Monitoring the Levels of Essential and Trace Metals in Groundwater along Fuoni Area in Zanzibar

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Abstract: Physico-chemical parameters of groundwater resources were studied in Fuoni area allocated at West District of Zanzibar Island. In June 2014, water samples were collected from ten groundwater sources for physico-chemical analysis. The chemical parameters include twenty metals (Al, As, Be, Ca, Cd, Co, Cr (III), Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Tl, V and Zn). Inductively Coupled Plasma Emission Spectroscopy (ICP-OES) determined the dissolved metal concentrations. The levels of total dissolved solid (TDS), turbidity, electrical conductivity (EC), and pH were also determined using Horiba multi-parameter water quality meter. There was no detection for the levels of Al, Be, Cd, Co, and Mn in all water samples. Notably, the physico-chemical parameters suggest that the groundwaters in this area are generally good for domestic use per World Health Organization (WHO) standards. Nevertheless, 40% of the analyzed water samples had elevated levels of calcium as compared to WHO guideline for calcium. Turbidity levels in majority of water samples were beyond the recommended guideline value. Both Sr/Ni ratio and Li/Ni ratio were greater than 1. Furthermore, four heavy metals namely, Cu, Fe, Zn, and Pb were used in a multivariate hazard analysis. The hazard analysis aimed at evaluating a potential human health risks associated with water consumption from the study area. The analysis included, heavy metal evaluation index (HEI), heavy metal pollution index (HPI), degree of metal contamination (C_d), and hazard quotient which yields hazard index (HI). Generally, there was no apparent risk to water consumers from being exposed to studied metals. Nevertheless, knowledge and awareness of the quality of drinking water is crucial, hence, the presence of trace and heavy metals in water sources necessitates the need of regular monitoring of water sources. Therefore, a good and sustainable management of drinking water quality is an inevitable factor in preventing and controlling of the waterborne diseases.

Keywords: Hazard Index, Sr/Ni Ratio, Thallium, Fuoni, Zanzibar

1. Introduction

Fuoni is a newly and ever growing area in west District of Zanzibar Island. Groundwater from wide diameter hand dug wells and bore hole wells is the principal water resources in this area. Groundwater, such as borehole water and well water, and surface water, such as lakes, rivers, and streams are the two principal natural sources of fresh water [15]. Over the last decade, groundwater resource has become the potential source of domestic water supply in worldwide [10].

Intriguingly, various water quality analysis, and public health surveys have shown that groundwater resources are vulnerable to contaminants. These contaminants may include

species such as waterborne pathogens, toxic elements, and other chemicals or biological species [3]. Over the last few years, surface water and groundwater resources are among the most important environmental issues due to heavy metals contamination and human industrial activities [9, 13, 21]. In recent study, groundwater quality, water type, and sources of contaminants have been explored using Piper, Stiff plots and multivariate statistical techniques [2].

Groundwater quality is important in many sectors, such as agriculture, aquaculture, and industries [27]. However, the lack of sufficient clean and safe water along with inadequate

sanitary infrastructures leave millions exposed to high-level of health risks, which can intensify the harshness on their daily life [1]. The United Nation had estimated that 1.7 billion people do not have adequate supply of portable drinking water [7]. Cholera, diarrhea, and other waterborne diseases have been estimated to cause 2.2 million deaths

every year [28].

Some of the heavy metals are essential for growth, development, and health, while others are categorized as toxic species on living organisms [25]. Table-1 summarizes the health impacts and medical implication of some physico-chemical parameters.

Table 1. Water-Quality Criteria, Standards and Health Impacts and Medical Implication of Selected Parameters.

Parameter	Standard SMCL	Health Impacts and or Medical Implication
Fe	300 µg/L	It can promote growth of certain kinds of bacteria that clog pipes and well openings
Pb	15 µg/L	A cumulative poison and toxic in small concentrations. It can cause lethargy, loss of appetite, constipation, anemia, abdominal pain, and gradual paralysis in the muscles
Li	-	Beneficial in concentration range of 250-1,250 µg/L. It may help in strengthen the cell wall and in improving resistance to genetic damage and to disease
Mn	50 µg/L	It causes gray or black stain on enamel, porcelain, and fabrics. It can promote growth of certain kinds of bacteria that clog pipes and wells
Hg	2 µg/L	It is not essential or beneficial role in human or animal nutrition. Some mercury compounds, such as mercuric chloride and alkyl mercury, are very toxic. Potential health effects of exposure to some mercury compounds in water include severe kidney and nervous system disorders
Ni	20 µg/L	It is very toxic to some plants and animals. Toxicity for humans is believed to be very minimal
Se	50 µg/L	It is essential to human and animal nutrition in minute concentrations. However, even a moderate excess may be harmful or potentially toxic if ingested for a long time. Potential human health effects of exposure to elevated selenium concentrations include liver damage
Sr	-	Its importance in human and animal nutrition is not known, but believed to be essential. Its toxicity is believed to be very minimal
Zn	5000 µg/L	It is essential and beneficial in metabolism; its deficiency in young children or animals will retard growth and may decrease general body resistance to disease. Appears to have no ill effects even in fairly large concentrations (20,000-40,000 mg/L), but can impart a metallic taste or milky appearance to water
Turbidity	1&5 NTU	Associations between drinking water turbidity and GI illness have been found in two settings, in people of various ages, diarrheal illness and lab-confirmed cryptosporidiosis

SMCL = Secondary Maximum Contaminant Level

Heavy metal contamination has become a significant problem in several community and agricultural areas over the years due to the application of commercial agrochemicals on agricultural production [23]. However, heavy metals originating from anthropogenic sources have been found in all components of the environment [4, 11, 12]. In recent years, more attention has been devoted to pollutants in the environment due to increase in anthropogenic contribution by heavy metals [8, 14]. Heavy metals can eventually dispersed and accumulated in the soil as well as surface and groundwater and may therefore affect adverse human health effect to living organisms [6, 22, 24]. The International Agency for Research on Cancer (IARC) has categorized Cd and its compounds as group 1 human carcinogen, and classified inorganic Pb compounds as probably human carcinogen (Group 2A) and organic Pb as possible human carcinogen (group 2B) [5]. Therefore, human health risk assessment plays significant role in the process of estimating the nature and probability of adverse health effects in humans associated with the exposure to hazards in contaminated environments [26].

Groundwater signifies an important source of drinking water, however, its quality might be threatened by a factors such as geological variation (such as soil type), water and soil chemistry. There are also other anthropogenical-enhanced factors, which lead to groundwater contaminations. For instances all activities conducted around the drinking water sources, onsite leaky septic tanks, and pit latrines. All these factors influence the transportation, distribution, and fate of the chemicals, and other contaminants in the groundwater aquifers [20].

As water quality is an environmental determinant of health, the knowledge, and awareness of the quality of drinking water remains crucial. The management and sustainability of good drinking water quality is an important factor in prevention and control of the waterborne diseases. Thus, the present study highlights the levels of some physico-chemical parameters of groundwater resources along Fuoni area in Zanzibar Island. The levels of pH, turbidity, electrical conductivity (EC), total dissolved solid (TDS) and hazard indices were also investigated.

2. Materials and Methods

2.1. Sampling

In June 2014, ten water samples were collected from different sites along Fuoni area. The sources of the collected water samples were; open hand dug wells and closed hand dug wells. Samples were collected in pre-cleaned polyethylene bottles. The handling, storage and preparation of the samples were done in accordance with the standard EPA method 2007

2.2. Analytical Procedure

Turbidity, pH, EC and TDS were measured using Horiba multiparameter water quality meter, while an Inductively Coupled Plasma-Optical Emission Spectrometry, ICP-OES (Thermo Scientific iCAP 6000) was used to determine the

levels of metals. Prior to water sampling, all the glass bottles were cleaned, and rinsed thoroughly with the sampled water. All reagents used were of analytical grade. Samples for the analysis of chemical parameters were filtered using disposable Merck 0.45µm filter Millipore. Thus, the analysis yielded the concentrations of metals, which correspond to the dissolved concentrations. The ground water samples were stored at 1- 4°C temperature prior to chemical analysis in the laboratory. Metal analyzed include Al, As, Be, Ca, Cd, Co, Cr (III), Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Se, Sr, Ti, V and Zn.

3. Result

SPSS version 16 was used for the data analysis. The summary of the descriptive statistics of the analyzed parameters in water samples is presented in Table-2.

Table 2. Summary of the Descriptive Statistics of the analyzed parameters in water samples.

Parameter	Range	Minimum conc. (mg/L)	Maximum conc. (mg/L)	Mean	Std. Deviation	WHO/ US EPA guideline
As	0.0005	BDL	0.0005	0.00005	0.000158	0.01 ^a
Ca	132.913	5.787	138.7	71.8317	51.96642	100 ^a
Cr (III)	0.0228	BDL	0.0228	0.01422	0.00798	-
Cu	0.0261	BDL	0.0261	0.005	0.00766	2 ^a
Fe	0.0015	BDL	0.0015	0.00015	0.000474	0.3 ^a
Li	0.0818	0.0123	0.0941	0.04261	0.029475	-
Mg	5.6856	0.2914	5.977	2.86706	1.875713	50 ^a
Na	68.35	4	72.35	24.3087	24.62121	175 ^a
Ni	0.005	BDL	0.005	0.00282	0.001623	0.02 ^b
Pb	0.0014	BDL	0.0014	0.00024	0.000515	0.015 ^a
Sr	0.0254	0.0064	0.0318	0.01669	0.007629	-
Ti	0.0568	0.0159	0.0727	0.04106	0.016209	0.002 ^a
V	0.059	BDL	0.059	0.03614	0.020756	-
Zn	0.1743	BDL	0.1743	0.02848	0.05461	3 ^a
pH	1.95	6.53	8.48	7.389	0.682845	6.5-8.5 ^a
EC	347	121	468	310.9	109.1985	1000 ^a
Turbidity	7.67	0	7.67	1.812	2.785789	<1 ^c &<5 ^d
TDS	223	81	304	209	76.59417	500 ^a

^aAs per WHO guideline, ^bAs per US EPA; ^cIf water was disinfected by chlorine, ^d If water was not disinfected
EC in µS/cm, Turbidity in NTU, all other parameters in mg/L except pH no unit

Notably, in the study area, the levels of Mn, Co, Cd, Be, Ni, Se, and Al were detected of all in water samples.

3.1. Concentration of Zn in Water Samples

The range of zinc in water samples was BDL – 0.1743 mg/L (Table-2; Figure-1). In all the aquifers in the study area, none of the samples analyzed for zinc exceeded the WHO standard (Figure A1). With this regard, consumption of

drinking water from the study area can be a potential source for zinc mineral beneficial in human metabolism. Its deficiency can cause deterioration in the growth of young children or animals, which in turn may increase their general resistances to disease.

However, because the soil is a potential reservoir of all the metals in Earth crust, thus the occurrence and the detected concentrations of the trace metals in water sources is not an anomalous event [17].

Figure 1. Concentration of Zn in water samples.

3.2. Concentration of Mg in Water Samples

The range of magnesium in water samples was 0.2914 – 5.77 mg/L (Table-2; Figure-2). None of the samples analyzed for magnesium exceeded the WHO standard. Thus, consumption of drinking water from the study area can serve as a potential source of magnesium mineral beneficial for human consumptions.

Figure 2. Concentration of Mg in water samples.

3.3. Concentration of Cu and Ni in Water Samples

The ranges of copper and nickel were BDL – 0.0261 mg/L, and BDL – 0.005 mg/L, respectively (Table-2; Figure-3). The values of these parameters in each sampling station were within the WHO and USEPA recommended guideline values.

Remarkably, the ratio of lithium to nickel in all water samples has been found to be greater than a unit (Figure A1). This observation suggests that in the study area, the relative abundance of lithium is higher as compared to nickel. Similar trend of lithium to nickel ratio was revealed in recent study at North region of Zanzibar Island [17].

Figure 3. Concentrations of Cu and Ni in water samples.

3.4. Concentrations of Sr, Li, Tl, As, and Cr III in Water Samples

The ranges of strontium, lithium, thallium, and chromium (III) in the analyzed samples were; Sr: 0.0064 – 0.0318 mg/L;

Li: 0.0213 – 0.0941 mg/L; Tl: 0.0159 – 0.0727 mg/L;

As: BDL - 0.0005 mg/L, and Cr (III): BDL – 0.0228 mg/L (Table-2; Figure-4). The values of thallium for all water samples (100%) in the study area exceeded the WHO recommended guideline, anthropogenic sources could be influential factor for the presence of thallium in water

samples. Moreover, recent study also reveals the occurrence of thallium in Zanzibar water resources [18]. The presence of contaminants in groundwater could be a consequence of anthropogenic activities, such as improper disposal of used electronic devices (e-wastes), tires, and other waste materials. Besides, the application of fertilizers, pesticides, and metal-containing paints can lead to considerable groundwater pollution [17]. Currently, there is no guidelines are available yet for chromium (III), lithium, and strontium.

Figure 4. Concentrations of Sr, Li, Tl and Cr III in water samples.

3.5. Concentrations of Na and Ca in Water Samples

The ranges of sodium and calcium in the analyzed samples were 4 – 72.35 mg/L and 5.787 – 138.7 respectively (Table-2; Figure-5). None of the analyzed sample had sodium and calcium concentration beyond the WHO guideline. The consumption of water from the study can serve considerable amount of these minerals required human daily metabolism.

Figure 5. Concentrations of Na and Ca in water samples.

3.6. TDS, EC, Turbidity, and pH in Water Samples

The ranges of TDS, EC, turbidity, and pH were; 81-304 mg/L, 121-468 $\mu\text{S}/\text{cm}$, 0 – 7.67 NTU, and 6.53 – 8.48 respectively. Basically, the values of these parameters were within the WHO recommended guideline value (Table-2). The EC correlates positively with TDS ($r^2 = 0.884$), and these two parameters exhibit regular patterns within the sampling sites (Figure-6). Contrarily to the pattern shown between TDS and EC, the pH and turbidity exhibit an irregular pattern, which signifies poor correlation between these two parameters (Figure-7).

Figure 6. Levels of EC and TDS in water sources.

Figure 7. Levels of pH and turbidity in water sources.

3.7. Hazard Indices (HEI and HI)

The ranges of these two parameters were; 0.00114 – 0.0967313, and 0.001193 – 0.058102, respectively. At varying degree, all water samples have shown some levels of HEI and HI (Figure-8, Figure A2).

Figure 8. Metal Hazard indices (HEI and HI) in water sources.

3.8. HPI, HEI, and C_d Levels in Water Samples

Four metals namely; Cu, Fe, Zn, and Pb were used to depict the level HPI, HEI and C_d . The values of HPI and C_d for each water samples have been found to be less than zero. Negative values for HPI and C_d were also reported in recent study conducted in groundwater sources at Urban

environment in Zanzibar Island [19]. The values of HEI were in the range of 0.00114 – 0.096713 (Figure A2). This observation can be taken as indication of low level of metallic pollution in the study area. Remarkably, the correlation between C_d and HEI was found to be very strong with Pearson coefficient of 1 (Figure-9).

Figure 9. HEI- Cd Correlation in water sources.

3.9. Chronic Daily Intake of Cu, Fe, Zn, and Pb

The chronic daily intake was measured separately using copper, iron, zinc, and lead. The trend for the daily intake of these metals was: ADD:Zn > ADD:Cu > ADD: Pb > ADD: Fe (Figure A2). Remarkably, strong correlation ($r^2 = 0.896$) was shown between the ADD of copper and zinc (Figure-10).

Figure 10. ADD: Cu-Zn Correlation in water sources.

3.10. Correlation Between the Analyzed Parameters in the Water Sources

While strong positive correlations existed for some of the analyzed parameters, some negative correlations were also observed. As an example, thallium has shown strong positive correlations with magnesium and sodium. Thallium relationship with magnesium and sodium were found to have

Pearson correlation values of 0.974 and 0.833 respectively (Table-3). The correlation between same parameters is not necessarily constant, and it can differ remarkably from one study area to another. In the analytical chemistry perspective, the correlation matrix is a fundamental and pervasive concept, and it does not necessarily mean the presence of causality among the analyzed parameters [19].

Table 3. Correlation matrix for the selected physico-chemical parameters.

Parameters	Ca	Cr III	Cu	Li	Mg	Na	Ni	Sr	Tl	Zn
Ca	1									
Cr III	0.227	1								
Cu	0.36	0.14	1							
Li	0.235	-0.815	0.022	1						
Mg	-0.26	0.564	-0.047	-0.785	1					
Na	-0.363	0.085	-0.334	-0.352	0.805	1				
Ni	-0.002	0.602	-0.018	-0.632	0.758	0.668	1			
Sr	0.268	0.302	-0.224	-0.259	0.477	0.595	0.801	1		
Tl	-0.226	0.515	-0.085	-0.759	0.974	0.833	0.758	0.538	1	
Zn	0.123	0.164	0.946	-0.139	0.044	-0.267	0.049	-0.267	0.022	1

4. Conclusion

Notably, the physico-chemical parameters in the present study suggest that the groundwaters in the study area are generally good for domestic use per World Health Organization (WHO) standards. Essential and trace metals

may occur in environments (water, air and soil) due to natural processes and various anthropogenic activities. Since some of heavy metals have been classified as probable and possible human carcinogens. It is necessary to perform regular monitoring programs of these metals and complemented by human risk assessment if possible.

Appendix

Sample sites	As	Ca	Cr	Cu	Fe	Li	Mg	Na	Ni	Pb	Sr	Tl	V	Zn	Sr/Ni Ratio	Li/Ni Ratio
1	BDL	31.56	0.0146	0.0005	BDL	0.0314	5.381	67.38	0.005	BDL	0.0215	0.0591	0.0337	0.0041	4.3	6.3
2	0.0005	16.17	0.0151	BDL	0.0015	0.0123	2.873	16.1	0.0031	BDL	0.0168	0.0406	0.0424	0.0137	5.4	4.0
3	BDL	112.9	0.0183	0.0022	BDL	0.0462	1.493	4	0.0016	0.0014	0.0088	0.0327	0.0396	0.0059	5.5	28.9
4	BDL	49.19	0.0157	0.001	BDL	0.0194	5.977	72.35	0.0042	BDL	0.0241	0.0727	0.0414	0.0007	5.7	4.6
5	BDL	5.787	BDL	0.0019	BDL	0.0941	0.2914	11.04	BDL	0.001	0.0153	0.0159	BDL	BDL	N/A	N/A
6	BDL	106.7	0.0154	0.0261	BDL	0.0436	2.908	8.341	0.0028	BDL	0.0105	0.04	0.0371	0.1743	3.8	15.6
7	BDL	19.31	0.0188	0.0049	BDL	0.0155	3.393	21.2	0.0033	BDL	0.0178	0.0475	0.0517	0.0644	5.4	4.7
8	BDL	111	0.0228	0.0053	BDL	0.0228	3.647	8.966	0.002	BDL	0.0139	0.0417	0.0565	0.01	7.0	11.4
9	BDL	138.7	0.0215	0.0051	BDL	0.0492	2.271	20.44	0.0049	BDL	0.0318	0.0355	0.059	0.0086	6.5	10
10	BDL	127	BDL	0.003	BDL	0.0916	0.4362	13.27	0.0013	BDL	0.0064	0.0249	BDL	0.0031	4.9	70.5

Figure A1. Detected levels of analyzed parameters in water sources.

Cd	HPI	HEI	HI	CDI:Cu	CDI:Fe	CDI:Zn	CDI:Pb
-3.99868	-1.04678	0.00132	0.001193	1.57E-05	0	0.000129	0
-3.98976	-1.04584	0.01024	0.001435	0	4.71E-05	0.000431	0
-3.90329	-1.04095	0.096713	0.016548	6.91E-05	0	0.000185	0.000044
-3.99886	-1.04749	0.00114	0.0016	3.14E-05	0	0.000022	0
-3.93143	-1.04288	0.068567	0.01188	5.97E-05	0	0	3.14E-05
-3.93904	-1.08331	0.06096	0.058102	0.00082	0	0.005478	0
-3.98222	-1.05307	0.01778	0.014227	0.000154	0	0.002024	0
-3.9927	-1.05365	0.0073	0.009138	0.000167	0	0.000314	0
-3.99318	-1.05336	0.00682	0.008686	0.00016	0	0.00027	0
-3.99638	-1.05035	0.00362	0.004904	9.43E-05	0	9.74E-05	0

Figure A2. Estimates of Hazards Indices and Chronic daily Intake of Zn, Fe, Cu, and Pb.

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