Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24419

163 (2019) 26–35
September

Health implication of anion contents in different brands of bottled water samples consumed in some parts of south west Nigeria

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Received 13 July 2018; Accepted 14 May 2019

ABSTRACT

In recent time, many bottled water factories in Nigeria are producing water for consumption without standard operation procedures for quality water treatments. Twenty-one samples of different brands of bottled water samples were purchased in and around three densely populated states in Southwest Nigeria. The concentrations of phosphate, nitrate, chloride and nitrite anions in the bottled water samples were analyzed using ascorbic acid method, UV–visible spectrophotometry and argentometric titration. Statistically, the regression analysis indicates that nitrate correlated with nitrite and the significance F value of 1.7×10^{-3} which is lower than the critical value of 5×10^{-3} with p-value of 1.7×10^{-3} also in good agreement. The principal component analysis strongly revealed that high factor scores of nitrite may be due to Aquarite bottled water with a combined contribution of about 65% in all the nitrites found in the 21 samples. The value of 0.80 mg L^{-1} for nitrite in Aquarite exceeds the World Health Organization, European Economic Community and Standard Organization of Nigeria guidelines by factors of 4, 1.6 and 4, respectively. The anion contents in Nirvana bottled water were found to be lower than the International Reference Standards. The exposure dose, lifetime average daily dose and hazard quotient from the bottled waters were below the permissible limits. This study suggests the need for greater awareness of the risks of anion contents in drinking water, and the appropriate authority should consider the constant increase in production of untreated or poorly treated bottled water as well as the global growth in environmental pollution.

Keywords: Bottled water; Anions; Chronic daily intake; Health risk; UV–visible spectrophotometry; Ascorbic acid, Argentometry

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1944-3994/1944-3986

1. Introduction

Safe drinking water is very important for human beings. The demand for safe drinking water has been on the increase globally. However, some countries such as Nigeria lack access to safe drinking water [1] which may result in adverse effects on human health especially on the long term. Most people there depend on bottled water as it is seen as a safer alternative to other sources of water such as tap water, but that is not always the case. In the developing and underdeveloped regions of the world, over a third of all deaths are caused by water pollution [2]. According to a survey conducted by Igali [3], it was estimated that about 65 million Nigerians have no access to safe drinking water, which is over one third of the Nigerian population. They are at risk of adverse health conditions as a result of poor water quality. High level of anion contamination in bottled water is a major concern for human health risks. The global growth in bottled water consumption with most waters not meeting the required quality standards has brought about the need to monitor drinking water quality (whether sachet or bottled water) for potential risks as well as its major source: groundwater.

The adverse effect that has been associated with anion contamination in bottle water include problems ranging from skeletal fluorosis to dental fluorosis for fluoride contamination [4].

Groundwater quality is affected by both natural and artificial sources. It depends on all the processes and reactions that act on the water from the moment it is in the atmosphere to the time it is discharged and it varies from place to place and with the depth of the water table [4]. The quality of groundwater can vary from one rock type to another and also within aquifers along groundwater flow paths [5]. It has been observed that exposure of ground water to dangerous amounts of chemicals such as anions is increasing due to the increase in industrialization and socio-economic activities [6,7]: sources include improper disposal of waste and excessive use of fertilizers thereby making groundwater unsafe for use without proper treatment. Various anions in water have been found by previous studies to have varying effects on human health. The aim of this study is to assess the concentrations of nitrate, nitrite, chloride and phosphate in selected bottle water samples and the exposure risk of the general to the general public that relies on these bottled water samples for consumption.

2. Geology and geographical location of the study area

The study area covered Lagos State, Oyo State and Ogun State in Southwest Nigeria. Lagos state lies at latitude 6.6080°N and longitude 3.6218°E, Oyo State lies at latitude 8.1196°N and longitude 3.4196°E while Ogun State lies at latitude 6.9075°N and longitude 3.5813°E. Table 1 presents the geologies of the water bearing formation of the study area and possible factors that could affect the level of the anions in the bottled water samples.

2.1. Lagos State

Lagos State is bounded on the north and east by Ogun State, on the west by the Republic of Benin and on the south by the Atlantic Ocean. It has a total area of 3,577 km^2 about 22% of which is water. Lagos State lies mostly within the Dahomey basin. Stratigraphically, the basin is divided into Abeokuta Formation, Ilaro Formation, Coastal Plain Sands and Recent Alluvium Sediments [8,9]. Deposition of Cretaceous sequence in the eastern Dahomey Basin began with the Abeokuta Group, consisting of the Ise, Afowo and Araromi formations [10,11].

2.2. Ogun State

Ogun State is an inland state and is bounded to the North by Oyo and Osun States, to the South by Lagos State, to the East by Ondo State and to the West by Benin Republic. Ogun state lies in the eastern Dahomey basin along with other south-western Nigerian states including Oyo and Lagos. The geology of Ogun state is composed of basement complex rocks and sedimentary rocks which are Late Cretaceous to Early Tertiary in age [8–11]. It consists of intercalations of clay containing sediments. The rock is soft and easily crumbled but in some places cement is found due to the presence of silica and iron oxide. Stratigraphically, the sedimentary rock of Ogun state consists of the Abeokuta group, Imo group, Ewekoro, Oshosun, Ilaro and Benin formations [11,12].

Table 1
Geologies of the water bearing formation of the study area and possible factors that could affect the level of the anions in the bottled water samples

Geology	Chemical composition	Citation	Possible cause
Lagos and Ogun			
• Coastal sands • Ilaro formation • Abeokuta group • Alluvium sediments	• Chloride (from saline water) • Nitrate • Nitrite • Carbonate • Bicarbonate • Heavy metals, etc.	[13] [14] [15]	• Direct contact of the soil and outcrops with sea water rich in chloride, nitrate, nitrite and others
Oyo			
• Basement complex • Magmatic gneiss • Granitic intrusion	• Rich in iron, zinc and other heavy metals • Low In anion concentration	[16] [17]	• Multi-ferous geochemical factors such as weathering and volcanism

2.3. Oyo State

Oyo State is also an inland state. It is bounded to the north by Kwara State, to the south by Ogun State, to the east by Osun State and to the west jointly by Ogun State and the Republic of Benin. Area is of Precambrian age and occurs within the basement complex of southwestern Nigeria. It is composed primarily of banded gneiss in which hornblende-biotite rich bands alternate with quartz-oligoclase rich bands. The banded gneiss, which originated as part of a sedimentary sequence, contains large lenses of granite gneiss and thin intercalated layers of amphibolites and quartzite [18]. The basement rock is divided into five major groups which are the metaigneous rocks, charnockitic rocks, migmatite–gneiss complex, older granites and unmetamorphosed dolerite dykes [19].

3. Materials and methods

3.1. Collection of water samples and analysis

A total of 21 bottled water samples were randomly purchased in late October 2017 and tested for their anion content (phosphate, nitrate, chloride and nitrite) from January to February 2018. Also, the regions of their source water were identified along with the geologies and mineralogy that could possibly contribute to the anion content of the source water in those regions. Out of the 21 bottled water samples selected, 17 were produced in Lagos State, 3 were produced in Ogun State and 1 was produced in Oyo State. The concentration of the anions in the various bottled water samples was determined through different methods. Levels of phosphate were determined through ascorbic acid method, chloride was determined through argentometric titration while nitrate and nitrite were determined using Genesys 10 UV-Visible Spectrophotometry (Thermo Fisher Scientific, Loughborough).

3.2. Determination of phosphate

Phosphate level of bottled water samples was determined via ascorbic acid method spectrophotometry [20]. A stock solution was prepared with 0.11 g of KH_2PO_4 (Sigma-Aldrich) accurately weighed in distilled water and diluted to 250 cm^3 in a volumetric flask (stock solution and different concentrations of 0.20, 0.40, 0.60, 0.80 and 1.0 mg L^{-1} was prepared. 1.7600 g of ascorbic acid (Sigma-Aldrich) was weighed in volumetric flask and made up to 100 cm^3.

Combined reagent preparation of 500 cm^3 of 2.5 M H_2SO_4 mixed 50 cm^3 potassium antimony tartrate solutions (Sigma-Aldrich) as solution A and 150 cm^3 ammonium molybdate solution (Sigma-Aldrich) as solution B, the two solutions are equally mixed with 300 cm^3 ascorbic acid solution as solution C, then these were thoroughly mixed. Thereafter, to each 25 cm^3 of the sample and standard, 4 cm^3 of combined reagent was added and made up to the mark with distilled water. These were allowed to stand for 30 min prior to the absorbance reading at 880 nm [21].

3.3. Determination of nitrate

A modified Method 352.1:EPA for nitrogen and nitrate (Colorimetric, Brucine) by spectrophotometry was adopted for this analysis. Apparatuses used were analytical weighing balance, UV-visible spectrophotometer (Genesys 10), 50 mL volumetric flask, 10 mL pipette and 250 mL beaker. Reagents used where brucine 2.5% (JT Baker, New Jersey), Concentrated H_2SO_4, KNO_3 (Sigma-Aldrich, Germany).

Nitrate of bottled water samples was analyzed measuring absorbance at the wavelength of 470 nm. 0.16 g of KNO_3 (Merck, Germany) were accurately weighed on an analytical balance and dissolved in distilled water, then 0.5 cm^3 of chloroform (Sigma-Aldrich, Germany) was added as preservative in 100 cm^3 volumetric flasks and made to the mark. 10 cm^3 of the stock solution was pipetted into 100 cm^3 volumetric flask, from this 0, 1, 2, 3, 4 and 5 mL each were taken into five different 50 mL flasks to have 0, 0.2, 0.4, 0.6, 0.8 and 1.0 ppm concentration. Thereafter, 2 mL of colour developer brucine solution was added, followed by 10 mL of concentrated sulphuric acid and mark with distilled water to mark. This was allowed to stand for 10 min for colour to develop. All the standard stock solutions were treated in likewise manner prior to spectrophotometric analysis.

3.4. Determination of nitrite

The concentration of nitrite in the bottled water samples was determined spectrophotometrically using Hanna HI 3873 Nitrite water test kit with one sachet of HI 3873-0 nitrite reagent in accordance with the instruction (Hanna, UK).

3.5. Determination of chloride

The concentration of chloride in the bottled water samples was determined through argentometric titration (MOHR'S Method) using a silver nitrate standard solution of 0.1 M $AgNO_3$ (Sigma-Aldrich, Germany) with potassium chromate as an indicator [22]. Materials used where burette 50 mL, conical flask 250 mL, measuring cylinder 100 mL, $AgNO_3$ solution and 2% K_2CrO_4 (Sigma-Aldrich) solution. 25 cm^3 of bottled water samples were placed into 250 cm^3 conical flasks with 1.0 mL of 2% potassium chromate indicator and titrated against 0.1 M $AgNO_3$ [22]. The readings were taken in triplicates.

3.6. Statistical evaluation for anion contents in the samples of selected bottled water

Exploratory analysis of both nitrites and nitrates present in all the bottled water samples was performed using descriptive statistics. Statistical implications and principal component analysis were also executed to identify the contributions of both nitrates and nitrites to the water samples. Data evaluation was carried out using the statistical analysis tool of XLSTAT 20.7.54791.0, 2017 version and data analysis functions on EXCEL application

3.7. Equation models for risk analysis used in this study according to USEPA

$$D = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{EF}}{\mathrm{BW}} \tag{1}$$

where D = exposure dose (mg kg^{-1} d^{-1}); C = contaminant concentration (mg L^{-1}); IR = water intake rate (L d^{-1}) = 2 L d^{-1} (adult) and 1 L d^{-1} (children); EF = exposure frequency (d/year) = 350 d; BW = body weight (kg) [23].
Ingestion LADD of drinking water =

$$\text{LADD} = \frac{\text{EPC} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{AT} \times \text{BW}} \tag{2}$$

where LADD = lifetime average daily dose (mg kg^{-1} year^{-1}); EPC = exposure point concentration (mg L^{-1}); IR = water ingestion rate (L d^{-1}) = 2 L d^{-1} (adult) and 1 L d^{-1} (children) [24,25]; BW = body weight (70 kg for adult, 10 kg on the average for children [25,26]; AT = average time (d) 25,550 (obtained from 70 year × 365 d) [24,25]; EF = exposure frequency (d/year) = (365 d year^{-1}); ED = exposure duration (year) = 70 years for adult, 6 years for children 1–6 years old [25,26].

$$\text{HQ}i = \frac{\text{LADD}}{\text{RFD}} \tag{3}$$

where LADD = lifetime average daily dose from Eq. (2); RFD = reference dose: RED for NO_2 = 0.19998, RED for NO_3 = 49.99500, RED for Cl = 250.026411 [27].

4. Results and discussion

The measured anions contents in the 21 different brands of bottled water samples are shown in Table 2. The concentrations of four anion contents (phosphate, nitrate, chloride and nitrite) in the bottled water samples were measured and presented in mg L^{-1}.

In this study, the concentration of nitrite (NO_2^-) varies from 0.002 to 0.8 mg L^{-1} with a mean value of 0.05889 mg L^{-1}. The highest value of 0.8 mg L^{-1} for nitrite was found in Aquarite bottled water, which was produced in Isolo, Lagos State, while the lowest value of 0.002 mg L^{-1} was found in both De Ren and Duslama bottled water. De Ren premium table water was produced in Sangotedo, Lagos, while Duslama table water is produced in Agege, Lagos State. The concentration of nitrite in some of the bottled water samples was not detected since it was found to be below the detectable limit.

Comparing the highest value of nitrite (0.8 mg L^{-1}) found in Aquarite bottled water to various standards, it can be observed in Table 2 that the concentration of nitrite found in this present study is higher by a factor of 3–4 when compared with the World Health Organization (WHO) standards and Standard Organization of Nigeria (SON) standards. It is higher by a factor of 1.6 when compared with the [18], 1998 standards and lower by a factor of 0.2 when compared with the [28] standards. This high value of nitrite may be from the water bearing formation (aquifer) considering [18] that high contents of nitrite were found in some boreholes in the study area. It may thus be due to the interconnectivity of the subsurface aquifer seepage between the underline geology of the study area and the Atlantic Ocean around the region

The nitrate (NO_3^-) concentration in the samples varied from 0.2 to 5.0 mg L^{-1} with a mean value of 1.214 mg L^{-1} as shown in Table 2. The maximum value of 5.0 mg L^{-1} was found in Cascade-Eden Table Water which is produced in Ilupeju, Lagos State, while the minimum value of 0.2 mg L^{-1} was observed in both Bigi and Cubby bottled water samples. Bigi premium drinking water is produced in Ososa, Ogun State while Cubby table water was produced in Olokonla-Ajah, Lagos State. Nitrate concentration in Nirvana premium table water is produced at Badagry Lagos State was below the detectable limit; hence it was not reported.

Table 2
Concentrations of the four anions in the 21 bottled water samples (mg L^{-1})

Sample ID	NO_2^-	NO_3^-	PO_4^{2-}	Cl^-
Aquarite	0.80	4.00	0.006	28.40
Hebron	0.04	1.40	0.010	28.43
La Verne	0.02	1.20	0.011	14.22
Varich Cool	NIL	0.40	0.018	28.42
KlienAby	0.06	2.00	0.015	21.30
Cubby	NIL	0.20	0.006	28.44
Sopetie	0.003	0.80	0.019	28.38
Cascade	0.009	1.20	0.020	28.42
Cway Ultra	NIL	0.40	0.003	28.37
Latinum	0.006	1.00	0.008	28.41
Nirvana	NIL	NIL	0.016	28.40
UPS	NIL	0.40	0.009	28.39
Cici	NIL	0.40	0.014	28.38
Bigi	NIL	0.20	0.009	28.39
Southern Spa	0.09	1.80	0.006	28.41
Vessi	0.04	1.40	0.004	28.40
De Ren	0.002	0.60	0.005	28.37
Enni	0.06	1.70	NIL	28.43
Cascade-Eden	0.10	5.00	0.009	28.38
LikWid	0.004	0.60	0.013	28.42
Duslama	0.002	0.80	0.013	28.39
Mean Values	**0.05886**	**1.214**	**0.01019**	**27.38**
WHO [1]	0.2	**50**	–	–
USEPA [16]	3.5	**40**	–	**250**
EEC [13]	0.5	**50**	–	**250**
SON	0.3	**50**	–	**250**

We compared the maximum concentration of nitrate observed by this study in Cascade-Eden Table Water to Standards established by WHO, SON, USEPA and EEC as shown in Table 2. It is to be noted that the value observed in this study is considerably lower when compared with the standards set by WHO, SON, EEC and USEPA. Concentration of phosphate (PO_4^{2-}) amongst the 21 selected bottled water samples ranged from 0.003 to 0.02 mg L^{-1} with an average value of 0.01019 mg L^{-1}. The highest value of phosphate was observed in Cascade Table water while the lowest value was found in Cway Ultra drinking water. Cway Ultra drinking water was produced in Isolo, Lagos while Cascade Table water is produced in Ilupeju, Lagos State. Also, phosphate concentration was not recorded for Enni premium table water as it was below the detectable limit.

For chloride (Cl^-), the concentration varied from 14.2 to 28.4 mg L^{-1} with a mean value of 27.39 mg L^{-1}. as shown in Table 2. The minimum value was found in La Verne premium water while the maximum value was observed in all the other samples apart from KlienAby table water which had a concentration of 21.3 mg L^{-1}. Comparing the highest value observed in this study to the US EPA, SON and ECC standards, it can be found that the concentration of chloride in this study is much lower by a factor of 0.1 as shown in Table 2.

4.1. Risk assessment of water ingestion exposure dose due to anions in the samples

In this study, the risk analysis of anions due to ingestion dose exposure was calculated using a model suggested by [29], shown in Eq. (1).

The water ingestion exposure dose for the four anions was calculated using an average body weight of 70 kg for adults as presented in Tables 3 and 4, respectively.

For the risk assessments due to anion contents in drinking water, certain fatal cases of methaemoglobinaemia have been reported in adults after the consumption of high amounts of nitrate ranging from 4 to 50 g [30]. A study has shown that a common birth defect has been associated with consuming excess anions of nitrite by pregnant mothers which is called methaemoglobinaemia [21]. The water ingestion exposure dose for adults with an average body weight of 70 kg for nitrite (NO_2^-) ranged from 0.00001 to 0.0229 mg kg^{-1} $year^{-1}$ while the water ingestion exposure dose for children with an average body weight of 10 kg for nitrite (NO_2^-) ranged from 0.0002 to 0.0800 mg kg^{-1} $year^{-1}$ for children.

In this study, for chloride (Cl^-), the water ingestion exposure dose for adults varied from 0.40571 to 0.8114 mg kg^{-1} $year^{-1}$ while for children, it varied from 1.4200 to 2.8400 mg kg^{-1} $year^{-1}$.

4.2. Evaluation of lifetime average daily dose

The chemical toxicity risk was evaluated using the lifetime average daily dose (LADD) of the anions through the ingestion of bottled water and comparing it with the reference dose (RFD) of 0.6 mg kg^{-1} $year^{-1}$ [27] used as a standard criterion for different elements in several foreign organizations, The values for both adults and children are presented in Tables 5 and 6, respectively.

The LADD for adults with an average body weight of 70 kg for nitrite (NO_2^-) ranged from 0.00006 to 0.02192 mg kg^{-1} $year^{-1}$ with a mean dose of 0.00161 mg kg^{-1} d^{-1} while that of children ranged from 0.00019 to 0.07671 mg kg^{-1} $year^{-1}$ with a mean dose of 0.00564 mg kg^{-1} $year^{-1}$. The highest dose for nitrite was found in Aquarite bottled water while the lowest dose was found in both De Ren and Duslama bottled water.

For nitrate (NO_3^-), the LADD varied from 0.00548 to 0.13699 mg kg^{-1} $year^{-1}$ with a mean dose of 0.03327 mg kg^{-1}

Table 3
Water ingestion exposure dose (D) of four anions for adults with average body weight of 70 kg

Sample ID	D (NO_2^-) mg kg^{-1} $year^{-1}$	D (NO_3^-) mg kg^{-1} $year^{-1}$	D (PO_4^{2-}) mg kg^{-1} $year^{-1}$	D (Cl^-) mg kg^{-1} $year^{-1}$
Aquarite	0.0229	0.1143	0.0002	0.8124
Hebron	0.0011	0.0400	0.0003	0.8104
La Verne	0.0006	0.0343	0.0003	0.4057
Varich Cool	NIL	0.0114	0.0005	0.8104
KlienAby	0.0017	0.0571	0.0004	0.6086
Cubby	NIL	0.0057	0.0002	0.8114
Sopetie	0.0001	0.0229	0.0005	0.8114
Cascade	0.0003	0.0343	0.0006	0.8103
Cway Ultra	NIL	0.0114	0.00009	0.8114
Latinum	0.0002	0.0286	0.0002	0.8114
Nirvana	NIL	NIL	0.0005	0.8112
UPS	NIL	0.0114	0.0003	0.8113
Cici	NIL	0.0114	0.0004	0.8114
Bigi	NIL	0.0057	0.0003	0.8112
Southern Spa	0.0026	0.0514	0.0002	0.8113
Vessi	0.0012	0.0400	0.0001	0.8114
De Ren	0.0001	0.0171	0.0001	0.8103
Enni	0.0017	0.0488	NIL	0.8112
Cascade-Eden	0.0029	0.1429	0.0002	0.8114
LikWid	0.0001	0.0171	0.0004	0.8102
Duslama	0.0001	0.0229	0.0004	0.8114
USEPA, 1989	0.33	7.0	–	–

Table 4
Water ingestion exposure dose of four anions for children with average body weight of 10 kg

Sample ID	D (NO_2^-) mg kg^{-1} year^{-1}	D (NO_3^-) mg kg^{-1} year^{-1}	D (PO_4^{2-}) mg kg^{-1} year^{-1}	D (Cl^-) mg kg^{-1} year^{-1}
Aquarite	0.0800	0.4000	0.0006	2.8400
Hebron	0.0040	0.1400	0.0010	2.8400
La Verne	0.0020	0.1200	0.0011	1.4200
Varich Cool	NIL	0.0400	0.0018	2.8400
KlienAby	0.0060	0.2000	0.0015	2.1300
Cubby	NIL	0.0200	0.0006	2.8400
Sopetie	0.0003	0.0800	0.0019	2.8400
Cascade	0.0009	0.1200	0.002	2.8400
Cway Ultra	NIL	0.0400	0.0003	2.8400
Latinum	0.0006	0.1000	0.0008	2.8400
Nirvana	NIL	NIL	0.0016	2.8400
UPS	NIL	0.0400	0.0009	2.8400
Cici	NIL	0.0400	0.0014	2.8400
Bigi	NIL	0.0200	0.0009	2.8400
Southern Spa	0.0090	0.1800	0.0006	2.8400
Vessi	0.0040	0.1400	0.0004	2.8400
De Ren	0.0002	0.0600	0.0005	2.8400
Enni	0.0060	0.1700	NIL	2.8400
Cascade-Eden	0.0100	0.5000	0.0009	2.8400
LikWid	0.0004	0.0600	0.0013	2.8400
Duslama	0.0002	0.0800	0.0013	2.8400

Table 5
Lifetime average daily dose of the four measured anions for adults with average body weight of 70 kg in the water samples

Sample ID	NO_2^- LADD (mg kg^{-1} year^{-1})	NO_3^- LADD (mg kg^{-1} year^{-1})	PO_4^{2-} LADD (mg kg^{-1} year^{-1})	Cl^- LADD (mg kg^{-1} year^{-1})
Aquarite	0.02192	0.10959	0.00016	0.77808
Hebron	0.00110	0.03836	0.00027	0.77808
La Verne	0.00055	0.03288	0.00030	0.38904
Varich Cool	NIL	0.01096	0.00049	0.77808
KlienAby	0.00164	0.05480	0.00041	0.58356
Cubby	NIL	0.00548	0.00016	0.77808
Sopetie	0.00008	0.02192	0.00052	0.77808
Cascade	0.00025	0.03288	0.00055	0.77808
Cway Ultra	NIL	0.01096	0.000082	0.77808
Latinum	0.00016	0.02740	0.00022	0.77808
Nirvana	NIL	NIL	0.00044	0.77808
UPS	NIL	0.01096	0.00025	0.77808
Cici	NIL	0.01096	0.00038	0.77808
Bigi	NIL	0.00548	0.00025	0.77808
Southern Spa	0.00247	0.04932	0.00016	0.77808
Vessi	0.00110	0.03836	0.00011	0.77808
De Ren	0.00006	0.01644	0.00014	0.77808
Enni	0.00164	0.04658	NIL	0.77808
Cascade-Eden	0.00274	0.13699	0.00025	0.77808
LikWid	0.00011	0.01644	0.00036	0.77808
Duslama	0.00006	0.02192	0.00036	0.77808

Table 6
Lifetime average daily dose of the four anions for children with average body weight of 10 kg

Water samples	NO_2^- LADD (mg kg^{-1} year^{-1})	NO_3^- LADD (mg kg^{-1} year^{-1})	PO_4^{2-} LADD (mg kg^{-1} year^{-1})	Cl^- LADD (mg kg^{-1} year^{-1})
Aquarite	0.07671	0.38356	0.00058	2.72329
Hebron	0.00384	0.13425	0.00096	2.72329
La Verne	0.00192	0.11507	0.00106	1.36164
Varich Cool	NIL	0.03836	0.00173	2.72329
KlienAby	0.00575	0.19178	0.00144	2.04247
Cubby	NIL	0.01918	0.00058	2.72329
Sopetie	0.00029	0.07671	0.00182	2.72329
Cascade	0.00086	0.11507	0.00192	2.72329
Cway Ultra	NIL	0.03836	0.00029	2.72329
Latinum	0.00058	0.09589	0.00077	2.72329
Nirvana	NIL	NIL	0.00153	2.72329
UPS	NIL	0.03836	0.00086	2.72329
Cici	NIL	0.03836	0.00134	2.72329
Bigi	NIL	0.01918	0.00086	2.72329
Southern Spa	0.00863	0.17260	0.00058	2.72329
Vessi	0.00384	0.13425	0.00038	2.72329
De Ren	0.00019	0.05753	0.00048	2.72329
Enni	0.00575	0.16301	NIL	2.72329
Cascade-Eden	0.00959	0.47945	0.00086	2.72329
LikWid	0.00038	0.05753	0.00125	2.72329
Duslama	0.00019	0.07671	0.00125	2.72329

year^{-1} while that of children varied from 0.01919 to 0.4794 mg kg^{-1} year^{-1} with a mean dose of 0.1164 mg kg^{-1} year^{-1}. The maximum dose of 0.136986 mg kg^{-1} year^{-1} was found in Cascade-Eden Table Water while the minimum dose of 0.00548 mg kg^{-1} year^{-1} was observed in both Bigi and Cubby bottled water.

The LADD of phosphate (PO_4^{2-}) amongst the bottled water samples ranged from 0.00008 to 0.00055 mg kg^{-1} year^{-1} with a mean dose of 0.00028 mg kg^{-1} d^{-1}. For children, it varied from 0.00029 to 0.00192 mg kg^{-1} year^{-1} with a mean dose of 0.00098 mg kg^{-1} year^{-1}.

For chloride (Cl^-), the water ingestion exposure dose for adults varied from 0.389041 to 0.778082 mg kg^{-1} d^{-1} with a mean dose of 0.7503 mg kg^{-1} year^{-1} while varying from 1.36164 to 2.72329 mg kg^{-1} year^{-1} with a mean dose of 2.62600 mg kg^{-1} year^{-1} for children. Comparing the highest value observed for chloride to the USEPA Reference Standard, it can be observed that the value determined from this present study is lower by a factor of 0.00130. All the values found in this present study were below the reference standard of 0.6 mg kg^{-1} year^{-1} according to Rahama [30]

4.3. Evaluation of hazard quotient

The risk analysis of hazard quotient (HQ) due to anion contents was determined using Eq. (3)

Considering adults, the hazard quotient for nitrite (NO_2^-) ranged from 0.00027 to 0.10960 with a mean value of 0.00806; for nitrate (NO_3^-), the hazard quotient varied from 0.00011 to 0.00091 with an average value of 0.00065 while

Table 7
Hazard quotient of the 3 anions for adults using WHO Reference Standards for nitrite and nitrate and US EPA Standards for chloride with an average body weight of 70 kg

Sample ID	HQ (NO_2^-)	HQ (NO_3^-)	HQ (Cl^-)
Aquarite	0.1096	0.00219	0.00311
Hebron	0.00548	0.00077	0.00311
La Verne	0.00274	0.00066	0.00156
Varich Cool	0	0.00022	0.00311
KlienAby	0.00822	0.00110	0.00233
Cubby	0	0.00011	0.00311
Sopetie	0.00041	0.00044	0.00311
Cascade	0.00123	0.00066	0.00311
Cway Ultra	0	0.00022	0.00311
Latinum	0.00082	0.00055	0.00311
Nirvana	0	NIL	0.00311
UPS	0	0.00022	0.00311
Cici	0	0.00022	0.00311
Bigi	0	0.00011	0.00311
Southern Spa	0.01233	0.00099	0.00311
Vessi	0.00548	0.00077	0.00311
De Ren	0.00027	0.00033	0.00311
Enni	0.00822	0.00093	0.00311
Cascade-Eden	0.01370	0.00274	0.00311
LikWid	0.00055	0.00032	0.00311
Duslama	0.00027	0.00044	0.00311

for chloride (Cl^-), the hazard quotient varied from 0.00156 to 0.00311 with an average value of 0.00300. For children, the hazard quotient ranged from 0.00096 to 0.38360 with a mean value of 0.02822 for nitrite (NO_2^-), from 0.00038 to 0.00959 with an average value of 0.00233 for nitrate (NO_3^-) and, for chloride, from 0.00545 to 0.0109 with a mean value of 0.0105. These values of the hazard quotient are lower than 1 according to USEPA and WHO standards

Table 8
Hazard quotient of three anions for children using WHO Reference Standards for nitrite and nitrate and US EPA Standards for chloride with an average body weight of 10 kg

Sample ID	HQ_i (NO_2^-)	HQ (NO_3^-)	HQ (Cl^-)
Aquarite	0.38360	0.00767	0.01089
Hebron	0.01918	0.00269	0.01089
La Verne	0.00959	0.00230	0.00545
Varich Cool	0	0.00077	0.01089
KlienAby	0.02877	0.00384	0.00817
Cubby	0	0.00038	0.01089
Sopetie	0.00144	0.00153	0.01089
Cascade	0.00432	0.00230	0.01089
Cway Ultra	0	0.00077	0.01089
Latinum	0.00288	0.00192	0.01089
Nirvana	0	NIL	0.01089
UPS	0	0.00077	0.01089
Cici	0	0.00077	0.01089
Bigi	0	0.00038	0.01089
Southern Spa	0.04315	0.00345	0.01089
Vessi	0.01918	0.00269	0.01089
De Ren	0.00096	0.00115	0.01089
Enni	0.02876	0.00326	0.01089
Cascade-Eden	0.04795	0.00958	0.01089
LikWid	0.00192	0.00115	0.01089
Duslama	0.000959	0.00153	0.01089

4.4. Statistical analysis using principal component analysis

4.4.1. Summary of regression analysis

From Table 9, the regression result indicates that the R^2 supports the fact that the nitrate reduces to nitrites because the value 0.4113586 tends towards zero (0) than one (1). Even the significance F-value is less than 0.05 which validates the value of R^2 and shows these results are statistically reliable. So also p-value of 0.0005007 which is less than critical value of 0.005 further shows that nitrates reduces to nitrite that is as the nitrates reduces, nitrites increases in all the 21 bottles of water. Also, Table 10 shows the factor score of the 21 bottled water samples.

From Fig. 1, it is discovered that nitrite concentration in Aquarite table water contributes 65% to the total nitrites in the 21 samples which means Aquarite with 65% of nitrites will be more toxic to human health as compared with Nirvana with both nitrite and nitrate value of 0%. This nitrite value is enough to turn human haemoglobin to methaemoglobin which kills infants less than 3 months of age quicker than adults.

4.4.2. Factor scores

The regression analysis in Fig. 2 indicates that nitrate reduces to nitrite, which may lead to the toxicity of nitrite exposure to humans. In addition, the oxidation has a major biological effect on humans which prevent the transportation of oxygen to the blood tissues. The condition called methaemoglobinaemia is reached when the reduced oxygen transported becomes manifest clinically when the concentration reach 10% and these causes

Table 9
Regression analysis of nitrites and nitrates of the 21 samples

Regression Statistics								
		Multiple R			0.6413724			
		R square			0.4113586			
		Adjusted R Square			0.3803775			
		Standard error			0.9750272			
		Observations			21			
ANOVA								
	Df	SS	MS	F	Significance F			
Regression	1	12.622832	12.622832	13.277716	0.0017271			
Residual	19	18.062882	0.950678					
Total	20	30.685714						
	Coefficients	Standard Error	t Stat	p-value	Lower 95%	Upper 95%	Lower 95.0%	Upper 95.0%
Intercept	0.9434885	0.2253736	4.1863311	0.00050069	0.4717761	1.4152008	0.4717761	1.4152008
NO_2^- (mg L^{-1})	4.6009241	1.2626512	3.64386	0.00172712	1.9581648	7.2436833	1.9581648	7.2436833

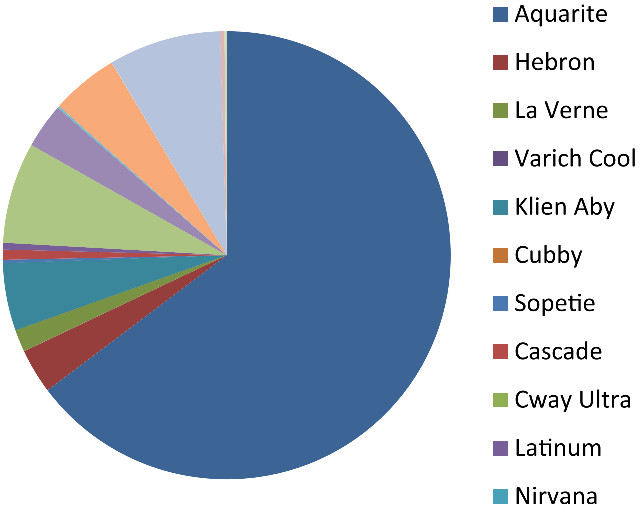

Fig. 1. Chart showing the percentage of nitrite in each of the 21 bottle water samples.

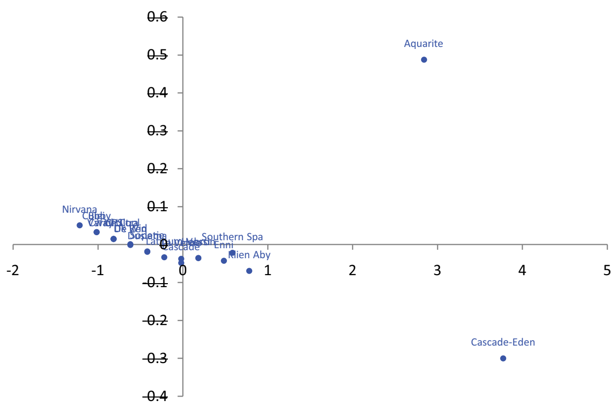

Fig. 2. Graph showing the factor score of F1 against F2 for the 21 bottle samples.

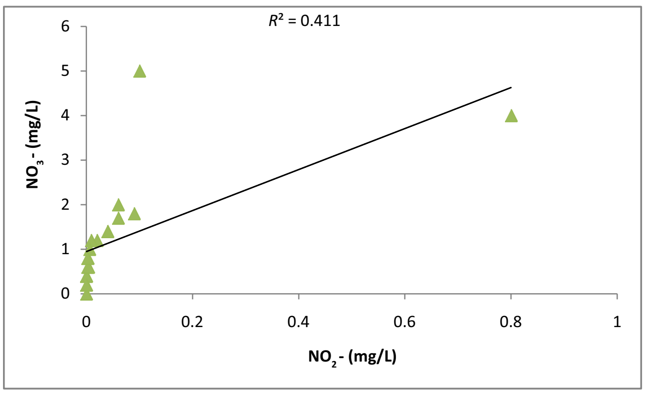

Fig. 3. Graph showing the factor score of F1 against F2 for the 21 bottle samples.

cyanosis and asphyxia at higher concentration. In infants under 3 months of age, methaemoglobin is less than 3% while in adults (humans) it is less than 2% according to USEPA [20]. The correlation between the nitrate and nitrite indicates a close to strong positive correlation with a value of 0.04114 as shown in Fig. 3

Table 10
Factor score of the 21 bottled water samples

Water sample	F1	F2
Aquarite	2.841	0.487
Hebron	0.183	–0.036
La Verne	–0.018	–0.037
Varich Cool	–0.816	0.015
KlienAby	0.783	–0.070
Cubby	–1.015	0.033
Sopetie	–0.418	–0.018
Cascade	–0.019	–0.048
Cway Ultra	–0.816	0.015
Latinum	–0.218	–0.033
Nirvana	–1.215	0.051
UPS	–0.816	0.015
Cici	–0.816	0.015
Bigi	–1.015	0.033
Southern Spa	0.586	–0.022
Vessi	0.183	–0.036
De Ren	–0.617	–0.001
Enni	0.484	–0.043
Cascade-Eden	3.774	–0.300
LikWid	–0.617	0.001
Duslama	–0.418	–0.019

5. Conclusions

The anion contents (nitrite, nitrate, phosphate and chloride) in 21 bottled water samples which are produced in some parts of Southwest Nigeria were investigated. Significantly, the consumption of all the brands of bottled water used for this present study were revealed to be safe for the general public except for Aquarite bottled water with a nitrite concentration of 0.8 mg L that exceeded the WHO, EEC and SON standards. The mean values of the analyzed anions were distinctly lower compared with previous studies reported in literature in Nigeria and other countries. This study suggests the need for greater awareness of the risks of anion contents in drinking water by the appropriate authorities considering the constant increase in production of untreated or poorly treated brands of bottled water as well as the global growth in environmental pollution. In addition, this the higher value observed for nitrite may be from the water bearing formation (aquifer). The findings of this study will help in establishing a baseline for the public exposure of anion contents from bottle water ingestion as well as monitoring the raw water source (aquifer) before sitting water factory. There is need for a separate agency to be created by the Nigerian government for the sole purpose of monitoring groundwater quality. Further studies also need to be carried out using more sensitive equipment such as ICP-AES coupled with ion chromatography for suitable water analysis. Other techniques are spectrophotometry, electrochemistry and ion chromatography. More so, this study considers the anion contents in the bottled water samples but higher risks for human health could derive from the microbiological parameters. The data from this investigation could be useful in establishing a baseline of bottled water toxicity risk exposure to the general public in Nigeria

Acknowledgements

The authors would like to thank the Covenant University Management for their financial support as well as the Chemistry Department, Covenant University for the use of their Analytical Chemistry laboratory for this present study. Also, to Maxico Hydrosolutions Consult Ltd. for the supply of field materials for this study

Symbols

D	—	Exposure dose, mg kg^{-1} d^{-1}
C	—	Contamination concentration, mg L^{-1}
LADD	—	Lifetime average daily dose, mg kg^{-1} d^{-1}
EPC	—	Exposure point concentration, mg L^{-1}
IR	—	Water ingestion rate, L d^{-1}
BW	—	Body weight, kg
AT	—	Averaging time, that is, years of life, years
EF	—	Exposure frequency, d/year
ED	—	Exposure duration, years
RFD	—	Reference dose
HQ_i	—	Hazard quotient

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