Trace Elements and Physico-chemical Quality of the Well Waters in Mahitsy, Province of Antananarivo, Madagascar

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The proposed study area of Mahitsy is located in the province of Antananarivo. Only 14.38% of the population in the rural zone has access to safe drinking water. Most of human population use wells or springs as the main source of drinking water. Wells are generally less than 20 meters deep and they are not properly sealed. Well waters investigated in January 2004 have a very large range of trace constituent and chemical composition in the zone of interest. Manganese concentrations range is 8 µg/L – 1115 µg/L and concentrations of barium vary in the range of 55 µg/L – 4967 µg/L. 67% of monitored well waters are of manganese concentration higher than 50 µg/L and 44% contain barium with a concentration higher than 700 µg/L. Total dissolved solids vary between 8 mg/L and 881 mg/L and well water pHs are acidic (4.28 – 5.94). Nitrate concentrations monitored in Mahitsy groundwaters show that, 54% of the well water samples exceed 50 mg/L (WHO guidelines value) and 84% exceed 13.5 mg/L (indicative value of human activities). The nitrate content ranges from 4 to 489 mg/L. Groundwater nitrate correlates positively with chloride and potassium. That would suggest that the high content of nitrate may result from the septic tank, the cesspool and the animal wastes storage, located next to the well. However, people draw water from ground water for domestic purposes, as the water infrastructure remains undeveloped in the studied area. The measurement of trace constituents are performed using Total Relflection X-ray Fluorescence (TXRF) analytical method and the major ions are determined by Ion Chromatograph (IC) system.

1. INTRODUCTION

Water is nowadays considered as a precious resource since it is the main source of life. However, it may also be a cause of lots of troubles, which could affect to some extent human health. Therefore, there is an increasing concern on water pollution of both natural and human origin. Water quality assessment is now becoming a necessity.

Although the Province of Antananarivo is rich in freshwater resources, their quality is not well-known. According to the Tableau de Bord Social [1], only 14.38% of the population in the rural zone has access to safe drinking water. In Mahitsy, groundwater is an important water resource. However, groundwater is highly vulnerable to contamination and no comprehensive studies have been completed on groundwater quality in the study zone. Wells are generally less than 20 meters deep and they are not properly protected from surfacial pollution.

Contaminants occurring in large concentrations are nitrate (NO_3^-), manganese (Mn) and barium (Ba).

The purpose of this work is to provide an overview of ongoing groundwater quality studies in Mahitsy to better understand the processes, which control pollution in the phreatic aquifer.

2. REGIONAL, GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The study site is located in Mahitsy, Province of Antananarivo. It stretches from 17° 43' S to 20° 17' S, and from 45° 28' E to 48° 3' E. The study site experiences an altitude tropical climate, which is marked by distinct summer (November – April) and winter (May – August) seasons. The average annual rainfall is around **1200 mm** in the study area. The main storm events occur during wet season in summer. The mean annual air temperature ranges from 16 °C to 24 °C.

The zone is predominantly rural. Agricultural land uses and cattle breeding dominate the population activities.

The province of Antananarivo lies within the Central High plateau section. It consists of crystalline rocks of Precambrian age [2]. The crystalline basement incorporates mainly gneisses, granites or migmatites.

Mahitsy is located in the hydrogeological zone of the crystalline high plateau zone with rainfall higher than 800 mm. Well waters tap upper aquifer. The water table varies in the range of 2 m to 19 m under the land surface. The well depth ranges from 5 m to 20 m, depending on the sampling site topography.

3. SAMPLING AND ANALYSIS

The sampling campaign was carried out in the area of Mahitsy in January 2004. 16 water samples were collected from private wells. The sampled wells are of two types: relatively protected well (RPW) and open-air well (OAW). They are all traditional wells.

Temperature, pH, redox potential (Eh), Electrical Conductivity, Total Dissolved Solids (TDS) and Dissolved Oxygen (DO) were measured in field using portable mulitmeter. The alkalinity was also determined in-situ by acid titration (with 0.16 N H_2SO_4). For the remaining analysis, samples were collected and passed through a 0.2 µm filter and the other elements in solution were determined in the laboratory : an ionic chromatograph was used for the determination of cation and anion concentrations. TXRF method was employed to measure the trace element concentrations in the sampled water. The detection limits for ions were within 0,25 mg/L. The trace element detection limits ranged between 8 µg/L and 55 µg/L. The analytical precision varied within 5%.

4. WATER CHEMISTRY

Two groups of well water can be distinguished on the basis of major ion concentrations. The first type is Ca, Mg – HCO_3 and the second one is K, Na – Cl - NO_3. The first group is weakly mineralized with HCO_3^- as a dominant anion and presents a pH value more than 5.5. It is represented by 2 wells located in Fidasiana and Andohanosy. The remaining sampled waters belong to the second group. Water in this category is highly polluted by NO_3^-. The contents of NO_3^- and Cl^- control the mineralisation of the well waters.

Measured well water temperatures ranged from 21.9 to 25.2 °C and averaged 23.2 °C. Only well water sampled in Tandrokomby had temperature outside the interval values recommended by the standards . Measured specific conductivity values varied from 33 to 1830 µS/cm and an average value of 483.6 µS/cm. The pH values were in range of 4.6 and 5.9 and averaged 5.2. All of well waters had unusually low pH values and violated water quality standards for pH. This is likely a natural condition, since the well is of a shallow depth and badly protected against infiltration from land surface. Sampled water presented a Eh value ranging from 64 to 140, indicating oxidizing conditions at the locations. The concentration of DO in well water can significantly affect many geochemical or biological processes such as oxidation or reduction of nutrients. Measured concentrations of DO varied from 1.16 to 3.64 mg/L. The mean concentration value was 2.80 mg/L. The TDS values varied from 16 to 881 mg/L and averaged 234 mg/L.

Well water samples had concentrations of sodium ranging from 2.1 to 130 mg/L with a mean value of 37.3 mg/L. The potassium concentrations varied between 3.6 and 235 mg/L and averaged 48 mg/L. 6 samples of 12 had potassium concentration at of above 12 mg/L, which is the recommended value for the potassium. The mean value of chloride was 48.2 mg/L and the concentration ranges are from 1.8 to 204 mg/L. Sampled water contained nitrate in concentrations of 9.9 to 489 mg/L. The mean value of nitrate level was 160 mg/L. Only 6 of 16 samples analyzed for nitrate contain concentration below the maximum allowed value (50 mg/L) proposed by the drinking water quality standards. Most of

water samples had sulfate concentrations below the minimum detection limit (0.25 mg/L), except 4 samples with 39 mg/L of sulfate as a maximum value.

Iron contents were between 8 µg/L and 213 µg/L with a mean value of 40 µg/L. One water sample collected in Mahitsy county town had a concentration exceeding 200 µg/L. Manganese was present in concentration lower than 8 to 976 µg/L. 10 of the 16 samples had a concentration higher than 50 µg/L, which is the maximum allowed value given by the water quality standards. Barium was very variable, with a range of less than 55 to 4967 µg/L and 7 water samples of 16 presented a concentration value exceeding 700 µg/L (maximum allowed value proposed by the French water quality standards). Strontium contents were in concentrations of less than 12 to 874 µg/L, with an average of 174 µg/L. Elements such chromium, arsenic, lead and mercury were present in concentrations of less than 9 µg/L, 10 µg/L, 21 µg/L and 20 µg/L, respectively.

5. DISCUSSION

5.1. Nitrate

The following concentration criteria is used to identify if measured nitrate in well waters could be of anthropogenic origin or not [3] :

- nitrate concentration less than 0.9 mg/L, indicating natural or background level,
- nitrate concentration between 0.9 mg/L and 13.5 mg/L, representing transitional level,
- nitrate concentration more than 13.5 mg/L, showing an eventual human influence on water quality.

Results show that around 18% of collected samples contained nitrate in concentration between 0.9 mg/L and 13.5 mg/L and more than 81% of sampled well water were of nitrate level higher than 13.5 mg/L. Among them, 77% had nitrate concentration exceeding the maximum allowed value (50 mg/L).

Therefore, most of well waters sampled in Mahitsy appear to be contaminated by human activities. With regards to the well localization, the nitrate contamination may be due to the infiltrations from latrines, livestock park, storage of animal manure and storage of domestic rubbish. Actually, some are located close to wells.

Figure 1 exhibits that the higher the nitrate content in well water, the greater the chloride and sodium concentration levels are. However, high level of nitrate with high content of chloride may suspect human and animal waste influence [4]. High concentrations of nitrate occurred in wells located in Mahitsy county town.

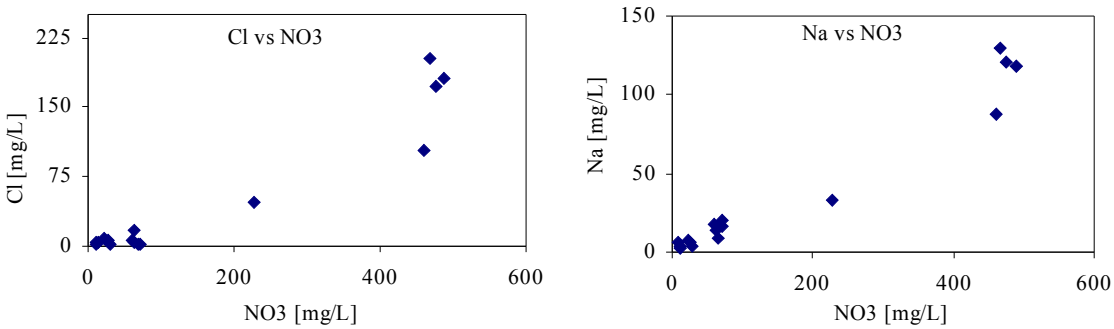

Figure 1. Plots of Cl^- and Na^+ versus nitrate in water collected in Mahitsy

5.2. Total Dissolved Solids

More than 68% of the samples collected from wells in Mahitsy area contain TDS lower than 100 mg/L. When water mineralisation is low with a pH value higher than 5.5 (case of samples collected from wells in Tandrokomby and Fidasina), water-rock interaction exert control on the TDS level. The water type (Ca, Mg – HCO_3) reflects such situation. However, figure 2 indicating the correlation between Cl^- and TDS, and NO_3^- and TDS showed that the more TDS value increases, the more pollution processes influence the TDS level.

Indeed, the presence of nitrate at high concentration in well waters seems to correlate with the TDS value. A random distribution of data for the plots of Ca^{++}, Mg^{++}, HCO_3^-, SO_4^{--} against TDS (figure 3) supports the previous hypothesis.

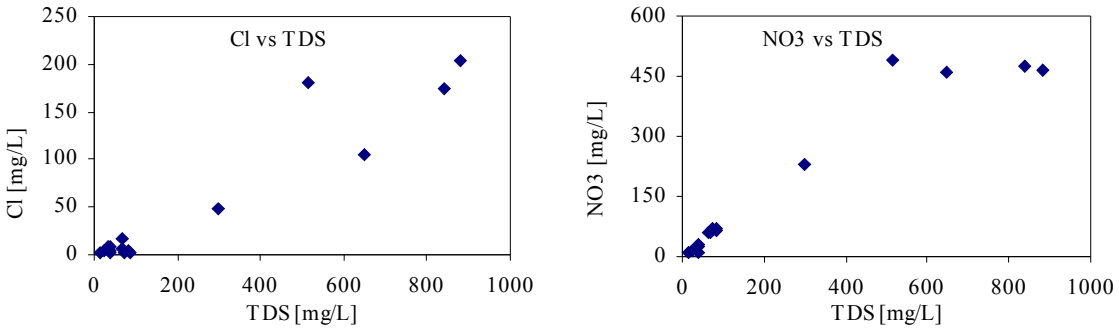

Figure 2. Plots of Cl^- and NO_3^- versus TDS for all water sampled in the study area

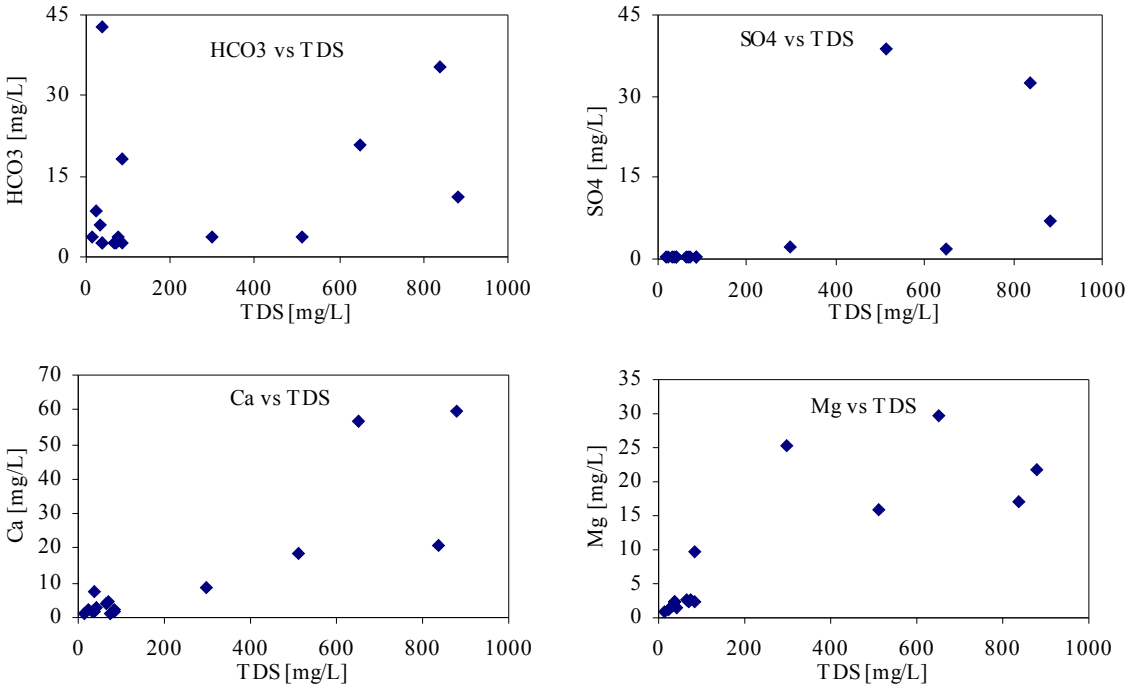

Figure 3. Plots of HCO_3^-, SO_4^{--}, Ca^{++} and Mg^{++} versus TDS for all water sampled in the study area

5.3. Manganese

More than 12% of water samples were of manganese concentrations below 20 µg/L and 25% of manganese levels between 20 µg/L and 50 µg/L. However, at concentration of around 20 µg/L in domestic water, manganese can produce

black precipitates, which may form coatings on the water pipes. 37.5% of sampled water contained manganese at concentration greater than 150 µg/L. At such concentration, Griffin [5] states that manganese can stain laundry and cause objectionable tastes in beverages. High concentrations of manganese were observed in well water featured by high level of nitrate.

5.4. Barium

The maximum concentration of barium in a sample of well water was 4967 µg/L, measured at a site in Fidasina. More than 31% of collected samples contained barium in concentration greater than 1000 µg/L. They were located in Fidasina, Antanivao and in Mahitsy county town. Elevated concentrations of barium were found in water containing nitrate greater than 50 mg/L.

6. CONCLUSION

Groundwater quality was assessed in Mahitsy by assessing 16 well water samples. At the scale of this investigation, well waters were contaminated by nitrate in Mahitsy. 60% of sampled waters contained nitrate of concentration exceeding 50 mg/L. Elevated nitrate occurred in well water collected in Mahitsy county town. It went with high content of manganese and barium. The maximum concentrations of manganese and barium were 976 µg/L and 4967 µg/L, respectively. The pH values ranged from 4.60 to 5.90 and the redox potential indicated oxidizing conditions ($64 < Eh < 140$). The TDS level varied between 16 mg/L and 881 mg/L. Most of the sampled waters were weakly mineralized (TDS < 100 mg/L). The correlations between nitrate concentrations, and chloride and sodium concentrations suggested relatively high concentrations of nitrate in well water may be caused by human activities such as latrines, animal manure storage, and domestic wastes stockpiling located near the wells.

More detailed study would be necessary to identify the contaminant water source. Use of isotope techniques may be useful as they could provide valuable information for such purposes.

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