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Investigating the Presence and Levels of Some Selected Chemical Parameters in Borehole Water of Ga-Matlala in Limpopo Province, South Africa: Determining the Potential Risks

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ABSTRACT: The safety of borehole water is highly questionable, yet most people in the African continent still depend on borehole water as the primary source for everyday use. To investigate the potential health risk of borehole water on the community, this study analyzed the presence and levels of various chemical parameters in borehole water of Ga-Matlala area in Limpopo province, South Africa. Twenty-four water samples were collected from selected eight villages of ga-Matlala during both the dry and rainy seasons. Techniques such as UV/vis spectrophotometric method, EDTA titrimetric method, Cl^- argentometric method and FAAS were used to determine fluoride, nitrate, hardness, calcium, chloride ion and magnesium. In the rainy season, hardness ranged from 146.10 to 1136.49 mg/L, calcium ranged between 252.54 to 448.2 mg/L. In the dry season, hardness ranged between 157.69 to 1003.80 mg/L, calcium concentration ranged between 183.43 and 385.37 mg/L. The recommended limits set by regulatory authorities were exceeded in both seasons. Fewer samples recorded chloride concentration $\geqslant$ 100 mg/L in both seasons. Magnesium concentrations were between 0.72 and 1.35 mg/L in both seasons. Fluoride concentration exceeded the maximum permissible level by regulatory bodies in most samples. In the rainy season, the lowest concentration was 1.94 mg/L, and a maximum was 3.22 mg/L. The nitrate concentration in both seasons was around 0.3 mg/L. Magnesium concentrations were within the acceptable levels. The elevated levels of chemicals in borehole may lead to dental fluorosis, risk of kidney stones and cancer in human beings. It is therefore recommended that risk awareness action should be undertaken, and treatment interventions should be considered.

KEYWORDS: Chemical parameters, borehole water, EDTA titrimetric method, Cl^- argentometric method, health risk

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Introduction

The supply of drinking water in rural areas is a major challenge in developing countries world-wide. Around 94% in both urban and especially rural areas depend on groundwater as a main source of water supply.[1] Groundwater is assumed to be safe for drinking, but the quality of most groundwater has not been established.[2] The quality of groundwater is affected by many parameters, such as total ionic content, pH, total dissolved solids, organic compounds, water hardness, fluoride, calcium, nitrate, and others.[3] The contamination of drinking water could be natural, based on factors such as geological, chemical, and physical characteristic of the area supplying the water or because of anthropogenic sources such as industrialization, mechanization, pesticides use, and fluoridation of drinking water affect the quality of water.[4]

Water can be classified as either soft, hard, or extreme hard water and the presence of calcium and magnesium in water, at a particular concentration affects water hardness (Table 1). The World Health Organization (WHO) indicated that water hardness has moderate health benefits to humans,[5] but the association between health risks including colon, rectal and pancreatic cancers, vascular diseases, and water hardness has long been established.[6-8] Higher concentration of calcium carbonate may also cause serious damage to coffee makers, boilers, kettles, and other equipment that hold water resulting in negative economic impact for both industries and households as they cause appliance corrosion.[9] Thus, communities using extremely hard water for their daily household activities are further burdened in spending a considerable amount of money on maintenance of household utensils to keep them functioning.[10]

Human exposure to chemicals is through ingestion, inhalation, and dermal contact.[11] The ingestion of food and water is the main way fluoride enters the human system, but water is the main source of fluoride in the human body.[12] According to the World Health Organization (WHO), the maximum permissible level of fluoride is 1.5 mg/L, while in South Africa the Department of Water Affairs and Forestry (DWAF) has set a maximum of 1.0 mg/L. Higher concentrations of fluoride in water can result in diseases such as dental fluorosis, bone density deterioration, muscle spasm and many other negative health challenges. Dental fluorosis is estimated

Table 1. Table showing the classification of water into hard, soft water by DWAF and WHO.

CLASSIFICATION (WHO)	HARDNESS IN MG/L (WHO)	DESCRIPTION OF HARDNESS (DWAF)	HARDNESS IN MG/L (DWAF)
Soft	0-60	Soft	0-50
Moderately hard	61-120	Moderately soft	50-100
Hard	121-180	Slightly hard	100-150
Very hard	⩾181	Moderately hard	150-200
		Hard	200-300
		Very hard	>300

to be affecting over more than 200 million people from different countries in Africa, Asia, Europe, South America, North America, and Australia.[13,14] In South Africa, especially in the rural areas, many black people are suffering from dental fluorosis. This could be because they are relying solely on groundwater for drinking purposes.[15,16] The consumption of lower concentrations of fluoride in drinking water has been associated with the prevention of dental caries.[17] An excess intake of nitrate of more than 50 mg/L may result in cancer, central nervous system birth defect, hypertension, diabetes, respiratory tract infection and change in the immune system.[18] The possible occurrence of methaemoglobinaemia in bottle-fed infants under the age of six months is the main risk associated with excess nitrate in drinking water (Hunault et al., 2007).[19] The maximum acceptable concentration of nitrate for drinking water is 50 mg/L NO_3^-.[5] Water with elevated concentration of chlorides does not have negative health impact on human, however, high chloride concentration affects the taste of water as well as food products, it causes metal corrosion, and it is harmful to plants (Shukla & Arya, 2018).[20] Standards set for chlorides in public drinking water may not exceed 250 mg/L.[21]

The analysis of chemical parameters in drinking water is very crucial, it helps in reducing health challenges encountered as a result of drinking water containing concentrations exceeding the maximum permissible level (MPL). Thus, it is imperative to reduce these chemical parameters in groundwater before any consumption and/or usage by human beings. Most rural communities in South Africa depend solely or mostly on untreated groundwater for daily activities. In the Capricorn District Municipality, most people are relying on boreholes for drinking water (Figure 1).

The community of Ga-Matlala rely mainly on directly abstracted, untreated borehole water for drinking and cooking and there are no regular quality control checks of the borehole water from the area (Figure 2). There were no studies performed on the quality of borehole water from Ga-Matlala, and thus, there is no data on the chemical composition of the borehole water from ga-Matlala, and their levels. The municipality has indicated that the groundwater quality in some parts of the municipality is not suitable for human consumption. Geological nature of Ga-Matlala area is mountainous and may be contributing immensely towards the elevated levels of fluoride, calcium, hardness, and other salts contents present in the drinking water.[22] The capital of the Ga-Matlala tribal chieftaincy and headquarters of the Bakone Traditional Council is in Setumong village. The area is located about 48 km northwest of the city of Polokwane on the Matlala Road. The aim of the study was to investigate the presence and levels of chemical parameters in borehole water in selected villages at Ga-Matlala area and interpret the potential negative health risks to the community members. Observably, some members of the community in this area presents manifestation of dental discoloration. In South Africa, especially in the rural areas, many black people are suffering from dental fluorosis. This could be because they are relying solely on groundwater for drinking purposes (Mc Caffery, 2001).[23]

Methods

Sample collection

Borehole water samples from eight villages, namely Setumong (Set), Sedie (Sed), Maineleng (Mai), Mamphulo (Mam), Madietane (Mma), Manamela (Man), Phetole (P) and Dibeng (D), from the ga-Matlala area were collected from randomly selected taps during both the rainy and dry seasons in 2021 and 2022. Three representative samples were collected randomly from each village making a total of 24 water samples. The water samples were collected in sterile 1000 ml polyethene plastic bottles for each sample. Prior to sampling, the taps were opened, and water was left to run for a minimum of 2 minutes. All the samples were transported to the laboratory and stored in 4°C in the refrigerator.

Reagents and apparatus

All used reagents were of analytical grade except where stated otherwise. Doubly distilled water was used for all preparations. All apparatus were washed with tap water using detergent and finally rinsed with distilled water.

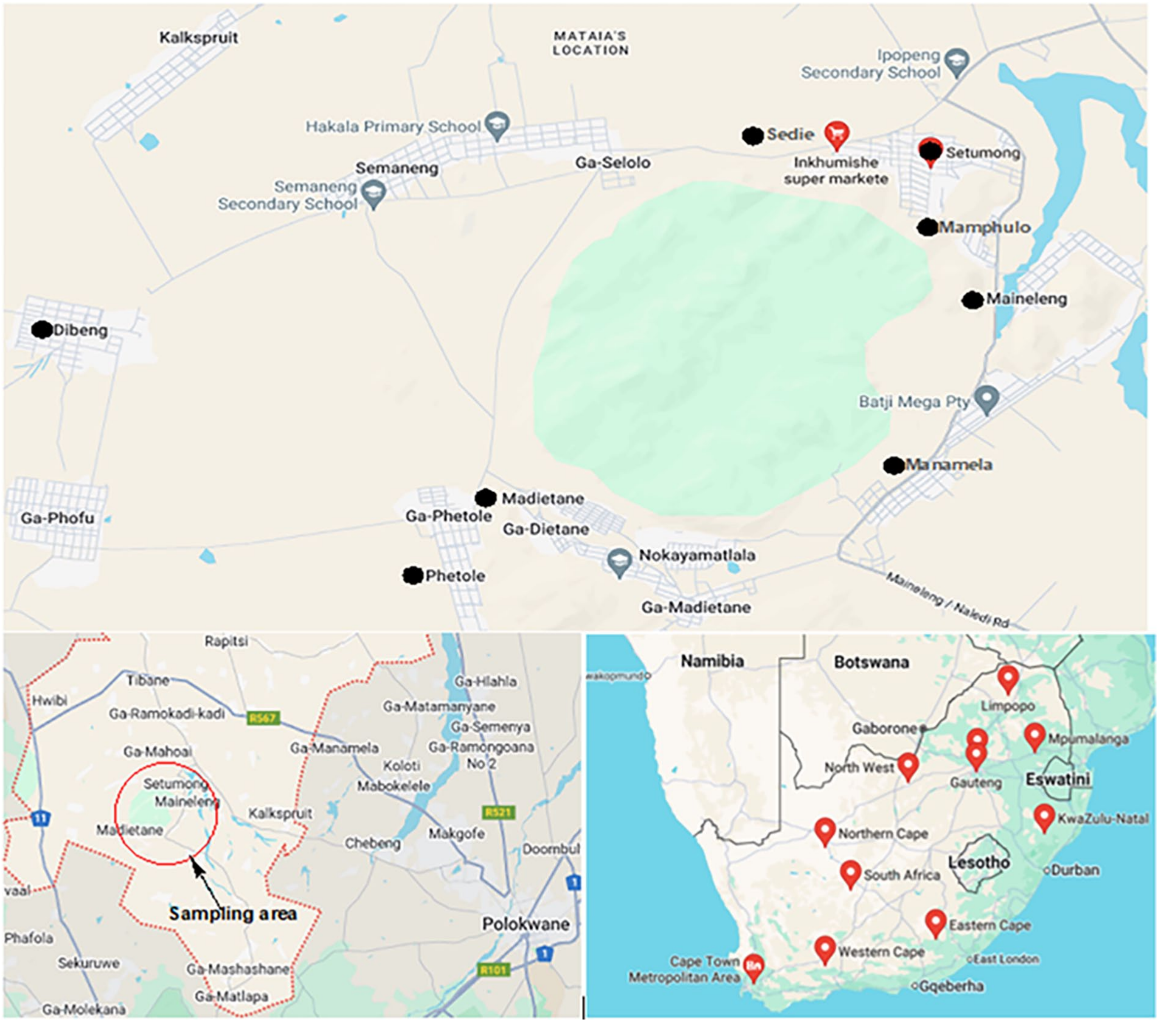

Figure 1. Map of the sampling area in Polokwane, Limpopo Province, South Africa.

Figure 2. Jojo tanks used for storage of municipal borehole water at Setumong, ga-Matlala.

Sample analysis

The total hardness and calcium concentrations were determined using standard EDTA titrimetric method, while magnesium concentration was determined using flame atomic absorption spectrophotometer (FAAS) (APHA, 1998).[24] The chloride ion concentration was determined using the Cl^- argentometric method described in the Standard Methods of Water and Wastewater (APHA, 1995 and 1998).[25] Fluoride was determined using the Alizarin red spectroscopic method described by Kalpesh and Logesh[1]. The determination of nitrate was done using the Ultraviolet spectrophotometric screening method described by Obeidat et al.[26] Borehole water samples collected in the dry season were boiled for about 5 minutes, cooled to room temperature and analyzed for total hardness, calcium, fluoride, chloride, and nitrate concentrations The samples were also analyzed prior to boiling. The analysis was done in triplicates.

Determination of water hardness and calcium concentration using EDTA titrimetric method

Standard EDTA solution. About 3.274 g analytical reagent grade disodium ethylene diamine tetra acetic acid dihydrate (EDTA) was weighed and dissolved in distilled water. The solution was made to a mark in a 1000 ml volumetric flask.

Standard calcium carbonate solution: Standard calcium carbonate was prepared by weighing 1.000g calcium carbonate into a 500 ml Erlenmeyer flask. About 1 + 1 HCl was added slowly to the $CaCO_3$ until it was completely dissolved. To the solution, 200 ml of distilled water was added, and the solution was boiled for a few minutes. A few drops of methyl red indicator were added to the cool solution and the solution was adjusted to an intermediate orange color by adding 3 N NH_4OH or 1 + 1 HCl. The solution was transferred to a 1000 ml volumetric flask and made to the mark.

Buffer solution. About 1.179 g disodium salt EDTA and 780 mg magnesium sulphate were dissolved in 50 ml distilled water. The solution was added to 16.9 g NH_4Cl and 143 ml concentrated NH_4OH with mixing, and then diluted with distilled water to a 250 ml mark in a volumetric flask.

Eriochrome black T. About 0.2 g of Eriochrome black T was mixed with 100 g sodium chloride and ground together in a mortar. The mixture was stored in a tightly stoppered ottle, and 0.2 g of the ground mixture was used for titration.

Standardization of EDTA. About 25 ml of standard calcium carbonate was pipetted into a 250 ml conical flask and diluted with 25 ml distilled water. One ml of the buffer solution was added, followed by about 0.2 g of EBT. EDTA solution was used for titration and the color changed from violet to blue and then to a distinct blue.

Determination of hardness / calcium in water samples

Hardness and calcium concentration of all the water samples was tested by using EDTA titrimetric method. To about 50 ml of the water sample, 1 ml of buffer (for hardness determination) or 2 ml of NaOH (for calcium determination) was added, followed by about 0.2 g of EBT. EDTA solution was used for titration and the color changed from violet to blue and finally to a distinct blue.

Determination of magnesium using atomic absorption spectrometry

Preparation of magnesium standards. Magnesium stock solution was prepared by dissolving 0.1658 g MgO in a minimum amount of 1 + 1 HNO_3. About 10 ml concentrated HNO_3 was added, and the solution was made to the mark in a 1000 ml volumetric flask. Calibration standards in the range 0.5-10.0 µg/ml Mg were prepared. The absorbance was measured at 285.2 nm and the results are expressed as µg/ml Mg.

Digestion of the water sample—Nitric acid digestion

About 100 ml of the well-mixed, acid preserved sample was transferred to a 250 ml beaker. 5 ml of concentrated HNO_3 and a few boiling chips were added. The water was boiled slowly and evaporated on a hot plate to the lowest volume possible (about 10 to 20 ml). Concentrated HNO_3 was continuously added until digestion was complete. The walls of the beaker were rinsed with water and the sample was filtered. The filtrate was transferred to a 100 ml volumetric flask and the beaker was rinsed further with two 5 ml portions of water, which were then added to the volumetric flask. The volumetric flask was filled to the mark with distilled water and mixed thoroughly.

Determination of chloride concentrations using Cl^- Argentometric Method

Potassium chromate indicator solution: 50 g K_2CrO_4 was dissolved in 300 ml distilled water. Silver nitrate solution was added until a definite red precipitate was formed. The solution was left to stand for 12 hours overnight, filtered and then diluted to the mark with distilled water in a 1000 ml volumetric flask.

Standard silver nitrate titrant, 0.0141 M: 2.395 g $AgNO_3$ was dissolved in distilled water and diluted to 1000 ml mark. The solution was stored in the dark.

Standard sodium chloride, 0 0141 M: 824 mg NaCl (dried at 140°C) was dissolved in distilled water and diluted to 1000 ml mark in a volumetric flask.

Procedure. A sample of 100 m1was used for the titration. The pH was adjusted to a range of between 7 and 10 by adding either 1 M H_2SO_4 or 1 M NaOH. One ml of K_2CrO_4 indicator solution was added. The solution was titrated with standard $AgNO_3$ to a pinkish-yellow end point.

Spectrometric determination of fluoride

Standard Fluoride solution: 1.507 g ammonium hydrogen difluoride ($NH_4F.HF$) was weighed and dissolved in distilled water; the solution was transferred to a 1000 ml volumetric flask and made to the mark with distilled water. A serial dilution of the stock solution was prepared in the range 0.5, 1.0, 1.5, 2.0, 2.5 mg/L.

Alizarin Red Solution: 0.7520 g alizarin red was weighed and dissolved in distilled water. The solution was made to the mark in a 1000 ml volumetric flask.

Zicornyl Acid Solution: 0.3438 g of zicornyl acid chloride octahydrate ($ZrOCl_2.8H_2O$) was dissolved in 500 ml distilled water. 33.30 ml of concentrated sulphuric acid was slowly added, with stirring, followed by the slow addition of 101 ml concentrated hydrochloric acid (HCl). The mixture was cooled and later made to the 1000 ml mark with distilled water.

Sample analysis for fluoride

To a 100 ml of both the sample and standard, 5.0 ml each of alizarin red and Zicornyl acid solutions were added. The

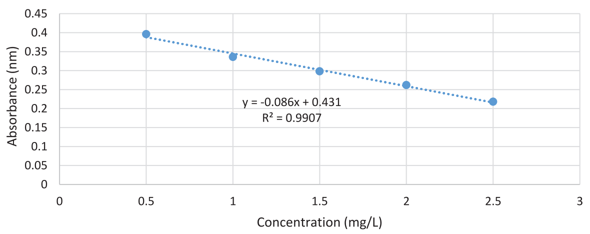

Figure 3. A plot of the calibration curve for spectrophotometric determination of fluoride concentration (520 nm).

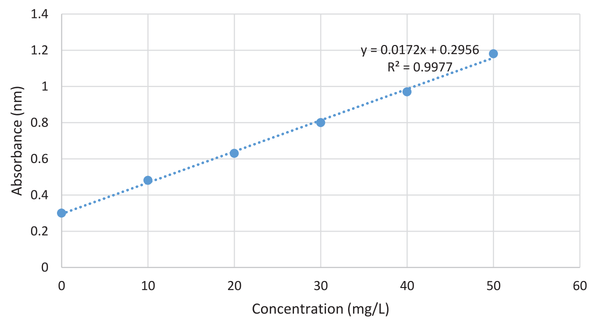

Figure 4. A plot of the calibration curve for spectrophotometric determination of nitrate concentration (205 nm).

solutions were mixed thoroughly and allowed to stand for one hour for full color development. After 1 hour absorbance readings for both the samples and the standards were taken at 520 nm (Figure 3) and the fluoride concentration of the samples was determined and expressed in mg/L.

Determination of nitrate - NO_3^- Ultraviolet (UV) spectrophotometric screening method

The concentration of nitrate in water samples collected from ga-Matlala was determined by spectrophotometric method. The UV absorbance was measured at 205 nm with Shimadzu UV Spectrophotometer, UV-1800, at 205 nm, using quartz cells of 1 cm light path and at 275 nm to determine interferences due to dissolved organic matter. A standard curve for the nitrate concentration was prepared by dissolving 0.7280 g KNO_3 in 1000 ml distilled water and diluted to the mark in a 1000 ml volumetric flask to prepare the stock nitrate solution. The solution was preserved with 2 ml $CHCl_3$/L. Potassium nitrate (KNO_3) was dried in an oven at 105°C for 24 h prior to use.

The intermediate nitrate solution: 100 ml of the stock solution was diluted to the mark in a 1000 ml volumetric flask. The solution was preserved with 2 ml $CHCl_3$.

Preparation of standard curve: calibration standards in the range 0-50 mg NO_3-N/L were prepared. About 1 ml HCl was added and the solution was mixed thoroughly. The calibration curve was made from the difference between the absorbance data recorded at 205 nm and the absorbance data obtained when determining interferences at 275 nm (Figure 4).

The standard curve was used to determine nitrate concentration of the water samples from ga-Matlala area. The results are expressed as mg/L NO_3.

Treatment of the sample: The samples were treated in the same manner as the standards.

Health risk assessment methodologies

The human exposure risk assessment methodologies have been described in literature.[27-29] The exposure through ingestion and dermal absorption are common for water.[27,28,30] The numeric expressions for risk assessment as obtained from the USEPA Risk Assessment Guidance for Superfund (RAGS) methodology[27] are given as follows:

$$Exp_{ing} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT} \quad (1)$$

$$Exp_{derm} = \frac{(C_{water} \times SA \times KP \times ET \times EF \times ED \times CF)}{(BW \times AT)} \quad (2)$$

Where, Exp_{ing} is the exposure dose through ingestion of water (mg/kg/day); Exp_{derm} is the exposure dose through dermal absorption (mg/kg/day); C_{water} is the average concentration of the estimated chemicals in water (mg/L); IR is ingestion rate (2.2 L/day for adults and 1.8 L/day for children); EF is exposure frequency (365 days/year); ED is exposure duration (70 years for adults; and 6 years for children); BW is average body weight (70 kg for adults; 15 kg for children); AT is the averaging time (25,550 days for adults; 2190 days for children); SA is the exposed skin area (18,000 cm^2 for adults; 6600 cm^2 for children); ET is exposure time (0.58 h/day for adults; 1 h/day for children); CF is unit conversion factor (0.001 L/cm3); and Kp is dermal permeability coefficient (cm/h), 0.001 (Asare-Donkor et al., 2016).[27,28,31] Potential non-carcinogenic risks due to exposure to contaminants were determined by comparing the calculated contaminant exposures from each exposure route with the reference dose (RfD).[27] The hazard quotient (HQ) which is a numeric estimate of the systemic toxicity potential posed by a single element within a single route of exposure was calculated using the relation:

Non-carcinogenic risk assessment

$$HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD_{ing/derm}} \quad (3)$$

where $HQ_{ing/derm}$ is hazard quotient via ingestion or dermal contact and $RfD_{ing/derm}$ is oral/dermal reference dose (mg/kg/day). The RfD_{ing} and RfD_{derm} values were obtained from the literature.[32] The HQ indicates whether little or no adverse health effects are likely to be caused by fluoride and/or nitrate when the borehole water is consumed or through dermal absorption by both adults and children. The overall potential non-carcinogenic effects posed by more than one chemical is a conservative assessment tool used to estimate high end risk

Table 2. The RfD's of non-carcinogenic factors.

NON-CARCINOGENIC	NITRATE	FLUORIDE
RfD_{ing} (mg/kg/day)	0.36	0.06[a]
RfD_{derm} (mg/kg/day)	0.18	1[a]

[a]EPA 2012 support of Summary Information on the IRIS.

rather than low end risk to protect the public. Cumulative hazard quotients is calculated from the sum of HQs for each chemical and expressed as hazard index (HI).[27]

$$HI = HQ_1 + HQ_2 + HQ_3 + \dots + HQ_n \quad (4)$$

If HI is less than unity (HI < 1), no chronic risks were assumed to occur at the site but if HI > 1, it implies that the non-carcinogenic health risks are likely to occur.[27,33,34]

Statistical analysis

Differences between groups were analyzed for statistical differences using analysis of variance (ANOVA) or student *t*-test, where applicable. Differences between groups were regarded as statistical different when $p < .05$ value was recorded.

Results and Discussion

The study was aimed at investigating the presence and levels of chemical parameters in borehole water and to assess any potential negative health implications on the community of Ga-Matlala area in Limpopo province, South Africa resulting from the chemical content in the borehole water samples. The average calcium and total water hardness results for both seasons were recorded and compared in Table 2. The average chloride and magnesium results for both seasons are shown in Table 3. Table 4 presents the fluoride and nitrate concentrations of borehole water samples from Ga-Matlala and Table 5, presents the percentage of borehole water samples from Ga-Matlala that are within or/and are exceeding the recommended guidelines, during both the rainy and dry seasons.

The results obtained in this experiment have indicated that all the borehole water samples from the selected villages in this study, collected during the rainy season contain fluoride concentrations exceeding the maximum allowed levels. Fluoride concentrations in the rainy season, have shown a range of 1.94 mg/L from sample 1 collected at Maineleng to 3.22 mg/L from sample 3 collected at Madietane. The average fluoride concentration in the villages assessed varied following the order, Sed > Set > Mam > Mma > D > Man > P > Mai, during the rainy season. The concentrations of all the samples are above the maximum allowed concentration by both DWAF (S.A.) and WHO.[35] The maximum allowed concentration for fluoride set by DWAF (S.A.) is 1 mg/L while for the WHO and EU is 1.5 mg/L. During the dry season, 54% showed fluoride levels exceeding the maximum permissible levels. The lowest recorded concentration was 0.02 mg/L while the highest concentration was 2.46 mg/L. During the dry season, the average fluoride concentration followed the order, Set > Sed > P > Mam > Mma > Mai > D > Man. Studies have indicated higher concentrations of fluoride affect human health negatively, causing skeletal and dental fluorosis and many other deadly physiological disorders.[13] The effects of high fluoride content in water may not be felt immediately but in the long run the negative impact starts to show. The development of skeletal fluorosis may take up to 30 years.[1]

During both the rainy and dry season, all the collected borehole water samples from Ga-Matlala area recorded higher concentration of total water hardness. The total water hardness levels ranged between 146.10 and 1136.49 mg/L $CaCO_3$ during the rainy season and between 157.69 and 1003.80 mg/L $CaCO_3$ during dry season. The Department of Water Affairs and Forestry (SA) (DWAF) has classified water with 0-50 mg/L $CaCO_3$ as soft water, moderately soft water ranges between 50-100 mg/L, slightly hard water 100-150 mg/L, and 150-200 mg/L is considered moderately hard water and 200-300 mg/L, while >300 mg/L is very hard water. The World Health Organization classifies any drinking with concentration between 121 and 180 mg/L as hard water while concentration ⩾181 mg/L is considered very hard water. The recorded water hardness in borehole water samples from Ga-Matlala area falls in the range of hard and very hard water according to WHO classification, and moderately to very hard water by the classification of the Department of Water Affairs and Forestry (SA) (DWAF) for both seasons. During the rainy season, the average total hardness levels were high in the following order, D > P > Mma > Man > Mai > Mam > Set > Sed. In the dry season, the hardness levels followed the order, P > D > Mma > Mam > Man > Mai > Sed > Set. Hard water has been reported to be beneficial to humans, it has the potential to relieve constipation in some cases. Reports show the skin disorder, eczema, in some children has been associated with exposure to hard water.[36] The Taiwanese scientists also highlighted a negative association of various types of cancer morbidity/mortality with the hardness of water and calcium.[37,38] Yang and Hung[39], reported a negative relationship between colon cancer mortality and drinking water hardness. Also, a decline in the reproductive health of men, attributed to the use of hard water, has been reported. In India, reproductive failure and stillbirths were reported in hardwater regions.[40] In the previous study conducted in the Greater Giyani Municipality in the Limpopo province, South Africa by Samie et al.[41], the total hardness of the borehole water used by schools was also found to be above the acceptable limits by both the local and international regulatory authorities (DWAF & WHO).

Water hardness is simply defined as the amount of dissolved calcium and magnesium, with hard water being regarded as that with high levels of dissolved minerals (calcium and magnesium) and perceived to be prevalent in groundwater/borehole water.[36] The phenomenon of seasonal variation in the

Table 3. Average calcium and total hardness concentrations (mg/L) (±SD) from borehole water samples collected at Ga-Matlala during rainy season, dry season (pre-boiling) and after boiling.

SEASON									
VILLAGE	SAMPLE NO.	RAINY	DRY-PRE BOILING	DRY-AFTER BOILING	ANOVA	RAINY	DRY-PRE BOILING	DRY-AFTER BOILING	ANOVA
		CALCIUM RAINY	CALCIUM	CALCIUM	*P*-VALUE	HARDNESS RAINY	HARDNESS	HARDNESS	*P*-VALUE
Setumong	1	267.68 ± 8.89	183.43 ± 1.18	246.63 ± 1.18	.00078*	200.00 ± 2.94	194.22 ± 1.11	207.68 ± 4.84	.00861*
	2	252.54 ± 6.73	224.28 ± 1.78	292.88 ± 0.44	.00089*	194.22 ± 2.94	173.07 ± 1.92	201.91 ± 1.11	.00294*
	3	286.94 ± 9.64	242.01 ± 0.89	272.07 ± 1.18	.00094*	196.14 ± 1.09	257.68 ± 4.00	274.99 ± 2.94	.00083*
Sedie	1	270.52 ± 2.11	221.20 ± 0.44	290.57 ± 0.77	.00087*	153.80 ± 2.89	182.69 ± 4.84	203.83 ± 1.11	.00425*
	2	263.96 ± 3.80	221.97 ± 0.77	245.09 ± 0.89	.00102*	146.10 ± 1.97	194.22 ± 1.92	207.68 ± 2.94	.00321*
	3	274.38 ± 3.35	208.09 ± 0.77	256.66 ± 1.94	.00124*	150.00 ± 2.22	213.45 ± 4.00	196.07 ± 2.22	.00215*
Maineleng	1	291.69 ± 2.92	226.60 ± 1.18	252.03 ± 1.18	.00107*	240.38 ± 5.09	234.60 ± 2.22	259.60 ± 1.87	.00687*
	2	294.00 ± 3.96	186.51 ± 1.18	253.57 ± 0.45	.00085*	230.76 ± 1.11	200.00 ± 4.00	232.68 ± 1.11	.00198*
	3	310.44 ± 5.39	243.55 ± 0.45	278.23 ± 0.77	.00058*	238.45 ± 1.92	234.6 ± 2.00	238.45 ± 3.33	.01986*
Mamphulo	1	273.61 ± 0.77	222.74 ± 0.44	260.50 ± 0.77	.00168*	221.14 ± 2.94	173.07 ± 1.11	198.07 ± 2.94	.00098
	2	273.35 ± 0.92	221.14 ± 0.45	263.87 ± 0.89	.00158*	221.14 ± 1.11	180.8 ± 0.89	196.54 ± 0.77	.00134*
	3	300.81 ± 14.42	224.28 ± 0.89	262.05 ± 1.18	.00067*	178.83 ± 3.85	167.30 ± 2.94	196.14 ± 1.11	.00966*
Madietane	1	275.40 ± 0.44	254.34 ± 0.45	342.98 ± 0.77	.00034*	259.60 ± 2.84	338.27 ± 1.21	519.21 ± 1.92	.00016*
	2	273.09 ± 1.18	265.13 ± 6.58	297.50 ± 1.18	.00306*	234.60 ± 2.94	317.30 ± 4.84	378.83 ± 4.84	.00038*
	3	272.30 ± 3.21	277.47 ± 1.18	310.61 ± 1.60	.00074*	496.10 ± 4.84	332.68 ± 4.83	424.98 ± 1.92	.00069*
Manamela	1	257.42 ± 3.53	223.40 ± 1.54	217.34 ± 0.89	.00276*	253.83 ± 4.84	271.14 ± 3.53	348.06 ± 2.94	.00082*
	2	257.42 ± 3.35	237.39 ± 0.89	206.55 ± 0.44	.00399*	213.45 ± 3.79	244.22 ± 3.33	290.37 ± 1.11	.00072*
	3	258.45 ± 7.28	198.85 ± 0.44	269.76 ± 0.45	.00292*	296.10 ± 2.94	299.83 ± 3.98	248.07 ± 1.11	.00506*
Phetole	1	308.80 ± 5.41	275.92 ± 0.77	385.37 ± 0.89	.00019*	592.20 ± 2.94	726.90 ± 2.94	903.81 ± 2.94	.00006*
	2	289.28 ± 5.83	271.16 ± 0.44	311.38 ± 1.18	.00278*	249.99 ± 1.11	361.52 ± 1.11	405.75 ± 2.94	.00088*
	3	363.79 ± 4.81	385.37 ± 0.44	470.15 ± 0.77	.00016*	859.58 ± 4.07	923.04 ± 2.94	1142.26 ± 4.05	.00013*
Dibeng	1	341.67 ± 3.21	255.89 ± 1.18	147.2 ± 1.18	.00057*	634.59 ± 2.94	157.69 ± 4.00	125.00 ± 2.91	.00001*
	2	296.06 ± 6.65	254.34 ± 0.44	262.82 ± 0.77	.00456*	392.29 ± 1.11	322.90 ± 5.86	344.21 ± 1.11	.00079*
	3	448.82 ± 14.47	385.37 ± 0.77	363.79 ± 0.89	.00095*	1136.49 ± 2.94	1003.80 ± 2.94	1382.63 ± 1.11	.00094*

*significant difference, $p < .05$.

Table 4. Average chloride and magnesium concentrations (mg/L) (±SD) from borehole water samples collected at Ga-Matlala during rainy season, dry season (pre-boiling) and after boiling.

SEASON								
VILLAGE	SAMPLE NO.	RAINY	DRY-PRE BOILING	DRY-AFTER BOILING	ANOVA	RAINY	DRY	*T*-TEST
		CHLORIDE	CHLORIDE	CHLORIDE	*P*-VALUE	MAGNESIUM RAINY	MAGNESIUM DRY (PRE-BOILING)	*P*-VALUE
Setumong	1	60.83 ± 0.76	64.98 ± 0.58	81.47 ± 0.58	.00285*	1.15 ± 0.00	1.07 ± 0.00	.0389*
	2	61.78 ± 0.29	85.97 ± 1.40	74.48 ± 1.00	.00345*	1.14 ± 0.00	1.06 ± 0.00	.0423*
	3	73.12 ± 0.29	142.46 ± 0.29	151.45 ± 0.29	.00147*	1.14 ± 0.00	1.14 ± 0.00	1.00
Sedie	1	63.13 ± 0.76	63.98 ± 0.76	65.98 ± 0.76	.05120	1.16 ± 0.00	1.07 ± 0.00	.0392*
	2	63.33 ± 0.76	72.98 ± 0.29	74.48 ± 0.58	.00564*	1.16 ± 0.00	1.08 ± 0.00	.0379*
	3	62.63 ± 0.76	65.48 ± 0.50	68.47 ± 0.50	.05241	1.08 ± 0.00	1.17 ± 0.00	.0376*
Maineleng	1	57.81 ± 0.76	62.98 ± 0.29	71.48 ± 0.29	.00121*	1.21 ± 0.00	1.10 ± 0.00	.0401*
	2	58.31 ± 0.29	64.97 ± 0.58	70.98 ± 0.50	.00126*	1.21 ± 0.00	1.11 ± 0.00	.0398*
	3	57.81 ± 0.76	62.48 ± 1.80	70.49 ± 0.58	.00121*	1.21 ± 0.00	1.12 ± 0.00	.0345*
Mamphulo	1	67.14 ± 0.29	103.97 ± 0.45	83.47 ± 0.50	.00116*	1.14 ± 0.00	1.10 ± 0.00	.0364*
	2	66.98 ± 0	102.77 ± 0.76	80.93 ± 0.76	.00119*	1.16 ± 0.00	1.11 ± 0.00	.0247*
	3	62.98 ± 1.04	106.47 ± 0.58	74.48 ± 0.58	.00112*	1.15 ± 0.00	1.09 ± 0.00	.0266*
Madietane	1	102.13 ± 1.15	154.45 ± 0.50	159.45 ± 0.29	.00164*	1.20 ± 0.00	1.15 ± 0.00	.0241*
	2	106.63 ± 0.29	106.47 ± 0.29	129.46 ± 0.29	.00324*	1.19 ± 0.00	1.12 ± 0.00	.0221*
	3	76.80 ± 1.76	92.47 ± 0.29	93.97 ± 1.00	.00288*	1.18 ± 0.00	1.11 ± 0.00	.0249*
Manamela	1	95.97 ± 0.87	81.97 ± 0.75	93.47 ± 0.50	.00394*	1.19 ± 0.00	1.11 ± 0.00	.0238*
	2	60.98 ± 0.87	43.49 ± 1.04	52.98 ± 0.50	.00248*	1.19 ± 0.00	1.09 ± 0.00	.0319*
	3	47.48 ± 0.50	84.97 ± 0.58	58.98 ± 0.50	.00198*	1.23 ± 0.00	1.09 ± 0.00	.0302*
Phetole	1	350.74 ± 0.76	354.39 ± 0.58	441.86 ± 0.50	.00098*	0.88 ± 1.11	1.24 ± 0.00	.0142*
	2	144.54 ± 0.29	166.44 ± 0.50	182.94 ± 0.29	.00297*	1.16 ± 0.00	1.27 ± 0.00	.0129*
	3	327.73 ± 0.58	329.90 ± 0.50	435.86 ± 2.07	.00099*	1.25 ± 0.00	1.35 ± 0.00	.0389*
Dibeng	1	591.15 ± 1.26	33.99 ± 0.50	42.49 ± 0.29	.00001*	1.25 ± 0.00	0.72 ± 0.00	.0122*
	2	188.77 ± 0.76	199.93 ± 0.50	248.92 ± 0.29	.00324*	1.00 ± 0.00	1.18 ± 0.00	.0348*
	3	806.41 ± 1.26	569.82 ± 0.50	788.25 ± 0.76	.00309*	1.41 ± 0.00	1.27 ± 0.00	.0401*

*significant difference, $p < .05$.

Table 5. Fluoride and nitrate concentrations (mg/L) from borehole water samples collected at Ga-Matlala during rainy season and dry seasons.

SEASON									
VILLAGE	SAMPLE NO.	RAINY	DRY (PRE BOILING)	DRY (AFTER BOILING)	ANOVA	RAINY	DRY (PRE BOILING)	DRY (AFTER BOILING)	ANOVA
		FLUORIDE	FLUORIDE	FLUORIDE	*P*-VALUE	NITRATE	NITRATE	NITRATE	*P*-VALUE
Setumong	1	2.37	2.17	2.34	.0264*	0.35	0.34	0.34	.998
	2	2.38	2.19	2.27	.0232*	0.35	0.34	0.34	.998
	3	2.19	2.36	2.20	.0281*	0.35	0.34	0.34	.998
Sedie	1	1.94	2.07	2.21	.0198*	0.35	0.34	0.34	.998
	2	2.12	2.04	2.32	.0302*	0.35	0.34	0.34	.998
	3	2.08	2.01	1.81	.0363*	0.35	0.34	0.34	.998
Maineleng	1	2.04	0.82	1.34	.00564*	0.35	0.34	0.34	.998
	2	1.99	0.77	1.10	.00461*	0.35	0.34	0.34	.998
	3	3.06	0.49	0.67	.00012*	0.35	0.34	0.34	.998
Mamphulo	1	3.13	1.97	2.23	.00324*	0.35	0.34	0.35	.999
	2	3.15	1.95	2.01	.00684*	0.35	0.35	0.34	.999
	3	3.15	1.96	2.19	.00724*	0.35	0.30	0.30	.894
Madietane	1	3.09	1.16	0.78	.000762*	0.31	0.35	0.35	.961
	2	3.11	1.02	1.29	.00231*	0.35	0.34	0.34	.998
	3	3.18	1.63	2.03	.00452*	0.35	0.34	0.34	.998
Manamela	1	3.14	0.87	0.91	.00024*	0.35	0.35	0.35	1.00
	2	3.07	0.02	0.02	.00008*	0.35	0.35	0.35	1.00
	3	3.14	0.38	0.70	.00036*	0.35	0.35	0.35	1.00
Phetole	1	2.62	2.46	2.53	.0223*	0.35	0.35	0.35	1.00
	2	2.54	1.65	1.87	.00584*	0.35	0.35	0.35	1.00
	3	3.22	1.98	0.96	.00124*	0.35	0.35	0.35	1.00
Dibeng	1	2.51	0.28	0.50	.00049*	0.35	0.35	0.35	1.00
	2	2.45	0.02	0.51	.00024*	0.35	0.35	0.35	1.00
	3	2.47	0.96	0.96	.00021*	0.35	0.34	0.34	.998

*significant difference, $p < .05$.

total hardness of water is not adequately reported on, and therefore not well understood. However, Hajek and Knapp[42] highlighted the breadth of ecological consequences resulting from the shifts in the seasonality of water availability in that it requires rigorous assessment. On this basis, it could be suggested that variation in the total hardness of borehole water from Ga-Matlala during the dry and rainy seasons could be one of the consequences of shifts in the seasonal availability of groundwater/ borehole water in the area.

The calcium concentration in borehole water samples ranged between 183.43 and 448.00 mg/L during the rainy season and between 252.54 and 385.37 mg/L during dry season. All the borehole water samples from Ga-Matlala area reported the calcium concentrations that are more than double the acceptable limit of 75 mg/L set by the WHO[21] in both seasons, and thus posing a health risk to the community. Although water source rich in calcium have benefits to the bone density in humans and animals,[43,44] intake of exceedingly higher amounts of calcium over a long period may raise the risk of health challenges such as kidney stones in human beings.[45] The average calcium levels in the rainy season were high in D > P > Mai > Mam > Mma > Sed Set > Man, while in the dry season P > D > Mma > Mam > Man > Mai > Sed > Set. Furthermore, the results showed magnesium concentrations within the borehole samples in the range

Table 6. Observed chemical levels in borehole water from Ga-Matlala collected during rainy and dry seasons that are within/ exceeding recommended guideline levels.

CHEMICAL PARAMETERS	RAINY SEASON		DRY SEASON		WHO MAXIMUM PERMISSIBLE LIMIT
	SAMPLES WITH LEVELS WITHIN GUIDELINE VALUES	SAMPLES WITH LEVELS EXCEEDING GUIDELINE VALUES	SAMPLES WITH LEVELS WITHIN GUIDELINE VALUES	SAMPLES WITH LEVELS EXCEEDING GUIDELINE VALUES	
Fluoride	ND	24 (100%)	11 (46%)	13 (54%)	1.5 mg/L
Calcium	ND	24 (100%)	ND	24 (100%)	75 mg/L
Hardness	ND	24 (100%)	ND	24 (100%)	500 mg/L
Chloride	19 (79.17%)	5 (20.83%)	21 (87.5%)	3 (12.50%)	250 mg/L
Magnesium	24 (100%)	ND	24 (100%)	ND	30 mg/L
Nitrate	24 (100%)	ND	24 (100%)	ND	50 mg/L

ND: not detected.

between 0.88 and 1.25 mg/L during the rainy season and 0.72 and 1.35 mg/L during the dry season. The results therefore indicated the magnesium concentrations in the borehole water samples from Ga-Matlala area to be within the acceptable limit set by international regulatory authority, WHO. The average magnesium levels were similar in all the villages. A study conducted in the North-West by Mpenyana-Monyatsi L and Momba (2012),[46] reported that the concentration of calcium was found to be above the acceptable limits in 43% of borehole water samples.

The observed chloride concentrations within the water samples ranged between 47.48 and 806.41 mg/L during rainy seasons and between 33.99 and 569.82 mg/L during dry seasons. The results indicate that in the rainy season, 20.8% of borehole water and 12.5% samples collected in the dry season exceeded the WHO acceptable level set at 250 mg/L (Table 6). The concentrations of chloride exceeding 250 mg/L may result in the water having a salty taste and health implications affecting both the heart and the kidneys (WHO, 2008).[47] Residents may suffer from gastrointestinal tract problems such as diarrhoea, nausea, inflammatory bowel disease.[48] The average chloride levels were higher in D > P > Mma > Set > Mam while the other villages, Sed, Man and Mai recorded a similar average chloride concentration.

The chemicals in drinking water are not consumed as drinking water only, but the community rely heavily on the borehole water for preparation of beverages and in cooking. In the study we evaluated the effect of increased temperature on the levels of the chemical parameters assessed. The samples collected in the dry season were boiled for about 5 minutes and levels of total hardness, calcium, chloride, fluoride, and nitrate were assessed. Total hardness increased in 87.5% samples, 83.33% showed an increase in calcium concentrations. 79.17% borehole water samples recorded an increase in chloride concentrations while 70.8% reported an increase in fluoride concentrations. The concentration of nitrate did not show any change after the water was boiled. The increase in levels of the chemical parameters after the water was boiled, therefore highlights an increase in the rate of negative health risks in the Ga-Matlala community. The high levels of chemicals in the borehole water are due to the geology of the area of Ga-Matlala. There are no mining activities and/or usage of pesticides by the community that could affect the quality of borehole water. Okofo et al.[49] highlights that groundwater quality can be affected on a local scale by the mineralogy of the geological formations in contact with the water.

The dose exposure through ingestion for fluoride ranged between 0.06 and 0.10 mg/kg/day for adults aged 70 years in the rainy season and 0.28 and 0.57 mg/kg/day for children. In the dry season, the dose exposure through ingestion ranged between 0.01 and 0.07 for adults and 0.05 and 0.26 mg/kg/day for children. Results of exposure dose of fluoride through dermal absorption ranged between 0.01 and 0.03 mg/kg/day during both the rainy and dry seasons, for both adults (70 years) and children (6 years) as reported in Table 7. Children have higher fluoride exposure values through ingestion and dermal absorption in both the dry and rainy seasons than adults, and thus have high health risk due to groundwater usage. But, as an ion, fluoride has low membrane permeability and limited absorption, especially from dilute aqueous solutions at neutral pH.[50] The exposure dose through ingestion of nitrate in borehole water (mg/kg/day) ranged between 0.01 and 0.013 mg/kg/day for adults (70 years) and 0.04 mg/kg/day for children (6 years) during both the rainy and dry seasons. The calculated HQ for nitrate was 0.048 and 0.054 mg/kg/day for adults and 0.11 mg/kg/day for children. The HQ for fluoride is more than 1 in all the villages assessed in this study, for both adults and children during the rainy season. It ranges between 1.02 and 1.7 for adults and 3.52 and 9.52 for children. In the dry season, 50% of the villages reported HQ less than 1 for adults while the other 50% reported HQ more than 1. During dry season, the HQ range for adults was 0.12 to 1.19 and for kids it ranged between 0.84 and 4.35. The calculated HQ was greater than 1 for children in 6 villages (Table 8). Adults and children in

Table 7. Results of exposure dose through ingestion of fluoride in borehole water (mg/kg/day) from selected villages of Ga-Matlala during the dry and rainy seasons.

SEASON	AGE (YEARS)	SAMPLING AREA							
		SETUMONG	SEDIE	MAINELENG	MAMPHULO	MADIETANE	MANAMELA	PHETOLE	DIBENG
Rainy	Adults (70)	0.07	0.06	0.07	0.10	0.10	0.10	0.09	0.08
	Children (6)	0.28	0.37	0.28	0.57	0.38	0.37	0.34	0.30
Dry	Adults (70)	0.07	0.06	0.02	0.06	0.04	0.01	0.06	0.01
	Children (6)	0.26	0.25	0.08	0.24	0.16	0.05	0.24	0.05

Table 8. Results of the calculated Hazard quotient for potential non-carcinogenic risk of fluoride and cumulative hazard indices (HI) in borehole water from selected villages of Ga-Matlala during the dry and rainy seasons.

SEASON	AGE (YEARS)		SAMPLING AREA							
			SETUMONG	SEDIE	MAINELENG	MAMPHULO	MADIETANE	MANAMELA	PHETOLE	DIBENG
Rainy	Adults (70)	HQ	1.19	1.02	1.19	1.70	1.70	1.70	1.53	1.35
		HI	1.24	1.07	1.24	1.75	1.75	1.75	1.58	1.40
	Children (6)	HQ	3.52	6.18	3.52	9.52	6.35	6.19	5.69	5.02
		HI	3.61	6.31	3.65	9.65	6.38	6.32	5.82	5.15
Dry	Adults (70)	HQ	1.19	1.02	0.34	1.02	0.68	0.18	1.02	0.12
		HI	1.24	1.07	0.39	1.07	0.73	0.23	1.07	0.17
	Children (6)	HQ	4.35	4.19	1.34	4.01	2.68	0.84	4.02	0.84
		HI	4.48	4.32	1.47	4.14	2.71	0.97	4.15	0.97

Ga-Matlala area are exposed to water with higher fluoride concentrations than the reference dose. A higher HQ is usually associated with higher potential non-carcinogenic risks but HQ less than 1 indicates a lower risk toxicity.[34] Nguyen et al., reported fluoride HQ through ingestion of 1.9 to 2.2 and HQ through dermal exposure of 4.7×10^{-4} to 8.6×10^{-4}.[32] The calculated cumulative hazard quotients (HI) is more than one unity (HI>1) for both adults and children during the rainy season in all the selected villages of Ga-Matlala. Non-cancer risks are likely to occur when HI >1. This indicates that consumption of borehole water from these villages poses a potential health risks to both the adults and children in the area due to consumption of borehole water for long time. During the dry season, HI >1 in four villages for adults and for children HI >1 in six villages.

Conclusion

The study shows that there is an acute fluoride problem at the selected villages of Ga-Matlala. It has revealed that 100% of the borehole water from the sampling locations, collected in the rainy season, and 54% collected in the dry season, have fluoride concentrations above 1.5 mg/L that was determined by WHO as the maximum allowed level. 100% of the collected borehole water samples from Ga-Matlala area in the Limpopo province recorded higher total water hardness and calcium concentrations during both seasons. The results revealed that on average, the total hardness and calcium concentrations in borehole water samples from ga-Matlala are higher than the recommended limits by both local and global regulatory authorities. The concentration of calcium is more than double the recommended limits by WHO. The drinking water from Ga-Matlala may be beneficial to the community by relieving health complications such as constipation and increasing the bone density, but, they are also at risk of developing kidney stones, colon, rectal cancer, a decline in the reproductive health of men in the area, possible still births and many other negative health effects associated with high levels as a result of the levels of chemicals in their drinking water. The chloride ion concentration was higher in fewer samples, whereas magnesium was within the acceptable limits. Nitrate concentrations are below the recommended limit of 50 mg/land poses no health risks. Thus, there is an immediate required deflouridation intervention and public awareness programs to educate communities about challenges they may face due to the quality of the borehole water they consume daily. There are currently no updated sources documenting the chemical parameters of borehole or underground water in the different areas of South Africa. The communities are thus not aware of the health risks they might encounter because of the water. Adults and children in Ga-Matlala area are exposed to water with higher fluoride concentrations than the reference dose. A higher HQ is usually associated with higher health risks but HQ less than 1 is considered a lower risk. It is therefore recommended that risk awareness action should be undertaken, and treatment interventions should be considered prior to the usage of borehole water from the area for household consumption. Ms Mabe was the student working on the project under the supervision of Prof Gololo and Dr Molefe. The authors have all contributed immensely to the work.

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