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RELATIVE LEVELS, FACTORS AND IMPACTS OF NITRATES AND FLOURIDES IN SOME GROUNDWATER BODIES IN THE LUBOMBO AND MANZINI REGIONS OF SWAZILAND

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Abstract: Enhanced nitrates and fluorides are crucial human health hazards in drinking water. Water samples from 24 groundwater systems, made up of 12 from each of the Lubombo and Manzini regions, were analyzed for NO_3-N (mg/L) and F^- (mg/L). Spectroscopic method was used for the analysis of NO_3-N while the Fluoride ion selective electrode was used for the F^- analysis. The relative abundance and other usual parameters employed revealed a greater degree of contamination of the Lubombo groundwater systems by NO_3-N, relative to those of the Manzini region. This is depicted by the % $\bar{X}_P(NO_3 - N) \geq MCL$ being 16.7% and 8.3% for the Lubombo and Manzini regions respectively. On the other hand, the Manzini region groundwater systems were slightly more contaminated with F^- than those of the Lubombo region. Most of the sampling points had NO_3-N (mg/L) with 83.3% and 91.7% of the sampling points having $NO_3\text{-N} \geq F^-$ in the Lubombo and Manzini regions respectively.

Keywords: Nitrate fertilizers, MCL, methemoglobinemia, dental and skeletal fluorosis, NO_3-N and F^- contamination.

1. Introduction: The presence and levels of nitrates in a water body is a strong indicator of its nutrient status and degree of pollution [1-4]. The current sharp rise in domestic, agricultural and industrial activities have resulted in corresponding increase in the degree of groundwater as well as surface water contamination by both nitrates and fluorides worldwide. A significant percentage of the world's population, especially the rural and sub-urban dwellers, depends on groundwater for drinking and other domestic purposes [4-8].

Hazardous health effects of drinking water that contains *NO_3-N* at levels greater than or equal to 10 mg/L, the fixed maximum contaminant level, results in adverse effects including the infant methemoglobinemia (the blue baby syndrome or oxygen starvation), goiter, malformation of infant nervous system (due to material transfer), spontaneous abortion, chromosome change,

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genotoxic effects in infants and cancer [2-5, 7, 9, 10]. The levels of F^- in drinking water determine whether consumption of that water will be beneficial or hazardous to the consumer [3]. A [F^-] of 1.00 mg/L in toothpaste is recommended for prevention of tooth decay. Consumption of water with lower levels of [F^-] can cause tooth decay, [F^-] above the 1.5 mg/L recommended MCL can cause dental fluorosis [11-21]. Long term intake of F^- at levels greater than or equal to 4 mg/L can result in loss of bone marrow while higher level doses of 20-450 mg/L for 10-20 years can cause crippling, skeletal fluorosis, changes in infant tooth structure and even death [3, 19, 20].

NO_3-N is transported into groundwater from both natural and anthropogenic sources. The natural sources include: atmospheric deposition, human and animal waste, soil erosion and fossil fuels while anthropogenic sources include inorganic fertilizers (the chief contributor), industrial discharges, urban and farm runoff [1, 2, 5, 7, 8]. The main sources of the F^- in groundwater bodies are fluorospar (CaF_2) and cryolite (Na_3AlF_6). Factors that influence the levels of both the nitrate nitrogen and fluorides in groundwater bodies include: land use, population density, intensity of industrial and agricultural activities, rainfall pattern, soil water content, soil and rock type of the immediate vicinity of the groundwater (which determine aquifer vulnerability), and topography. In addition, NO_3-N levels are also influenced by the depth of the groundwater system and nitrogen loading of the immediate vicinity of the sampling point [1, 8, 14, 16-18, 22].

2 Methodology

2.1 Sampling and sample preservation

The water samples were collected using pre-washed 1 L polyethylene bottles. These samples were collected from 19 boreholes, 4 springs and 1 shallow well in the Lubombo and Manzini regions of Swaziland. Sampling was carried out in each sampling point at intervals of 4 weeks 5 times. In all the sampling trips, 4 samples were collected from each sampling point. The water samples were kept over ice in a cooler box immediately after sampling then transported to the analytical Chemistry Laboratory. The samples were kept in a chest freezer at 4 ^oC until analysis which was carried out within 24 hours.

2.2 Experimental procedure

2.2.1 *Nitrate nitrogen*

A 100 ppm NO_3-N was prepared using anhydrous KNO_3 (AR). Serial dilution of the stock solution was done to obtain 5, 10, 20, 30 and 40 ppm NO_3-N solutions which were used to calibrate the UV-spectrophotometer. The programme for the analysis of NO_3-N was selected and the wavelength was set at 500 nm. The detailed analytical procedure is as described in our previous work [2, 7] and in the HACH Company Manual [26].

2.2.2 *Fluorides*

A 100 ppm F^- solution was prepared using anhydrous NaF (AR). The stock solution was diluted serially to obtain1.0, 1.5 and 2.0 ppm F^- standards which were used for the calibration of the fluoride ion-selective electrode. For each analysis of standard or sample, 25 ml were transferred into a beaker. Thereafter the electrode was immersed in the solution and the reading was taken after 3 minutes which was enough equilibration time. The electrode was recalibrated prior to each set of measurements.

2.2.3 *Validation*

Four replicate analyses were carried out for each sampling point in each sampling session for both NO_3-N and F^-. Estimated reagent blanks were deducted from the readings before using them in the determination of the mean values of the replicates. NO_3-N reference standard solution from HACH Coy and prepared F^- standards were used following similar experimental procedures as for the samples to validate the methods. Percentage recovery and the Student t-test statistic were also used for the validation.

Results and Discussions

Table 1: Pooled Means and their relative values to X_0* and MCL** for NO_3-N (mg/L) in groundwater samples

Sampling point	Range	$X_P \pm S_P$	X_P / X_0	X_P /MCL
LUBOMBO REGION				
KM	4.25-10.61	6.26±0.74	2.09	0.63
EB	10.48-15.79	12.78±1.90	4.26	1.28
SL	3.84-5.00	4.18±0.67	1.39	0.42
NK	0.11-1.00	0.56±0.57	0.19	0.06
TK	0.27-3.15	1.46±0.85	0.49	0.15
MF	0.13-1.57	0.93±0.50	0.31	0.09
KK	6.27-9.48	7.58±0.32	2.53	0.76
LM	11.44-26.51	17.61±1.34	5.87	1.76
TB	5.11-10.32	7.30±0.82	2.43	0.73
TW	6.07-6.57	6.29±1.12	2.10	0.63
TP	7.79-8.89	8.27±0.36	2.76	0.83
HL	1.46-3.25	2.32±0.55	0.77	0.23
MANZINI REGION				
MT	9.18-12.42	10.70±0.35	3.57	1.07
LO	4.86-11.00	8.10±0.54	2.70	0.81
MH	3.80-5.80	4.93±0.59	1.64	0.49
SG	3.50-5.60	5.00±0.61	1.67	0.05
ML	2.40-5.10	4.02±0.42	1.34	0.40
MA	2.50-4.10	4.00±0.36	1.33	0.40
MO	2.60-4.10	3.72±0.50	1.24	0.37
NG	1.90-3.80	2.70±0.48	0.90	0.27
MC	0.83-2.00	1.56±0.54	0.52	0.16
LU	0.60-2.10	1.48±0.26	0.49	0.15
TS	1.10-1.90	1.55±0.43	0.52	0.16
MK	1.20-1.80	1.42±0.39	0.47	0.14

*X_0 (NO_3-N) = 3.0 mg/L is NO_3-N levels in naturally occurring groundwater (unaffected by human activities)
**MCL = Maximum Contaminant Level (10.00 mg/L for NO_3-N for drinking water)

Sampling points abbreviations:

LUBOMBO REGION	MANZINI REGION
KM - KaMswati	MT - Manzini Town
EB - Emboleni	LO - Logoba
SL - Sihlongwaneni	MH - Mhlaleni
NK - Nkalashane	SG - Sgodvweni
TK - Tsambokhulu	ML - Malkerns
MF - Mafucula	MA - Mahlanya
KK - Kuhlamukeni	MO - Moneni
LM - Lomahasha	NG - Ngwane Park
TB - Timbutini Primary School	MC - Manzini Central School
TW - Timbutini Well	LU - Ludzeludze

TP - Tsambokhulu Primary School TS - Tsekwane Butchery
HL - Hhalane MK - Mankayane

Table 2: Pooled Means and their relative values to X_0* and MCL** for F^- (mg/L) in groundwater samples

Sampling point	Range	$X_P \pm S_P$	X_P / X_0	X_P /MCL
		LUBOMBO REGION		
KM	0.11-0.33	0.35±0.21	0.70	0.23
EB	0.17-0.24	0.18±0.04	0.36	0.12
SL	0.11-1.29	0.36±0.11	0.72	0.24
NK	0.16-2.00	0.61±0.28	1.22	0.41
TK	0.48-1.51	0.88±0.06	1.76	0.59
MF	0.50-1.98	1.62±0.11	3.24	1.08
KK	0.21-0.59	0.37±0.10	0.74	0.25
LM	0.19-0.23	0.22±0.04	0.44	0.15
TB	0.17-2.55	1.29±0.07	2.58	0.86
TW	0.01-0.23	0.13±0.08	0.26	0.09
TP	0.42-1.36	0.94±0.15	1.88	0.63
HL	0.17-0.53	0.38±0.02	0.76	0.25
		MANZINI REGION		
MT	0.12-0.25	0.19±0.11	0.38	0.13
LO	0.16-0.27	0.22±0.04	0.44	0.15
MH	0.11-0.21	0.18±0.03	0.36	0.12
SG	0.10-0.18	0.13±0.02	0.26	0.09
ML	0.08-0.18	0.11±0.02	0.22	0.07
MA	0.10-0.16	0.13±0.03	0.26	0.09
MO	0.07-0.20	0.13±0.05	0.26	0.09
NG	0.08-0.20	0.14±0.05	0.28	0.09
MC	0.10-0.17	0.13±0.03	0.26	0.09
LU	0.06-0.17	0.13±0.03	0.26	0.09
TS	5.00-6.18	5.64±0.53	11.28	3.76
MK	0.06-0.09	0.08±0.04	0.16	0.05

*X_0 = Optimum F^- level for drinking water (0.50 mg/L)
**MCL = Maximum Contaminant Level (1.50 mg/L) for F^- in drinking water

Table 3: Relative abundance of NO_3-N : F^- (mg/L) per sampling point in terms of $X^*_{P(rel)}$ and $N_{MCL(rel)}$

Sampling point	$\bar{X}_P(NO_3-N)$	$\bar{X}_P(F^-)$	$\bar{X}_P(rel)$	$N_{MCL}(rel)$
		LUBOMBO REGION		
KM	6.26±0.74	0.35±0.21	17.89	2.74
EB	12.78±1.90	0.18±0.04	71.00	10.67
SL	4.18±0.67	0.36±0.11	11.61	1.75
NK	0.56±0.57	0.61±0.28	0.92	0.15
TK	1.46±0.85	0.88±0.06	1.66	0.25
MF	0.93±0.50	1.62±0.11	0.57	0.08
KK	7.58±0.32	0.37±0.10	20.49	3.04
LM	17.61±1.34	0.22±0.04	80.04	11.73
TB	7.30±0.82	1.29±0.07	5.66	0.85
TW	6.29±1.12	0.13±0.08	48.38	7.00

TP	8.27±0.36	0.94±0.15	8.80	1.32
HL	2.32±0.55	0.38±0.02	6.11	0.92
		MANZINI REGION		
MT	10.70±0.35	0.19±0.11	56.32	8.23
LO	8.10±0.54	0.22±0.04	36.82	5.40
MH	4.93±0.59	0.18±0.03	27.39	4.08
SG	5.00±0.61	0.13±0.02	38.46	0.55
ML	4.02±0.42	0.11±0.02	36.55	5.71
MA	4.00±0.36	0.13±0.03	30.77	4.44
MO	3.72±0.50	0.13±0.05	28.62	4.11
NG	2.70±0.48	0.14±0.05	19.29	3.00
MC	1.56±0.54	0.13±0.03	12.00	1.78
LU	1.48±0.26	0.13±0.03	11.38	1.67
TS	1.55±0.43	5.64±0.53	0.27	0.04
MK	1.42±0.39	0.08±0.04	17.75	2.80

$$* X_{P(rel)} = \frac{\bar{X}_P(NO_3 - N)}{\bar{X}_p(F^-)} \qquad **N_{MCL(rel)} = \frac{N_{MCL}(NO_3 - N)}{N_{MCL}(F^-)} \qquad N_{MCL} = \frac{\bar{X}_P}{MCL}$$

Table 4: Comparison of some pertinent parameters for groundwater levels of NO_3-N (mg/L) and, F^- (mg/L) in the Lubombo and Manzini regions

PARAMETER	LUBOMBO		MANZINI	
	NO_3-N	F^-	NO_3-N	F^-
Absolute range (mg/L)	0.11 – 26.57	0.10 – 2.55	0.18 – 12.42	0.06 – 6.18
Pooled mean, X_P range (mg/L)	0.56±0.37 – 17.61±1.34	0.13±0.08 – 1.62±0.11	1.42±0.30 – 10.70±0.35	0.08±0.04 – 5.64±0.53
Pooled regional mean (mg/L)	6.30±0.79	0.61±0.17	4.10±0.47	0.65±0.16
% with $\bar{X}_P \geq$MCL	16.7	8.3	8.3	8.3
% with $\bar{X}_P$ = C[1] MCL (NO_3-N)	8.3	-	8.3	-
% with $\bar{X}_P$ = C[1] MCL (F^-)	-	8.3	-	0
% with $\bar{X}_P \geq X_0$ (NO_3-N)	66.7	-	58.3	-
% with $\bar{X}_P \geq X_0$ (F^-)	-	83.3	-	91.7

$\bar{X}_P$ = pooled mean
MCL = Maximum Contaminant Level (10 mg/L (NO_3-N) and 1.5 mg/L (F^-) in drinking water
C^1MCL = concentration considered to be critically close to MCL i.e. $8.0 \leq X_0 < 10$ mg/L NO_3-N and $1.1 \leq X_0 < 1.5$ mg/L for F^-
$X_0(NO_3\text{-}N) = 3.00$ mg/L

$X_0(F^-) = 0.50$ mg/L

Table 5: Relative abundance parameters for NO_3-N (mg/L) and F^- (mg/L) in groundwater systems of the Lubombo and Manzini regions of Swaziland

Parameter		Lubombo Region	Manzini Region
$\bar{X}_P/X_0(NO_3\text{-}N)$	Range %	0.19 – 5.87	0.47 – 3. 57
	≥1.00	66.7	58.3
$\bar{X}_P/MCL(NO_3\text{-}N)$	Range %	0.06 – 1.76	0.05 – 1.07
	≥1.00	16.7	8.30
$\bar{X}_P/X_0(F^-)$	Range %	0.13 – 1.62	0.08 – 5.64
	≥1.00	16.7	8.30
$\bar{X}_P/MCL(F^-)$	Range %	0.09 – 1.08	0.05 – 3.76
	≥1.00	8.30	8.30
$\bar{X}_P$ (rel)	Range %	0.57 – 80.05	0.27 – 56.32
	≥1.00	83.3	91.7
N(MCL)	Range %	0.15 – 11.73	0.04 – 8.23
	≥1.00	58.3	83.3

$\bar{X}_P$, X_0 and MCL – are as previously interpreted in Table 4

$\bar{X}_P$ (rel) and N(MCL) – as earlier interpreted in Table 3

The method validation tests gave a mean recovery of 96.5% for the NO_3-N using the UV spectroscopic technique described earlier on, while a 98.7% recovery was obtained for the fluoride ion-selective electrode method employed for the analysis of F^- in the samples. Additionally, the Student t-test employed for the same data sets showed that there were no significant differences between the true values of the standards of NO_3-N (mg/L) and F^- (mg/L) and those obtained experimentally using the respective methods employed for the analyses of the two water parameters under investigation in this study.

From Tables 1, 2 and 4, it can be seen that both the absolute and pooled mean ranges for the NO_3-N (mg/L) values in the Lubombo region are higher than those for the Manzini region. Similar observations hold in the cases of the calculated pooled regional means for which the value for the Lubombo region (6.30±0.79) mg/L is approximately 1.5 times higher than that for the Manzini region (4.10±0.42) mg/L NO_3-N, as well as for the percentage of the sampled groundwater points having their pooled mean values greater than the MCL (miximum contaminant level) of which the percentage for the Lubombo region is twice as high as that for the Manzini region. The two regions are at par only with respect to the percentage of the sampled points with average NO_3-N (mg/L) values critically approaching the MCL i.e. 8.3% in each region. Similarly, the percentage of groundwater systems with pooled mean NO_3-N (mg/L) values greater than $\bar{X}$ is higher in the Lubombo region than in the Manzini region. This is an indication of stronger anthropogenic contaminant influence on the groundwater systems of the Lubombo region relative to that of the Manzini region. These observations confirm again that the Lubombo region of Swaziland still remains the heart beat in farming activities of the nation, being as it is the chief sugar cane planting belt and the main agricultural and economic domain with the accompanying intensive application of nitrate and other fertilizers. This is corroborated by the fact that nitrogen nitrate fertilizer application has long been identified as the most prominent and most notorious source of groundwater, as well as surface water contaminant by nitrates. (1, 2, 3, 7).

Another important factor that can most possibly account for the relatively high levels of NO_3-N in the groundwater systems in the Lubombo region is the rock types in the region, namely, the Lebombo rhyolites, the sabie river basalts and the rheognimbrites. The first two types are relatively soft, thereby enhancing easy leaching of nitrates into the groundwater table. This phenomenon, in addition to the high solubility of nitrates and their poor affinity for soil further enhance the nitrate levels in most of the groundwater systems in the Lubombo region.

Based on the parameters in Table 4 and some of our previous work [7], the degree of groundwater contamination by nitrate in these regions seems to be worsening. For instance, the percentage of the groundwater yet uncontaminated from anthropogenic sources in the Lubombo region was 40% some 3 years earlier but at the time of the present work stood at 33.3% and for the Manzini region it was 69.5% but has since reduced to 41.7%. a similar trend is followed on considering the % $\bar{X}_P \geq$ MCL factor which for the Lubombo region was 15% but rose to 16.7% while for the Manzini region it increased from 0% to 8.3% within a space of 3 years [7].and, as it has been shown, the number of groundwater systems being contaminated through anthropogenic means are also on the increase in both regions.

The fluoride levels in the sampled groundwater systems in the two regions are generally lower than those of the nitrate from the same sampling points. On comparison of F^- levels at regional bases, the % with $\bar{X}_P$ (F^-) < X_0 for Manzini is greater than that of Lubombo region as shown in Table 4. This depicts likelihood of a greater incidence of tooth decay in the areas of Manzini region where these groundwater bodies are located relative to their counterparts in the Lubombo region.

The generally much lower concentrations of the F^- relative to those of the nitrates in the groundwater samples in the two regions are accountable for by limited fluoride loading sources from the environment especially anthropogenic ones and the relatively stronger affinity of F^- for soil. This causes a slow percolation through soil and some being trapped in the soil, and ultimately fewer ions get leached into the water table of the groundwater [20].

From Tables 1, 2, 3, and 5, the relative abundance of NO_3-N (mg/L) and F^- (mg/L) in the sampled groundwater systems in the two regions are shown in terms of some parameters. These parameters, particularly summarized in Table 5, enable us to see at a glance the actual pollution of the groundwater systems by these species in each sampling point as well as at regional levels. They provide a more vivid and indeed a better quantitative basis for comparison of the degree of groundwater pollution by these species. Employing the $\bar{X}_P/X_0$, and $\bar{X}_P$/MCL relative abundance parameter for instance, help us to deduce how much each point has been contaminated relative to X_0 or MCL. These parameters confirm a greater degree of pollution of the Lubombo region groundwater systems by nitrates as they demonstrate higher peak values and percentage greater than or equal to one relative to those of the Manzini region.

The $\bar{X}_P$/MCL (F^-) parameter demonstrates higher peak values and greater ranges for the Manzini region groundwater systems relative to those of Lubombo, confirming a greater degree of contamination of the former by fluorides. The $\bar{X}_P$(rel) values show a higher relative peak value (80.00) and a much greater range (79.43) for the Lubombo region groundwaters relative to the respective values of 56.32 and 56.05 for the Manzini region to further the higher level of nitrate pollution of the Lubombo region groundwater systems. Considering the issue of correlation between the NO_3-N and F^- (mg/L) levels in the respective sampled points, we have to compare the $\bar{X}_P$(NO_3-N) and $\bar{X}_P$(F^-) values on a point to point basis and see whether or not they correlate in their vulnerability between the peak and minimum values for the two species.

From Table 3 we can observe some good correlation between the values of the NO_3-N and F^- (mg/L) for the Manzini region while there is no such correlation in the Lubombo region, indeed, it is like a negative correlation between these species for the later. The descending plots in each of the two regions show these facts more clearly. In view of these conflicting observations, a further and more comprehensive study has to be carried out to obtain a true picture and clearer conclusion on this.

Conclusion

Absolute parameters such as X_0, MCL, estimated parameters such as $\bar{X}_P$, C^1MCL, pooled mean ranges and evolved relative abundance parameters such as $\bar{X}_P/X_0$, $\bar{X}_P$/MCL and $\bar{X}_P$ (rel) enabled us to come up with some findings. The groundwater systems of the Lubombo region are polluted to a greater extent than those of the Manzini region by NO_3-N while the opposite holds for the case of F^- pollution of the same groundwater systems. The dominant factors that are most likely to be responsible for these observations are the higher degree of agricultural activities (farming) in the Lubombo region and the greater population density coupled with the much greater industrial activities in the Manzini region. The fact that the % $\bar{X}_P(F^-) < X_0$ for Manzini is greater than that of Lubombo implies greater expected increase of tooth decay cases in Manzini in the consumers of such water. Practically, cases of tooth decay has been observed in the Lubombo region probably because the Manzini region is more urbanized compared to the Lubombo, more people depend on untreated water in the rural Lubombo region than in Manzini [29]. However, because the C(MCL) for both regions is the same (8.3%) and low implying that dental and skeletal fluorosis is unlikely in both regions. Correlation between the levels of nitrates and fluorides in the groundwater systems of the two regions are at variance as it is positive in the case of Manzini region while it is non-existent for those in the Lubombo region.

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