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Study of the Mineralization of the Quaternary and Pliocene Aquifers of the Department of Diffa (South-East Niger)

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ABSTRACT

The aim of this study is to characterize the hydrogeochemical and microbiological context of the captured aquifers, for a better understanding of the mineralogical and microbiological quality of groundwater in the Diffa department. The results showed that the temperature of the quaternary and Pliocene aquifers ranged from 23,3°C to 43,2°C, and 25,5°C to 38,7°C, respectively, with averages of $30,17 \pm 3,37^{\circ}C$ and $33,68 \pm$ 5,28°C, respectively. The pH of the waters vary respectively between 6.75 and 8.53 and 6, 3 and 6, 82 with respective averages of 7, 46 ± 0 , 46 and 6, 53 ± 0 , 20. The conductivities vary respectively between 30 and 7770 µS/cm, and 627 and 1680 µS/cm with respective averages of 764, 1 µS/cm and 1065µS/cm. Most of the water samples have physicochemical parameters below the standards set by the WHO. However, these water points have contents higher than the standards, in manganese (70, 21%), bicarbonates (54, 89%) and conductivity (51, 06%). The ACPN and the CHA indicated that the mineralization of the analyzed waters was controlled by three (3) phenomena including mineralization by hydrolysis of minerals, infiltration and by oxidationreduction. The Piper diagram showed that 71, 42% of the quaternary groundwater belongs to the bicarbonate family and 28, 58% to the chloride family. All Pliocene groundwater is chlorinated. Bacteriological analysis revealed that 14, 70% of the waters analyzed were of poor quality. Indeed, all the quaternary groundwater is contaminated. This contamination is the consequence of recent pollution of human or animal origin.

INTRODUCTION

The conservation of the quality of the environment is a pervasive concern in our societies at the eve of the 21st century. The alteration of the natural environment, particularly water resources, has gradually become a global concern.

In Africa, groundwater in urban and rural areas is subjected to multiple constraints due to high population growth and inadequate or lack of sanitation (Groen J. et al., (1988), Boubakar Hassane A (2010)).

Sewerage systems, septic tanks, urban and industrial wastewater and solid waste are the main sources of groundwater pollution in urban areas. In peri-urban and rural areas, the use of agricultural inputs contributes significantly to the degradation of groundwater and river quality (Boubakar Hassane A, 2010).

In Niger, the population growth experienced by the country after its independence, which rose from 3 million inhabitants in 1960 to 17,138,707 (INS, 2014), has resulted in an increase in primary needs of the population, including access to drinking water for urban and rural populations. Thus, according to the report, *Agir pour l'eau et l'assainissement au Niger (Acting for Water and Sanitation in Niger)* of the *Solidarité-Eau programme* of December 2013, 50% of Niger Republic citizens and 64% of the inhabitants of Diffa do not have access to drinking water and barely 20% of Niger Republic citizens and 3% of the inhabitants of Diffa have access to improved sanitation facilities to relieve themselves. This great demographic pressure on natural resources results in increased production of waste of all kinds. Thus, for the past few decades, the studies carried out on water resources in Africa by Kouassi *et al.*,(2008, 2010 and 2012a), (Kouassi *et al.* 2011) and (Boubakar Hassane A., 2010) have reported numerous pollution sources both at the level of surface and groundwater, in several localities of which the department of Diffa. The present study, which focuses on the Diffa department, was undertaken in order to better understand the physicochemical and microbiological qualities of the groundwater resources of the aquifers tapped in this area.

The objective of this study is to characterize the hydrogeochemical and microbiological context of the aquifers collected, for an understanding of the mineralogical and microbiological quality of the groundwater of the Diffa department.

To attain the objective of this study, field and laboratory work was carried out in both hydrogeochemical and microbiological analyzes.

The data collected were processed using a combination of a variety of statistical methods, including Standard Principal Component Analysis (SPCA) and Hierarchical Ascending Classification (HAC).

Presentation of the study area Geographical location

The department of Diffa, with a surface area of 55076 Km² is located in the south-eastern part of Niger, and in the north-western part of the Lake Chad basin (Diffa region). It is bordered to the east by the department of Bosso, to the north by the department of N'guigmi, to the west by the department of Maïné-Soroa and to the south by the Federal Republic of Nigeria (Figure 1). It is partly located in the Sahelian band whose rainfall is characterized by great spatial and temporal variability. Low rainfall and surface runoff is compensated by groundwater resources.



Figure No. 1: Location map of the Diffa department

The relief of the study area is characterized essentially by the dune systems of the Kadzell and the valleys of the Komadougou Yobé. As outcropping geological formations, they are dominated by deposits dating from the Quaternary period, notably the alluvial deposits of the Kadzell, the current deposits of the Komadougou Yobé, the ferruginous sandstones of the Continental Terminal observed in places in the valley of the Komadougou Yobé and the Agadem massif/mount. To these are added the deposits of the Tal cord and those of the ancient and recent ergs of the Manga dune system (BRGM, 1966 geological reconnaissance map of the Manga).

The Komadougou Yobé is the only river in the department. Its hydrological regime is defined by the upstream watershed in Nigeria. Its flow, which starts with the rainy season (July) reaches its maximum in November or December and becomes nil a few months later.

The two main aquifer systems exploited in the region are the Quaternary sand and sandy-clay series, between 0 and 100 m deep, containing the water table; and the Pliocene sands and silts, between 250 and 400 m deep, containing a captive artesian water table (Greiger, 1979). These two aquifers extend into Chad and Nigeria (UNDP-UNESCO-CBLT, 1972, Leduc C. *et al.*, 1998).

The Pliocene aquifer



The Pliocene water table is only identified towards the centre of the Lake Chad basin. Its piezometric level, which apparently varies very little, is between 310 and 320 m.

It is captive everywhere and the boreholes are often artesian. These fossil waters are moderately mineralized (700 to 3600 μ S/cm). The roof of the Pliocene aquifer is constituted by thick and uniform clays. Geological (the thickness and homogeneity of these clays), hydrodynamic (the persistence of a very strong difference in charge, which can exceed 40 m) and hydrochemical (the contrast of chemical and isotopic facies) considerations indicate the absence of significant communication between the two (2) Pliocene and Quaternary aquifers south of the 15°N parallel. The waters are sodium sulphate, for two thirds of the analyzes, or sodium chloride (Schneider 1969, UNDP-UNESCO-CBLT 1972, Leduc C. *et al.*, 1998).

Groundwater

The Quaternary zone, which varies in depth from 0 to 100 m, appears to flow from the northern edge of the Mounio crystalline massif/mount towards the center of the Lake Chad basin. The hydraulic gradient varies from 0.1 to 2.5‰. The piezometry varies very little during the year except along the Komadougou Yobé River (up to 2 m) whose flooding recharges the water table. The Kadzell zone is a depressed water table whose only explanation seems to be evaporation, necessarily reduced due to the great depth, combined with very low permeability. There are obviously significant variations in facies in the Quaternary sedimentation, linked to the wanderings of the Komadougou Yobé, variations in the level of the lake, and the succession of arid and wet episodes. The present surface of the Kadzell, which is very clayey, and its northern edge of recent dunes illustrate this sedimentary variability. However, the whole constitutes a thick and continuous aquifer (Leduc C., 2003).

MATERIALS AND METHODS

The analysis of the physicochemical parameters covered forty-seven (47) water points including forty-two (12) cemented wells and thirty (30) boreholes capturing the water table of the Manga and five (05) capturing the Pliocene water table. The bacteriological analysis covered thirty-four (34) water points.

These 47 water points are distributed in thirty-eight (38) villages in three (03) communes of the department of Diffa. These 47 water points were selected by the systematic sampling method. A bacteriological analysis was carried out only on thirty-four (34) water points. These samples were analyzed at the Water Quality Monitoring Laboratory of the Regional Directorate of Hydraulics and Sanitation (DRH/A) in Diffa.

Several analytical methods were used/Analytical Methods

The Physical Reader Method for the determination of the parameters of conductivity (Cond) and temperature (T^o C) by a conductivity meter branded WTW and the hydrogen potential (pH) by a pH meter branded Waterproof.

The spectrophotometric method: spectrophotometry is a quantitative method of analysis which consists in measuring the absorbance or optical density of a given chemical substance, generally in solution. A spectrophotometer type HACH DR/2010 was used to determine the following chemical parameters:

Sulphate (SO_4^{2-}) determined by pouring the reagent (Sulfaver 4) into 10 ml of a sample contained in a tube and stirring until a homogeneous solution is obtained. This solution was measured with a spectrophotometer at a wavelength of 650 nm.

Nitrates (NO_3^{-}): Nitrate ions were determined by pouring the reagent (Nitraver3) into 10 ml of the sample contained in a tube and shaking until the reagent was dissolved. This solution was measured with a spectrophotometer at a wavelength of 520 nm.

Fluorides (F-): Fluoride ions were complexed with the SPADNS reagent at the wavelength of 625 nm.

Manganese (Mn $^{2+}$): Manganese was oxidized to permanganate using manganese periodate in an acidic medium. The compound thus formed could be determined spectrometrically at a wavelength of 425 nm.

Total iron ions (FeT): the reagent used was forever 1 and 2 in a 10 ml sample, the solution obtained was analyzed spectrophotometrically at a wavelength of 510 nm to determine the iron content.

Potassium (K+) ions were determined by molecular absorption photometry. The principle consists in complexing the potassium ion from the reagents; potassium 1, potassium 2 and potassium 3 in 10 ml of the sample. The solutions thus obtained were placed in a Wagtech 7100 photometer.

The volumetric method was an assay technique used in analytical chemistry to determine the concentration of a chemical species in solution. The following parameters were determined by this method;

Chlorides (Cl-) were determined by measuring the sample with mercuric nitrate, the reagent used was diphenylcarbon. At the turn (dark blue color), the chloride was equal to the amount of mercuric nitrate poured to obtain the turn*4*800/20;

Calcium (Ca²⁺) was calculated from the Calcium Hardness (Dcal) which was determined by assaying the specimen with 20% EDTA by pouring one (1) to three (3) drops of Sodium Hydroxide and Buffer Hardness 1 and NaOH, the reagent used was Calver. At the turn (blue color), the Dcal value was given by: Dcal = the amount of EDTA added*4*800/20 and Ca= Dcal*0.4; The total hardness or water content (TH) was determined by assaying the sample with EDTA, and with manver as reagent used by pouring two (2) to three (3) drops of buffer solution into the sample before starting the assay. At the turn (dark blue color), the TH=quantity of EDTA poured to obtain equilibrium*4*800/20;

The Complete Alkalometric Titration (TAC) was determined by assaying the sample with sulfuric acid and with bromocresol as reagent, at equilibrium (pink colour). The TAC was equal to the quantity of sulphuric acid poured to obtain equilibrium*4*800/20;

Magnesium was calculated from the magnesium hardness (Dmg) where Dmg=TH-Dcal and Mg=Dmg*0.243;

Bicarbonates (HCO₃²⁻) were determined from TAC by the following relationship: $[HCO_3^{2-}]$ =TAC*1.22.

The method by calculation of the ions

Here only the sodium ions were determined by the ion calculation method using the ion balance of water, i.e. the sum of the cations equals that of the anions.

The bacteriological analysis method.

The bacteriological analysis concerned thirty-four (34) water points for which typical (faecal and total) and atypical coliforms were determined by filtering 100 ml of each sample through membranes (filter papers) which were inoculated into the culture media, all of which were placed in an incubator of the AQUASAFE MSL50 brand. There were two (2) inoculation batches for each sample (i.e. for each sample 100 ml* 2 were filtered through two (2) different membranes), one for the determination of faecal coliforms incubated at 44°C for 24 hours and the other for total coliforms incubated at 37°C for 18 hours. Atypical coliforms were determined in each of the two (2) batches. The number of yellow spots observed on each membrane incubated at 44 °C for 24 hours corresponds to the number of faecal coliforms per 100 ml of sample water.

The number of yellow spots observed on each membrane incubated at 44 °C for 24 hours corresponds to the number of faecal coliforms per 100 ml of water of the sample filtered through that membrane and that of the membrane incubated at 37 °C for 18 hours corresponded to the number of total coliforms. The sum of the black spots observed on the two (2) membranes of the same sample, i.e. one in the first batch and the other in the second batch, corresponded to the number of atypical coliforms per 100 ml of water of the sample concerned.

All the physicochemical parameters determined were analyzed and processed using descriptive statistical methods which made it possible to compare the average contents of the Quaternary and Pliocene groundwater. Also, comparisons of the parameters of the water points within the same water table and the average of each parameter to its standard set by the WHO (WHO, 2017) were made. These parameters were the subject of descriptive statistical analyzes and Standard Principal Component Analysis (SPCA) coupled with Hydrochemical Methods for the study at the origin of the mineralization phenomena. The NPAC thus used made it possible to characterize the quality of the groundwater, but also to contribute to the planning of a follow-up control of this one. Finally, an Ascending Hierarchical Classification (AHC) of water point data was carried out. As for the bacteriological data, they were subjected to a simple descriptive analysis in order to classify the waters.

Results of the hydrogeochemical and microbiological characterization

Spatialization of sampling sites

The distribution of sample collection sites across the mapping provided an overview of the mesh. The sites concerned were shown in Figure 2.



Figure No. 2: Distribution map of sampling sites

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Results of descriptive statistics

All the data obtained following the analyzes of the physicochemical parameters of fortyseven (47) samples taken were subjected to basic statistical tests with the Mini tab software, including the test of two (2) samples which consisted in comparing the parameters of the Pliocene water table and those of the Quaternary. The results of this test are given in Table 1. This table shows that among the parameters tested, only the pH (P=000) and the HCO_3^{2-} (P=0.001) of the two (2) aquifers show significant differences because their probabilities are lower than the usual threshold of significance which is 0.05.

The results of the normality test, which consisted in verifying the normality of the distribution of each parameter around its regression line, are given in Table 2.

Table No. 1: 7	Fest results for	comparison of	two (2) slicks:	Q (Quaternary	sheet) and P
(Pliocene shee	et)				

Echantillons	Ν	Variables	Moyenne	Ecart-type	P-value	
Q	42	nЦ	7,46	0,46	0.000	
Р	5	pm	6,53	0,20	0,000	
Q	42	т	30,17	3,37	0.220	
Р	5	1	33,68	5,28	0,220	
Q	42	Cond	764,1	1260	0 203	
Р	5	Colla	1065,4	437	0,275	
Q	42	HCO ₂ -	203,82	104,6	0.001	
Р	5	11003	125,51	30,38	0,001	
Q	42	Cl	42,04	69,47	0.095	
Р	5	CI	200,4	161,20	0,095	
Q	42	SQ. ²⁻	177,3	442,1	0 231	
Р	5	504	413,6	356,6	0,231	
Q	42	F -	0,68	0,39	0.312	
Р	5	1	0,46	0,39	0,312	
Q	42	NO ₂ -	6,46	7,70	0.927	
Р	5	1103	6,02	9,78	0,927	
Q	42	N_{2}^{+}	87,79	141,64	0.24	
Р	5	114	172	141,65	0,24	
Q	42	K^+	9,64	10,38	0.659	
Р	5	К	8,65	3,35	0,057	
Q	42	FeT	0,17	0,20	0.445	
Р	5	101	0,51	0,88	0,775	
Q	42	Mn^{2+}	0,60	0,31	0.402	
Р	5	14111	0,86	0,6	0,402	
Q	42	Ca^{2+}	50,96	31,45	0.892	
Р	5	Cu	47,74	48,41	0,072	
Q	42	Mg2+	8,42	10,41	0.126	
Р	5	141621	34,24	29,70	0,120	

Table No. 2	Results o	of the normality test
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Variables	Ν	Min	Max	Moyenne	Ecart-type	P-value
nЦ	42	6,75	8,53	7,46	0,46	0,038
pm	5	6,3	6,82	6,53	0,20	0,015
т	42	23,3	43,2	30,17	3,37	0,10
1	5	25,5	38,7	33,68	5,28	0,150
Cond	42	30	7770	764,1	1260	0,010
Collu	5	627	1680	1065,4	437	0,150
HCO-	42	81,98	585	203,82	104,6	0,010
псоз	5	83,94	161,04	125,51	30,38	0,150
Cl	42	0,8	328	42,04	69,47	0,010
CI-	5	46,86	432	200,4	161,20	0,150
SO. ²⁻	42	0	920	177,3	442,1	0,010
304	5	118	940	413,6	356,6	0,150
Б	42	0	1,8	0,68	0,39	0,150
1'-	5	0	0,9	0,46	0,39	0,150
NO. ⁻	42	0,5	37,84	6,46	7,70	0,010
NO ₃	5	0,4	23,4	6,02	9,78	0,010
No^+	42	0	847	87,79	141,64	0,010
INA	5	3	348	172	141,65	0,150
K +	42	3	58,4	9,64	10,38	0,010
К	5	4,5	12,42	8,65	3,35	0,150
FoT	42	0	0,78	0,17	0,20	0,010
101	5	0	2,08	0,51	0,88	0,010
Mn^{2+}	42	0	1,3	0,60	0,31	0,150
IVIII	5	0	1,5	0,86	0,6	0,150
Ca^{2+}	42	14,2	164	50,96	31,45	0,010
Ca	5	1,92	128	47,74	48,41	0,094
$M\alpha^{2+}$	42	0	50,55	8,42	10,41	0,010
Mg ²⁺	5	1,94	64	34,24	29,70	0,150

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Variables	Ν	Min	Max	Moyenne	Ecart-type	P-value
лЦ	42	6,75	8,53	7,46	0,46	0,038
pm	5	6,3	6,82	6,53	0,20	0,015
т	42	23,3	43,2	30,17	3,37	0,10
1	5	25,5	38,7	33,68	5,28	0,150
Cond	42	30	7770	764,1	1260	0,010
Cond	5	627	1680	1065,4	437	0,150
UCO.	42	81,98	585	203,82	104,6	0,010
HCO3	5	83,94	161,04	125,51	30,38	0,150
Cl	42	0,8	328	42,04	69,47	0,010
CI	5	46,86	432	200,4	161,20	0,150
SO ² -	42	0	920	177,3	442,1	0,010
504-	5	118	940	413,6	356,6	0,150
Б-	42	0	1,8	0,68	0,39	0,150
Г	5	0	0,9	0,46	0,39	0,150
NO	42	0,5	37,84	6,46	7,70	0,010
NO ₃	5	0,4	23,4	6,02	9,78	0,010
N_{0}^{+}	42	0	847	87,79	141,64	0,010
Ina	5	3	348	172	141,65	0,150
\mathbf{V}^+	42	3	58,4	9,64	10,38	0,010
K	5	4,5	12,42	8,65	3,35	0,150
EaT	42	0	0,78	0,17	0,20	0,010
гет	5	0	2,08	0,51	0,88	0,010
M. 2+	42	0	1,3	0,60	0,31	0,150
1 V1 11	5	0	1,5	0,86	0,6	0,150
$C a^{2+}$	42	14,2	164	50,96	31,45	0,010
Ca	5	1,92	128	47,74	48,41	0,094
M~2+	42	0	50,55	8,42	10,41	0,010
NIg ⁻¹	5	1,94	64	34,24	29,70	0,150

This table shows that for the Pliocene sheet, only the pH, nitrates and iron do not follow a normal distribution law because the P values are below 0.05 (Pearson's significance threshold). On the other hand, for the quaternary layer, only fluoride and manganese ions follow a normal distribution.

Table 3 shows the difference between the mean of each parameter and its set standard. The standard values are maximum allowed values, they are compared to the values of the mean of a parameter by the following relationship: T= (Sample mean-Fixed standard)/ ErT.mean.

The above table shows that only conductivity and manganese have averages above their standards and only for the Pliocene water table.

Variables	Ν	Moyenne	Ecart-T	Т	ErT.moyenne	Р	Normes
пЦ	42	7,46	0,46	-0,45	0,07	0,65	6 5 <nu<8 5<="" td=""></nu<8>
pm	5	6,53	0,20	-10,89	0,09	0,00	0,3 <u>≤</u> µ11 <u>≤</u> 8,5
т	42	30,17	3,37	5,13	0,52	0,07	25 à 30
1	5	33,68	5,28	2,62	2,36	0,059	25 a 50
Cond	42	764,1	1260	1,87	194,4	0,068	400
Colla	5	1065,4	437	3,40	195.45	0,027	400
HCO2 ⁻	42	203,82	104,6	-2,86	16,14	0,007	250
neos	5	125,51	30,38	-9,16	13,59	0,001	250
C1-	42	42,04	69,47	-19,40	10,72	0,00	250
CI	5	200,4	161,20	-0,69	72,07	0,53	230
SQ4 ²⁻	42	177,3	442,1	-3,26	68,22	0,002	400
504	5	413,6	356,6	0,09	156,48	0,94	100
F-	42	0,68	0,39	-13,69	0,06	0,00	1.5
	5	0,46	0,39	-5,90	0,18	0,004	1,0
NO ₃ -	42	6,46	7,70	-36,66	1,19	0,000	50
1,03	5	6,02	9,78	-10,05	4,38	0,001	00
Na^+	42	87,79	141,64	-5,13	21,86	0,000	200
	5	172	141,65	-0,44	63,35	0,681	200
\mathbf{K}^+	42	9,64	10,38	-1,47	1,60	0,148	12
	5	8,65	3,35	-2,23	1,5	0,090	
FeT	42	0,17	0,20	-4,06	0,03	0,000	0.3
	5	0,51	0,88	0,53	0,40	0,627	0,0
Mn ²⁺	42	0,60	0,31	4,22	0,05	0,163	0.4
	5	0,86	0,6	1,71	0,27	0,00	.,.
Ca^{2+}	42	50,96	31,45	-10,10	4,85	0,000	100
Cu	5	47,74	48,41	-2,41	21,65	0,073	100
$M\sigma^{2+}$	42	8,42	10,41	-25,89	1,61	0,000	50
1115	5	34,24	29,70	-1,19	13,28	0,301	50

Table No. 3: Results of comparison of parameters to standards

Results of Normalized Principal Component Analysis (NPCA)

The standardized principal component analysis (NPCA) covered fifteen (15) variables: pH, temperature, conductivity, water content, bicarbonates, chlorides, sulphates, fluorides, nitrates, sodium, potassium, iron, manganese, calcium and magnesium. The results obtained from the CNPA are presented in Tables 4, 5 and 6. Table 4 gives the eigenvalues, the variances expressed for each factor and their cumulative values.

F1F2Valeur propre5,5932,737Pourcentage Total de la variance
exprimée37,3018,30Cumul de la variance exprimée (%)37,3055,60

Table No. 4: Eigenvalues and percentages expressed for the main axes

The F1 factor is expressed with a variance of 37.30% and the F2 factor with 18.3% of the variance expressed.

The total variance expressed by the first two (2) factors is 55.60%. The contribution of the different variables in the definition of the main factors is given in Table 5. Each factor is defined by a certain number of essential variables in highlighting the chemical process of the waters.

Variable	F1	F2
pН	0,06	0,82
Т	-0,19	-0,61
Cond	-0,89	0,30
TH	-0,84	-0,22
HCO ₃ -	-0,46	0,68
Cl ⁻	-0,57	-0,63
SO_4^{2-}	-0,93	0,19
F-	-0,19	0,25
NO_3^-	0,12	0,08
Na ⁺	-0,91	0,15
\mathbf{K}^+	-0,77	0,40
FeT	-0,44	-0,26
Mn^{2+}	-0,26	-0,40
Ca ²⁺	-0,79	-0,09
Mg ²⁺	-0,55	-0,43

Table No. 5. Correlations between variables and factors

Table 5 shows that the factor F1 is defined by the electrical conductivity Cond (r=-0.89), the Hydrometric Titer TH (r=-0.84), sulphate ions SO_4^{2-} (r= -0.93) sodium ions Na+(r= -0.91), potassium ions K+(r=-0.77) and calcium ions Ca²⁺ (r=-0.79).

The F2 factor is defined by the hydrogen potential pH (r= 0.82), the bicarbonate ions HCO32-(r= 0.68) and to within a degree by the chloride ions (Cl-).

Analysis of the correlation matrix

The relationship between all the variables taken in pairs and the correlation coefficients are given by the correlation matrix Table 6, based on the critical correlation coefficient r = 0.64 (Mangin A., 1974).

	pН	Т	Cond	TH	HCO ₃ ⁻	CI S	O4 ²⁻ F	NO₃ Na ⁺ K	† FeT	Mn ²⁺	Ca ²⁺	Mg	g ²⁺		
pН	1														
Т	-0,50	1													
Cond	0,13	0,11	1												
TH	-0,12	0,09	0,56	1											
HCO3	0,46	-0,28	0,55	0,23	1										
C1 ⁻	-0,54	0,41	0,28	0,66	-0,12	1									
SO4 ²⁻	0,08	0,14	0,98	0,64	0,50	0,36	1								
F	0,05	-0,11	0,15	0,19	0,28	-0,03	0,11	1							
NO_3	-0,09	-0,06	-0,04	-0,14	0,10	-0,20	-0,08	0,13 1							
Na^+	0,01	0,19	0,95	0,58	0,51	0,46	0,96	0,11 -0,14	1						
\mathbf{K}^{+}	0,17	-0,03	0,83	0,43	0,54	0,16	0,79	0,21 -0,04	0,78	1					
FeT	-0,13	0,20	0,22	0,43	0,05	0,17	0,35	-0,02 -0,10	0,26	0,21	1				
Mn ²⁺	-0,34	0,18	0,10	0,22	-0,14	0,27	0,16	0,08 0,11	0,16	0,15	0,23	1			
Ca ²⁺	-0,04	0,03	0,57	0,93	0,22	0,55	0,61	0,20 -0,16	0,56	0,53	0,34	0,18	1		
Mg ²⁺	-0,31	0,21	0,3	4 0,0	5 3 0,0	07 0,	,54 (0,44 -0,05	0,08	0,35	0,12	0,39	0,21	0,35	1

Table No. 6: Correlation matrix

The analysis of this table shows the existence of correlations between conductivity and the following ions: SO42- (0.98), Na+ (0.95) and K+ (0.83). Thus, variations in the dissolved ionic charges are entirely or partly related to variations in the contents of these different ions. This also indicates that these different parameters tend to evolve together, either by concentration under the effect of evaporation or by the addition of ions from common sources for example. TH is correlated with the following ions: Ca²⁺ (0.93), Cl-(0.66), SO₄²⁻ (0.64) and Mg²⁺ (0.63). SO₄²⁻ ions are also very well correlated with Na+ (0.96) and K+ (0.79).

Analysis of the space of the variables in the factorial plane

The first two main components are shown in Figure 3. This design accounts for 55.6% of the variance for the analysis of the variables used.

The F₁ factor with 37.30% of the total variance is represented by conductivity (Cond), Water Title (TH), sulphate ions (SO₄²⁻), sodium ions (Na+), potassium ions (K+) and calcium ions (Ca²⁺). Of these ions, only the average SO₄²⁻ ions in the Pliocene sheet is slightly above the norm. SO₄²⁻ ions are mainly anthropogenic in origin and are introduced into the subsoil either by leaching from applied fertilizers or by the discharge of wastewater. Calcium (Ca²⁺) and sodium (Na⁺) probably come from the infiltration of lake water containing salts as the groundwater is fed by this lake.

The F_1 factor, therefore, expresses mineralization through the infiltration of surface and groundwater.

The factor F_2 with 18.3% of the total variance is represented much more by the pH and HCO_3^{2-} ions. Thus, waters with an acidic tendency (pH lower than 7) characteristic of the Pliocene table would be essentially due to the geological process involving the decrease of bicarbonate ions and the release of hydrogen ions. This factor could be related either to the dissolution of calcite that may be contained in the earth's crust. The Cl- could come from the dissolution of halite whose content is above the norm in 40% of Pliocene groundwater and in only 4.76% of Quaternary groundwater.

The F_2 factor, therefore, expresses the mineralization of the water by the residence time phenomenon (water-rock contact). The mineralization of groundwater is probably acquired by the phenomenon of infiltration of surface and underground water and that of dissolution or residence time (water-rock contact).



Figure No. 3: Projection of the variables in the space of the factorial plane F1×F2



Figure No. 4: Projection of the samples in the space of the factorial plane F1-F2

The graphical representation in the factorial space of the statistical units (Figure 4) shows the distribution of the water points as a function of the factors F1 and F2. The analysis of this graph shows three (3) main groupings of water points and a fourth (water point) isolated.

The first group is composed of the waters of three boreholes of the quaternary water table B4 (Kindjandi2), B13 (Garin Wanzam1) and B15 (Garin Wanzam3). These waters are the most mineralized with contents exceeding the norms in sulphates, sodium, bicarbonates and a slight iron overflow with pHs with a basic tendency (pH>7). These waters are much more concentrated around the F1 factor. Analysis of the figure shows that the degree of vulnerability to pollution evolves along the F1 axis from right to left, as the contents of the determining parameters increase from right to left.

Thus, on the extreme left, we find water point B5 (Kindjandi3) which is the most polluted (water not acceptable for human consumption). So the factor F1 is the axis of mineralization by infiltration of water into the quaternary water table and it is the axis of pollution.

The second group is made up of water from four (4) water points including two cemented wells PC2 (Messa) and PC4 (Karjim Tilo) and two wells drilled in the Pliocene table A4 (Messa) and A5 (Kabi). The waters of these water points are mineralized with contents exceeding the standards in sulphates, sodium, iron, and/or calcium, chloride and manganese, with acidic pH values (pH<7). These waters are concentrated around the F2 factor, which

represents an axis of mineralization to a low degree by water-rock contact (residence time), as all the water points of the Pliocene table are at the top of the F1 axis. This could probably be explained by the fact that waters with longer residence times are at the top of the axis, those with shorter residence times are at the bottom of the axis and those under the influence of mixing with older waters are around the axis. It also represents the oxidation-reduction axis because the average magnesium content of the Pliocene water table.

The third group consists of thirty-nine (39) water points. On the whole, the parameters of these waters are below standards. Nevertheless, fifteen (15) of these have conductivities slightly exceeding the standards. These water points are concentrated around the origin of the axes of F1 and F2; these are the water points that are not vulnerable to pollution.

The fourth consists of a single isolated B5 water point (Kindjandi well). This is the water point with the highest conductivity value (7770 μ s/cm). With several parameters exceeding the standards: TH (384° F) against 10 ° F (standard), HCO₃^{- (434.2 mg/l)} against 250 mg/l (standard), SO₄²⁻ (2560 mg/l) against 400 mg/l, Na+(847 mg/l) against 200 mg/l, Mn^{2+ (0.9 mg/l)} against 0.4 mg/l, Ca²⁺ (121.6 mg/l) against 100 mg/l and K+ (58.4 mg/l) against 12 mg/l.

The values of the measured parameters show that this water is not acceptable for human consumption.

Results of the Hierarchical Ascending Classification (HAC)

Hierarchical classification is said to be ascending when one starts from a situation where all individuals are alone in a class and then grouped together in larger and larger classes.

The dendrogram (Figure 5) derived from the HAC showed two main groupings of variables.



Figure No. 5: Dendrogram from the Ascending Hierarchical Classification (AHC)

The first grouping consists of pH, Cond, SO4²⁻, Na⁺, K⁺, HCO3⁻, F- and NO3⁻.

This grouping reflects the residence time mineralization and the phenomenon of water infiltration into the water table by leaching.

The second grouping is made up of Cl-, Ca^{2+,} FeT, Mg²⁺ and Mn ²⁺, could account for the residence time mineralization and an oxidation-reduction mechanism.

Results of the hydrochemical facies analysis

The Piper diagram allows the characterization of the geochemical facies of the waters.





Figure No. 6: Hydrochemical facies of the Quaternary a) and Pliocene b) zone of the Departments of Diffa

The groundwater chemical facies of the Diffa Department are given by the Piper diagram (**Figures 6 a and b**). The representations of the results of chemical analyzes in the Piper diagrams allowed the identification of the following water families:

• The family of calcium and magnesium bicarbonate waters (18 points of the quaternary water table);

• The family of sodi-potassium bicarbonate waters (12 points of the quaternary water table);

• The family of chlorinated sodium and potassium or sulphate sodium waters (8 points of the quaternary water table and 4 points of the Pliocene water table);

• The family of calcium and magnesian chlorinated and sulphated waters (4 points of the quaternary water table and one point of the Pliocene water table).

Thus, the fact that only quaternary groundwater is classified as calcium and magnesium bicarbonate, sodium and potassium bicarbonate could be explained by local factors related to anthropogenic pollution around structures where the water table is shallower and/or by the infiltration factor of lake water containing either potassium or sodium salt into the water table.

Results of bacteriological analysis

The bacteriological analysis was carried out on the waters of 20 boreholes and 9 cemented wells of the quaternary water table and on the five (5) boreholes of the Pliocene water table and concerned the following coliforms: faecal coliforms, total coliforms and atypical bacteria. Concentration in water, i.e. 200 colonies per 100 ml or more. They can falsify the results of microbiological water analyzes. The analysis of bacteriological results showed that the water points in the villages of Kindjandi1 (B5), Wogam Koura (B2), Gonidi (PC3) and Karjim Tilo (PC5) belong to class III, i.e. poor quality water, with coliform levels above 100 colonies/100 ml. The water from borehole B24 (Diffa/Afounori district) belongs to class II, i.e. water of poorer quality, with coliform levels between 10 and 100 and the remaining 29 water points belong to class I, i.e. good quality water, with coliform levels below 10 coliforms/100 ml.

The water points belonging to Class III are used for the needs of people and livestock and the one belonging to Class II is located in the centre of Diffa. Degradation of the bacteriological quality of these water points may be due to the creation of conditions for decomposition of organic matter and infiltration of biological pollutants.

DISCUSSIONS

The analyzes carried out on the waters of two (2) aquifers collected from the department of Diffa show that all the waters of the Pliocene aquifer are mineralized with an average conductivity of 1065.4 μ S/cm and those of the Quaternary aquifer are moderately mineralized (18 out of the 42 water points exceed the norm) with an average conductivity of 764.1 μ S/cm. All the waters of the Pliocene table have a pH of less than 7 with an average of 6.53 pH units and those of the quaternary table have a pH that varies greatly between acidity and basicity with an average of 7.46 pH units.

On the whole, the waters are classified among those that are very hard with the exception of that of a borehole in the quaternary aquifer (Mourimadi) which is classified as soft. Average water temperatures are 30.17°C for the quaternary table and 33.68°C for the Pliocene table.

Analysis of the physicochemical parameters has shown that groundwater is chemically diverse, but is nevertheless acceptable for human consumption with the exception of water from a single water point in the quaternary aquifer (Kindjandi3).

Descriptive analysis of the data showed that the chemical parameters influencing water mineralization are bicarbonate, chloride, sulphate, sodium, potassium and calcium. Abnormal (above standard) concentrations of these variables may be due to several sources. This high variability of physicochemical parameters between water points is consistent with those found by Rim Z., (2008) and (Leduc C., 1997) which show that in the Diffa region, the geochemistry of major ions is much less homogeneous. The main reasons for this are the larger surface area of the area, thus the greater range of geological situations encountered, and especially the diversity of the surface-ground relations that significantly mark the water table. Electrical conductivities measured in wells and boreholes vary between 100 and 9000 μ S/cm. The highest values are found on the western edge of Lake Chad and in the centre of the basins in the Maïné-Soroa and Goudoumaria region. According to Rim Z., (2008), the mineralization of the water table is generally low (106 to 400 μ S /cm) but can exceed 5,000 μ S /cm in areas subject to evaporation (lakeshore, basins), where it shows a very high spatial and temporal variability. For the Pliocene zone, mineralization is average (760 to 3,600 μ S /cm) and correlates with spatial variations in electrical conductivity.

Sodium is the dominant cation for almost all groundwater analyzes. Thus, the correlation matrix indicates that the chemical parameters influencing water mineralization are sulphate, sodium, calcium, manganese and potassium. Indeed, the Principal Component Analysis has highlighted two weak factors of water mineralization, the mineralization by acid hydrolysis and infiltration and that of oxidation-reduction. Rim Z., (2008) and (Leduc C., 1997). The projection of individuals in the factor space showed that the groundwater of Diffa is divided into three (3) groups:

- The first group is composed of water from 3 boreholes (Kindjandi 2, Garin Wanzam 1 and 2) of the quaternary water table. These waters are mineralized with contents exceeding the norms in sulphates, sodium, bicarbonates and a slight excess of iron with basic pH.

- The second consists of water from two wells drilled in the Pliocene table (Messa and Kabi) and two cemented wells (Messa and Karjim Tilo). These waters are the most mineralized with acidic pH and levels of sulphate, sodium, iron, and/or calcium, chloride and manganese exceeding the standards.

- The third consists of 38 quaternary groundwater points and one water point of the Pliocene water table. This group includes the least mineralized waters with conductivities mostly below the norm, and pH close to neutral. One can observe isolation of a water point (the B5 well of Kindjandi) which is the most mineralized, which has as Cond=7770 μ S/Cm, it is the only water point whose water is unacceptable for human consumption.

The Ascending Hierarchical Classification (AHC) has highlighted two main groupings of variables. The first consists of pH, Cond, SO_4^{2-} , Na^+ , K^+ , HCO_3^- , F^- and NO_3^- . This group accounts for residence time mineralization or hydrolysis of carbonate and silicate minerals. It also indicates mineralization by water infiltration into the water table.

The second group consists of Cl⁻, Ca²⁺, FeT, Mg²⁺ and Mn²⁺. It (group) accounts for residence time mineralization or the phenomenon of hydrolysis of minerals, and the presence of iron and manganese in the group indicates that there is an oxidation-reduction mechanism. These results are in agreement with those of RIM Z., (2008), which indicates that the residence time in the aquifer is very long; the low mineralization again reflects the poverty of the continental sediments in soluble elements.

The hydrochemical study highlighted four (4) facies, including that of bicarbonates (calcareous and magnesian and sodi-potassium) which predominates in the quaternary aquifer (18 water points for calcareous and magnesian bicarbonates and 12 water points for sodipotassium bicarbonates), i.e. 71.43%.

This result is consistent with those found by several authors who worked in Niger. Thus, according to these results, the bicarbonate facies is the most dominant in the Quaternary water table (Rim Z., 2008; Sandao, 2013; Zangui, 2015, Haoua A., *et al.*, 2014).

The results of the microbiological analyzes revealed a significant presence of fecal coliform bacteria (Escherichia coli) and fecal streptococci in the waters of four (4) water points (B5 Kindjandi1, B2 Wogam Koura, PC3 Gonidi and PC5 Karjim Tilo), i.e. 11.77% of the total of 34 analyzed. The presence of these bacteria is probably due to pollution of human or animal origin as all these waters are from the quaternary water table. The poor quality water points are located in areas where most people defecate in the open air. In addition, these water points are used as watering places for farm animals.

CONCLUSION

The study of the hydrogeochemical characteristics of the Diffa department water resources was carried out using a combination of the methods of analysis of variance, analysis of descriptive statistics, multivariate statistics and analysis of hydrochemical facies. This study made it possible to highlight the different physicochemical and bacteriological characteristics of the waters of the sampled sites.

The physicochemical analyzes showed that most of the waters of the Diffa department have a pH in accordance with the standard. Most of the chemical quality parameters were below the WHO drinking water standard. All the water points have very hard water except for one water point in the quaternary aquifer which has soft water.

The graphical representation of the projection of the individuals in the factor space highlighted three (3) groups of waters. The first is made up of three (3) water points of the quaternary aquifer, these waters are the most mineralized (highest conductivities) of those acceptable for human consumption with basic pH and high contents of sulphate, sodium, bicarbonate and total iron.

The second is made up of water from two water points of the Pliocene table and two cemented wells of the Quaternary table. These waters are moderately mineralized and all have a pH below 7 and high levels of sulphate, sodium and total iron.

The third is made up of 38 water points from the Quaternary table and one from the Pliocene table. This group presents less mineralized waters with conductivities mostly below the norm and a pH close to neutral.

The Standard Principal Component Analysis (SCA) and the HAC indicated that the low mineralization of the waters of the Diffa department was controlled by three (3) phenomena. These are mineralization by hydrolysis, by rainfall and soil leaching and oxidation-reduction.

The classification of the results of chemical analyzes of the waters obtained from the Piper triangular diagram identified four (4) facies with predominantly calci-magnesian bicarbonates, followed by sodi-potassium bicarbonates, sodium and potassium chlorides or sodium sulphate and calcium and magnesium chloride and sulphate waters. Moreover, bacteriological analyzes showed that only the waters of five (5) water points were affected out of the thirty-four (34) analyzed. Generally speaking, the aquifers collected for drinking water in the Department of Diffa were not threatened by a remarkable pollution of anthropic origin, however, there were some rare polluted water points due to the inexistence of modern hydraulic infrastructures and the lack of sanitation.

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