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PHYSICO - CHEMICAL ANALYSIS OF HOUSEHOLD DRINKING WATER AND WATER SOURCES IN THE LIMPOPO PROVINCE, SOUTH AFRICA

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Abstract – In the present study, the physico-chemical characteristics of drinking water samples and its potential health implications from different districts in Northern South Africa were determined. Water samples were collected from households, boreholes or Rivers from which local populations collect water for drinking. Physicochemical parameter analysis were processed and compared with the standard values set by the South African standard (DWAF). The pH range of the samples varied between 5.12 and 8.96 units. The turbidity from homes and rivers varied from 0.17 NTU to 21.74NTU. With the mean values of physicochemical analysis as follows Fluoride (0.45mg/L), Chloride (107.39 mg/L), Nitrate (95.91 mg/L), Phosphate (65.30 mg/L), Cadmium (7.67μg/mL), and Lead (21.93 μg/mL). Of all the samples tested, 49 (87.5%) had no fluoride at all while 3(5.4%) samples had a concentration above the recommended limit. The high levels observed could be detrimental to the health of the population.

INTRODUCTION

Water sources are commonly contaminated by microorganisms as well as chemical substances which make it unsuitable for human consumption. Therefore it is important that the quality of such water sources be evaluated and monitored regularly. In South Africa, it is estimated that about 70% of the water used in both rural and urban areas is surface water drawn from rivers, streams, lakes, ponds and springs although ground water in the form of Borehole has recently been increasingly used (Wessels et al., 2010). In South Africa; the chemical constituents of drinking water are regularly measured by water providers such as the Department of Water Affairs, and Municipalities (DWA 2014; DWAF 2004). However, epidemiological studies focusing on the level of chemical contaminants in drinking water as well as the potential human health outcomes are very scarce. Groundwater is water below the topsoil and above impervious bedrock. When groundwater collects in and saturates relatively porous fractured bedrock and soil, it is said to be in an aquifer. The water table is a depth below which the soil and fractured bedrock (i.e., the aquifer) is saturated with water. The water table can vary from season to season and year to year, often resulting into a considerable variation of the weight of the pore water, which has loading effects on the groundwater flow in the underlying confined aquifer (Wang et al., 2012). For a well to produce water reliably, it must be deep enough so that water can be pumped from the aquifer under virtually all weather conditions. Aquifers are recharged from above by precipitation and runoff. In South Africa as well as in many countries around the world, ground water is used as a main source of drinking water by a sizable proportion of the population, especially those in the rural area, where access to portable water is a challenge. However, the contents of this water in terms of chemistry and other characteristics depend on several factors including the nature of the rock where the water is situated. In relation to health related impact of the chemical contents of this water on human and animal health, it is important to

understand the chemical composition of water sources and drinking water particularly in rural communities where access to treated water is often very limited.

Different types of wells are often used for water provision mostly in rural areas such as those in the Limpopo Province. They include dug wells which are usually shallow holes of 3 to 10 m deep, lined with rock, brick, tile, or concrete, with a pump in a nearby pump house or in the dwelling. They are easy to contaminate and unreliable in most cases. Driven wells usually use a pipe that is driven through gravel or sandy soil. These wells also tend to be shallow, usually approximately 15 m deep with the pump generally installed at the top of the well or in the dwelling. Driven wells are relatively easy to contaminate because of their shallowness but can be installed rapidly and inexpensively if the geologic conditions are right. Dug wells and driven wells are often the water source at camps or vacation homes as well as many rural households in South Africa (Abiye, 2011).

Some chemical substances found in water sources could be both beneficial and detrimental to human and animal health. For example, Fluoride (F^-) contributes positively to teeth and bone formation and their health due to its inhibition of enzymes of cariogenic bacteria. However, excess F^- is responsible for fluorosis, dental caries, osteosclerosis, calcification of tendons and ligaments, and bone deformity (Zhang et al., 2012). Chloride (Cl^-) is a major constituent in mammalian blood and most abundant electrolyte in serum, with a key role in the regulation of body fluids, electrolyte balance (Kenrick Berend et al., 2012) and part of the circulatory system. However; Cl^- in excess (in the consumption of NaCl) is associated with hypertension. Furthermore, chemical substances could work in synergy to cause harm to the host. For example, excessive amounts of Br^- are usually exacerbated by high levels of F^- and Iodine (I). The chemical composition of well water varies according to the region, underlying geologic formation, and environmental contamination and can be harmful, beneficial, or merely undesirable (Mande et al., 2011). For example, some fluoride is desirable in drinking water, whereas iron is undesirable. Many other chemicals, some of them potentially toxic, can contaminate well water, with their presence or absence attributable to naturally occurring geologic factors or dispersion from industry, farms, or business. The presence of nitrates is particularly problematic for infants, pregnant or nursing women. Nitrate contamination of drinking water may result in human health affects including interference with blood's ability to deliver oxygen to the body generally resulting in a condition known as methoglobinemia, or blue baby syndrome. The health effect of Nitrate contamination of drinking water varies from country to country. Ecologic studies of stomach cancer in countries such as Slovakia, Spain, and Hungary of historical measurements and exposure levels near or above the maximum contaminant level (MCL) have found positive correlations of stomach cancer incidence or mortality to nitrate levels in the water (Gulis et al., 2002). In Slovakia, incidence of non-Hodgkin lymphoma (NHL) and colon cancer was significantly elevated among men and women exposed to public supply nitrate levels of 4.5–11.3 mg/L nitrate-N (Gulis et al., 2002). However, there was no association with bladder and kidney cancer incidence. In Spain, there was a positive correlation between nitrate levels in public supplies and prostate cancer mortality, but no relation with bladder and colon cancer (Morales-Suarez-Varela et al., 1995). Too much sodium has been identified as a risk factor for high blood pressure (Khan et al., 2010). Other potential health effects include cancer, disruption of thyroid function, birth defects and miscarriages. Recommendations have been made on the maximum level of different chemicals species in drinking water for which there is not or minimal health risks. Although several studies have determined the concentration of these chemicals in sewage (El-Nahhal et al., 2014), very few studies have described the occurrence of these chemicals in drinking water particularly in the Limpopo Province.

Chemical contaminants are approached by investigating the possibility that the contamination exists on the homeowner's or on an adjacent homeowner's property, such as from agricultural application of nitrogen-containing fertilizers, pesticide application, or fuel tanks (Obiri Danso et al., 2008). If the water supply cannot be remediated further and the well is still contaminated or the chemicals in question are naturally occurring, then it is possible to filter out or treat for virtually any chemical or biological contaminant. However, treatment can become complex and/or expensive and can require meticulous or professional maintenance. In the present study, we determined the physico-chemical content of household drinking water as well as some River and Boreholes water from 22 different villages in the Limpopo Province including rivers, boreholes, springs, dams and water from municipal taps and their potential health impacts in relations to the guidelines and standard sets by South African regulatory authority for adequate monitoring.

METHODOLOGY

Study Area

Limpopo province is geographically located at the Northern part of South Africa. The province is with a total area of 125,754 km^2 (48,554 sq. mi) bounded on the north by Zimbabwe and Botswana, on the east by Mozambique and on the south and west by the provinces of Mpumalanga, North West and Gauteng (Aurecon, 2010; Wikipedia contributor, 2017). Limpopo is characterised by sparsely populated rural areas that have low densities with rural population mainly involved in mining or agricultural activities (Aurecon, 2010; Census, 2011). It is considered to be a poor province with approximately 87% of its people living in rural areas and with 23% of households having no access to piped water (Massyn et al., 2016).

Sample collection

Water samples were collected aseptically with sterile sampling bottles. The samples were transported within 2 hours of collection in a cool box containing ice packs to the Department of Microbiology, at the University of Venda in the microbiology laboratory for analysis. Ethical clearance for the study was obtained from the University of Venda and authorization was obtained from the Department of Water Affairs in the Vhembe District. The consent of the household heads was obtained before sample collection.

Determination of physical properties

Turbidity was measured using the HACH DR/2010 Spectrophotometer. Twenty five millilitres of a well-mixed sample were measured into a clean sample cell. Another sample cell was filled with distilled water. The intensity of light scattered and absorbed by the sample was compared to that measured for standard Formazin suspensions and was read at a wavelength of 860 nm. The Temperature of the water samples was also measured as well as the pH of the samples.

Determination of chemical properties

The chemical quality of the water samples was established by carrying out an anion analysis using a Metrohm 850 professional ion chromatograph. Heavy metals were determined by use of a Varian 220 atomic absorption spectrophotometer coupled to a GTA 110 electrothermal atomiser.

Determination of anions

Merck multi-element anion standard of 1000mg/L was used. The anions present in the standards were fluoride, chloride, bromide, nitrate, phosphate and sulphate. Deionised water from a Millipore water purifier with a conductance of 0.054 ìS/cm was used for the dilution of standards. The standards for the

Fig. 1. Map of the municipalities in Limpopo province of South Africa (List of municipalities in Limpopo, 2017)

calibration curves were produced by serial dilution of the bulk standard. The calibration curves were made up of four stands of concentration 1 mg/L, 5 mg/L, 10mg/L and 20 mg/L. The calibration curves produced for each anion had a minimum correlation coefficient of 0.99.

Determination of Lead and Cadmium

Merck standards of 1000 mg/L of both Lead and cadmium were used for the determination using the Varian atomic absorption spectrometer. The instrument was used in the electrothermal mode with a partitioned graphite tube. The standards were prepared using the ultrapure water from the Millipore purifier for serial dilution. The calibration curves produced for both elements had a minimum correlation coefficient greater than 0.99. The process of producing a calibration curve was done by sampling each component of the standards three times. The samples were also sampled in triplicate for each determination.

Data analysis

The data were entered in Microsoft Excel programme and descriptive statistics were computed. Statistical tests were performed using the SPSS programme.

RESULTS

Turbidity

The turbidity of the water samples collected from homes and rivers varied from 0.17 NTU to 21.74NTU. Of all the samples, 37 (50.7%) had a turbidity less than 1NTU, while 28 (38.4%) had a turbidity between 1 and 5NTU and 8 had a turbidity more than 5NTU. Samples from Thulamela and Mutale, two municipalities in the Vhembe District, had the highest turbidity measurements in comparison to samples from other regions (Table 1). The turbidity of all the river samples were above 1NTU while most (66.7%) of the communal tap water had turbidity less than 1NTU (Table 2). Only 41% of the borehole water samples had turbidity less than 1NTU. In Tubatse District the turbidity of tap water sources was all within the recommended values while in Mutale District, the turbidity of tap water was the lowest (Table 3).

pH of the water samples

The pH of a solution is defined as the negative logarithm to the base ten of the hydrogen ion concentration, given by the expression:

$$pH = -\log 10\,[H^+].$$

Table 1. Turbidity of water samples from different municipalities in the Limpopo province

Municipality	Turbidity			
	<1NTU	1- 5 NTU	>5NTU	Total
Capricorn	6(86%)	1(14%)	0	7
Elias Motswaledi	6 (75%)	2 (25%)	0	8
Greater Giyani	8 (67%)	4 (33%)	0	12
Makhado	6 (55%)	5 (46%)	0	11
Mutale	1 (6%)	11 (61%)	6 (33%)	18
Thulamela	2 (33%)	3 (50%)	1 (17%)	6
Tubatse	3 (75%)	0	1 (25%)	4
Waterberg	5 (71%)	2 (29%)	0	7
Total	37(51%)	28 (38%)	8 (11%)	73

Table 2. Turbidity of water samples from different sources used by population for drinking

Source	Turbidity range			Total
	<1NTU	1 - 5 NTU	>5NTU	
Borehole	10 (42%)	11 (46%)	3 (13%)	24
House	8 (57%)	5 (36%)	1 (7%)	14
River	0	1 (25%)	3 (75%)	4
Spring	1 (25%)	3 (75%)	0	4
Communal tap	18 (67%)	8 (30%)	1 (4%)	27
Total	37 (51%)	28 (38%)	8 (11%)	73

Where $[H^+]$ is the hydrogen ion concentration. At pH less than 7, water is acidic, while at pH greater than 7 water is alkaline.

The pH of the samples varied between 5.12 and 8.96 units. The South African standards indicate that the normal pH of water used for drinking and other domestic purposes should be between 6 and 9. However, it also indicates that "the pH of most raw waters lies in the range of 6.5 - 8.5" and outside this range, there might be slight negative side effects or discomfort. For example, aluminium solubility begins to increase at pH 6, and amphoteric oxides may begin to dissolve at a pH of greater than 8.5. Very slight effects on taste may be noticed on occasion. Therefore in the present study we considered the normal pH range to be between 6.5 and 8.5 units. Considering this range, 3 samples had pH bellow 6.5 while 12 were above 8.5 making a total of 15 (17%) outside of our normal pH range.

Water samples from the rivers all had pH within the recommended limits while tap samples had 6.7% samples with pH less than 6.5 and 13.7% of the samples had pH more than 8.5 (Table 4).

Temperatures

The temperature of the water normally varies from 0-35 degrees Celsius, depending on the source depth and season. The temperature of water affects some of the important physical properties and characteristics of water and solubility of dissolved gases (example; oxygen and carbon dioxide). Chemical and biological reaction rates increase with increasing temperature. In the rural areas of the Limpopo Province, where the water samples were collected, the temperature of water varied from 20º – 26ºC depending on the time of collection and kind of source.

Chemical profiles of water samples

Several chemicals including Fluoride, Chloride, Nitrate, Phosphate, Cadmium and Lead were tested in the water samples and the classification was done according to South African Standards. Table 5 shows the range of the values obtained for each of the chemicals tested.

Fluoride

A total of 56 samples were analyzed for fluoride. Of

Table 3. Turbidity of water sources by district in rural areas in the Limpopo Province

Municipality	Turbidity	Water source					Total
		Borehole	House	River	Spring	tap	
Capricorn	High	0	0	0	0	1 (20%)	1 (14%)
	Normal	1 (100%)	1 (100%)	0	0	4 (80%)	6 (86%)
	Total	1	1	0	0	5	7
Elias Motswaledi	High	0	0	0	1 (50%)	1 (50%)	2 (29%)
	Normal	1 (100%)	2 (100%)	0	1 (50%)	1 (50%)	5 (71%)
	Total	1	2	0	2	2	7
Greater Giyani	High	3 (38%)	0	0	0	1 (25%)	4 (33%)
	Normal	5 (63%)	0	0	0	3 (75%)	8 (67%)
	Total	8	0	0	0	4	12
Makhado	High	0	0	1 (100%)	1 (100%)	3 (38%)	5 (46%)
	Normal	1 (100%)	0	0	0	5 (63%)	6 (55%)
	Total	1	0	1	1	8	11
Mutale	High	9 (100%)	4 (100%)	1 (100%)	1 (100%)	2 (67%)	17 (94%)
	Normal	0	0	0	0	1 (33%)	1 (6%)
	Total	9	4	1	1	3	18
Thulamela	High	2 (67%)	0	1 (100%)	0	1 (50%)	4 (67%)
	Normal	1 (33%)	0	0	0	1 (50%)	2 (33%)
	Total	3	0	1	0	2	6
Tubatse	High	0	0	1 (100%)	0	0	1 (25%)
	Normal	0	0	0	0	3 (100%)	3 (75%)
	Total	0	0	1	0	3	4
Waterberg	High	0	2 (33%)	0	0	0	2 (29%)
	Normal	1 (100%)	4 (67%)	0	0	0	5 (71%)
	Total	1	6	0	0	0	7

High = values above 1NTU, Normal =Less than 1NTU.

Table 4. pH in different municipalities by water sources

District	Borehole			House			River			Spring			Tap		
	Less than 6.5	6.5 - 8.5	More than 8.5	Less than 6.5	6.5 - 8.5	More than 8.5	Less than 6.5	6.5 - 8.5	More than 8.5	Less than 6.5	6.5 - 8.5	More than 8.5	Less than 6.5	6.5 - 8.5	More than 8.5
Capricorn	0	1(100%)	0	-	2 (100%)	0	-	-	-	-	-	-	0	5 (71%)	2 (29%)
Elias motswaledi	0	1(100%)	0	-	5 (71%)	2 (29%)	-	-	-	-	1 (50%)	1 (50%)	0	3 (75%)	1 (25%)
Greater Giyani	0	8(100%)	0	-	-	-	-	-	-	-	-	-	0	2 (100%)	0
Makhado	0	2(100%)	0	-	2 (40%)	3 (60%)	-	2 (100%)	-	-	1 (100%)	0	1 (11%)	7 (78%)	1 (11%)
Mutale	1(11%)	7 (78%)	1 (11%)	-	4 (100%)	0	-	1 (100%)	-	-	1 (100%)	0	1 (50%)	1 (50%)	0
Thulamela	0	3(100%)	0	-	-	-	-	1 (100%)	-	-	-	-	0	2 (100%)	0
Tubatse	-	-	-	-	-	-	-	1 (100%)	-	-	-	-	0	4 (100%)	0
Waterberg	0	0	1(100%)	-	6 (100%)	0	-	-	-	-	-	-	-	-	-
Total	1 (4%)	22 (88%)	2 (8%)	-	19 (79%)	5 (21%)	-	5 (100%)	-	-	3 (75%)	1 (25%)	2 (7%)	24 (80%)	4 (13%)

these samples, 49 (87.5%) had no fluoride at all while 4 (7.1%) samples had a concentration bellow 1mg/L. The recommended value for fluoride in drinking water is less than 1mg/L according to South African standard. Three samples (5.4%) had a concentration value more than 1mg/ml. The three samples with high fluoride content were from Giyani Municipality (1) and Elias Motswaledi Municipality in the Sekhukhune District (2).

According to WHO standards the acceptable fluoride content is less than 1.5mg/L. Considering this criterion, only two samples from the Sekhukhune District were out of limit. Turbidity was not associated with the presence of fluoride in water samples since the turbidity of the samples with high fluoride content was less than 1. The samples with high fluoride content (SA standards) were from boreholes for two samples and home for one. The household from which the sample was collected probably collected water from the bore hole located in the same area.

Chloride

The recommended limit of chloride in drinking water in South Africa is 200 mg/L or less. Of the 65 samples tested for chloride, 59 (90.8%) had concentrations of chloride that were within the recommended limit of <200mg/L while the rest (9.2%) were out of this limit.

Most water samples had a chloride concentration between 0 and 200mg/L. The highest concentrations of chloride (>600mg/L) was found in Capricorn while those between 200 and 600mg/L were found in Elias Motswaledi, Makhado, Mutale andTubatse Municipalities (Table 6). All the three samples from springs had chloride contents within the recommended limits while less household samples had chloride values within the recommended limits (Table 7).

Nitrate

A total of 65 samples were tested for nitrate. Out of these only 12 (18.5%) were within the recommended limit according to South African standards of less than 5mg/L. Considering the American standard of less than 10mg/L, only 14 samples were within these limits while 47 (72.3%) of the samples had a nitrate content more than 20mg/L. Table 8 bellow shows the distribution of the nitrate content of the samples.

More samples (66.7%) in the Makhado District had nitrate content within the recommended limits while none of the samples collected in Capricorn,

Table 5. Distribution of measured parameters in the samples. The minimum, mean, maximum and median values are given for the different chemicals.

Statistical characteristics	Chemicals and concentrations					
	Fluoride (mg/L)	Chloride (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Cadmium (µg/ml)	Lead (µg/ml)
Number tested	56	65	65	65	42	41
Mean	-.45196	107.3999	95.91218	65.30406	7.67	21.93
Std. Error of Mean	.097195	15.47846	12.548390	10.954690	1.492	2.973
Median	-.76150	71.6100	59.84100	28.59800	4.40	21.00
Mode	-.909[a]	1.64[a]	-1.145[a]	-.913[a]	0	0
Std. Deviation	.727344	124.79136	101.168351	88.319533	9.671	19.039
Variance	.529	15572.884	10235.035	7800.340	93.528	362.493
Range	3.877	725.03	406.057	342.454	49	62
Minimum	-1.028	1.64	-1.145	-.913	0	0
Maximum	2.849	726.67	404.912	341.541	49	62
South African Standard	<1mg/L	<200	<10	-	<5	<20
WHO standard	<1.5	<250	<50	-	<3	<10

Table 6. Distribution of chloride content in different Municipalities in the Limpopo Province

Municipality	Chloride (mg/L)				Total
	<100 mg/L	100 - 200 mg/mL	200 - 600 mg/L	>600 mg/L	
Capricorn	0	7 (78%)	0	2 (22%)	9
Elias Motswaledi	12 (86%)	1 (7%)	1 (7%)	0	14
Greater Giyani	4 (67%)	2 (33%)	0	0	6
Makhado	9 (75%)	2 (17%)	1 (8%)	0	12
Mutale	3 (43%)	3 (43%)	1 (14%)	0	7
Thulamela	5 (83%)	1 (17%)	0	0	6
Tubatse	2 (50%)	1 (25%)	1 (25%)	0	4
Waterberg	3 (43%)	4 (57%)	0	0	7
Total	38 (59%)	21 (32%)	4 (6%)	2 (3%)	65

Table 7. Distribution of chloride content by water sources

Source	Chloride mg/L				Total
	<100mg/L	100 - 200 mg/mL	200 - 600mg/L	>600mg/L	
Borehole	11 (52%)	8 (38%)	2 (10%)	0	21
House	11 (50%)	7 (35%)	1 (5%)	1 (5%)	20
River	4 (80%)	1 (20%)	0	0	5
Spring	3 (100%)	0	0	0	3
Communal tap	9 (56%)	5 (31%)	1 (6%)	1 (6%)	16
Total	38 (59%)	21 (32%)	4 (6%)	2 (3%)	65

Table 8. Distribution of nitrate in water samples from boreholes, homes and rivers in the Limpopo Province

Range	Frequency	Percent
<5 mg/L	12	18.5
5-10 mg/L	2	3.1
10.0-20 mg/L	4	6.2
>20 mg/L	47	72.3
Total	65	100

Elias Motswaledi, Tubatse and Waterberg Districts had nitrate content within the recommended limits (Table 9).

Eighty percent of the samples collected directly from the rivers had a nitrate content within the recommended limits while none from the 20 samples collected directly from the household stored water had nitrate content within the recommended limits (Table 10).

Table 9. Distribution of nitrate in different municipalities in the Limpopo Province

Municipality	Nitrate (mg/L)				Total
	<5mg/L	5 - 10mg/L	10 - 20mg/L	>20mg/L	
Capricorn	0	0	1 (11%)	8 (89%)	9
Elias Motswaledi	0	1 (7%)	2 (14%)	11 (79%)	14
Greater Giyani	1 (17%)	0	0	5 (83%)	6
Makhado	8 (67%)	1 (8%)	0	3 (25%)	12
Mutale	2 (29%)	0	1 (14%)	4 (57%)	7
Thulamela	1 (17%)	0	0	5(83%)	6
Tubatse	0	0	0	4 (100%)	4
Waterberg	0	0	0	7 (100%)	7
Total	12 (19%)	2 (3%)	4 (6%)	47 (72%)	65

Table 10. Distribution of nitrate by water sources in the Limpopo Province

Sources	Nitrate mg/L				Total
	<5mg/L	5 - 10mg/L	10 - 20mg/L	>20mg/L	
Borehole	3 (14%)	0	2 (10%)	16 (76%)	21
House	0	1 (5%)	0	19 (95%)	20
River	4 (80%)	0	0	1 (20%)	5
Spring	1 (33%)	0	2 (66.7%)	0	3
Communal tap	4 (25%)	1 (6%)	0	11 (69%)	16
Total	12 (19%)	2 (3%)	4 (6.2%)	47 (72%)	65

Phosphates

Sixty five samples were analyzed for phosphates and only 5 (7.7%) had concentrations of less than 0.1mg/L as recommended by the South African standards. Most of the samples (58.5%) had phosphate content between 1 and 50mg/L. About 80% of the water samples had phosphate levels above 1mg/L (Table 11). Only samples from Makhado and Thulamela municipalities had phosphate contents within the recommended limit 33.3% and 16.7% respectively. All the other municipalities had phosphate content above the recommended limit (Table 12). More spring water samples and River water samples had phosphate content within the recommended limit as opposed to boreholes and household stored water (Table 13). High levels of phosphate in the samples were associated with high pH (pH above 8.5) (÷2=8.765; p=0.012) but were not associated with turbidity.

Table 11. Phosphate content distribution in the water samples from the different district in the Limpopo Province

Range	Frequency	Percent
<0.1mg/L	5	7.7
0.1 - 1mg/L	2	3.1
1 - 50 mg/L	38	58.5
>50mg/L	20	30.8
Total	65	100.0

Cadmium

Forty two samples were analysed for cadmium of which 22 (52.4%) had a concentration within the limits recommended by the South African standards (<5μg/L) while, 8 (19%) had a concentration of more than 10μg/L) (Table 14). Cadmium levels were higher in Waterberg District than the orther regions of the Limpopo Province (Table 15). About 85% of the borehole water samples had cadmium content within the recommended limits. However, 44% of the communal waters and about 51% of the household water samples had a cadmium content above the recommended 5 μg/L (Table 16). There was no significant association between the turbidity of the samples and the cadmium content of the water. But, 63.6% of the samples that had a pH value within the recommended limits had cadmium content within the recommended limit compared to only 42.9% of the samples that had too high or too low pH that had cadmium content within the recommended limit. But the difference was not statistically significant.

Lead

Of the 41 samples tested 13 (31.7%) had a

Table 12. Distribution of phosphate content in different Municipalities in the Limpopo Province

Municipality	Phosphate mg/L				Total
	<0.1mg/L	0.1 - 1mg/L	1 - 50mg/L	>50mg/L	
Capricorn	0	0	4 (44%)	5 (56%)	9
Elias Motswaledi	0	1 (7%)	7 (50%)	6 (43%)	14
Greater Giyani	0	0	6 (100%)	0	6
Makhado	4 (33%)	0	8 (67%)	0	12
Mutale	0	1 (14%)	5 (71%)	1 (14%)	7
Thulamela	1 (17%)	0	5 (83%)	0	6
Tubatse	0	0	1 (25%)	3 (75%)	4
Waterberg	0	0	2 (29%)	5 (71%)	7
Total	5 (8%)	2 (3%)	38 (59%)	20 (31%)	65

Table 13. Distribution of phosphate by water sources in the Limpopo Province

Source	Phosphate mg/L				Total
	<0.1mg/L	0.1 - 1mg/L	1 - 50mg/L	>50mg/L	
Borehole	1 (5%)	1 (5%)	16 (76%)	3 (14%)	21
House	0	1 (5%)	9 (45%)	10 (50%)	20
River	1 (20%)	0	3 (60%)	1 (20%)	5
Spring	1 (33%)	0	1 (33%)	1 (33%)	3
Communal tap	2 (13%)	0	9 (56%)	5 (31%)	16
Total	5 (8%)	2 (3%)	38 (59%)	20 (31%)	65

Table 14. Cadmium content distribution in drinking water samples from Limpopo Province.

Range	Frequency	Valid Percent
<5μg/L	22	52.4
5 - 10 μg/L	12	28.6
>10 μg/L	8	19.0
Total	42	100.0

concentration less than 10 μg/L as recommended by South African standards. Most of the samples had a lead concentration between 20 and 50 μg/L (Table 17). More than 60% of the borehole water samples had a lead content higher than the recommended 20 μg/L.

Most samples from Elias Motswaledi Municipality had lead content within the recommended limit while fewer samples from Makhado and Waterberg were within the recommended limit (Table 18). All the 2 River water samples had levels of lead within the recommended limit as opposed to only 16.7% of the borehole samples that had lead contend within the recommended limit (Table 19). There were no association between lead content and the turbidity as well as the pH of the samples ($p>0.05$).

DISCUSSION

The objective of the study described in this chapter

Table 15. Distribution of cadmium content in drinking water samples from boreholes, homes and rivers in different municipalities in the Limpopo Province

Municipality	Cadmium μg/mL			Total
	<5 μg/L	5 - 10 μg/L	>10 μg/L	
Capricorn	5 (71%)	2 (29%)	0	7
Elias Motswaledi	7 (58%)	4 (25%)	2 (17%)	13
Makhado	2 (67%)	1 (33%)	0	3
Tubatse Municipality	2 (50%)	2 (25%)	1 (25%)	4
Thulamela	0	0	1	1
Waterberg	3 (33%)	3 (33%)	3 (33%)	9
	3 (75%)		1 (25%)	5
Total	22	12	8	42

Table 16. Distribution of cadmium by water sources in the Limpopo Province

Source	Cadmium μg/mL10			Total
	<5 μg/L	5 - 10 μg/L	>10 μg/L	
Borehole	6 (86%)	0	1 (14%)	7
House	10 (48%)	6 (29%)	5 (24%)	21
River	0	2 (100%)	0	2
Spring	1 (33%)	2 (67%)	0	3
Communal tap	5 (56%)	2 (22%)	2 (22%)	9
Total	22 (52%)	12 (29%)	8 (19%)	42

Table 17. Lead content distribution in drinking water samples in the Limpopo Province.

Range	Frequency	Valid Percent
<10 μg/L	13	31.7
10 - 20 μg/L	5	12.2
20 - 50 μg/L	19	46.3
>50 μg/L	4	9.8
Total	41	100.0

was to determine the level of chemical contaminants in household water as well as water sources such as rivers, dams and boreholes in the rural areas of the Limpopo Province. High levels of nitrate, phosphate as well as heavy metals including lead and cadmium were discovered in the water samples. Nitrate as a source of Nitrogen for plants occurs naturally in both soil and water. It is among the most common contaminants of water sources worldwide. It is globally accepted that estimate that fertilizers are the largest contributor to anthropogenic nitrogen worldwide; other major sources include animal and human waste, nitrogen oxides from utilities and automobiles, as an oxidizing agent and in the production of explosives, glass making as well as in leguminous crops that fix atmospheric nitrogen (Speijers et al., 2011; Fields, 2004). These organic and inorganic sources of nitrogen are transformed to nitrate by mineralization, hydrolysis, and bacterial nitrification. Under reducing conditions, nitrate can be biologically transformed to nitrogen gas through denitrification. Nitrate not taken up by plants or denitrified migrates to streams and groundwater. It has been suggested that the presence of nitrates in spring water is associated with agricultural activity, from oxidation of nitrogenous waste products in human and animal excreta, including septic tanks, as well as from wastewater treatments (Speijers et al., 2011; Townsend and Whittemore, 2005; Lewis et al.,

Table 18. Distribution of the lead contend in drinking water samples in different municipalities in the Limpopo Province

Municipality	Lead μg/mL				Total
	<10 μg/L	10 - 20 μg/L	20 - 50 μg/L	>50 μg/L	
Capricorn	3 (50%)	1 (17%)	1 (17%)	1 (17%)	6
Elias Motswaledi	7 (54%)	1 (8%)	5 (39%)	0	13
Makhado	0	2 (67%)	1 (33%)	0	3
Tubatse	2 (40%)	0	3 (60%)	0	5
Thulamela	0	0	0	1 (100%)	1
Waterberg	1 (11%)	2 (22%)	6 (67%)	0	9
	0	0	2 (50%)	2 (50%)	4
Total	13 (38%)	5 (12%)	19 (46%)	4 (10%)	41

Table 19. Distribution of lead by water sources in the Limpopo Province

Source	Lead μg/ml				Total
	<10 μg/L	10 - 20 μg/L	20 - 50 μg/L	>50 μg/L	
Borehole	1 (17%)	1 (17%)	4 (67%)	0	6
House	5 (24%)	3 (14%)	10 (48%)	3 (14%)	21
River	2 (100%)	0	0	0	2
Spring	2 (67%)	0	1 (33%)	0	3
Communal tap	3 (33%)	1 (11%)	4 (44%)	1 (11%)	9
Total	13 (32%)	5 (12%)	19 (46%)	4 (10%)	41

1980). The high levels of nitrates observed in this study could probably be attributed to poor sanitation, probably leaching of nitrates from the nearby pit latrines or a possible contamination by animal wasteand wastewater treatment. Nitrate contamination of spring water from domestic sewage has been observed elsewhere in Africa (Haruna et al., 2005). In Nigeria, for example, nitrate levels in shallow wells were demonstrated to correlate with high human population density (Malomo et al., 1990; Langgennegger, 1981). Recent data from the United States indicate that about 22% of domestic wells in agricultural areas of the country exceeded the maximum contaminant level (MCL) (U.S. Geological Survey, unpublished data). In contrast, 3% of public supply wells in major aquifers (typical sources for public water supplies) exceed the MCL.

Cadmium is a common environmental pollutant, which is widely distributed in the aquatic environment. Studies have indicated that Cadmium may be introduced into the environment byweathering of minerals and soils, paints, pigments, plastic stabilizers, atmospheric deposition from non-ferrous metal mining and smelting operations, coal combustion and other industrial operations such as electroplating and fossil fuel, fertilizer, and sewage sludge disposal (Rahmanian et al., 2015; Merian, 1991).

The concentration of Cd in unpolluted water is usually less than 0.001 mg/L and the WHO level of Cd in drinking water is 0.01 mg/L (Nkono et al., 1997). The South African guideline for Cd is 0.005 mg/L (DWAF 1998, 1996). In the present study we found that about 48% of all the water samples tested had cadmium levels above the limits recommended by the South African Department of Water Affairs with the hihest values recorded at Waterburg District. These values was as a results of major mining activities in the various localities. In fact it should be noted that in the region where samples were collected, some residents indicated that the presence of the mine has been worrisome to the population as the mine often dumped the used water in the local river. This could be a potential source of the metals in the river although further studies are needed to confirm this hypothesis. Previous studies in Thohoyandou showed that the concentration ranges of all the metals measured were below the international guidelines and acceptable concentrations for drinking water except the values for Cd and Pb (Okonkwo and Mothiba 2005). Similarly studies in South Africa and Tanzania have indicated that Cadmium concentration was generally high in all the water sources with mean concentration range of 0.77 to 2.24 mg/L (Mwegoha and Kihampa, 2010; Fatoki et al., (2004). The authors further indicated that factors such as the dumping of agricultural wastes, addition of impure chemicals during water purification (in the case of pipe borne water), leaching of metals from wastes site to the ground water plus rural and urban water run-off could be responsible for the observed high concentrations of Cd. In the present study, we found similar results in a greater area of the Province.

Fluoride is essential for normal bone growth, but its higher concentration in the drinking water poses great health problems and fluorosis is common in many parts of the world including South Africa. The present study did not show high concentration of fluoride in the samples tested. It is estimated that too high fluoride intake normally gives rise to teeth mottling (dental fluorosis) and related problems. Chronic endemic fluorosis is a condition which is caused by an excess of fluorides in drinking water and which affects the calcification of the teeth, resulting in what is commonly known as dental fluorosis. Previous studies have shown that the majority of dental fluorosis sufferers (mainly blacks) in South Africa live in rural areas. Studies in the Western Cape have indicated that the prevalence of fluorosis (scores 2, 3, 4 and 5) among school children was 47% in Sanddrif, 50% in Kuboes (Two areas of low fluoride) and 95% in Leeu Gamka (an area of high fluoride) (Grobleri et al., 2001). This study showed a positive association between high Fluoride levels in the drinking water and dental caries in the areas affected. Different studies have shown that the occurrence of dental fluorosis in the majority of cases in South Africa are related to the fluoride content of groundwater used for drinking purposes (WRC, 2001). In the present study, only two water samples had high fluoride content indicating a low level of contamination of water sources from the region with this chemical. A study by Ncube and Schutte (2005) indicated that fluoridation of groundwater is not advisable since the occurrence of low fluoride ion concentrations in groundwater is not a national problem. They further indicated that alternatives to water fluoridation should be looked into for such areas. These could include salt fluoridation, milk fluoridation, or the use of fluoride supplements such as fluoride drops or tablets or fluoridated vitamins. In Malawi, fluoride levels in most water samples tested were way above the WHO guideline value of 1.5 mg/L free fluoride with levels of up to 8.6 mg/L in borehole water that have been reported in Ulongwe in Machinga District, while subsequent studies found positive correlation between the pH of the water and fluoride concentrations (Sajidu et al., 2008). Further studies are needed in Limpopo Province to determine any potential correlation between dental fluorosis and the level of fluoride in drinking water sources with particular reference to borehole waters.

Lead is one of the most common water sources contaminants around the world. Lead interferes with a variety of body processes and is toxic to many organs and tissues including the heart, bones, intestines, kidneys, and reproductive and nervous systems and is particularly toxic to children causing potentially permanent learning and behavior disorders (Payne, 2008). Symptoms include abdominal pain, confusion, headache, anemia, irritability, and in severe cases seizures, coma, and death (Shadick et al., 2000). Although lead can be found in soil, it is commonly found in water sources. In Tanzania, the concentration of lead in river water exceeded the WHO (2004) drinking water limit of 0.01mg/L (Mwegoha and Kihampa, 2010). In that study, maximum concentrations of lead could be attributed to the inflowing channel from a certain wastewater stabilization pond which consisted of various wastes from industrial and domestic effluents, including automobile garages and car wash, which discharge mixtures of oil and car washing into the stream leading to the river. In the present study, more than half of the samples tested had higher lead levels. These results are similar to those found in Nigeria where the concentration of Pb was generally high in all the water samples tested from all the four towns considered in that study (Oluyemi et al., 2010). The lowest values recorded were found in streams located in a serene environment on the outskirt of the town where no industrial or domestic activities are taking place. While on the contrary, the high concentration of the elements in a river (6.69 mg/L) was considered to be as a result of the direct release of domestic waste containing Pb from human activities at the riverbank and vehicular exhausts. The highest value of Pb (6.98 mg/L) recorded for the pipe borne water was the same in all the towns in the Local Government since the pipe borne water was from the same source. It was indicated that the values obtained could be associated with the wearing of lead from metal pipes into the water during water distribution although other possible source of this element was suggested to be the geology of the area since its value was generally high, even in ground-water (boreholes and hand-dug wells). Another study in Southern Nigeria showed that Data obtained showed that all the untreated water samples contained lead concentrations in the range of 1.0 - 12.0 ppb, with a mean value (X) of 4.9 ± 0.18 ppb (Abiola, 2010). In Kenya, all the fish samples tested from Lake Victoria had lead levels above the WHO maximum limit of 0.2 (μg/g) while Lead content in soil samples ranged from 0.2 to 3.9 (μg/g) indicating that there is considerable risk of lead poisoning from drinking water and eating some foods from these sites (Makokha et al., 2008). Previous studies in the Thohoyandou region showed that early morning tap water ush had Pb level of 20.6 ± 5.6 μg Pb L^{-1} which is higher compared to the WHO and FDA maximum permissible concentrations of 10 μg L^{-1} and 15 μg L^{-1} respectively (Okonkwo and Maribe, 2004). In the present study, we did not investigate the potential source of contamination; however, the nature of the pipes used could be implicated. It should also be noted that human activities in the rivers could conataminate the water sources. For example, it is common to find in rural areas people washing cars in the rivers. The potential role of the mines is also to be further investigated as the Limpopo Province is home to several mines as well.

Phosphorous is a vital nutrient for all living things and is a common constituent of agricultural fertilizers, manure, and organic wastes in sewage and industrial effluent (Howard Perlman, 2016). Cellular phosphates compounds trap energy generated from food consumed and transfer it to activities that demand it for locomotion, reproduction and growth. Without phosphorus to build these energy compounds, cell life cannot exist (Wagner, 1974). Phosphorus occurs naturally as phosphates and its introduction in aquatic environment is a major cause of eutrophication (Howard Perlman, 2016; Lindsy et al., 1960). Most phosphates are dissolved but some are in combination with suspended particles in the water and may contribute to turbidity. Phosphorus is normally very low (< 1mg/L) in clean portable water sources and usually not regulated (Nduka et al., 2008). In the present study, the phosphate content of about 31% of the samples was higher than 50 mg/L.

The water phosphate content depends on several issues such as fertilizers, human and animal waste that infiltrate the ground to get to drinking water sources. All the samples collected from households had phosphate concentration above 0.1 mg/L while less than 10% of all the samples had a phosphate concentration less than 1 mg/L. The source of phosphate in the present study could not be determined. However, the possibility of Agricultural contamination or human waste through sewage cannot be ruled out. Further investigations are warranted.

Chlorine gas is highly toxic but chloride irons are essential for life (Duffus, 1996). Though chloride anion is present in natural water, high chloride content may indicate pollution by sewage, industrial waste or intrusion of seawater or saline water into fresh water aquifer (Bertram and Balance 1996). Chloride occurs in all natural waters in varying concentrations. In the present study, the chloride concentration varied between 1.64 mg/L and 726.67 mg/L. The lowest concentration of chloride was found in rivers and springs while boreholes and household water samples had the highest prevalence of high chloride concentration. It has been suggested that the concentration of chloride is usually greater in groundwater than surface water especially if salt deposits are in the area. A study in Tanzania found that all the samples collected from households had chloride levels that exceeded the WHO limits (Napacho and Manyele, 2010). Chloride in small concentrations are not harmful to humans in drinking water, and with some adaptation, the human body can tolerate water with as much as 200 mg/L chloride ion. However, above a concentration of 250 mg/L chloride, the water may taste salty (Hauser, 2001). High chloride content in process waters may promote pipe corrosion. Removal of chloride from portable water is very difficult and generally requires desalination.

This saltiness could be due in part to the high chloride content in the water samples. However, further studies are needed to confirm this hypothesis.

The spatial distribution of chemical properties and concentrations vary within the same region and the different regions as well. In our study, there was a variation of the chemical properties of water samples among the different districts. A study conducted on the quality of sachet water samples in the Cape Coast Municipality of Ghana in 2002 - 2004, showed that pH and conductivity exceeded WHO guidelines while the major cations including sodium and potassium were bellow WHO limits, therefore did not seem to pose any health dangers. Studies in Oman have indicated that the concentrations of most of the elements were less than the permissible limits of national Omani standards and WHO guidelines for drinking water and domestic use and do not generally pose any health and environmental problems. However there were high levels of electrical conductivity, total dissolved solids, chloride, and sodium absorption ratio (Ghrefat *et al.*, 2011). In Nigeria, the maximum permissible limit for phosphate as P in water system that will reduce the likelihood of algae growth is < 5 mg/L (FEPA/FMENV 1991). A study in Nigeria reported the concentrations for Chloride ranged between 3.64 and 184.04 mg/L with nitrate ranging between 1.08 and 53.03 mg/L while the highest phosphate value observed was 23.07 mg/L (Oluyemi *et al.*, 2010). These values were much lower compared to those obtained in the present study. Related study in Nigeria also reported high levels of phosphate in wells that were used for drinking water (Ololade *et al.*, 2009). Also, in a Ghanaian study, measured major anions (i.e., chloride, sulphate, and nitrates) were within the WHO drinking water guideline (Dadoo *et al.*, 2006). No exceedances were recorded for iron and lead, unlike in our study where many samples had lead contents above both national (DWAF) and international (WHO) limits.

In order to improve the chemical quality of these water sources, there is need to utilise or develop technologies that could help eliminate those substances in the water sourcesto yield better results for sustainability of human existence.

CONCLUSION

Contamination of water as it affects the physicochemical species is an attribute of anthropogenic and natural sources and this species in high amount will results in negative health impacts. This study indicates a very low prevalence of fluoride contamination in the areas tested in the Limpopo Province. However, the prevalence of nitrate, chloride, lead and cadmium contamination was very high. Statistically significant association relationship between high pH and high phosphate content in water was reported in this study. The salty flavour of water reported in the study might be related to the high content of salts in the water.

There is need to further investigate the extent of low fluoride contamination in the Province in relation to the occurrence of fluorosis in the local populations. The study was not able to identify potential sources of contamination from the chemical substances investigated in these locality. Therefore, further studies are needed in order to identify potential sources of contamination as well as the potential effect of high levels of chemicals such as nitrate in the population particularly newborn babies in the Province. Measures are needed in order to reduce the salt concentration of water used by rural communities in the Limpopo Province.

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