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RESEARCH PAPER

The geochemistry of the main pools in the humid compound "Guerbes-Sanhadja" (Algerian North-East)

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Abstract

The compound of the humid area Guerbes –Sanhadja is located in Ben Azzouz town in the east of Skikda, Algeria. It is of 42.110ha.The main physicochemical parameters of the eight big basins that are considered as the most representative of the whole humid area measured on the ground show that all the pools studied have almost a neutral pH. The electric conductivity of the set of pools show that their waters allow a reasonable exploitation Except a pool which has a high salinity level in Ain Nechma (AN 2) the chemical analyses of these waters allows also to note that the quantities of salt are different from one site to another, which can be explained by the influence of the substratum, the reason is the anthropogenic effect (pumping, uncontrolled dump sites, wastewater disposal). The obtained results show that on the whole, the waters of the pools in the compound Guerbes-Sanhadja are rich in calcium and bicarbonate with the dominance of a chemical feature with calcium-bicarbonates type.

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Introduction

The humid zones are lands of transition between aquatic ecosystems and terrestrial ecosystems (Raven, 2009). Those zones constitute remarkable ecosystems that cover essential functions. They work as reservoirs of biodiversity that contain vegetation and animal species that are often of great interest from a bio-geographical point of view (Dajoz, 2008).

There are many birds, mammals, reptiles, amphibians, fish and invertebrates (Rebah, 2005). They intervene in the hydrological regime by storing large quantities of water, curbing floods and returning water slowly during periods of drought. They ensure the purification of running and underground water. They allow irrigated or special crops agricultural activities. Finally, they have a social role, as they have always been frequented by walkers, fishermen, artists and painters in search of natural landscapes (Dajoz, 2008). Hydrological conditions are the determining factor in the physicochemical characteristics of wetland waters. They condition the inputs of solids and dissolved substances, especially nutrients, sometimes contaminants and their impact on wetlands (Fustec *et al.*, 2000). All over the world, wetlands are drained to be transformed to agricultural land, for industrial arrangements either in port or urban development, or threatened by the abandonment of traditional pastoral farming practices. These humid zones still require human activity to maintain open extremely fragile environments. The Ramsar International Convention (Iran), signed in 1971, establishes a global network of humid zones to establish and sustain local protection (Chauveau, 2007).

The geographical position of Algeria, its physical configuration and the diversity of its climate is identified by its important wealth of wetlands, especially in the North-East which contains many freshwater lakes, swamps and plain floods. (Anonymous, 2013). Among the Algerian sites on the Ramsar list is the humid Guerbès-Sanhadja complex. The remarkable flora and fauna of this region originates from at least three (3) elements: its geomorphological and therefore pedological diversity, its role as a bioclimatic junction, resulting in a highly rich biodiversity (Boumezbeur, 2001). The wet complex of Guerbes-Sanhadja remains little studied, due to its geographical marginalization of major university centers (CFS, 2012). Our investigation aims to study the main physico-chemical parameters of the water in some humid depressions in this complex.

Presentation of the study zone

The Plain of Guerbès contains wetlands of international importance that are considered perfect examples, rare and sometimes unique of natural wetland type in North Africa and in the whole Mediterranean region (Samraoui et de Belair, 1997); (Boumazbeur, 2001). The Guerbès-Sanhadja Wetlands Complex covers the eastern coastal area of Skikda. It is bordered by the coastal dune hills to the north, the Chettaibi coastal massif to the east and the internal part of the alluvial plain to the south (CFS, 2012).

This set of 42000 hectares, from 0 to 190 meters altitude with geographical coordinates, (Fig.1):

- Longitude : 7°8'E à 7°25'E
- Latitude : 36°46' à 37°N
- It is shared between three sub-watersheds. It is the Kebir-Magroun coastal sub-basin that covers most of the surface of the wetland (23000 ha), followed by the sub-basins of Kebir-Hammam and coastal Filfila. (CFS, 2012).

Materials and methods

Sampling

Water samples were collected during the summer season (May 28, 2014) from eight sites, number 19 samples (Fig 2).

Water samples were collected during the summer season (May 28, 2014) determined parameters on the ground:

-Electrical conductivity (EC), pH, temperature (°C) in the field using a multi settings.

Laboratory analysis

-Calcium (Ca^{+2}) and magnesium (Mg^{+2}) were determined by complexometry, the different methods of volumetric metering with EDTA,

- Sodium (Na^+) and potassium (K^+) measured by flame photometry.
- Chlorides (Cl^-) were analyzed by $AgNO_3$ titrimetry
- Carbonates (CO_3^{-2}) and Bicarbonates (HCO_3^-) by titrimetry with sulfuric acid,
- Sulfates (SO_4^{-2}), Nitrates (NO_3), nitrites (NO_2) and ammonium (NH_4) by spectrophotometry.

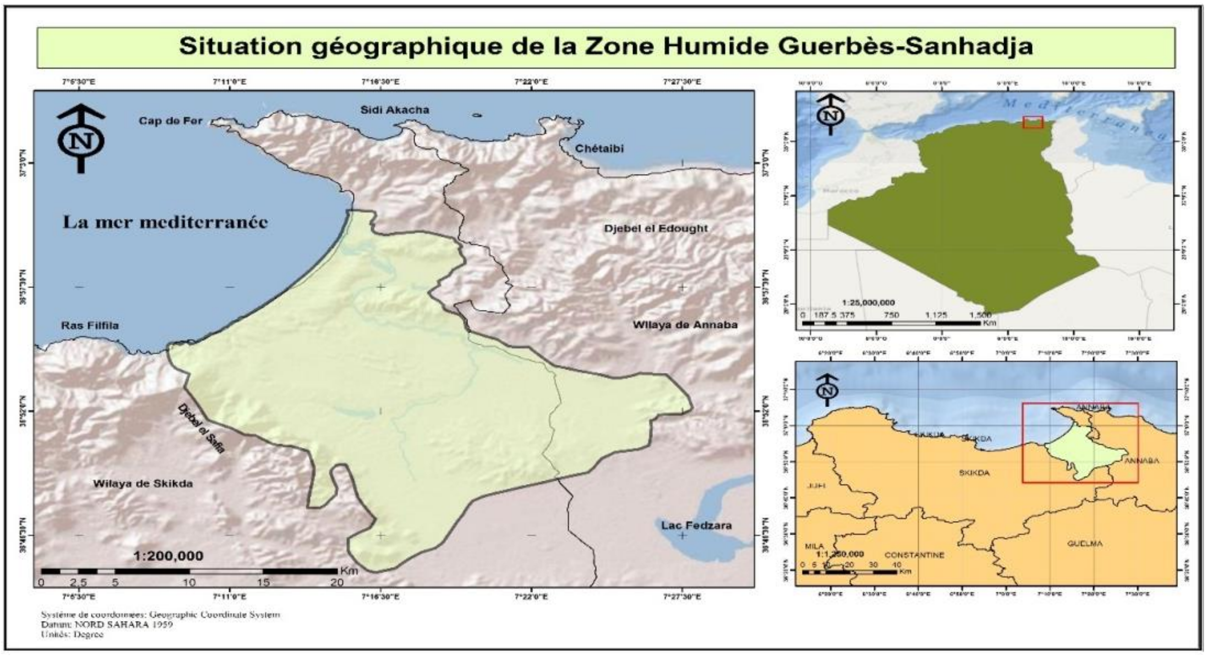

Fig. 1. The Geographical location of the Humid Compound "Guerbes-Sanhadja".

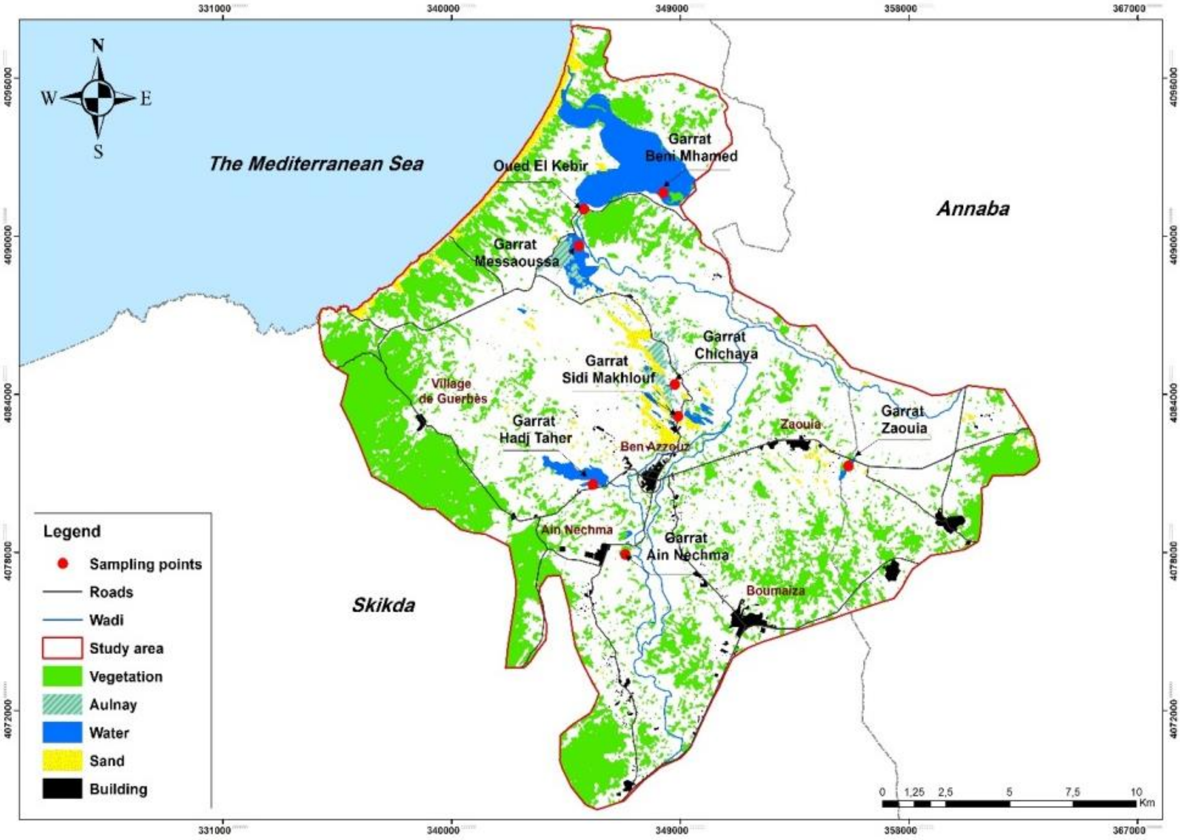

Fig. 2. Location of sampling points.

Table 1. The main pools.

Nº	Main Pools	Surfaces (ha)	Coordinates	Number of Samples
E1	Bnimhamed (BM)	1100	36°56 .53'N 7°14.162'E	(BM1, BM2, BM3)
E2	Oued El Kebir (K)	/	/	(K1)
E3	Msawsa(M)	392	36°56 .06' N 7°14,71'E	(M1)
E4	Chichaya (CH)	50	36°53 .85'N 7°18 .19'E	(CH1, CH2)
E5	Hadj Taher (HT)	112	36°51 .78' N 7°15.36' E	(HT1, HT2, HT3, HT4, HT5)
E6	Sidi Makhlouf (SM)	11	36°53.09'N 7°18 .36'E	(SM1, SM2)
E7	Zaouia (Z)	12	36°52' N 07°21'E	(Z1, Z2, Z3)
E8	Ain Nechma (AN)	01	36°50 .27' N 7°15.96' E	(AN1, AN2)

Results and discussion

Chemicals Facies

The Piper diagram

The hydro chemical facies can be classified based on the dominant ions using the piper diagram (Ravikumar et Somashekar, 2013). Piper diagrams were used to display the relative concentrations of major cations and anions on two separate tri-linear plots, with a central parcel where the points of the two tri-linear parcels are projected. The central rhomboid field (quadrilateral field) is used to show the overall chemical character of the water (Piper, 1944; Guleret *et al*, 2002). The representation of concentrations in major elements on the Piper diagram, shows that the waters sampled are generally sodium chlorides facies, the latter common in environments rich in evaporites (halite [NaCl] of marine origin).

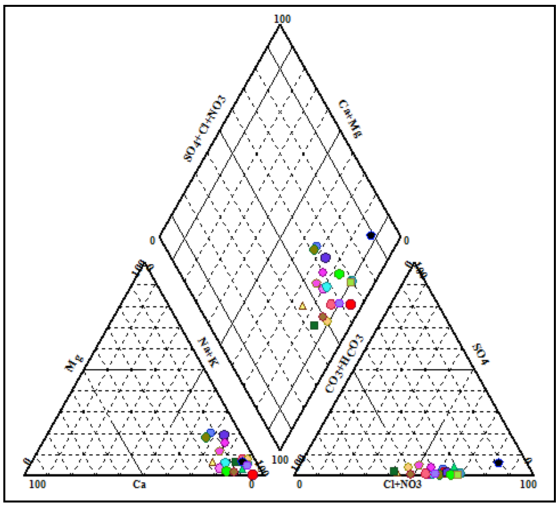

Fig. 3. Diagramme de Piper représentant les principaux faciès des eaux (Guerbes-Sanhadja).

Diagramme de durov (1948)

The Durov diagram (1948) gives more information on the hydro-chemical profile and the evolution of groundwater quality. It helps to identify the types of hydro-chemical profiles, classify groundwater types and can indicate the mixing of different types of water and ion exchange in the study area. The graph makes it easy to distinguish Na + -HCO$_3^-$, Ca^{2+} - HCO$_3^-$, Na$^+$ - Cl$^-$ and Ca^{2+} - Cl$^-$ samples. The waters of the Guerbes-Sanhadja compound have a chemical facies: chlorid-sodium (Cl$^-$ - Na$^+$) (Fig. 4).

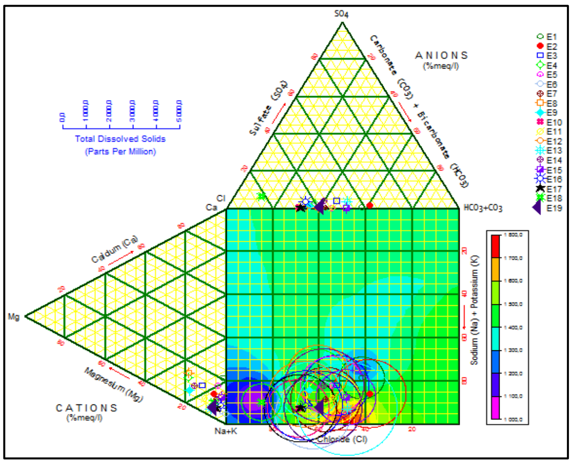

Fig. 4. A Diagram of the main concentration of elements (Guerbes-Sanhadja).

Saturation index (SI)

In order to explain the mineralization acquisition mechanisms, we used the "Diagram" software to determine the saturation indicator of some specific minerals (Table 2). The saturation of the waters with the matrix is often expressed either by the saturation rate (= (PAI / Ks)* 100), or by the saturation index (SI = log (PAI/Ks), where PAI is the product of the activity of the ions concerned and Ks is the product of the solubility of the mineral considered. The saturation index is the most used form for water. The water is neutralized (balanced) with the mineral when IS=0, it is under-saturated when IS<0 is supersaturated when it is>0. When a solution is under-saturated for a mineral, it will have a tendency to dissolve.

The results obtained indicate a saturation of the minerals with regard to the halite (NaCl), and an under saturation with regard to the gypsum ($CaSO_4$, $2H_2O$), the aragonite ($CaCO_3$), the dolomite CaMg $(CO_3)_2$ and anhydrite ($CaSO_4$) in the study area (Table 1). The majority of the samples are undersaturated relative to calcite ($CaCO_3$), except (Z1) and (Z2) which are supersaturated.

Calculation of the mineral saturation index in water indicates that only carbonate minerals tend to precipitate, especially in the form of dolomite, calcite and aragonite. While minerals, in this case, halite, gypsum and anhydrite, tend to dissolve. Therefore a possible dissolution of these minerals can contribute to the acquisition of salt load in the water (Fig. 5).

Table 2. Indicators of saturation of the minerals in the humid compound Guerbes-Sanhadja.

N°	Échantillons	SI Calcite	SI Aragonite	SI Dolomite	SI Gypse	SI Anhydrite	SI Halite
E1	AN1	-1.03	-1.18	-2.95	-3.04	-3.26	-6.00
E2	AN2	-1.10	-1.24	-2.31	-2.51	-2.73	-5.65
E3	BM1	-1.47	-1.62	-2.86	-2.21	-2.44	-5.61
E4	BM2	-1.17	-1.32	-2.06	-2.34	-2.57	-5.56
E5	BM3	-0.88	-1.03	-2.23	-2.95	-3.19	-5.46
E6	CH1	-0.69	-0.84	-2.30	-2.87	-3.10	-5.21
E7	CH2	-0.41	-0.55	-1.01	-3.06	-3.29	-5.39
E8	K1	0.08	-0.06	0.36	-3.00	-3.23	-5.59
E9	M1	-2.48	-2.63	-4.44	-2.94	-3.18	-5.52
E10	HT1	-2.39	-2.54	-4.65	-3.32	-3.55	-5.32
E11	HT2	-1.51	-1.66	-2.75	-3.41	-3.65	-5.64
E12	HT3	-1.36	-1.51	-3.46	-2.95	-3.19	-5.28
E13	HT4	-2.17	-2.31	-3.87	-2.48	-2.71	-5.22
E14	HT5	-1.52	-1.66	-2.76	-2.07	-2.30	-5.32
E15	SM1	-1.66	-1.81	-3.95	-3.28	-3.51	-5.65
E16	SM2	1.59	0.44	0.91	-2.26	-2.48	-5.20
E17	Z1	0.16	0.02	0.50	-0.02	0.50	-5.20
E18	Z2	0.05	-0.10	0.19	-0.10	0.19	-5.28
E19	Z3	-0.15	-0.29	-0.14	-0.29	-0.14	-5.54

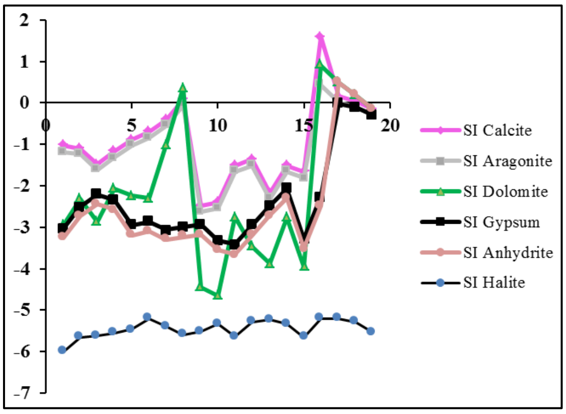

Fig. 5. Saturation Index (SI).

The Quality of Waters

Different standards of chemical quality have been established to assess the suitability of water for domestic use or irrigation. In the present study, the suitability for different uses is based on the concentration of its major ion constituents, The SAR and the Electrical conductivity (EC).

Sodium adsorption rate (SAR)

The sodium concentration in the irrigation water is determined by the SAR which is considered a very important parameter (Brindha and Kavitha, 2014) expresses the sodium concentration or the alkaline hazard for the determination of the quality of the water used for irrigation purposes. High salinity reduces the osmotic activity of plants and prevents water from reaching the branches and leaves of plants resulting in low production (Deepali *et al.*, 2010).

In addition, high Na^+ and low Ca^{+2} irrigation water promotes ion exchange by Na + saturation, destroying soil structure due to dispersion of clay particles (Todd, 1980). Also affect its fertility (Subba Rao, 2006). The SAR is calculated, using the following formula:

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\frac{\mathrm{Ca}^{++}+\mathrm{Mg}^{++}}{2}}}$$

Table 3. The Classification of Waters according to SAR (Todd 1959; Richards, 1954).

SAR	Classes of Water	Number of Samples
<10	Excellent	7
10–18	Good	7
18–26	Doubtful	4
>26	Inappropriate	1

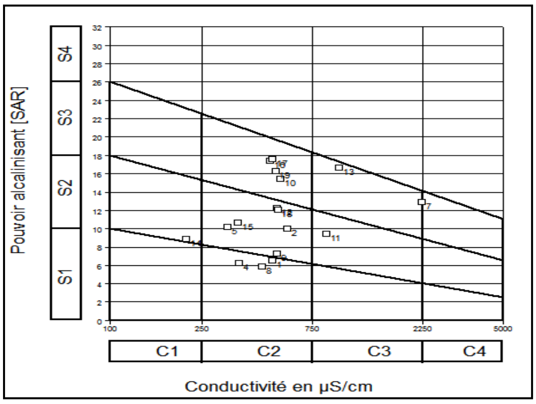

Fig. 5. The diagram of Richards applied to Waters of the Study Zone.

Statistical approach

This multi-faceted analysis, applied to hydro-chemical studies allows presenting graphically the maximum of information and the correlations between the variables and the points of observation. In the ACP has been used to distinguish the contribution of natural processes of chemical composition.

We performed a ACP on reduced centric variables using Xl stat software on a set of 13 physicochemical parameters obtained from 19 points of water.

The variables taken into account are: T, pH ,CE, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-}, Cl^{-}, SO_4^{2-}, NO_2^{-}, NO_3^{-}, Factor 1 expresses (30.93%) of the variance of the data and shows an opposition between NO_3, NO_2, HCO_3, Ca^{2+} and CO_3.

Table 4. The Classification of Ground Waters based on the Diagram.

Number of Samples	N° of Samples	Total percentage	Classes of Water	Irrigation status
1	E14	5.26%	-Low risk of salinity. -Average risk of sodium.	appropriate
4	E1 E4 E8 E9	15.78%	-Average risk of salinity. - Low risk of sodium.	appropriate
7	E2 E3 E5 E9 E12 E15 E18	36.84%	-Average risk of salinity. -Average risk of sodium.	Appropriate under specific conditions
3	E10 E19 E17	15.78%	-Average risk of salinity. -High risk of sodium.	Appropriate under specific conditions
1	E11	5.2%	-High risk of salinity . -Average risk of sodium.	Appropriate under specific conditions
2	E7 E13	10.52%	-High risk of salinity. -High risk of sodium.	- Inappropriate

This first interpretation shows an origin of salinity or a phenomenon of mineralization. The deduction in the positive part of the axis is a state of alkalinity whereas in the negative part corresponds to acidity in opposition between the pH and the bicarbonates. According to the F2 axis (16.95%), an opposite evolution between T, pH, K and Mg The interpretation of the results provided by the ACP, has shown that the waters of the region are almost polluted, we will try to highlight the forms of pollution (natural or anthropogenic, mineral or organic) detected after some performed analyses.

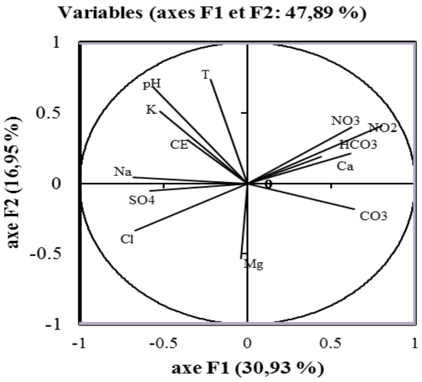

Fig. 5. The Spatial Distribution of variables according to axes F1–F2.

Table 5. Correlation of parameters with factors.

	T°C	pH	CE	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	CO_3^{--}	Cl^{-}	SO_4^{--}	NO^{-}_{2}	NO^{-}_{3}
T°C	1												
pH	0.715	1											
CE	-0.018	0.212	1										
Ca^{2+}	-0.112	-0.103	-0.175	1									
Mg^{2+}	-0.280	-0.172	-0.229	0.092	1								
Na^{+}	0.228	0.371	0.177	-0.226	-0.216	1							
K^{+}	0.275	0.571	0.306	0.270	-0.123	0.236	1						
HCO_3^{-}	-0.048	-0.135	-0.066	0.452	0.047	-0.218	-0.274	1					
CO_3^{2-}	-0.079	-0.466	-0.522	0.364	-0.081	-0.217	-0.408	0.110	1				
Cl^{-}	-0.050	0.211	0.055	-0.178	0.195	0.753	0.036	-0.269	-0.363	1			
SO_4^{2-}	0.129	0.205	0.149	-0.126	0.397	0.238	0.482	-0.450	-0.301	0.189	1		
NO_2^{-}	0.206	-0.160	-0.109	0.179	-0.214	-0.447	-0.153	0.129	0.372	-0.552	-0.205	1	
NO_3^{-}	0.083	-0.168	-0.066	0.451	-0.109	-0.413	-0.265	0.839	0.277	-0.529	-0.448	0.640	1

Table 6. Matrix of correlations.

	F1	F2
T°C	-0.218	0.739
pH	-0.561	0.679
CE	-0.357	0.306
Ca^{2+}	0.440	0.187
Mg^{2+}	-0.038	-0.532
Na^{+}	-0.681	0.043
K^{+}	-0.519	0.514
HCO_3^{-}	0.617	0.210
CO_3^{2-}	0.638	-0.182
Cl^{-}	-0.668	-0.333
SO_4^{2-}	-0.583	-0.055
NO_2^{-}	0.620	0.397
NO_3^{-}	0.803	0.412

Matrix of correlations

A good correlation was observed between HCO_3- and NO_3, NO_2 and NO_3, NO_3 and Cl^-; NO_2 and Cl^-, K^+ and SO_4^-, CE and CO_3^-, pH and CO_3^-, pH and $K^{+,}$ pH and T°C, indicating that these elements have the same origin (Chidambaram and Ramanathan, 2000)(Table 5). Almost all the minerals analyzed have shown a good correlation with the conductivity, because the latter increases with the dissolution of minerals by ion exchange or oxidation-reduction reaction in a water system (Subba Rao, 2002).

Conclusion

In this study, we tried to determine the physical and chemical properties of the waters of the main pools in the wetlands of the Guerbes-Sanhadja compound. Eight pools considered as the most representative of the complex were the subject of this work. The results obtained in the field show a strong relationship between physico-chemical parameters such as pH, temperature and electrical conductivity. The different analyses carried out in the laboratory show high levels of chlorides and bicarbonates, generally due to the dissolution of geological formations (gypsum and halite), this increase results in a high electrical conductivity. Their origin is multiple because they are in an urban area with strong agricultural activities (fertilizer). Climatic factors (high temperatures, lack of rainfall) play a major role in this increase.

With regard to the chemical features of pool waters, the most abundant feature is sodium chloride (Cl - Na +), which is common in environments rich in (NaCl halite). For the saturation index, the results indicate under saturation of the minerals with respect to (NaCl), gypsum ($CaSO_4$, $2H_2O$) and aragonite ($CaCO_3$), dolomite CaMg $(CO_3)_2$ and the anhydrite ($CaSO_4$) throughout the watershed (Tab.1). The majority of the samples correspond to under saturation of calcite ($CaCO_3$), with the exception of four samples which are supersaturated. Therefore, a possible dissolution of these minerals can contribute to the acquisition of the salt load in the water. Regarding the adsorbed sodium level (SAR); water samples are classified as C1S2, C2S1, C2S2 and C2S3 were the dominant classes. These waters are suitable for plants that have tolerance to salt, however its use can cause problems for clays. Salinity must be controlled, irrigation of tolerable crops to salts on well-drained soils.

Oxidation-reduction processes play an important role in the quality of water. The characteristics of the redox potential of water can be a good indicator of their degradation. The studies must give special importance to the following minerals: iron, nitrogen and sulfur. This component has unfortunately not been addressed in this study because of certain constraints.

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