

*Full Length Research Paper*

# Messinian salinity crisis impact on the groundwater quality in Kert aquifer NE Morocco: Hydrochemical and statistical approaches

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Groundwater's studies at middle Kert aquifer in northeast of Morocco are very important due to the semi-arid character and its geological history. The region is recognized by messinian salinity crisis already 5.6 Ma. Water chemistry is mainly dominated by dissolution of evaporate rocks (Halite and Gypsum) related to outcropping and basement limits developed in Messinian age. Freshwater with total dissolved solids 740 mg/l (average value) in Tafersite district is chemically distinct from saline water with total dissolved solids of 9803 mg/l in the south zone. In wadis, water is  $SO_4$ -Cl-Ca type; they are influenced by the surrounding highlands located at the south of the plain. The investigation reveals that weathering of evaporated rocks is the processes responsible for high  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$  and  $SO_4^{2-}$  concentrations. Also, hydro chemical data displays that freshwater observed in the northwest part reflect the influence of freshwaters coming from metamorphic massive of Tamsamane. The factorial analysis reveal three sources of salinization, the principal one is described above, whilst the dissolution of carbonates and human influence represented by  $NO_3^-$ , played only a secondary role.

**Key words:** Salinization, groundwater, Messinian crisis, hydrochemistry, statistical, Kert aquifer, NE Morocco.

## INTRODUCTION

The messinian salinity crisis was a geological event during which Mediterranean Sea went into complete desiccation throughout the Messinian age from 5.6 to 5.33 Ma (Roveri et al., 2008). The principal cause of this event was the isolation of Mediterranean basin from the Atlantic Ocean for a longer period after the closure of Atlantic gateways. Several messinian salt deposits are outcropping in many basins like Sorbas and Nijar in south Spain (Braga et al., 2006; Soria et al., 2008) and in

northeastern Moroccan Neogene basins. A major question remains concerning the impact of messinian salinity crisis on the groundwater quality. Many works in northeastern of Morocco showed that salinity increases in the majority of aquifers. In shallow coastal aquifer of Saidia, the water is brackish (Melloul et al., 2007). In Triffa plain the electrical conductivity varies between 600 and 11 120  $\mu$ S/cm, and the chemical facies is Cl-Na (Elmandour et al., 2008). In Bou Arg unconfined aquifer, in northeastern Mediterranean coast, the higher values of hydraulic conductivity facilitates seawater intrusion (El yaouti et al., 2009). The causes of this salinization are almost similar in all of the aquifers and linked to geological, geochemical contexts of the plains, dissolution of gypsum

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indicated by high sulfate concentrations, and other phenomena, such as oxydoreduction reaction and ionic exchange. Thus, the problems associated with natural saline groundwater, salt-water intrusion, and upcoming of saline water due to over-pumping in agricultural and industrial zones are major concerns in many regions in the global world.

Water resources available in northeast of Morocco are scarce, vulnerable to salinization and increasingly becoming major complicating factors in the socio-ecologic and ecopolitic problems of the region. The main reasons for this issue are related to their reception input of many different water sources (seawater, rivers, sebkha and anthropogenic sources) in the one hand, in the other hand the often density populated regions. Considering the quantity and quality of water needed to satisfy the socioeconomic development in the region, freshwater is the most binding constraint and present great challenge. Like in many parts of Morocco, salinization is presented generally where aquifers are located in the rifain southern corridor or in contact with Mediterranean Sea (Elgettafi et al., 2007). This problem becomes more disturbing when it is combined with arid climate and after the long dry periods. During the last decade, the deterioration of superficial water and groundwater is a problem for the local authorities and a major scientific concern. The continued stress on land and water resources has disturbed the natural balance and has accelerated the natural salinization process, particularly in arid and semi arid climatic region. To put a limit to these dramatic changes, in 1995, the Moroccan government has adopted a 10-95 law for using the water resources. Now, 10-95 law by the high council for water and climate formulates general guidelines for the national water policy and examines the national strategy for observing climate change and its impact on water resources.

Freshwater strongly affected by interaction with minerals of the geological reservoir (Manno et al., 2007; Melish et al., 2008), is primarily controlled by weathering of aluminosilicates, dissolution of carbonate and evaporate minerals and cation exchange reactions. Thus, the knowledge of groundwater chemistry is the first requirement for many practical purposes. Hydrochemistry is an essential tool for understanding the groundwater evolution (Pilla et al., 2006). It provides information on the water provenance, residence time, flow direction and relation with surface waters. The challenge is to understand the salt sources, and the mechanisms which are responsible in incrementing groundwater salinity, in order to manage and share these water resources under those specific climate change and population growths (Elgettafi et al., 2011). The aim of this study was to investigate the geochemical characteristics of water in order to identify the main hydro geochemical process controlling the chemical composition based on major ion

chemistry and statistical method.

## Study area

### *Geological setting*

The Kert basin, which covers a total area of about 250 km<sup>2</sup>, is located in the northeastern part of Morocco and extends between latitudes 34°55' and 35°54'N, and longitudes 3°19' and 3°34'W (Figure 1). The Kert River is the important river in the Kert basin, which is mostly characterized by a seasonal flow regime. This stream with a total long rounded 90 km and a catchments area rounded 2710 Km<sup>2</sup> (Zielhofer et al., 2008). The Kert depression received during the Miocene to Villafranchian a very mixed and varied thick marine and continental sedimentation. It is limited to the east by the western Gareb range. The massive metamorphic of Tamsamane, which limits the plain in the north and northwest was affected by a compressive tectonic event generating a N120°E fracture cleavage associated with green shale (Frizon de Lamotte, 1985). In the south part we found intra rifain nappes and marls of Miocene. The Jurassic and Cretaceous deposits mostly constitute of carbonates rocks; limit the plain in the southern part (Figure 1). Several studies have been done to date the opening of Kert basin. During early-middle Tortonian, a series of conjugate strike-slip faults (N70°E to N90°E) occurs east of Nekor fault, related to the formation of Kert basin (Ait Brahim et al., 2002). While, Azdimoussa et al. (2007) suggest that the younger normal fault system records N-S extension controlling the formation of the Kert Basin dates the Messinian-Pliocene age. In the Messinian, Kert basin deepened with the Messinian Sea level rise (Haq et al., 1987). It is known that in the occidental Mediterranean Neogene basin the sedimentological history is marked by evaporite series related to messinian salinity crisis caused by closing of Gibraltar strait. Whereof, Hervouet (1985) defined a complex tectono-sedimentary (Gareb-Kebdana chaotic unit) extending from Kebdana in the east towards the Midar city in the west, often composed by a gypseous marl. In the west of plain, the scrapes were principally a fragment of gravity-driven nappes of internal and external rifain domain slid westward along the foreland (Hervouet, 1985). The plain contains a transgressed post nappe deposits (Azdimoussa, 1999). The micro paleontological dating of the sedimentary filling the Kert basin indicates late Miocene and Pliocene ages (Feinberg, 1986).

### *Hydrogeological setting*

The hydrogeology character of the study area were described by Carlier (1973), based on data obtained from pumping tests and electrical geophysics. There is an

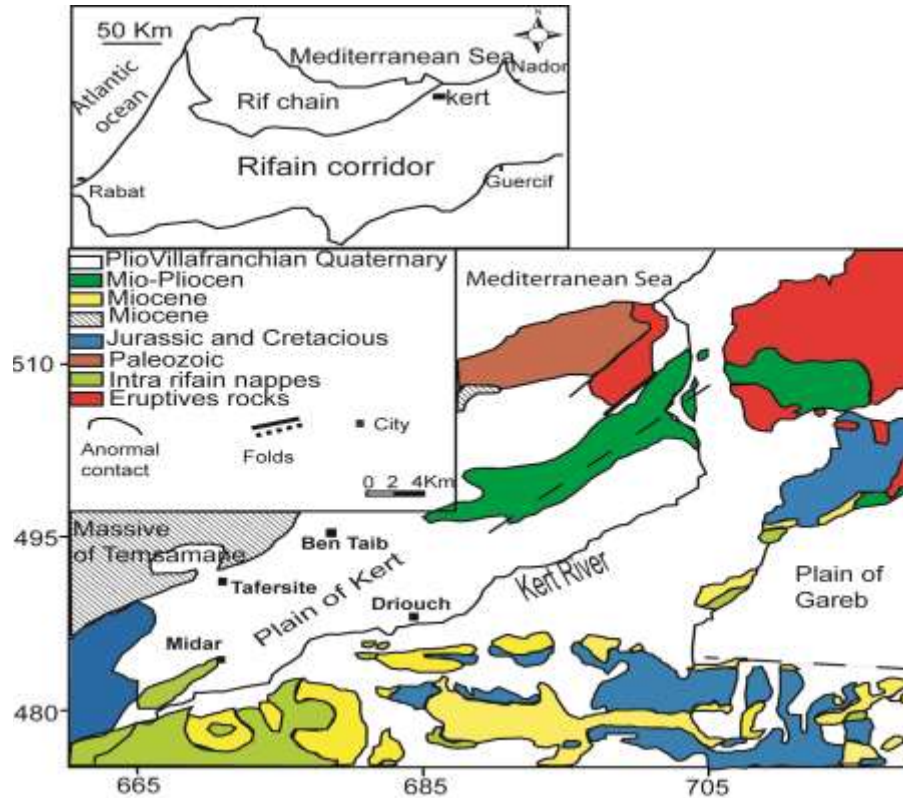


Figure 1. Geological map of Middle Kert plain (Carlier, 1973).

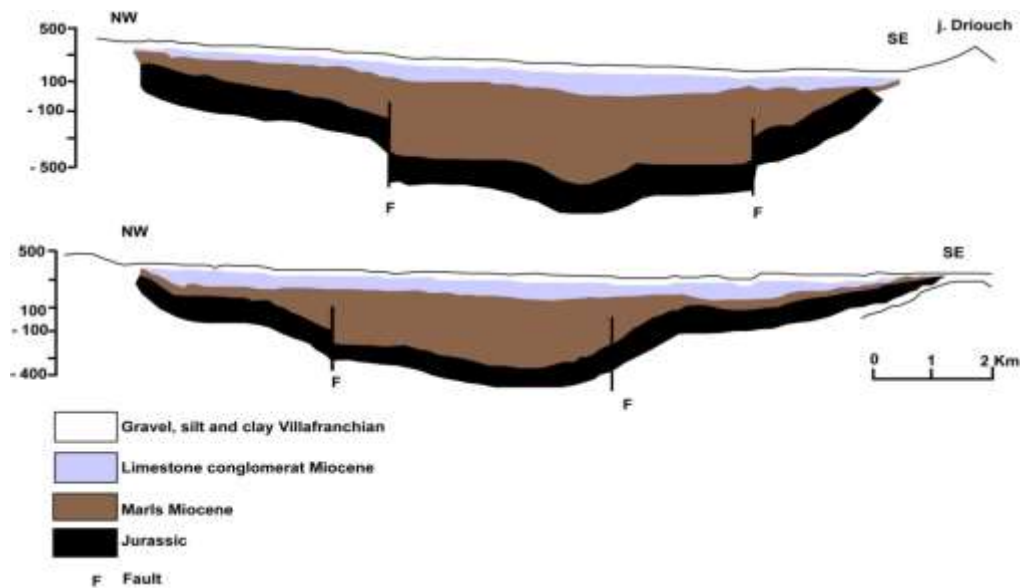


Figure 2. Hydrogeological cross section in the Kert plain (Carlier, 1973).

unconfined aquifer, which extends under the Kert plain and flows on the Miocene blue marls (substratum of aquifer). The strata of various hydrogeological formations

can be identified as follows (Figure 2). The substratum of the aquifer is represented by the Miocene transgressed marls, which is overlaid by a contemporary deposit made

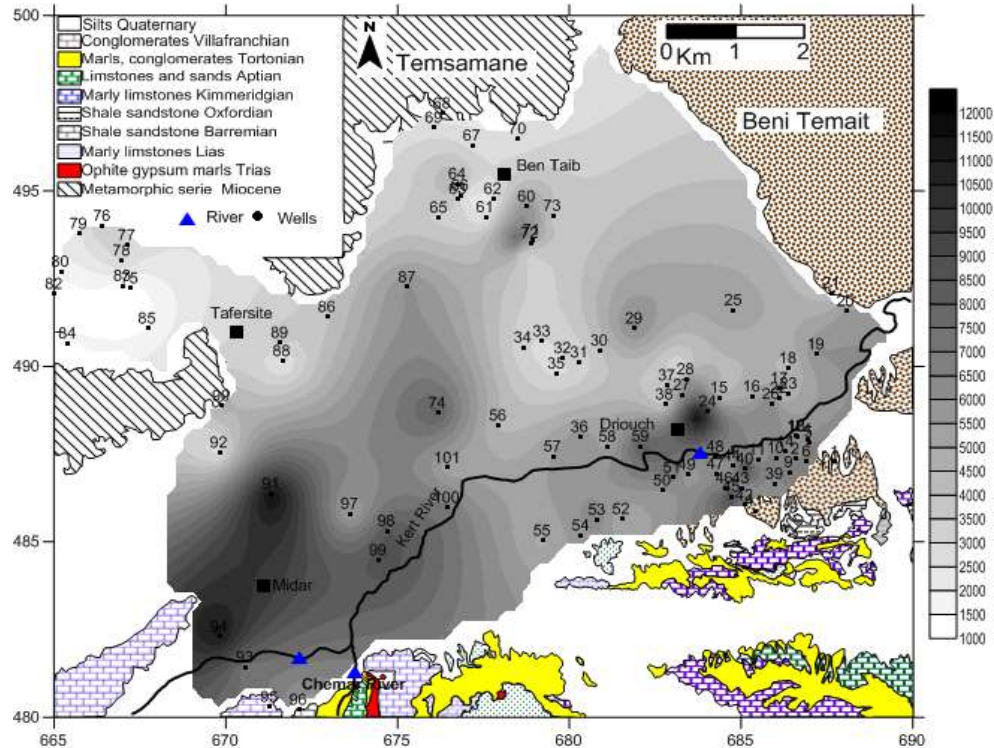


Figure 3. Electrical conductivity map of groundwater in Kert aquifer.

up of limestone and conglomerate. We assume that the Miocene formation contains the gypsum as well as the one outcrop in the region. The series end with gravel, silt and clay Villafranchian age. Two vertical faults have controlled the Kert basin during the Miocene. These faults have collapsed the center of the plain and have raised the borders north and south. Consequently, the aquifer might be hydraulically connected through those faults with the underlying Jurassic unit. Two exploratory boreholes were drilled in this latter unit in order to find an aquifer in the deep resisting formation determined by geophysics (Zeryouhi, 1971). The first borehole number is 1635/6 with the depth of 801m ( $X = 685.18$   $Y = 486.85$  Lambert coordinates) and the second borehole number is 1636/6, 684 m in depth ( $X = 679.14$   $Y = 484.05$  Lambert coordinates). Both of them had not given the expected result.

Thirty-two Pumping tests were performed on the plain. Permeability and transmissivity computed using classical Theis-Jacob method amount from  $0, 4 \cdot 10^{-5}$  to  $18 \cdot 10^{-5}$  m/s and from  $0, 1 \cdot 10^{-3}$  to  $34 \cdot 10^{-3}$  m<sup>2</sup>/s, respectively. Storage coefficient estimated from these tests is 0.3 to 3.5%. The piezometric head contour map realized in 2008 (Elgettafi, 2011) shows that in northern part water flow from Northwest to Southeast. The second water flow as the major direction is from West to East in centre plain. Tamsamane massif metamorphic located on the

northwestern side is considered as a recharge zone for the studied groundwater. The discharge fields are situated in the extreme East. Kert River is characterized by a seasonal flow regime and it is in connection with aquifer.

## MATERIALS AND METHODS

### Water sampling

A total of 94 wells and 3 surfaces waters samples (Kert in Midar, Kert in Driouch and Chemar) were collected during two field trips in July and in December, 2008. Locations of water sampling points are showing in Figure 3. All the data in the study area are listed in Table 1. The pH,  $T_p$ , and specific electrical conductivity (EC) measurements were made *in situ*. The electrical conductivity was measured simultaneous with temperature by a VWR EC300 instrument, previously calibrated by the conductivity solution HI 70031 (HANNA). pH measurements were carried out using a glass electrode connected to a VWR pH100-meter, after calibration with pH 4.01 and 7.00 buffer solutions. Each sample was stored in new polypropylene bottle, pre-washed with HNO<sub>3</sub> and rinsed with deionized water. The bottles were capped without leaving any head space and stored in a refrigerated container for transport to the laboratory and kept cool until analysis. All of the water samples, were analyzed for major cation ( $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ) major anions ( $Cl^-$ ,  $SO_4^{2-}$ ,  $HCO_3^-$ ,  $NO_3^-$ ), and total dissolved solids (TDS), in Hydraulic Laboratory of Moulouya Agency, Oujda, using standard analytical procedures.  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$  and  $HCO_3^-$  were determined by titrimetric methods. The concentration of  $Na^+$ ,  $K^+$ ,  $SO_4^{2-}$  and  $NO_3^-$

**Table 1.** Hydrochemical analyses of groundwater in Kert aquifer (electrical conductivity, total dissolved solids, temperature, sodium, potassium, calcium, magnesium, chloride, bicarbonates, sulphate and nitrates, KD, Kert in Driouch; KM, Kert in Midar; CH, Chemar).

| ID wells | EC    | TDS  | Th | Ph   | Na   | K  | Ca  | Mg  | Cl   | HCO <sub>3</sub> | SO <sub>4</sub> | NO <sub>3</sub> |
|----------|-------|------|----|------|------|----|-----|-----|------|------------------|-----------------|-----------------|
| 1        | 6470  | 4966 | 24 | 7.41 | 1240 | 7  | 212 | 250 | 1659 | 298              | 1258            | 17              |
| 2        | 6310  | 4944 | 21 | 7.22 | 1120 | 5  | 240 | 315 | 1399 | 292              | 1460            | 34              |
| 4        | 5860  | 4393 | 22 | 7.32 | 720  | 5  | 200 | 243 | 1249 | 305              | 1317            | 32              |
| 5        | 6990  | 5093 | 23 | 7.07 | 620  | 5  | 440 | 157 | 1499 | 280              | 816             | 14              |
| 6        | 6780  | 5324 | 22 | 7.05 | 560  | 5  | 444 | 174 | 1549 | 274              | 781             | 22              |
| 9        | 7190  | 5855 | 22 | 7.02 | 600  | 6  | 400 | 187 | 1374 | 280              | 1181            | 18              |
| 10       | 7260  | 5322 | 26 | 7.2  | 640  | 6  | 420 | 218 | 1629 | 286              | 1338            | 38              |
| 11       | 5810  | 4317 | 20 | 7.09 | 660  | 5  | 408 | 153 | 1099 | 305              | 1132            | 35              |
| 12       | 5940  | 4413 | 20 | 7.16 | 520  | 5  | 424 | 155 | 1349 | 317              | 1111            | 39              |
| 13       | 6313  | 4600 | 19 | 7.4  | 550  | 5  | 408 | 170 | 1409 | 347              | 1030            | 35              |
| 14       | 6050  | 4112 | 20 | 7.21 | 560  | 5  | 320 | 182 | 1449 | 280              | 1022            | 26              |
| 15       | 4460  | 2991 | 22 | 6.95 | 630  | 8  | 268 | 68  | 1124 | 549              | 663             | 31              |
| 16       | 5120  | 3222 | 21 | 6.98 | 780  | 7  | 280 | 72  | 1084 | 610              | 740             | 35              |
| 17       | 5240  | 3602 | 22 | 6.77 | 720  | 8  | 192 | 162 | 1189 | 610              | 920             | 28              |
| 18       | 4210  | 2944 | 23 | 6.99 | 600  | 6  | 180 | 133 | 974  | 610              | 765             | 23              |
| 19       | 6060  | 3998 | 21 | 6.96 | 830  | 7  | 248 | 148 | 1774 | 427              | 736             | 18              |
| 20       | 5640  | 4369 | 23 | 7.06 | 920  | 8  | 172 | 223 | 1584 | 366              | 618             | 23              |
| 21       | 3980  | 2853 | 22 | 7.36 | 680  | 6  | 116 | 155 | 1074 | 366              | 438             | 20              |
| 22       | 4540  | 2986 | 22 | 6.75 | 960  | 9  | 168 | 140 | 924  | 854              | 850             | 15              |
| 23       | 4780  | 3196 | 21 | 6.89 | 1000 | 9  | 148 | 165 | 1049 | 841              | 830             | 16              |
| 24       | 12300 | 9803 | 21 | 6.96 | 2500 | 6  | 300 | 464 | 3398 | 317              | 1683            | 145             |
| 25       | 5570  | 4641 | 21 | 7.19 | 840  | 5  | 521 | 29  | 1599 | 305              | 430             | 15              |
| 26       | 6720  | 3814 | 21 | 6.8  | 800  | 9  | 240 | 140 | 1399 | 628              | 813             | 11              |
| 27       | 6050  | 4249 | 22 | 7.25 | 1120 | 6  | 352 | 65  | 1374 | 408              | 1166            | 31              |
| 28       | 5860  | 3976 | 23 | 7.02 | 1200 | 5  | 360 | 77  | 1369 | 390              | 1054            | 20              |
| 29       | 6360  | 5133 | 22 | 7.17 | 1160 | 5  | 376 | 140 | 2099 | 305              | 644             | 18              |
| 30       | 3970  | 2592 | 26 | 6.8  | 680  | 5  | 232 | 102 | 674  | 744              | 689             | 19              |
| 31       | 3070  | 2053 | 23 | 7.21 | 460  | 4  | 184 | 70  | 704  | 335              | 361             | 10              |
| 32       | 3040  | 2143 | 25 | 7.16 | 480  | 4  | 220 | 60  | 669  | 317              | 550             | 18              |
| 33       | 2970  | 1945 | 24 | 7.22 | 420  | 4  | 168 | 85  | 684  | 292              | 320             | 9               |
| 34       | 3050  | 2287 | 26 | 7.21 | 500  | 4  | 240 | 80  | 664  | 292              | 520             | 22              |
| 35       | 2840  | 1800 | 23 | 7.24 | 440  | 5  | 192 | 89  | 554  | 353              | 507             | 18              |
| 36       | 5920  | 4621 | 22 | 7.08 | 1000 | 5  | 432 | 211 | 1159 | 335              | 1444            | 28              |
| 37       | 4280  | 2739 | 22 | 7.1  | 680  | 13 | 240 | 70  | 1009 | 366              | 532             | 11              |
| 38       | 3480  | 2244 | 22 | 7.06 | 700  | 5  | 240 | 72  | 689  | 414              | 656             | 27              |
| 39       | 6010  | 4227 | 23 | 7.32 | 1280 | 7  | 320 | 228 | 1874 | 286              | 997             | 2               |
| 40       | 9800  | 7871 | 22 | 7.14 | 2100 | 8  | 581 | 352 | 2949 | 305              | 2029            | 9               |
| 41       | 6821  | 3104 | 24 | 7.21 | 1040 | 9  | 228 | 116 | 1199 | 402              | 1066            | 6               |
| 42       | 6320  | 2233 | 23 | 7.45 | 720  | 10 | 180 | 189 | 1289 | 347              | 1108            | 8               |
| 43       | 5820  | 5780 | 22 | 7.27 | 1900 | 7  | 432 | 296 | 2664 | 268              | 1519            | 7               |
| 44       | 6010  | 2635 | 22 | 7.1  | 920  | 6  | 368 | 165 | 1024 | 335              | 1472            | 6               |
| 45       | 9800  | 5614 | 23 | 7.13 | 2000 | 8  | 521 | 291 | 2499 | 305              | 2013            | 8               |
| 46       | 6820  | 2882 | 22 | 7.11 | 1040 | 7  | 320 | 216 | 1399 | 323              | 1562            | 7               |
| 47       | 6320  | 2806 | 21 | 7    | 1000 | 6  | 360 | 170 | 1099 | 366              | 1558            | 6               |
| 48       | 5820  | 2904 | 22 | 7.12 | 760  | 4  | 372 | 162 | 1024 | 335              | 1489            | 6               |
| 49       | 5500  | 2901 | 23 | 7.22 | 600  | 5  | 236 | 123 | 774  | 317              | 1148            | 13              |
| 50       | 5800  | 3750 | 22 | 7.31 | 820  | 8  | 240 | 182 | 1124 | 427              | 1305            | 7               |
| 51       | 6990  | 4783 | 21 | 6.85 | 840  | 6  | 420 | 194 | 1454 | 317              | 1313            | 36              |

Table 1. Contd.

|     |       |      |      |      |     |      |     |     |      |      |      |      |
|-----|-------|------|------|------|-----|------|-----|-----|------|------|------|------|
| 52  | 4910  | 3251 | 21   | 7.56 | 750 | 5    | 216 | 167 | 1334 | 292  | 1289 | 7    |
| 53  | 6400  | 4326 | 22   | 6.85 | 880 | 6    | 300 | 194 | 1324 | 396  | 1307 | 8    |
| 54  | 5860  | 3864 | 21   | 7.27 | 800 | 5    | 276 | 160 | 1349 | 311  | 1250 | 7    |
| 55  | 4830  | 3381 | 21   | 7.16 | 730 | 5    | 240 | 145 | 819  | 323  | 1419 | 6    |
| 56  | 4390  | 2319 | 22   | 6.94 | 700 | 8    | 184 | 77  | 749  | 854  | 593  | 8    |
| 57  | 5540  | 3618 | 22   | 7.1  | 620 | 5    | 360 | 145 | 914  | 317  | 1564 | 15   |
| 58  | 5310  | 3449 | 23   | 7.15 | 630 | 5    | 318 | 145 | 874  | 323  | 1444 | 14   |
| 59  | 8360  | 5828 | 22.5 | 7.17 | 790 | 6    | 525 | 252 | 1774 | 280  | 1736 | 41   |
| 60  | 6040  | 4079 | 23.5 | 7.2  | 480 | 6    | 448 | 128 | 1849 | 183  | 416  | 43   |
| 61  | 2410  | 1306 | 22   | 7.56 | 290 | 3    | 116 | 68  | 509  | 256  | 324  | 16   |
| 62  | 2460  | 1286 | 23   | 7.52 | 290 | 3    | 136 | 61  | 514  | 250  | 326  | 52   |
| 63  | 3710  | 2254 | 22   | 7.16 | 400 | 4    | 224 | 92  | 864  | 286  | 414  | 12   |
| 64  | 4860  | 2364 | 21   | 7.16 | 470 | 5    | 381 | 182 | 1359 | 329  | 883  | 9    |
| 65  | 3320  | 2231 | 22   | 7.34 | 340 | 3    | 212 | 124 | 769  | 347  | 660  | 0    |
| 66  | 2000  | 1101 | 22   | 7.66 | 270 | 6    | 128 | 58  | 394  | 323  | 393  | 103  |
| 67  | 2840  | 1683 | 23   | 7.32 | 310 | 3    | 212 | 70  | 649  | 341  | 405  | 81   |
| 68  | 2160  | 1122 | 23   | 7.52 | 260 | 2    | 160 | 63  | 469  | 366  | 442  | 19   |
| 69  | 2700  | 1577 | 22   | 7.31 | 300 | 4    | 168 | 83  | 569  | 366  | 550  | 35   |
| 70  | 2570  | 1548 | 22   | 7.58 | 300 | 5    | 140 | 92  | 659  | 305  | 432  | 36   |
| 71  | 8550  | 5572 | 22.5 | 6.85 | 850 | 8    | 533 | 201 | 2124 | 762  | 1168 | 38   |
| 72  | 3450  | 2159 | 21.5 | 7.36 | 400 | 5    | 220 | 78  | 934  | 317  | 420  | 36   |
| 73  | 3620  | 2355 | 22   | 7.7  | 370 | 5    | 240 | 102 | 969  | 274  | 381  | 36   |
| 74  | 8240  | 3559 | 22   | 6.74 | 610 | 9    | 357 | 63  | 424  | 719  | 1187 | 6    |
| 75  | 1120  | 377  | 21   | 7.44 | 42  | 0.34 | 88  | 27  | 109  | 274  | 91   | 10   |
| 76  | 3580  | 1502 | 22   | 7.24 | 150 | 1    | 272 | 53  | 374  | 329  | 412  | 21   |
| 77  | 2850  | 1065 | 23   | 7.18 | 150 | 0.67 | 160 | 36  | 284  | 329  | 269  | 6    |
| 78  | 3250  | 1332 | 23   | 7.1  | 130 | 0.67 | 212 | 53  | 324  | 335  | 387  | 0    |
| 79  | 2400  | 861  | 23   | 7.26 | 80  | 0.33 | 136 | 29  | 239  | 335  | 148  | 5    |
| 80  | 1750  | 615  | 23   | 7.3  | 70  | 0    | 100 | 29  | 199  | 335  | 69   | 9    |
| 81  | 1190  | 389  | 22   | 7.36 | 140 | 0.33 | 92  | 34  | 174  | 305  | 126  | 4    |
| 82  | 1080  | 357  | 21   | 7.5  | 160 | 0.67 | 80  | 27  | 124  | 280  | 142  | 4    |
| 83  | 1120  | 349  | 22   | 7.52 | 180 | 0    | 80  | 22  | 134  | 280  | 132  | 8    |
| 84  | 1700  | 750  | 22   | 7.33 | 40  | 0.67 | 160 | 39  | 174  | 262  | 306  | 0.42 |
| 85  | 1490  | 546  | 21   | 7.37 | 80  | 0.67 | 116 | 46  | 124  | 329  | 232  | 0.33 |
| 86  | 3860  | 1682 | 23   | 7.19 | 360 | 1.67 | 220 | 75  | 529  | 311  | 626  | 1    |
| 87  | 6130  | 2500 | 23   | 7.57 | 470 | 6    | 180 | 104 | 999  | 183  | 695  | 2    |
| 88  | 2180  | 821  | 23   | 7.4  | 210 | 2    | 152 | 44  | 249  | 274  | 412  | 0    |
| 89  | 3720  | 1551 | 22   | 7.2  | 300 | 5    | 232 | 49  | 514  | 366  | 526  | 0    |
| 90  | 4800  | 1869 | 24   | 6.88 | 440 | 3    | 232 | 87  | 574  | 713  | 687  | 0    |
| 91  | 11800 | 4381 | 22   | 6.47 | 990 | 18   | 244 | 151 | 1499 | 1329 | 822  | 0    |
| 92  | 2520  | 724  | 23   | 7.24 | 260 | 2    | 160 | 97  | 189  | 579  | 856  | 0    |
| 93  | 7190  | 3726 | 23   | 7.11 | 570 | 5    | 348 | 243 | 799  | 323  | 2013 | 1    |
| 94  | 11300 | 5926 | 22   | 6.23 | 660 | 5    | 553 | 211 | 1174 | 1311 | 306  | 1    |
| 95  | 7130  | 3074 | 23   | 6.95 | 610 | 5    | 280 | 170 | 1079 | 488  | 1295 | 3    |
| 96  | 5440  | 2442 | 22   | 6.99 | 440 | 2    | 268 | 116 | 634  | 366  | 844  | 0    |
| 97  | 5180  | 2323 | 22   | 7.04 | 500 | 4    | 160 | 194 | 564  | 457  | 1542 | 0    |
| 98  | 8570  | 4008 | 21   | 6.73 | 670 | 4    | 360 | 255 | 1109 | 579  | 1840 | 1    |
| 99  | 8780  | 4286 | 22   | 6.85 | 510 | 4    | 472 | 223 | 1049 | 549  | 1876 | 0.2  |
| 100 | 7160  | 3409 | 22   | 7    | 520 | 3    | 400 | 145 | 764  | 427  | 1815 | 0.4  |
| 101 | 5080  | 2416 | 21   | 7.13 | 390 | 3    | 296 | 121 | 624  | 445  | 1256 | 1    |



Table 1. Contd.

| Wadis |      |      |     |   |     |    |     |     |      |    |
|-------|------|------|-----|---|-----|----|-----|-----|------|----|
| KD    | 4850 | 3928 | 560 | 5 | 737 | 39 | 780 | 165 | 1642 | 27 |
| KM    | 4070 | 3877 | 460 | 7 | 705 | 29 | 840 | 165 | 1673 | 0  |
| CH    | 5130 | 4212 | 740 | 7 | 753 | 97 | 900 | 165 | 1550 | 0  |

was measured by atomic absorption spectrophotometry. The values of Charge Balance Errors are less than or equal 5%, which is an acceptable error for the purpose of this study:

$$CBE = \frac{\sum \text{Cations} - \sum \text{Anions}}{\sum \text{Cations} + \sum \text{Anions}}$$

The theoretical partial pressure of CO<sub>2</sub> in water (P<sub>CO<sub>2</sub></sub>) was calculated with thermodynamic model PHREEQC (Parkhurst and Appelo, 1999).

### Statistical method

Generally, hydrological and geochemical processes are difficult to understand on account of their complexity. However, based on hydro chemical composition, statistical method can show the correlations between them. A correlation analysis was applied to describe the degree of relation between two or more hydro chemical parameters. A high correlation coefficient near 1 or -1 means a good relationship between variables, and a correlation coefficient around 0 means no relationship.

The correlation coefficient is:

$$r_{xy} = \frac{\sum_{i=1}^N (x_i - \bar{x}) \cdot (y_i - \bar{y})}{\sqrt{\sum_{i=1}^N (x_i - \bar{x})^2} \cdot \sqrt{\sum_{i=1}^N (y_i - \bar{y})^2}}$$

This expression is simply the sum (over all samples) of the product of the deviations of the  $x_i$  measurements and the  $y_i$  measurements on each sample from the mean values  $\bar{x}$  and  $\bar{y}$  respectively for the complete set of samples.

Principal component analysis (PCA) and factor analysis (FA) were applied to explain relationships between variables and thus, infer the processes that control water chemistry (Helina et al., 2000). The main purpose of FA is to reduce the contribution of less significant variables to simplify even more of the data structure coming from PCA. This method starts by coding all variables to have zero means and unit variances, and find the eigenvalues and corresponding eigenvectors. Then, the data were transformed to factors. The factor extraction was done with a minimum acceptable eigenvalue as 1 (Mahlknecht, 2004). Orthogonal rotation of these initial factors to terminal factor solution was done with Kaiser's varimax scheme (Kaiser, 1958). The operation finish by factors scores coefficients, which are derived from the matrix loading.

## RESULTS AND DISCUSSION

### Water hydrochemical

Analyses of chemical results show a large variation in

chemical compositions and also indicate low salinity of some groundwater samples (Tafersite region). TDS values are 349 to 9803 mg/l, knowing that the values greater than 1000 were considered indicative of salinity (Petalas and Diamantis, 1999; Jalali, 2006) nevertheless, in arid zone where the water is scarce; water bad quality is currently used. SEC values are in the range of 1080 to 12300  $\mu\text{s}/\text{cm}$ . Generally, the ionic content of groundwater of the study area is high, the dominant cations are Na<sup>+</sup> and Ca<sup>2+</sup> (max value are 2500 and 581, respectively) and the dominants anions are Cl<sup>-</sup> and SO<sub>4</sub><sup>-</sup> (max value are 3398 and 2029, respectively). HCO<sub>3</sub><sup>-</sup> ranges from 183 to 1329 mg/l; the high concentration corresponds to the low values of pH. Water CO<sub>2</sub> partial pressures range between 10<sup>-2.3</sup> and 10<sup>-0.1</sup> atm, and all of the samples had P<sub>CO<sub>2</sub></sub> over values significantly above of the atmosphere because of the possible contribution of biologic respiration. As to NO<sub>3</sub><sup>-</sup> the over concentration is seen in some wells, it means that the contamination is local, and is likely to be derived from the use of traditional fertilizers (animal waste). A significant feature of these waters is their weak acidic character, with pH values in the range 6.23 to 7.66, and temperature ranges from 19°C to 26°C, reflecting that water circulates in the same depth. The geochemical modeling program PHREEQC (Parkhurst and Appelo, 1999) was used to calculate aqueous speciation and the thermodynamic equilibrium conditions of waters with respect to the main mineral phases present in the aquifer. Saturation indices, defined as SI=log (IAP/Kt), IAP being the ion activity product of the mineral-water reaction and Kt the thermodynamic equilibrium constant at the measured temperature, were calculated by ion activities. Thus, SI=0 indicates a thermodynamic equilibrium state, and values >0 and <0 denote super saturation and under saturation, respectively. All the groundwater samples are supersaturated with respect to calcite and dolomite (from 0.04 to 0.83 and from 0.3 to 1.61 respectively), and under saturated with respect to gypsum and halite (from -1.52 to -0.32 and from -6.8 to -3.8, respectively).

As for the wadis's samples they all show high salinity. They are 5130  $\mu\text{s}/\text{cm}$  in Chemar and 4850  $\mu\text{s}/\text{cm}$  in Kert near Driouch city. The oversaturation in Kert wadi (4850  $\mu\text{s}/\text{cm}$ ) is detected after its connection with Chemar Wadi. The dominant cations are Na<sup>+</sup> and Ca<sup>2+</sup> (max value are 740 and 817 mg/l, respectively), and dominant anions are SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> (max values are 1720 and 900 mg/l, respectively) (Table 1).

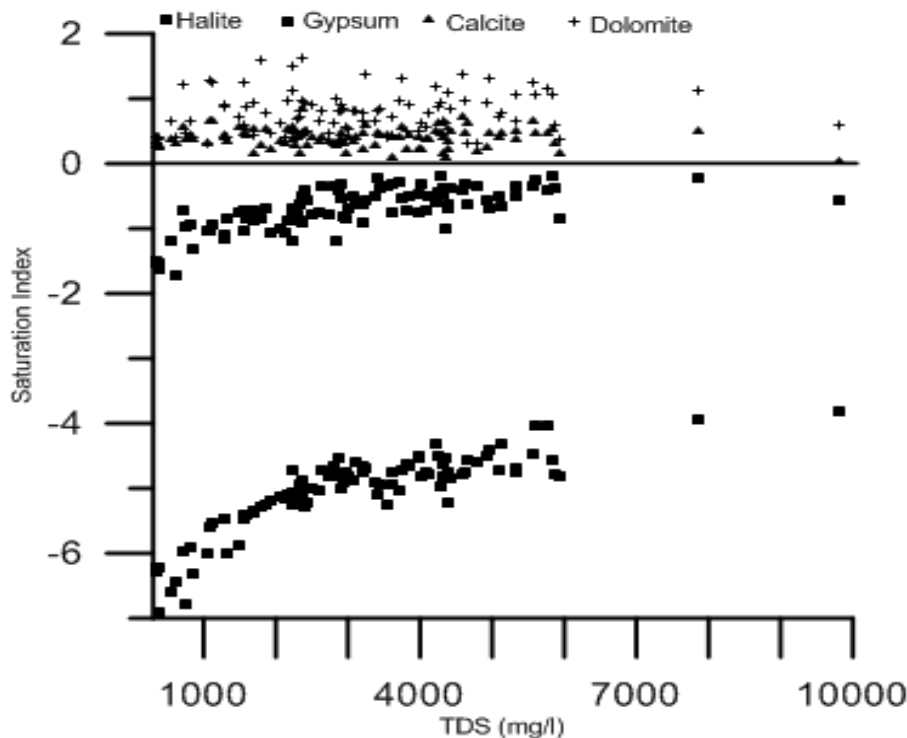


Figure 4. Relationships between TDS and SI of Halite, Gypsum, Calcite and Dolomite.

### Geochemical process

The spatial distribution of electrical conductivity indicates some contrast (Figure 3). There is a pronounced increase in electrical conductivity from the northwest margin to the centre of the field. Only one zone that consists of freshwater is distinguished which located in Tafersite in the northwest part of the study area. TDS is about 740 mg/l and EC= 1957  $\mu\text{s}/\text{cm}$ , and abundance orders  $\text{mE}/\text{l}$   $\text{Ca} > \text{Na} > \text{Mg}$  and  $\text{HCO}_3 > \text{Cl} > \text{SO}_4$ . The water type is  $\text{HCO}_3$ -Ca. The low degree of mineralisation of these waters which are in contact with metamorphic massive of Tamsamane suggest the laterally alimentation by fresh waters. Salinity values increase from North to South, corresponding to the main groundwater flow direction and exceed 11 000  $\mu\text{s}/\text{cm}$  in Midar and Driouch (Figure 3). This salinity increase could be explained by: probably a longer contact-time with rocks during water circulation and/or depend on the distance from a source of freshwater. The second zone consists of the remaining samples that we find towards the south and presents a most important percentage. It is different from other samples in terms of its high salinity (average TDS= 3667, EC=5931).  $\text{Na} > \text{Ca}/\text{Mg}$  and  $\text{Cl} > \text{SO}_4 > \text{HCO}_3$  are dominant cation and anion element respectively. The significant character of these waters is that they are located in the zone where the upper Miocene marls both outcrop and are at 4 m of depth. Secondly the zone is crossed by kert wadi. It appears that groundwater quality is represented

by a wide range of concentrations mainly dominated by evaporite rock dissolution.

This kind of waters is frequently observed in Neogene basin in northeastern of Morocco. In order to identify the salinization sources for middle Kert aquifer and to delineate the areas of influence, the hydrochemistry was analyzed graphically by means x-y plots and equilibrium state of the water with respect to a mineral phase which was determined by calculating a saturation index (SI) using analytical data.

Figure 4 shows the plots of SI against TDS for all the investigated water. It can be seen that all the groundwater samples are supersaturated with respect to calcite and dolomite. No clear tendency between carbonates Si and TDS evolution is found in all groundwater samples. That suggests the sensitivity of carbonates minerals to precipitation. Also, all the groundwater samples are under saturated with respect to halite and gypsum suggesting the dissolution of evaporates minerals. Saturation with respect to those latter is approached with increasing TDS content, although no samples reach saturation especially halite SI. This means that these elements are not limited by mineral equilibrium and variable degrees of continuous dissolution of halite and gypsum is occurred.

The same behavior is known in Bou Areg aquifer NE Morocco. Evaporates mineral phases are minor or absent in the host rock aquifer as suggested by El yaouti et al. (2009) is not supported by this study. The dissolution of



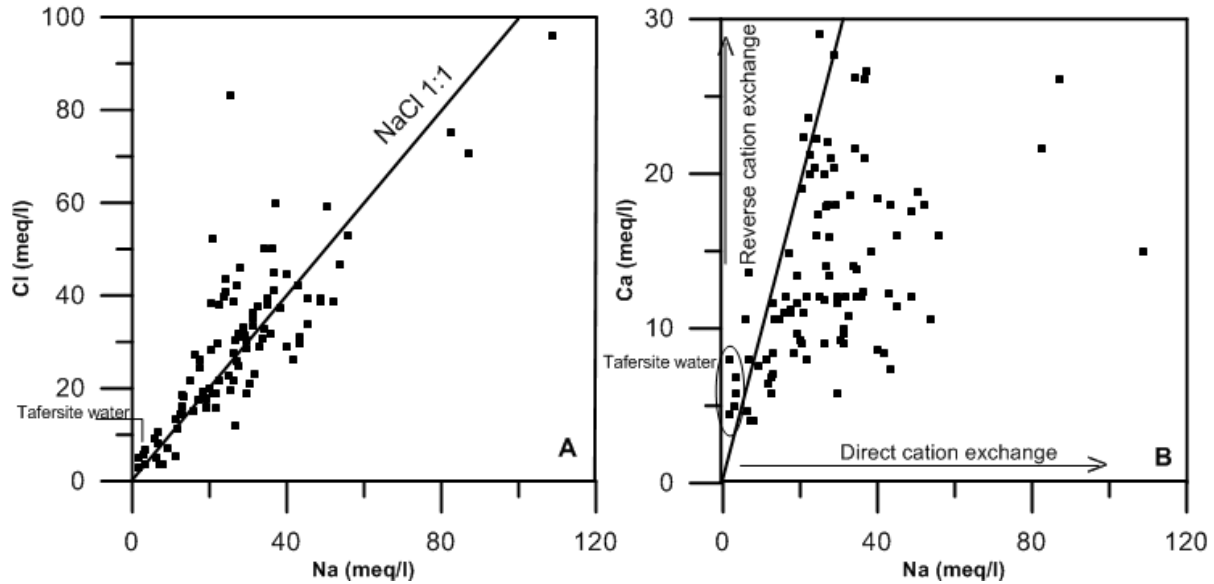


Figure 5. Relationships Na vs Cl (A) and Na vs Ca (B).

gypsum in these waters should also tend to maintain saturation or super saturation with respect to carbonate minerals. Thus, increasing of  $\text{Ca}^{2+}$  and Ca/Mg ratio causing by gypsum dissolution generates systematically the phenomenon of dedolomitisation which explains the over-saturation of calcite and dolomite.

The Na-Cl scatter gram shows that generally,  $\text{Na}^{2+}$  increases linearly with  $\text{Cl}^-$  along the NaCl 1:1 line of halite minerals (Figure 5A); suggesting that the processes controlling the  $\text{Cl}^-$  ion concentration are also affecting  $\text{Na}^{2+}$ . That may be a result of weathering rock rich in NaCl (Halit), which is highly soluble and easily dissolved. Through, chloride has a conservative behavior (Tellam and Lloyd, 1986). Some wells show an excess of  $\text{Na}^+$  with respect of Na/Cl ratio of halite minerals. This could be due to a further water source for  $\text{Na}^+$ . Thus,  $\text{Na/Cl} > 1$  may be explained by different ways.

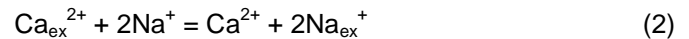
- (i) Dissolution of evaporate Na- $\text{SO}_4$  minerals.
- (ii) Ca-Na exchange according to the reaction:



- (iii) The high concentration of  $\text{Na}^+$  is related to the important water-rock interaction.

A look at the evolution of Ca relative to Na (Figure 5B) shows a mixing trend between fresh and saline water. In Tafersite region low salinity shows an excess of  $\text{Ca}^{2+}$  with respect Na-Ca line. This behavior is due to the freshwater coming laterally from the metamorphic massive of Tamsamane which border the plain in the north. It is shown by piezometric map that the aquifer is supplied by

the Tamsamane Mountains. This mixture diluted the groundwater within various degrees. The water has been enriched more by  $\text{Ca}^{2+}$  according to the reaction 2, than other wells (Figure 5B). We can explain that by reverse cation exchange.



Assuming that Na derives from different sources and that Cl is only from halite and also since the Na/Cl ratio it was concluded that the studied waters have been affected by cation exchange reactions causing low salinity (removed  $\text{Na}^+$ ), and the excess of  $\text{Na}^+$  in high salinity reflect extra source of  $\text{Na}^+$ .

There are several soluble sedimentary minerals that release  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  upon dissolution. The principal source of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  is the dissolution of gypsum ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ) and anhydrite ( $\text{CaSO}_4$ ). The dissolution of gypsum is fast and just a few residence time of water in gypsum land increase strongly the saturation index of gypsum. In the Ca- $\text{SO}_4$  diagram water in Tafersite region low mineralization depict different trends than other samples. Those samples have greater concentration of  $\text{Ca}^{2+}$  relative to  $\text{SO}_4^{2-}$  (Figure 6). It is widely accepted that  $\text{SO}_4^{2-}$  depletion has been caused by the biological reduction or precipitation of gypsum as a result of extensive evaporation. However, the condition under which precipitation of gypsum took place have not yet been clarified ( $\text{Sig} < 0$ ). Although, the majority of samples show a high concentration of  $\text{SO}_4^{2-}$  (Figure 6), Sulphate concentrations are variable, and increase content occurs from the recharge area (Tafersite) in the northern part towards the south. This increase may be due to the dissolution of gypsum and/or oxidation of

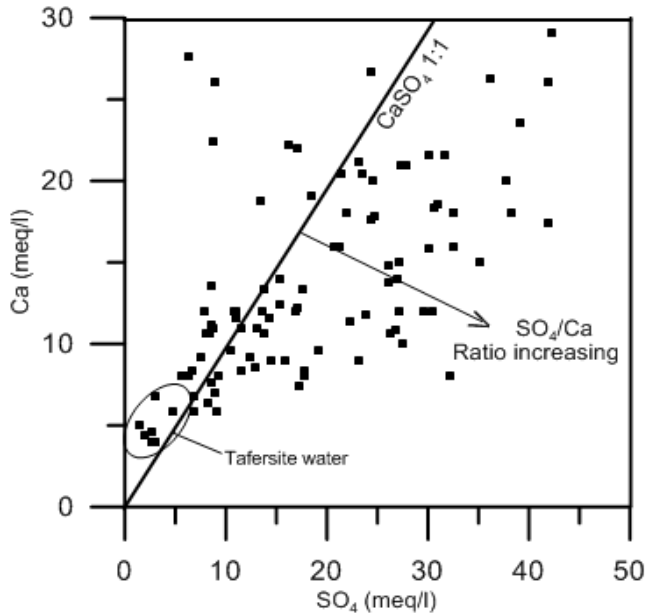


Figure 6. Relationships between SO<sub>4</sub> and Ca.

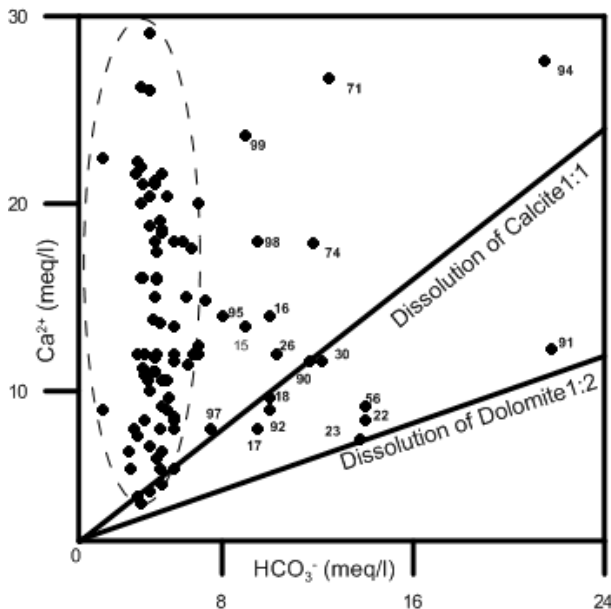
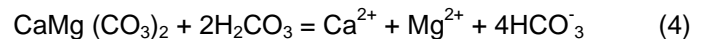
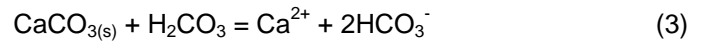


Figure 7. Relationships between HCO<sub>3</sub><sup>-</sup> and Ca<sup>2+</sup>.

sulfide minerals. Also, the Kert wadi which crossed the plain in the south and hydraulically connects with groundwater is an additional source of SO<sub>4</sub><sup>2-</sup>. The dissolution of gypsum is also accompanied by cation exchange reactions. The most important exchange reactions are the water softening reactions in Tafersite region, where Ca<sup>2+</sup> and Mg<sup>2+</sup> in the water exchange with

sorbed Na<sup>+</sup> as ground water moves through clayey material. A deficit of Ca<sup>2+</sup> showing in Figure 6 could be linked to cation exchange and carbonate precipitation, the both factors are known that remove the Ca<sup>2+</sup> from groundwater and decrease its concentration. Their content of SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> seems to be influenced by waters circulating within Miocene formation. Generally, gypsum deposits typically contain some magnesium; the dissolution of gypsum will also result in an increase in concentration of Mg<sup>2+</sup> in water. The removal of Ca<sup>2+</sup> and Mg<sup>2+</sup>, through the dissolution of evaporate minerals, may cause a disturbance in carbonate chemical equilibrium. This is confirmed by the water oversaturation index with respect to calcium and dolomite. Besides local geology (Miocene substratum) these waters are also influenced by the lithology of the catchment area. On regional scale, the surface geology in south region is dominated by gypsum marls Messinian age, which is crossed by Kert Wadi.

The total dissolved inorganic carbon (TDIC) is equivalent to the groundwater HCO<sub>3</sub><sup>-</sup> content for the observed pH range. The solubility of calcite and dolomite is largely controlled by CO<sub>2</sub> fugacity and pH, according to following reactions:



As shown previously, increasing the P<sub>CO2</sub> from 10<sup>-2.3</sup> to 8.10<sup>-0.1</sup> atm increases the total of amount of HCO<sub>3</sub><sup>-</sup> in solution from 250 to 1329 mg/l and lowers the pH from 7.66 to 6.23. So, these data are consistent with a reaction scheme in which meteoric waters flowing through the soil zone gain high CO<sub>2</sub> pressure and then are driven towards saturation by reaction with the carbonate minerals of the soil and host rocks. Figure 7 shows a series of samples which show an increase in calcium content independently of bicarbonate concentration, this reflects the dominance of gypsum dissolution to increase Ca<sup>2+</sup> concentration and tends to exclude its relation with weathering of carbonates.

**Correlation matrix**

The Pearson's correlation matrix to find the relationships between two or more variables was carried out using Stat graphics plus 5.1 software as shown in Table 2. Samples showing r > 0.6 are considered to be strongly correlated, whereas r < 0.6 shows poor correlation. EC shows a good correlation with Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> suggest that these elements are the principal source of salinization. The same for, Cl<sup>-</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> have a good correlation between them. These data suggest that water from different samples has the same geochemical properties. Also, the good correlation of these aqueous species with Cl<sup>-</sup> suggests that all of these

**Table 2.** Descriptive statistics of hydro chemical data (electrical conductivity, total dissolved solids, temperature, sodium, potassium, calcium, magnesium, chloride, bicarbonates, sulphate nitrates and pressure of CO<sub>2</sub>).

| Factor           | EC   | Ca   | Mg    | Na    | K     | Cl    | SO <sub>4</sub> | HCO <sub>3</sub> | NO <sub>3</sub> | P <sub>CO2</sub> | pH |
|------------------|------|------|-------|-------|-------|-------|-----------------|------------------|-----------------|------------------|----|
| EC               | 1    |      |       |       |       |       |                 |                  |                 |                  |    |
| Ca               | 0.73 | 1    |       |       |       |       |                 |                  |                 |                  |    |
| Mg               | 0.76 | 0.53 | 1     |       |       |       |                 |                  |                 |                  |    |
| Na               | 0.71 | 0.52 | 0.77  | 1     |       |       |                 |                  |                 |                  |    |
| K                | 0.60 | 0.29 | 0.39  | 0.55  | 1     |       |                 |                  |                 |                  |    |
| Cl               | 0.77 | 0.68 | 0.80  | 0.87  | 0.53  | 1     |                 |                  |                 |                  |    |
| SO <sub>4</sub>  | 0.70 | 0.59 | 0.78  | 0.66  | 0.37  | 0.58  | 1               |                  |                 |                  |    |
| HCO <sub>3</sub> | 0.34 | 0.03 | 0.02  | 0.09  | 0.46  | -0.01 | -0.15           | 1                |                 |                  |    |
| NO <sub>3</sub>  | 0.10 | 0.06 | 0.23  | 0.22  | 0.14  | 0.31  | 0.007           | -0.15            | 1               |                  |    |
| P <sub>CO2</sub> | 0.43 | 0.21 | 0.10  | 0.08  | 0.32  | 0.06  | -0.004          | 0.84             | -0.14           | 1                |    |
| pH               | -0.6 | -0.4 | -0.25 | -0.74 | -0.41 | -0.25 | -0.28           | -0.74            | 0.14            | -0.68            | 1  |

**Table 3.** Loading of the components obtained from principal component analysis, with three factors, Eigenvalue derived by factor analysis, and cumulative % explained by factors.

| Factor           | 1     | 2     | 3     |
|------------------|-------|-------|-------|
| Cl               | 0.85  | -     | -     |
| SO <sub>4</sub>  | 0.88  | -     | -     |
| HCO <sub>3</sub> | -     | 0.88  | -     |
| NO <sub>3</sub>  | -     | -     | 0.88  |
| Ca               | 0.77  | -     | -     |
| Mg               | 0.88  | -     | -     |
| Na               | 0.83  | -     | -     |
| pH               | -     | -0.82 | -     |
| P <sub>CO2</sub> | -     | 0.91  | -     |
| Eigen value      | 4.816 | 2.281 | 0.971 |
| % variance       | 48.16 | 22.81 | 9.71  |
| Cumulative %     | 48.16 | 70.97 | 80.68 |

species have behaved in a predominantly conservative manner with little water-reservoir rock interaction once the waters entered in the aquifer.

### Factor analysis

The Varimax rotation Factor Analysis (FA) was used as an alternative tool for corroboration of the concept obtained from hydrochemistry analysis. The Stat graphics plus 5.1 were used for extracting factors through the principal extraction method. The calculated factor loading, together with communalities and percentages of variance explained each factor, are listed in Table 3. The three retained factors explain about 80.65% of total variance of the data set (Table 3).

Factor 1 explains more than 48.31% of the variance. This factor is interpreted as related mainly to salinization

of groundwater due to dissolution of evaporitic rocks. The main contributors are Cl<sup>-</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, correlate positively with EC. Association between Ca, Mg, Na, Cl and SO<sub>4</sub> suggest dissolution of gypsum and halite. This is also supported by geological investigations. The occurrence of process of this factor is especially in aquifer basement and Miocene marly-gypsum outcrops in the southern of plain. The component of the salinization factor is similar to dissolution evaporate process in NE of Morocco (Elmandour et al., 2008; El yaouti et al., 2009), and SE Spain (Ceron et al., 2000).

Factor 2 explaining about 22.58% of total variance, includes HCO<sub>3</sub><sup>-</sup>, pH and P<sub>CO2</sub>. This is strongly P<sub>CO2</sub> controlled the weathering. The higher concentration in HCO<sub>3</sub><sup>-</sup> may be caused by carbonate dissolution driven by the increase of P<sub>CO2</sub> and the decrease of pH. This process is predominant in Midar region. The weathering of carbonate rocks in this region causes the high HCO<sub>3</sub>

concentration throughout the aquifer.

Factor 3 concerns  $\text{NO}_3^-$  (anthropogenic contamination) and contributes to total variance for about 9.75%. The high concentration is a particular case. That can be derived from sewage affluent and/or animal waste. Maximum observed  $\text{NO}_3^-$  concentration of groundwater in the study area is 145 mg/l, which is essentially higher than Moroccan standards for drinking water.

## Conclusion

The present study shows that the Kert region consists of deposits from the Jurassic to Villafranchian ages. The geological and geophysics study show that the reservoir is formed by detrital deposits of average permeability and it is based on marl substratum upper Miocene (Messinian) age.

Natural recharge in the study area is extremely limited to northwest part of area study (Tafersite region), and is identified in the Tamsamane metamorphic massive.

The hydro chemical data clearly indicate the contribution of local geology in salinity increasing of groundwater. The identified potential source of salinization includes dissolution of evaporate sediments which comprise the aquifer substratum. So, the abundance of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  in the groundwater is attributed to gypsum and halite dissolution. The reverse cation exchange process is important here because it has effectively increased  $\text{Ca}^{2+}$  concentration in Tafersite region at the expense of  $\text{Na}^+$ . This process is confirmed by salinity value rise and concentration variation, as a consequence of the dissolution of the aquifer material and cation exchange reactions between groundwater and the clay fraction. Generally, the groundwater have a similar chemical composition, they must have formed at the same time and from the same origin seawater masses. The water evolved from Messinian (upper Miocene) seawater that underwent evaporation during Mediterranean desiccation. Factor analysis is a powerful tool that gives an important clue for understanding geochemical processes that control the groundwater salinization. The statistical results show 3 factors (F1, F2 and F3), that explained 80.65% of the total variance in the groundwater quality. Factor 1 is the principal source of groundwater mineralization included  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Factor 2 is the carbonates processes include  $\text{HCO}_3^-$ ,  $\text{P}_{\text{CO}_2}$  and pH. Factor 3 represented by  $\text{NO}_3^-$  explained the human impact.

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