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Full Length Research Paper

Geochemistry and ionic interaction in the Bizerte Lagoon waters (Northern Tunisia)

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The Bizerte Lagoon is classified in the category of medium salinity environments. The lagoon geochemistry, with regard to the major ions, is essentially controlled by the continental contributions and interactions with the marine environment. The geochemical analyses of the major ions as well as their behaviour in the lagoon water permitted to describe the eventual ability of a solution chemical composition, to precipitate different minerals. Sampling and geochemical analysis of the principal ions (Ca^{++}, K^+, Na^+, Mg^{++}, Cl^-, SO_4^{2-} and HCO_3^-) at the water surface (0 to 2 m) and at the bottom (over 2 m) of the lagoon (9 stations), in the Channel (3 stations) and in the bay of Bizerte (3 stations), was performed monthly during one year. The results for the Bizerte Lagoon waters show that only carbonates and gypsum can precipitate.

Key words: Water, Bizerte lagoon, ionic ratio, precipitation.

INTRODUCTION

The Bizerte Lagoon with an ellipsoidal shape (surface area: ~ 150 km^2) is a littoral lagoon in north-eastern Tunisia, which has two connections with surrounding environment; the first one is continental with the Garaet Ichkeul (the most important fresh water surface in Tunisia (Ouakad, 2007)) by the intermediary of Wadi Tinja, and the second one with the Mediterranean sea by a long channel. The Bizerte region has a sub-humid climate with 600 to 800 mm annual rainfall. Two seasons are distinguished. Winter extends from November to April, with maximum precipitation in February (219.5 mm). Summer and the rest of the year are dry without any freshwater input from Wadis. The drainage network that feeds the lagoon has a catchment of 252 km^2 (Kallel, 1989). The annual balance of water exchanges between the Bizerte Lagoon and the Mediterranean Sea shows that in winter a surplus of fresh water of approximately 534 (±26.03) Mm^3 are lost from the lagoon. However, during the summer, because of the lack of precipitation and strong evaporation, there is an incursion of marine water 84 (±2.45) Mm^3 towards the lagoon (Ben et al., 2009). Generally, water of the Bizerte Lagoon principal affluent shows temperatures oscillating between 11.1 and 20.8°C, with a neutral pH to slightly alkaline (7.13 to 9.22). This water is very rich in dissolved oxygen between 5.8 and 9.5 mg/l. The water salinity varies between 0.5 to 3.8 psu. Only the water of Wadi Tinja during the summer season and Wadi Rharek during all the year, present high contents of dissolved salts.

The mineralization of the streaming water of Bizerte Lagoon drainage basin is rather important. The analysis of the major elements shows for the majority of this water a sulphate-calcareous to chloride calcareous stable facies. Only Wadi Rharek water shows sodium chloride facies (Ben et al., 2010). During the summer season, Wadi Tinja water shows an important concentration in sodium ions and chlorides, with the phenomenon of marine water intrusion from the Bizerte Lagoon towards the Garaet Ichkeul (Ben et al., 2008). Wadi Rharek water presents constantly such high contents of these ions, resulting from scrubbing the Triassic terrains of Djebel Kchabta crossed by this Wadi (Crampon, 1971; Mathlouthi, 1985). The rest of Wadis water presents balanced contents of major ions which could be originated by the hydromorphic soils scrubbing (Ben et

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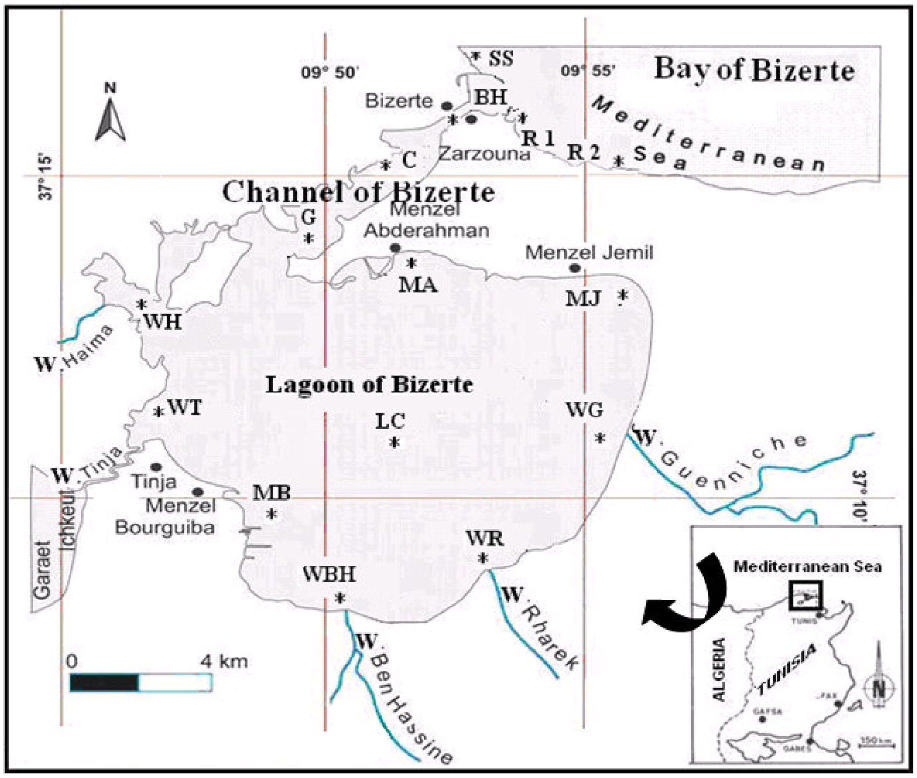

Figure 1. Samplings localisation in the Bay, the channel and the lagoon of Bizerte. SS, Sidi Salem; R1, R'mel 1; R2, R'mel 2; BH, Before Harbour; C, Channel; G, Gully; WH, Wadi Haima; WT, Wadi Tinja; MB, Menzel Bourguiba; WBH, Wadi Ben Hassine; WR, Wadi Rharek; WG, Wadi Guenniche; MJ, Menzel Jemil, MA, Menzel Abderhman and LC, Lagoon Centre.

al., 2010). So, physicochemical parameters, as well as the contents of major ions at Bizerte Lagoon waters are then influenced by those of marine water in summer period and those of the principal affluent in winter period.

The mixture zones of fresh and salty waters constitute an important environment of marine chemical reactions, which are consecutive to the sudden change of environmental conditions (Ouakad, 2007). This type of environment corresponds to estuary, delta or coastal lagoon with continental and marine influences. The biological activity is as important as the geochemical processes. We actually know more than ten enzymes families of carbonic anhydrases, and are universally present in the living organisms. They are used to catalyse in a reversible way the transformation of CO_2 into bicarbonate (Villeneuve, 2002). The Bizerte Lagoon ecosystem is affected by several physicochemical, hydrological and geochemical processes. In order to better understand the processes operating in this disturbed lagoon environment, a geochemical analysis of the major ions was carried out.

The obtained results enabled us to elucidate parameters responsible for precipitation of some minerals.

METHODOLOGY

Monthly water samples were collected from 15 stations in the Bizerte Lagoon between 37° 8' and 37° 14' of northern latitude and 9° 46' and 9° 56' of eastern longitude (Figure 1). Two samples were taken at each station; one at surface and one at bottom (2 m depth, using a hydrological bottle). These samples intended to determine "in situ" physico-chemical parameters. At the laboratory, each water sample undergoes the necessary dilution in order to determine the concentration of major ions (Ca^{++}, K^{+}, Na^{+} and Mg^{++}) using atomic absorption spectrometry of THERMO-ELEMENTAL-SOLAAR-S4 type (Rodier et al., 2005). The alkalinity was determined by titration with the sulphuric acid M/100. The water alkalinity corresponds to the presence of hydroxides, carbonates and bicarbonates. The chlorides were determined by titrimetrically with silver nitrate ($AgNO_3$) (Rodier et al., 2005).

The sulphates were determined with barium chloride ($BaCl_2$. $2H_2O$). The method of sulphates determination is the precipitation of barium sulphate and the determination of the amount of precipitate by turbidimetry (Rodier et al., 2005).

RESULTS AND DISCUSSION

Physico-chemical parameters of water

The spatio-temporal variation of salinity during winter and

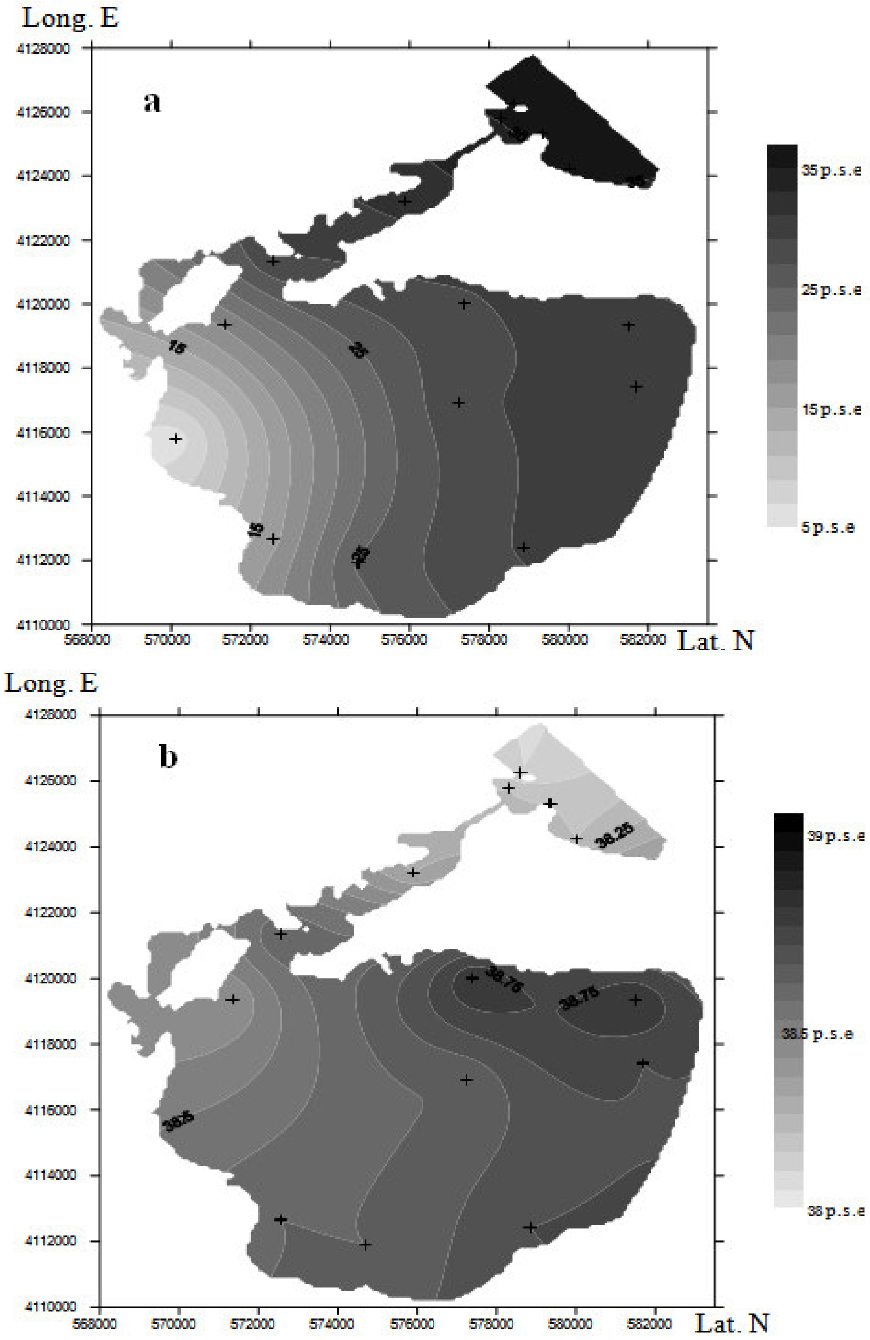

Figure 2. Spatio-temporal variation of Bizerte Lagoon water salinity. a) Surface water (in winter), b) Surface water (in summer).

spring showed that the lagoon water is less saline (from 5.9 to 29.1 psu) than the bay water (always higher than 30 psu) (Figure 2a). This variation is related to the impact of fresh water contributions by Wadi Tinja (Ben et al., 2008). The salinity homogenisation of lagoon waters occurs in summer period (between 36 and 38 psu) (Figure 2b). It should be noted, that the lagoon waters salinity indicated to a small rise compared to bay waters during summer. These results permitted to classify the Bizerte Lagoon, according to the classification of Mars (1966), in the category of the medium salinity environments. The monthly variation of dissolved oxygen (DO) concentrations in Bizerte Lagoon water shows two different periods. These are a winter period, when the concentrations oscillate between 7 and 11 mg/l (Figure 3a) and a summer period, when the concentrations vary

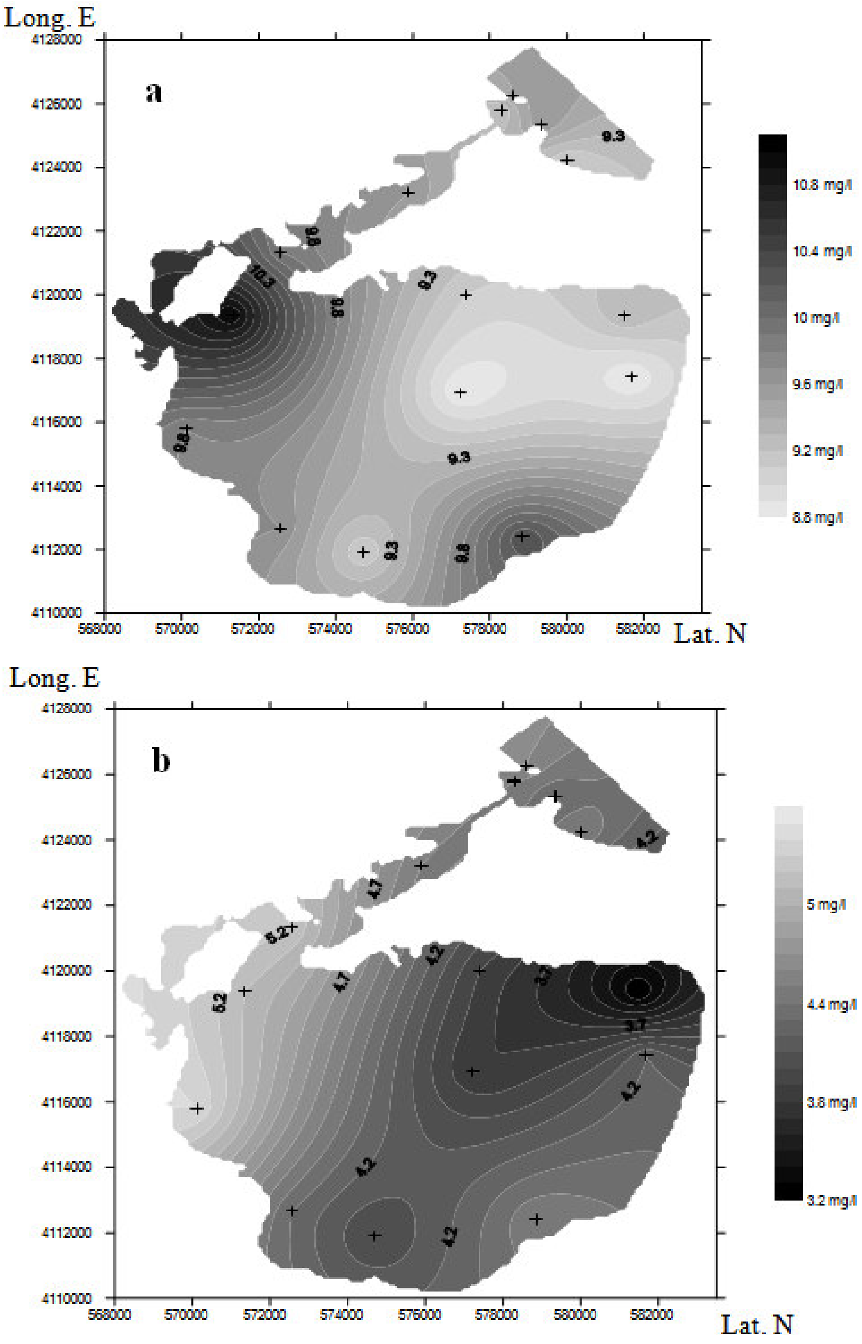

Figure 3. Spatio-temporal variation of the dissolved oxygen concentrations in the Bizerte Lagoon water. a) Surface water (in winter) b) Surface water (in summer).

between 3 and 6 mg/l (Figure 3b).

Geochemistry of water

The bulk geochemical analysis results of the major ions in the lagoon and bay of Bizerte water shows two different periods: The first is a winter period during which the sodium concentrations at station (WT) oscillate between a minimum of 1.82 g/l and a maximum of 9.32 g/l (Figure 4a). The potassium contents do not exceed 0.35 g/l, with a minimum of 0.07 g/l. The magnesium concentrations oscillate around 1g/l with a minimum of 0.22 g/l and calcium concentrations are up to 0.35 g/l, and can have low values up to 170 mg/l on the prodeltaic station of Wadi Tinja. The chlorides concentrations are

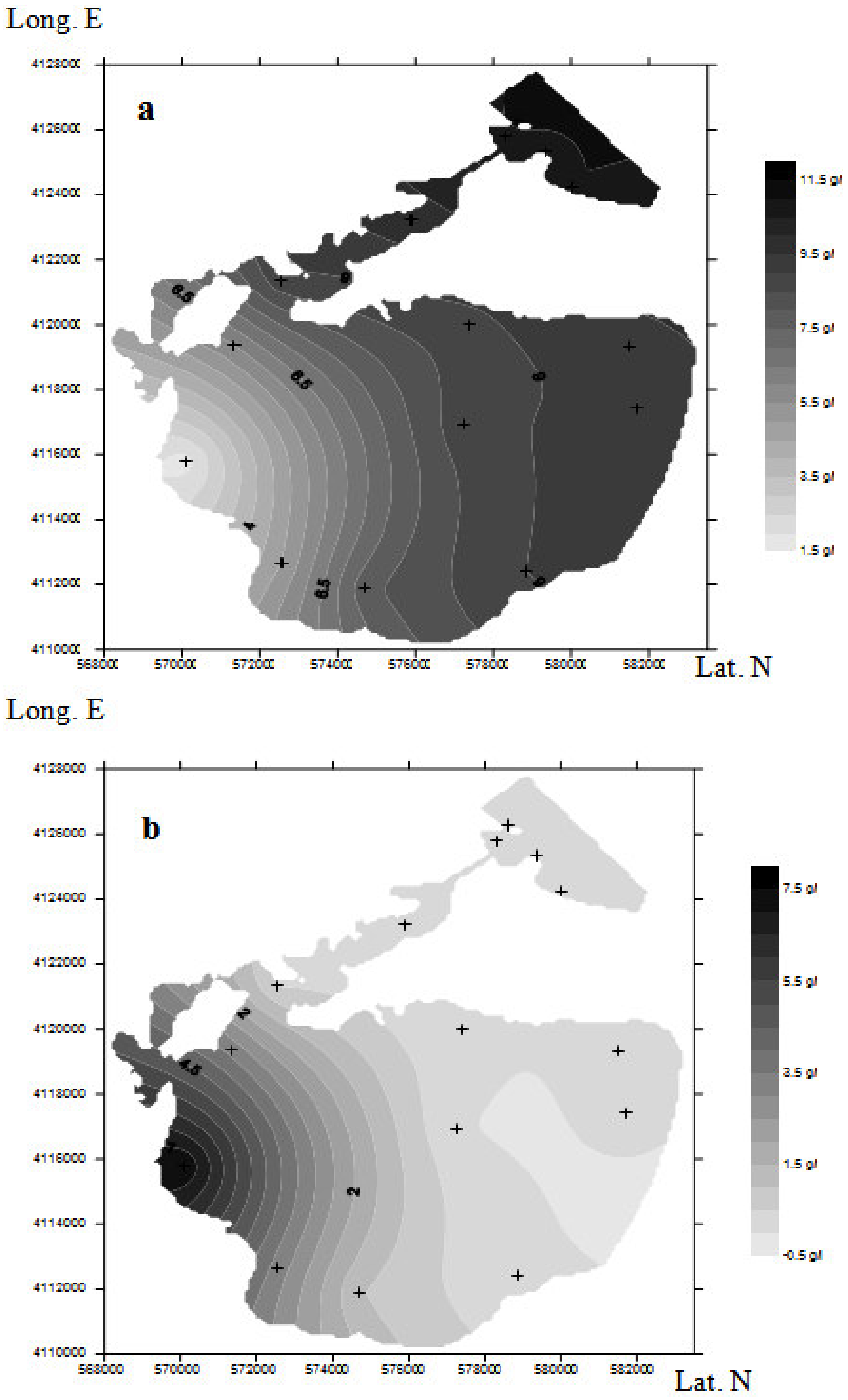

Figure 4. Spatial variation of the sodium content of Bizerte Lagoon water. a) Surface water (in winter), b) Differences in concentrations between surface and bottom water (in winter).

lower than 17g/l with a minimum of 3.28 g/l at the mouth zone of Wadi Tinja. The sulphate concentrations are lower than 2.5 g/l, with a minimum of 0.46 g/l at the surface water station (WT). During the rainy period (in winter), the lagoon water has lower concentrations of major ions than the bay water. It is due to the important continental fresh water contributions, in particular of the Garaet Ichkeul through the Wadi Tinja (Ben et al., 2009). Under these conditions, concentric aureoles around the zones of Wadi mouths are observed (Figure 4a).

It is during this winter period, when the lagoon water stratification develops, that is the surface water is less enriched in major ions than the bottom water. For example, the difference in sodium concentrations between surface and bottom waters becomes very important. At the station WT, the sodium concentration in surface water is 1.82 g/l, whereas at the bottom water it is 9.29 g/l during January (Figure 4b). In the summer period, the sodium concentrations are homogeneous and vary between 10.00 and 11.98 g/l. The potassium concentrations are higher than 0.40 g/l, with a maximum of 0.43 g/l and magnesium concentrations reach 1.43 g/l at several stations. The calcium concentrations are higher than 0.40 g/l, with a maximum of 0.45 g/l. The sulphate concentrations are around 2.5 g/l. Generally, the lagoon and the bay waters showed a homogenisation of bicarbonate concentrations during the year of study, with concentrations from 0.12 to 0.15 g/l. It is only during the winter season and due to the important continental fresh water input rich in bicarbonate, that the stations at the Wadi mouths show surface water richer in bicarbonate than those at the bottom.

In winter, the surface water at the station WT shows high bicarbonate concentration of 0.22 g/l (Figure 5a) compared to 0.15 mg/l for bottom water (Figure 5b). The bicarbonate concentrations in the Bizerte Lagoon are low compared to other environment; this is due to the effectiveness of exchanges between the lagoon and the sea, fresh water inflow, and also to the water dilution. Thus, the lagoon water alkalinity distribution is homogeneous with little variations of pH. The chemical composition of the solution, which is concentrated by evaporation, is variable, but generally, the content of dissolved salts increases. However, the ionic ratios remain constant as far as no salts precipitate.

The obtained results showed a negative correlation between Ca^{++} and HCO_3^- (R = - 0. 77; p= 0.05), which indicated that Ca^{++} is not only related to the carbonate rocks dissolution. Indeed, besides this last process, HCO_3^- may be provided by the atmospheric CO_2 diffusion into the lagoon (Villeneuve, 2002).

Behaviour of the major ions

Mg^{++}/Ca^{++} ratio

The temporal distribution of this ratio varies considerably for surface water between summer and winter. Concerning summer values, it was found to be around 3.3 compared to value of 1.4 in winter. The bottom water shows a constant and high ratio. The reduction in the Mg^{++}/Ca^{++} ratio in the surface water of the Bizerte Lagoon during winter period observed especially at the Wadis mouths is due to the important fresh water input. On the other hand, its increase during the summer season could be due to the combined effect of marine water intrusions and the impact of evaporation. This increase is dependent on the precipitation of calcite in the basin, but the involved quantities are low compared to the concentrations of Ca^{++} and Mg^{++}, in water.

During the year of the study, the Bizerte Lagoon bottom waters showed a high Mg^{++}/Ca^{++} ratio. This water is a little richer in Mg^{++} than surface waters, probably because more Ca^{++} was lost by calcite precipitation.

A part of Mg^{++} is lost by the transformation of calcite into magnesium calcite and aragonite. This transformation contributes to the increase of Ca^{++} ions in the basin interstitial waters. The relative increase in this ratio promotes the precipitation of the gypsum, but this increase is possibly limited by the calcic carbonates dolomitization of the lagoon sedimentary filling. Ultimately, we can priori assume that the geochemistry of the Bizerte Lagoon waters, with regard to Ca^{++} and Mg^{++} is primarily controlled by the marine environment.

SO_4^{2-}/Ca^{++}, SO_4^{2-}/Cl^-, Na^+/Cl^- and HCO_3^-/Cl^- ratios

During the summer season, the increase in the SO_4^{2-}/Ca^{++} ratio (6.66 compared to 2.94 in winter) should result in the precipitation of the gypsum partly, but this increase is controlled by the calcite precipitation in the lagoon sedimentary filling. It should be noted that precipitation of gypsum tends to lower the SO_4^{2-}/Cl^- ratio. This ratio increases again, if halite precipitates, with resulting decrease in the Na^+/Cl^- ratio (Medhioub, 1979). However, under these conditions, SO_4^{2-}/Cl^- and Na^+/Cl^- ratios do not show any notable seasonal variations, which may be explained by limited precipitation of gypsum and the absence of halite precipitation. The minimum values of HCO_3^-/Cl^- ratio are reached during the summer season (0.006 compared to 0.01 in winter), which is probably caused by an increase in temperature and precipitation of carbonates. Bottom waters show a low HCO_3^-/Cl^- ratio during all year of the study. This could be related to several phenomena such as:

1. The presence of evolved waters at the surface, which lost a part of their bicarbonate,
2. The photosynthetic activity which can contribute to the calcium carbonate precipitation.

Chemical evolution of waters and saturation test

The possible aptitude of a solution of given chemical composition to precipitate minerals can be checked by the calculation of saturation ratios. The ratio of the ion activities product Q and the theoretical solubility product Ksp is calculated:

$$\Omega = Q/Ksp$$

Three cases can be distinguished:

$Q < Ksp$: Ω is lower than 1 and the solution is under

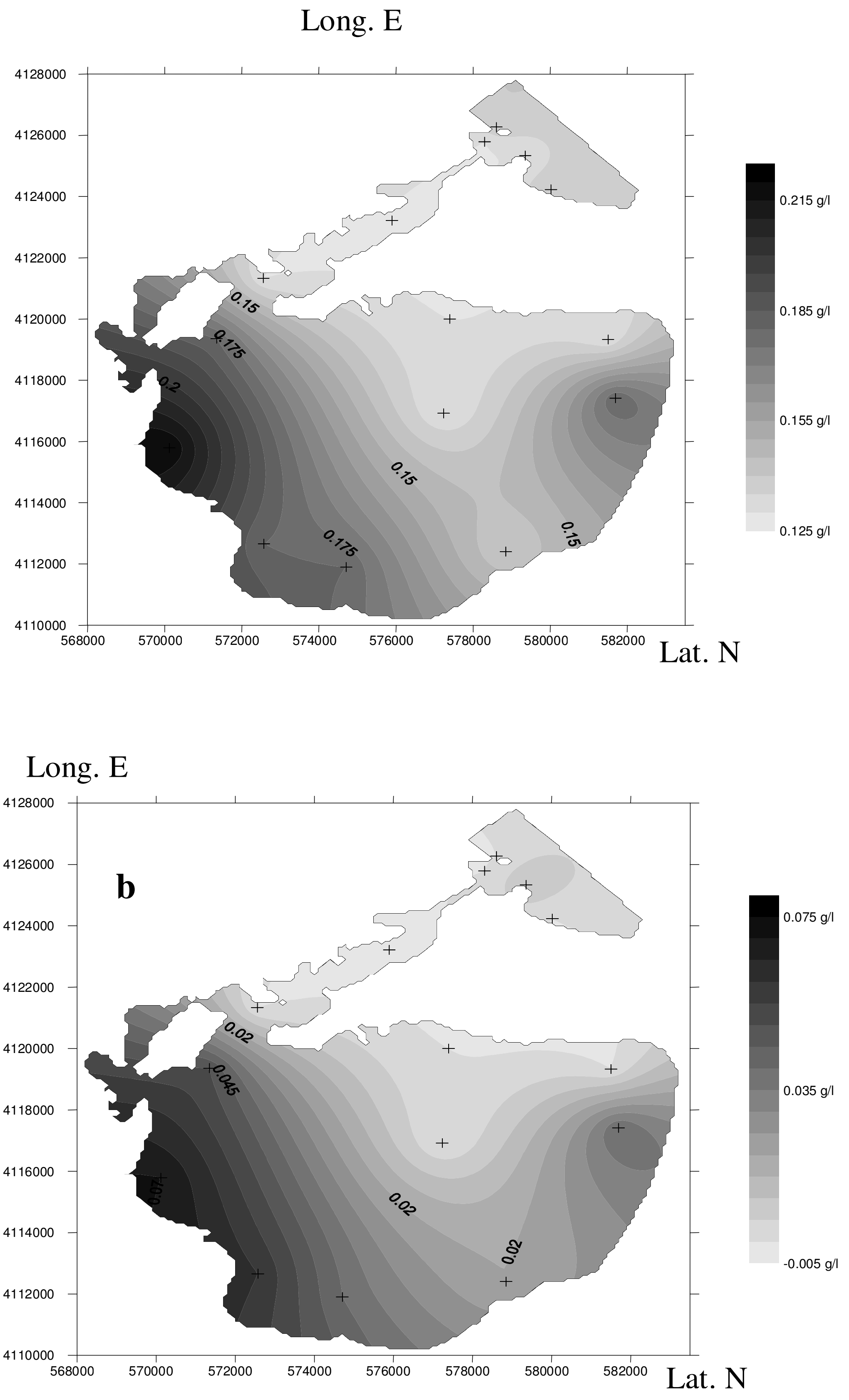

Figure 5. Spatial variations of the bicarbonate concentrations in the Bizerte Lagoon water. a. Water surface concentrations (in winter). b. Variation in concentrations between surface and bottom water (in winter).

Table 1. Saturation ratios calculated for some minerals at 25°C.

Minerals	Log Ksp $_{299,\ 15°K}$	Log Q		Ω = Q / Ksp	
		Winter	Summer	Winter	Summer
Calcite	- 8.36 (a)	- 4.80	- 4.57	1.74	1.83
Aragonite	- 8.22 (b)	- 4.80	- 4.57	1.71	1.79
Dolomite and/or magnesium calcite	- 17.0 (c)	- 8.89	- 7.43	1.91	2.28
Gypsum	- 4.60 (d)	- 4.32	- 3.74	1.06	1.22

(a) Plummer and Bussenberg (1982), Sass and al. (1983), (b) Morse and al. (1980), (c) Truesdell and Jones (1974), (d) Naumov al. (1971).

saturated with respect to a mineral considered.

Q = Ksp: Ω is equal to 1 and the solution is at equilibrium with a mineral considered.

Q > Ksp: Ω is higher than 1 and the solution is oversaturated with respect to a mineral considered (Stumm and Morgan, 1970). The over saturation state is unstable and should theoretically evolve in time towards equilibrium. It could be a slow process due to a precipitation delay related to crystals germination phenomena, to the kinetics reaction etc (Ben, 1988). In particular, the impurities in carbonate minerals (Sr in calcite and aragonite, Mg in magnesium calcite) can not only inhibit (or conversely activate) the precipitation of minerals, but also change the value of a relevant mineral solubility product (Tagorti, 1990).

It is in this context that preliminary evaporation tests of the brine of Sebkha El Adhibate (South-western Tunisian, on the Libyan border) were carried out in order to determine the useful salt sequences deposited (ONM, 1986 in Bouhlila, 1997). The Works of Ben (1988: paralic basin of El Kantara-Gourine, South-eastern of Tunisia), of Tagorti (1990: lagoon complex: Sebkha Halk el Mengel and Assa El jerbia (the Sahel of Tunisia) and of Darragi, (1992: Natron Lake (Tanzania) allowed the simulation of a wider variety of natural brines. From the data on the activity coefficients for ionic species, the stochiometric products are calculated and compared to the theoretical solubility products for minerals. In our case the calculation of Q is based on the concentration of the ionic species and not on activities. The calculations are based on empiric equations proposed by Pitzer and Mayorga (1973). The results are given in Table 1.

Following Table 1, four minerals could precipitate at the water-sediment interface in the Bizerte Lagoon. In spite of obtaining these values from calculations on the basis of concentrations and not activities of the ionic species, they probably are a little bit higher but confirm the possibility of precipitation of these minerals. The calculation of the thermodynamic balance and of the saturation index (SI) by Chaouni Alia and Al., (1997) allowed to specify that the minerals whose potential of dissolution is very high, such as anhydrite, halite, epsomite and brucite, will be dissolved if they are present in the sediments of the Bou-Areg plain (North-Eastern Morocco). Whereas, the solution is in chemical balance or is slightly supersaturated compared to calcite ($- 0.12 < SI < +0.93$).

Conclusion

The concentrations of main ions in the Bizerte Lagoon waters, that is Na$^+$, K+, Ca^{++}, Mg^{++}, Cl$^-$, HCO$_3^-$and SO$_4^{2-}$, are primarily controlled by the continental contributions and the interactions with the marine environment. During summer (the dry season), lagoon waters are concentrated by strong evaporation and they become increasingly enriched in sulphate, magnesium, and calcium. Based on saturation ratios calculations, carbonate minerals and gypsum can precipitate at the water-sediment interface in the Bizerte Lagoon.

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