Geochemical study of Shallow Aquifer in the Sedimentary Basement of Betioky, Southwestern of Madagascar

L.P. Fareze*, J. Rajaobelison, V. Ramaroson, F.F.A. Razafitsalama
Institut National des Sciences et Techniques-Madagascar, P.O Box 4279, 101 Antananarivo, Madagascar
mamypfarez@gmail.com

Abstract

Hydrochemical studies were undertaken for understanding the evolution of chemical process in the sedimentary aquifer basement of Mahafaly region, southwest of Madagascar. Four mainly groundwater types have been observed according to the geological formation: i. less mineralized groundwater with type of Na-Ca-Cl-HCO₃, from the phreatic aquifer of Isalo sandstone and clays formation covered by sandy shells in the Betioky hill, ii. more mineralized groundwater with type of Na-SO₄-Cl or Na-SO₄-Cl from Isalo sandstone formation at the east, iii. more mineralized groundwater dominated by Na-Ca-Mg-SO₄-Cl-HCO₃ water type, from the phreatic aquifer of the Jurassic and cretaceous formation, iv. groundwater from the alluvium formation at the Sakamena basin with Na-Ca-SO₄-HCO₃ water type. Saturation index results indicated that all groundwater in the study zone have negative values corresponding to under saturation of gypsum and halite while more samples have positive values on calcite and dolomite. Halite, calcite and gypsum dissolution, exchange of cation and precipitation of calcium bicarbonate are identified as dominants chemical processes conducting the evolution of groundwater mineralization in sedimentary aquifer of Betioky basin.

Keywords: Geochemical, Groundwater, Mineralization, Mahafaly, South-western of Madagascar.

Introduction

The sedimentary basin of Betioky is located at the Mahafaly peneplain in the south-western part of Madagascar. Groundwater which is the potential water resource in this region is affected by pollution from agricultural activity and mining exploitation. Lack of drinking water supply is one reason hindering the economic development in the Mahafaly region because the access rate of drinking water is less than 38% [1]. Since 2000, several projects were implemented to help the local population for their domestic utility. High groundwater mineralization was then found in some part of the area with electrical conductivity value reaches up to 5000µS/cm. Geochemical studies were conducted to identify the source of the groundwater pollution in the study zone using chemical and environmental isotopes [2]. So, the objective within this work is to characterize the geochemical evolution of groundwater for controlling its quality in this region. Hydrochemical studies must be identified and understood to evaluate the reasons of groundwater quality changes and to set up a plan for their protection[3]. This study was elaborated within the frame of IFS grants, which contributed financially in collaboration with INSTN-Madagascar and the NGOs working on the water supply field in the district of Betioky.

Description of area: The study zone is cantered at the Betioky city, between 23°15'S and 24°10' S latitudes and the 44°10'E and 45°00' E longitudes. The district of Betioky is surrounded by the district of Toliara in the north, by the district of Benenitra at the east boundary and the district of Ampanihy limits the study area in the south. The district consists of wide plains through which the Onilahy river flows westwards through the Mahafaly karstic plateau. The total geographical area of the study zone is 4500 km² with about 000100 inhabitants. The altitude of the plains varies between 100 m to 400 m. Globally, the district forms a large area of peneplain, where the middle part constitutes the study zone. It is bounded in its eastern border by the Sakoa basin and in the west by the Mahafaly plateau. Thus, the whole area can be divided into three categories, the Betioky hill, the alluvial plains and the east valley in Sakamena and sakoa basins. The district has a semi-arid climate characterized by relatively high temperature with mean value of 25°C. The average rainfall precipitation is 500 mm/yr and it rains only during the summer season.

Geological and hydrogeological settings: The study zone is a sedimentary basin, mainly formed by Neocene continental with sandstone and sandy clay extending below a shell of red sands[4]. The zone belongs to the Karroo group which distinguishes three series of geological formation namely Sakoa, Sakamena and Isalo. The Sakoa formation on the eastern side of area is a glacial series in the base attributed in the Upper Carboniferous, following the Permian coal series and red series. The Sakamena formation involves in the base a powerful schist sandstone series of upper Permian following clay with septaria corresponding at the upper Triassic. The Isalo formation corresponds at the large group of continental wastes. The Isalo group is composed into three subgroups. The first belongs at Isalo I which consists of

massive sandstone but soft poorly cemented, cross-bedded without fossil. In the middle southern part of the island, Isalo II presents a continental facies, with soft sandstone cross-bedded, alternating with green or red clays. Sometimes, a silicified wood fossil which is very large (Araucarioxylon, Cedroxylon) is the rest of fish (Ceratodus) Reptiles (Précrocodiliens).

In the western part of the study zone, middle Jurassic ends definitively the Karroo system. In the upper Jurassic, a generalized marine transgression affects the deposits along western the coastal of Madagascar represent by a calcareous limestone, marls and clays containing in abundance of Ammonites and Belemnites. The upper Jurassic forms in the western coastal a median fairly narrow with 10 to 20km. These layers which enriched in glauconite can form an impermeable cover protecting the aquifer. Clays contain always a crystal of gypsum.

The Lower Cretaceous is quite predominantly continental and continental spike. Again, it is reported as gypsiferous at several levels. However, alluviums formed with clayey sands are found along the river.

Groundwater in the sedimentary aquifer of Mahafaly region drains a vast area starting at the upstream on the crystalline peneplains of Androy and mahafaly. It flows westwards up to the Onilahy River across various geological formations. All the way, the main recharge zone area is located at level of crystalline basement where precipitation is more important[5]. In this zone, runoff acts only during heavy rains created a flood river and then can temporary supply the main aquifer. The main aquifer is fresh water in upstream except a few points presenting a high salinity. Groundwater is more mineralized while following the direction in downstream through the different geological formation.

Methodology

Sampling campaigns were undertaken during August 2012 and July 2013. 46 water samples were collected from different water sites. The sites of water sampling for isotopes and chemical analysis are dug wells, boreholes, springs and rivers. Dug wells are installed in different geological zones while the nearby boreholes drain the shallow aquifer. Field measurements include pH, electrical conductivity, temperature, dissolved oxygen and alkalinity. Samples destined for chemical analysis are filtered by whatman paper with 0.45µm diameter and collected in a polyethylene bottle 50 ml. samples for cation analysis are added a few drops of sulfuric acid. Cation and anion analyses are performed by Ion chromatography (DX-120) at X-fluorescence and Environment laboratory of INSTN-Madagascar. All results are treated with AQUACHEM software for determining the chemical water types. Ionic balance accepted is less than 5% which represents 80% of the samples. PHREEQC package is utilized for indices saturation calculation of each sample.
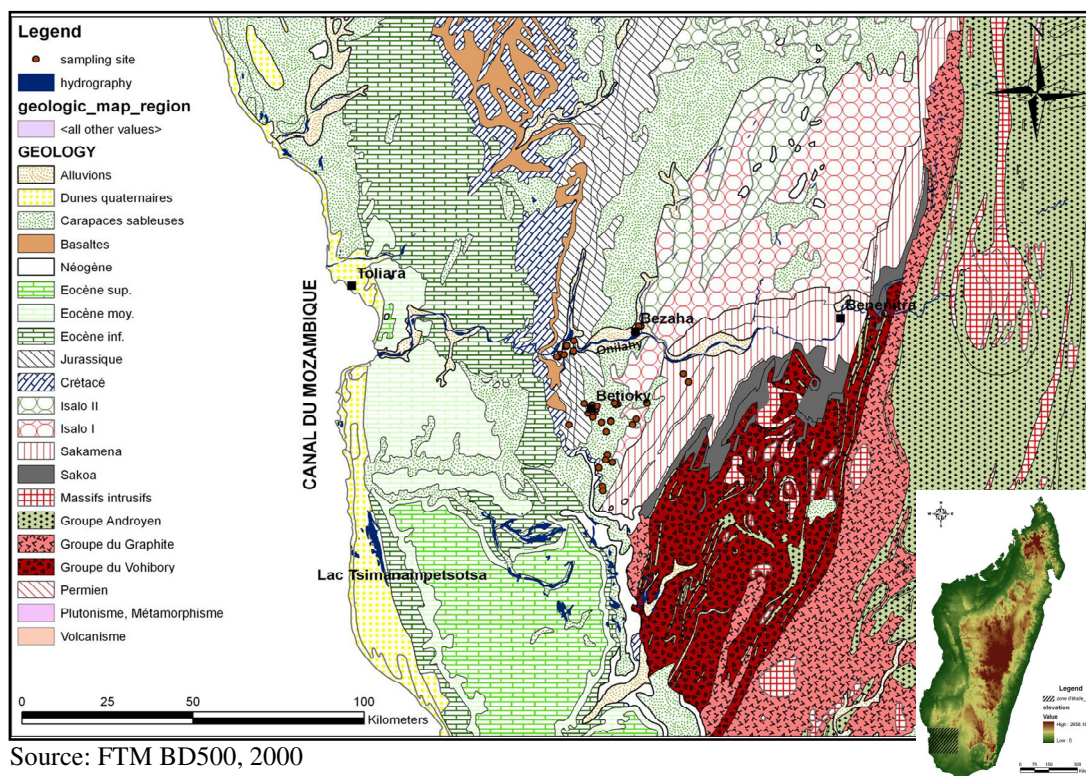

Figure-1
**Geological map of the study zone and sampling sites**

Results and Discussion

Hydrochemistry: The figure below shows the spatial distribution of the electrical conductivity (Figure-2) for the samples in the study area. The electrical conductivity value in Betioky hill is low with value not greater than 700µS/cm but it increases when mowing away from the recharge area. For the thermal springs, the electrical conductivity ranges from 79.9µs/cm to 147.9µs/cm corresponding to fresh water. In the eastern valley at the Sakamena basin, the maximum electrical conductivity is 883µs/cm. High mineralization with an electrical conductivity greater than 1800µs/cm is observed in groundwater at the western part due to the high nitrate concentration.

The mean pH value in the study zone is close to the neutral 7.13. For the groundwater in Betioky hill, the pH ranges from 6.63 to 7.94 while near of the river, it varies between 7.03 and 7.37. At the east valley to the Sakamena basin, the pH value ranges from 6.91 to 8.03. The dissolved oxygen values in groundwater samples at the Betioky hill varie between 2.16 mg/L and 7.06 mg/L with a mean value of 4.71 mg/L. This value increases to 5.07 mg/L at the east valley and ranges from 2.96 mg/L to 6.54 mg/L. Groundwater at the west and that near the river have dissolved oxygen values varying from 2.61 mg/L to 6.44 mg/L with a mean value of 4.89 mg/L.

Groundwater mineralization: Relative abundance of major ions is determined by their concentration in the collected samples. For the cations, the order is Na>Ca>Mg>K because of high sodium concentration, ranging from 8.45 mg/L to 789.97 mg/L, followed by Ca, ranging from 5.42 mg/L to 230.6 mg/L and Mg, which ranges from 8.45 mg/L et 124 mg/L. For the anions, relative abundance is Cl>SO_4>HCO_3, Cl is the dominant anion for all the samples, it ranges from 4.68 mg/L to 1443.37 mg/L, followed by SO_4, varying from 2.85 mg/L to 787.67 mg/L and HCO_3, which falls between 8.54 mg/L and 624 mg/L. Correlation of Spearman's values for the different ions and electrical conductivity is shown in Table-1. The contribution of each ion in the mineralization of groundwater is defined by the correlation coefficient (Table-1) with the electrical conductivity. Na, Mg and Ca ions contribute more in the groundwater mineralization with correlation coefficients of r^2=0.926, 0.921 and 0.913 respectively. For the anions, Cl and SO_4 contribute both in the ground water mineralization because they have correlation coefficients of 0.862 and 0.732 respectively. Thus, a correlation coefficient of 0.916 between Na and Cl indicates that they have a same origin. The same suggestion could be said of, Na and HCO_3 with r^2=0.747, and SO_4 and Ca on the one hand and SO_4 and Mg on the other hand, with positive correlation coefficients. The values are respectively 0.737 and 0.747.
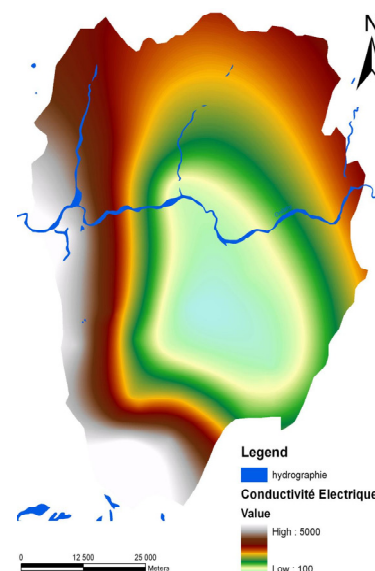
Figure-2
Spatial distribution of electrical conductivity on the groundwater in the sedimentary basin of Betioky
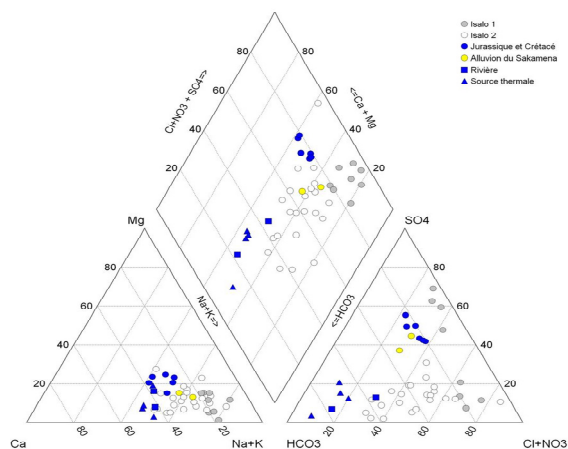
Table-1
Spearman correlation matrix of the chemical results for all samples

R^2	CE	Ca	Na	Mg	K	Cl	HCO_3	SO_4	NO_3
CE	1	**0.921**	**0.926**	**0.913**	0.533	**0.862**	0.669	**0.732**	0.323
Ca		1	**0.763**	**0.888**	0.521	0.678	0.651	**0.737**	0.423
Na			1	**0.789**	0.404	**0.916**	**0.747**	0.650	0.138
Mg				1	0.602	0.696	0.624	**0.704**	0.505
K					1	0.436	0.245	0.165	0.595
Cl						1	0.586	0.419	0.057
HCO_3							1	0.605	-0.067
SO_4								1	0.034
NO_3									1

Hydrochemical facies: Piper diagram were used to determine the patterns of spatial change in the hydrochemistry among geological units, along a line of section or along a path line[6,7]. The results of the chemical analyses of the wells in the study area were shown on the following figure (Figure-3) for hydrochemical facies.

Groundwater chemical type in the study zone is much dispersed and varies according their geographical and geological location. In fact four groups have been distinguished in the study area according to their chemical water type (Figure-3, Table-2). The first group is the ground water located at the Betioky hill with Na-Ca-Cl-HCO$_3$ type, probably as result of interaction with different rocks along the flow path from the recharge zone having a Na-Ca-HCO$_3$-Cl water type.

The second group belongs to the groundwater in the alluvium plain. Groundwater in this area has a mixed cation Na-Ca-Mg-SO$_4$-Cl-HCO$_3$ type. Groundwater is more mature in this zone. The third group is the groundwater in the alluvium Sakamena basin with a Na-Ca-SO$_4$-HCO$_3$ type. Groundwater in this part of the study area is mixed with river. The fourth group is the groundwater in the Isalo sandstone formation in the east valley with a Na-SO$_4$-Cl or Na-Cl type. It may be due to the ascending of high mineralized deep groundwater in this zone.

Table-2
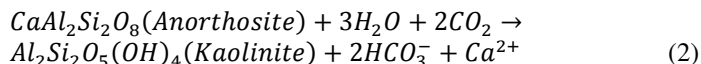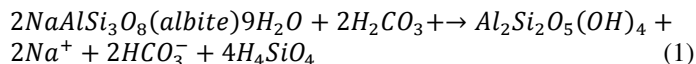**Different chemical type of water samples in the study zone**

Zone	Geological formation	Location	Water type
A	Isalo 2	Betioky hill	Na-Ca-HCO$_3$-Cl
B	Sakamena	Sakamena basin	Na-Ca-SO$_4$-HCO$_3$
C	Isalo 1	South and east valley	Na-Cl or Na-SO$_4$-Cl
D	Jurassic and cretaceous	Near the river	Na-Ca-Mg-SO$_4$-Cl-HCO$_3$
river	Alluvium	Tongobory	Na-Ca-HCO$_3$
Springs	Isalo 2	Bezaha	Ca-Na-HCO$_3$

Geochemical process: Gibbs plot was used to define the main chemical process controlling the chemistry of groundwater in the study zone[8]. The most of the data point plots in the rock dominance zone on the diagram of Gibbs (Figure-4). It indicates that interaction of water-rocks controls majorly the groundwater chemistry of this area.

Figure-3
Piper diagram for all well water samples
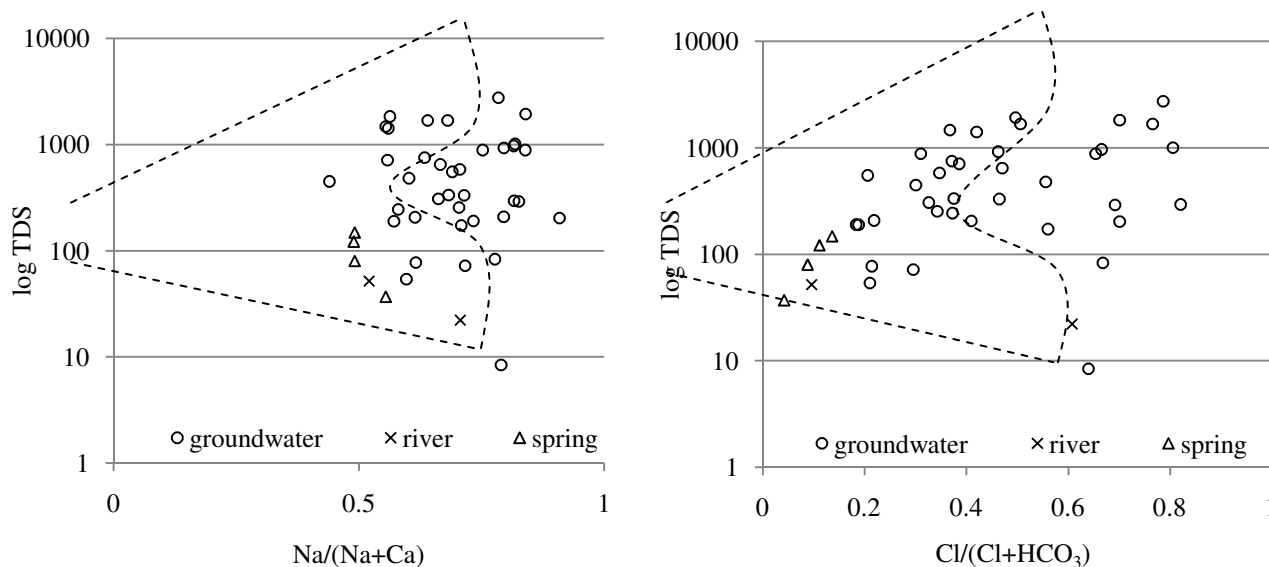
Figure-4
Gibbs diagram for all samples

For the shallow groundwater which is tapped in sandstone, clay and coarse sand, alteration of silicates minerals are probable sources of major cations[9]. Weathering of silicate is the principal geochemical process which controls the most groundwater mineralization. It can be illustrated by the following equations:

$$2NaAlSi_3O_8(albite)9H_2O + 2H_2CO_3 + \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4 \quad (1)$$

$$CaAl_2Si_2O_8(Anorthosite) + 3H_2O + 2CO_2 \rightarrow Al_2Si_2O_5(OH)_4(Kaolinite) + 2HCO_3^- + Ca^{2+} \quad (2)$$

In the sedimentary aquifer system, silicates weathering processes cannot take place as the pH value of between 4 and 6.5 However, the minimum pH value obtained on groundwater in the study area is 6.56 meaning that weathering of silicate minerals should not be the major source of mineralization for studied aquifer system. Since the geological formation of the study area is enclosed by silicified wood then alteration of feldspars anorthosite can be assumed the major source of ions present in groundwater in the clay and sandstone formation of the Isalo aquifer the degree of contribution silica must be justified by the analysis of SiO_4 in the collected water samples[10,11].

While the correlation graph between Ca^{2+} and HCO_3^- (Figure-5) has two trends forming different groups of waters. The first group is the water with type of Na-Ca-Cl-HCO_3 having a Ca/HCO_3 ratio less than 1. It assumes that dissolution of calcite in the calcareous marl formation occurs but depleted of Ca^{2+} becomes from cation exchange. The second group is the water with Na-Ca-Mg-SO_4-Cl-HCO_3 type having Ca/HCO_3 ratio more than 1. It means that calcite and gypsum dissolution occurs simultaneously in the aquifer which increases the calcium concentration.

On the other hand, silicate minerals dissolution may contribute to the groundwater mineralization in the Jurassic and Cretaceous formation with is justifying by the good correlation between Na and HCO_3 (Figure-5) but it is not the principal source of ions in the groundwater.
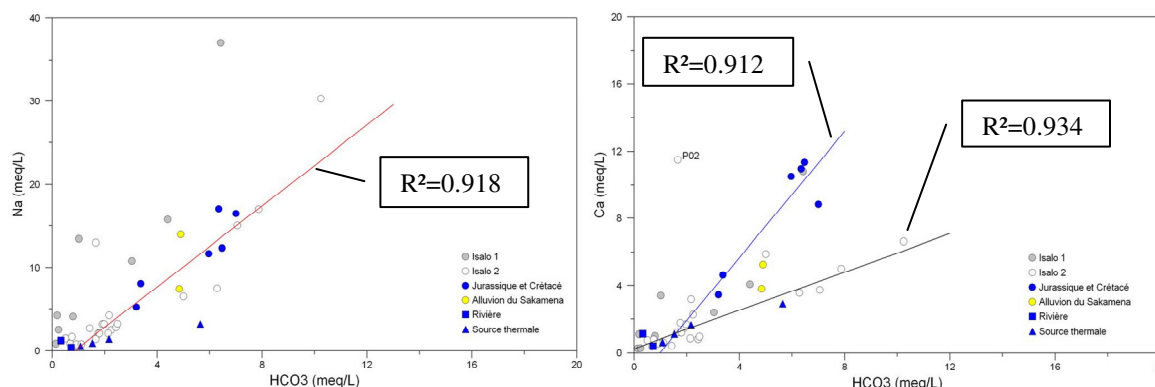

Figure-5
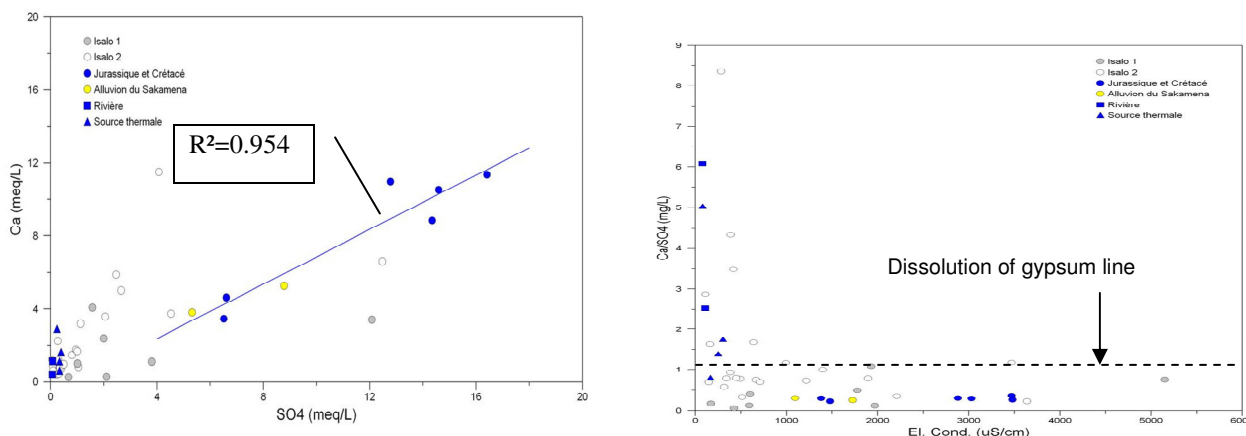**Graph of HCO_3^-, Na^+ and Ca^{2+}**

Figure-6
Correlation between SO_4^{2+}, Ca^{2+} and Ca/SO_4 ratio with electrical conductivity

For groundwater where sulfate is the major anion occurs from dissolution of gypsum because the coefficeient of correlation is 0.954 but, lower Ca^{2+}/SO_4^{2-} (Figure-6) ratio can be interpreted as results of $CaCO_3$ precipitation causing by the reaction forming sandstone of materials in the zone [12].

A positive correlation (r^2=0.916) between sodium and chloride ions is observed. Some point plots along the equiline, which indicates that dissolution of halite from saline clayed formation in Sakamena basin is the probable source of chloride ion in the groundwater in this area, and it is the effect of high evapotranspiration marking by the semi arid zone. Therefore, Na/Cl ratio (Figure-7) more than to 1 for another sample indicates that cation exchange is evidently introduced in the geochemical process on this groundwater[13].

This assumption is again identified by the relationship between Na^+ and Ca^{2+} (Figure-8). All the samples are plotted below the equiline indicating that Ca^{2+} present in groundwater replaces Na^+ releases from clay minerals. Moreover, Ca /Mg ratio is superior than 1 suggests that cation exchange can be responsible of Mg^{2+} ion content in the groundwater sample with Na-Ca-Mg-SO4-Cl-HCO_3 type.

Saturation index: Saturation index (SI) is defined as the logarithm of the quotient of the ion activity product (IAP) and solubility product constant (KSP). PHREEQC was applied to calculate the saturation index for each sample [14].

$$SI = \log \frac{IAP}{K_{SP}} \tag{3}$$

The IAP is function of ionic strength, temperature and complex formation. It was been calculated from the activity determined analytically by the concentrations. It is similar with solubility product but using equilibrium solubility data corrected to the appropriate water temperature. The saturation index indicates a saturation of solution in equilibrium with a mineral phase.
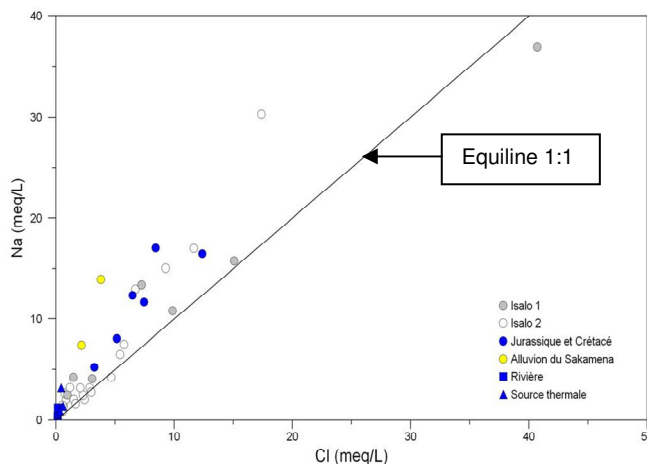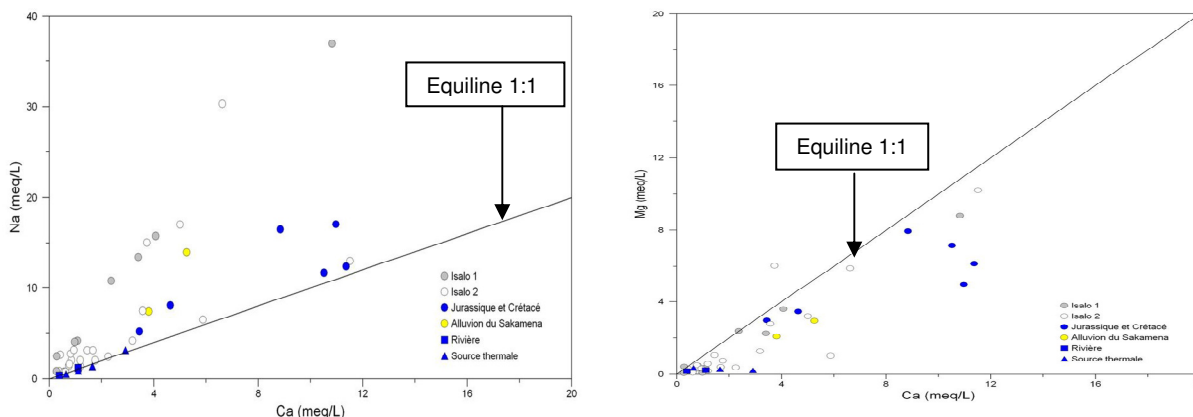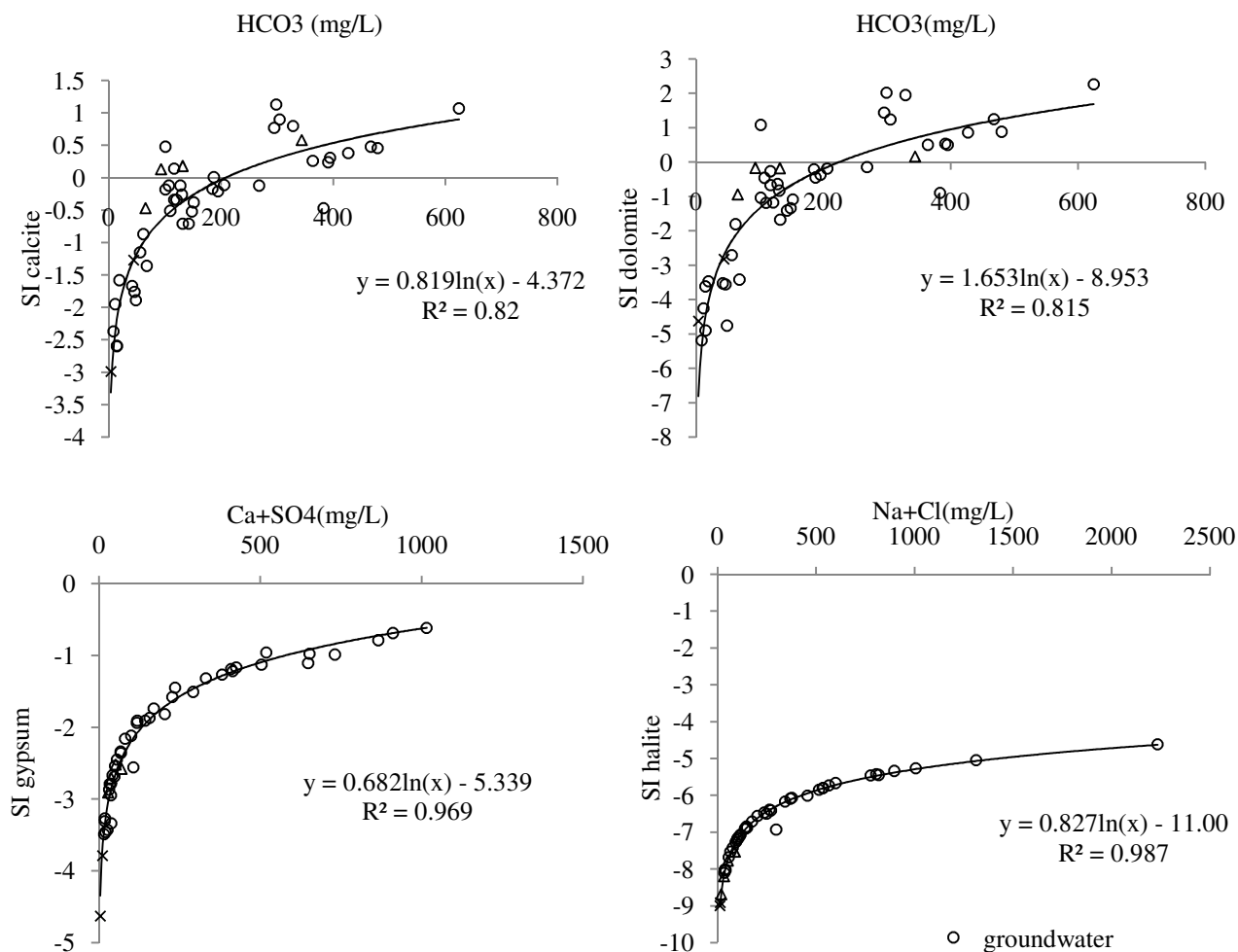

Figure-7
Graph of Na and Cl

Figure-8
Graph of Na^+, Mg^{2+} and Ca^{2+}

Figure-9
Saturation Indexes for all samples

Positive saturation indexes value means that oversaturation of calcite and dolomite dominates on the groundwater samples from Jurassic and cretaceous formation (Figure-9). Dolomite dissolution increases Ca^{2+}, Mg^{2+}, and HCO_3^- concentration into the solution and it means that under-saturation of dolomite occurs and oversaturation means that calcite and dolomite precipitates in the system. On the other hand, all water samples under-saturate of gypsum and halite. Under-saturation with respect to gypsum shows that groundwater could feasibly dissolve gypsum and then, Ca^{2+}, and SO_4^{2-} ion concentrations in the solution would increase [15]. The saturation indexes of gypsum versus $Ca+SO_4$ (mg/L) concentrations graph gives a good correlation coefficient close to 1, this indicates that dissolution of gypsum increases Ca^{2+}, and SO_4^{2-} concentrations in the samples. Some samples have a saturation index value close to zero meaning that they are in equilibrium with the mineral phase or oversaturated of calcite and dolomite simultaneously provoking a more dissolution and high mineralization following the direction of the groundwater flow.

Conclusion

Hydrochemical data analyses of samples collected in the sedimentary aquifer of Mahafaly region were investigated to identify geochemical processes for the groundwater mineralization. The results show that four different types of water were observed in the study zone according to their geological formation such as Na-Ca-HCO₃-Cl type, Na-(SO₄)-Cl type, Na-Ca-Mg-SO₄-Cl-HCO₃ type and Na-Ca-SO₄-HCO₃ type respectively at the Isalo sandstone clays formation, Isalo sandstone formation, Jurassic and cretaceous formation, and Sakamena alluvium formation. Carbonate minerals dissolution namely calcite and halite following cation exchange product more ions for the groundwater in the Isalo group, while dissolution of gypsum and calcite with cation exchange are the dominant mineralization processes for the groundwater in the Jurassic and cretaceous formation and the Sakamena alluvium.

Acknowledgements

References

1. Ministry of Water. (2012). Report on the environmental status in Madagascar. Antananarivo, Madagascar.

2. Li X., Zhang L. and Hou X. (2008). Use of hydrogeochemical and environmental isotopes for evaluation of groundwater in Qingshuihe basin, Northwestern China. *Hydrogeological Journal*, 16, 335-348.

3. Elango L. and Senthilkumar L. (2013). Geochemical process controlling the groundwater quality in lower Palar river basin, southern India. *Indian Academy of Science, Journal of Earth System*, 122(2), 419-432.

4. Bésairie H. and Collignon M. (1971). Geology of Madagascar. Geological annals of Madagascar, 35, Antananarivo, Madagascar.

5. Aurouze J. (1959). Hydrogeological of southern Madagascar. Thesis. Université de Paris, France.

6. Raji B. and Alagbe S. (1997). Hydrochemical facies in parts of the Nigerian basement complex. *Environ. Geol.*, 29, 46-49.

7. Domenico P. and Schwartz F. (1998). Physical and Chemical Hydrology. John Wiley & Sons Inc., New York, USA.

8. Gibbs R.J. (1970). Mechanisms controlling world water chemistry Science. 17, 1088-1090.

9. Bowser C.J. and Jones B.F. (2002). Mineralogic control on the composition of natural waters dominated by silicate hydrolysis. *American Journal of Science.*, 302, 582-662.

10. Bésairie H. and Collignon M. (1946). Geology of Madagascar. Geological annals of Madagascar, 12. Antananarivo, Madagascar.

11. Nicolini E. (1980). Isotopes of the zones on precipitations recorded in Antananarivo and IAEA station networks of occidental Indian Ocean. Thesis, Université Pierre Marie Curie, Paris 6, France.

12. Guyot L. (2002). Hydrogeological recognition for water supply in the plain coastline of semi-arid zone, southwestern of Madagascar. Thesis, Université de Nantes, France.

13. Liu F., Song X., Yang L., Zhang Y., Han D. and Ma Y. (2015). Identifying the origin and geochemical evolution of groundwater using hydrochemistry and stable isotopes in the Subei Lake basin, Ordos energy base, Northwestern China. *Hydrology Earth System Science*, 19, 551-565.

14. Parkhurst D.L. and Appelo J.C.A. (1999). User's guide to PHREEQC: A computer program for speciation, reaction path, advective transport and inverse geochemical calculation. USGS Investigation No 99-4259, Denver Colorado, United States of America.

15. Stumm W. and Morgan J.J. (1996). Aquatic chemistry: Chemical equilibria and rates in natural waters. John Wiley and Sons, New York, United States of America.