

Hydrogeochemistry and Health Risks Assessment of Some Groundwaters Suitability for Drinking Within the Urban Region of Unguja Island, Zanzibar

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Abstract: Majority of the Island inhabitants depends on groundwaters for drinking therefore the hydrogeochemistry and health risks assessment with respect to WHO standards is absolutely essential for protection policy formulation. The groundwater samples for analyses were collected from selected four wells within each (Chukwani-Mbweni, DarajaMbovu - Amani and Mwanakwerekwe) suburb during the moderate rainy season of January 2020. The selection was based on their strategic positions taking into consideration relevant geographical and environmental factors commensurable with this study. Various contaminants and physiochemical parameters were determined using Atomic Absorption spectroscopy, GC/MS, Temp/pH/TDS/EC meter and DR/3900 spectrophotometer. Chemical Oxygen Demand values were also determined. Microbial contamination was determined using the MPN technique. The results show that these groundwaters are slightly alkaline, microbially contaminated, have high C.O.D. values ranging from 188.5 to 305.7 mg/L indicating the existence of some organic based endocrine disruptive elements, and disparities in water quality parameters with respect to the recommended WHO standards thus ascertaining possible public health risks. The research recommends the need for continuous monitoring, assessment and treatment of these raw groundwaters for drinking at the point of collection rather relying on the old conventional boiling method or drinking as it is.

Keywords: Unguja, Hydrogeochemistry, Ground Waters, Quality Parameters, Endocrine Disruptive Chemicals, Health Risks

1. Introduction

Unguja Island of Zanzibar has a current estimated population of 1.8 million with approximately 22% having access to clean water supplied by Zanzibar Water Authority (ZAWA). This surplus is not sufficient and reliable since at times it is supplied twice a week [38] despite the improvement on palatable groundwater supplies initiated by the help of African Development Bank [1]. Majority rely on drinking either boiled or un-boiled raw groundwater since they cannot afford buying continuously treated bottled water [81, 10]. Groundwater is regarded as a reliable and resilient

water resource for most rural and urban areas of Island of Unguja due to its distributed, subsurface storage and perennial availability as was once reported by [30, 28]. This Island is surrounded by sea with no fresh water body, thus ground water reserve in Unguja Island is only nourished by seasonal rainfall [8]. Therefore, it is also paramount to have a clear understanding of hydrologic system since it forms the gateway for providing information for the groundwater resource management [55, 83] and source for the natural constituents formulating these groundwaters.

Stratigraphically, the Island is shaped by thick sedimentary rocks with a predominating north-south fault direction and

characterized by Karstic formation, sinkholes and caverns suggesting periods of higher sea level, marine erosion with wave cut cliffs and platforms, reworked marine and fluvial sediments plus tilting rocking with a raised sea cliffs and submerged coastal reefs [80]. Consequently, the Island surface has only quaternary and tertiary (Miocene) sediments which are mainly sand, cemented sandstone with several forms of limestone weathered coral rock while these thin quaternary deposits covers most of the Miocene soils [68]. The sedimentary formations, in particularly the sand-clay dominated aquifers, have high primary porosity and permeability [33, 22]. This facilitates rapid infiltration and rise of water table after heavy rainfall particularly in the areas where underlying formations are of clayey type [69]. Therefore, this Island poses its delineated ground water resources in terms of lens which float above deeper saline aquifer [29, 39]. The drainage is mainly westerly but also predominantly subsurface except in areas with heavy sticky clay formation.

Lithologically, groundwaters are hosted within either basement (old, crystalline rocks of metamorphic and /or intrusive origin) or sedimentary terrains and the water movements is usually controlled by secondary porosity resulting from chemical weathering, faulting and fracturing [50, 83, 90] consequently these groundwaters have varying degrees in color and taste though contaminants in groundwater are usually colourless and odourless [73]. These waters are pumped from an aquifer to earth's surface either via a private well or a city water system for use. Excessive groundwater withdrawals lead to water shortage, and decline in the water quality due to saltwater intrusion [37].

Among the marine rocks, metals do exist either in salts of carbonates, chlorides or as hydroxides or in ionic forms depending on the extent of its complexation and oxidation state. Thus, groundwater constituents are the product of natural mechanistic reactions within the geological environment inside an aquifer and are regulated by residence time, flow path, rock type and level of rock-water interaction in addition to evaporation-precipitation [11, 58, 21]. Therefore, most of the inorganic contaminants in groundwater are of geogenic origin as a result of dissolution of the natural mineral deposits within the Earth's crust [9, 60, 74, 32]. Their concentrations vary from region to region depending on many factors such as the above-mentioned geological structures, soil, water acidity and particulate matter concentration [73, 12, 57]. Consequently, these affects the uniformity of water quality parameters. There are no mining activities on the Island therefore the low pH associated with acid mine drainage (AMD) which contributes to the solubility of potential toxic metals eventually entering into the groundwaters basin is absent. Therefore, the knowledge of hydrogeochemistry for groundwater is one of the important concepts in assessing the quality of water in Unguja Island.

Apart from the natural geogenic contaminants, potential anthropogenic source of groundwater contamination is domestic sewage especially onsite sanitation systems like pit

latrines, cesspits and soak away pits, poor sewage disposal system [43, 64]. The landfills leachates and septic systems, haphazard disposal from agricultural chemicals (e.g. fertilizers, pesticides, etc.), nanoparticles, hydrocarbons, microplastics, underground pipes, road salts, industrial and household cleaning products creates seepage to ground waters [31, 26]. These contribute to groundwater contamination thus posing threat to human health, ecological services, and sustainable socioeconomic development [47, 48]. These organic and inorganic contaminants are common theme reported in groundwater studies and acts as one of the main sources for lethal endocrine disruptive chemicals (EDC). These EDC are associated with serious health risk such as cancer, sexual hormone imbalances, stomach health issues, brain malfunction, kidney failure, liver cirrhosis [53, 45, 40, 18] consequently they weaken human body immune system [41]. Studies too have shown that physical-chemical components of drinking water have an ability to cause adverse health effects after prolonged periods of exposure and accumulation in our body organs, especially chemicals that have toxic properties and are carcinogenic [52].

Urbanization, agricultural practices, industrial activities, geological disturbances, and climate change all pose significant threats to groundwater quality. Poor sanitation is linked to microbial contaminants which are responsible to transmission of diseases such as cholera, diarrhea, hepatitis A, typhoid and polio. Despite waste waters do get filtered when passing through the soil but microbial contaminants, particularly viruses, do not easily get trapped therefore ground waters needs to be disinfected when used for mass consumption and requires periodical microbial checking.

Despite the use of ground water for drinking may assist in increasing the level of mineral nutrients uptake in the local population, however, it must be also augmented by a nutritious food supply in order to satisfy normal dietary requirements [20]. In 2010, the UN General Assembly explicitly recommended sufficient, safe, acceptable, physically accessible and affordable water for personal and domestic use which must be sustained without causing unacceptable environmental, health, economic or social consequences. Therefore, these raw groundwaters requires regular hydrogeochemistry assessment, protection, and some treatment and purification before they are used for drinking and other domestic purposes [60, 12]. The natural purification processes for contaminated groundwater can take decades or even hundreds of years, even if the source of contamination is cut off [76, 69] because it moves slowly and isn't exposed to the natural cleansing benefits of air, sunlight and micro-organism [57]. Once contaminated, remediation is challenging and costly, because groundwater is located in subsurface geological strata, (the wells aren't too deep ranging from 8 to 12 meters in these Unguja regions) and residence times are long [84, 83, 73].

Therefore, the objectives of this research includes hydrogeochemically assessing groundwater from selected suburbs against the WHO drinking water standards, to determine the contaminants (quantitatively and

qualitatively), microbial contamination levels, possible health risks and suitable recommendations. The suburbs Chukwani/Mbweni, Daraja Mbovu - Amani and Mwanakwerekwe zones were chosen considering their environmental, geographical (high population, topography, economic, social, poor drainage, perennial waste water reserves, etc.) factors and their strategic positions according groundwater zonation on hydrogeological map of Unguja [29] within the urban center. The groundwater wells chosen are well centralized and point water collections by the majority surrounding communities.

2. Materials and Methods

2.1. The Instruments Used

Glass-ware used for titrimetric analysis, electronic weighing balance, Temp/pH/TDS/EC meter model MI1399 (cost effective, easy to use and water resistant), Hach DR/3900 Spectrophotometer (multicomponent anion analyzer, easy to operate, robust and fast), Atomic absorption spectroscopy (AAS) is preferred for trace heavy metal ions because of its low cost and short analysis time [85] and Gas chromatograph-Mass spectroscopy (GC-MS) used for identification of hydrocarbon derivatives in the samples, Turbidity meter (Hach 2100HQ, USA). Incubator, test tubes, sterilized plastic bottles, petri-dishes and oven used for microbial assay.

2.2. The Reagents Used

The analytical grade reagents includes MacConkey Agar (CM0007), SPADN, APHA, Sodium chloride, Potassium dichromate ($K_2Cr_2O_7$), Ferrous ammonium sulphate, Ammonium chloride, Sulphuric acid, etc; Spectroscopic grade reagents e.g. Alcohol, Hexane, Acetonitrile, De-ionized water, etc.; Standard EDTA titrant (0.01 M), Eriochrome black T indicator, Ferroin indicator, Deionized water, Distilled water ACS grade anions standards and Ammonia buffer solution; HPLC grade reagents include Distilled water, Dichloromethane and Anhydrous Sodium sulfate. Manufacturers are Sigma-Aldrich (USA) and Brüggemann GmbH & Co. KG.

3. Methods Description

3.1. Groundwater Sampling

The raw groundwater samples were taken from three (3) regions within Unguja Island which are D/Mbovu- Amani, M/Kwerekwe and C/Mbweni Zones. Samplings were done in the month of January when the region is experiencing moderate rainfall and humid conditions. From each strategically selected well within each zone, three liters of groundwater were taken into sterilized plastic bottles for further analysis. They were transported in a cooler box.

3.2. Water Preservation

Sample plastic containers were sterilized according to the

laboratory standard sterilization procedures. The sterilized sample bottles were then rinsed three times with the sampled raw ground water before transferring the unfiltered groundwater into the well labeled sterilized 1-liter sample bottles. The unfiltered groundwater samples were preserved at 4°C climatic conditions and in sterilized chamber prior to analysis.

3.3. Physical Parameters Determinations

The pH, temperature, total dissolved solid (TDS), and electrical conductivity were determined in situ by the portable Temp/pH/TDS/EC multiparameter model MI1399 (cost effective, easy to use and water resistant) according to the manufacturer's instruction. The pH meter was calibrated against pH buffer of 7, 9 and 12. Each reading was taken after 2 minutes taking the precautionary measures after every measurement. In case of turbidity, approximately 25 ml of the sample taken then agitated until all air bubbles disappeared. The quantity was transferred into the sample cell and the turbidity was measured in nephelometric turbidity units (NTU) using turbidity meter (Hach 2100HQ, USA).

3.4. Anions Determination

The anions were qualitatively tested using the silver nitrate test to observe the precipitate and anionic constituents confirmed using the Hach DR/3900 split-beam Spectrophotometer (320 – 1100 nm) programmed with calibrations for water management test requirements and to counter interferences caused by other chemical species. The method for analysis used was based on standard procedures established by APHA 1998 [7] with each anion having its characteristic wavelength of absorption.

3.5. Cations Determination

Samples were digested and analyzed with Atomic Absorption Spectroscopy (Varian Model: AA240) using standard methods established by APHA [7] for metals determination. The digestion procedure was done by carefully adding 5ml of concentrated nitric acid (anal grad) into 50 ml of water sample on a hot plate for about 30 min to concentrate the mixture to about 15 ml. Approximately 1 ml of the concentrated nitric acid was added periodically to the mixture during the heating processes in the fuming chamber until a clear solution was obtained, cooled, then transferred into 25 ml standard flask and made to the mark using de-ionized water. Blank samples were prepared using the same procedure for background corrections.

3.6. Most Probable Number (MPN) Determination for Coliforms

The most probable number (MPN) analysis is a statistical method based on the random dispersion of microorganisms per volume in a given sample using the multiple tube technique, including the presumptive and confirmatory tests according to established standards (Duksbrough, 2000). In this method, measured volumes of water were added to a

series of tubes containing a liquid indicator growth medium. The media receiving one or more indicator bacteria showed growth and a characteristic colour change. The colour change was absent in those receiving only an inoculum of water without indicator bacteria. From the number and distribution of positive and negative reactions, the MPN of indicator organisms in the sample was estimated with reference to statistical tables. For the confirmatory tests, tubes from the presumptive test were re-incubated for an additional 24 hours at 37°C, then inoculated onto Eosin methylene blue agar plates using the streaking method and finally the plates were incubated in an inverted position at 37°C for 24 hours.

3.7. Determination for Organic Species Using GC-MS Spectrometry

GCMS-QP2010 Ultra Shimadzu was used. The MS is merchandised with firmware advanced scanning speed protocol (ASSP) that optimizes the ion transmission hardware parameters with a highly efficient data collection algorithm, acquisition speed up to 20000 μ /sec and 100HZ, very sensitive. The electron ionization source was kept at the 300°C. Chromatographic separation was performed using DIOXIN2 column (40m length, internal diameter 180 μ m and phase thickness 0.18 μ m with a helium flow of 1 ml/min; The column temperature was programmed starting at 40°C - hold for 5min- ramp at 10°C /min up to 250°C then ramp at 6°C upto 330°C -hold % min; transfer line temperature-330°C. 2 μ L of sample were introduced into the injector heated at 270°C in splitless mode; after 75 s, the injector was purged with a flow of helium at 20mL/min. The results were automatically found and quantified using target analyte basing on accurate masses of the molecular ions and certain characteristic fragmented ions as one of the criteria for finding and matching the analytes.

Sample Preparation for the GC-MS machine:

The raw groundwaters from various well in each region were mixed to give a zonal sample and as a result we had three main zonal samples to run. 1 ml of groundwater sample was placed in a 5-mL vial, added 1 ml of dichloromethane and shaken for 1 minute. Calculated amount of internal standards (2 – 100ng) was added to the organic phase using a syringe, then sodium sulphate approximately 1.5 g was introduced in portions periodically. After binding of aqueous phase with sodium sulphate, 2 μ L of the extract was injected into GC in splitless mode.

3.8. Determination for Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) this is used to determine the quality of pollution in water. The higher chemical oxygen demand indicates the higher organic pollution in the sample water.

20 ml of groundwater sample was introduced in a 250 ml round bottom flask added 10 ml of freshly prepared 0.25 N $K_2Cr_2O_7$, a pinch of Ag_2SO_4 and $HgSO_4$ then 20 ml of dil H_2SO_4 and finally refluxed for 2.5 hours. The refluxed mixture was then cooled, transferred to a 500 ml conical flask, and diluted to approximately 300 ml by distilled water, then added 3 drops of ferroin indicator and titrated against freshly prepared 0.25 N Mohr's salt till the endpoint of wine-red color achieved. Let the titre value be X ml.

Blank titration was performed using distilled water in place of sample solution and refluxed for the same time then titrated against the 0.25 N Mohr's salt. Let the titre value be Y ml.

Calculations:

$$C. O. D \text{ in mg/litre} = \frac{(Y - X) \times N \text{ of Mohr's salt} \times 1000 \times 8}{\text{Volume of ground water sample}}$$

3.9. Determination of Hardness

50 ml of the groundwater sample was taken into a conical flask, added 1 ml of buffer solution then 5% Na_2S solution. To the mixture was added approximately 150 mg of Eriochrome black T-NaCl mixture and swirled till the sample solution turned wine red. The content was then titrated with EDTA solution until blue coloration is obtained signifying the end point.

Calculation:

$$\text{Hardness, mg of } CaCO_3/\text{liter} = \frac{\text{ml of 0.01 M EDTA used} \times 1000}{\text{Volume of ground water sample}}$$

$$1000 \text{ cc } 1M \text{ EDTA} \equiv 1000g \text{ } CaCO_3$$

$$1ml \text{ 0.01 M EDTA} \equiv 1 \text{ mg of } CaCO_3$$

3.10. Data Analysis

Data obtained were subjected to statistical analysis and reported on the basis of mean deviation.

4. Results

The concentrations for cation parameter using the Atomic Absorption spectrophotometer are shown in table 1 below in comparable with the W.H.O. guideline values for drinking water.

Table 1. Cations Concentrations.

Parameter	C/Mbweni Zone mg/L	D/Mbovu-Amani Zone mg/L	M/Kwerekwe Zone mg/L	W.H.O. Limit values mg/L
Cd	0.01 \pm 0.02	0.01 \pm 0.03	0.02 \pm 0.01	0.003
Mg	140.1 \pm 0.25	72.2 \pm 0.05	138.3 \pm 0.02	150.0
Mn	0.15 \pm 0.01	0.19 \pm 0.01	0.16 \pm 0.01	0.1
Na	245.5 \pm 0.00	156.26 \pm 0.04	210.3 \pm 0.02	200
Pb	-	0.24 \pm 0.00	-	0.01
Zn	-	-	-	3.0
Fe	0.07 \pm 0.01	0.09 \pm 0.02	0.02 \pm 0.00	0.03
Cu	0.022 \pm 0.00	0.085 \pm 0.01	0.051 \pm 0.00	2.0
K	43.83 \pm 0.01	11.53 \pm 0.02	34.99 \pm 0.02	20

Parameter	C/Mbweni Zone mg/L	D/Mbovu-Amani Zone mg/L	M/Kwerekwe Zone mg/L	W.H.O. Limit values mg/L
Ca	223.67 ± 0.02	251.39 ± 0.04	333.12 ± 0.01	200
Al	0.21 ± 0.01	0.88 ± 0.01	0.92 ± 0.01	0.2
Cr	0.01 ± 0.00	0.02 ± 0.00	0.01 ± 0.01	0.05
Se	0.02 ± 0.01	0.01 ± 0.02	0.01 ± 0.00	0.01
As	0.02 ± 0.00	0.05 ± 0.01	0.03 ± 0.01	0.05

The anions were qualitatively tested using the silver nitrate test and precipitates were obtained. The results for anionic constituents with their concentrations confirmed using the Hach DR/3900 split-beam Spectrophotometer (320 – 1100 nm) are shown in table 2 below.

Table 2. Anions Concentrations.

Parameter	C/Mbweni Zone mg/L	D/Mbovu –Amani mg/L	M/Kwerekwe mg/L	W.H.O limit values (mg/L)
Flourides	1.65 ± 0.01	1.55 ± 0.03	1.24 ± 0.01	1.5
Sulfates	415 ± 0.04	85.5 ± 0.01	158 ± 0.02	400
Sulphides	0.01 ± 0.00	0.02 ± 0.01	-	0.05
Nitrates	52.67 ± 0.04	1.15 ± 0.01	6.21 ± 0.01	10
Phosphates	3.44 ± 0.03	0.02 ± 0.00	1.02 ± 0.01	0.5
Chlorides	260.2 ± 0.02	158 ± 0.02	251 ± 0.04	250
Carbonates	253 ± 0.02	58 ± 0.04	288 ± 0.02	300
Bicarbonates	200.2 ± 0.01	62 ± 0.02	310 ± 0.01	300

Table 3. Physical parameters and C.O.D results.

Parameters	C/Mbweni Zone	D/Mbovu- Amani Zone	M/Kwerekwe Zone	W.H.O Guideline value
pH	8.4 ± 0.5	7.2 ± 0.2	7.7 ± 0.3	6.5 – 8.5
Conductivity (µs)	2368 ± 25.3	1484 ± 45.4	1742 ± 56.1	1000 µs
TDS	1539 ± 15	1080 ± 8	940 ± 11	1000 mg/L
Temperature	23.5 ± 2.1°C	18.2 ± 1.8°C	20.5 ± 1.5°C	≥ 15°C
Turbidity	3.8 ± 0.3	2.5 ± 0.4	3.2 ± 0.2	5 NTU
C.O.D	305.3 ± 0.4 mg/L	189 ± 0.5 mg/L	244.6 ± 0.2 mg/L	50 µg/L

The tables 4 (a and b) shows the comparative values of hardness parameters for these raw groundwaters with respect to the standard values.

Table 4. The Standards for Water Hardness by Water Quality Association (WQA).

Hardness Level	Soft	Slightly Hard	Moderately Hard	Hard	Very Hard
mg/L or ppm	Less than 17.1	17.1 to 60	60 to 120	120 to 180	180 and above

Table 5. Experimental results of Hardness from the three zones.

Parameter	C/Mbweni Zone	M/Kwerekwe Zone	D/Mbovu-Zone
Hardness (mg/L)	158.7 ± 5	115.4 ± 4	73.5 ± 5

The GC/MS qualitative results of these raw groundwaters from the three zones are shown in the tables 6-8.

Table 6. The GC/MS qualitative results of Chukwani/Mbweni Zone.

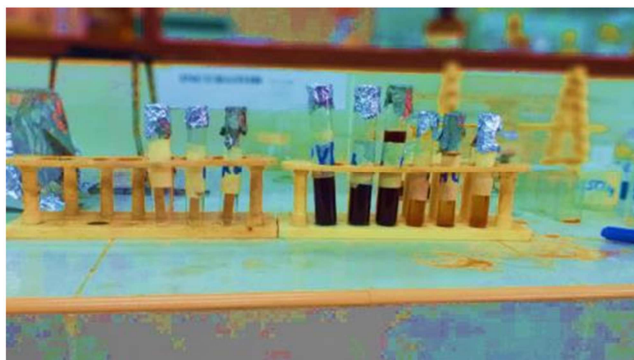
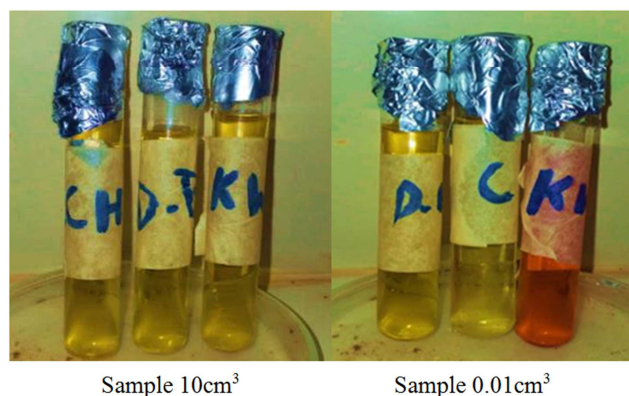
S/N	NAME OF THE COMPOUND	R. TIME	AREA	HEIGHT
1	Phenol, 2,4-bis(1,1-dimethylethyl)-	7.132	676173	381479
2	Phthalic acid, 2,7-dimethyloct-7-en-5-yn-4-yl isobutyl ester	9.811	137253	103904
3	Terpinylformate,	10.047	64633	30118
4	Dietilphthalate	3.214	3456	10989
5	Dichloroacetic acid, heptadecyl ester	10.61	8619	57753
6	5-ethenyl-5-methyl-2,4-oxazolidinedione	7.745	173235	116723
7	3-methyl-2-pentanone	9.253	208327	143606
8	1,1-dichloro-1-nitroethane	4.472	9455	30678
9	1,4-dichlorobenzene	4.012	9276	30761
10	9-t-Butyltricyclo[4.2.1.1(2,5)]decane-9,10-diol	13.448	130563	77010
11	Bromoacetic acid, octadecyl ester	15.021	67343	39101
12	17α-ethynylestradiol	5.654	5687	3482

Table 7. The GC/MS qualitative results of DarajaMbovu- Amani Zone.

S/N	NAME OF THE COMPOUND	R. TIME	AREA	HEIGHT
1	Trifluoroacetic acid, pentadecyl ester	9.25	88293	62661
2	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	9.806	59981	43322
3	Dibutyl phthalate	10.123	113881	85214
4	Methyl phthalate	10.438	307779	216451
5	Dichloroacetic acid, heptadecyl ester	10.604	105680	73113
6	Oxirane, tetradecyl-	11.209	99994	12840
7	5-methyl-2-hexanone	7.543	3214	4011
8	Bromoacetic acid, biphenyl	15.016	2101	2276
9	diethylphthalate, 1,2,4-trimethylbenzene	5.671	55324	4262
10	Oxirane, hexadecyl-	17.967	356564	55822
11	1,2,3,4-tetrahydronaphthalene	4.967	22403	5948
12	Diethylstilbestrol	5.81	2401	2211

Table 8. The GC/MC qualitative results of M/Kwerekwe-Zone.

S/N	NAME OF THE COMPOUND	R. TIME	AREA	HEIGHT
1	Trifluoroacetic acid, pentadecyl ester	7.741	80570	49520
2	Dichloroacetic acid, heptadecyl ester	9.249	103400	71613
3	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	9.805	65115	46106
4	Dibutyl phthalate	10.122	124460	92870
5	Dichloroacetic acid, heptadecyl ester	10.604	113311	80208
6	[1,1'-Biphenyl]-2,3'-diol, 3,4',5,6'-tetrakis(1,1-dimethylethyl)-	12.83	28705	20460
7	3-Chloropropionic acid, heptadecyl ester	13.173	3000	1964
8	2- Bromopropionic acid, octyl ester	13.557	13839	9028
9	Bis(2-ethylhexyl) phthalate	13.815	350632	238192
10	Sulfurous acid, octadecyl 2-propyl ester	14.534	5669	3981
11	Vinclozolin	4.875	4332	1895
12	Citalopram	4.789	4876	2113

Microbial concentration coloration of MPN test (10cm^3 , 0.1cm^3 and 0.001cm^3)**Figure 1.** Shows photo-shot results for MPN test at different concentrations.

The table 6 Showing statistical results from figure 1 of 9

tubes at each of 0.1, 0.01 and 0.001 ginocula, the MPNs and 95% confidence interval.

Table 9. Microbial contamination statistical results.

Pos. tubes			MPN/g	Conf. lim.	
0.1	0.01	0.001		Low	High
3	3	0	280	100	710
3	3	2	430	100	1100
3	3	3	430	150	1100

5. Discussion

The quality of drinking water is a powerful environmental determinant of health which must be noted as a basic human need [84, 58]. The experimental data obtained shows disparities in anions and cations concentrations in addition to the hydrocarbons derivatives realized from these groundwaters against the WHO drinking water quality standards. The average concentration of calcium was found to be more in M/kwerekwe ground water and above the WHO limit incomparable to other zones. The presence of both magnesium and calcium sulfates and /or chlorides in water contributes to the water hardness with C/Mbweni groundwaters having the highest value (Table 5). All these groundwaters are not soft (Table 5) comparing with the standards (Table 4) therefore requires softening. The existence of calcium and magnesium may be attributed to the natural occurrence of gypsum which is abundant within the Island. It has also been realized that most mineralization of infiltrating low-mineral rainwater occurs during recharge when carbonate dissolution and

silicate weathering occurs leading to increased levels of Ca, Mg, Na and K [14, 69]. From health perspective, hardness upto 500mg/L is safe but more than this cause laxative effects [59]. Magnesium, though within the range of WHO drinking standards (Table 1) is a dietary mineral for humans and a very important ingredient for many enzymes in our body including DNA replication however too much overdose leads to nerve depression, urine retention, cardiac arrest, low blood pressure, personality changes, vomit and diarrhea [88]. But Lower magnesium intake is associated with worse knee pain and function in radiographic knee osteoarthritis, especially among individuals with low fiber intake [71, 17]. Excess calcium reacts with the naturally occurring pyrophosphates chemical within our bodies to form calcium pyrophosphate dihydrate (CPPD) crystals which collects in the cartilage causing joints swelling, pains in knees, wrist, ankles, shoulders and other joints particularly to age sets above fifty years. This types of arthritis disease known as pseudogout [78, 65].

No Zinc was detected in all the waters therefore health risks associated with Zinc such as skin irritation, pancreas damage, anemia, etc may be tied to a different cause. Cadmium, though occurs in small concentrations (0.001 – 0.002 mg/L) below the recommended limit of 0.003 mg/L, a lifetime body accumulation at levels exceeding 0.005 mg/L can cause renal failure, liver, sensory disturbance, convulsions, lung damage, shock, salivation, bone and blood damage [62]. The major sources of cadmium are decayed debris which had accumulated then solidified into rocks and underground mineralization via bacterial process then finally reach into groundwater bodies [27]. Chromium (III) with accumulation of 0.1 mg/L causes similar effects as cadmium in addition to affecting internal hemorrhage and respiratory disorders while chromium (IV) can cause dermatitis and ulceration [75]. It is quite interesting that lead, which may have originated mainly from household faucets, dumped solder joints, a concentration of 0.24 mg/L has been realized from D/Mbovu- Amani Zone groundwaters against the recommended 0.01 mg/L. It is highly toxic even at relatively low concentrations [15, 4]. Its accumulation in human body over some time causes serious damage to brain, kidney, nervous and red blood cells. For infants, large amount of lead can cause delays in physical and mental development since it attacks brain and the central nervous system [89]. Generally, selenium is found in traces in the soils and its accumulation leads to foul breath, vomiting and diarrhea, irritability, fatigue, hypertension [42]. Naturally, sedimentary aquifers are found to contain excessive arsenic levels and fluoride levels in addition to Calcium, Magnesium, iron, sodium, and Potassium [14] but are often associated with the carcinogen arsenic since its harmfulness outweighs the benefits of the salubrious minerals. Studies have shown that consumption of arsenic (a natural component of earthcrust) over periods of 5 to 25 years its inorganic form leads to cancer and skin lesion, negative impacts on cognitive development and increased deaths in young adults while its organic form rarely it does not generally accumulate in the body [89, 79]. Aluminum

concentration detected though decimal < 0.2 mg/L, however, prolonged intake leads to alzheimer's and parkinson's disease, senility and pre-senile dementia [89]. Its anthropogenic release in waters is most probably from wastes water effluents and solid wastes containing food cans, cookware [6, 16, 26]. Indeed, there is a lot of imported kitchenware materials, canned food and beverages containers made of aluminum found within the Island and their disposal system is worrying. These heavy metals (atomic weight lies between 63.5 and 200.5, sp. gr. > 4.0) Al, Pb, Cd and As do exist in these groundwater in colloidal, particulate and dissolved phases [34, 2] with their occurrence attributed to natural origin (e.g. eroded minerals within sediments, leaching of ore deposits and volcanism extruded products) or of anthropogenic origin (i.e. solid waste disposal, industrial or domestic effluents, harbour channel dredging) [51]. The concentrations of sodium are not very worrying though excessive sodium in drinking water is also an issue when combined with the normal dietary level intakes, may lead to hypertension and cardiometabolic diseases particularly in pregnant women [14, 5] and among infants it causes hypernatraemia and serious neurological damage [63]. Too much potassium intake may result into a significant health effects in people with kidney disease or other conditions such as heart disease, coronary artery disease, hypertension, diabetes and adrenal insufficiency [46] while no significant health effects associated with calcium have been reported at those found concentrations.

The high values of C.O.D reported in table 3 indicates the levels of organic pollutants into the groundwater system. These values ascertain the existence of poor waste disposal systems, infiltration of domestic sewer systems into the groundwater basin, landfill leachates and the intrusion of fertilizers, pesticides [44, 34]. C/Mbweni zone has the highest value due to the existence fertilized irrigated small vegetable farms in addition to the poor disposal system which includes wastes from households (domestic wastes), salons, landfills leachates, etc.

Organic compounds such as phthalates, oxiranes, biphenyls, carboxylic acids derivatives dichloronitroethanes, phenolic derivatives, diethylstilbestrol, etc. used as plasticizers, fungicides, detergents, pesticides, fertilizers, contraception/ personal care products, and cosmetic formulations, are grouped as endocrine disruptive chemical. The qualitative assessment using the GC-MS spectroscopic machine revealed the presence of these EDC organic compounds in every groundwaters (Tables 6, 7, 8). The existence of these EDC elements is evident by the high C.O.D values (Table 3). For example, in table 6, the phthalates derivative compounds, Vinclozolin compounds such as 5-ethenyl-5-methyl-2,4-oxazolidinedione, 1,4-dichlorobenzene, 1,1-dichloro-1-nitroethane, are EDC associated with fertilizers, pesticides, etc. Their existence is associated with small irrigated artificially fertilized vegetable farms within C/Mbweni zone. Compound such as 17 α -ethinylestradiol, diethylstilbestrol is associated with personal health care products. The lethal EDC elements such as

phthalates, esters, biphenyl and ketonic derivatives apart from being components of plasticizers, fungicides, detergents, flavoring and essence components, they are also associated more with effluents from personal health care and cosmetic application industry which indeed is a rampant business due to the influence of Unguja Island social setups. These infiltrates into groundwater system due to poor waste disposal system, and poor sewage disposal system found within the residential area. The C/Mbweni Zone and D/Mbovu- Amani Zone has more concentrations of these EDC contaminants since these populated residential areas have a lot of beautification centers (Salons) in addition to contaminants from domestic waste disposal. In these regions Cosmetics shops are on the increase implying increase in cosmetics products consumptions consequently cosmetics and personal care products effluents are also on the rise. Pesticides such as 1,2,3,4-tetrahydronaphthalene, 1,4-dichlorobenzene, etc has also been detected in D/Mbovu-Amani and C/Mbweni groundwaters incomparable to M/kwerekwe waters. These severe water contaminants/infiltrates into ground water systems and are resistant to natural degradation [55, 54, 26, 23]. Studies have shown that EDC's have serious health consequences such as brain disorders, pubertal timing variations, ovulatory disorders, prostrate and breast cancer, unusual sexual misbehavior, male infertility, immune abnormality, blue baby syndrome, hypospadias, reduced anogenital distance leading to UTI cases particularly in women, cryptorchidism, low IQs, structural anomalies, disrupted hypothalamic estrogenic receptor distribution, alteration of nitric oxide syntheses signaling, affectations of human immune function, and disrupted behavior in children associated with early life BPA exposure, especially in girls, oligospermia to mention but a few [45, 77, 24].

The concentration of flouride ranges from 1.65 to 1.24 mg/L. These concentrations cannot lead to skeletal fluorosis which flourishes with concentrations between 3 – 6 mg/L [86, 72, 67, 19] but can cause slight dental fluorosis [3]. Low concentrations of flouride have been considered beneficial to prevent dental carries [86, 49, 61]. The nitrate concentrations ranges from 53.7 – 1.15mg/L with C/Mbweni zone having above the WHO mark of 10 mg/L. The main source is likely from fertilizers used in the vegetable farms [25], nitrogen fixation from atmosphere by legumes, bacteria, poor waste water disposal system and sludge. The M/kwerekwe and D/Mbovu - Amani zones do not have irrigated small farms consequently nitrate existence in groundwater may be attributed to poor waste water disposal system and natural occurrence. Above 40 mg/L is known to cause blue baby syndrome or methemoglobinemia in children [67]. Studies have revealed that nitrates cannot be removed from drinking water by boiling [70] therefore it easily finds its way into the human body unless removed using alternative purification methods. The high chloride levels (260 and 251 mg/L) may be an indicator of pollution by sewage or irrigation leachates [66]. The contents of bicarbonates and carbonates have no known

adverse health effects but their dominant concentrations suggest water – rocks interactions. Apart from anthropogenic sources such as gypsum, microbial degradation of organic matter which releases phosphorous in phosphate forms and domestic sewage, excess phosphates in C/Mbweni zone ground waters may be attributed to excess use of fertilizers in those nuclear small farms [25]. Since phosphates are not very mobile in soil, there are transported easily by percolating waters into the groundwater basin and such quantities reported of 3.44 mg/L are not very harmful to man [56]. The sulfate concentration is found to range from 85 to 415 mg/L. Drinking waters with sulphate concentrations above 200 mg/l like C/Mbweni Zone waters may lead to gastrointestinal irritation and bowel discomfort [70, 87]. This high value most likely is associated with effluents from infiltration from sulphate based fertilizers used in the farms [25] in addition to wastewater discharges particularly from households. M/kwerekwe zone has the largest food market in Unguja Island, large waste water disposal pond and several waste dumps. Most likely the infiltration of these landfill leachates [26] in addition to weathering of geomorphological structures/mineral into the groundwater basin leads to the stated sulfated concentration.

From the cation and anion concentrations, three major likely hydrochemical facies are Ca-Cl, mixed Ca-Mg-Cl and Na-Cl meaning that the samples are saline with low to high sodium hazard. This signifies that these regions are to some appreciable extent affected by saltwater contamination due to seawater intrusion [37], domestic sewage and saltpan deposits. C/Mbweni zone is leading since it is closer to the sea than the rest. These aspects do confirm why we have high EC, TDS and Chloride values particularly in the C/Mbweni zone. This too concurs well with the pH values which have been found to fall within the W.H.O. range but on the higher side indicating these groundwaters are slightly alkaline. This also commensurate well with the moderate hardness found and supports the problems of variable tastes, odour and colour [15] experienced by locals. Studies have shown that temperatures above 15°C enhances the growth of nuisance organisms hence concurs well with the microbial contamination levels reported (Table 9). The microbial contamination is so much attributed to poor sanitations signifying fecal contamination due to poor sewage disposal systems and seepages from various wastes dumps acting as vehicles for microbes into groundwater basins [11, 35]. The presences of microbial contamination is also supported by the high pH values or alkalinity which is found to decrease the germicidal potential of chlorine [88]. The conductivity ranges from 1429 – 2393.3 μ S above the WHO limits with C/Mbweni zone leading the track. These parameter depends on presences of total dissolved ionic components in water, their total concentrations, mobility, valence, relative concentration and temperature [58, 91]. High concentrations of Na, K, Mg and Ca could be the main game changer behind conductivity levels among these zones. The values above the WHO limits cause stomach rambles and diarrhea [87], and also is an indicator for TDS values. Normally TDS indicates the sum of

all components dissolved in water e.g. K^+ , Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , etc. C/Mbweni Zone has the highest of around 1539 mg/L far beyond the recommended limits (Table 3). This may be attributed to the agricultural activities, low lying topographical position within the hydrological zoning and its closeness to the sea. Waters with high dissolved solids is known to cause impairment of physiological processes in the human, gastrointestinal irritation [36]. Despite of complains of gastrointestinal irritations, stomach rambles, etc. upto date there is no health based guidelines for TDS in Zanzibar.

Groundwaters normally have low turbidity because of the natural filtration that occurs as they penetrate through the soil [82]. This is evident from the low values of less than 3NTU but this does not signify that during treatment and purification we should not filter the water. Likewise, the appearance, taste, colour and odour do not really tell if the water is safe to drink.

From Ministry of Health (Revolutionary Government of Zanzibar) (2020 – 2019) bulletin and informative, cases such as, among others, brain disorders, UTIs, ovulatory disorders, low IQs, blue baby syndromes, immune abnormalities, arthritis and joint pains, gastrointestinal irritation and bowel discomfort, skin diseases, disrupted behavior in children associated with early life BPA exposure, kidney problems, sensory issues, fatigue, hypertension, etc. are on the rise but the question is, should we tie them on these contaminants' effects? These negative impacts of contaminated groundwater on human health are chronic and at times hard to diagnose [13] apart from waterborne diseases such as cholera, typhoid fever, etc. Therefore, more research needs to be done to ascertain the connection. The composite overall result shows the ingestion of these cations, anions, EDC elements and the nature of these ground waters as drinking water indicates that the total health risks are beyond the US EPA acceptable level of 10^{-6} per year [88] for consumption of groundwater sourced from three zones. This is worrying and a potential health risks to vulnerable individuals with the health risks to children higher than the risks to adults.

6. Conclusion

From the above results, it confirms that these groundwaters are contaminated, infected and not potable. These groundwaters requires purification and treatment to make them potable and palatable rather than relying on the conventional treatment of boiling which either destroys or deactivate microorganisms. To improve on these raw groundwaters suitability for drinking, it requires treating these waters through screening, sedimentation and filtration or aeration, to reduce and eliminate any form of contaminants before physical-chemical and microbial treatment for dissolved constituents and microbes respectively in order to conform with the latest drinking water quality standards laid by the World Health Organization (WHO).

7. Recommendations

When WHO standard or guideline is exceeded proper action is required. The government needs to initiate and improve on the existing Environmental Protection policy acts on the sources of these haphazard contaminants, decriminalize these nuclear/small vegetable farms within residential areas and regulate on the type of fertilizers, personal health care products and cosmetics suitable for use. The mass should be made aware on the consequences of contaminants. There is a need for exponential increase for suitable groundwater evaluation of groundwaters quality with the aim of safeguard public health and protecting the groundwater resources, and a proper coordination of health records on health issues associated with contaminant be well documented. This study also recommends medical hydrogeology framework may help in regionalizing water quality. This study proposes exponential hydrogeochemical evaluation of groundwater by using soft computing techniques or models which are accurate and reliable such as Piper plots and Durov plots suitable for demonstrating large amount of data and defining major trends of pollutants concentrations consequently leading to formulating suitable water treatment. The soil Permeability index and Water quality index analyses should be done in order to give the true status of the quality of groundwater resources for drinking purposes. Principal Component and Cluster water analyses should also be encouraged and latest methods for detecting and tracking the movement of groundwater contaminants are indeed appreciated. Radiochemical multi-elements analysis is recommended since decimal concentration of titanium ores have been identified along the ocean shores. There is also the need for case studies and remedial actions in controlling groundwater from natural sources, effects of groundwater contamination on the abiotic environment and novel techniques for assessing risks to human populations consuming these contaminated groundwaters.

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Competing Interest

The authors have declared that there are no competing interests exist.

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