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ANALYSIS OF NITRATES AND NITRITES IN SUBSOIL AND GROUND WATER SAMPLES IN SWAZILAND

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ABSTRACT. The concentrations of nitrate as nitrogen (NO_3–N) in mg/L and nitrite as nitrogen (NO_2–N) in µg/L were determined in water samples from 60 boreholes, 21 shallow wells and 7 springs located in the four regions of the country. For all the 88 sampling points nitrate levels vary within 0.05 ± 0.00 – 28.44 ± 0.80 mg/L NO_3–N, out of which 10.22% have mg/L NO_3–N ≥ MCL (maximum contaminant level) of 10 mg/L NO_3–N. Shallow wells recorded the highest NO_3–N% ≥ MCL of 20.0% followed by boreholes with NO_3–N % ≥ MCL of 8.33% while for springs, the NO_3–N % ≥ MCL was zero. On the other hand, NO_2–N (µg/L) from all the sampling points vary within (ND/0.30 ± 0.00 – 297.0 ± 0.50) µg/L NO_2–N, which were far below the recommended MCL of 1 mg/L (= 1000 µg/L).

KEY WORDS: Shallow wells, Boreholes, Springs, Nitrate fertilizers, Microbial conversion of nitrate, Methemoglobinemia, Maximum contaminant level (MCL)

INTRODUCTION

Groundwater is the major source of water for drinking and other domestic purposes in rural and suburban areas world-wide [1]. Current statistics reveals that ground water provides water for an average of 14-75% of the population of the developed and developing countries the world over [1-5], and could be as high as 95% of the population in some cases [4]. This observation makes the inclusion of groundwater in the basic background water quality assessment programme an inevitable step.

Subsoil waters (shallow wells and springs) and ground waters (deep waters such as boreholes), are susceptible to contamination by chemicals from the land surface including nitrates and nitrites due to their ability to percolate through the soil into the water bodies. Nitrate has been described as the most ubiquitous contaminant of subsoil and ground waters [3, 6].

Nitrates from uncontrolled, excessive application of nitrate fertilizers remain the highest contributor to elevated levels of nitrates and nitrites in subsoil and ground waters. Other significant artificial sources include animal manure, untreated or inadequately treated sewage, industrial wastes as well as nitrogen from automobile exhausts and industries, which are subsequently converted to nitrates/nitrites and then deposited in land [2, 7-10]. In addition, natural sources of nitrates and nitrites that inadvertently pollute ground waters include breakdown of organic matter through mineralization, hydrolysis and microbial action and nitrogen fixation [5, 11]. Nitrites in natural and drinking water also occur as an intermediate product of the conversion of ammonium ion to nitrate as well as in the nitrification process of ammonia [2, 11].

The high water solubility of both nitrate and nitrite coupled with their good mobility through soil enhance their leaching through soil into ground waters [2, 6, 7]. Due to their low volatility, the species accumulate continually and persist in underground waters for decades, especially the shallow wells which are more susceptible to nitrate/nitrite contamination [2, 5-7].

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Consumption of water with elevated concentrations of nitrate and nitrite by infants (usually less than six months old), and young animals can result in the development of methemoglobinemia – a fatal condition in which the affected baby suffers from oxygen deficiency in the blood due to reduction of O_2 uptake by the lungs, which in extreme cases can result in stupor, coma or even death. Also nitrite can react with secondary amines in human stomach to form the highly carcinogenic N–nitroso compounds [2, 7, 12-17]. Some spontaneous abortions had been linked with drinking of water drawn from shallow wells contaminated with nitrate [3, 5, 14], while oxidation of nitrite to nitrate by dissolved oxygen in water causes a depletion in the O_2 level in water [18].

Consequent on these and a host of other health hazards associated with elevated levels of nitrates and nitrites in drinking water, the U.S. Environmental Protection Agency (USEPA), has fixed maximum contaminant levels (MCL) of 10 mg/L for NO_3–N and 1 mg/L for NO_2–N, while WHO also fixes MCL of 10 mg/L for NO_3–N and 3 mg/L for NO_2–N in drinking water [2, 7, 12, 19-21]. Generally subsoil waters that are unaffected by human activities usually contain less than 3 mg/L NO_3–N [22]. Hence, for the safety of consumers, monitoring of the levels of nitrates and nitrites in ground waters is inevitable. Indeed, it has been recommended that nitrate/nitrite levels in drinking water should be monitored at a minimum interval of three years [23].

Swaziland has a vast number of ground water – consisting of boreholes, shallow wells and springs which are located mainly in the rural and sub-urban areas of the country and they are the major sources of drinking water. The current intensification of agricultural activities nation-wide, with the corresponding increase in the use of nitrate fertilizers coupled with the rapid growth in population and industrial sector as well as a number of other natural and artificial factors capable of enhancing the nitrate/nitrite levels in ground waters underscore the necessity for this type of study as a continuous exercise and at not too long time intervals. Such a study on a comprehensive basis was last carried out between 1986 and 1991 [24]. We report here the levels of NO_3–N mg/L and NO_2–N μg/L in selected subsoil and ground water samples from the four regions of the country. The automated spectrophotometric method has been employed for this analysis, based on its sensitivity and ease of operation [7, 13, 26-32].

EXPERIMENTAL

Instrumentation

The advanced water quality laboratory series HACH-DR 2010 datalogging, microprocessor – controlled spectrophotometer was used for the analysis of both NO_3–N and NO_2–N at programmed wavelengths and reaction times.

Reagents

Sodium nitrite (AR, from Merck Chemicals, RSA) was oven dried at 110 °C for 1 h and then cooled in a desiccator prior to weighing; NitraVer 5 nitrate and NitriVer 3 nitrite reagent powder pillows (both from HACH Chemical Company, U.S.A.); nitrate standards (HACH Chemical Company U.S.A.); bromine water and phenol were used. Distilled, de-ionised water was used for preparation of all the reagent solutions.

Samples were collected from sixty boreholes, twenty one shallow wells and seven springs located in the four regions of the country (see Figure 1 below and Table 1 under "Results and Discussions"). Samples were collected in 250 mL plastic bottles previously scrupulously cleaned with non-ionic detergent, rinsed with tap water and finally with distilled, deionised water. Four samples were collected from each site. The samples were transferred into a cooler box containing ice-chips, transported to the laboratory and stored in the refrigerator at about 4°C prior to analysis. These steps assure retardation of possible chemical or biological reactions in the sample. Refrigerated samples were usually allowed warm up to the room temperature, filtered and analyzed within 48 h after sampling [9, 27, 33, 34].

Analysis

NO_3–N (mg/L). After selecting the programme for the NO_3–N analysis, the wavelength was set at 500 nm and a 25 mL sample cell was filled with the water sample. To compensate for interference by nitrite, bromine water was added drop wise to develop a yellow colour, followed by adding a drop of phenol solution to produce a colourless solution. The contents of a NitraVer 5 nitrate reagent pillow were added. The cell was stoppered, shaken vigorously for 1 min and then allowed to stand for 5 min to complete the reaction. Another 25 mL cell containing the water sample but without the NitraVer 5 reagent, was used to zero the instrument, after which the concentration of the nitrate (NO_3–N in mg/L), in the prepared sample was read. Nitrate in an untreated sample is not detectable by this method.

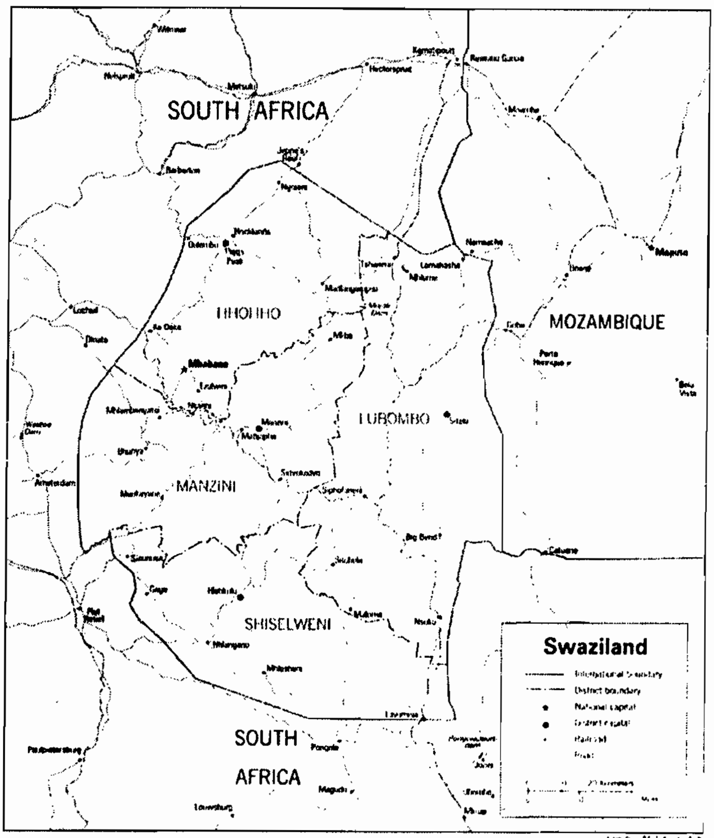

Figure 1. The four sampling regions in the country.

NO_2–N (mg/L). After selecting the programme for NO_2–N measurement and a wavelength of 507 nm, a 10 mL cell was filled with the water sample and the contents of a NitriVer 3 nitrite reagent emptied into it. The cell was then capped, shaken properly for 1 min and allowed to stand for 20 min for the completion of the reaction. Another 10 mL cell filled with the water sample, but without the NitriVer 3 nitrite reagent, was used to zero the instrument. It was then replaced with the cell containing the treated sample and the nitrite concentration read in mg/L NO_2–N.

For both NO_3–N and NO_2–N analysis, four readings were taken and the mean used for each of the sampling points. Also reagent blanks were determined for each set of reagent pillows and each of the results presented in this report was adjusted for blank measurement accordingly.

In order to validate the analytical method used, 25 mL of distilled deionised water samples were spiked with varying amounts of the 500 mg/L NO_3–N standard solution supplied by the HACH Company. The NO_3–N (mg/L) determined following the same procedure as above gave an average recovery of 99.2%. Similarly, using 10 mL distilled water and NO_2–N standards prepared using $NaNO_2$ (AR) and following the procedure for the analysis of NO_2–N, a 96.1% recovery was obtained.

RESULTS AND DISCUSSION

Table 1 shows the geographic regional distribution of the three ground water types sampled for the analysis of NO_3–N/NO_2–N. A total of 88 of them were used as sampling points with and average of 22 per region and a minimum of 20 per region to ensure a good degree of evenness in their sampling spread across the nation (see also Figure 1).

Table 1. Regional spread and type of the groundwater sampled for analysis of NO_3–N (mg/L) and NO_2–N (μg/L).

Region	Type of groundwater*			Total sampled per region
	Boreholes	Deep wells	Springs	
Hhohho (HHH)	12	7	5	24
Lubombo (LUB)	10	10	-	20
Manzini (MZN)	21	2	-	23
Shiselweni (SSN)	17	2	2	21
Total/type	60	21	7	88

*Four replicate samples were taken for analysis from each ground water type.

Tables 2 and 3 depict the mean and peak values of NO_3–N and NO_2–N, respectively, for each type of ground water sampled on geographic regional basis. With the exception of Manzini region, it is observed that in the remaining three regions, the mean values for both NO_3–N (mg/L) and NO_2–N (μg/L) are highest for shallow wells and lowest for springs. These results are in line with the usual observation and prediction that nitrate and nitrite contamination generally decreases with increasing depth of ground water. This is a consequence of the fact that the water table for a shallow well is closer to the land surface and hence more susceptible to potential sources of NO_3–N/NO_2–N contamination such as fertilizers, animal manure and septic systems. On the other hand, deeper ground water aquifers are much less susceptible to contamination from the land surface because such contaminants have to travel longer distances before reaching them [3, 5, 15, 35]. For similar reasons, the calculated mean peak values are highest for shallow wells and lowest for springs for both NO_3–N and NO_2–N. For nitrates, the mean peak values for the NO_3–N levels in both boreholes (42.25 ± 3.71 mg/L), and shallow wells (88.48 ± 3.22

mg/L), exceed the set MCL of 10 mg/L for drinking water. In contrast, the mean peak values for NO_2–N in all the samples are below the set MCL of 1000 μg/L for drinking water.

Table 2. Peak and mean regional levels of NO_3–N in groundwater samples. MCL = 10 mg/L.

Region	Mean (X_p+s_p) and peak values* (mg/L)		
	Boreholes	Shallow Wells	Springs
Hhohho	2.84 ±0.73 (6.2 ± 0.50)	8.78 ± 2.36 (23.93 ± 5.88)	1.34 ± 0.34 (2.76 ± 0.07)
Lubombo	5.16 ± 0.52 (28.44 ± 0.80)	8.64 ± 1.43 (27.21 ± 1.51)	- -
Manzini	3.59 ± 0.17 (13.01 ± 0.09)	0.60 ± 0.47 (1.0 ± 0.66)	- -
Shiselweni	3.59 ± 0.10 (11.27 ± 0.04)	5.30 ± 0.05 (8.52 ± 0.04)	0.46 ± 0.04 (0.47 ± 0.05)

X_p = pooled mean; s_p = pooled standard deviation. *Peak values are in brackets.

Table 3. Peak and mean regional levels of NO_2–N in groundwater samples. MCL = 1 mg/L = 1000 μg/L.

Region	Mean (X_p+s_p) and peak values* (μg/L)		
	Boreholes	Shallow Wells	Springs
Hhohho	8.48 ±0.88 (34.0± 1.5)	11.67± 1.80 (33.0 ± 3.91)	1.0 ± 0.07 (1.0 ± 0.1)
Lubombo	9.57 ± 1.87 (33.0 ± 2.20)	79.67 ± 4.87 (297.0 ± 5.0)	- -
Manzini	7.90 ± 1.60 (47.81 ± 5.5)	4.43 ± 0.43 (4.43± 0.61)	- -
Shiselweni	14.13 ± 0.57 (54.20 ± 0.61)	14.47± 0.77 (19.49± 0.91)	5.49± 0.71 (6.39 ± 0.30)

X_p = pooled mean; s_p = pooled standard deviation. *Peak values are in brackets.

Tables 4 and 5 give the broad picture of some categorized levels of NO_3–N (mg/L) and the number/percentage of groundwater types containing them on regional basis. From this point of view, we are able to quantify the percentage of each type of the ground water that is yet unaffected by human activities, i.e. those with NO_3–N concentrations ≤ 3.0 mg/L and those that have exceeded the EPA/WHO drinking water standard of 10 mg/L. We also consider that NO_3–N concentrations within the range 8.1-9.9 mg/L to be at critical levels of this species as further accumulation due to increased nitrogen inputs can increase their approach to the MCL. The number and percentages of each type of the ground water with NO_3–N concentrations exceeding the MCL regionally and nationally are also shown in Table 4 while those for NO_2–N are shown in Table 6.

First on the regional basis, Lubombo region has the highest percentage (15%) of ground water (all types) with NO_3–N levels ≥ MCL and the lowest percentage (40%) of ground water not contaminated by human activities (Tables 4 and 5). On ranking the regions in an increasing order with regards to the percentage of their ground water with concentrations ≥ MCL, we have:

HHH < MZN < SSN < LUB.

Table 4. Percentages of categorized ranges of NO_3–N concentrations (mg/L) in the groundwater samples on geographic regional basis. (MCL = 10 mg/L).

Region	0.00-3.00[a] (mg/L)		3.1-8.0 (mg/L)		8.1-9.9[b] (mg/L)		≥10.0 (mg/L)	
	No.	%	No.	%	No.	%	No.	%
Hhohho	14	58.3	7	29.2	1	4.2	2	8.3 (2.3)[c] (22.2)[d]
Lubombo	8	40.0	7	35.0	2	10.0	2	15 .0 (3.4)[c] 33.3)[d]
Manzini	16	69.6	5	21.7	0	0	2	8.3 (2.3)[c] (22.2)[d]
Shiselweni	13	61.9	5	23.8	1	4.8	2	9.5 (2.3)[c] (22.2)[d]
Grand total	51	58.0	24	27.3	4	4.5	9	10.2[c] (100.0)[d]

a: NO_3–N (mg/L) ≤ 3.0 indicative of nitrate concentrations in naturally occurring groundwater unaffected by human activities. b: Concentration range considered to be critically approaching the maximum contaminant level (MCL). c: Regional percentage of groundwater type ≥ MCL based on total (all types) sampled nationally. d: Regional percentage of groundwater type ≥ MCL based on the national total groundwater type ≥ MCL.

Table 5. Type, number and percentage of groundwater with nitrate (NO_3–N) concentrations ≤ 3 mg/L on geographic regional basis.

Region	Boreholes		Shallow wells		Springs		Regional total (all types)	
	No.	%	No.	%	No.	%	No.	%
Hhohho	7	58.3	2	28.6	5	100.0	14	58.3
Lubombo	6	60.0	2	20.0	-	-	8	40.0
Manzini	14	6.70	2	100.0	-	-	16	69.6
Shiselweni	10	58.8	1	50.0	2	100	13	61.9
Total per type	37	61.7	7	33.3	7	100	51	58.0

Table 6. Percentages of categorized ranges of NO_2–N concentration (μg/L) in the groundwater samples on geographic regional basis (MCL = 1mg/L =1000 μg/L).

Region	0.0-3.0 (μg/L)		3.1-999.0 (μg/L)	
	No.	%	No.	%
Hhohho	14	58.3	10	41.7
Lubombo	10	50.0	7	50.0
Manzini	11	47.8	12	52.2
Shiselweni	8	38.1	5	61.9
Grand total	43	48.9	45	51.1

This order is in consonant with expectation in view of the nature of the land use and the degree of urbanization of the respective regions [2, 5, 7, 10, 14-16, 35]. Lubombo region contains the sugar belt of the country as well as being in the lowveld where the most intensive agricultural activities are going on. Hence it is likely to receive the largest amount of nitrogen loadings resulting form applied inorganic fertilizers and animal manure (Table 2). These also account for the highest peak values observed [14, 15, 35]. On the other hand, the Hhohho and Manzini regions with the lowest percentages of ground water with NO_3–N concentrations ≥ MCL (10 mg/L), are the most urbanized with the capital (Mbabane) and the largest city in the country (Manzini), located within these regions, respectively. This means that their main sources of nitrogen inputs would be population density such as residential fertilizers, septic systems and urban animal wastes and to a lesser extent nitrogen loading from agricultural sources. On the same account, Manzini region has the highest percentage (69.6%), (Tables 4 and 5) of ground water that are unpolluted through human activities [5, 7, 15, 35].

Considering the nature of the ground water, the percentage (33.3%) of shallow wells uncontaminated by human activities is the lowest (Table 5) while no spring has been thus contaminated, i.e. 100% of the sampled springs fall under this category, and 61.7% of all the sampled boreholes are still unpolluted by human activities which is about twice the percentage for shallow wells in this category. The shallow water tables for the wells and the deep aquifers for the boreholes are the main supporting evidences for these observations. Another factor which could influence NO_3–N levels in this respect, but which is rather localized as per each ground water is the aquifer or water table vulnerability as determined by the soil texture in the immediate vicinity of the particular ground water [15, 35].

Table 6 shows three categorized levels of NO_2–N on geographic regional basis with about 49% of all the sampled ground water having concentrations of this species ≤ 3 μg/L and 0% ≥ MCL of 1mg/L for drinking water [2, 7, 12, 19-21]. The Shiselweni region, another highly agricultural area of the country has 61.9% (the highest) of the ground water sampled from there having NO_2–N concentrations on the high broad range, in support of our earlier reasons. On the other hand Hhohho region which is more significantly urbanized and most of its area being in the highveld has the highest percentage of ground water in lowest range (0-3.0 μg/L) and the lowest percentage of its groundwater containing the high range NO_2–N levels. The fact of this region being in the highveld area of the nation with the hilly and undulating landscape can enhance a fast flow of water through the drains and ditches into the streams below rather than allowing it to percolate to the groundwater. This would result in reduced NO_3–N/NO_2–N contamination of the groundwater even if the nitrogen inputs through agricultural, non-agricultural and population density are significant [2, 11, 14, 15, 35].

The fairly high percentage (52.2%) of groundwater containing the high range levels of NO_2–N in the Manzini region is probably linked to the fact that Manzini city is the largest city in the country and also harbours the largest industrial estate in the country. Thus additional sources of nitrogen inputs here would include atmospheric deposition from airborne nitrogen compounds (from factory and automobile exhausts) and leachates from factory wastes. The latter contribution in particular can result in enhanced levels of NO_2–N because of microbial action leading to production of nitrite as an intermediate product in the conversion of ammonium ion to nitrate and in the nitrification of ammonia in the effluents [2, 5, 11]. Tables 7 and 8 show the percentages of the groundwater type with nitrate and nitrite concentrations equal to or greater than the indicated EPA/WHO drinking water standards on regional basis and the overall concentration ranges of NO_3-N and NO_2-N in each type of groundwater. Tables 6, 7 and 8 reveal that none of the sampled groundwater (all types) contains NO_2–N with concentrations equal to or exceeding the USEPA/WHO MCL of 1 mg/L for drinking water. Indeed the values of NO_2–N concentrations in all the samples are far below the USEPA/WHO MCL, with the highest NO_2–N concentration being 297.0 μg/L – a value that is just about a third of the drinking water MCL of 1 mg/L (Table 8). Of all the groundwater sampled in the Hhohho region, 8.3% contain NO_3–N levels ≥ MCL, all of which are shallow wells, representing 28.6% of the shallow wells from the region, 2.3% of all the sampled groundwater (all types) and 22.2% of the total number of groundwater types with NO_3–N levels ≥ MCL (Tables 4, 7 and 8).

Table 7. Overall percentages of samples equal to or exceeding the MCL on regional basis.MCL for NO_3-N = 10.0 mg/L and MCL for NO_2-N = 1.0 mg/L.

Region	% ≥ MCL							
	NO_3–N				NO_2–N			
	Boreholes	Deep wells	Springs	Regional overall	Boreholes	Deep wells	Springs	Regional overall
Hhohho	0	28.6	0	8.3	0	0	0	0
Lubombo	10.0	20.0	-	15.0	0	0	-	0
Manzini	9.5	0	-	8.7	0	0	0	0
Shiselweni	11.8	0	0	9.5	0	0	0	0

Table 8. Overall ranges and % ≥ MCL for NO_3–N (mg/L) and NO_2–N (μg/L) in the various types of ground and subsoil waters analysed. MCL: NO_3–N = 10.0 mg/L; NO_2–N = 1000 μg/L.

Subsoil/ground water type	Ranges		% ≥ MCL	
	NO_3–N (mg/L)	NO_2–N (μg/L)	NO_3–N	NO_2–N
Boreholes	0.23 ± 0.06-28.44 ± 0.80	ND/0.30 ± 0.30 - 54.20 ± 0.610	8.3	0.0
Shallow wells	0.05 ± 0.00-27.21 ± 1.51	ND/9.44 ± 0.61 - 297.0 ± 0.50	20.0	0.0
Springs	0.45 ± 0.00 - 2.76 ± 0.07	ND/5.48 ± 0.30 - 6.39 ± 0.30	0.0	0.0
Grand overall.	0.05 ± 0.00 - 28.44 ± 0.80	ND/0.30 ± 0.30 - 297.0 ± 0.50	10.22	0.0

In the Lubombo region 15% of all types of groundwater sampled in that region have NO_3–N concentrations ≥ MCL. This is made up 10% of the boreholes and 20% of the shallow wells sampled in that region (Table 7). The 15% is equivalent to 3.4% of all types of sampled groundwater and 33.3% of the total number of groundwater with NO_3–N ≥ MCL (Tables 4, 7 and 8).

In the Manzini region, 8.7% of all the sampled groundwater has NO_3–N levels ≥ MCL all of which are boreholes and represents 9.5% of all the boreholes sampled from the region. On the other hand 9.5% of all the sampled groundwater from the Shiselweni region contains NO_3–N levels ≥ MCL all of which are also boreholes representing 11.8% of all the sampled boreholes from the region. For both Manzini and Shiselweni regions these percentages are each equivalent to 2.3% of the total sampled groundwater nationally (all types) and 22.2% of the national total ≥ MCL (Tables 4 and 7).

On ranking for the number/percentage of groundwater containing nitrates equal to or greater than the MCL of 10 mg/L for drinking water we have:

On the type basis: shallow wells > boreholes > springs.

On regional basis: Lubombo > Shiselweni > Manzini > Hhohho.

The first trend is in conformity with the prediction that nitrate concentrations in groundwater decreases with increasing depth consequent on reasons given earlier in this paper [2, 5, 14, 15, 35]. The regional variation pattern in this respect also conforms to the prediction that the nature and intensity of agricultural practices are the most dominant determinant of the nitrogen inputs in any given land surface and hence the extent of the nitrate levels as well as its contamination of the corresponding underground waters. As earlier reiterated the Lubombo region with its vast sugarcane and maize plantations remains the leading agricultural sector of the nation and this affirms our results as being in agreement with the findings and predictions of other authors.

CONCLUSION

Considering the fact that the nitrite concentrations in all the analyzed groundwater samples fall far below the maximum contaminant level (MCL) of 1 mg/L (1000 µg/L) for drinking water, the groundwater in these regions can thus be regarded as not being seriously contaminated by nitrite. On the other hand 10.2% of all the groundwater analyzed nationally have nitrate concentrations equal to or greater than the USEPA/WHO MCL of 10 mg/L, while 58% still remains uncontaminated by nitrate due to human activities. While these figures might be considered to be somehow encouraging with regard to nitrate contamination of the groundwater nationwide, it is by no means to disregard the need for a continued monitoring of their levels at short and regular intervals nationally. This is particularly important because of the increase in agricultural practices at commercial levels nationwide and much more so for areas such as the Lubombo region where 15% of the groundwater analyzed there have nitrate levels $\geq$ MCL and 10% with concentrations critically approaching the MCL.

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