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Multivariate statistical approach and water quality assessment of natural springs and other drinking water sources in Southeastern Nigeria

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Abstract

This baseline study investigated the physico-chemical and trace elements (including potentially toxic elements, PTEs) contents of ground and surface water sources used for domestic purposes in some districts within the shale bedrock terrain of Southeastern Nigeria. A total of 124 water samples from 13 natural springs, 24 streams, 80 boreholes and 7 hand-dug wells were collected from rural and urban areas and analysed by ICP-OES, GF-AAS and CV-AFS for 21 elements. The distribution pattern, sources of contamination, health risk of potentially toxic elements (PTEs), together with water quality index were investigated. The results were compared with national and international guidelines for drinking water. Al and Fe were implicated as the dominant pollutants in the water bodies. Water quality index (WQI) indicated that all the water sources had either excellent or good water quality (WQ) with the exception of a borehole, which had poor WQ. Different multivariate statistical approaches applied to evaluate the origins of the elements in the water bodies identified six source types that accounted for 70.88% of the total variance. Anthropogenic activities were considered to

contribute much of Cu, Pb, Cd, Cr, Li and P, while Al, As, Co, Fe, Se, Ni, Y and V were likely from crustal materials, minerals and ores, and natural environments. Both anthropogenic and natural sources accounted for the Hg, Mn and Zn. Cluster analysis (CA) was adopted to classify 124 sample points into two groups of water pollution, reflecting influences from crustal materials and anthropogenic sources. From the result of hazard quotient and index (HQ/HI), there is little or no health risks arising from PTEs in using water from the region.

Keywords: Geology, Hydrology, Environmental science, Natural hazard, Geochemistry

1. Introduction

In recent times, it has become very difficult, seemingly impossible, to meet increased demands and provide sufficient quality water to the population due to pollution (Stevanovic, 2010). Springs, streams, hand-dug wells and boreholes are some of the sources widely used for drinking purpose; in most case untreated (Owamah et al., 2013). Most often, these water sources could be polluted, making their potability disputable. Moreover, since the industrial revolution, environmental pollution has become a worldwide critical issue relating to both industrialized and developing countries-generation of inorganic pollutants such as heavy metals, and organic pollutants such as detergents, fertilizers, pesticides, pharmaceuticals, and biomaterials are the consequences. In general, microorganisms, organic compounds, and toxic heavy metals are the sources of contaminations of water (Verma et al., 2018), although many are products of natural mobilization of these elements, such as weathering reactions, biological activity, volcanic emissions, and rocks solubilization (Meng et al., 2016; Kumar et al., 2017; Funes Pinter et al., 2018), as well as geological sources (Karakaya and Karakaya, 2014; Kostic et al., 2016) through mine drainage of waters that are rich in elements, which can mix into the surface water. Water becomes unsuitable for drinking and other domestic uses when they are enriched with potentially toxic elements (PTEs) (Nazeer et al., 2014). More importantly, potential threats to human health and aquatic ecosystems make trace element pollution of water systems an ongoing environmental problem (Giri and Singh, 2014; Farahat and Linderholm, 2015). Groundwater and surface water are fundamentally interconnected. It is often difficult to separate the two, because they recharge each other, and hence they can also contaminate each other (Trček and Zojer, 2010). Quality assessment of springs could therefore present an idea of groundwater and surface water quality.

In most developing countries like Nigeria, water treatment and quality monitoring are limited to areas closest to the seat of power, while the rural population is left to use untreated waters as the cost of providing treated water is either unaffordable

or of less priority to the government. The adoption of poor management practice for potentially hazardous wastes such as e-waste management, the lax application of relevant environment-related legislations to protect human health and environment (Osibanjo and Nnorom, 2007; Nnorom and Osibanjo, 2008) and the lack of adequate infrastructure to manage wastes safely, have resulted in burying wastes, burning them in the open air or dumping into surface water bodies (Nnorom and Osibanjo, 2008). Hence, monitoring of water resources in terms of water quality especially PTEs content is vital to evaluate the risk of metal contamination towards public health (Magesh et al., 2017). Exposure to PTEs, especially at elevated amounts, are known to be sources of health problems such as reduced growth and development, damage of organs, impairment of the nervous system amongst other (Duruibe et al., 2007). For instance, lead and mercury are known to cause kidney malfunctioning and miscarriages in humans (Duruibe et al., 2007). They are also known to affect growth and development, even resulting in low intelligence in children (Duruibe et al., 2007).

In natural waters, the bioavailability of trace metals, including their toxicity, is thought to be related to their ability to cross biological barriers (e.g. plasma membrane) (Worms et al., 2008), thus, our study made use of dissolved concentrations of these elements to estimate their human health impact. Although several water studies have been conducted in Nigeria in recent years (Omaka et al., 2014, 2016, 2017; Adamu et al., 2015; Igwe et al., 2015; Nganje et al., 2015), spring waters, mainly used by majority of the rural populace have never received attention regarding their quality. To our knowledge, no comprehensive data are available on PTEs (especially Hg) levels in springs, streams, boreholes and hand-dug wells in the rural and most urban areas of southeastern region of Nigeria. Therefore, it is appropriate to understand the PTEs concentrations, distribution, likely sources, potential health risks, as well as evaluate the overall water quality index of drinking water sources in the southeastern Nigeria.

Multivariate statistical approaches, including cluster analysis (CA), correlation analysis, and factor/principal component analysis (FA/PCA) have been recognized as powerful tools for environmental studies. They reduce complex datasets to small number of factors without any loss of information, and reveal hidden relations between variables, thereby offering a better understanding of water quality and possible sources that affect the studied system (Singh et al., 2004).

A water quality index (WQI) describes the general situation of water bodies by changing water quality parameters levels into a numerical score using mathematical tools (Silvert, 2000; Boyacioglu, 2007). Contrary to most of the previous water quality indices and modifications, Canadian Council of Ministers of the Environment (CCME) made a successful attempt for the development of an efficient drinking water quality index (DWQI) (CCME, 2001). The Canadian DWQI compared observed

levels of water quality parameters to guidelines or standard values as benchmarks instead of standardizing observations by subjective rating curves. Since then, several modifications (Hurley et al., 2012; Mohebbi et al., 2013; Abtahi et al., 2015, 2016) have been made on DWQI, with the view to (i) accommodate parameters measured at different frequencies within any particular study period; (ii) assign weight factors for input parameters and account for two important sub-indices — health-based index and acceptability index; (iii) ultimately develop a generic water quality index that is applicable to drinking source water worldwide, in lieu of a site-specific water quality index. Moreover, Hurley et al. (2012) identified site specificity as a primary challenge to index development and pointed out that parameters of concern at one location and thus necessitating monitoring may not be of concern elsewhere and therefore are rarely monitored. They further noted that if a consistent set of parameters is not monitored on routine basis at all times, then alternative indices are required that can incorporate all parameters of concern at all location (Hurley et al., 2012).

When hard to eliminate toxic elements are present in water in excess amount, they can cause serious health problems to humans (Ozdes et al., 2011). It therefore becomes necessary to assess the degree of element toxicity in the water sources, which will inform the users to take precautionary measures, where government intervention is not realizable as in the case of the areas under study. The hazard quotient (HQ) and hazard index (HI) have been used extensively for aquatic risk assessments (EPA, 2004). HQ could be communicated on short or long-term basis. The latter is expressed as the ratio between exposure through individual pathways and the reference dose (RfD), while the former is the ratio of estimated weekly intake (EWI) to the provisional tolerable weekly intake (PTWI). Moreover, the HI, which is the sum of the HQs from all applicable pathways (e.g. oral and dermal) can be used to evaluate the total potential non-carcinogenic risk posed by pollutants (in this case, PTEs) through more than one pathway (Meng et al., 2016). The potential for adverse effects on human health or the necessity for further study would be indicated if the $HI > 1$.

Therefore, this study was conducted as a baseline survey of some physicochemical parameters and water contamination by PTEs. The aim of the study was to determine the concentrations of dissolved Al, As, Cd, Co, Cr, Cu, Hg, Li, Mn, Ni, P, Pb, Se, V, Y, Zn, Ca, K, Mg, Na, and Fe using complex equipment suitable for their detections. The objectives are (1) examining the distribution pattern of elements across 124 sampling sites; (2) investigating the sources of PTEs using multivariate statistics; (3) employing Water Quality Index (WQI) approach for water quality index study; and (4) evaluating the hazard impact on human health posed by PTEs using Hazard Quotient/Index (HQ/HI). The results will implicate water sources with unacceptable metal levels, and such information will be necessary in driving government policy formulations and action towards initiating provision of water treatment facilities. The data generated by this study will augment existing data base, guide further

investigations and provide a framework needed for effective groundwater management.

2. Materials and methods

2.1. Description of the study areas

2.1.1. Location and topography

This study was carried out in Abia and Imo states in the southeast geopolitical zone of Nigeria, located within latitudes $4^{\circ}15'N$ and $6^{\circ}58'N$ and longitude $6^{\circ}50'E$ and $7^{\circ}59'E$ (Fig. 1). The study areas are well characterized by distinct dry (November – March) and wet (April – October) seasons (Nganje et al., 2015). Other geographical and meteorological settings of the states are well described in *Annual Abstract of Statistics* (2012) and *National Population Commission* (2009). The people, especially rural dwellers are known for farming and trading, with the civil servants residing mostly in the urban centres. The topography and physiography of these areas have been reported in literature (Omaka et al., 2017). Most parts of the sampled locations, especially the urban areas have good road networks, whereas most roads in the rural areas leading to the streams and springs are pedestrian.

2.1.2. Geology and hydrogeology

There are two principal geological formations in the states namely Bende-Ameki and the coastal plain sands otherwise known as Benin Formation, which is found around Aba, Umuahia, some parts of Imo state and its adjoining areas due to their proximity to the Atlantic Ocean (Fig. 2). Bende-Ameki formation overlies the impervious Imo shale group of Paleocene age, which is characterized by lateral and vertical variations in lithology (Akaninyene and Igboekwe, 2012). This geology formation comprises namely: the upper coal measure (Nsukka formation), false bedded sandstone (Ajali sandstone), lower coal measures (Mamu formation). The Nsukka formation consist of an alternating succession of sandstone, dirty shale and sandy shale with thin coal seam at various horizons (Nwajide, 2006). The Ajali sandstone consist of friable, poorly-sorted sandstones. The Mamu also has its type section at Mamu River Enugu district. It consists of distinctive assemblages of sandstone, shales, mudstone and sandy shale with coal seams at several horizons well bedded fine medium sandstone that are white or yellow in colour. Generally, these do not allow easy flow of runoff waters in the area and thus streets/road which do not have adequate drainage system are always flooded (Nwajide, 2006). The Asu River Group is predominantly shaley, with occurrences of siltstone, mudstone and limestone. In some areas, either boreholes or springs are difficult to locate. This is believed to be due to aquifer depth, topography and geology of the areas as described by Nganje et al. (2015) pointing to low permeability of the underlying impermeable shale rocks.

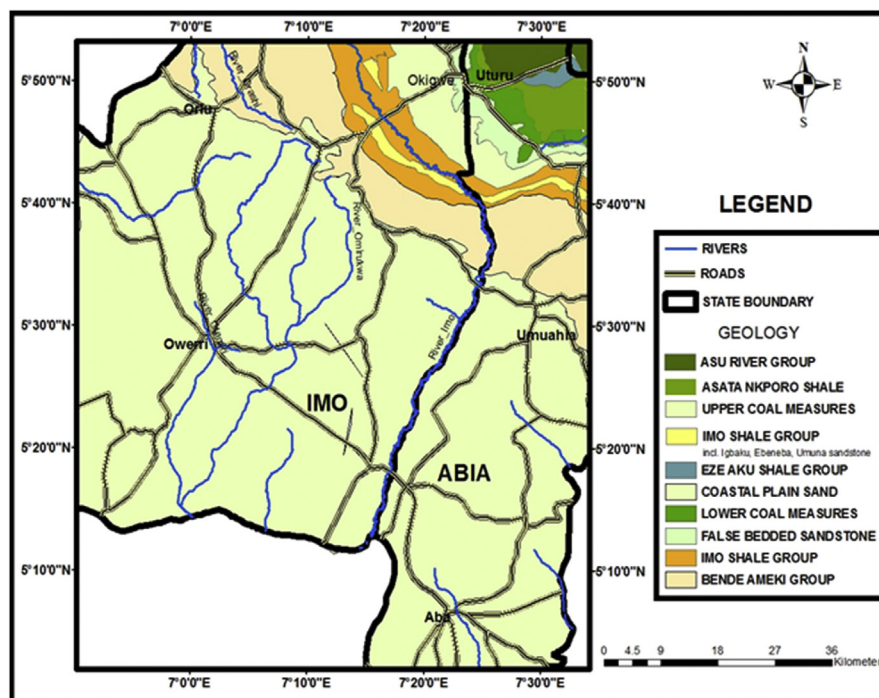


Fig. 2. Geology map of the study areas.

$\pm 0.071 \mu\text{g/mL}$ As (Lot No. H2AS02109) standards from INORGANIC VENTURES (Christiansburg, USA) traceable to NIST and pH buffers 4 and 7 (VMR chemicals, Belgium). Equipment used were: PerkinElmer[®] Optima 7300 DV ICP-OES interfaced to WinLab32[™] version 5.5 (PerkinElmer[®], Inc. Norwalk USA); PerkinElmer[®] Optima 8300 DV ICP-OES interfaced to Syngistix[™] version 3.0 (PerkinElmer[®], Shelton CT USA); GF-AAS model AA280Z (Agilent Technologies, Inc. Australia) with Zeeman background correction feature; and CV-AFS model PE-1000 (Nippon Instruments Corporation, Takatsuki Japan); HI9811-5 meter (HANNA Instruments, Romania).

2.3. Sampling and sample preparation

Stratified random sampling method was used, in which three senatorial districts of both states were sampled. Sixty-two samples were randomly collected from both urban and rural settlements from each state, making a total of 124 samples; and this is comprised of 13 springs (identified codes: SP1 – SP13); 24 streams (ST14 – ST37); 7 hand-dug wells (DW38 – DW44) and 80 boreholes (BH45 – BH124). The study was carried out between October 2017 and July 2018, across the two seasons. Supplementary Table 1S shows the sample codes, names, types and coordinates of the sampled stations. For borehole and hand-dug well samples, consent was sought from either the owners or caretakers who freely gave their names whereas those who preferred not to, were designated as *anonymous*.

Water sampling and preservation were performed in accordance with the procedure prescribed in [APHA \(2012\)](#). All sampling containers were pre-treated by soaking in 10% nitric acid (HNO_3) overnight, washed with Citranox® acid cleaner and detergent (NY, USA) and triple rinsed with double deionized water (18.2 MΩcm at 25 °C) from Milli-Q water purification system. Borehole taps were allowed to run at maximum flow for at least 3 minutes, followed by a reduction in the flow rate before sample collection. Hand dug wells were sampled by first agitating the water severally with the plastic sampler before collection. During sampling, 500 mL polyethylene container was used, then filtered into 100 mL polyethylene container through 0.45 μm membrane filter. In all cases, container was rinsed three times with the sample to be collected and filtrate was then acidified to pH below 2 with 0.5 mL conc. HNO_3 . Samples were stored in ice chest and taken to the laboratory where it was kept at 4 °C in the refrigerator prior to analysis not later than seven days of sampling. In situ tests, such as temperature, pH, Conductivity, and Total Dissolved Solids (TDS) were carried out using portable meters. Meters were calibrated each sampling day using the respective standards.

In the laboratory, sample preparation was done in accordance with procedures of [ASTM D1976](#). Reagent blanks, using demineralized water were also prepared in the same manner and used at 10% insertion rate.

2.4. Determination of Al, Cd, Co, Cr, Cu, Li, Mn, Ni, P, Se, V, Y, Zn, Ca, K, Mg, Na and Fe using ICP-OES

2.4.1. Instrument optimization and performance evaluation

The optimized instrument parameters are presented in Supplementary Table 2S. To check for efficiency in atomization, excitation and ionization processes in ICP, ionic (280.271 nm) to atomic (285.213 nm) lines intensity ratio of magnesium was used. The ratio obtained during the study was between 12.9 and 16.7.

Method detection limit (MDL) was determined as described by [EPA \(1994\)](#) and presented in Supplementary Table 3S together with the corresponding wavelengths of detection. Each calibration used a minimum of four points over the concentration range of 0–500 and 0–5000 μg/L for trace and major elements respectively. Calibration was linear and correlation coefficients for all elements were >0.999. Samples and blanks were analysed, and each reported result (after auto blank subtraction) was an average of three replicate measurements. Due to lack of Certified Reference Material (CRM), the accuracy of the equipment (ICP-OES 7300DV) was verified using validated Optima 8300 ICP-OES and spike recovery method. All these were done for quality control purposes. Result showed less than 5% error for both equipment (Supplementary Table 3S). Method precision was carried out by re-determining selected random replicate samples. The coefficient of variation was 1.79–4.37%.

For recovery studies, some water samples were fortified at different levels and taken through the entire analytical process with their corresponding unfortified samples. The recoveries varied from 93.6 to 114.8% (Supplementary Table 4S).

2.5. Determination of As and Pb using GF-AAS

2.5.1. Instrumentation and method validation

Graphite furnace atomic absorption spectrometer interfaced to SpectrAA version 5.1 and equipped with transversely heated platform atomizer (THPA) was used. An arsenic ultrAA HC and lead ultrAA HC lamps (Agilent technologies), operated at a current of 10 mA respectively were used as the line sources and optimized. The detections were performed at 193.7 and 282.3 nm, field of 0.8 T, and spectral slit width of 0.5R and 0.5 respectively. Omega platform tube (Agilent Part No. 6310003700) was used for THPA, and PSD-120 auto sampler was used for sample introduction into the atomizer tube.

Argon (Ar) with purity of 99.999% (BOC special Prod/Twisco, Nigeria) was used, while peak area was applied exclusively for signal evaluation and quantification. The matrix modifier used was 0.1%(m/v) Pd+0.03%(m/v) Mg+0.05%(v/v) Triton X-100 + 2% citric acid+0.6%(v/v) HNO₃ solution. Bulk standard (30 µg/L) was prepared by serial dilution from the stock, while working standards (1, 3, 5 and 8 µg/L) were auto prepared by the equipment. Dilution of over ranged concentrations was performed automatically. Sample (30 µL) was injected on 'hot inject' mode, with modifier introduction on 'pre-inject' mode. The graphite furnace temperature program for the analysis is presented in Supplementary Table 5S.

Method detection limit for As and Pb was 0.5 and 0.7 µg/L respectively. The RSD for randomly selected replicate samples was 2.16 and 2.77%. The recoveries varied from 99 to 107% for As and 88–102% for Pb (Supplementary Table 6S).

2.6. Determination of Hg using CV-AFS

2.6.1. Instrumentation and optimization

Measurement of Hg was done using PE-1000 Nippon mercury analyser (Supplementary Fig. 1S), equipped with auto sample changer and interfaced to PE1000-Win version 1.6.4, which offers a direct sample matrix analysis with patented catalysts and combustion tubes that eliminate external and cumbersome acid/alkali pre-treatment and reduction processes. The equipment was operated as recommended by the manufacturer for water sample type, and in accordance with EPA method 245.7 (EPA, 2005). The determined MDL was 0.03 µg/L. RSD on selected replicate samples was 2.2%. The recoveries varied from 101 to 107% (Supplementary Table 6S).

2.7. Water quality index

Water quality index (WQI), which is based on calculation that reflects the integrated impact of different water quality variables (Meng et al., 2016) was performed. In the present study, having considered only elements as input parameters, water quality index was calculated based on the factor loadings of the individual elements in a principal component (PC) and the associated Eigen values. Assigned weight was then calculated as relative loading values on the same PC multiplied by relative Eigen values. WQI was calculated as given below:

$$WQI = \sum \left[w_i \times \left(\frac{c_i}{s_i} \right) \right] \times 100 \quad (1)$$

where w_i represents the weight attributed to each parameter i . The value of w_i is assigned based on the eigenvalues for each principal component and factor loading for each parameter from the PCA results and represents the relative importance of each individual water quality parameter for drinking purpose (Wang, 2018). In Eq. (1), c_i is the element's concentration in water samples while s_i is the Nigerian Standard for Drinking Water Quality for each element. Water sources were then classified based on the calculated WQI values where $0 \leq WQI \leq 50$ indicates excellent water quality; $50 < WQI \leq 100$ indicates good water quality; $100 < WQI \leq 200$ indicates poor water quality; $200 < WQI \leq 300$ indicates very poor water quality, while $WQI > 300$ represents water that is unsuitable for drinking (Meng et al., 2016).

2.8. Health risk assessment

Hazard quotient (HQ) and hazard index (HI) have been extensively used for aquatic risk assessments and they are recommended by the U.S. Environmental Protection Agency (EPA, 2004). For short-term risk assessment, intake of toxic metals was calculated through estimated weekly intake (EWI) and acute HQ following Eqs. (2) and (3) below (Lin et al., 2015):

$$EWI = \frac{IR \times C_w \times 7 \text{ days}}{BW} \quad (2)$$

$$HQ = EWI/PTWI \quad (3)$$

where PTWI is provisional tolerable weekly intake of metals (FAO, 2004, 2010, 2011), which is the maximum amount of a contaminant to which a person can be exposed per week over a lifetime without an unacceptable risk of health effects; IR is the ingestion rate (2 and 0.64 L/day for adults and children, respectively); C_w is the average element concentration in each water source ($\mu\text{g/L}$) and BW is the average body weight (70 kg for adults and 15 kg for children). According to

Leung et al. (2008) if EWI/PTWI ratio exceeds 1 ($HQ > 1$) there is a serious possibility for development of some health issues.

For long-term risk assessment, we explored the two major routes of metals exposure to human: ingestion and dermal absorption and these were assessed using the Average Daily Dose ($ADD_{\text{ingestion}}$ and ADD_{dermal}), Hazard Quotient ($HQ_{\text{ingestion}}$ and HQ_{dermal}) and Hazard Index ($HI_{\text{ingestion}}$ and HI_{dermal}) (Singh et al., 2018). HQ is the ratio of exposure through individual pathways to the reference dose (RfD). HI is the sum of the HQs for individual waterborne element from both exposure routes.

$$ADD_{\text{ingestion}} = \frac{C_w \times IR \times EF \times ED}{BW \times AT} \quad (4)$$

$$ADD_{\text{dermal}} = \frac{C_w \times SA \times K_p \times ET \times EF \times ED \times 10^{-3}}{BW \times AT} \quad (5)$$

$$HQ_{\text{ingestion}} = \frac{ADD_{\text{ingestion}}}{RfD_{\text{ingestion}}}; HQ_{\text{dermal}} = \frac{ADD_{\text{dermal}}}{RfD_{\text{dermal}}} \quad (6)$$

$$RfD_{\text{dermal}} = RfD_{\text{ingestion}} \times ABS_{GI} \quad (7)$$

$$HI = \sum HQ_s \quad (8)$$

Considering Eqs. (4), (5), (6), (7), and (8), $ADD_{\text{ingestion}}$ and ADD_{dermal} represent the average daily dose from ingestion and dermal absorption respectively, and are given in $\mu\text{g}/\text{kg}/\text{day}$; C_w is the average element concentration in each water source ($\mu\text{g}/\text{L}$); BW is the average body weight (70 kg for adults and 15 kg for children); IR is the ingestion rate (2 and 0.64 L/day for adults and children, respectively); EF is the exposure frequency (365 days/year); ED is the exposure duration (30 and 6 years for adults and children, respectively); AT is the average time ($ED \times 365$ days/year); SA is exposed skin area (18,000 cm^2 for adults and 6600 cm^2 for children); ET is exposure time (0.58 and 1 h/day for adults and children, respectively); K_p is the dermal permeability coefficient in water (cm/h); RfD is the corresponding reference dose ($\mu\text{g}/\text{kg}/\text{day}$) and ABS_{GI} is the gastrointestinal absorption factor (dimensionless). These values were referenced from EPA (2004) and Wang (2018) and are presented in Table 7.

For $HI < 1$, no risks from non-carcinogenic effects are expected, while $HI > 1$ indicates a likelihood of adverse health effects and the probability of such effects increases with the increase in the HI values (Wu et al., 2018).

2.9. Data analysis

Descriptive statistics was performed on parameters obtained from individual water sources. For comparison of the spatial differences of the water quality parameters in the sources, one-way analysis of variance (ANOVA) was conducted in this study ($p < .05$). Correlation matrix, Factor/Principal Component Analysis (FA/PCA) and hierarchical agglomerative Cluster Analysis (CA) were also used to explore the possible sources of PTEs by reducing the dimensionality of the dataset to several influencing factors (Li et al., 2011).

All data processing was conducted using Microsoft Office Professional Plus 2013, Statistical Package for Social Sciences (SPSS[®]) version 16 (SPSS inc., USA) and STATISTICA[®] version 10 (StatSoft, Inc. 2011). The sampling locations were fixed by Global Positioning System and the coordinates were plotted using ArcGIS[®] 10.4 software. It is worth mentioning that values that were very low and below the method detection limit (<MDL) were treated as 'zero' while only detectable concentrations were used for statistical analysis.

3. Results and discussion

3.1. Summary of Kolmogorov-Smirnov/Shapiro-Wilk tests of data

Kolmogorov-Smirnov (K-S) and Shapiro-Wilk (S-W) statistics were used to test the normal distribution of the data. Normal Q-Q plots were used to visualize the normality of data, while p-value was used to confirm parameters that showed normal distribution. The result showed that 21 elements together with pH, conductivity and TDS (Table 1) did not conform to a normal distribution, whereas average temperature showed normal distribution.

The results obtained from the K-S and S-W tests together with large standard deviation values for the parameters that depicted no normal distribution indicated that the mean values might have been affected by the presence of outliers, which corresponded to samples with extremely low or high values. Nevertheless, this study made use of arithmetic means for comparisons because the results reported in the guidelines are generally given as arithmetic means.

3.2. Physicochemical characteristics

The water quality parameters (water temperature, pH, conductivity and TDS) in the water samples from the drinking water sources are listed in Table 1. Small variation was observed in the temperature values of hand-dug wells, which varied from 28.0 to 29.2 °C; whereas springs, streams and boreholes had larger variations ranging from 27.1 – 31.0, 26.8–31.6 and 25.5–32.7 respectively. The relatively large variation

Table 1. Summary of physico-chemical and trace elements concentrations of drinking water sources from Southeastern Nigeria.

		Temp	pH	Cond	TDS	Ca*	K	Mg	Na	Fe	Al	As	Cd
		°C		µS/cm	mg/L	mg/L				µg/L			
Springs (n = 13)	Min	27.1	3.6	20	10	0.06	0.02	0.09	0.74	0	10	0.00	0.00
	Max	31.0	6.8	370	194	15.64	16.31	3.52	39.24	520	1100	0.06	0.43
	Median	28.3	4.7	30	17	0.91	1.73	0.19	2.85	17	100	0.00	0.00
	Mean	28.3	5.1	65	35	2.10	2.69	0.55	5.20	130	224	0.01	0.03
	SD	1.1	1.0	94	49	4.18	4.27	0.92	10.30	180	309	0.02	0.12
Streams (n = 24)	Min	26.8	4.4	10	5	0.21	0.17	0.10	0.59	30	20	0.00	0.00
	Max	31.6	6.9	202	107	15.24	8.60	2.09	16.47	4740	1309	2.65	0.00
	Median	28.5	5.9	30	16	0.73	0.96	0.29	1.41	747	119	0.10	0.00
	Mean	28.6	5.8	47	25	2.42	1.68	0.53	3.47	1345	237	0.32	0.00
	SD	1.5	0.6	45	24	3.45	2.05	0.54	4.17	1203	307	0.56	0.00
Dug wells (n = 7)	Min	28.0	4.3	20	11	0.90	0.30	0.07	0.82	10	30	0.00	0.00
	Max	29.2	5.4	270	151	10.53	6.10	2.02	31.91	770	289	0.19	0.00
	Median	28.6	4.6	70	41	1.80	2.80	0.54	4.64	39	123	0.02	0.00
	Mean	28.5	4.7	91	50	4.64	3.12	0.75	7.64	152	129	0.05	0.00
	SD	0.5	0.4	84	47	4.30	1.95	0.63	10.90	277	81	0.07	0.00
Boreholes (n = 80)	Min	25.5	3.1	10	5	0.14	0.00	0.07	0.28	0	0	0.00	0.00
	Max	32.7	6.3	510	286	13.43	14.19	3.01	50.46	1260	3312	1.27	1.03
	Median	29.1	4.7	50	25	0.51	0.66	0.22	1.62	10	41	0.00	0.00
	Mean	28.9	4.7	61	33	1.19	1.65	0.44	3.64	46	138	0.13	0.04
	SD	1.5	0.6	64	35	1.94	2.53	0.53	6.22	148	408	0.29	0.16

(continued on next page)

Table 1. (Continued)

		Temp	pH	Cond	TDS	Ca*	K	Mg	Na	Fe	Al	As	Cd	
		°C		µS/cm	mg/L	mg/L				µg/L				
Total (n = 124)	Min	25.5	3.1	10	5	0.06	0.00	0.07	0.28	0	0	0.00	0.00	
	Max	32.7	6.9	570	286	15.64	16.31	3.52	50.46	4740	3312	2.65	1.03	
	Median	28.9	4.8	45	23	0.59	0.94	0.24	1.77	19	49	0.00	0.00	
	Mean	28.8	5.0	61	32	1.72	1.84	0.49	4.00	312	166	0.15	0.03	
	SD	1.4	0.8	65	36	2.83	2.66	0.59	6.73	742	369	0.35	0.14	
	K-S Test^a	0.20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	S-W Test^b	0.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Co	Cr	Cu	Hg	Li	Mn	Ni	P	Pb	Se	V	Y	Zn
		µg/L												
Spring (n = 13)	Min	0.00	0.00	0.00	0.00	0.00	0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	3.23	1.55	2.71	0.02	2.49	129	3.26	6.12	0.00	22.88	1.89	2.67	71.55
	Median	0.58	0.00	0.19	0.00	0.00	5.7	0.00	0.01	0.00	0.00	0.07	0.32	0.00
	Mean	0.80	0.23	0.67	0.00	0.68	18.5	0.50	1.05	0.00	5.02	0.30	0.64	9.91
	SD	0.90	0.51	0.91	0.01	0.98	34.4	1.02	1.82	0.00	7.60	0.52	0.89	21.26
Stream (n = 24)	Min	0.00	0.00	0.00	0.00	0.00	3.3	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	11.11	7.27	5.06	0.02	1.58	66.1	5.36	9.30	0.86	40.89	2.88	2.69	85.86
	Median	0.70	0.17	0.59	0.01	0.00	22.8	0.48	1.83	0.00	0.00	0.18	0.00	0.00
	Mean	1.42	1.37	1.02	0.01	0.09	25.7	1.00	2.63	0.09	5.22	0.69	0.24	6.56
	SD	2.28	1.98	1.29	0.01	0.33	14.6	1.44	3.04	0.23	10.66	0.90	0.69	18.47
Dug well (n = 7)	Min	0.00	0.00	0.07	0.00	0.00	4.9	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	4.82	3.99	3.76	0.02	6.74	154	5.64	7.67	32.34	12.52	0.02	5.25	97.69
	Median	0.22	1.60	0.87	0.02	0.17	7.9	2.83	0.00	0.62	1.52	0.00	0.00	2.77
	Mean	1.64	1.58	1.19	0.01	1.54	47.4	2.62	1.25	5.18	3.87	0.00	0.83	24.31

(continued on next page)

Table 1. (Continued)

Borehole (n = 80)	SD	2.05	1.64	1.32	0.01	2.52	68.5	2.59	2.86	12.00	5.07	0.01	1.96	37.65
	Min	0.00	0.00	0.00	0.00	0.00	2.5	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	6.32	30.21	185	0.25	7.24	351	9.28	184	15.42	39.44	1.41	28.52	139
	Median	0.45	0.00	7.86	0.01	0.00	14.6	0.00	8.88	0.80	0.00	0.00	0.16	0.00
	Mean	0.81	3.46	16.26	0.02	1.27	32.8	1.14	17.84	1.66	1.76	0.24	1.28	10.29
Total (n = 124)	SD	1.07	8.48	26.27	0.04	2.02	57.3	2.05	26.56	2.82	5.40	0.37	3.74	23.22
	Min	0.00	0.00	0.00	0.00	0.00	0.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Max	11.11	30.21	185	0.25	7.24	351	9.28	184	32.34	40.89	2.88	28.52	139
	Median	0.53	0.00	2.60	0.01	0.00	15.0	0.00	4.80	0.24	0.00	0.00	0.00	0.00
	Mean	0.98	2.61	10.83	0.01	1.00	30.8	1.13	12.20	1.38	2.89	0.32	0.99	10.32
	SD	1.44	6.96	22.31	0.03	1.81	50.3	1.92	22.68	3.68	7.02	0.55	3.09	23.18
	K-S Test^a	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	S-W Test^b	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

* Major elements concentrations are in mg/L; trace elements are in µg/L.

^a Kolmogorov Smirnov test with Lilliefors Significance Correction.

^b Shapiro-Wilk test.

observed for these water sources (springs, streams and boreholes) could be attributed to their exposure to sunlight compared to the hand-dug wells. However, the average temperature recorded for all the sources was 28.8 °C. The drinking water sources were generally acidic. Only two springs and four streams had pH values that are in the range of 6.5–6.9, which corresponded to Nigerian Standard Drinking Water Quality limit of 6.5–8.5 (NSDWQ, 2007). The overall conductivity (10–570 $\mu\text{S}/\text{cm}$) and TDS (5–286 mg/L) of the water sources were generally low with the highest being 1.7 times lower than NSDWQ limit. The elements, Ca, K and Na were found in ranges of 0.06–15.64, 0.00–16.31 and 0.28–50.46 mg/L respectively and these are below the NSDWQ limits. The observed range for Mg is 0.07–3.52 mg/L and Mg concentration exceeded the recommended limit of 0.2 mg/L (NSDWQ, 2007) in about 57 % of the total samples studied.

3.3. Spatial variability of trace elements in water sources

Analysis of variance (ANOVA, Supplementary Table 7S) indicated no statistical differences ($p < .05$) for Al, Cd, Co, Cr, Mn, Hg, Ni, Se, Y and Zn for the different water sources. However, the mean contents of As, Cu, Fe, Li, P, Pb and V for the sources were statistically different. The higher Fe concentrations observed for streams could be as a result of oxidation and reduction processes within the water bodies. Insoluble Fe in the stream sediments, might be reduced into dissolved speciation under a reducing condition and diffuse upward. More so, Supplementary Fig. 2S elucidated the discrepancies in elements content for the different water sources. The average concentrations of these elements are in the following order: Al > Fe > Mn > Zn > Se in springs; Fe \gg Al > Mn > Zn > Se in streams; Fe > Al > Mn > Zn > Se in hand-dug wells and Al > Fe > Mn > Zn > Se in boreholes. All the water sources investigated had very low Cd and Hg contents that ranged from 0 – 1.0 and 0–0.3 $\mu\text{g}/\text{L}$ respectively.

Considering the spatial distribution of the elements determined, it was concluded that Al, Mn, Se and Zn demonstrated the same pattern of distribution with no significant difference, which indicates that they are likely from the same source. The concentrations of Cu, Pb and P were higher in boreholes compared to the other water sources. These elements could be anthropogenic in nature and may result from leaching from the plastic water tanks and corrosion of metallic tanks. The streams were loaded with Fe and Al, which could result from crustal materials.

3.4. Extent of water sources contamination

Guidelines for drinking water established by WHO (2017), EPA (2018) and NSDWQ (2007) were used as benchmark to evaluate the level of contamination by PTEs (Table 2). Only the average concentrations of Al (for springs and streams), and Fe (for streams) were higher than the respective limits established by WHO,

Table 2. Comparison of data from present study (trace elements, µg/L) with drinking water guidelines and data from literature.

		Al	As	Cd	Cr	Hg	Pb	Se	V	Zn	Fe	Mn	Co	Ni	Cu
Country	NSDWQ	200	10	3	50	1	10	-	-	3000	300	200	-	20	1000
	EPA	-	10	5	100	2	15	10	-	-	200	50	-	20	2000
	WHO	200	10	3	50	6	10	40	-	-	300	100	-	70	2000
Our study	Nigeria Springs	224	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	9.9	130	19	<MDL	<MDL	<MDL
	Streams	237	<MDL	<MDL	1.4	<MDL	<MDL	<MDL	0.70	6.6	1345	26	1.4	<MDL	1.0
	Boreholes	138	<MDL	<MDL	3.5	<MDL	1.7	<MDL	<MDL	10.3	46	33	<MDL	<MDL	16.3
	Dug wells	129	<MDL	<MDL	1.6	<MDL	5.2	<MDL	<MDL	24.3	152	47	1.6	<MDL	1.2
Omaka et al. (2014)	Nigeria Boreholes	-	670	0.0	19.6	-	8.0	-	-	44.5	792	129	-	12.0	56.0
Adamu et al. (2015)	Nigeria Stream	-	2.0	-	-	20.0	48.0	-	-	66.0	1497	131	-	2.0	-
Igwe et al. (2015)	Nigeria Boreholes & wells	-	<1.0	<1.0	-	-	<1.0	<1.00	-	<10	-	-	-	-	<1.0
Nganje et al. (2015)	Nigeria Streams	4160	1.9	1.8	4.8	-	38.9	-	1.8	1083	3169	575	10.7	19.0	18.9
	Dug wells	4180	1.7	1.0	3.9	-	39.1	-	1.7	2169	1931	434	4.5	47.3	22.2
	Boreholes	2973	1.7	3.0	3.3	-	254.6	-	1.6	1050	1710	401	6.1	8.8	12.8
Omaka et al. (2017)	Nigeria Boreholes	-	1563	173	-	-	2.1	-	-	1434	315	2179	-	6.2	11.1
	Dug wells	-	2277	167	-	-	3.5	-	-	1468	291	1873	-	7.8	4.8
Kumar et al. (2016)	India Tube wells	-	32.1	0.1	0.3	-	3.2	0.6	-	30.8	-	452	0.3	1.4	3.5
Kostic et al. (2016)	Serbia Tap water	17.8	4.7	0.2	ND	-	ND	ND	ND	183	10	1	ND	0.1	3.0
	Well	ND	52.0	1.31	ND	-	3.4	1.2	0.2	469	540	92	0.3	1.9	4.4
Karakaya and Karakaya (2014)	Turkey Stream	10.2	65.7	13.7	-	-	24.3	12.7	1.6	3.2	57	0.5	77.6	7.7	5.0
	Spring	3.7	1.7	2.4	-	-	28.3	0.5	1.1	0.4	4	3.6	2.8	3.9	0.3

NSDWQ Nigerian Standard for Drinking Water Quality, WHO World Health Organization, EPA United States Environmental Protection Agency.

EPA and NSDWQ. Nevertheless, some 22 individual sampling stations had Al, while 3 stations had Pb concentrations higher than the established limits. Although Al was not originally considered to be a significant health hazard in drinking water, it has been recently shown to pose a potential danger to persons suffering from kidney disorders (EPA, 2001). Al is indicted as one of the causes of neurological problems (Mir-Marqués et al., 2012) and a contributory factor to Alzheimer disease (EPA, 2001). Additionally, Se content of water from ten (10) sampling stations were above the permissible limit set by EPA. Manganese was found above NSDWQ limit in samples from six (6) sampling points while Fe was found above the stated established limits in 26 sampled water stations. Furthermore, the mean metal values from this study were compared with mean values reported in literatures within and outside Nigeria (Table 2). The average levels of As and Cd in boreholes (1563.2 and 173.4 µg/L) and dug wells (2276.8 and 167.0 µg/L) respectively were reported for this region, which is not in agreement with our study nor others conducted in Nigeria (Table 2).

3.5. Statistical analysis

Cluster analysis, correlation matrix, factor and principal component analysis were some of the useful statistical approaches applied to the dataset.

3.5.1. Cluster analysis

Samples from all water sources were used for classification based on spatial resemblances of variables by hierarchical cluster analysis (CA) using the average linkage method (between groups). Fig. 3 shows the dendrogram with two statistically

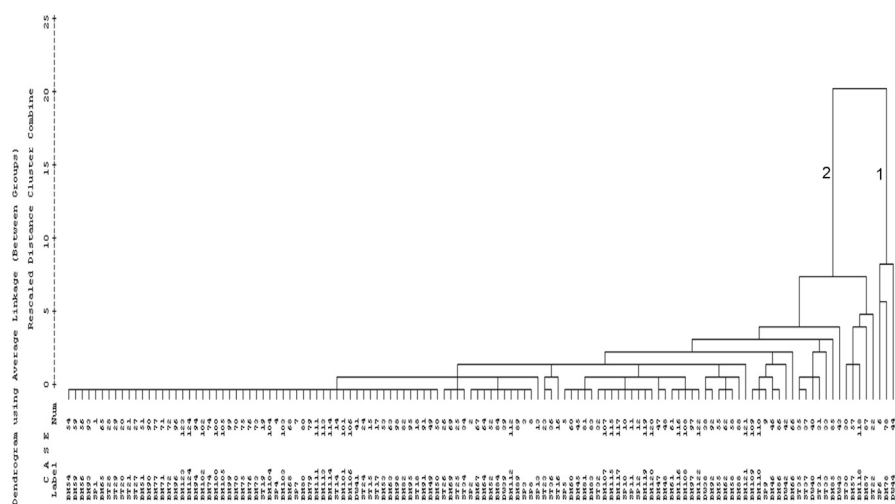


Fig. 3. Dendrogram based on agglomerative hierarchical clustering for 124 drinking water sampling sites.

different clusters at $(D_{link}/D_{max}) \times 100 < 25$, each consisting of two subgroups. Cluster 1 contained only 3 sites, while cluster 2 contained the remaining 121 sampling sites, with a subgroup containing 5 sites and the other subgroup, 116 sites. On the basis of average trace elements concentrations, cluster 1 and cluster 2 were assigned as group of moderate pollution and low pollution by trace elements respectively. Samples in cluster 1 contained pollutants believed to have come from crustal materials, whereas majority of sampling points in cluster 2 possessed pollutants with possible anthropogenic or natural origin, depending on the subgroup.

3.5.2. Correlation matrix

Correlation matrix was used to identify inter-relationships between the 21 elements (Table 3). The classification method adopted by Wang (2018) was used. In this classification, $r < 0.3$ was considered of no relevance; $0.3 < r < 0.5$ as 'less relevance'; $0.5 < r < 0.8$ as median relevance; and $r > 0.8$ as of high relevance (Wang, 2018). Generally, strong positive correlations ($p < 0.01$) with correlation coefficients varying from 0.815 – 0.981 were observed for the pairs of Mg-K; Cu-P; Al-Y and Ca-Mg, which were found to be of high relevance. Median relevance was observed for Ca-K-Na-Mg; Hg-Y; Cr-Mn, Al-Ca; Mg-Al and Na-Al with correlation coefficients varying from 0.500 – 0.791, while the pairs of Al-Hg; Cr-Hg; Mn-Mg and Mn-Na showed less relevance with correlation coefficients from 0.472 – 0.479. The correlation of the elements with TDS showed that median positive correlation exists between TDS and Ca, K, and Mg varying from 0.703 to 0.740, while the pairs of Na-TDS correlated significantly with high relevance of 0.879 (Table 3). Almost all trace elements did not significantly correlate with TDS except Hg and Y, which had less and median positive correlations respectively (Table 3). Total dissolved solid (TDS) indicates the level of dissolved constituents in the water body. High dissolved constituents and low ionic activity can therefore suggest the occurrence of pollutant loading, reduced oxygen and therefore the presence of a contaminant plume in the water body (Ezekwe et al., 2012). Thus, the positive relationship between TDS and Hg suggests that constant monitoring of mercury in these drinking water sources is vital, especially at elevated TDS. Helena et al. (2000) suggested that elements with high correlation coefficients in the water body could have similar hydrochemical characteristics.

3.5.3. Factor and principal component analysis

Principal Component Analysis (PCA) was used to additionally probe the sources of the elements by extracting some dominating influencing factors from the standardized data set (Helena et al., 2000). The factor contribution or variables with minor significance obtained by PCA were further reduced using factor analysis (FA) with a varimax rotation method. Kaiser-Meyer-Olkin (KMO) and Bartlett's

Table 3. Correlation matrix of elements in drinking water sources from Southeastern Nigeria.

	TDS	Ca	K	Mg	Na	Fe	Al	As	Cd	Co	Cr	Cu	Hg	Li	Mn	Ni	P	Pb	Se	V	Y	Zn	
TDS	1																						
Ca	0.740**	1																					
K	0.703**	0.758**	1																				
Mg	0.734**	0.839**	0.826**	1																			
Na	0.879**	0.791**	0.745**	0.766**	1																		
Fe	-0.049	0.102	-0.016	0.068	-0.018	1																	
Al	0.618**	0.500**	0.421**	0.509**	0.677**	0.024	1																
As	-0.056	-0.063	-0.138	-0.066	-0.052	0.382**	-0.06	1															
Cd	-0.027	-0.096	-0.11	-0.047	-0.013	-0.085	-0.05	0.116	1														
Co	0.181*	0.151	0.131	0.15	0.160	0.246**	0.048	0.027	-0.029	1													
Cr	0.028	-0.085	-0.138	0.016	0.052	-0.032	0.055	0.258**	0.639**	-0.12	1												
Cu	-0.076	-0.145	-0.091	-0.105	-0.088	-0.159	-0.094	0.083	0.115	-0.02	0.016	1											
Hg	0.407**	0.195*	0.126	0.232**	0.442**	-0.090	0.479**	0.082	0.142	-0.154	0.479**	0.006	1										
Li	0.000	-0.165	-0.159	-0.057	-0.046	-0.178*	-0.026	0.145	0.584**	0.031	0.775**	0.032	0.341**	1									
Mn	0.428**	0.324**	0.231**	0.474**	0.472**	0.006	0.380**	0.015	0.141	0.054	0.532**	-0.037	0.428**	0.343**	1								
Ni	0.037	-0.018	-0.02	-0.020	-0.005	-0.046	-0.026	-0.128	-0.118	0.251**	-0.154	0.047	-0.161	0.017	0.017	1							
P	-0.101	-0.158	-0.122	-0.118	-0.099	-0.147	-0.110	0.094	0.169	-0.03	0.083	0.981**	0.021	0.067	-0.003	0.057	1						
Pb	-0.040	-0.077	-0.074	-0.054	-0.068	-0.117	-0.055	-0.028	-0.024	-0.022	-0.065	0.423**	-0.04	-0.045	-0.081	0.087	0.419**	1					
Se	-0.084	-0.093	-0.025	-0.062	-0.093	0.126	0.005	-0.081	-0.014	0.173	-0.034	-0.110	-0.104	0.000	-0.05	0.234**	-0.132	-0.070	1				
V	-0.095	0.058	-0.009	0.003	-0.052	0.323**	0.147	0.223*	-0.099	0.143	-0.158	0.093	-0.132	-0.214*	-0.155	-0.042	0.089	0.026	-0.140	1			
Y	0.611**	0.391**	0.312**	0.419**	0.665**	-0.106	0.815**	-0.062	0.059	0.070	0.197*	-0.051	0.575**	0.099	0.525**	0.006	-0.048	-0.040	-0.000	-0.140	1		
Zn	0.110	0.101	0.200*	0.214*	0.089	-0.004	0.029	-0.116	0.170	0.186*	0.180*	0.213*	0.099	0.294**	0.230*	0.031	0.207*	0.120	-0.010	0.008	0.020	1	

Bold: strong positive correlation coefficients.

*Correlation is significant at the 0.05 level (2-tailed).

**Correlation is significant at the 0.01 level (2-tailed).

sphericity test (Li et al., 2011) were used to assess the suitability of the data for factor analysis. The excellent value of KMO (0.681) and Bartlett's sphericity test significance (<0.001) buttressed the adequacy of our data for FA. Presented in Table 4 is the results of FA/PCA, including the eigenvalues, variance and communalities. In doing this, only independent factors with eigenvalues greater than 1 were extracted.

The factor loadings were classified as 'strong', 'moderate', and 'weak' according to the absolute loading values of >0.75 , $0.75-0.50$, and $0.50-0.30$, respectively (Liu et al., 2003). Six independent factors were extracted, accounting for 70.88% of the total variance. The first factor, which accounted for 16.92% of the total variance, had strong positive loadings of Ca (0.86), K (0.89) and Mg (0.90); moderate loading of

Table 4. Varimax rotated component matrix for elements in water (the significance of Kaiser-Meyer-Olkin (KMO) and Bartlett's sphericity test is < 0.001).

Eigenvalues	3.55	2.83	2.78	2.41	1.74	1.57	
Variance (%)	16.92	13.48	13.22	11.50	8.31	7.45	
Cumulative (%)	16.92	30.40	43.62	55.12	63.43	70.88	
Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communalities
Ca	0.86	-0.11	0.25	-0.11	0.07	-0.04	0.83
K	0.89	-0.11	0.11	-0.06	-0.08	-0.02	0.83
Mg	0.90	0.02	0.25	-0.07	0.02	-0.01	0.87
Na	0.75	-0.01	0.56	-0.05	-0.02	-0.01	0.87
Fe	0.06	-0.05	-0.07	-0.21	0.78	0.18	0.69
Al	0.38	-0.11	0.80	-0.03	0.08	0.04	0.80
As	-0.17	0.21	0.08	0.02	0.72	-0.16	0.62
Cd	-0.05	0.75	-0.03	0.06	-0.00	-0.09	0.58
Co	0.27	0.05	-0.11	0.02	0.30	0.65	0.60
Cr	-0.11	0.89	0.26	-0.05	0.06	-0.13	0.89
Cu	-0.06	0.07	-0.02	0.94	0.04	-0.04	0.90
Hg	0.06	0.34	0.73	0.01	-0.04	-0.20	0.69
Li	-0.12	0.88	0.09	-0.01	-0.10	0.06	0.81
Mn	0.34	0.47	0.50	-0.04	-0.03	0.07	0.59
Ni	-0.04	-0.10	0.02	0.13	-0.15	0.72	0.57
P	-0.08	0.12	-0.01	0.94	0.05	-0.05	0.91
Pb	-0.04	-0.09	-0.01	0.64	-0.08	0.03	0.43
Se	-0.15	-0.01	0.04	-0.18	-0.06	0.66	0.50
V	0.06	-0.23	-0.06	0.16	0.67	-0.07	0.54
Y	0.26	0.06	0.88	-0.01	-0.10	0.08	0.86
Zn	0.41	0.44	-0.22	0.29	-0.05	0.19	0.53

Extraction method: Principal component analysis.

Rotation method: Varimax with Kaiser Normalization.

Na (0.75) and weak loadings of Al (0.38), Mn (0.34) and Zn (0.41). Factor 1 can be attributed to natural contribution because of the elements involved. Factor 2 explains 13.48% of the total variance and was correlated with Cd (0.75), Cr (0.89), Li (0.88), Zn (0.44), Hg (0.34) and Mn (0.47), which are elements that have mixed natural and anthropogenic origins. Factor 3, which accounted for 13.22% of the total variance had strong positive loadings of Al (0.80) and Y (0.88), moderate loadings of Hg (0.73) and Na (0.56); and is weakly correlated with Mn (0.50). Although the aluminium concentrations in our study was high, its high occurrence in almost all water sources sampled led us to attribute factor 3 to natural contribution. Aluminium is a major component of crustal materials (Kumar et al., 2001), and thus, could be the source of Al. Mercury was generally very low and could be of natural origin. Factor 4 explained 11.50% of the total variance and was correlated with Cu (0.94), Pb (0.64) and P (0.94) only. The slightly elevated levels of Pb and Cu observed in borehole water samples indicates that they could be of anthropogenic origin. Fe (0.78), As (0.72) and V (0.67) were loaded in factor 5, which explained 8.31% of the total variance. Fe is ubiquitous in water bodies while As in drinking water is typically caused by the weathering and dissolution of arsenic bearing rocks, minerals and ores (EPA, 2018). More so, the lower values of As and V suggests that factor 5 could be attributed to the weathering of rocks. The remaining elements: Co (0.65), Ni (0.72) and Se (0.66) were loaded in factor 6, which accounted for 7.45% of the total variance. Their low values suggested that they could be from natural sources. Additionally, standardized biplot (Fig. 4), which plots variables and cases, and shows how variables

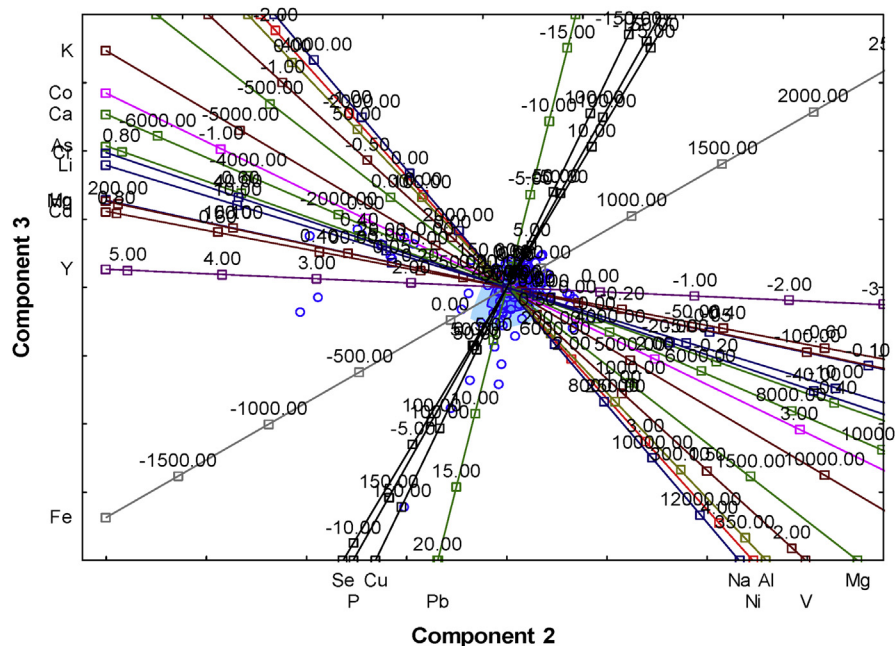


Fig. 4. Standardized biplot based on concentration of metals in drinking water sources in the space of second and third components.

are correlated was employed together with unrotated loadings (Fig. 5) to visualize the factor loadings of the variables.

3.5.4. Water quality index

The weights of 21 variables (w_i) were obtained based on the FA/PCA results and summarized in Table 5. The water quality index (WQI) calculated using Eq. (1) ranged from 3.75 – 70.58, 7.51–71.04, 5.81–45.92 and 1.52–132.34 for samples from springs, streams, hand-dug wells and boreholes respectively. However, the WQI values calculated based on the average concentrations of dissolved elements at the different water sources ranged from 12.99 – 33.30, with an average of 20.01, which indicated excellent water quality for the water bodies under study. Nevertheless, one borehole can be categorized as being of ‘poor quality’ considering the high values of the parameters determined including TDS, Al, Hg, Pb, when compared to other sources of drinking water in the districts.

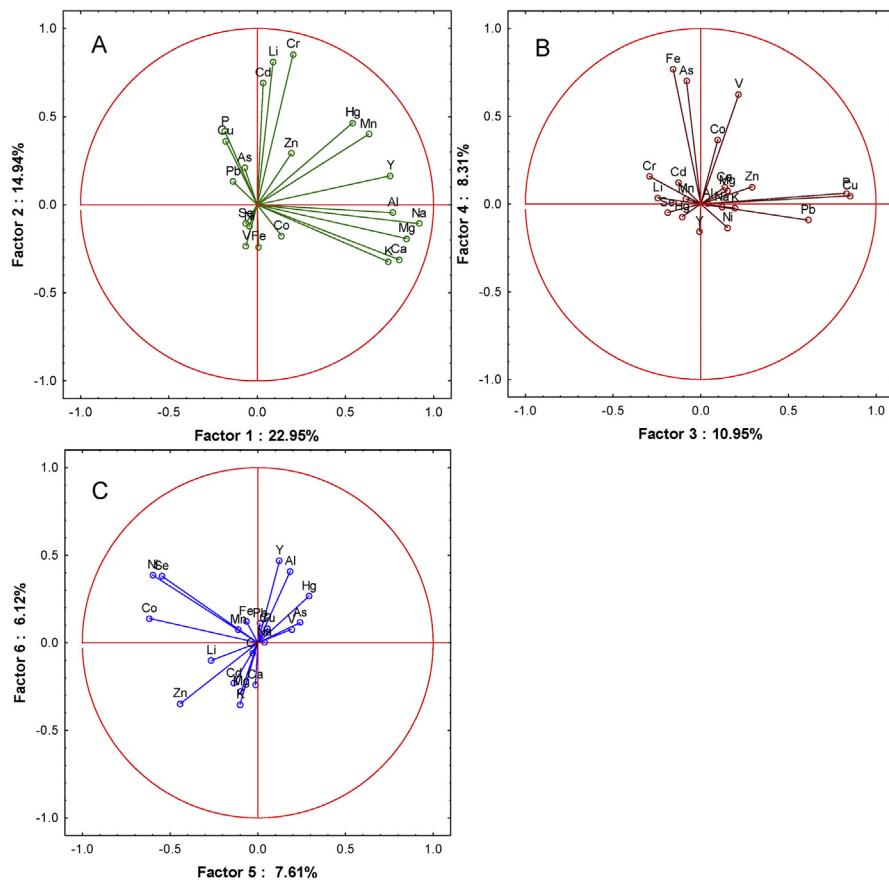


Fig. 5. Plots of loadings (unrotated) based on concentration of metals in drinking water sources in the space of (A) first and second; (B) third and fourth; and (C) fifth and sixth factors.

Table 5. Calculated weights for the 21 metals determined in the drinking water sources.

PC	Eigen value	Relative eigen value	Variable	Loading value	Relative loading value on same PC	Weight (relative eigen value × relative loading value)
1	3.55	0.24	Ca	0.86	0.25	0.06
			K	0.89	0.26	0.06
			Mg	0.90	0.26	0.06
			Na	0.75	0.22	0.05
			Total	3.40	1.00	
2	2.83	0.19	Cd	0.75	0.25	0.05
			Cr	0.89	0.30	0.06
			Li	0.88	0.30	0.06
			Zn	0.44	0.15	0.03
			Total	2.96	1.00	
3	2.78	0.19	Al	0.80	0.27	0.05
			Hg	0.73	0.25	0.05
			Mn	0.50	0.17	0.03
			Y	0.88	0.30	0.06
			Total	2.91	1.00	
4	2.41	0.16	Cu	0.94	0.37	0.06
			P	0.94	0.37	0.06
			Pb	0.64	0.25	0.04
			Total	2.52	1.00	
5	1.74	0.12	Fe	0.78	0.36	0.04
			As	0.72	0.33	0.04
			V	0.67	0.31	0.07
			Total	2.17	1.00	
6	1.57	0.11	Co	0.65	0.32	0.04
			Ni	0.72	0.35	0.04
	14.88		Se	0.66	0.33	0.04
			Total	2.03	1.00	

3.5.5. Potential health risk assessment

Human toxicity by metals varies depending on duration – acute or chronic. Kostic and co-workers observed that the chronic HQ (1.7×10^{-3}) estimated for arsenic in tap water was different from acute HQ (1.31) calculated based on weekly intake, which suggested potential high risk for human health (Kostic et al., 2016). The average hazard quotient (HQ) for the water samples expressed through estimated weekly intake (EWI) and provisional tolerable weekly intake

(PTWI) were generally lower than one ($HQ < 1$) for all metals (Table 6), indicating little or no potential non-carcinogenic risk arising from using the water from the various sources for drinking and other domestic applications. The HQ and HI values for intake of the trace elements (using the mean values) by ingestion and dermal pathways for adults and children are given in Table 7. Both $HQ_{\text{ingestion}}$ and HQ_{dermal} values for both adults and children, and for all elements were generally lower than 1 ($HQ < 1$), indicating little or no potential non-carcinogenic concern via oral intake and dermal absorption. However, compared with adults, higher $HQ_{\text{ingestion}}$ and HQ_{dermal} (higher HI) values were observed for children suggesting that children are more sensitive than adults, when exposed to PTEs in water. Generally, the HI values for adults and children for all elements under study were much smaller than 1, with HI values for children being higher than adults'. Shown in Fig. 6 is the variation of average Hazard Index (HI_{Average}) of all the elements for both adults and children. It could be seen that springs and boreholes had lower HI than streams and hand-dug wells, while hand-dug wells had highest HI values amongst other sources in the region. This suggests that, though little or no health risks are expected to occur by drinking water from all sources, those that drink from hand-dug wells and streams are exposed more.

Table 6. Potential short-term human health risk regarding to metals in water sources.

	PTWI*	Springs		Streams		Hand-dug wells		Boreholes	
		HQ Adult	HQ Children	HQ Adult	HQ Children	HQ Adult	HQ Children	HQ Adult	HQ Children
Al	2000	2.2E-02	3.3E-02	2.4E-02	3.3E-02	1.3E-02	1.9E-02	1.4E-02	2.1E-02
As	15	1.2E-04	1.8E-04	4.2E-03	1.8E-04	7.0E-04	1.1E-03	1.8E-03	2.7E-03
Cd	7	9.3E-04	1.4E-03	0.0E+00	1.4E-03	0.0E+00	0.0E+00	1.1E-03	1.7E-03
Co	700†	2.3E-04	3.4E-04	4.1E-04	3.4E-04	4.7E-04	7.0E-04	2.3E-04	3.5E-04
Cr	23.3	2.0E-03	2.9E-03	1.2E-02	2.9E-03	1.4E-02	2.0E-02	3.0E-02	4.4E-02
Cu	3500	3.8E-05	5.7E-05	5.8E-05	5.7E-05	6.8E-05	1.0E-04	9.3E-04	1.4E-03
Fe	5600	4.7E-03	6.9E-03	4.8E-02	6.9E-03	5.4E-03	8.1E-03	1.6E-03	2.4E-03
Hg	1.6	4.8E-04	7.2E-04	9.9E-04	7.2E-04	1.5E-03	2.3E-03	2.2E-03	3.2E-03
Mn	1400	2.6E-03	3.9E-03	3.7E-03	3.9E-03	6.8E-03	1.0E-02	4.7E-03	7.0E-03
Ni	35	2.9E-03	4.3E-03	5.7E-03	4.3E-03	1.5E-02	2.2E-02	6.5E-03	9.7E-03
Pb	25	0.0E+00	0.0E+00	7.1E-04	0.0E+00	4.1E-02	6.2E-02	1.3E-02	2.0E-02
Se	35	2.9E-02	4.3E-02	3.0E-02	4.3E-02	2.2E-02	3.3E-02	1.0E-02	1.5E-02
Zn	7000	2.8E-04	4.2E-04	1.9E-04	4.2E-04	6.9E-04	1.0E-03	2.9E-04	4.4E-04

* PTWI Provisional tolerable weekly intake is in $\mu\text{g}/\text{kg}$.

† No PTWI was given for Co, thus Maximum tolerable limit was used (EVM, 2002).

Table 7. Potential long-term human health risk regarding to metals in water sources.

		Kp	RfD_{ingestion}	RfD_{dermal}	HQ_{ingestion}		HQ_{dermal}		HI	
		cm/h	µg/kg		Adult	Child	Adult	Child	Adult	Child
Springs	Al	1.0E-03	1000	200	6.4E-03	9.6E-03	1.7E-04	4.9E-04	6.6E-03	1.0E-02
	As	1.0E-03	0.3	0.285	8.8E-04	1.3E-03	4.8E-06	1.4E-05	8.8E-04	1.3E-03
	Cd	1.0E-03	0.5	0.025	1.9E-03	2.8E-03	2.0E-04	5.8E-04	2.1E-03	3.3E-03
	Co	4.0E-04	0.3	0.06	7.6E-02	1.1E-01	7.9E-04	2.3E-03	7.6E-02	1.2E-01
	Cr	1.0E-03	3	0.075	2.2E-03	3.2E-03	4.5E-04	1.3E-03	2.6E-03	4.5E-03
	Cu	1.0E-03	40	8	4.8E-04	7.1E-04	1.2E-05	3.7E-05	4.9E-04	7.5E-04
	Fe	1.0E-03	700	140	5.3E-03	7.9E-03	1.4E-04	4.1E-04	5.4E-03	8.3E-03
	Hg	1.0E-03	0.3	0.021	3.7E-04	5.5E-04	2.7E-05	8.1E-05	3.9E-04	6.2E-04
	Mn	1.0E-03	24	0.96	2.2E-02	3.3E-02	2.9E-03	8.5E-03	2.5E-02	4.1E-02
	Ni	2.0E-04	20	0.8	7.2E-04	1.1E-03	1.9E-05	5.5E-05	7.4E-04	1.1E-03
	Pb	1.0E-04	1.4	0.42	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
	Se	1.0E-03	5	4.2	2.9E-02	4.3E-02	1.8E-04	5.3E-04	2.9E-02	4.3E-02
	V	1.0E-03	1	0.01	8.6E-03	1.3E-02	4.5E-03	1.3E-02	1.3E-02	2.6E-02
Zn	6.0E-04	300	60	9.4E-04	1.4E-03	1.5E-05	4.4E-05	9.6E-04	1.5E-03	
Streams	Al	1.0E-03	1000	200	6.8E-03	1.0E-02	1.8E-04	5.2E-04	7.0E-03	1.1E-02
	As	1.0E-03	0.3	0.285	3.0E-02	4.5E-02	1.7E-04	4.9E-04	3.0E-02	4.6E-02
	Cd	1.0E-03	0.5	0.025	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
	Co	4.0E-04	0.3	0.06	1.4E-01	2.0E-01	1.4E-03	4.2E-03	1.4E-01	2.1E-01
	Cr	1.0E-03	3	0.075	1.3E-02	1.9E-02	2.7E-03	8.0E-03	1.6E-02	2.7E-02
	Cu	1.0E-03	40	8	7.3E-04	1.1E-03	1.9E-05	5.6E-05	7.4E-04	1.1E-03
	Fe	1.0E-03	700	140	5.5E-02	8.2E-02	1.4E-03	4.2E-03	5.6E-02	8.6E-02
	Hg	1.0E-03	0.3	0.021	7.5E-04	1.1E-03	5.6E-05	1.7E-04	8.1E-04	1.3E-03
	Ni	2.0E-04	20	0.8	1.4E-03	2.1E-03	3.7E-05	1.1E-04	1.5E-03	2.2E-03

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Table 7. (Continued)

	Kp	RfD _{ingestion}	RfD _{dermal}	HQ _{ingestion}		HQ _{dermal}		HI		
		cm/h	µg/kg	Adult	Child	Adult	Child	Adult	Child	
Dug wells	Pb	1.0E-04	1.4	0.42	1.8E-03	2.7E-03	3.2E-06	9.3E-06	1.8E-03	2.7E-03
	Se	1.0E-03	5	4.2	3.0E-02	4.5E-02	1.9E-04	5.5E-04	3.0E-02	4.5E-02
	V	1.0E-03	1	0.01	2.0E-02	2.9E-02	1.0E-02	3.0E-02	2.9E-02	5.8E-02
	Zn	6.0E-04	300	60	6.2E-04	9.3E-04	9.8E-06	2.9E-05	6.3E-04	9.6E-04
	Al	1.0E-03	1000	200	3.7E-03	5.5E-03	9.6E-05	2.8E-04	3.8E-03	5.8E-03
	As	1.0E-03	0.3	0.285	5.0E-03	7.5E-03	2.8E-05	8.2E-05	5.1E-03	7.6E-03
	Cd	1.0E-03	0.5	0.025	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
	Co	4.0E-04	0.3	0.06	1.6E-01	2.3E-01	1.6E-03	4.8E-03	1.6E-01	2.4E-01
	Cr	1.0E-03	3	0.075	1.5E-02	2.2E-02	3.1E-03	9.3E-03	1.8E-02	3.1E-02
	Cu	1.0E-03	40	8	8.5E-04	1.3E-03	2.2E-05	6.6E-05	8.7E-04	1.3E-03
	Fe	1.0E-03	700	140	6.2E-03	9.3E-03	1.6E-04	4.8E-04	6.4E-03	9.7E-03
	Hg	1.0E-03	0.3	0.021	1.2E-03	1.7E-03	8.6E-05	2.5E-04	1.2E-03	2.0E-03
	Mn	1.0E-03	24	0.96	5.6E-02	8.4E-02	7.4E-03	2.2E-02	6.4E-02	1.1E-01
	Ni	2.0E-04	20	0.8	3.7E-03	5.6E-03	9.8E-05	2.9E-04	3.8E-03	5.9E-03
Boreholes	Pb	1.0E-04	1.4	0.42	1.1E-01	1.6E-01	1.8E-04	5.4E-04	1.1E-01	1.6E-01
	Se	1.0E-03	5	4.2	2.2E-02	3.3E-02	1.4E-04	4.0E-04	2.2E-02	3.3E-02
	V	1.0E-03	1	0.01	9.8E-05	1.5E-04	5.1E-05	1.5E-04	1.5E-04	2.9E-04
	Zn	6.0E-04	300	60	2.3E-03	3.5E-03	3.6E-05	1.1E-04	2.4E-03	3.6E-03
	Al	1.0E-03	1000	200	3.9E-03	5.9E-03	1.0E-04	3.0E-04	4.0E-03	6.2E-03
	As	1.0E-03	0.3	0.285	1.3E-02	1.9E-02	7.0E-05	2.1E-04	1.3E-02	1.9E-02
	Cd	1.0E-03	0.5	0.025	2.2E-03	3.3E-03	2.3E-04	6.9E-04	2.5E-03	4.0E-03
	Co	4.0E-04	0.3	0.06	7.8E-02	1.2E-01	8.1E-04	2.4E-03	7.8E-02	1.2E-01

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Table 7. (Continued)

	Kp	RfD_{ingestion}	RfD_{dermal}	HQ_{ingestion}		HQ_{dermal}		HI	
	cm/h	µg/kg		Adult	Child	Adult	Child	Adult	Child
Cr	1.0E-03	3	0.075	3.3E-02	4.9E-02	6.9E-03	2.0E-02	4.0E-02	6.9E-02
Cu	1.0E-03	40	8	1.2E-02	1.7E-02	3.0E-04	8.9E-04	1.2E-02	1.8E-02
Fe	1.0E-03	700	140	1.9E-03	2.8E-03	4.9E-05	1.4E-04	1.9E-03	2.9E-03
Hg	1.0E-03	0.3	0.021	1.6E-03	2.4E-03	1.2E-04	3.6E-04	1.8E-03	2.8E-03
Mn	1.0E-03	24	0.96	3.9E-02	5.8E-02	5.1E-03	1.5E-02	4.4E-02	7.3E-02
Ni	2.0E-04	20	0.8	1.6E-03	2.4E-03	4.2E-05	1.2E-04	1.7E-03	2.5E-03
Pb	1.0E-04	1.4	0.42	3.4E-02	5.1E-02	5.9E-05	1.7E-04	3.4E-02	5.1E-02
Se	1.0E-03	5	4.2	1.0E-02	1.5E-02	6.3E-05	1.8E-04	1.0E-02	1.5E-02
V	1.0E-03	1	0.01	6.9E-03	1.0E-02	3.6E-03	1.1E-02	1.0E-02	2.1E-02
Zn	6.0E-04	300	60	9.8E-04	1.5E-03	1.5E-05	4.5E-05	9.9E-04	1.5E-03

Kp is the Dermal permeability coefficient; RfD is Reference dose; HQ is the Hazard quotient and HI is the Hazard Index.

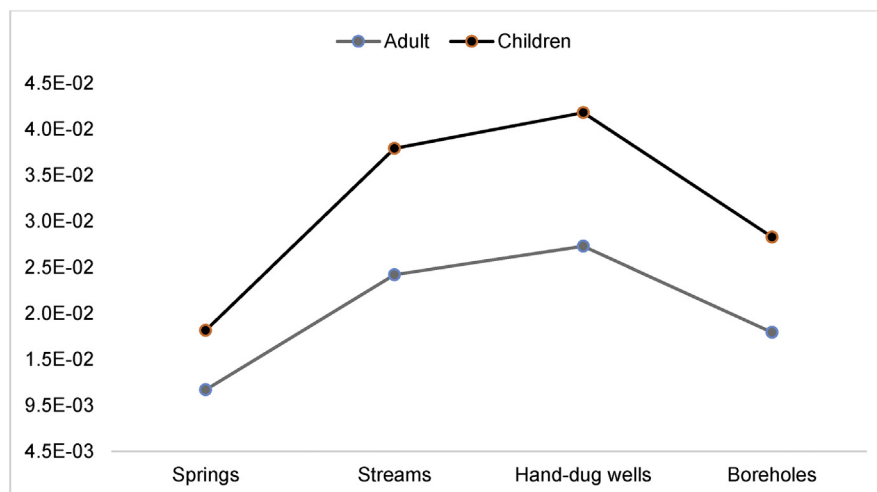


Fig. 6. Average Hazard Index (HI) for children and adults in water sources.

4. Conclusion

This study determined the concentrations of elements of nutritional and potentially toxic importance in drinking water sources in Abia and Imo states, Southeastern Nigeria. The drinking water sources were generally characterized by low pH values, indicating deviation from the set limits. Multivariate statistical techniques were used to characterize PTEs in natural springs and other drinking water sources based on: (1) likely origin (2) inter relationships, (3) extent of involvement in water contamination, and (4) their ability to cause harm to unsuspecting consumers. The overall average concentrations of elements in the water sources were found in this order of magnitude: Fe > Al > Mn > Cu > Zn > P > Se > Cr > Pb > Ni > Li > Y > Co > V > As > Cd > Hg. However, Fe, Al, Mn, Se and Zn were the dominant elements. When compared with drinking water guidelines set by WHO, EPA and NSDWQ, mean concentration of Al in springs (244.0 µg/L) and streams (237.3 µg/L) together with Fe in streams (1344.5 µg/L) were higher than the set limits. Moreover, Pb, Mn, Al and Se were found above their respective permissible limits in 3, 9, 21 and 11 sampling stations respectively, while Fe levels were above its permissible limit in about 92% of samples from streams. In comparison, the average values of the elements obtained in this study were lower than those earlier reported in some studies in this region. Moreover, cluster analysis grouped the individual water bodies into moderate and low pollution, reflecting influences from crustal materials and anthropogenic sources respectively. Water quality index (WQI) approach indicated that all drinking water sources had either excellent or good water quality (WQ) with the exception of a borehole, which had poor WQ. From the result of hazard quotient and index (HQ/HI), there is little or no potential non-carcinogenic health risks in using water from the sources studied in this region for drinking and domestic purposes. Nevertheless, consuming water from the springs and/or boreholes has less

adverse human health impact than the other sources. In the region under study, virtually all households including children do not have access to treated municipal water supply, therefore there is need for constant monitoring of drinking waters. Though little or no health risks are expected to occur by drinking water from all sources investigated, those that consume water from hand-dug wells and streams without treatment, are likely to be at higher health risk.

Declarations

Author contribution statement

Ugochukwu Ewuzie: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Innocent Nnorom: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Sunday Eze: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

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