Groundwater Quality Assessment around Sub-Urban Zone, Antananarivo Area, In Using Hydrochemical Approach

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ABSTRACT: The study area is located in Madagascar High land, precisely at Analamanga region, including a large plain culminate on the elevation around 1250 m. About sixty percent of its peoples do not have access on drinking water distributed by the water supply company. Most of their population use wells as water supply system. However, the wells are highly exposed on pollutants because of its location, situated inside the residential area and close to the anthropic activity and household waste.

The hydrochemical analysis was carried out on the water sample from the well. Measurement of major ions were performed at JIRAMA’s laboratory where the Ca²⁺ and Mg²⁺ concentrations are obtained through the volumetric titration method in using solution EDTA, the HCO₃⁻ through alkalinity titration and complete alkalinity titration, Cl⁻ in using the acid titration, SO₄²⁻ concentration is defined with barium ethanoate; organic matter was measured in using permanganate oxidisability; Na⁺ concentration is determined through the electrical conductivity method, and the colorimetric titration method was used to determine iron, ammonium, nitrate and nitrite concentration in solution. Some Radionuclide elements (U and Th) and barium concentration analysis were also done. The test was done in using ICP-MS method (Inductively Coupled Plasma Mass Spectrometry).

Water TDS test give the concentration value range between 10mg / L to 1200 mg / L. Waters are slightly acid with low pH, included to 4.4 and 6.87. Also, the observation done on water temperature at two seasons winter and summer show that it change and follow the ambient temperature. The chemical analysis gives high rate of nitrate cation which is in balance with both chloride and sodium concentrations. Approximately 10 % of the 31 monitored wells had nitrate concentrations above the WHO standard and more than 50 % had a TDS above 13.5 mg / L.

The result analysis done under this study conduct us to consider that the water resources inside the sub-urban zone are vulnerable on human activities, household waste, animal and human defections, and industrials discharges.

KEYWORDS: Sub-urban, Antananarivo, groundwater, cation, anion, hydrochemistry.

I. INTRODUCTION

In front of the water drinkable demand increase caused by the population increase and the urbanization development, the water potentiality assessment is unavoidable under the water sustainable management. The present study is done in order to understanding chemical quality change of groundwater in sub-urban site, around Antananarivo area. The study area is included in the Highland of Madagascar, the soil is constituted by metamorphic crystalline rock and the alluvium at the lowlands part. [5]. The map showed that the lowlands areas
located on the alluvial deposits (Betsimitatata plain) are most vulnerable of pollutants than the weathered area situated in interfluve zone. Ralaimariso in 2004 [6] studied the hydrochemical setting in the crystalline aquifer of Highlands in Ambohitrakoho site, out of urban area. The groundwater mineralization is considerably low, even in lowland cover by flat and alluvial deposits. Groundwater electrical conductivities are between 15μS/cm and 60μS/cm at the mountain background and they are less than 120 μS/cm for the altered aquifer of interfluve system. There are three types of chemical groundwater, sodium magnesium for water spring located on the mountain base, sodium bicarbonate for the water from the altered aquifer zone, and calcium bicarbonate and magnesium in the arena aquifer zone. [7] The effect of industry activity on the groundwater and surface water were studied.

Also, we are done the groundwater sampling for the chemical analysis of major ions and some radionuclide elements, in 31 wells located around Antananarivo urban area (see figure 1). The process and the interpretation of the analysis results conduct us on groundwater quality assessment and to see the vulnerability degree of this resource in sub-urban area.

II. GEOMORPHOLOGICAL AND GEOLOGICAL SETTING

The study area belongs to the Centre Highland part of Madagascar. It is formed by the succession of lateritic hills, valley and alluvial plains in lowlands zone. Antananarivo is surrounded by the alluvial plain composed of lacustrine deposit during the quaternary. Three rivers crossed this plain, Ikopa, Sisaony and Mamba. They follow generally the South-East North-West direction (see Figure 1).

The old towns are installed on isolate hills surrounding by the Bestimitatatata plain which is before transformed to paddy field and occupied progressively by the habitation. The elevation varies from 1240m to 1540m.

Weathered zones are lithologically heterogeneous. Its types were depended on rock nature [7]. The lateritic layer may reach 40m depth in some area [8].

Figure 1: Sampling points and geomorphologic setting of the study area
The regional geological setting conducts us on the differentiation of the aquifer type. The study area is formed principally by two types of rocks: granitic and schist. Some schist composed by the graphite series is associated with gneiss. Weathered formation from the two types of rock are completely different, also the aquifer system inside these layers.

The lateritic rocks are crossed by depressions and formed the valleys and shallows covered by alluvial deposit. These lower zones drained the regional water, such as surface than underground, which joined after the river network [9].

Some litho-stratigraphic sections deduced from the drilling done one Antananarivo plain, North West of Antananarivo town, drive us on the identification of the different potential aquifers and the impermeable layer which limit the aquifers. We can deduce from the four successive interest layers from top to bottom, hydrogeologically: thin sandy layer form the perched aquifer, confined aquifer form by sand isolate from the upper aquifers by an argillaceous layer, micaceous-clay arena constitute the aquifer in weathered zone and the fracture and fissured aquifer of basement(Figure 3).
Physico-chemical analyses was done on the 31 waters samples from the well and spring located around Antananarivo town (figures 1 and 2). Samples were filtered in using the 0.2μm paper pores and stored in polyethylene bottles 1.5 liters volume. The samples were immediately brought to the laboratory and then analysed as soon as possible in order to minimize the change in the hydrochemical properties.

Note that the measure of the pH, temperature, electrical conductivity and TDS were done with multi-parameter HANNA high-precision in-situ before the sampling. The variation of pH and TDS may be interpreted as existence of contamination.

The standard procedure, APHA 1995 was followed during the chemical analysis of major and minor ions. For the alkalinity, HCO₃⁻ and CO₃²⁻ titration, the standard sulphuric acid (0.02N) were used in using phenolphthalein and methyl orange indicator paper. Also, the titration of radionuclide elements (U and Th) and barium was done with ICP-MS (Inductively Coupled Plasma Mass Spectrometry) method.

Increase of water mineralization is result of either rock chemical elements dissolution or anthropological pollutant. After the analysis and determination of the mineralization types that we can define the mineralization origin.

IV. RESULTS AND DISCUSSION

Results

Groundwaters chemistry:

TDS and pH are the parameters which allow controlling easily physical and chemical characteristics of waters. Their variation translates contamination of the water resources (FEPS).

The results reveal that all samples are slightly acid. The pH range between 4.4 during wet season and 6.87 for dry season. The mean pH is 5.6.

The TDS value is 13 mg/L for the minimum, corresponding to dry season and 1295 mg/L for wet season. TDS for wells corresponding to samples 3, 29 and 30 indicate a poor quality of water according to the WHO standard value.

Organic matters (OM) are results of urban sewer discharge, and pollutants from food industry or slaughterhouse [10], [11].
The mean values of OM from the two seasons is 1.28 mg/L and 0.25 mg/L. Samples number 12 and 4 present concentrations equal to 5 mg/L and 4mg/L in dry season. These values do not exceed the WHO standard level. However, the presence of OM in the groundwater means interaction of water with a peaty formation under the surface and which is diluted during wet season.

The mean value of the electrical conductivity of the samples is 211μS/cm and 246μS/cm. The malagasy standard is fixed a maximum of 3000 μS/cm and the rainwater have electrical conductivity equal 90 μS/cm [12].

Ammonium concentration is less than 1mg/L for all samples except the sample 3 where the value is 4.31 mg/L in dry season. This is probably due to home wastewater discharge.

Presence of nitrates in groundwater is an indice of pollution from agriculture, urban, or industry. In this study, the samples 3, 4, 7 and 16 have respectively nitrate concentrations equal to 199.24 mg/L, 70.48 mg/L, 81.39 mg/L, 144.36 mg/L et 53.01 mg/L.

Nitrate concentrations range between 0.042 mg/L à 0.035 mg/L. Samples 3, 13, 15, 22, 30 et 31 exceed the maximum content level of the malagasy standard value.

Discussion :

a)- Nitrate

Table 1 shows statistic description of major ions and TDS.

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>Std. Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>31</td>
<td>.80</td>
<td>82.00</td>
<td>13.4710</td>
<td>16.77185</td>
</tr>
<tr>
<td>Magnesium</td>
<td>31</td>
<td>1.22</td>
<td>43.50</td>
<td>7.2052</td>
<td>9.33783</td>
</tr>
<tr>
<td>Sodium</td>
<td>31</td>
<td>1.15</td>
<td>144.26</td>
<td>23.9298</td>
<td>32.10368</td>
</tr>
<tr>
<td>Bicarbonates</td>
<td>31</td>
<td>4.88</td>
<td>135.42</td>
<td>21.6058</td>
<td>27.79029</td>
</tr>
<tr>
<td>Sulfates</td>
<td>31</td>
<td>.00</td>
<td>20.17</td>
<td>3.5623</td>
<td>5.00131</td>
</tr>
<tr>
<td>Chlorites</td>
<td>31</td>
<td>1.77</td>
<td>220.01</td>
<td>37.2548</td>
<td>49.61129</td>
</tr>
<tr>
<td>Nitrates</td>
<td>31</td>
<td>.00</td>
<td>199.24</td>
<td>18.6223</td>
<td>38.48656</td>
</tr>
<tr>
<td>TDS</td>
<td>31</td>
<td>13.00</td>
<td>1198.00</td>
<td>256.4516</td>
<td>303.58742</td>
</tr>
</tbody>
</table>

Nitrate concentration in groundwater is defined as follow [13], [14]:
- nitrate concentration less than 0.9 mg/L, indicate a natural value or background noise,
- nitrate concentration between 0.9 mg/L and 13.5 mg/L, correspond to transitional stage,
- nitrate concentration above 13.5 mg/L, shows a possible influence of the resources.

The results shows that 25,80% of the water samples have nitrate concentrations that exceed 13.5 mg/L during dry season and 51,6% during wet season. Among them, 37,5% in dry season and 25% in wet season exceed the maximum content level acceptable for WHO and Malagasy standard level (50 mg/L).

Consequently, we can resume that pollutions of the groundwater for the study area came from anthropic activities. Pollutants like nitrate in water may come from latrine infiltration, or leaching from waste storage in the surface. The increases of contaminant concentration after rainy season confirm this observation. Table 2 give correlation matrix between major ions and TDS.
Table 2: Correlation matrix of major ions and TDS (Red for dry season and blue for wet season)

<table>
<thead>
<tr>
<th></th>
<th>Ca++</th>
<th>Mg++</th>
<th>Na+</th>
<th>HCO3-</th>
<th>SO4--</th>
<th>Cl-</th>
<th>NO3-</th>
<th>TDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca++</td>
<td>1</td>
<td>.528(*)</td>
<td>.541(**)</td>
<td>0.162</td>
<td>.434(*)</td>
<td>.563(**)</td>
<td>0.314</td>
<td>.594(**)</td>
</tr>
<tr>
<td>Mg2+</td>
<td>.613(**)</td>
<td>1</td>
<td>.778(**)</td>
<td>0.111</td>
<td>.497(**)</td>
<td>.823(**)</td>
<td>.686(**)</td>
<td>.864(**)</td>
</tr>
<tr>
<td>Na+</td>
<td>.584(**)</td>
<td>.646(**)</td>
<td>1</td>
<td>0.032</td>
<td>.601(**)</td>
<td>.974(**)</td>
<td>.785(**)</td>
<td>.876(**)</td>
</tr>
<tr>
<td>HCO3-</td>
<td>0.298</td>
<td>0.227</td>
<td>0.161</td>
<td>1</td>
<td>-0.055</td>
<td>0.034</td>
<td>-0.214</td>
<td>0.153</td>
</tr>
<tr>
<td>SO4--</td>
<td>.752(**)</td>
<td>.379(*)</td>
<td>.384(*)</td>
<td>.603(**)</td>
<td>1</td>
<td>.623(**)</td>
<td>.728(**)</td>
<td>.500(**)</td>
</tr>
<tr>
<td>Cl-</td>
<td>.578(**)</td>
<td>.645(**)</td>
<td>.995(**)</td>
<td>0.122</td>
<td>.356(*)</td>
<td>1</td>
<td>.788(**)</td>
<td>.927(**)</td>
</tr>
<tr>
<td>NO3-</td>
<td>0.192</td>
<td>0.152</td>
<td>.623(**)</td>
<td>-0.169</td>
<td>0.171</td>
<td>.604(**)</td>
<td>1</td>
<td>.654(**)</td>
</tr>
<tr>
<td>TDS</td>
<td>.668(**)</td>
<td>.768(**)</td>
<td>.953(**)</td>
<td>0.141</td>
<td>.416(*)</td>
<td>.956(**)</td>
<td>.499(**)</td>
<td>1</td>
</tr>
</tbody>
</table>

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

Figure 4 shows that higher the nitrate concentration and chlorites and sodium concentration increase. This may indicates that water quality is influenced by human and animal wastes [15].
Three groups of groundwater types are identified: Cl-SO₄-Na water; Cl-CaSO₄-Mg water; and CaHCO₃-Mg water. Figure 5 shows piper diagramme for the 31 analysed groundwater.

Figure 6 shows the situation of the well of the sample 3 which had the highest concentration of nitrate, chlorites and sodium.
Figure 6: Profile view of the well in sample 3

b)-Total Dissolves Salt (TDS):

About 13% of the waters samples have TDS higher than 600 mg/L. When mineralization is high, pH is low. In this case, dissolution of the pollutants from the surface throw the infiltration of the rainwater take control of the total mineralization. The Cl-SO_{4}-Na and Cl-CaSO_{4}-Mg water types highlight this situation. Figure 7 show that higher the TDS, and the pollution from human activities influence the groundwater quality. Indeed, table 2 shows significant correlation between TDS and Cl^{-}, Na^{+} and NO_{3}^{-}. A random distribution of Ca^{2+}, Mg^{2+}, HCO_{3}^{-} and SO_{4}^{2-} according to the TDS (figure 7) verify also this hypothesis.
Figures always reflect the high correlation between TDS and major elements, especially for $\text{Ma}^{2+}$ and $\text{Cl}^{-}$ and $\text{Mg}^{2+}$.

Figure 7: Plots of $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{HCO}_3^-$ and $\text{SO}_4^{2-}$ Vs TDS
The mean temperature of the waters range from 17.9 to 21.6°C. The variation of the T° according to the altitude is high (3.7°C for only 30 meters). In 2005, Antonio Jorge de Lima Gomes and Vallya Mannathal Hamza found a variation of the geothermal energy between 16 to 24°C/Km [16]. It means that the aquifer is vulnerable to the variation of the temperature and to the climate change. Figure 8 shows the variation of the temperature between rainy and dry season.

![Figure 8: Variation of the temperature of the groundwater from winter time to summer time.](image)

c-) Uranium and Barium:

According to the WHO standard for drinking water, uranium concentrations are relatively low (0.02 to 0.16 ppb). Barium concentration is low as well except one sample from the north parts of the study area where the barium concentration is equal to 3223 ppb. It means that the groundwater resources for the study area do not present risk of exposure to uranium radioactivity. At high concentrations, barium causes vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles and convulsions and paralysis following stimulation of the central nervous system [17], [18]. For the case of the study area, the maximum concentration of barium recorded is largely low than the mean daily intake of barium from food, water and air (estimated to be slightly more than 1 mg/day). It is then considered as to be not yet a risk. However, it is interesting to make a study on this subject and to better understand the evolution of the barium in groundwater of the study area.

V. CONCLUSION

Thirty one water samples from wells or sources were analyzed to study the groundwater quality. Among the 31 samples, only three have nitrate concentration more than the maximum contaminate level (50mg/L) of the WHO for the both two seasons. However, the aquifer is vulnerable to pollutants from human activities in the surface. TDS range from 13 to 1198 mg/l. More than 50% of the water samples have low mineralization. Waters are slightly acid (pH range from 4.4 to 6.87). Concentration of nitrate, chloride and sodium is correlated; that means that the contamination from human activities in the surface is significant (latrine, animal wastes, storage of domestic wastes). High concentration of Barium (3223 ppb) is recorded and concentration of uranium is low.
REFERENCES


