Assessment of fluoride, pH and nitrate levels in Gokwe waters, Zimbabwe

T. Ngarivhume[1]*, E.Togarepi[1] and N. Mpofu[2]

[1]*Chemistry Department, Bindura University of Science Education, P. Bag 1020, Bindura.
Corresponding author: tngarivhume@yahoo.com
[2] The Government Analyst Laboratory Box CY 231, Causeway, Harare.

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Abstract

The fluoride, pH, and nitrate levels in waters from Gokwe districts were determined using ion selective methods, pH meter, and UV-vis, respectively. The water sources (44) included boreholes (26), artesian wells (7), rivers (9) and dams (2). Most boreholes from high fluoride areas (HFA) of Goredema, Chireya and Nemangwe (17/18) had average fluoride levels of 8.60 and 6.73 mg/L, well above the WHO guideline (1.5 mg/L); while all sources in Njelele, a low fluoride area (LFA), had average fluoride levels of 0.13 and 008 mg/L during the dry and wet seasons, respectively. Artesian wells in Goredema, Chireya and Nemangwe reported an average fluoride level of 3.80 mg/L during the dry season. All waters from rivers and dams reported fluoride and nitrate levels below the WHO guidelines during both seasons. Many artesian wells (4/7) and very few boreholes (3/26) reported nitrate levels above WHO guidelines (11 mg/L). The pH from all sources was found to be within the WHO guideline (6-9) and slightly higher in areas with higher fluoride levels.

Key words: Fluorides, Fluorosis, Water quality

Introduction

Fluoride is naturally occurring in many water sources around the world and its concentrations range from insignificant to 50 ppm (Boehnke and Delumyea, 2000).

In Canada, fluorides of up to 0.3 ppm are introduced in drinking water. Fluoride supplements are advocated for children whose water was not fluoridated. Almost all toothpastes contain fluorides of approximately 0.3 ppm. A zero concentration of fluoride leads to dental caries. Fluoride prevents dental caries in three ways; that is, surface fluorides may kill bacteria making them less able to produce acids, fluoride incorporated into crystals on tooth surface makes the surface resistant to acids and fluorides increase the speed to remineralization (Canadian Pediatrics Society, 2002).

Ingestion of high levels of fluorides can lead to dental fluorosis. Secondary teeth are at the greatest risk of developing fluorosis at the ages of 15 to 24 months (Canadian Pediatrics Society, 2002). It is during the transition and maturation stages in enamel development in which the fluoride ions become incorporated into the enamel structure and the matrix become porous.

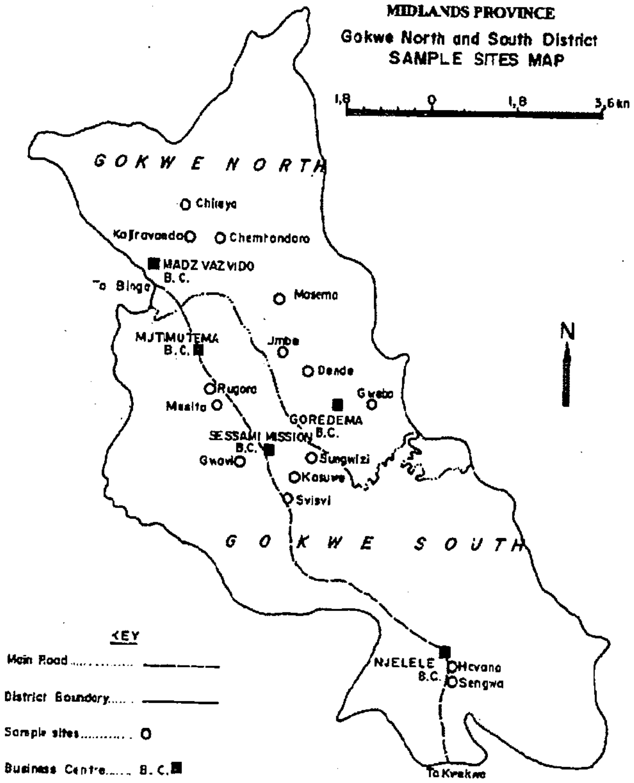
From research carried out in China, it was found out that apart from causing dental and skeletal fluorosis, fluorides are carcinogenic (The Fluoride Action Network, 2000; Radojevic and Bashkin, 1999). An investigation on 157 children aged between 12-13 years born and bred in an area where burning of fluoride rich coal was a common practice, revealed that excessive fluorides intake since childhood would reduce mental work capacity and hair zinc content (The Fluoride Action Network, 2000). According to WHO (1996), South African Water Quality Guidelines, (SAWQG) (1993) and Suckling (1943), recommended that fluoride concentration in drinking water must not be greater than 1.5 ppm.

In Zimbabwe, researchers established that there is a relationship between fluoride ion concentrations in drinking water and the prevalence of dental fluorosis in Gokwe and Chimanimani districts (Tobayiwa et al, 1991; Frencken and Sithole, 1995). In Gokwe, artesian wells waters were found to contain 5 to 10 ppm fluoride ions concentrations. In Chimanimani water from hot springs was found to contain 5 to 6 ppm fluoride ion concentration. In both cases dental fluorosis was found to be very severe. However, specific sources were not identified, so that village based water treatments could be explored. The objective of the study was to determine the water quality of different sources during the dry and wet seasons in Gokwe.

Materials and methods

Water sampling

High-density polyethylene 500 ml sample containers were cleansed with distilled hot water several times with and then without soap, followed by five rinses in deionised water and then finally two rinses with sample water. All glassware used were also cleaned in the same way and then dried in an oven at 180 ± 2 °C for 1 h and then cooled in desiccators before they were used (Radojevic and Bashkin, 1999). Two replicates of forty-four samples were collected per season. Samples were collected from rivers (9), dams (2), artesian wells (7) and boreholes (26). Figure 1 shows the location of the study areas. Samples were refrigerated at 4 °C until analysis.



Laboratory analysis

Fluorides were determined at the Government Analyst Laboratory, Harare, using ion selective electrode method (Tobayiwa et al, 1991). The pH of the water samples was determined by a pH meter that was calibrated using 4, 7 and 10 pH buffers. The probe was rinsed with distilled water between samples. The nitrate content of the samples was determined following the procedure of Radojevic and Bashkin (1999).

Results and Discussion

Fluoride levels

Fluoride concentrations were found to be very high in borehole water samples from HFA as shown in Table 1. The average fluoride levels in wet and dry seasons were 6.70 ± 3.41 and 8.60 ± 3.16 ppm respectively. Both levels were far above the 1.50 ppm recommended by WHO (1996) and SAWQG (1993) in hot dry climates.

Table 1: Boreholes samples (HFA)

Parameter season source	pH		nitrate/ppm		Fluoride/ppm	
	wet	dry	wet	dry	wet	dry
Goredema 1	7.7	8.8	ND	0.1	9.4	12.0
Goredema 2	7.7	6.9	ND	0.6	0.5	0.8
Gwebo	8.5	8.1	ND	0.4	9.2	12.0
Denda	8.4	7.9	ND	4.4	10.6	10.0
Umbe	8.9	8.2	ND	1.3	5.4	8.0
Kajiravanda	8.5	8.1	6.6	0.6	7.2	12.0
Katsvanzva	8.4	6.5	ND	0.6	4.8	14.0
Sungwizi	8.5	7.9	0.7	ND	6.4	6.0
Kamhondoro	8.5	7.8	3.1	0.4	12.8	12.0
Mutora	8.2	7.9	3.7	ND	12.8	6.0
Muuyu	8.5	7.9	ND	ND	8.2	8.0
Time	8.8	8.2	ND	ND	3.2	8.0
Gwave	8.6	8.5	ND	ND	5.2	8.0
Cotco	8.0	8.2	ND	1.3	3.8	6.0
Musita	8.5	7.8	0.2	3.0	4.8	8.0
Chikweru	7.5	7.9	ND	ND	3.2	6.0
Masakadza	8.5	7.0	1.0	3.0	9.0	8.0
Rugora	7.1	7.8	0.5	2.6	4.6	10.0
N	18	18	18	18	18	18
Mean	**8.3**	**7.7**	**0.9**	**1.0**	**6.7**	**8.6**
S	0.49	7.7	1.79	1.38	3.41	3.16
S^2	0.24	7.7	3.22	1.90	11.6	9.96

The boreholes were drilled to a depth of about 30 m. The source of fluoride could be fluoride rich coal. Underground water could have flowed from neighbouring Zhombe-Simuchembu coalfields. Other possible sources of fluoride include fluoride rich rocks such as fluoropatite, $Ca_5F(PO_4)_3$ and fluospar, CaF_2.

Fluoride concentration decreased during the wet season probably due to the dilution effect by rains. It is also possible that as water percolates into the aquifer, it may carry polyvalent metal ions such as *Al*(III), Fe(III) and Se (III) which will complex fluoride ions and remove them from solution (Cotton, 1988). Boreholes in the LFA had fluoride levels that were within the acceptable levels during both the wet and dry seasons, as can be seen from Table 2. Artesian wells in HFA had average fluoride levels of 3.80 ppm, during the dry season, which is above the WHO recommended level. In the wet season the artesian wells had acceptable fluoride levels. (Tables 3 and 4)

Table 2: Boreholes samples (LFA)

Parameter season source	pH		nitrate/ppm		Fluoride/ppm	
	wet	dry	wet	dry	wet	dry
Kasuwe	7.76	7.00	14.90	4.90	0.05	0.20
Njelele	7.58	7.20	0.70	12.60	0.02	0.10
Hovano	7.60	7.09	12.60	16.40	0.12	0.10
Maganza	7.25	7.39	6.60	20.10	0.03	0.10
Nhliziyana	7.44	7.86	ND	0.80	0.20	0.20
Mawire	7.87	7.83	ND	ND	0.07	0.10
Sengwa	7.70	7.05	12.60	9.60	0.06	0.10
Makubaza	7.30	7.58	ND	1.00	0.10	0.10
N	8	8	8	8	8	8
mean	**7.56**	**7.34**	**5.92**	**8.18**	**0.08**	**0.13**
S	0.22	0.34	6.58	7.70	0.06	0.05
S^2	0.04	0.12	43.25	59.27	0.00	0.00

Table 3: Artesian Wells Samples (HFA)

Parameter season source	pH		nitrate/ppm		Fluoride/ppm	
	wet	dry	wet	dry	wet	dry
Umbe	8.33	7.65	ND	15.00	0.80	8.00
Denda	7.80	7.04	12.40	15.60	0.40	2.00
Mutodi	7.63	7.64	107.50	88.10	0.70	1.40
N		3	3	3	3	3
mean	**7.92**	**7.44**	**39.97**	**39.57**	**0.63**	**3.80**
S	0.37	0.35	58.81	42.03	0.21	3.65
S^2	0.13	0.12	3459.0	1766.7	0.04	13.32

Table 4: Artesian Wells samples (LFA)

Parameter season source	pH		nitrate/ppm		Fluoride/ppm	
	wet	dry	wet	dry	wet	dry
Bachi	7.76	7.33	ND	3.90	0.17	0.40
Mhofu	7.56	7.15	2.20	4.70	0.06	0.20
Mbanje	7.47	7.81	ND	54.00	0.04	0.40
Mashizha	6.99	7.32	ND	4.30	0.30	0.10
N	4	4	4	4	4	4
mean	**7.45**	**7.40**	**0.55**	**16.73**	**0.14**	**0.28**
S	0.33	0.28	1.10	24.85	0.12	0.15
S^2	0.11	0.08	1.21	617.63	0.01	0.02

The depth of the artesian wells ranged from 8 to 12 m. During the dry season, fluoride levels ranged from 1.4 to 8.0 ppm. The lower levels of fluorides in artesian wells as compared to boreholes could be due to depth difference. Water in boreholes could have had more exposure to fluoride rich rocks and coal than artesian well waters.

Dam and river water samples from HFA had fluoride levels that were within the acceptable levels except for Umbe river that had 1.80 ppm during the dry season as can be seen from Table 5. In the LFA water from boreholes, artesian wells and dams and rivers had acceptable levels of fluorides ($0.21 \pm 4.0 \times 10^{-5}$ mg/L and $0.11 \pm 4.0 \times 10^{-5}$ mg/L for dry and wet seasons respectively) (see Tables 2, 4 and 6) (WHO, 1996; SAWQG, 1993).

Table 5: Rivers and Dams Samples (HFA)

Parameter season source	pH		nitrate/ppm		Fluoride/ppm	
	wet	dry	wet	dry	wet	dry
Denda river	8.38	7.91	ND	0.40	0.20	0.80
Umbe river	7.97	8.03	2.5	8.50	0.10	1.80
Umbe dam	7.92	7.69	ND	5.40	0.08	0.60
Ume river	7.40	7.68	ND	10.2	0.03	0.80
Gwave river	7.64	7.97	ND	0.90	0.03	0.40
Sasme river	7.10	7.68	ND	0.10	0.09	0.20
Ganye river	7.62	7.70	ND	8.10	0.09	0.20
Chomumvuri	7.43	7.91	ND	8.20	0.10	0.20
Svisvi river	7.46	7.66	2.7	8.40	0.15	0.20
N	9	9	9	9	9	9
mean	**7.66**	**7.80**	**0.58**	**5.58**	**0.10**	**0.58**
S	0.38	0.15	1.15	4.03	0.05	0.52
S^2	0.14	0.02	1.32	16.2	0.00	0.27

Nitrate levels

WHO adopted the concentration of 11.3 ppm NO_3-N as its guideline value for drinking water based on long-term exposure (WHO, 1996). Boreholes in HFA had nitrate levels, which were within the WHO guidelines. (Table 1) Some of the boreholes in LFA had levels which were above the WHO guidelines, as can be seen from Table 2. Most boreholes (23/26) and all rivers and dams had nitrate levels that were within acceptable levels. (Tables 1,2,5 and 6)

Some of the artesian wells had very high levels of nitrates as can be seen from Tables 3 and 4. Mutodi had 107.5 and 88.0 ppm during the wet and dry seasons respectively. High levels of nitrates were found in areas where the soil was sandy. The wells with high nitrate content were situated in gardens

In all cases the pH was found to be within the WHO (1996) and SAWQG, (1993) recommended range of 6 to 9 for drinking water. (Tables 1 6). In most natural waters pH is controlled by the carbon dioxide-bicarbonate equilibrium:

$$CO_2 (g) + H_2O(l) \rightleftharpoons H^+_{(aq)} + HCO^-_3 (aq)$$

An increase in carbon dioxide concentration will lower the pH. The pH is also affected by the fluoride ions because F^- ions are small and highly charged hence they may extract H^+ ions from water leaving OH^- ions in water (The Fluoride Action Network, 2000). Exposure to extreme pH values will result in irritation of eyes, skin and mucous membranes.

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

Table 6: Rivers and dams samples (LFA)

Parameter season source	pH		nitrate/ppm		Fluoride/ppm	
	wet	dry	wet	dry	wet	dry
Kasuwe river	7.19	7.02	ND	ND	0.20	0.20
Mapfumo Dam	7.60	7.87	ND	8.9	0.08	0.60
N	2	2	2	2	2	2
mean	**7.40**	**7.45**	**0**	**4.45**	**0.14**	**0.40**
S	0.29	0.60	0	6.29	0.08	0.28
S^2	0.08	0.36	0	39.6	0.01	0.08

where there is perennial growing of vegetables and continuous use of both organic and inorganic fertilizers. Leaching is high in sandy soils.

Exposure to high levels of nitrates in drinking water may lead to methaemoglobinemia in infants. Nitrates are converted to nitrites, which facilitates oxidation of Fe^{2+} in haemoglobin to Fe^{3+} that does not bind dioxygen (Radojevic and Bashkin, 1999; Huheey, 1993).

$$[Fe(II)\text{-}O\text{-}O\text{-}H]^{1+} + H\ O_2 \xrightarrow{NO_2^-} [Fe(III)HO]^{3+} + H\ O_2$$

Nitrate can also combine with amines in food to produce carcinogenic nitrosamines in the stomach (Solomons, 1996).

$$(CH_3)_2NH + HCl + NO_2^- \longrightarrow (CH_3)_2N\text{-}N\text{=}O$$

However, NO_3^- in the stomach of any one who is not an infant is rapidly reduced to NO that kills pathogenic bacteria.

Correlations

As can be seen from Table 7, there was a significant correlation at α = 0.05 and α = 0.01 level between fluoride levels and pH (p = 0.00). This implies that to a lesser extent the pH (r = 0.28) is dependant on the fluoride concentrations. Samples with higher fluoride levels were slightly more basic.

$$F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-_{(aq)}$$

No significant correlation was established between nitrate and fluorides, and between pH and nitrates, as all p values were above 0.01 and 0.05 significant levels.

The quality of water is not only dependent on pH, NO_3^- and F^-. There are other factors such as total dissolved solids, biological oxygen demand, mineral content and microorganism that affect water quality.

Table 7: Overall Correlations

	pH	**Nitrates**	**Fluorides**
pH	1.000	0.057	0.281
Pearson correlation (2-tailed)		0.717	0.048
N	44	43	44
Nitrate	0.057	1.000	-0.275
Pearson correlation (2-tailed)	0.717	0.075	-
N	43	44	44
Fluoride	0.281	0.275	1.000
Pearson correlation (2-tailed)	0.045	0.075	-
N	44	44	44

Conclusion

River and dam water had acceptable fluoride and nitrate levels, during the two seasons, in both HFA and LFA. The perennial sources of drinking water in HFA are boreholes and artesian wells that had high fluoride levels. Boreholes had higher F^- ion concentrations than artesian wells. In LFA, boreholes and artesian wells had acceptable fluoride levels, suggesting that the probable cause of the difference in fluoride concentrations could be the catchments of these water sources.

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