



Health risk assessment of heavy metals and physicochemical parameters in natural mineral bottled drinking water using ICP-MS in South Africa

Samuel Odumu Ogana John¹ · Stephen Friday Olukotun^{1,2} · Tebogo Gilbert Kupi¹ · Manny Mathuthu¹

Received: 4 March 2024 / Accepted: 5 August 2024 / Published online: 14 August 2024
© The Author(s) 2024

Abstract

The contamination of natural mineral bottled drinking water with trace, heavy metals and rare-earth elements is a growing concern globally, especially in regions with limited access to safe drinking water sources. In South Africa, the safety of bottled water remains a critical issue due to potential health risks associated with heavy metal exposure. This study aimed to evaluate physicochemical parameters alongside to assess the health risks due to heavy metals in natural mineral bottled drinking water available in South Africa, using inductively coupled plasma mass spectrometry analysis. A total of 21 bottled water samples from different brands were collected and analysed for heavy metal concentrations including Pb, Cd, As, Cr, Ni, Ba and Hg, as well as physicochemical parameters such as pH, conductivity, dissolved oxygen and total dissolved solids among others. The results revealed physicochemical parameters were within acceptable ranges, indicating overall water quality. Varying levels of heavy metals across different brands observed with concentrations of Al, Fe, Mg, Ca, K and Mn in some samples exceeding permissible limits set by WHO and SAWQG for drinking water quality. The mean concentration of the heavy metals is in the decreasing toxicity order of Sr > Al > Ba > Mn > Cu > Cr > Zn > Fe > As > Co > U > Ni > Cs > Pb > Cd > Hg. The mean values of the chronic daily intake (CDI) for the concentration of heavy metals for adults are in the order of Cr > Fe > Sr > Ba > Mn > Cu > Zn > Li > V > As > Ni > Be > Pb > Hg > Cd and were below acceptable limits. The estimated values of both HQ and HI (with mean of 2.07E−03 and range of 0.00 to 1.76E−02) for the heavy metals are all found to be less than 1. The total mean value of ILCR is 4.67E−06, and range of 0.00 to 2.76E−05, which is insignificant and within the permissible level of the cancer risk guidance limit of 1.00E−06 to 1.00E−04. The results show that consumption of natural mineral bottled drinking water of South Africa is safe and may not cause any significant health risk to the populace. However, the long-time potential effects due to the few exceeded metals levels needed to be considered. Our findings contribute to the ongoing discourse on water quality assurance, offering insights into the overall integrity of the natural mineral bottled water supply chain in South Africa. This research not only serves as a foundation for regulatory measures but also underscores the significance of maintaining high-quality standards in the bottled water industry for public health and environmental sustainability.

Keywords Health risk · Natural mineral water · Physicochemical parameters · Trace elements · Heavy metals · ICP-MS · Bottled drinking water · Public health

✉ Samuel Odumu Ogana John
samjoh2014@gmail.com
Stephen Friday Olukotun
olukotunsf@yahoo.com
Tebogo Gilbert Kupi
tebogo.kupi@nwu.ac.za
Manny Mathuthu
manny.mathuthu@nwu.ac.za

¹ Center for Applied Radiation Science and Technology (CARST), North-West University, Cnr Albert Luthuli Road and University Drive, Mmabatho 2735, South Africa
² Department of Physics and Engineering Physics, Obafemi Awolowo University, Ile-Ife 220282, Nigeria

Introduction

The significance of safe drinking water to the quality of human health and well-being cannot be overemphasised. The growing demand for reliable and safe drinking water with persisting concerns regarding the quality and safety of bottled water, especially where there is limited alternative sources of portable water, makes it necessary to assess potential contaminant of health impact (Madzunya et al. 2020; John et al. 2021; Kekes et al. 2023). The accessing of safe and pure drinking water and sanitation has been considered as human right to be enjoyed by all and sundry as the United Nations in 2010 General Assembly so declared in the sustainable development goals (Hodgson and Manus 2006; UN 2010; Kekes et al. 2023). However, due to climate change, increase in population and anthropogenic activities, scarcity of water resources and its contamination with the attendants health risk becomes inevitable (Momba et al. 2006; WHO 2022; Altunisik 2023; Ehsan et al. 2024). Globally and in South Africa in particular, where issues of water scarcity and contamination could be prevalent, the safety of natural mineral bottled drinking water has become a subject of scrutiny (Petraccia et al. 2006; Hodgson and Manus 2006; Odendaal 2024).

The popularity of bottled water worldwide is unprecedented with its use in the year 2020 of more than 450 billion litres, having annual global production of greater than 6 billion gallons and still growing (Statista 2022). This underscores the importance of bottled water with its requirement in some parts of the world increasing due to unsafe nature of other alternative sources like tap water. Having many advantages of being safe, pure, containing flavour, the comfort it provides and health benefits among others (Altunisik 2023; Feru 2004).

The bottled drinking water, formerly referred to as packaged water, available on the South African market are of various types, which are of groundwater sources. They include natural water, mineral water, spring water, natural mineral carbonated sparkling water. They are often collected and packaged directly from the source or undergo some industrial processing before packaging. Additionally, due to geological settings and possible microplastic pollution, the need of continuous monitoring of the safety and quality in compliance to standards is pertinent (Altunisik 2023; Feru 2004). Natural mineral bottled drinking water have useful benefit to the health of humans because of the presence of mineral elements like calcium, magnesium, iron, potassium, zinc, sodium, bicarbonate, etc., which the body needs to maintain good health. However, these elements must be in moderation as elevated levels can be of potential health hazards of the kind of carcinogenic and non-carcinogenic impact. And must comply with the South

African National Standard (SANS) 241, for safe and clean drinking water (Hodgson and Manus 2006; DOH 2006, 2010; SANS 2015).

The drinking water is one of the exposure pathways of humans to potential contaminants of health impact, in the environment (SAWQG 1996; WHO 2020). The excessive ingestion and overaccumulation of trace elements, heavy metals and rare-earth elements have some health risk of concern. For instance, Mn is an important trace element, as its deficiency could lead to anaemia, impairment in growth and abnormalities in the skeleton (SAWQG 1996; WHO 2022). However, ingestion of high concentration of Mn in drinking water could cause severe health risk impact such as neurological effects with diminished cognitive ability, temporarily suggested Parkinson's disease (SAWQG 1996; WHO 2022). Cr is a heavy metal of carcinogenic attributes and portends risk of acute toxicity, slight nausea and increasing risk of cancer induction, especially gastrointestinal cancer over prolonged exposure (SAWQG 1996; WHO 2020; Naz et al. 2016). Zn is essential for physiological and metabolic processes in living organism, but in high concentration it can have severe, acute toxicity, disturbances in electrolytes and renal damage possibility (Pillai 1983; SAWQG 1996). Pb has acute and or irreversible effects on human health like neurological impairment, respiratory disorder and anaemia, with high sensitivity to Pb toxicity by children which could damage their brain (SAWQG 1996; Abdul et al. 2012). Cd as carcinogenic heavy metal, elevated concentrations with long-term exposure put individuals in high risk of kidney damage, with effect that is potentially acute or irreversible on human health (SAWQG 1996). Other elements of concerns are also discussed which provide understanding of the need for continuous monitoring of route of ingestion in compliance with standards (Momba et al. 2006; Hodgson and Manus 2006; SANS 2015).

Studies on water quality and safety in South Africa have been reported (Grabow 1986; Momba et al. 2006; Mathuthu and Olobatoke 2016; Njinga et al. 2016; Mathuthu et al. 2021), but not on natural mineral bottled drinking water also using different analytical procedures other than ICP-MS, which makes this baseline study and novel. This study aims at assessing the health risks related to trace elements, heavy metals and rare-earth elements contamination in natural mineral bottled drinking water available in South Africa. Using a modern highly sensitive, accurate, effective analytical technique, known as inductively coupled plasma mass spectrometry (ICP-MS) (Ogana et al. 2019; Wilschefski and Baxter 2019). We evaluated the concentrations of trace elements, heavy metals and rare-earth elements in various bottled drinking water brands. More so, we examined key physicochemical parameters like potential hydrogen (pH), electrical conductivity, dissolved oxygen (DO), total dissolved solids (TDS), salinity and oxidation reduction

potential (ORP) to provide a comprehensive assessment of the drinking water quality (Jindal and Sharma 2011). The significance of this research lies in its potential to shed light and provide baseline data on the extent of trace elements, heavy metal contamination and rare-earth elements in natural mineral bottled drinking water and its implications for public health. By identifying and quantifying trace elements, heavy metal concentrations and rare-earth elements, we can better understand the associated health risks (Liang et al. 2019) and inform regulatory measures to ensure the safety of bottled drinking water products. Furthermore, this study contributes to the existing body of knowledge regarding water quality assessment in South Africa, ensuring the adherence to stringent quality standards, safeguarding public health and promoting transparency within the bottled drinking water industry, while providing valuable insights for policymakers, regulatory agencies and consumers alike.

Materials and methods

Study area

The area for this study is South Africa, which covers 1,219,602 km² surface area and stretches from latitude 22°S to 35°S and longitude 17°E to 33°E, bordered by Namibia, Botswana, Zimbabwe, Mozambique and Eswatini up inlands, but landlock Lesotho in the south-east region. It is also bordered by the Atlantic Ocean south-westwards and the Indian ocean by south-eastwards, see Fig. 1, and has an estimated population of about 60.5 M people (GCIS 2022). Due to its subtropical location, the warm temperate condition of the area is accounted for by the interior plateau altitude and the oceans besides the country, which moderates it. South Africa has an annual rainfall of about 500 mm and is relatively dry. The temperatures compared to other countries having similar altitudes tend to be lower, owing to the elevation above sea level, thereby requiring more consumption of drinking water by the people. It is endowed with natural mineral resources such as gold, platinum, uranium, diamond, coal and a lot more with many rivers and



Fig. 1 The Map of the Republic of South Africa showing provinces and cities (NOP 1998)

mountains of geological significance to the aquifers related to natural water sources.

Sampling

A total of twenty-one different commercial natural mineral bottled drinking water samples were collected from the South African shopping malls and taken to the laboratory for analysis. The sample brands are the topmost and most consumed commercial bottled drinking water across South Africa, following a mini survey conducted and online search, prior to the sample collection (AoPrice 2023; Mascha 2023). The various bottled drinking water are of the type—natural-still spring water, mineral water, natural carbonated sparkling water, flavoured sparkling water and alkaline ionised water. The sampling was done according to a standardised method by the South African Water Quality Guidelines (SAWQG 1996) and the American Public Health Association (APHA 1999). The samples were collected, stored in the refrigerator at a temperature of 2–4 °C in laboratory and analysed within the month of September, 2023.

Physicochemical parameters

The physicochemical parameters of the drinking water samples were determined based on the standardised methods for

the examination of water by the South African Water Quality Guidelines (SAWQG 1996) and the American Public Health Association (APHA 1999). BANTE 900-UK Benchtop Multiparameter Water Quality Meter, with S/N 230223-003, by BANTE Instruments, was used together with 913 pH Meter Ω Metrohm—Swiss made and BIOBASE MS-S280-Pro Magnetic Stirrer device (Fig. 2). The average value from the various instruments was used. The calibration of equipment using standard and buffer solutions was performed, using standardised procedures, and the calibration curves are shown in Figs. 3, 4. The physicochemical parameters measured include potential hydrogen (pH), temperature, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), salinity, resistivity, potential and oxidation reduction potential (ORP) and discussed, as shown in Figs. 5, 6.

ICP-MS analysis

The glassware and materials used were decontaminated using 10% (v/v) HNO_3 , then rinsed with ultrapure, deionised water, (18 $\text{M}\Omega$ cm) obtained from Hitech Laboratory Water Purification System (Lasec Laboratory Solution Provider, UK) as shown in Fig. 2, also used in the preparation of all the solutions. It was ensured that only reagents of analytical grade were used.

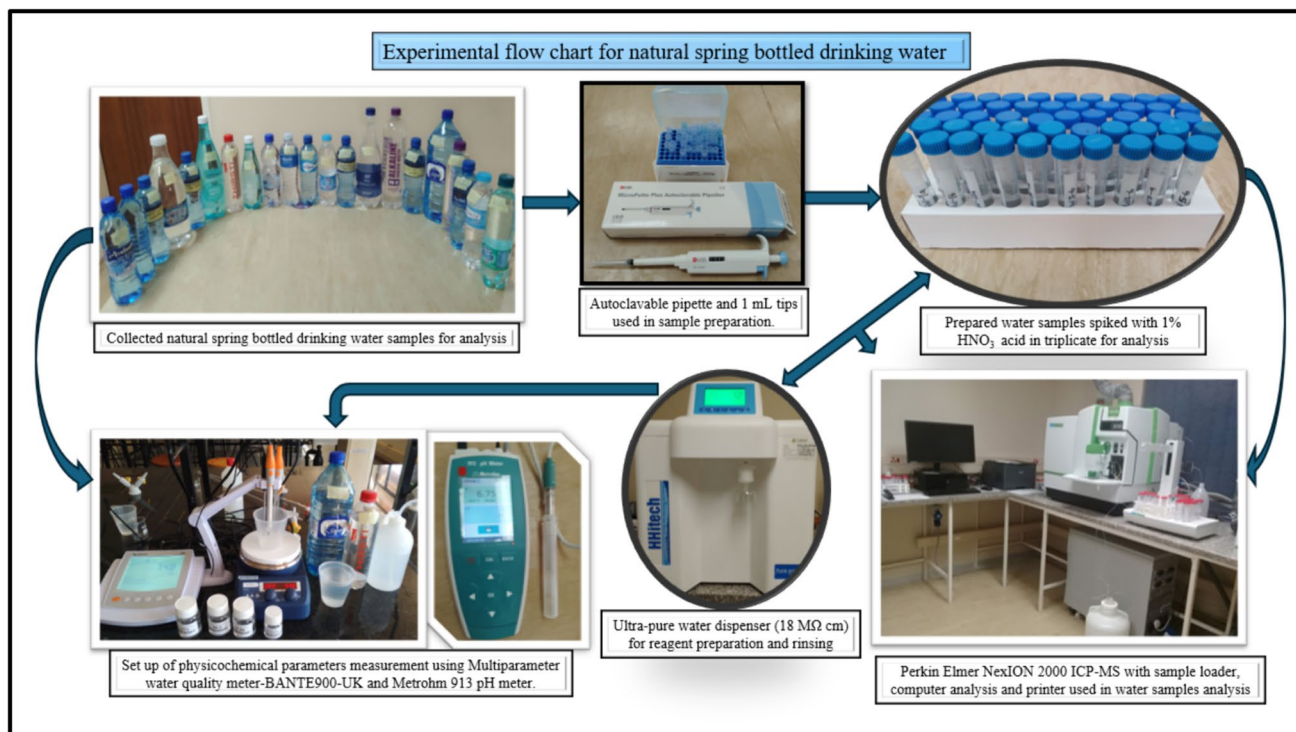


Fig. 2 Pictorial description of the experimental set-up for natural spring bottled drinking water sample collection, preparation and analysis using ICP-MS technique

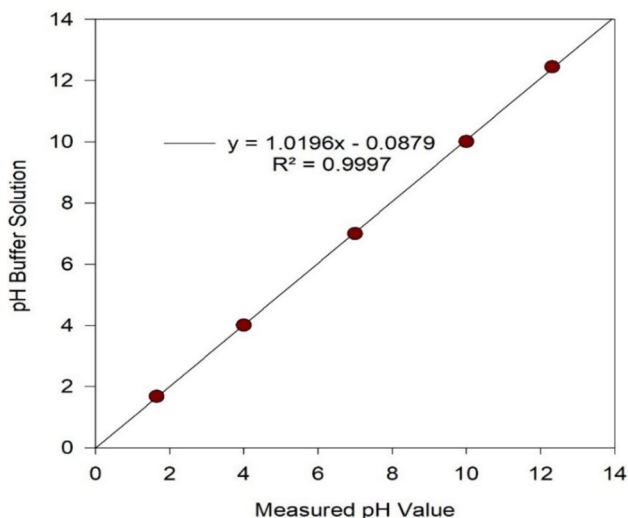


Fig. 3 pH calibration curve for the pH and related physicochemical parameters measurement in this study

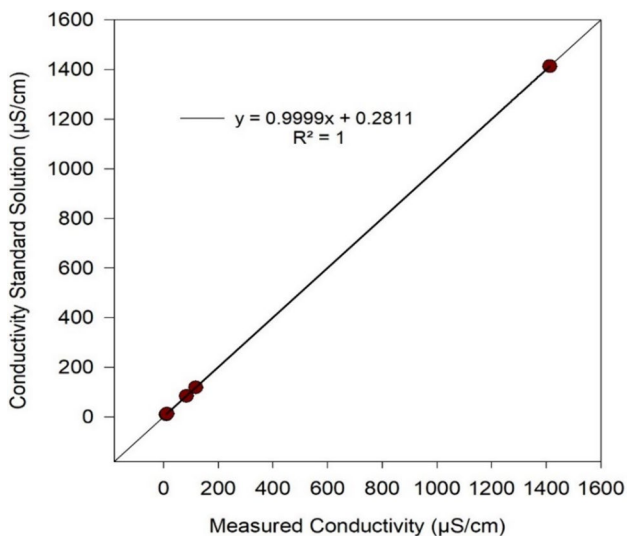


Fig. 4 Calibration curve for electrical conductivity and related physicochemical parameters measurement in this study

The water samples were analysed for their chemical content such as the trace elements, heavy and rare-earth elements using the inductively coupled plasma mass spectrometry (ICP-MS) PerkinElmer NexION 2000, as shown in Fig. 2. The ICP-MS detection limit for the respective metals analysed in the drinking water samples ranged between 0.5 and 5.0 ng/L. The instrument analyses sample by producing ions (ionizations) through the inductively coupled plasma to a mass spectrometer which separates and detects ions from the samples. The quadruple KED mode setting enables measurement with no or insignificant elemental interferences (Pruszkowski 2021). The total

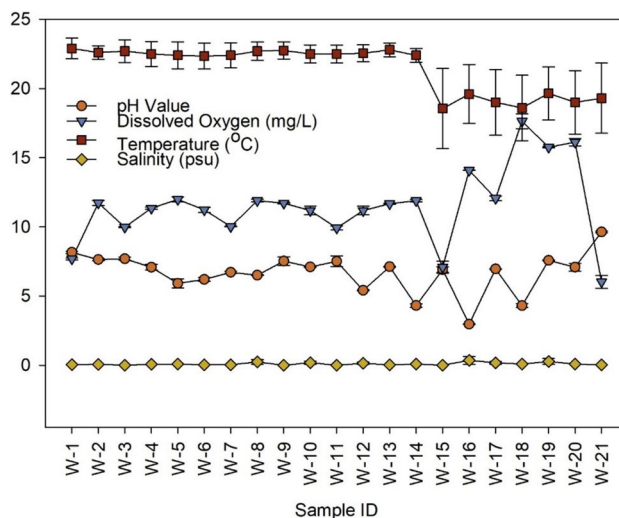


Fig. 5 Results of the physicochemical parameters for pH, dissolved oxygen (mg/L), temperature (°C) and salinity (psu) measured in this study; whiskers represent standard deviation

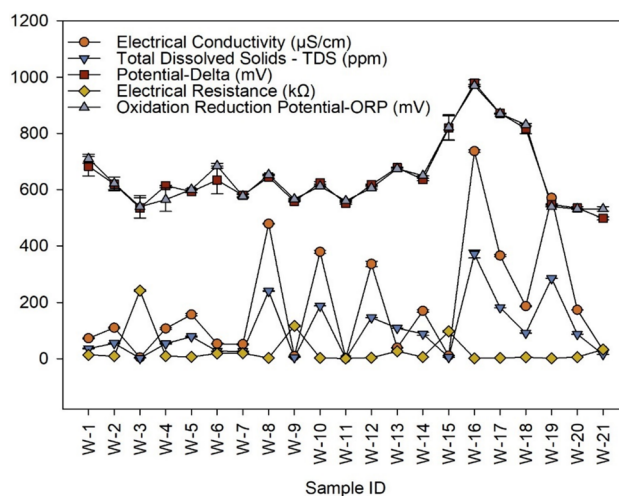


Fig. 6 Results showing the physicochemical parameters for electrical conductivity (EC), total dissolved solids (ppm), potential delta (mV), electrical resistance (kΩ) and oxidation reduction potential (mV) measured in this study; whiskers represent standard deviation

quant analysis method was used, with ^{103}Rh and ^{209}Bi as the internal standards.

Assessment of human health risk

The assessment of human health risks entails weighing the amount of possible evidence concerning the potential of a given contaminant that could cause harmful health effect when a person is exposed to toxic and harmful substances over a given time duration (USEPA 1989). The assessment of human health risk due to individual potentially toxic

metal is performed by estimating the level of risk, and classified in terms of carcinogenic or non-carcinogenic health risk (Bempah and Ewusi 2016; Mohammadi et al. 2019). Ingestion of drinking water is one of the most important rout through which humans are being exposed to harmful and toxic contaminants of significant health impacts. In this study, the determination of the carcinogenic or non-carcinogenic health hazards due to ingestion of bottled drinking water in South Africa was done using the general exposure pathway equations (Eqs. 1–4) adopted from (USEPA 1989; Wu et al. 2009; Bempah and Ewusi 2016; Mohammadi et al. 2019), for the adult age group. The levels of the exposure of humans to heavy metal were calculated using Eq. 1, chronic daily intake (CDI)(mg/kg-day) as:

$$CDI = \frac{CW \times IR \times ABS_{gi} \times EF \times ED}{BW \times AT} \quad (1)$$

where CW (mg/L) is the heavy metal concentration in drinking water, IR (L/day) is the ingestion rate – 2.0 L/day used in this study (USEPA 1989; SAWQG 1996), ABS_{gi} (no unit) is the gastrointestinal absorption factor – 0.001 used in this study (Mohammadi et al. 2019), EF (days/year) is the exposure frequency – 365 days/year used in this study; ED (years) is the exposure duration – 70 years lifetime (USEPA 1989; SAWQG 1996); BW (kg) is the body weight of the exposed adult person – 70 kg used in this study as average, age specific values (USEPA 1989; SAWQG 1996) and AT (days/year) is the average time, a non-carcinogenic effect period of exposure that is pathway-specific, derived as $ED \times 365$ days/year, i.e. 25,550 days/year used in this study (USEPA 1989; SAWQG 1996).

The computed CDI of the heavy metals was used to calculate the hazard quotient, HQ a non-carcinogenic health risks quantity, from Eq. 2

$$HQ = \frac{CDI}{RfD} \quad (2)$$

where RfD (mg/kg/day) is the reference oral-ingested dose, values for each heavy metal as used in this study are presented in Table 4, column 8.

The estimated values of HQ less than 1 are within the acceptable level of non-carcinogenic risk, whereas the value with HQ greater than 1 is considered as unacceptable risk with the potential of causing adverse health hazard impact on human (USEPA 2011). Hazard index (HI), a non-carcinogenic health risk parameter, is the sum of all the HQs of the individual contaminants, and it provides the estimated values of the whole potential health risks. It is determined based on USEPA guidelines using Eq. 3

$$HI = \sum_{k=1}^n HQ_{HM} \quad (3)$$

where HQ_{HM} represents the individual heavy metal's HQ being added up, respectively.

The values of HI as computed are being compared to the standard values to ascertain the level or possibility of whether there is non-carcinogenic health impact on the humans. Hence, for HI value less 1 imply there is no non-carcinogenic health risk whereas for HI values greater than 1, for an exposed person imply there are chances of non-carcinogenic health risk impact to occur (Bempah and Ewusi 2016; Mohammadi et al. 2019).

The incident lifetime cancer risk (ILCR) (unitless) can be used to estimate the probability of cancer health risk due to the consumption of drinking water and consequent exposure to a given dose of heavy metals therein, for a lifetime (USEPA 1989). In this study, the ILCR, for the drinking water samples, was calculated using Eq. 4, which is a linear low dose cancer equation.

$$ILCR = CDI \times SF \quad (4)$$

where SF (mg/kg-day) is the cancer slope factor, an estimate which is contaminant specific. The values of SF for individual toxic metal used in this study are presented in Table 5 column 5. The permissible range value for the ILCR is between 1.00E–06 and 1.00E–04 for both single and multicarcinogenic elements. This means that, based on the exposure circumstance, computed values of ILCR greater than 1.00E–04 are regarded as unacceptable risks whereas those below 1.00E–06 are regarded as not to pose any significant health risk (USEPA 1989; Wu et al. 2009; Bempah and Ewusi 2016).

The computation of the various parameter and data in this study was done using the statistical packages Microsoft Excel and Sigma Plot version 15.0, where the formulas described above, Eqs. 1–4 and statistical analysis were performed, and the respective results presented in the tables in result and discussion section.

Results and discussion

The results of physicochemical parameters and ICP-MS analysis of the bottled natural mineral drinking water samples from South Africa are presented as follows:

Calibration of the instrument

Figures 3, 4 present the calibration curves of the instruments used in measuring the physicochemical parameters of the various drinking water samples. Figure 3 shows the plot of standard pH buffer solution against the measured pH values. The calibration points are 1 to 5—USA (pH 1.68, 4.01, 7.00, 10.01, 12.45), with temperature compensation of 0 to 100 °C and accuracy of ± 0.002 pH. The measured pH

values compare well with the standard pH values yielding a correlation coefficient, R^2 of 99.97%. Figure 4 shows the calibration curve plot of the conductivity standard solution ($\mu\text{S}/\text{cm}$) against the measured EC values. There are 1 to 4 calibration points (12.88, 84, 111.8 and 1413, $\mu\text{S}/\text{cm}$), at the temperature compensation of 0 to 100 °C and accuracy of $\pm 0.5\%$ F.S. The result shows a very good correlation R^2 of 100%. The calibration results both at 95% confidence level show high level of sensitivity and accuracy of the instrument for the measurement, with good reliability.

Physicochemical parameters

Figures 5, 6 present the results of the measured physicochemical parameters, with their respective errors shown as whiskers which represent standard deviation (SD). Figure 5 shows results of pH, dissolved oxygen (DO) (mg/L), temperature (°C) and salinity (psu or g/L). Figure 5 shows results of electrical conductivity (EC) ($\mu\text{S}/\text{cm}$), total dissolved solid (TDS) (ppm or mg/kg), delta (mV), electrical resistance (k Ω) and oxidation reduction potential (ORP) (mV).

The pH of water samples ranged from 2.964 ± 0.013 to 9.632 ± 0.390 with a mean value of 6.680 ± 0.129 and standard deviation of 1.472, as shown in Fig. 4. The lower limit of the pH range value is measured from fruit

flavoured sparkling bottled water sample, whereas the upper limit is from alkaline ionised still water sample. The mean value is within both the recommended guidelines of South African Water Quality Guideline—Target Water Quality Range (TWQR) of (6.0–9.0) and World Health Organization—WHO of (6.5–8.5). The water samples that are outside the pH permissible limit are specialised bottled drinking water containing some additive fruit flavours, carbonated and alkaline ionised, considered to be responsible for the pH variation. The statistical analysis of the physicochemical parameters in the bottled drinking water quality of the samples is presented in Table 1. The pH in this study correlates with DO, potential delta and ORP, see Table 2, and is comparable with the indicated values on the label of the bottled water brand.

Dissolved oxygen of the water samples ranged from 6.480 ± 0.015 to 17.145 ± 0.535 mg/L, with a mean value of 11.603 ± 0.179 mg/L and standard deviation of 2.684, see Fig. 4. The value in this study is within the permissible limit of ≥ 6.0 mg/L, an indication that the water samples contain the required dissolved oxygen needed for healthy body. One of the sources of oxygen for blood oxygenation is from water and the level of which is very important to be in checked and follow the recommended value (Patil et al. 2012).

Table 1 Statistical analysis of the physicochemical parameters in the bottled drinking water samples in South Africa

Parameters	pH	EC ($\mu\text{S}/\text{cm}$)	TDS (ppm)	DO (mg/L)	Temp. (°C)	Delta (mV)	Salinity (psu)	Resistivity (k Ω)	ORP (mV)
No. of Samples	21	21	21	21	21	21	21	21	21
Minimum	2.96 ± 0.01	1.38 ± 0.00	0.70 ± 0.03	6.48 ± 0.02	18.55 ± 0.49	497.95 ± 0.61	0	0.89 ± 0.04	531.4 ± 0.25
Maximum	9.63 ± 0.39	737.0 ± 9.39	371 ± 13.88	17.15 ± 0.54	22.9 ± 2.89	979.15 ± 49.11	0.35 ± 0.29	242 ± 3.27	970.0 ± 44.70
Arithmetic Mean	6.68 ± 0.13	192.57 ± 2.25	99.62 ± 1.48	11.60 ± 0.18	21.42 ± 1.26	649.39 ± 12.51	0.09 ± 0.04	29.70 ± 0.60	653.21 ± 10.44
Median	7.08 ± 0.08	110.05 ± 1.67	78.35 ± 0.61	11.63 ± 0.15	22.40 ± 0.89	619.8 ± 4.57	0.06 ± 0.00	6.35 ± 0.12	612.3 ± 4.45
Mode	N/A	N/A	N/A	11.39 ± 0.32	22.50 ± 0.49	N/A	N/A	N/A	N/A
Standard deviation	1.47	208.03	102.2	2.68	1.70	123.79	0.1	57.47	123.45
SA WQG	6.0–9.0	0–700 ($\mu\text{S}/\text{cm}$)	0–450	≥ 6.0	N/A	N/A	0–1	N/A	N/A
WHO permissible limits	6.5–8.0	1500	<600	≥ 6.0	N/A	N/A	N/A	N/A	N/A

*EC: electrical conductivity, TDS: total dissolved solids, Temp.: temperature, Delta: potential, ER: electrical resistance, ORP: oxidation reduction potential, SA WQG: South Africa Water Quality Guideline, WHO: World Health Organization

Table 2 Pearson correlation coefficient of the analysed physicochemical parameters in the bottled drinking water samples in South Africa

Parameter	pH	EC	TDS	DO	Temp	Delta	Salinity	ER	ORP
pH	1								
EC	-0.494	1							
TDS	-0.485	0.981	1						
DO	-0.543	0.507	0.519	1					
Temp	-0.126	-0.285	-0.260	-0.290	1				
Delta	-0.617	0.450	0.472	0.202	-0.449	1			
Salinity	-0.476	0.998	0.981	0.495	-0.270	0.442	1		
ER	0.273	-0.417	-0.422	-0.304	0.110	-0.193	-0.430	1	
ORP	-0.598	0.402	0.421	0.160	-0.454	0.987	0.394	-0.180	1

*EC: electrical conductivity, TDS: total dissolved solids, Temp: temperature, Delta: potential, ER: electrical resistance, ORP: oxidation reduction potential

The temperature of the water samples, as shown in Fig. 5, ranged from 18.55 ± 0.489 to 22.90 ± 2.898 °C, with a mean of 21.42 ± 1.258 °C and standard deviation of 1.701. Water temperature is significant to physicochemical parameters, such as pH, DO, TDS, EC, salinity and ORP (Patil et al. 2012) but showed low and negative correlation between them in this study.

Salinity of water samples ranged from 0 to 0.35 ± 0.29 psu, with a mean value of 0.09 ± 0.04 psu and standard deviation of 0.1 (see Fig. 5 and Table 1). The permissible limit is in the range of 0–1 which is not exceeded by the water samples results.

The electrical conductivity of the water samples ranged from 1.382 ± 0.00 to 737 ± 9.389 $\mu\text{S}/\text{cm}$ with a mean value of 192.57 ± 2.247 $\mu\text{S}/\text{cm}$ and a standard deviation of 208.03 as shown in Fig. 6. The range and mean value are within both the recommended guidelines of South African Water Quality Guideline—Target Water Quality Range (TWQR) of (0–700 $\mu\text{S}/\text{cm}$) and World Health Organization—WHO of (1500 $\mu\text{S}/\text{cm}$) (SAWQG 1996; WHO 2022). In this study, EC is found as shown in Table 2 to statistically correlate very strongly with TDS, DO and salinity water properties, and comparable with (Joshi et al. 2009).

The total dissolved solids of the water samples ranged from 0.701 ± 0.033 to 371 ± 13.880 ppm, with a mean value of 99.623 ± 1.478 ppm and a standard deviation of 102.2, see Fig. 6. The range and mean value are within both the recommended guidelines of South African Water Quality Guideline—Target Water Quality Range (TWQR) of (0–450 ppm) and World Health Organization—WHO of (<600). The values are also comparable with the indicated values on the label of the water bottle. TDS as an important water quality property that tells the quantity of dissolved solids such as minerals and salts is found in this study to correlate very strongly with dissolved oxygen, conductivity and salinity as shown in Table 2.

The potential delta of the water samples ranged from 497.95 ± 0.612 to 979.15 ± 49.112 mV with a mean value

of 649.39 ± 12.514 mV and standard deviation of 123.79 (see Fig. 6 and Table 1). From Table 2, delta correlated significantly with ORP, a related parameter to DO and slightly with salinity.

The resistivity parameter of the water ranged from 0.895 ± 0.00 to 242 ± 3.266 k Ω with a mean value of 29.701 ± 0.601 k Ω and standard deviation of 57.474 as shown in Fig. 6 also in Table 1. It is an important water quality parameter which tells its ability to resist electrical current, correlates inversely with the TDS and EC and is usually higher in fresh water than saline water. It provides information on groundwater potential indicating the absence of dissolved solids or contaminants which ensures water purity for consumption (Hodlur et al. 2006; Fajana 2020).

Oxidation reduction potential also known as redox potential shows how free electrons and oxidising or reducing agent are available in drinking water (James et al. 2004). In this study, ORP has values ranging from 531.4 ± 0.245 to 970 ± 44.703 mV with a mean of 653.121 ± 10.437 mV and standard deviation of 123.454 (see Fig. 5 and Table 1). Although there is no recommended value for the ORP, the values observed here suggest drinking water rich in redox agent enough for body electrolytic balance. A correlation of 0.160 was observed between ORP and DO, suggesting that low or higher value of ORP in drinking water does not necessarily implied that there is less or a lot of DO present and is comparable with findings by (James et al. 2004; Austin et al. 2009).

Table 2 shows the Pearson correlation coefficient of the analysed physicochemical parameters in the bottled drinking water samples in South Africa. Values that are close to 1 and -1 or where $R > 0.8$ have high correlation, those whose values of R in the range of 0.4 to 0.8 correlates moderately, whereas those close to 0 have low correlation or there is no significant interaction between the parameters involved (Abdessamed et al. 2023). The range of Pearson's coefficient is from -0.617 and 0.273; -0.422 and 0.981; and -0.123 and 0.987. The

Table 3 Concentrations and summary statistics of trace, rare-earth elements and heavy metals (mg/L) in commercial bottled drinking water in South Africa using ICP-MS (mean concentration ± SD) number of samples 21

Elements	Maximum (mg/L)	Minimum (mg/L)	Mean (mg/L)	Stdev	WHO (2004, 2022) (mg/L)	TWQR-SA (1996) (mg/L)
Li	0.0170 ± 0.0003	0.00	0.0020 ± 3.03E-05	0.0038	N.G	N.G
Be	0.0007 ± 0.0005	0.00	0.0226 ± 8.07E-05	0.0002	N.G	N.G
C	734.809 ± 231.514	0.00	132.0857 ± 24.6992	231.7373	N.G	N.G
Na	6.8165 ± 0.1740	0.00	1.4854 ± 0.0242	2.4467	< 20	0–100
Mg	42.5622 ± 0.3265	0.00	8.5293 ± 0.0645	12.6673	30	0–30
Al	0.2442 ± 0.0138	0.00	0.0301 ± 0.0014	0.0703	0.2	0–0.15
Si	14.5449 ± 0.1292	0.00	3.7496 ± 0.0267	4.3139	N.G	N.G
P	0.0537 ± 0.0005	0.00	0.0037 ± 6.97E-05	0.0119	N.G	N.G
Cl	21.5009 ± 1.9979	0.00	3.6316 ± 0.2814	6.3116	5	N.G
K	93.6178 ± 8.1812	0.00	11.7508 ± 5.2044	21.3885	10	0–50
Ca	288.8297 ± 4.1015	0.00	80.8176 ± 0.6389	116.0008	75	0–32
Ti	0.1838 ± 0.0026	0.00	0.0364 ± 0.0007	0.0575	N.G	N.G
V	0.0042 ± 7.78E-05	0.00	0.0005 ± 1.48E-05	0.0010	N.G	0–0.1
Cr	0.0213 ± 0.0083	0.00	0.0036 ± 0.0007	0.0062	0.05	0–0.05
Mn	0.1569 ± 0.0005	0.00	0.0080 ± 3.8E-05	0.0341	0.08	0–0.05
Fe	0.2807 ± 0.0092	0.00	0.0021 ± 0.1921	0.0027	0.3	0–0.1
Co	0.0034 ± 3.54E-05	0.00	0.0002 ± 2.36E-06	0.0007	N.G	N.G
Ni	0.0019 ± 2.83E-05	0.00	9.21E-05 ± 2.36E-06	0.0004	0.07	N.G
Cu	0.0423 ± 0.0007	0.00	0.0054 ± 7.78E-05	0.0107	2	0–1
Zn	0.0567 ± 0.0006	0.00	0.0027 ± 2.93E-05	0.0124	3	0–3
As	0.0009 ± 2.12E-05	0.00	0.0002 ± 3.37E-06	0.0002	0.01	0–10
Se	0.04975 ± 0.0696	0.00	0.0025 ± 0.0033	0.0152	0.04	0–20
Br	0.1434 ± 0.0729	0.00	0.0406 ± 0.0048	0.0502	N.G	N.G
Rb	0.1033 ± 0.0729	0.00	0.0016 ± 0.0035	0.0224	N.G	N.G
Sr	1.1535 ± 0.07225	0.00	0.0733 ± 0.0040	0.2489	N.G	N.G
Zr	0.0011 ± 0.0006	0.00	0.0002 ± 7.27E-05	0.0003	N.G	N.G
Ag	0.0053 ± 5.66E-05	0.00	0.0003 ± 1.08E-05	1.64E-05	0.01	N.G
Cd	3.50E-05 ± 7.07E-06	0.00	2.86E-06 ± 6.73E-07	8.60E-06	0.003	0–5
Sb	0.0006 ± 1.414E-05	0.00	0.0002 ± 3.70E-06	4.81E-06	0.02	N.G
I	0.0731 ± 0.0026	0.00	0.0099 ± 0.0003	0.0163	N.G	N.G
Cs	0.0005 ± 1.41E-05	0.00	4.93E-05 ± 1.01E-06	0.0001	N.G	N.G
Ba	0.2235 ± 0.0063	0.00	0.0241 ± 0.0007	0.0627	1.3	N.G
La	0.0066 ± 0.0002	0.00	0.0004 ± 1.52E-05	0.0014	N.G	N.G
Ce	0.0067 ± 0.0002	0.00	0.0004 ± 1.28E-05	0.0015	N.G	N.G
Nd	0.0004 ± 1.41E-05	0.00	3.07E-05 ± 1.68E-06	9.58E-05	N.G	N.G
Hg	0.0005 ± 0.0007	0.00	2.52E-05 ± 3.43E-05	0.0001	0.006	0–1
Pb	0.0004 ± 0.0002	0.00	2.88E-05 ± 1.11E-05	9.95E-05	0.01	0–10
Th	7.00E-05 ± 7.07E-06	0.00	6.43E-06 ± 1.01E-06	1.78E-05	N.G	N.G
U	0.0029 ± 0.0002	0.00	0.0002 ± 1.45E-05	0.0007	0.03	N.G

*N.G.: not available, Stdev. and SD: Standard deviation, WHO: World Health Organization guidelines, TWQR-SA: Total Water Quality Range of South Africa

parameters (pH) show a negatively moderate correlation with EC, TDS, DO, salinity and ORP. A very strong significant correlation is observed between salinity and EC, TDS with values of R as 0.998 and 0.981, respectively. ORP and delta also show high correlation of 0.987. A

very low correlation is observed between pH and temperature, resistivity; dissolved oxygen (DO) and delta, ORP; resistivity and ORP, temp and delta.

Concentrations of trace, heavy and rare-earth elements

Table 3 presents the concentrations (mg/L) of lithium (Li), beryllium (Be), carbon (C), sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), bromine (Br), rubidium (Rb), strontium (Sr), zirconium (Z), silver (Ag), cadmium (Cd), antimony (Sb), iodine (I), caesium (Cs), barium (Ba), lanthanum (La), cerium (Ce), neodymium (Nd), mercury (Hg), lead (Pb), thorium (Th) and uranium (U), measured utilising the ICP-MS analysis.

The concentration of Al in the water samples ranges from 0 to 0.245 ± 0.013 mg/L, with a mean value of 0.0301 ± 0.0014 mg/L and a standard deviation of 0.070. The permissible limit and guideline level for Al are 0.2 and 0–0.15, respectively (WHO 2004, 2022 and SAWQG 1996). 4.76% of the samples exceeded the limit, and it is of the natural carbonated water sample type. Al is used in the treatment of water and as food additives (WHO 2022). In domestic water, Al where there is Fe or Mn has aesthetic effects, in relation to discolouration and relates to causing Alzheimer's disease as well as chronic neurological disorders such as dialysis dementia (SAWQG 1996; Abdul et al. 2012). Fe concentration in the water samples ranges from 0 to 0.281 ± 0.009 mg/L with a mean of 0.086 ± 0.002 mg/L and standard deviation of 0.113. The permissible limit of Fe in drinking water is 0.3 and 0–0.1 mg/L, respectively (WHO 2004, SA WQG, 1996). 23.81% of the samples exceeded the South African Water Quality Guideline but is below the WHO recommendation. The excessive ingestion and overaccumulation of Fe may cause haemorrhage, metabolic acidosis, cardiac depression and tissue damage (SAWQG 1996; Abdul et al. 2012). The concentration of Cu in the water samples range from 0 to 0.042 ± 0.001 mg/L with a mean of 0.005 ± 0.0001 mg/L and standard deviation of 0.011. None of the samples showed high Cu concentration above the permissible limit. However, Cu is considered an essential nutrient but at higher doses is observed to cause gastrointestinal irritation, nausea and vomiting (SAWQG 1996; USEPA 1999). Zn concentration in the drinking water samples ranges from 0 to 0.057 ± 0.001 mg/L with mean of 0.002 ± 0.0002 mg/L and standard deviation of 0.012. Only 4.76% of the water samples contain Zn and the concentrations are below the acceptable limit of 3 mg/L set by both (SAWQG 1996; WHO 2022). Zn is a trace element that is essential for physiological and metabolic processes in living organism, but in high concentration it can have severe, acute toxicity, disturbances in electrolytes and renal damage possibility (Pillai 1983; SAWQG 1996).

The concentration of Pb in the water samples is in the range of 0 to 0.0004 ± 0.0002 mg/L with a mean of $2.88E-05 \pm 1.11E-05$ mg/L and standard deviation of $9.95E-05$, shown by only 9.52% of the samples. The desirable limit of Pb in drinking water is 0.01 mg/L (WHO 2022) and 0–10 mg/L (SAWQG 1996), and is not exceeded by the Pb concentration. However, the acute and or irreversible effects of high level of Pb on human health include neurological impairment, respiratory disorder and anaemia, with high sensitivity to Pb toxicity by children which could damage their brain (Abdul et al. 2012; SAWQG 1996). The concentration of Mg in the drinking water is in the range of 0 to 42.562 ± 0.326 mg/L, mean of 8.529 ± 0.0645 mg/L and standard deviation of 12.667. The permissible limit of Mg in drinking water is 30 mg/L (WHO 2022; SAWQG 1996). The mean value of Mg is below acceptable limit whereas the maximum value (recorded from natural carbonated sparkling water) is above the permissible limit. Magnesium carbonate is one of the common minerals of magnesium and could inform the reason why the permissible limit is exceeded in this water sample (Nerbrand et al. 2003). Mg has a property of bitter taste and makes it provide natural protection against the ingestion of concentrations that could be potentially harmful. However, high levels of Mg in drinking water may cause diarrhoea, severe scaling and health problems (Kozisek 2020; Abdul et al. 2012; SAWQG 1996). However, Mg in drinking water was found to play a protective role against cardiovascular disease (Kozisek 2020). The concentration of Ca in the water samples ranges from 0 to 288.829 ± 4.102 mg/L, mean of 80.818 ± 0.639 mg/L and standard deviation of 116.001. The permissible limit of Ca in drinking water is 75 mg/L (WHO 2022) and 0–32 mg/L (SAWQG 1996). 28.57% of the water samples exceeded the permissible limit set by WHO whereas 42.86% of the water samples are above the recommended level by SAWQG. Natural mineral spring water were the samples type found with the elevated levels of Ca. In human diet, Ca is an important mineral element having a range of 500 to 1400 mg per day total dietary intake, considered to play protective role against cardiovascular disease and moderate the toxicity of other heavy metals (SAWQG 1996). However, studies showed that major cardiovascular risk factors correlated significantly with the content of Ca in water (Nerbrand et al. 2003; Kozisek 2020). K concentration in the drinking water is in the range of 0 to 93.618 ± 8.181 mg/L, mean of 11.751 ± 5.204 mg/L and standard deviation of 21.388. The recommended limit of K in drinking water is 10 mg/L (WHO 2004) and 0–50 mg/L (SAWQG 1996). 23.81% and 4.76% of the samples exceed the WHO and SAWQG permissible limit, respectively. However, the daily recommended requirement of K is > 3000 mg as it is essential element in human and found widely in the environment including natural drinking water at concentrations levels of no health

concern (WHO 2022). However, elevated levels of K cause hyperkalaemia and have adverse effects on high-risk groups such as infants or persons with renal disease, kidney and heart disease, diabetes as well as those under medication that interfere with functioning of K in the body (WHO 2009).

The concentration of Mn in the water samples ranges from 0 to 0.1569 ± 0.0005 mg/L, mean value of $0.0080 \pm 3.8E-05$ mg/L and standard deviation of 0.0341. The permissible limit of Mn in drinking water is 0.08 mg/L (WHO 2022) and 0–0.05 mg/L (SAWQG 1996). 4.76% of the water exceed both permissible limits of Mn in drinking water, and it is observed in spring water sample type. It could be attributed to its natural occurrence in groundwater, or contamination from the water bottling process (WHO 2022; Feru 2004). Mn is an important trace element, as its deficiency could lead to anaemia, impairment in growth and abnormalities in the skeleton (SAWQG 1996; WHO 2022). However, ingestion of elevated levels of Mn in drinking water could cause severe health effects such as neurological effects with diminished cognitive ability, temporarily suggested Parkinson's disease (WHO 2022; SAWQG 1996). The concentration of Cr in the analysed drinking water ranges from 0 to 0.0213 ± 0.0083 mg/L, mean of 0.0036 ± 0.0007 mg/L and standard deviation of 0.0062. The permissible limit of Cr in drinking water is 0.05 mg/L (WHO 2022; SAWQG 1996) and is not exceeded in this study. Cr is one of the heavy metals of carcinogenic attributes. If found in high concentrations in drinking water, it portends risk of acute toxicity, slight nausea and increasing risk of cancer induction, especially gastrointestinal cancer over prolonged exposure (SAWQG 1996; WHO 2020; Naz et al 2016). Ni concentration in the water samples ranges from 0 to $0.0019 \pm 2.83E-05$ mg/L with mean value of $9.21E-05 \pm 2.36E-06$ mg/L and standard deviation of 0.0004. 9.52% of the samples yielded that results while others have zero values. The permissible limit of Ni in drinking water 0.07 mg/L is not exceeded in this study. Ni is also one of the heavy metals that has attributes of carcinogen through ingestion route (DHHS 2002). The concentration of Cd in the drinking water ranges from 0 to $3.50E-05 \pm 7.07E-06$ mg/L, mean of $2.86E-06 \pm 6.73E-07$ mg/L and standard deviation of $8.60E-06$. The results are produced by only 14.29% of the samples and are below the permissible limit of 0.003 mg/L and 0–5 mg/L, respectively (WHO 2022; SAWQG 1996). However, Cd is one of the carcinogenic heavy metals, elevated concentrations with long-term exposure put individuals in high risk of kidney damage, effect for which is potentially acute or irreversible on human health (SAWQG 1996).

The concentration of Na ranges from 0 to 6.8165 ± 0.1740 mg/L mean of 1.4854 ± 0.0242 mg/L and standard deviation of 2.4467. Guidance level of Na is < 20 mg/L (WHO 2022) and 0–100 mg/L (SAWQG

1996) and is not exceeded by the drinking water samples in this study. As an essential element, the body of humans needs Na whose functions include the regulation of fluids, transmission of nerves impulses, contraction of impulses as well as relaxing (Jeffery et al 2014). However, high concentrations of Na in drinking water make it have very salty taste with tendency of causing nausea and vomiting. It increases the risk of severe health effects such as hypertension, disease of the heart and stroke, gastrointestinal track ulceration, disturbances of the central nervous system and possibility of pulmonary oedema (USEPA 2003; Jeffery et al 2014). The concentration of U in drinking water ranges from 0 to 0.0029 ± 0.0002 mg/L mean of $0.0002 \pm 1.45E-05$ mg/L and standard deviation of 0.0007, presented by 38.10% of the samples, while 61.90% of the samples recorded zero concentration. The acceptable limit of U in drinking water is 0.03 mg/L (WHO 2004) which is not exceeded by the drinking water samples in this study. U is a chemical element and a toxic heavy metal that is ubiquitous and has potential health effects (due to elevated levels and prolong exposure) of kidney damage, composition of urine changes and liver or bone cancer (WHO 2005; Kurttio et al. 2002). Ba concentration in the drinking water ranges from 0 to 0.2235 ± 0.0063 mg/L, mean value of 0.0241 ± 0.0007 mg/L and standard deviation of 0.0627. The recommended guideline level of Ba is 1.3 mg/L (WHO 2022) and is not exceeded by the water samples in this study.

The concentration of C in the drinking water samples ranged between 0 to 734.809 ± 231.514 mg/L with a mean value of 132.0857 ± 24.6992 mg/L and standard deviation of 231.7373, recorded by 61.90% of the drinking water samples, whereas 38.10% recorded zero. There is no permissible limit for C in drinking water.

The maximum concentrations of Al, Fe, Mg, Ca, K and Mn were above the permissible limits of the drinking water quality, while the other elements analysed did not exceed the limits, as provided by WHO and SAWQG. This may be due to factors such as the geological formation of the aquifer or bedrock for which water is in contact with, anthropogenic factors such as industrial processing, discharge of sewage and acid mined water seepage into soil, which could contaminate natural spring water (APHA 1999; Fajana 2020; USEPA 2012). This call for remedial action by relevant authority to mitigate the long-time effects this exceedence could have on the people consuming such water. The concentrations of the heavy metals analysed in the drinking water samples are presented in Fig. 7. The mean concentration of the heavy metals in the drinking water samples as measured was in the decreasing toxicity order of Sr > Al > Ba > Mn > Cu > Cr > Zn > Fe > As > Co > U > Ni > Cs > Pb > Cd > Hg. This order skewed the highly toxic heavy metals to the right, which is the low-level concentration region.

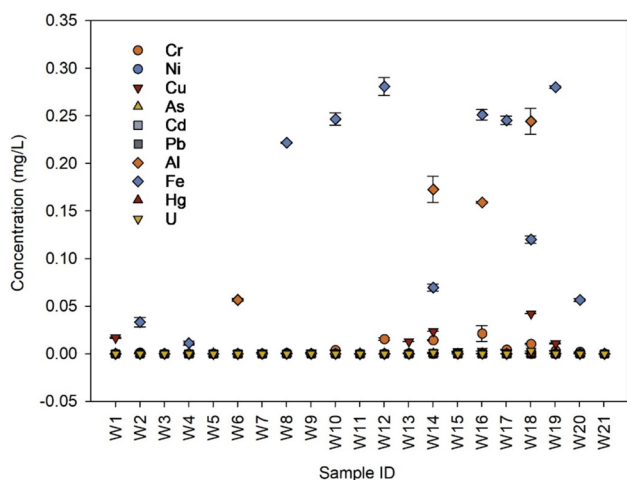


Fig. 7 Heavy metal concentrations of Cr, Ni, Cu, As, Cd, Pb, Al, Fe, Hg and U in the different bottled drinking water samples (mg/L) measured in this study with whiskers representing standard deviation

Assessment of human health risk

Assessment of non-carcinogenic risk

The assessment of health risks of humans involves estimating the kind and level of health effects people could be exposed to in an environment that is contaminated, especially by toxic chemicals. In this study, the computed chronic daily intake (CDI), hazard quotient (HQ) and hazard

index (HI) values for the adults due to heavy metals in the consumption of bottled drinking water of South Africa are shown in Table 4. The results showed that the mean levels of the CDI (mg/kg-day) are 6.31E-08 for Li, 2.54E-09 for Be, 1.13E-05 for Cr, 2.52E-07 for Mn, 2.72E-06 for Fe, 2.90E-09 for Ni, 1.71E-07 for Cu, 8.48E-08 for Zn, 5.52E-09 for As, 8.98E-11 for Cd, 7.59E-07 for Ba, 7.93E-10 for Hg, 9.05E-10 for Pb, 9.05E-06 for Sr and 1.41E-08 for V. Hence, the mean values of the CDI for the concentration of heavy metals for the adults are determined to be of the order of Cr > Fe > Sr > Ba > Mn > Cu > Zn > Li > V > As > Ni > Be > Pb > Hg > Cd. The estimated chronic daily intake values in the drinking water were all below the recommended permissible limit (USEPA 2011).

The estimated values of HQ as shown in Table 4 columns 5–7 for the heavy metals are all less than 1. Therefore, the health risk estimation of Li, Be, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Ba, Hg, Pb, Sr and V by their mean values showed an acceptable level of the non-carcinogenic health risk in all the bottled drinking water samples analysed from South Africa. The individual contributions of the heavy metals can be said to be in the order of Li > As > V > Ba > Fe > Cu > Sr > Hg > Mn > Pb > Zn > Cd > Ni > Be > Cr. The HI estimated value, which is the total of the HQs, as shown in Table 4 at the bottom of columns 5–7 has a mean of 2.07E-03 and a range of 0.00 to 1.76E-02, all of which falls below 1. It therefore suggests that consumption of bottled drinking water by the people of South Africa will not pose any non-carcinogenic health risk due to heavy metals exposure.

Table 4 Non-carcinogenic human health risks values of chronic daily intake (CDI), hazard quotient (HQ) and hazard index (HI) due to ingestion of heavy metals in bottled drinking water in South Africa

Heavy metal	Chronic daily intake (CDI) (mg/kg/day)			Hazard quotient (HQ)			RfD (mg/kg-day)*
	Mean	Minimum	Maximum	Mean	Minimum	Maximum	
Li	6.31E-08	0.00	5.28E-07	2.00E-03	0.00	1.68E-02	2.00E-02
Be	2.54E-09	0.00	2.15E-08	1.27E-07	0.00	1.08E-06	2.00E-03
Cr	1.13E-05	0.00	6.68E-07	3.78E-08	0.00	2.23E-04	3.00E-03
Mn	2.52E-07	0.00	4.93E-06	1.80E-06	0.00	3.52E-05	1.40E-01
Fe	2.72E-06	0.00	8.82E-06	9.06E-06	0.00	2.94E-05	3.00E-01
Ni	2.90E-09	0.00	5.94E-08	1.45E-07	0.00	2.97E-06	2.00E-02
Cu	1.71E-07	0.00	1.33E-06	4.28E-06	0.00	3.33E-05	4.00E-02
Zn	8.48E-08	0.00	1.78E-06	2.83E-07	0.00	5.94E-06	3.00E-01
As	5.52E-09	0.00	2.77E-08	1.84E-05	0.00	9.22E-05	3.00E-04
Cd	8.98E-11	0.00	1.10E-09	1.80E-07	0.00	2.20E-06	5.00E-04
Ba	7.59E-07	0.00	7.02E-06	1.08E-05	0.00	1.00E-04	7.00E-02
Hg	7.93E-10	0.00	1.59E-08	2.64E-06	0.00	5.29E-05	3.00E-04
Pb	9.05E-10	0.00	1.35E-08	6.47E-07	0.00	9.65E-06	1.40E-03
Sr	2.30E-06	0.00	3.23E-05	3.84E-06	0.00	6.04E-05	6.00E-01
V	1.41E-08	0.00	1.32E-07	1.41E-05	0.00	1.32E-04	1.00E-03
Hazard index (HI)				2.07E-03	0.00	1.76E-02	

*USEPA (2011), Mohammadi et al. (2019), Bempah and Ewusi (2016), Wu et al. (2009). RfD=Reference Dose

Assessment of carcinogenic risk

Assessment of carcinogenic risk is performed for heavy metals such as Cr, Ni, As, Cd and Pb that have potential of yielding cancer in humans due to exposure to same (USEPA 1989; Mohammadi et al 2019). Table 5 presents the estimated values of ILCR for the heavy metals, and the cancer slope factor (SF) in column 5, which was used together with the CDI in the determination of the ILCR. The results from this study showed total mean values of ILCR to be $4.67E-06$, and range of 0.00 to $2.76E-05$, which is insignificant as well as within the permissible level of the cancer risk guidance limit of $1.00E-06$ to $1.00E-04$ (Wu et al 2009). An indication that the consumption of bottled drinking water in South Africa is safe and without contamination with heavy metals that could cause carcinogenic health risk.

Table 6 presents the comparison of heavy metal concentration in drinking water from South Africa (present study) and other countries of the world and the water quality guideline values by international organisations, such as World Health Organization (WHO) and US Environmental Protection Agency (USEPA). The type of water considered in this comparison is of groundwater source. It can be observed that the concentration of heavy metals in the bottled drinking water from South Africa has values in a close order of magnitude to those of natural spring water from Iran but less than those reported by other countries of the world. Moreso, the concentrations are below the guideline values except for countries like Ghana and Nigeria which exceeded the limits. This variation could be due to the geological location variation across the world, anthropogenic factors as well as industrial water production processes (Oyeku and Eludoyin 2010; WHO 2022).

Conclusion

The purpose of this study is to investigate the composition and characteristics of the natural mineral bottled drinking water consumed in South Africa with the view to ascertain the potential health risks related with the exposure to heavy metal contaminants. Utilising specialised ICP-MS and physicochemical parameters system of analysis, the results showed varying concentration levels of trace, heavy and rare-earth elements across the various brands in relation to compliance with regulatory standards. Additionally, our findings underscore the importance of monitoring the concentrations of heavy metal in bottled drinking water. The physicochemical parameters, such as pH, EC, DO, ORP, resistivity and salinity among others, were found to be within the acceptable levels, showing overall water quality.

The maximum concentrations of Al, Fe, Mg, Ca, K and Mn in some samples were above the permissible limits of

Table 5 Carcinogenic human health risks values of incremental lifetime cancer risk (ILCR) due to the ingestion of heavy metals in the bottled drinking water by adults in South Africa

Heavy metal	Incremental lifetime cancer risk (ILCR)			Cancer slope factor (SF) (kg/day/mg)*
	Mean	Minimum	Maximum	
Cr	$4.65E-06$	0.00	$2.74E-05$	41
Ni	$2.43E-09$	0.00	$4.99E-08$	0.84
As	$8.28E-09$	0.00	$4.15E-08$	1.5
Cd	$5.48E-10$	0.00	$6.71E-09$	6.1
Pb	$7.70E-09$	0.00	$1.15E-07$	8.5
Σ ILCR	$4.67E-06$	0.00	$2.76E-05$	

*USEPA (2011), Mohammadi et al. (2019)

the drinking water quality, while those of other elements analysed did not exceed the limits, as provided by WHO and SAWQG. Samples with exceeding concentration limits are of the type—fruit flavoured carbonated sparkling drinking water. Hence, potential long-time effects this exceedence could have on the people consuming such water should be examined. The mean concentration of the heavy metals in the drinking water samples as measured was in the decreasing toxicity order of $Sr > Al > Ba > Mn > Cu > Cr > Zn > Fe > As > Co > U > Ni > Cs > Pb > Cd > Hg$. The mean values of the CDI for the concentration of heavy metals for adults are determined to be of the order of $Cr > Fe > Sr > Ba > Mn > Cu > Zn > Li > V > As > Ni > Be > Pb > Hg > Cd$. The estimated chronic daily intake values in the drinking water were all below the recommended permissible limit. The estimated values of both HQ and HI (with mean of $2.07E-03$ and range of 0.00 to $1.76E-02$) for the heavy metals are all found to be less than 1. Therefore, the health risk estimation of Li, Be, Cr, Mn, Fe, Ni, Cu, Zn, As, Cd, Ba, Hg, Pb, Sr and V by their mean values showed an acceptable level of the non-carcinogenic health risk in all the bottled drinking water samples analysed. Meanwhile, the results from this study showed total mean values of ILCR to be $4.67E-06$, and range of 0.00 to $2.76E-05$, which is insignificant as well as within the permissible level of the cancer risk guidance limit of $1.00E-06$ to $1.00E-04$. An indication that the consumption of bottled drinking water in south Africa may be safe and without contamination with heavy metals that could cause carcinogenic health risk. However, the long-time potential effects due to the few exceeded metals needed to be considered. The bottled drinking water from this study compares well with other countries but with less heavy metals concentration.

This study is limited to the assessment of the physicochemical parameters, trace and heavy metals and the health risk from most consumed natural spring commercial bottled water in South Africa, using the ICP-MS destructive

Table 6 Comparison of heavy metal concentration in drinking water from South Africa (present study) and other countries of the world and the water quality guideline values by international organisations

Country	Water type	Heavy metals mean concentrations (mg/L)										References
		Cr	Ni	Cu	As	Cd	Pb	Al	Fe			
South Africa	Natural mineral spring bottled water	0.0036±0.0007	9.21E-05 ± 2.36E-06	0.0054 ± 7.78E-05	0.0002 ± 3.37E-06	2.86E-06 ± 6.73E-07	2.88E-05 ± 1.11E-05	0.0301 ± 0.0014	0.0021 ± 0.1921	0.0021 ± 0.1921	0.0021 ± 0.1921	Present study
Ghana	Groundwater	1.0 ± 0.94	7.31 ± 4.48	35.03 ± 7.80	8.81 ± 13.16	0.44 ± 0.27	4.43 ± 3.34	512.59 ± 488.33				Bempah and Ewusi (2016)
Iran	Natural spring water	0.00508	0.00347	0.00679	–	0.00043	0.0032	–	–	–	–	Mohammadi et al. (2019)
India	Groundwater	0.01	0.05	0.06	0.01	0	0.02	0.11	0.14			Rasheed et al. (2012)
Ethiopia	Groundwater	0.146 ± 0.009	0.0037 ± 0.0006	–	0.395 ± 0.006	0.017 ± 0.002	0.069 ± 0.026	–	0.379 ± 0.234			Mebrahtu and Zerabruk (2011)
Nigeria	Groundwater	–	–	0.02 ± 0.04	–	–	2.4 ± 3.3	–	4.23 ± 6.4			Oyeku and Eludoyin (2010)
Turkey	Pump drinking water	0.00418 ± 0.00035	0.00216 ± 0.00019	0.00484 ± 0.00025	–	–	–	0.00621 ± 0.003	0.0346 ± 0.0003			Tuzen and Soyak (2006)
WHO Guideline	Drinking water	0.05	0.07	2.0	0.01	0.003	0.01	0.2	0.3			WHO (2022)
USEPA Guideline	Drinking water	0.05	0.1	1.0	0.01	0.005	0.05	0.15	0.3			USEPA (2012)

analytical technique. It could be further expanded to include more and all available and consumed natural mineral spring bottled commercial water, also utilising other methods like ion chromatography (for anions and cations components of physicochemical parameters), hyper pure germanium (HPGe) gamma spectrometry technique (for activity concentration levels of natural radionuclides and radiological health risk analysis) and or liquid scintillation counting (LSC) technique for hydrogen and tritium or gross alpha and beta in the drinking water.

This study contributes to the existing body of knowledge in safety of bottled drinking water, especially, in the context of human health risk due to exposure to heavy metals, by providing baseline data for reference. It also underscores the significance of stringent quality control measures and regular monitoring to ensure the safety as well as the integrity of the bottled water products. It will boost the safeguarding of public health and the confidence of consumers.

It is highly recommended that there should be continuous research on bottled drinking water to assess the sources and ingestion pathway of heavy metals contamination and human exposure, with potential mitigation strategies. Furthermore, there should be public awareness campaigns on the importance of quality of water whereby healthier drinking water practices could be achieved in the process.

Acknowledgements The authors wish to thank Mr Sizwe Loyilani of the Chemistry Analytical Laboratory of the North West University Mahikeng Campus for assisting with the physicochemical parameter's measurement. This research was supported by the Postdoctoral Research Fund of the North West University, South Africa.

Funding Open access funding provided by North-West University. Research and open access funding provided by North West University, Mahikeng Campus, South Africa, Research fund No NW 1G01487; 1D 01986.

Data availability All the data are within the article.

Declarations

Conflict of interest The authors have declared no conflict of interest and wish to state that this research was done based on principle of conducting responsible research with proper citation of sources, accurate reporting of data and avoidance of plagiarism and fabrication. Hence, no personal identifying information was included in the analysis or article.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will

need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Abdessamed D, Jodar-Abellan A, Ghoneim SSM, Almaliki A, Hussein EE, Pardo MA (2023) Groundwater quality assessment for sustainable human consumption in arid areas based on GIS and water quality index in the watershed of Ain Sefra (SW of Algeria). *Environ Earth Sci* 82:510–529. <https://doi.org/10.1007/s12665-023-11183-9>
- Abdul RM, Mutnuri L, Dattatreya PJ, Mohan DA (2012) Assessment of drinking water quality using ICP-MS and microbiological methods in the Bholakpur area, Hyderabad, India. *Environ Monit Assess* 184:1581–1592. <https://doi.org/10.1007/s10661-011-2062-2>
- Altunisik A (2023) Microplastic pollution and human health risk assessment in Turkish bottled natural and mineral waters. *Environ Sci Pollut Res* 30:39816–39825. <https://doi.org/10.1007/s11356-022-25054-6>
- AoPrice (2023) Top 10 best bottled water brands in South Africa. Retrieved from AoPrice: aoprice.com/top-10-best-bottled-water-brands-in-south-africa.html
- APHA (1999) Standard methods for the examination of water and wastewater, 20th edn. APHA, Washington
- Austin D, Carroll J, Alkons-Wolinsky R, Scharf R, Mericas D, Enoch M, Hicks D, Murphy P (2009) Whole lake oxygen dynamic studies: a prelude to engineering controls of internal phosphorus loading. In: Proceedings of the water environment federation, pp 1–18. <https://doi.org/10.2175/193864709793958138>
- Bempah CK, Ewusi A (2016) Heavy metals contamination and human health risk assessment around Obuasi gold mine in Ghana. *Environ Monit Assess* 188:261–274. <https://doi.org/10.1007/s10661-016-5241-3>
- DHHS (2002) Report on Carcinogens—Nickel Compounds and Metallic Nickel Fifteenth Edition. Department of Health and Human Services. New York: Human Health Services HHS. Retrieved from <https://ntp.niehs.nih.gov/sites/default/files/ntp/roc/content/profiles/nickel.pdf>. Accessed 06 Feb 2024
- DOH (2006). Foodstuffs, cosmetics and disinfectants Act, 1972 (Act No. 54 of 1972); Regulations relating to all Bottled Waters. Retrieved from Polity, Department of Health - Government Notices No. 29051; R.718: www.polity.org.za. Accessed 16 Feb 2024
- DOH (2010). Foodstuffs, cosmetics and disinfectants Acts, 1972 (Act No. 54 of 1972): Regulations Relating to all Bottled Waters: Amendment. Retrieved February 16, 2024, from Polity, Department of Health - Government Notice No. 33219; 455: polity.org.za
- Ehsan M, Shabbir H, Al-Quraishi AMF, Al-Ansari N, Ahmad Z, Abdelrahman K, Sohail MT, Manzoor Z, Shafi A, Elbeltagi A (2024) Groundwater delineation for sustainable improvement and development aided by GIS, AHP, and MIF techniques. *Appl Water Sci* 14:23–29. <https://doi.org/10.1007/s13201-023-02065-3>
- Fajana A (2020) Groundwater aquifer potential using electrical resistivity method and porosity calculation: a case study. *NRIAG J Astron Geophys* 9(1):168–175. <https://doi.org/10.1080/20909977.2020.1728955>
- Feru A (2004) Bottled natural mineral waters in Romania. *Environ Geol* 46:670–674. <https://doi.org/10.1007/s00254-004-1006-3>
- GCIS (2022) South Africa Yearbook (SAYB) 2021/22 (Originally published as South Africa Official Yearbook) (29th ed.) (M. Mokoena, Ed.) Pretoria: Government Communications (GCIS).

- Retrieved January 25, 2024, from <https://www.gcis.gov.za/official-guide-south-africa-202122>
- Grabow WOK (1986) Water quality assessment and control in South Africa. *South Afr J Sci* 82:342–348. https://doi.org/10.10520/AJA00382353_5486
- Hodgson K, Manus L (2006) A drinking water quality framework for South Africa. *Water SA* 32(5):1–6
- Hodlur GK, Dhakate R, Andrade R (2006) Correlation of vertical electrical sounding and borehole-log data for delineation of saltwater and freshwater aquifers. *Geophysics* 71(1):G11–G20. <https://doi.org/10.1190/1.2169847>
- James CN, Copeland RC, Lytle DA (2004) Relationships between Oxidation-Reduction Potential, Oxidant, and pH in Drinking Water 1–13. U.S. Environmental Protection Agency. Retrieved February 27, 2024, from https://cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=125092
- Jeffery SL, John H, Doug V (2014) Sodium in drinking water. Public Health Madison and Dane County -Healthy People and Places, 1–5. Retrieved February 6, 2024, from <https://www.publichealthmdc.com/documents/SodiumDrinkingWater.pdf>
- Jindal R, Sharma C (2011) Studies on water quality of Sutlej River around Ludhiana with reference to physicochemical parameters. *Environ Monit Assess* 174:417–425. <https://doi.org/10.1007/s10661-010-1466-8>
- John SOO, Akpa TC, Onoja RA (2021) Gross alpha and gross beta radioactivity measurements in groundwater from Nasarawa North district Nasarawa state Nigeria. *Radiat Prot Environ* 44:3–11. https://doi.org/10.4103/rpe.RPE_24_20
- Joshi DM, Bhandari NS, Kumar A, Agrawal N (2009) Statistical analysis of physicochemical parameters of water of river Ganga in Haridwar district. *RASAYAN J Chem* 2(3):579–587
- Kekes T, Tzia C, Kolliopoulos G (2023) Drinking and natural mineral water: treatment and quality-safety assurance. *Water* 15:2325–2364. <https://doi.org/10.3390/w15132325>
- Kozisek F (2020) Regulations for calcium, magnesium or hardness in drinking water in the European Union member states. *Regul Toxicol Pharmacol* 112:104589. <https://doi.org/10.1016/j.yrtph.2020.104589>
- Kurttio P, Auvinen A, Salonen L, Saha H, Pekkanen J, Mäkeläinen I, Väisänen SB, Penttilä IM, Komulainen H (2002) Renal effects of uranium in drinking water. *Environ Health Perspect* 110(4):337–342. <https://doi.org/10.1289/ehp.02110337>
- Liang G, Gong W, Li B, Zuo J, Pan L, Liu X (2019) Analysis of heavy metals in foodstuffs and an assessment of the health risks to the general public via consumption in Beijing, China. *Int J Environ Res Public Health* 16:909–918. <https://doi.org/10.3390/ijerph16060909>
- Madzunya D, Dudu VP, Mathuthu M, Manjoro M (2020) Radiological health risk assessment of drinking water and soil dust from Gauteng and North West Provinces, in South Africa. *Heliyon* 6:e03392. <https://doi.org/10.1016/j.heliyon.2020.e03392>
- Mascha M (2023) Bottled water of South Africa. Retrieved August 8, 2023, from Fine Waters. <https://finewaters.com>
- Mathuthu M, Olobatoke R (2016) Assessment of heavy metals and radionuclide concentrations in mafikeng waste water treatment plant. *J Water Resour Prot* 8:93–99. <https://doi.org/10.4236/jwarp.2016.81008>
- Mathuthu J, Mokhine ND, Mkiva N, Nde SC, Dennis I, Hendriks J, Palamuleni L, Kupi TG, Mathuthu M (2021) Determination of Water Isotope compositions for the IAEA WICO and North West Villages, South Africa. *Water* 13:2801–2810. <https://doi.org/10.3390/w13202801>
- Mebrahtu G, Zerabruk S (2011) Concentration and health implication of heavy metals in drinking water from urban areas of Tigray region, Northern Ethiopia. *Momona Ethiopian J Sci* 3:105–121. <https://doi.org/10.4314/mejs.v3i1.63689>
- Mohammadi AA, Zarei A, Majidi S, Ghaderpoury A, Hashempour Y, Saghi MH, Alinejad A, Yousefi M, Hosseingholizadeh N, Ghaderpoori M (2019) Carcinogenic and non-carcinogenic health risk assessment of heavy metals in drinking water of Khorramabad, Iran. *MethodsX* 6:1642–1651. <https://doi.org/10.1016/j.mex.2019.07.017>
- Momba MNB, Tyafa Z, Makala N, Brouckaert BM, Obi CL (2006) Safe drinking water still a dream in rural areas of South Africa. Case study: the Eastern Cape Province. *Water SA* 32(5):716–720
- Naz A, Mishra BK, Gupta SK (2016) Human health risk assessment of chromium in drinking water: a case study of Sukinda Chromite Mine, Odisha, India. *Expo Health* 8:253–264. <https://doi.org/10.1007/s12403-016-0199-5>
- Nerbrand C, Agréus L, Lenner RA, Nyberg P, Svärdsudd K (2003) The influence of calcium and magnesium in drinking water and diet on cardiovascular risk factors in individuals living in hard and soft water areas with differences in cardiovascular mortality. *BMC Public Health* 3:21–29
- Njinga RL, Tshivhase VM, Mathuthu M (2016) Chemical toxicity of surface-based drinking water sources due to natural uranium pollutant around princess gold mine environs in roodepoort South Africa. *Expo Health* 8:457–464. <https://doi.org/10.1007/s12403-016-0203-0>
- NOP (1998) South Africa—a Country Profile and Facts. Retrieved January 25, 2024, from Nations Online Project : https://www.nationsonline.org/oneworld/south_africa.htm
- Odendaal N (2024) Waning perceptions of drinking water quality underline need for urgent intervention. Johannesburg: Polity. Retrieved February 19, 2024, from <https://www.polity.org.za>
- Ogana JSO, Usman I, Akpa TC, Yusuf SD, Gurku UM, Ibrahim U (2019) Inductively coupled plasma mass spectrometry (ICP-MS): a modern analytical technique for nuclear forensic application. *Dutse J Pure Appl Sci* 5(2b):231–239
- Oyeku O, Eludoyin A (2010) Heavy metal contamination of groundwater resources in a Nigerian urban settlement. *Afr J Environ Sci Technol* 4(4):201–214
- Patil PN, Sawant DV, Deshmukh RN (2012) Physico-chemical parameters for testing of water—a review. *Int J Environ Sci* 3(3):1194–1207
- Petraccia L, Liberati G, Masciullo SG, Grassi M, Fraioli A (2006) Water, mineral waters and health. *Clin Nutr* 2:377–385. <https://doi.org/10.1016/j.clnu.2005.10.002>
- Pillai CK (1983) Heavy metals in aquatic environment, Water pollution and management (Varshay C.K.). Wiley, New Delhi
- Pruszkowski E (2021) Interferences in ICP-MS: Do we still have to worry about them? Technical Note. Retrieved January 19, 2024, from PerkinElmer: <https://resources.perkinelmer.com/lab-solutions/resources/docs/TCH-1815551-NexION-5000-ICP-MS-Interferences.pdf>
- SANS (2015). Drinking water; South African National Standards (SANS) 241-1: 2015. Retrieved February 21, 2024, from https://store.sabs.co.za/catalog/product/view/_ignore_category/1/id/2135761/s/sans-241-2015-ed-2-00-2/
- SAWQG (1996) South African Water Quality Guidelines—Domestic use (2nd ed., Vol. 1). Pretoria: Department of Water Affairs and Forestry. Retrieved January 19, 2024, from https://www.dws.gov.za/Groundwater/documents/Pol_saWQguideFRESHDomesticusevoll1.pdf
- Statista (2022) Retrieved February 22, 2024, from <https://www.statista.com/statistics/455422/bottled-water-consumption-ineurope-per-capita/>
- Tuzen M, Soylak M (2006) Evaluation of metal levels of drinking waters from the Tokat-Black Sea Region of Turkey. *Polish J Environ Stud* 15(6):915
- UN (2010) The Human Right to Water and Sanitation, A/RES/64/292 2010. New York, NY, USA: United Nations.

- USEPA (1989) Risk Assessment Guidance for Superfund; Human Health Evaluation Manual (Part A) (Vol. I). Washington DC: Office of Emergency and Remedial Response, U. S. Environmental Protection Agency. Retrieved February 7, 2024, from https://www.epa.gov/sites/default/files/2015-09/documents/rags_a.pdf
- USEPA (1999) National primary drinking water regulation. United States Environmental Protection Agency, New York
- USEPA (2003) Drinking Water Advisory: Consumer Acceptability Advice and Health Effects Analysis on Sodium. Washington DC: U. S. Environmental Protection Agency. Retrieved February 6, 2024, from https://www.epa.gov/sites/default/files/2014-09/documents/support_cc1_sodium_dwreport.pdf
- USEPA (2011) Exposure factors handbook: 2011 Edition. National Center for Environmental Assessment. Washington DC; EPA/600/R-09/052F. Retrieved February 14, 2024, from <http://www.epa.gov/ncea/efh>
- USEPA. (2012). Guidelines for Water Reuse U. S. Environmental Protection Agency, Office of Wastewater Management, Office of Water. www.epa.gov
- WHO (2004) Guidelines for drinking water quality. World Health Organisation, Geneva
- WHO (2005) Uranium in Drinking-water - Background document for development of WHO Guidelines for Drinking-water Quality. Geneva : World Health Organisation. Retrieved February 6, 2024, from <https://www.who.int/docs/default-source/wash-documents/wash-chemicals/uranium-background-document.pdf>
- WHO (2009) Potassium in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality. Geneva, Switzerland: World Health Organisation. Retrieved February 6, 2024, from https://cdn.who.int/media/docs/default-source/wash-documents/wash-chemicals/potassium-background.pdf?sfvrsn=4542eda3_4
- WHO (2020) Chromium in drinking-water_Background document for development of WHO Guidelines for drinking-water quality. 3. Geneva, Geneva, Switzerland. Retrieved from <https://iris.who.int/bitstream/handle/10665/338062/WHO-HEP-ECH-WSH-2020.3-eng.pdf>
- WHO (2022) *Guidelines for drinking-water quality: fourth edition incorporating the first and second addenda*. Switzerland: World Health Organisation. Retrieved 01 19, 2024, from <https://www.who.int/publications/i/item/9789240045064>
- Wilschefski SC, Baxter MR (2019) Inductively coupled plasma mass spectrometry: introduction to analytical aspects. *Clin Biochem Rev* 40(3):115–133. <https://doi.org/10.33176/AACB-19-00024>
- Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, Cheng SP (2009) Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section China. *Bull Environ Contam Toxicol* 82:405–409. <https://doi.org/10.1007/s00128-008-9497-3>

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.