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ANTHROPOGENIC FEATURES IN THE SINES (PORTUGAL) AND ESSAOUIRA (MOROCCO) COASTAL AQUIFERS: A COMPARATIVE STUDY OF THEIR HYDROCHEMICAL EVOLUTION BY A PRINCIPAL COMPONENT ANALYSIS.

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ABSTRACT

Considering the effects of climatic conditions on groundwater resources salinization and quality, a comparative study was conducted on the coastal aquifers of Sines (Portugal) and Essaouira (Morocco). Under the climatic and environmental conditions these two basins present different vulnerabilities to anthropogenic activities. Both aquifers correspond to sedimentary basins with similar structures and lithologies.

From the available physical, chemical and piezometric data, two series of results of each area were selected corresponding to two different years that were analysed by Principal Component Analysis (PCA).

Sines basin is characterised by a temperate climate. In the Sines aquifer the water-rock interaction process is the major mechanism responsible for the groundwater evolution, conferring a calcium-bicarbonate facies. Applying the PCA, punctual anthropogenic contamination was identified and linked to agricultural activities.

The water resources of the Essaouira basin are characteristic of a semi-arid climate, and are severely impacted by the climate (quantity and quality). PCA allowed the evaluation of the contribution of the Tidzi diapir in the water recharge that confers to the groundwater a sodium-chloride facies. Although this statistical method did not shown a nitrate contamination input in the Essaouira multi-aquifer, this polluent presents locally high values.

Also the very high evaporation and scarce precipitation activate the processes of salinization and contamination.

Key words: *hydrogeochemistry, salinization, Sines Basin (Portugal), Essaouira Basin (Morroco).*

RESUMEN

Considerando los efectos de las condiciones climáticas sobre la calidad y la salinidad de las aguas subterráneas, se ha llevado a cabo un estudio comparativo entre los acuíferos costeros de Sines (Portugal) y de Essaouira (Marruecos). Teniendo en cuenta las condiciones climáticas y el medio ambiente de estas dos cuencas, resultan distintas vulnerabilidades a las actividades antrópicas. Ambos acuíferos se localizan en cuencas sedimentarias de estructura y de litología idénticas.

Un Análisis de Componentes Principales fue realizado a partir de datos físicos, químicos y piezométricos conseguidos durante dos años en cada área.

La cuenca de Sines se caracteriza por un clima templado. En el acuífero de Sines el desarrollo de las interacciones agua-roca es mayoritariamente responsable de la modificación de las aguas subterráneas, confiriendo una facies calcio-bicarbonatada. Mediante un Análisis de Componentes Principales, se identificó una contaminación antropogénica puntual de origen agrícola.

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Los recursos en agua de la cuenca de Essaouira están dentro de un clima semiárido, dependiendo muchísimo de este (cantidad y calidad). La utilización de la citada metodología permitió evidenciar la contribución del diapiro Tidzi en las aguas de recargas, confiriendo una facies de cloruro sódico en las aguas subterráneas. Aunque este método estadístico no permitió la demostración de la contaminación por los nitratos en los diversos acuíferos de Essaouira, aquel contaminante se encontraba puntualmente en altas concentraciones. Por otra parte, la fuerte evaporación y las bajas precipitaciones amplían el fenómeno de salinidad y de contaminación.

Palabras clave: *hydrogeoquímica, salinidad, cuenca de Sines (Portugal), cuenca de Essaouira (Marruecos).*

Introduction

In coastal regions, the problems related with the increase of salinization and pollution in groundwater systems is generally associated to the effects of seawater (seawater intrusion by overexploitation of the system and by sea-salt-spray) and on the other hand by the anthropogenic activities such as domestic wastes, agriculture and industry. Also, intrinsic properties of aquifers (porous / fractured / karstic media, geological structure, permeability), and external factors such as climate may contribute to mitigate or worsen these problems.

Considering the effects of climatic conditions on groundwater resources salinization and quality, a comparative study was conducted on the coastal aquifers of Sines and Essaouira basins located on the Atlantic coastline, southern (Portugal), and southern (Morocco), respectively (Fig. 1). Both aquifers have similar structure and lithologies. However they are under different environmental and climatic conditions having different recharge rates.

Sines sedimentary basin is characterised by a temperate climate with a mean annual rainfall of about 650 mm/year and with a potencial evapotranspiration of about 750 mm/year (Lavaredas and Silva, 1999a). Opposite conditions are found at Essaouira basin located in a Moroccan semi-arid area with maximum annual rainfall of 300 mm/year and with a high potential evapotranspiration around 920 mm/year (Fakir, 2001).

Both sedimentary basins have an area of about 200 km^2. They are filled with Mesozoic and Cenozoic materials, which are overlaid with superficial Plioquaternary terrains (Fig. 1). In both sedimentary basins, one main aquifer was identified, supplying water for drinking and for agricultural activities.

Geological and Hydrogeological data

The Sines basin

The Sines sedimentary basin corresponds to a tectonical basin with a NE-SW orientation filled with Mesozoic and Cenozoic deposits (Fig. 2). The basin deposits contact by angular discordance to the E and S with Palaeozoic basement rocks, to the SW with the Sines Subvolcanic Massif and to the W, with Quaternary and Terciary deposits along the Deixa-o-Resto fault.

The local Mesozoic sequence begins with Triassic deposits consisting of sandstones, evaporites and carbonates series (Grés de Silves Formation) overlaid by tuffs of the Volcanic-Sedimentary complex.

Carbonate layers with clastic rocks at the top compose the Jurassic sequence. The Liassic is represented by dolomites, dolomitic marls and oolitic limestones with an average thickness of 100 m. Oolitic limestones, microcristaline limestones and rare dolomites and marls compose the Dogger, with a maximum thickness of 400 meters. The Malm with about 600 m is constituted by a sequence of conglomerates, limestones, clays and marls (Manuppela & Moreira, 1989).

Miocene deposits (clayey sandstones, marls and marly limestone), Plio-Pleistocene detrital (sands and clays) and recent alluvial and dune deposits partially covered by the Mesozoic formations.

In the Sines basin two hydrogeological systems were identified: the Mio-Pliocene and the Jurassic terrains (Fig. 2). These hydrogeological systems supply the entire region with some areas highly populated and industrialised. In the Mio-Pliocene system the recharge of the aquifer is made directly on the outcrop areas, while in the Jurassic terrains the recharge occurs directly in carbonate formations outcrops and furthermore receives some contribution from the Miocene layers. In the studied area the main discharge of the systems should be in the continental platform, although, some small natural springs occur inland.

In the Sines Basin the precipitation varies, from 600 mm to 765 mm at Santiago do Cacém and a potencial evapotranspiration is about 750 mm/year (Lavaredas and Silva, 1999a). Analysing the precipitation records it is possible to verify the influence of the relief in the amount of precipitation over Sines Basin. The values of mean annual precipita-

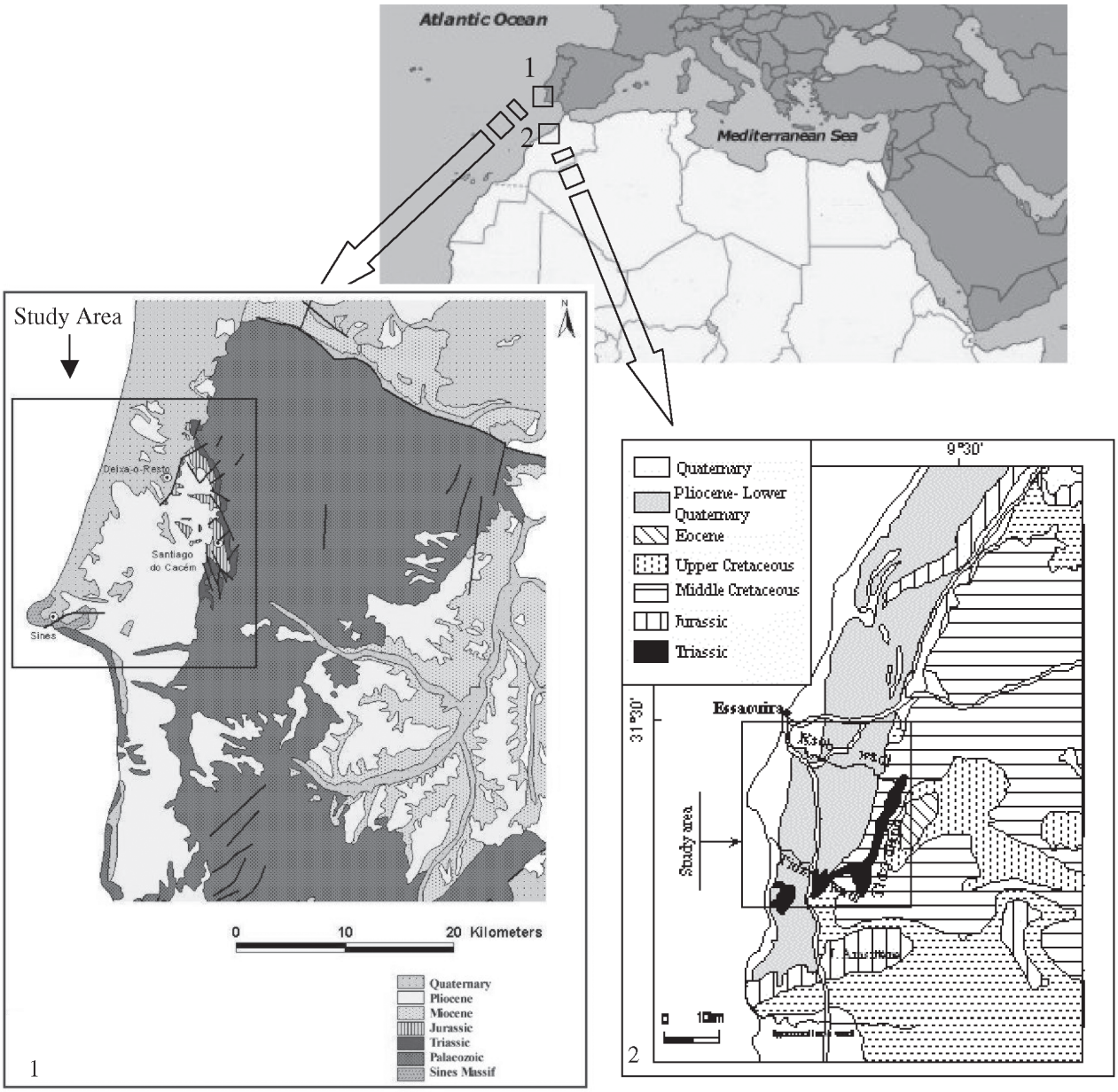

Fig. 1.—Location of the Sines (1) and Essaouira (2) basins.

tion increase to the interior when the altitude became higher (Grândola and Cercal mountains).

The main groundwater flow direction of Jurassic aquifer is from E to W towards the Atlantic Ocean. In the central part of the studied area, near Santo André Lagoon, as a result of a well concentrations supplying water to the Santiago do Cacém, a piezometric depression was identified (Fig. 3), although, the piezometric results reveal that the system does not present important variations in time from a season to another, which could be a result of a recharge contribution from the Tertiary formations to the Jurassic system.

The Essaouira basin

Covering the Palaeozoic bedrock, the sedimentary series range from the Triassic to the Quaternary. The sedimentary sequence begins with Triassic deposits having the same lithology as in Sines basin, outcroping in the E and S of the region. The

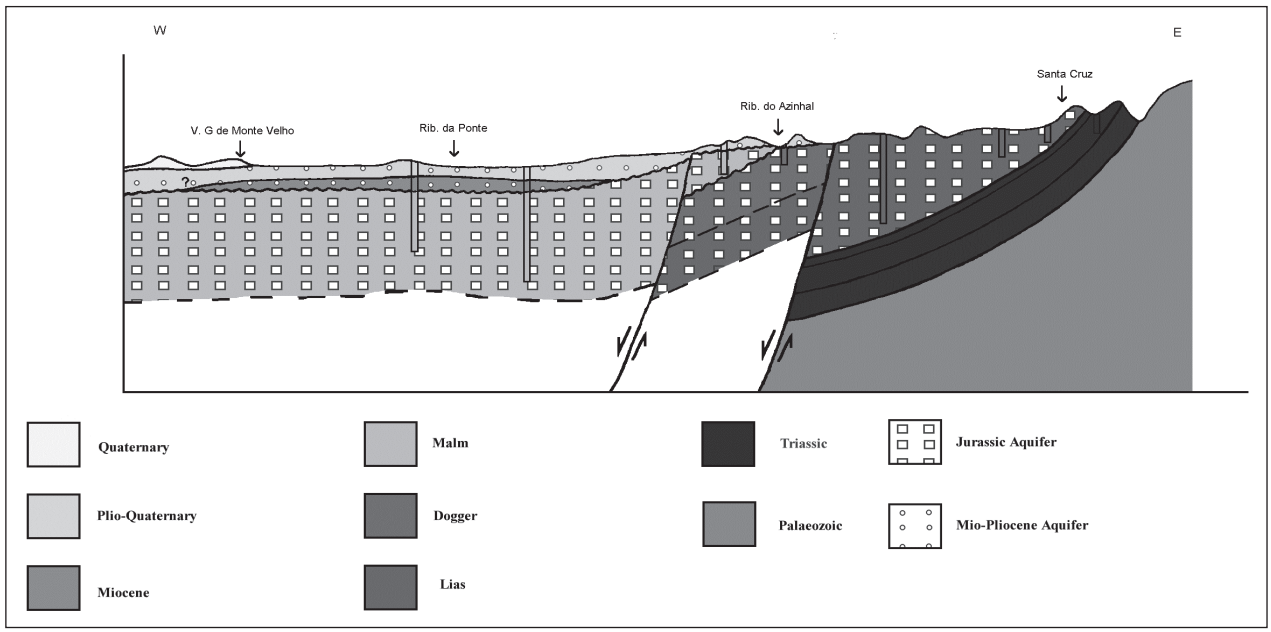

Fig. 2.—Geologic cross-section (adapted from Inverno *et al*., 1993).

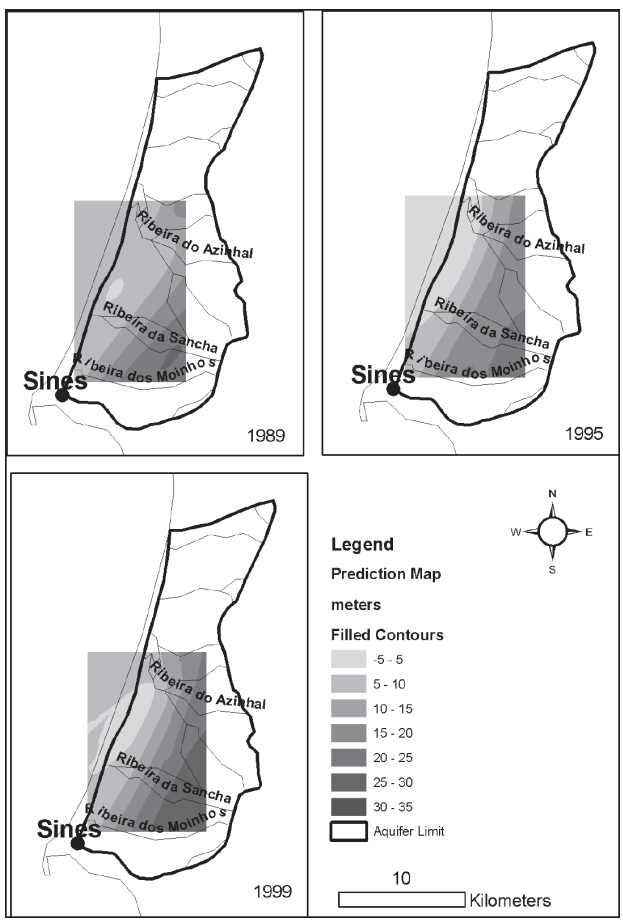

Fig. 3.—Sines basin piezometric map.

Carbonate rocks compose the Jurassic and marly sediments of lower Cretaceous to Cenomanian dominate the Cretaceous. The dolomitic limestones of the Turonian are covered by Senonian gypsy marls (Duffaud *et al*., 1966), which appear below the Plioquaternary detrital deposits of sands, sandstone and conglomerates. The geological structures delineate a syncline bordered by the Tidzi diapir of Triassic age which outcrops to the E and S.

In the Essaouira basin a multi-aquifer was identified constituted by detrital deposits of the Plioquaternary and dolomitic limestones of the Turonian.

The Plioquaternary is unconfined below the Senonian marls. However, in some places it can be in direct contact with the other Cretaceous and Triassic units. The Plioquaternary is generally up to 60 m thick.

The Turonian is confined by the Senonian marls and in direct contact with the Plioquaternary on the edges of the syncline structure.

For a few years, water has been withdrawn through drilling wells to supply the Essaouira tcity. At present, the Plioquaternary provides 47% of drinking water for Essaouira with about 64000 inhabitants and rural population. The total rate of extraction in this system is around 97 L/s (Agoumi, 1999; Hassani *et al*., 1998).

The piezometric levels in the Essaouira multi-aquifer present a general standardization through time (1990/2000). However, locally some piezometric variations can be identified. As a consequence of the weak thickness the sensibility to the droughts

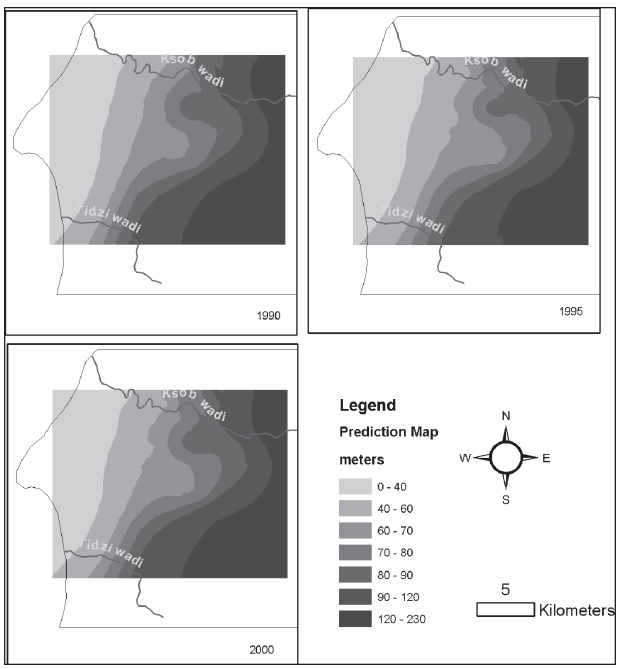

Fig. 4.—Essaouira basin piezometric map.

have an important impact in the water reservoir, as widespread drought periods that are affecting Morocco since 1978 (Agoumi, 1999; Hassani *et al*., 1998).

Morocco has a wide range of climate conditions: the coastal regions generally have a mild climate, the Atlas Mountains can be cold and wet during spring or even in summer, while the desert is hot and dry nearly all year. The Essaouira basin can be considered a semi-arid area with annual rainfall up to 300 mm/year and a very high potential evapotranspiration of about 920 mm/year (Agoumi, 1999; Hassani *et al*., 1998).

The main flow direction is from SE to NW towards the Atlantic Ocean, being the recharge area located near the Tidzi diapir (Fig. 4). The piezometric maps, since 1990 to 2000, show, in the N, a line deviation to the NE, indicating a possible contribution of the oued in the aquifer recharge.

Hydrochemical features

Several hydrogeological and hydrochemical studies have been performed in the basins of Sines and Essaouira, in order to evaluate their groundwater resources and to allow their chemical characterization and evolution along the flow paths (Bahir *et al*., 1999, 2000, 2001; Lavaredas and Siva, 1999a, 1999b; Galego Fernandes and Silva, 1999; Galego Fernandes *et al*., 2001a, 2001b).

To conduct the present comparative study, two campaigns were selected per basin: 1999 and 2001 for Sines and 1995 and 1996 for Essaouira. Concerning the Essaouira basin, the selection of the data considered that 1995 was a representative year of dry climatic conditions (mean rainfall of 200 mm) while 1996 was an exceptional rainy year (mean rainfall of 600 mm).

Considering that the chemical historical data in Sines basin groundwaters system presents a constant behaviour, the data selected correspond to the more

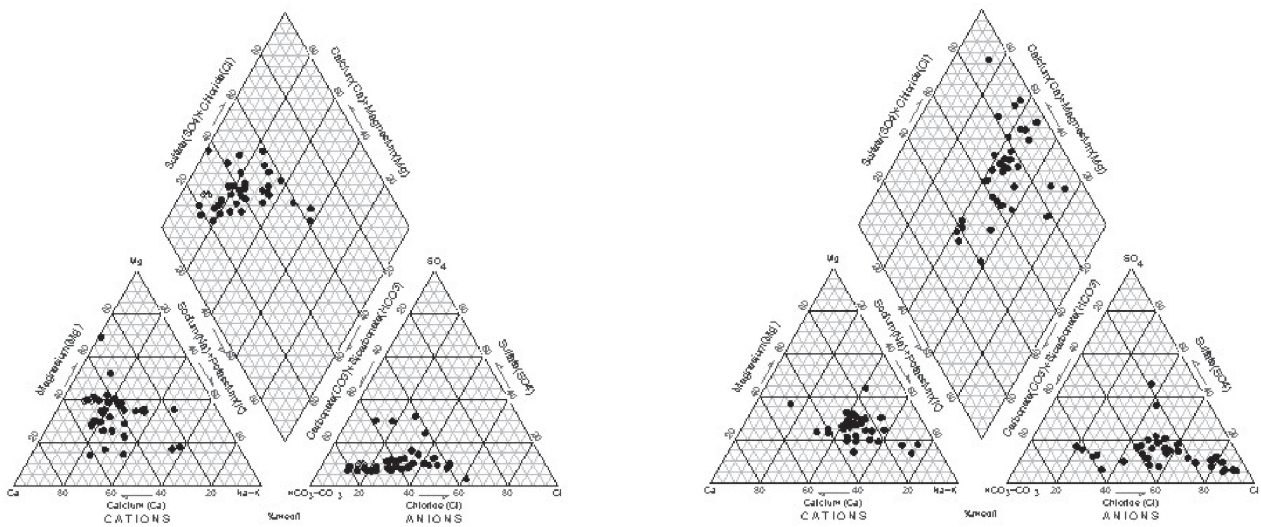

Fig. 5.—Piper diagram showing the ionic composition of groundwater: A) Sines basin; B) Essaouira basin.

Table 1.—**Comparison between the 1999 and 2001 campaigns in the Sines basin**

	1999					2001				
	Average	Standard deviation	Max	Min	Samples number	Average	Standard deviation	Max	Min	Samples number
EC (µS/cm)	729.2	258.3	1,420	175	38	708.3	224.9	1,179	235	20
pH	6.9	0.4	7.6	5.7		7.7	0.2	7.9	7.6	
Na (mg/l)	37.9	16.1	82.3	0.04	38					
Mg (mg/l)	30.8	13.9	57.3	5	38					
K	2.8	1.4	7.9	0,8						
Ca (mg/l)	65.9	28.2	120	5.75	38	67.0	27.3	101.6	4.8	20
HCO_3 (mg/l)	298.6	128.0	566	41	38	277.6	132.5	518	32	20
SO_4 (mg/l)	47.8	44.4	200.0	3.0	38	47.2	40.6	166.0	11.2	20
Cl (mg/l)	84.5	44.1	258.0	26.0	38	73.4	46.0	243.0	26.3	20
NO_3 (mg/l)	19.8	15.0	93.4	4.7	38	26.3	32.8	147.0	0.2	20
Fe	0.067	0.077	0.400	0.002						
CO_2	22.6	11.6	45.8	4.4						
Cu	0.008	0.024	0.144	0.001						
Al	0.083	0.098	0.597	0.007						
PO_4	0.033	0.031	0.130	0.002						
Mn	0.010	0.020	0.119	0.002						

Table 2.—**Comparison between the 1995 and 1996 campaigns in the Essaouira basin (adapted from Menanni *et al.*, 2001)**

	1995					1996				
	Average	Standard deviation	Max	Min	Samples number	Average	Standard deviation	Max	Min	Samples number
EC (µS/cm)						1,704.4	616.9	3,180	824.0	23
Na (mg/l)	269.4	126.1	591.7	105.6	33	308.9	122.9	736.0	144.9	23
Mg (mg/l)	73.8	25.0	140.0	26.2	33	64.3	28.8	116.6	13.9	23
Ca (mg/l)	142.6	71.2	325.0	53.2	33	163.0	55.4	282.4	76.4	23
HCO_3 (mg/l)	376.9	231.6	958.0	134.0	33	284.3	78.9	478.2	162.3	23
SO_4 (mg/l)	153.0	84.2	463.1	30.2	33	167.9	68.0	332.2	78.6	23
Cl (mg/l)	506.7	364.3	1,723	128.5	33	688.7	369.5	1,654	227.2	23
NO_3 (mg/l)	53.2	47.6	187.0	1.4	33	91.5	81.2	295.8	1.6	23

recent and complete campaigns (1999 and 2001). No data were available from 1995 to 1996 in Sines.

The chemical composition and the results of the statistical treatment are displayed in tables 1 and 2.

In the Sines basin, the groundwater is mainly of the calcium-bicarbonate type (Fig. 5a), related to the lithological composition of the reservoirs dominated by calcareous and dolomitic units.

Plotting the chemical results it is possible to see that the parameters with a higher dispersion are the bicarbonates, calcium, sulphates, chloride and nitrates (Fig. 6). The enrichment in chlorides and sodium is present in the waters located near the Moinhos River (in S of the area), from values of 70 to 200 mg/L and 25 to 70 mg/L, respectively. The increase in the salt concentration could be associated to different mechanisms: Hettangian evaporites lixiviation; mixture with actual seawater through the river substratum; and mixture with ancient seawater trapped in the sediments.

The similar distribution pattern of the content in chlorides, nitrates and sulphates, showing a significant difference between the medium and maximum values, thus allowing the identification of local contaminations inputs to the groundwater system.

The wide range values in the bicarbonate content, from 50 to 600 mg/L, is the result of the lateral geological variations of the layers conferring to the groundwater different contents of bicarbonate.

A standardisation of the results was performed, so that all the variables show the same importance in the system characterisation. Plotting the standardised parameters (Fig. 7) it is possible to verify that for some parameters, such as PO_4, Al, Cu, Mn, SO_4, NO_3 and Fe, the median is similar to the minimum presenting a significant difference with the

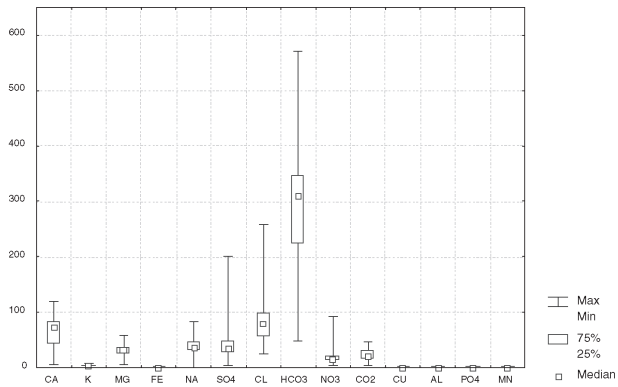

Fig. 6.—Box Plot of chemical analyses in the Sines basin.

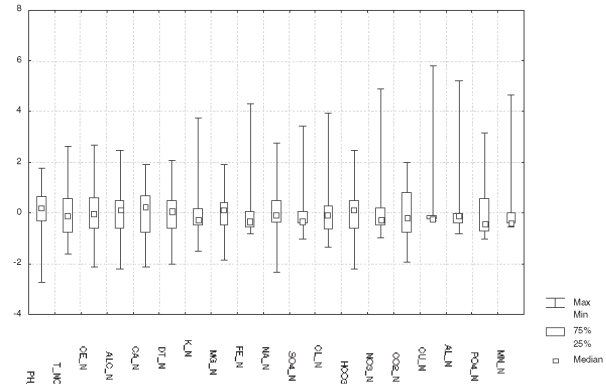

Fig. 7.—Box Plot of standardised parameters in the Sines basin.

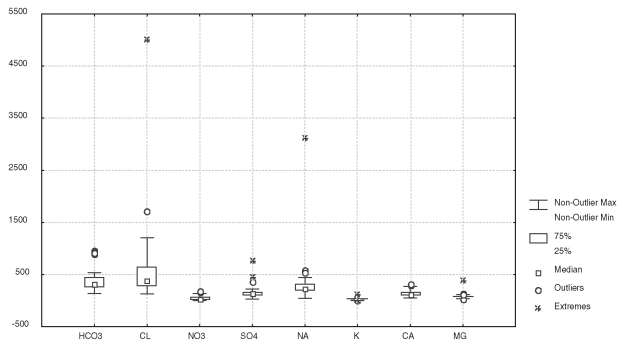

Fig. 8.—Box Plot of chemical analyses in the Essaouira basin.

maximum. This distribution seems to indicate an external origin, an anthropogenic source to the aquifer system, probably indicating pollution input to the groundwater by agricultural or cattle breeding activities.

In the Essouaira basin, in spite of the occurrence of calcareous and dolomitic levels, all waters are of Na-Cl-type (Fig. 5b). The chemical signature of these waters should be the result of the preferential recharge area that is located in the Tidzi diapir. A high correlation coefficient was found between electrical conductivity, chlorides and sodium contents, suggesting the large contribution of these elements to the groundwater chemical load. Nevertheless, occulted by chloride the groundwater is highly bicarbonate as a result of the presence of carbonate compounds in the reservoirs matrix.

Analysing the dispersion of the values of the parameters is probable that the difference between the maximum values and the average is a result of a punctual increase (Fig. 8). However, the present range is in majority a result of the oued contribution into groundwater recharge, leading to a dilution of the water mineralization. Another hypothesis to explain the range in mineralization could be the available time in the water rock interaction with the diapir that constitutes the basin. It is also important to consider the huge concentrations in chloride and sodium (5019 and 3133 mg/L), not included in the diagram because of the anomaly behaviour of the well number 45 located near the coastline on the NW of the area. These values could be a result of a local intrusion phenomena originated by over exploitation.

Hydrogeochemical evolution

Considering the numerous species involved in the chemical analyses, the sources of salinization were sought using Principal Component Analysis (PCA). PCA is a Factorial Analysis, in which graphs are generalised, taking into account all the elements involved, in order to achieve optimal data visualisation (Melloul, 1995). Using this statistical analysis a reduction of the observation dimensions species obtained in which the given objects are studied, by creating linear combinations of variables that characterize the studied objects (Mackiewicz and Ratajczak, 1993).

The Sines basin

The PCA was performed in the Sines basin physical-chemical data (27 cases and 17 variables) using STATISTIC 6 code. Six factors with eigenvalues over 1 were obtained (Tables 3 and 4):

Factor 1 contributes nearly 32.7% of the total variance of the system characterisation, showing a positive correlation with bicarbonate, conductivity, calcium and magnesium content. This factor represents the groundwater evolution and the importance of water-rock interaction processes. It emphasises that groundwater with a higher residence time has

Table 3.—**Factorial analyses in the Sines basin**

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
PH	0.413967	0.129105	0.120544	0.606931	–0.49159	–0.21335
T	0.15484	–0.30159	0.132867	0.793264	0.212014	–0.17598
EC	0.88723	0.187405	0.322347	0.015455	0.100405	0.086188
Ca	0.839664	0.225607	0.201784	0.136337	–0.06118	0.158545
K	–0.08279	0.131756	0.756965	–0.04986	0.009782	–0.1309
Mg	0.872236	0.211863	0.090179	–0.10358	0.153512	0.039057
Fe	–0.59128	0.218672	–0.13569	0.077108	0.490802	0.443039
Na	0.270834	0.02512	0.891028	0.011688	0.104109	0.044228
SO_4	0.339139	0.7387	0.2383	0.059692	0.119147	0.10917
Cl	0.342234	–0.0148	0.808232	0.131777	–0.04458	0.054879
HCO_3	0.935198	0.050347	–0.04276	–0.03069	–0.01687	0.070395
NO_3	0.104481	0.04036	0.120134	–0.01931	0.821959	–0.19554
CO_2	0.34118	–0.09942	0.097527	–0.87046	0.116494	–0.11611
Cu	0.213157	0.789385	–0.19936	0.012418	0.194734	0.001844
Al	–0.67417	6.64E-05	–0.23319	0.029066	0.246257	0.500445
PO_4	–0.02843	0.710394	0.229224	–0.17984	–0.29524	–0.00185
Mn	–0.22352	–0.04857	–0.02275	0.106387	0.212905	–0.79165

Table 4.—**Total variance of factors in the Sines basin**

	Eigenval	% total Variance	Cumul. Eigenval	Cumul. %
1	5.56	32.68	5.56	32.68
2	2.20	12.94	7.75	45.62
3	1.85	10.88	9.61	56.50
4	1.68	9.86	11.28	66.36
5	1.40	8.22	12.68	74.58
6	1.08	6.35	13.76	80.93

higher values in bicarbonate, calcium and magnesium, as related to the lithology of the aquifer.

Factor 2 represents 12.9% of the total variance and indicates a positive correlation between copper and sulphates. This could be a result of two phenomena: agriculture contamination by the use of pesticides or result of a contribution of malachites and azurites from the Triassic formations.

Factor 3, also with an important contribution to the waters evolution (10.9%), shows a positive correlation between sodium, chloride and potassium. Factor 3 probably represents the dissolution of evaporate minerals and its contribution to water mineralization.

Factor 4 represents 9.9% of the total variance and it is dominated by the temperature and carbon dioxide.

Factor 5 represents the groundwater contamination by nitrates, a hazard for humans in the area. Factor 6 displays a negative correlation with Mn, that may represent the lost of the Palaeozoic and/or the lost of the clays influence.

Plotting in a diagram the factor 5 *versus* factor 2 for all samples analysed, it is possible to identify the samples with higher contaminations. Samples where the factor 2 as a higher contribution, such as F11, F27 and F35, correspond to wells located in agricultural terrains where the use of fertilisers is more intensive. Sample F12 represents a groundwater sample with nitrate contamination (concentrations approximately of 100 mg/L), where factor 5 has a greater importance (Fig. 9).

Comparing the data of the 1999 and 2001 campaigns (Table 3), the concentrations of relevant chemical species, namely the nitrate concentration, are identical for the water samples, so no significant variation was verified.

The distribution of sodium and chloride, within Sines, allow the evaluation of the water hydrochemical evolution (Fig. 10).

The enrichment in chloride and sodium is mostly observed near the Moinhos River and Cascalheira River (NE of the area), with an increase of values from 70 to 200 mg/l in chloride and 25 to near 70 mg/l in sodium The increase of salt content in these locations could be associated with three different mechanisms: i) lixiviation of evaporitic materials from the Hettangian, ii) seawater mixing with infiltration by the river substratum and iii) ancient seawater trapped in the sediments during the basin formation.

The Essaouira basin

The application of the PCA method to Essaouira groundwater data allows the identification of 3 factors with eigenvalues greater than 1 (Table 5 and 6):

— Factor 1 represents 41% to the total variance of the groundwater system with a positive correla-

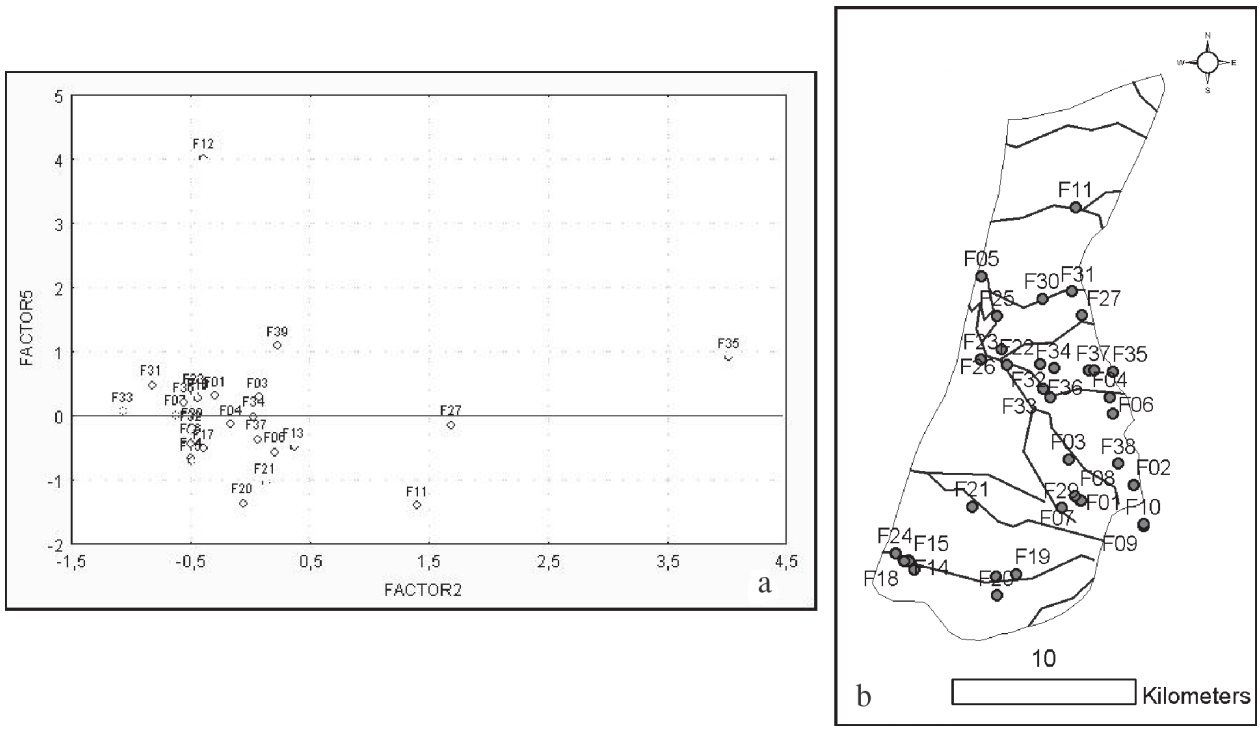

Fig. 9.—Factor 5 *versus* factor 2 to Sines Basin samples (a) and wells location (b).

tion between chloride, sodium, calcium and magnesium. This pattern materialises the water-rock interaction namely the dissolution of evaporate minerals and/or the contribution of Tidzi diapir in the water recharge.

— Factor 2 with a relevance of 19% to the groundwater characterization represents the sulphates content. These values could have natural or anthropogenic origins, resulting from evaporatic dissolution and/or the use of fertilisers.

— Factor 3 represents 17% of the total variance and it is probably the result of the influence of the bedrock in the water mineralization; factor 3 shows a high correlation with potassium.

The samples recovered after the exceptional rainfalls in January 1996, show a remarkable increase in Na^+ and Cl^+ concentrations when compared with the data of 1995 (Table 2). In fact, the infiltrated water in 1996 remobilized the salts trapped and concentrated in the soil and in the unsaturated zone during the long period of low precipitations.

However, dilution effects can be observed in a particular recharge environment. Indeed, spatial distributions of sodium and chloride for 1996 (Fig. 11) show that the lowest concentrations are in the NE area immediately southward of *Ksob wadi*. It highlights the aquifer recharge by *Ksob wadi* and the dilution originated by it. This recharge was also confirmed via water flow measurements in this *wadi* (Fekri, 1993).

The higher concentrations located in the central part of the area are a result of the influence of the

Table 5.—**Factorial analyses in the Essaouira Basin**

	Factor 1	Factor 2	Factor 3
HCO_3	–0.05209	0.56697	–0.59120
Cl	0.91966	–0.24626	0.20629
NO_3	0.51705	–0.59032	0.05719
SO_4	0.10906	0.82363	0.23708
Na	0.83928	0.23035	0.16783
K	0.03055	0.24041	0.85555
Ca	0.82401	–0.14683	–0.02267
Mg	0.83775	0.09662	–0.43083

Table 6.—**Total Variance of factor in the Essaouira basin**

	Eigenval	% total Variance	Cumul. Eigenval	Cumul. %
1	3.27	40.90	3.27	40.90
2	1.49	18.69	4.77	59.59
3	1.40	17.44	6.16	77.03

Fig. 10.—Spatial distribution of sodium and chloride in the Sines basin.

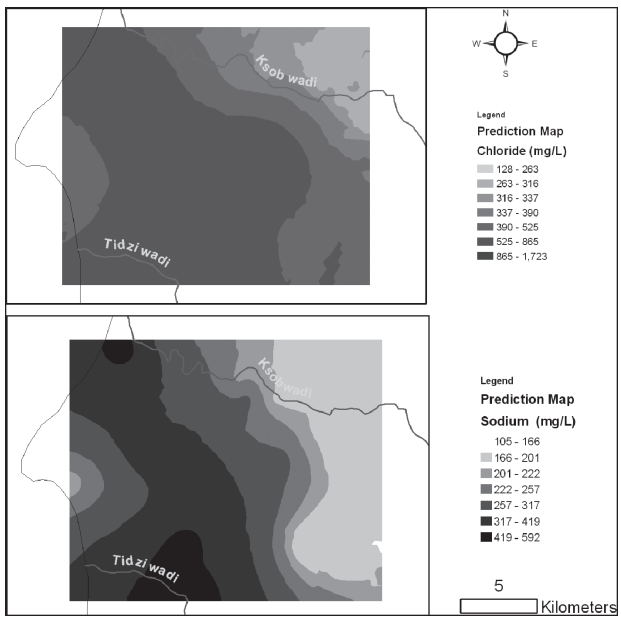

Fig. 11.—Spatial distribution of sodium and chloride in the Essaouira basin.

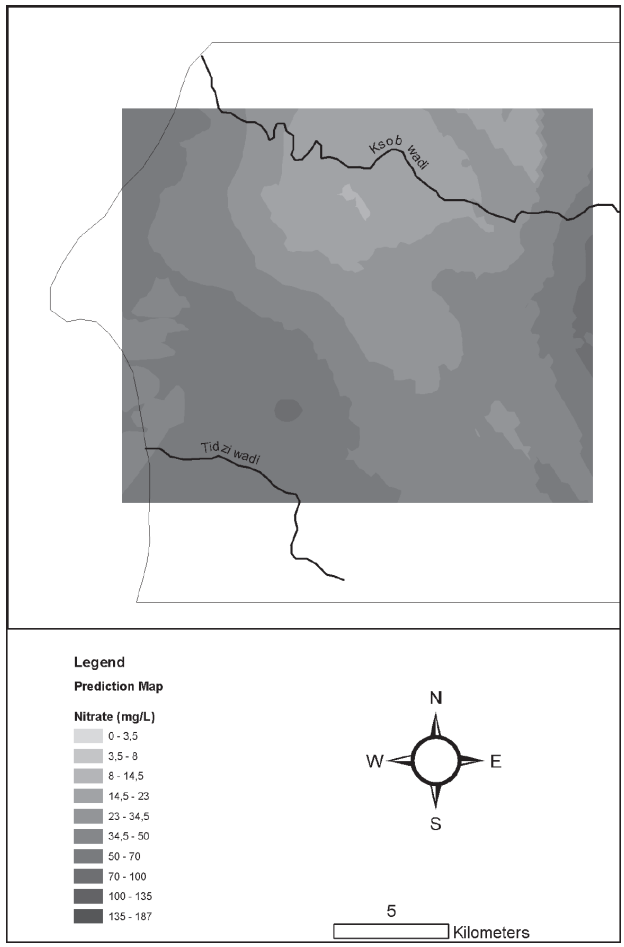

Fig. 12.—Spatial distribution of nitrate in the Essaouira basin.

Tidzi diapir in the water recharge, leading to high contents in sodium and chloride, according to the main flow direction. The evolution of these parameters does not indicate the main flow direction probably as related to the *Ksob wadi* recharge and the dilution effect generated by it.

Anthropogenic influence on the aquifers

Contamination

In 1995, nitrate concentrations in the groundwater system of Essaouira basin ranged from 1.4 to 187 mg/L (Table 2). The mean NO_3^- concentration was 53.5 mg/L and 45% of the groundwater samples exceeded 45 mg/L (Bahir et al., 2001), which is the World Health Organization maximum amount of NO_3^- content for drinking water.

In 1996 the nitrate content was higher than the one of the previous campaign, the concentration

ranged from 1.6 to 295.8 mg/L, with a mean value of 91.5 mg/L being 65% of the groundwater samples over 45 mg/L. The NO_3^- and Cl^- concentration increasing after the rains of 1996's supports the above hypothesis for the external origin of these elements as well as the salt remobilization phenomena triggered by precipitation after a long period of drought.

The nitrate distribution also indicates the oued contribution in the groundwater mineralization, by dilution the groundwater near this river assume lower concentrations in this pollutant (Fig. 12).

From the comparison of the two basins it is possible to see that in the Sines basin, nitrate concentrations are inferior (Table 1) and remain quite similar between 1999 and 2001 with mean values of 19.8 mg/L and 26.3 mg/L respectively.

Based on the different nitrate content at the Essaouira and Sines, one might think that important amount of fertilisers were used in intensive agricultural activities in Morocco. However, there are only weak agricultural activities there, less important than in Sines. In the Essaouira basin, the main source of nitrate is associated to wrong wells design, lack of head well protection (e. g. hand-dug wells with no casing and cover), lack of head well protection areas, traditional extraction methods, accumulation of livestock waste nearby the wells. The lack of prevention and environmental programs for the population seriously threatens the groundwater resources and leads to poor quality in the water supplies.

In relation to the sulphates, the origin in the both aquifers could be similar. In Essaouira sulphates are probably the result of evaporites and diapiric dissolution, but they could also be the result of the fertilisers. However, we haven't obtained any correlation between sulphates and other element that supports the different origins (Table 7).

Table 7.—**Correlation matrix in the Essaouira basin**

	HCO_3	Cl	NO_3	SO_4	Na	K	Ca	Mg
HCO_3	1.00	–0.38	–0.18	0.12	0.11	–0.15	–0.19	0.20
Cl	–0.38	1.00	0.52	–0.06	0.77	0.08	0.79	0.65
NO_3	–0.18	0.52	1.00	–0.39	0.36	0.04	0.38	0.33
SO_4	0.12	–0.06	–0.39	1.00	0.18	0.23	0.04	0.09
Na	0.11	0.77	0.36	0.18	1.00	0.26	0.46	0.59
K	–0.15	0.08	0.04	0.23	0.26	1.00	–0.06	–0.30
Ca	–0.19	0.79	0.38	0.04	0.46	–0.06	1.00	0.66
Mg	0.20	0.65	0.33	0.09	0.59	–0.30	0.66	1.00

In Sines the sulphate origin, suggested here, could be associated with the Hettangian dissolution or with the pesticides. These theories could be confirmed by the PCA and also by the correlation matrix (Table 8).

Conclusion

The hydrogeological system, in the Sines basin, supplies a highly populated and industrialised region. The amount of precipitation provides a consistent recharge, leading to an aquifer system that is not in hydraulic stress and does not present significant temporal variations in quantity and quality. The water-rock interaction process is the major mechanism responsible for the groundwater salinity. Some anthropogenic contaminations might also have influenced the water mineralization.

Table 8.—**Correlation matrix in the Sines basin**

	Ph	T	Cond	Ca	K	Mg	Fe	Na	SO_4	Cl	HCO_3	NO_3	CO_2	Cu	Al	PO_4	Mn
Ph	1.00	0.35	0.37	0.48	0.18	0.31	–0.49	0.15	0.14	0.28	0.39	–0.25	–0.43	0.07	–0.45	0.11	0.03
T	0.35	1.00	0.11	0.17	0.04	–0.01	–0.10	0.18	–0.03	0.22	0.10	0.12	–0.48	–0.15	–0.17	–0.36	0.23
COND	0.37	0.11	1.00	0.84	0.13	0.90	–0.40	0.52	0.54	0.64	0.83	0.16	0.30	0.25	–0.56	0.17	–0.18
Ca	0.48	0.17	0.84	1.00	0.07	0.67	–0.38	0.46	0.46	0.42	0.87	0.06	0.17	0.26	–0.51	0.26	–0.27
K	0.18	0.04	0.13	0.07	1.00	0.08	–0.08	0.53	0.24	0.39	–0.08	0.13	0.14	–0.01	–0.17	0.12	–0.02
Mg	0.31	–0.01	0.90	0.67	0.08	1.00	–0.36	0.30	0.53	0.37	0.80	0.16	0.39	0.34	–0.50	0.05	–0.17
Fe	–0.49	–0.10	–0.40	–0.38	–0.08	–0.36	1.00	–0.22	–0.05	–0.27	–0.44	0.18	–0.27	0.12	0.83	0.06	0.02
Na	0.15	0.18	0.52	0.46	0.53	0.30	–0.22	1.00	0.31	0.80	0.21	0.22	0.17	–0.05	–0.34	0.22	–0.07
SO_4	0.14	–0.03	0.54	0.46	0.24	0.53	–0.05	0.31	1.00	0.29	0.26	0.09	0.03	0.58	–0.21	0.40	–0.19
Cl	0.28	0.22	0.64	0.42	0.39	0.37	–0.27	0.80	0.29	1.00	0.24	0.01	0.06	–0.07	–0.39	0.16	–0.04
HCO_3	0.39	0.10	0.83	0.87	–0.08	0.80	–0.44	0.21	0.26	0.24	1.00	0.08	0.34	0.17	–0.52	0.14	–0.20
NO_3	–0.25	0.12	0.16	0.06	0.13	0.16	0.18	0.22	0.09	0.01	0.08	1.00	0.08	0.13	–0.08	–0.09	0.14
CO_2	–0.43	–0.48	0.30	0.17	0.14	0.39	–0.27	0.17	0.03	0.06	0.34	0.08	1.00	0.03	–0.26	0.03	0.00
Cu	0.07	–0.15	0.25	0.26	–0.01	0.34	0.12	–0.05	0.58	–0.07	0.17	0.13	0.03	1.00	–0.11	0.27	–0.13
Al	–0.45	–0.17	–0.56	–0.51	–0.17	–0.50	0.83	–0.34	–0.21	–0.39	–0.52	–0.08	–0.26	–0.11	1.00	–0.10	–0.02
PO_4	0.11	–0.36	0.17	0.26	0.12	0.05	0.06	0.22	0.40	0.16	0.14	–0.09	0.03	0.27	–0.10	1.00	–0.04
Mn	0.03	0.23	–0.18	–0.27	–0.02	–0.17	0.02	–0.07	–0.19	–0.04	–0.20	0.14	0.00	–0.13	–0.02	–0.04	1.00

The economic and social activities in the Essaouira basin depend heavily on groundwater. In this basin, the very high evaporation and scarce precipitation of the semi-arid climate activate the processes of salinization and contamination. In this context, the rainfall triggers a remobilization of residual chemical species and contaminants (sodium, chloride, nitrate) trapped and concentrated in the soil or seeped into the unsaturated zone during the long period of drought. This clearly shows the small potential of natural attenuation by precipitation of the semi-arid regions.

Considering the numerous elements involved in the chemical analyses, the sources of salinization were sought using Principal Component Analysis (PCA). In the Sines Basin 6 factors were obtained, that characterize the elements responsible for the water mineralization, such as bicarbonate, chloride, calcium, sodium. The anthropogenic influence in the water degradation is also important. The factors that correspond to the local pollution represent 21.6% (Factor 2 and 5) of the total variance of the system.

In Essaouira we identified the contribution of the Tidzi diapir in the water recharge and the water-rock interaction (the dissolution of evaporite minerals) that materialises 41% of the total variance. The other 2 factors depend on the bedrock influence in the water mineralization or even on the presence of anthropogenic contamination.

According to the climatic and environmental conditions and social and economical factors it is evident that each of the referred basins requires specific management measures to protect and to preserve the groundwater resources and to guarantee the water supplies. Rajagopal and Graham (1989) suggest three recommendations that might be useful in the Essaouira basin, where less management measures exist:

— The use of the water from Ksob wadi for artificial recharge of the aquifers. In fact, the most significant outflows of the wadi are related to occasional floods in winter. A small part feeds the aquifers and the rest is lost to the Atlantic Ocean.

— Improvement of the techniques of drilling, constructing and protecting wells.

— Public awareness and participation in water management.

Today, in Sines the protection measures to groundwater quality are respected. However, some nitrate contamination problems are still found as a result of some agricultural and cattle breeding activities, which lead us to suggests a rigorous control of possible contamination sources, such as effluents and others.

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