



Assessment the risk of impact of waste treatment center on groundwater quality in Oum Azza (Rabat, Morocco).

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Abstract

Water quality is very essential to human health. And, Groundwater quality assessment is necessary to guarantee sustainable safe use of water. Hence, in the region of study of Oum Azza, the presence the waste center treatment it could alter the quality of groundwater. In the present paper, hydrochemical, geochemical and multivariate statistical were used to assess the impact of waste treatment center Oum Azza on groundwater quality. Q-mode hierarchical cluster analysis (HCA) based on major ion contents and hydrochemical facies; defined three main chemical water types. The first, group 1, has low salinity (mean EC=813 μ S/cm) and abundance orders $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > NO_3^{-}$. With increased water-rock interaction, waters in group 2 and 3 become more saline, changing composition towards Cl-Ca-Mg and $HCO_3^{-} - Na^{+} - Mg^{2+}$. The principal component analysis (PCA) revealed, on part of the existence of phenomena governing groundwater mineralization particular, the water-rock interaction. And another part a tendency to nitrogen pollution localized at collected well water. These results contribute to a better understanding of the hydrochemical properties of groundwater in the area of study.

Keywords: PCA, Contamination, Mineralization, Facies, Waste treatment center, Oum Azza

1. Introduction

Water is the key resource for human living and uncountable human activities. In Morocco, owing to dependency on climatic and spatiotemporal irregularities; the water potential that is limited and substantially reduced, had been classify Morocco in category chronic water stress. Groundwater resources, dynamic in nature, are altered by such factors as the expansion of irrigation activities, urbanization and landfill leachate.

In fact, these factors reduce the groundwater quality. In addition, they present a health hazard to the rural population using well water without any treatment. Its quality of groundwater is an important factor influencing the human well-being. Hence monitoring and covering these important resources is essential [1]. In recent years, a growing number of studies stressed the critical Quality situation of several Moroccan groundwater; especially the pollution of groundwater by the leachate of garbage dump [2-4].

Oum Azza (Municipality of Rabat, Morocco) endows a waste treatment center, which provides an environmental advantage to the area. Howbeit, we cannot ignore the risk of eventual migration of leachate into groundwater. The study aims to assess the impact of waste treatment center Oum Azza on groundwater quality. The assessment is mostly based on hydrochemical analysis. Quality of groundwater for drinking water supply has been studied; through the spatiotemporal monitoring of physicochemical tracers. The water samples were collected during the wet period (March) and dry period (June) of 2010 from twelve wells in Oum Azza area. The quality of hydrochemical data obtained was assessed by two approaches; geochemical and multivariate statistical; PCA has been widely used to analyze and reduce the number of variables in environmental studies and HCA is one of the most broadly applied data clustering methods in groundwater classification.

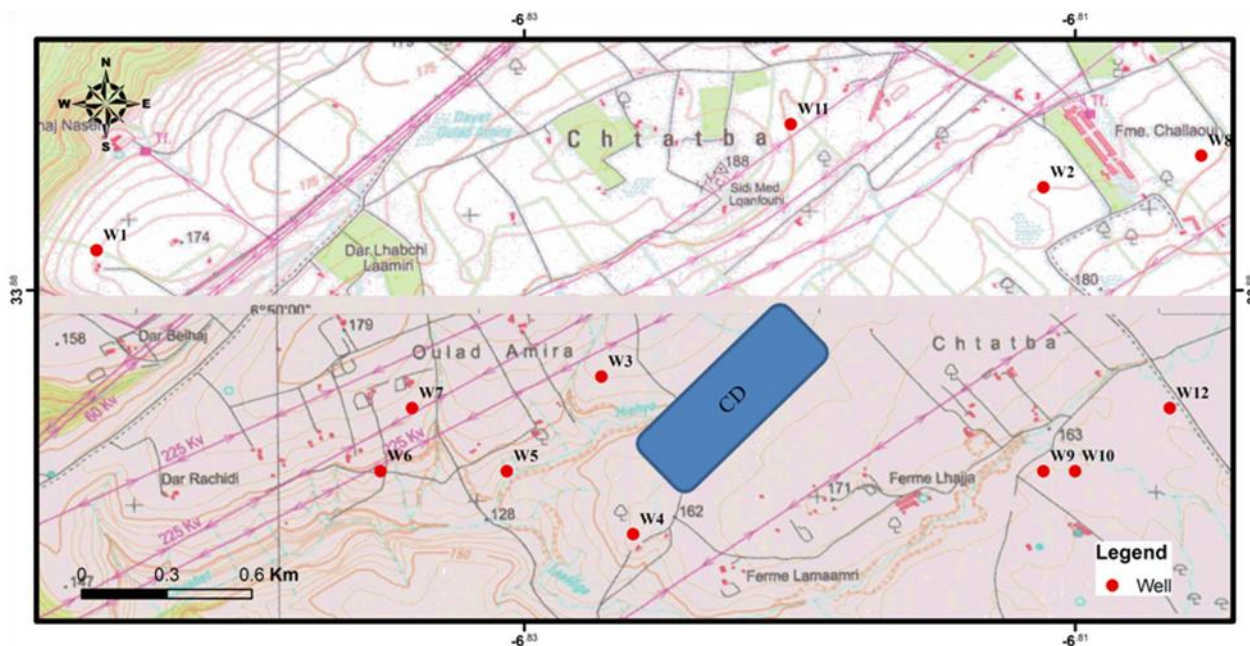


Fig.1. Map showing water sampling location. CD: Controlled dump.

2. Geology and hydrogeology

The area of study belongs to the Ain Ouda, located in the Nord west of Morocco (Fig.1). The climate of this area is semi arid, the annual precipitation being approximately 555 mm. The rainy season extends from October to April and a dry season covering the rest of the year. The mean monthly temperatures vary between 12, 6°C and 32, 5°C. The study area is marked by the predominance of primary fields, indeed the bedrock of the main formations in the region, which locally over much of the plateau consists mainly of schist of Visean age (Primary) fractured and cut by veins of quartzite. The major tectonic phase that affected the area since the Carboniferous does not allow us to precisely highlight a particular type of deformation. The aquifer system is developed at the interface of the base fractured and altered of Neogene and Quaternary plateaus. Groundwater flow is in a SE-NW direction (Fig.2).

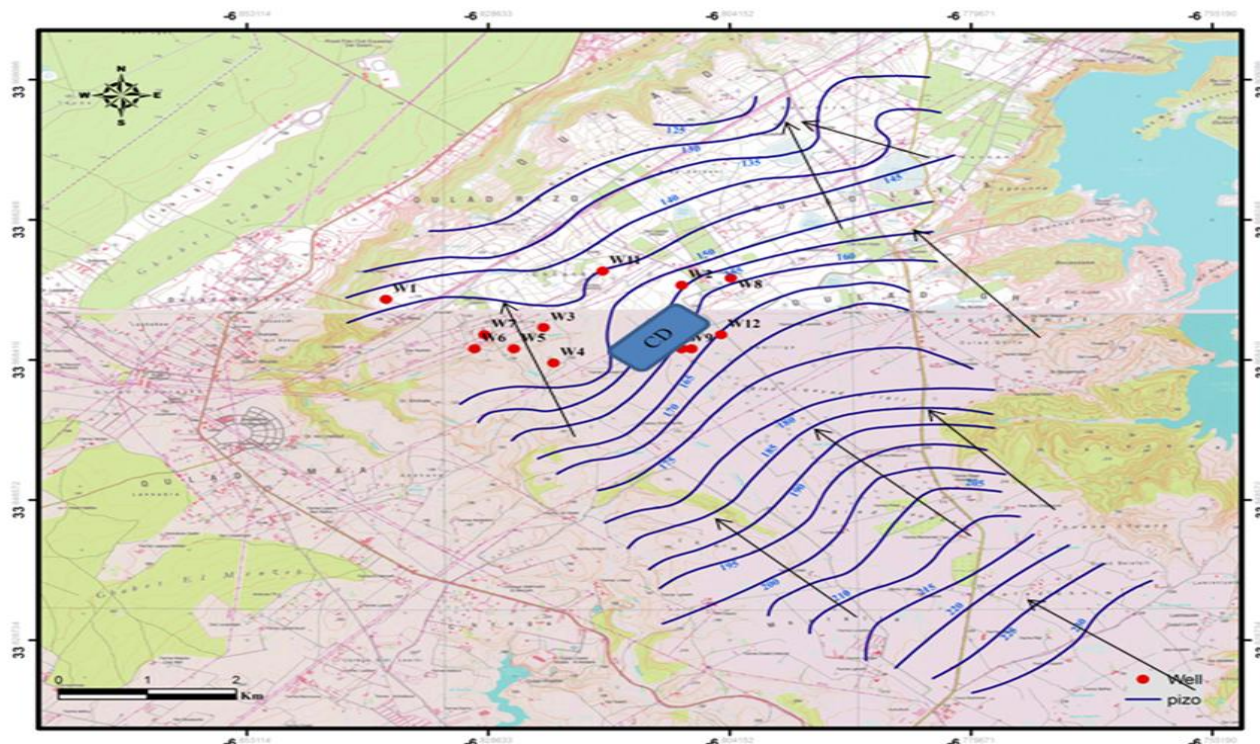


Fig.2. Potentiometric surface of the Oum Azza aquifer. CD: Controlled Dump

Sampling and analytical methods

The monitoring of evolution of physicochemical parameters was carried upon two campaigns in year 2010. A water sample was collected from each location during wet and dry season. The samples were collected with weighted bucket (50cm below the water well surface) to total 24. The water samples were taken in flasks and immediately transported at 4°C in the icebox to the laboratory (National hygiene Institute, Rabat). All Assessed parameters are determinate within at the end of each sampling day. Statistical analyses were performed by Xlstat computer software [5]. The quality of hydrochemical data was assessed by three approaches; geochemical and statistical analysis.

Twelve wells were selected; during rainy season (March 2010) and dry season (June 2010) from Oum Azza area. All samples were measured for physicochemical characteristics using standards methods. In situ field measurements were made on water samples for temperature (T), pH (315i\SET WTW), and electrical conductivity (EC) (315i\SET WTW) and dissolved oxygen (OD) (Oxi 330i\SET). Whilst the rest of parameters; nitrate, nitrite, ammonium, sulphate and orthophosphate were analyzed by spectrometry according to AFNOR standards NFT 90-013, NFT 90-012, NFT 90-015, NFT 90-040, NFT 90-023, using a jascov-530 molecular absorption spectrometer controlled by a computer. Sodium and potassium concentration were measured using flame photometer, according to AFNOR standards NFT 90-042. Alkalinity and hardness were measured using titration method. Organic matter were determined by oxidation with potassium permanganate in an acid hot medium. Chloride dosing was carried out by the standards titration method (Mohr method). Calcium and magnesium was determined by complexometric method using ethylenediaminetetracetic acid. All the water quality parameters are expressed in mg/L, except pH and hardness (°F).

3. Results and discussion

3.1 General Hydrochemistry

Statistics of the chemical composition of the groundwater samples are given in Table 1. The mean concentrations of the major ion in the samples groundwater are within the WHO [6] guidelines for drinking water. EC values of the groundwater samples of the studied area ranged from 474 to 2200 $\mu\text{s}/\text{cm}$. With a mean value exceeding the limits indicated by the WHO (750 $\mu\text{s}/\text{cm}$) of 1183 $\mu\text{s}/\text{cm}$ and 1131 $\mu\text{s}/\text{cm}$ for rainy and dry period, respectively. The pH values varied from 6, 63 to 7, 52 indicating that the water was fairly buffered during the two campaigns (Table1). The high values of total hardness 35 ° F (DC) and 43.70 ° F (RC) confirmed the severe charge by calcium and magnesium; witch classified those waters in the category "very hard water". The relative abundance of major cation was and majority of samples exceed the desirable limit of Ca (75mg/L) during two campaigning, but only 25 % of them exceed that of Mg (30mg/L). The abundance of major anions was $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$, the maximum HCO_3^- and Cl^- concentration of 658,8 mg/L (RC), 671 mg/L (DC) and 425,5 mg/L (RC), 372,45mg/L(DC)respectively are, however, higher than their respective WHO standards of 300 mg/L and 250 mg/L. the value of the nitrate during two campaigning in the study area consistent with the standard norms (50mg / L).Whilst, in dry period, the richness of nitrates located at the wells P6 (60mg/L). The evolution of ammonia nitrogen (NH_4^+) and nitrite nitrogen (NO_2^-) in analyzed samples shows a slight variation between the two sampling periods, however the summer revealed high concentrations of ammonium with value of 3.96 mg / L present on the well W6; exceeded the standard limit (0.5mg/L) and nitrite nitrogen with a concentration of 0.32 mg / L at the well W3. Exceed the recommended standard (0.1 mg/L).

The same organic matter concentration is within the recommended Moroccan and international standards (5mg/L), except for wells W4 and W5. This element has a dissimilar trend of dissolved oxygen. Indeed, in rainy season; the OD demonstrates elevated values. However, the low values are operated accounted during the dry period from 2.35mg/L to 6.45mg/L and from 3.22 mg/L to 8.03 mg/L during the wet period respectively. The wide variation is attributed to the phenomenon of evaporation during the dry period, is as in fact, a part of water is absorbed by the soil; while the other part is almost completely evaporated before attaint reaching the groundwater. It was clearly observed that the concentrations of the major elements undergo an appreciable change during two campaigns.

Multivariate statistical analysis

Various methods and multivariate statistical analysis are applied to analyze and explain the chemical components of groundwater. Q-mode hierarchical cluster analysis (HCA) and Components Principal Analysis (CPA) were jointly used to define evolution and the origin of chemical parameters of groundwater samples the one hand, the other hand to group the commonly collected water quality data and exhibits the correlations between chemical parameters and groundwater samples. The hydrochemical data obtained the two conducted campaigns (CE, Mg^{2+} , Ca^{2+} , Na^+ , K^+ , HCO_3^- , NO_3^- , NO_2^- , NH_4^+ , SO_4^{2-} , Cl^- , organic matter, and hardness) were utilized in this analysis.

Table.1. Statistical summary of hydrochemical parameters of groundwater of Oum Azza platea

	Ca ²⁺	Mg ²⁺	Na ⁺	k ⁺	NO ₃ ⁻	so ₄ ²⁻	HCO ₃ ⁻	Cl ⁻	F ^o	po ₄ ²⁻	NH ₄ ⁺	NO ₂ ⁻	E.C	TDS	O.M	OD	pH	T (°C)
WHO	75	30	50	10	50	250	300	250	50	0,5	0,5	0,1	750	500	5	___	6,5-8.5	25
Total (n=24)																		
Rainy period (n=12)																		
Min	40,88	15,56	45,6	0,9	5,8	2,5	109,08	56,8	17	0,05	0	0	623	404	0,44	3,22	6,51	18,06
Max	134,66	194,5	197,6	6,9	47,2	83,85	658,8	425,5	91	0,44	0,09	0,06	2200	1543	9,8	8,03	7,42	21,5
Mean	86,01	50,1	96,18	2,23	20,54	33,85	298,81	220,46	43,7	0,21	0,03	0,01	1183	973,5	3,63	6,6	7,03	19
Dry period (n=12)																		
Min	29,65	10,7	40,6	0,5	2,21	4,29	164,7	71	11,8	0,09	0	0	474	538	0,64	2,35	6,38	21,4
Max	206,01	55,94	229,8	6,4	60	60,94	671	372,45	61,4	0,48	3,96	0,32	1954	1296	9,5	6,45	7,44	24,9
Mean	91,96	30,24	127,86	3,78	21,76	28,21	360,92	202,94	35	0,24	0,45	0,04	1131	917	3,59	5,32	7,03	22,41

Hierarchical cluster analysis

Hierarchical cluster analysis (HCA) is used to test water quality data and determine if samples can be grouped into hydrochemical groups. The hierarchical cluster analysis method was used to group water samples into significant different clusters. The groundwater samples were classified by HCA into three main clusters (C1, C2 and C3) (Fig.3a)-in wet season, each representing a hydrochemical facies with mean for each parameter shown in table2. From a geochemical viewpoint, these groups are interpreted by plotting the representative points of water samples on Piper diagram [22] (Fig4).EC seems to be a major distinguishing factor with concentrations increasing in all major-ions following the order: Cluster1>C2>C3 (Table2.a).

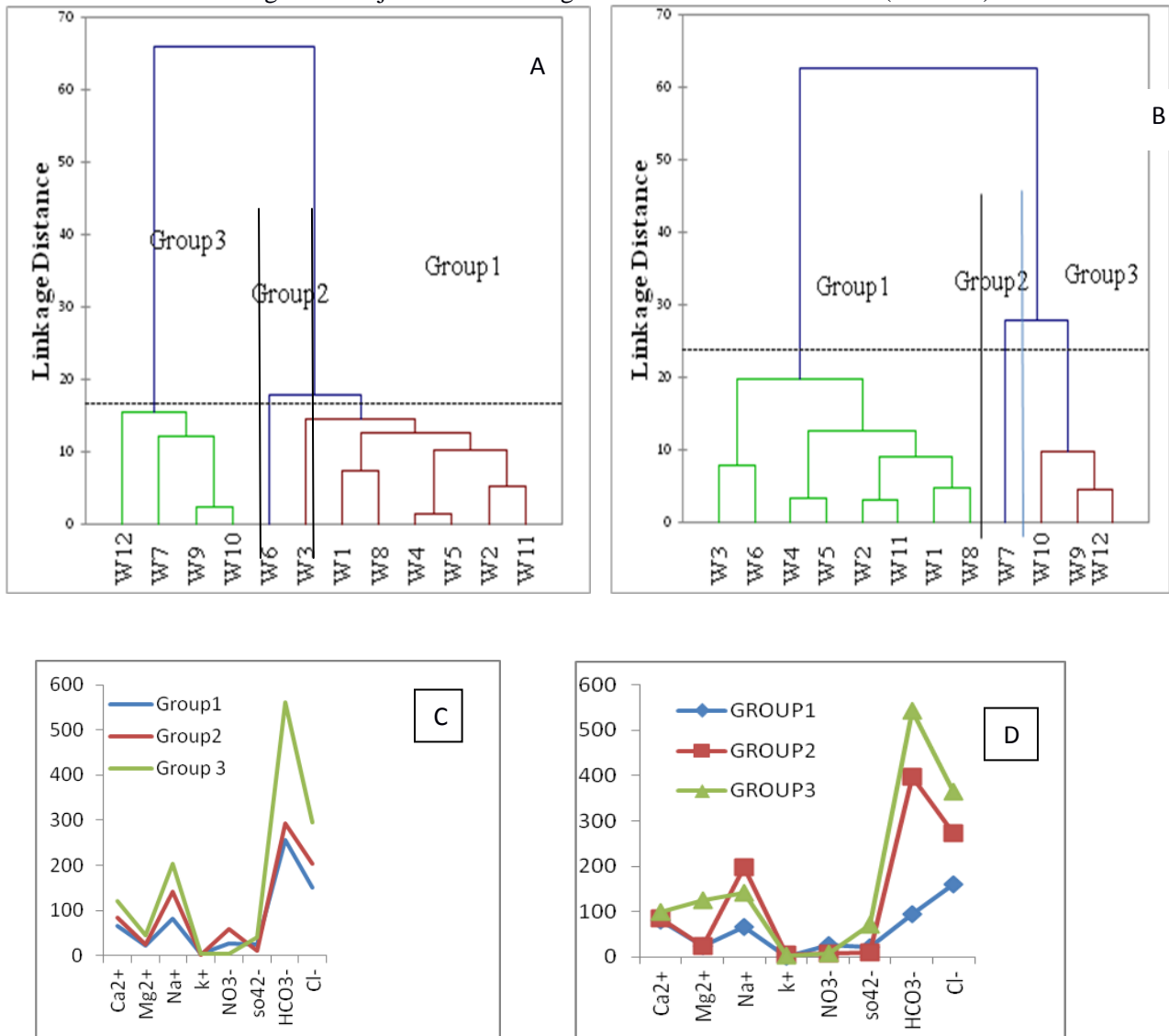


Fig.3. Dendrogram of the Q-mode b hierarchical cluster analysis. (a).Rainy season,(b) Dry season. (c) Average composition of the three groundwater groups (wet season). (d) Average composition of the three groundwater groups (Dry season).

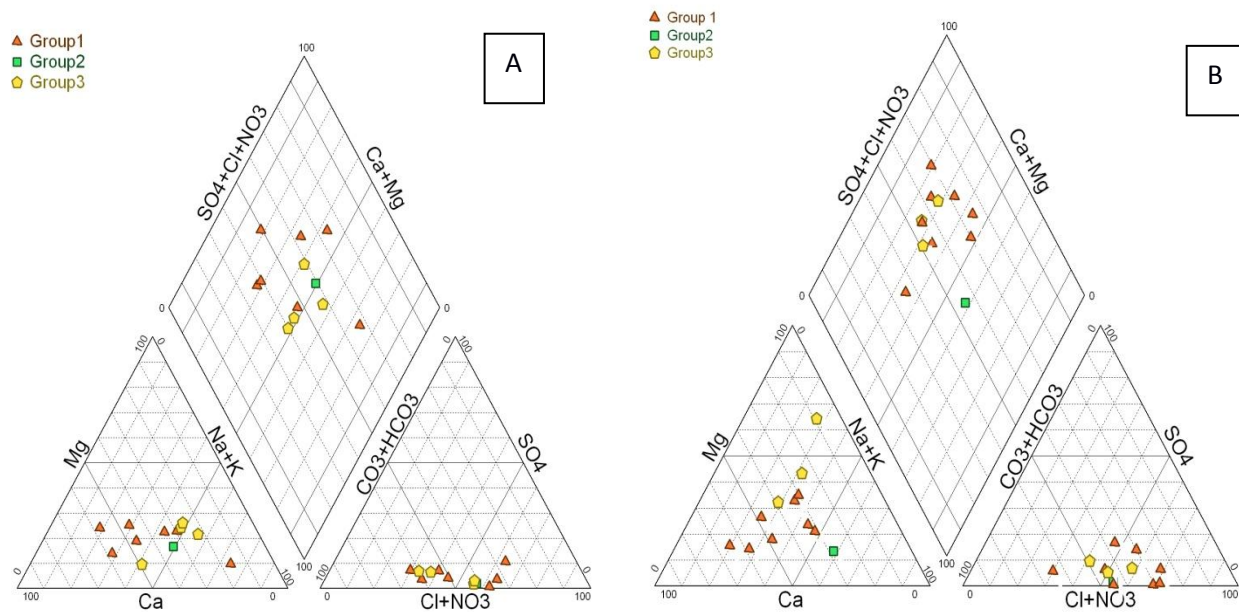


Fig.4. Piper diagram for water samples. (a) Dry season, (b) Rainy season

Table.2.a Mean parameter values of the three principal water groups (determined from HCA. Wet season)

	Ca ²⁺	Mg ²⁺	Na ⁺	k ⁺	NO ₃ ⁻	so ₄ ²⁻	HCO ₃ ⁻	Cl ⁻	TDS
GROUP1	81,12	25,19	66,51	1,9	27	23	94,92	159,84	580
GROUP2	85,74	24,75	197,6	6,2	6,82	11,23	397,5	273,95	1004
GROUP3	99	125	142	2	8	70	543	364	1353

Table.2.b. Mean parameter values of the three principal water groups (determined from HCA. Dry season)

	Ca ²⁺	Mg ²⁺	Na ⁺	k ⁺	NO ₃ ⁻	so ₄ ²⁻	HCO ₃ ⁻	Cl ⁻	TDS
Group1	66,88	22,31	82,24	2,83	26,20	23,60	256,20	150,11	757
Group2	84,96	25,29	141,6	0,5	60	11,77	292,8	202,35	819
Group 3	120,0	45,4	204,3	3,2	4,4	40,4	561,2	295,5	1277

The first cluster is characterized by low salinity with relatively TDS (580mg/L=averages) and abundance orders Ca²⁺>Na⁺>Mg²⁺>K⁺ and HCO₃⁻>Cl⁻>NO₃⁻>SO₄²⁻. These waters are classified as HCO₃⁻ alkaline earth water type. In addition showed in elevated concentration in NO₃⁻ from other cluster; reflecting anthropogenic pollution.

Group 2 is made up of water samples the cation composition which is dominated by Ca²⁺ and Na⁺, with anion classified Cl-Ca-Mg.

Group 3 has high salinity (TDS mean=1353 mg/L). On the basis of overall chemical composition, characterized by ion abundances Na⁺>Mg²⁺>Ca²⁺>K⁺ and HCO₃⁻>Cl⁻>SO₄²⁻>NO₃⁻. These waters are classified as HCO₃⁻-Na⁺-Mg²⁺.

HCA of dry period (Fig.3b) showed the same trend, except wells 6 and 7. indeed, the well 6 passed from group 1 to group 2, and the well 7 passed from Group 2 to Group 3. The variations of ionic composition are suggesting that the hydrochemistry of groundwater is controlled by water-rock interaction and anthropogenic pollution.

Principal component principal

Each component is typified by high or few loadings, and many near-zero loadings as mentioned by Davis [7] The first two components explain 45.32 % (F1) and 15.38 % (F2) of the variance,

Axis F1 accounts the greatest amount of the variance, and is characterized by highly positive loading in ions major, EC, and hardness. This major factor describes mineralization of groundwater by water soil/rock interaction. The association of bicarbonate, sodium, magnesium, and calcium; could report the same origin and a common mechanism of mineralization, the axis F1 expresses the phenomenon of mineralization related to the residence time of groundwater in the aquifer. In fact, Mg^{2+} , Ca^{2+} and HCO_3^- appear in the water after long contact with under-soil formation.

Axis 2 is defined by positive loading K^+ and by negative loading in NO_2^- and NH_4^+ . Fig.5a summarizes this information by showing the position of the loading of chemical parameters in the plane defined by the axis of components 1 and 2.

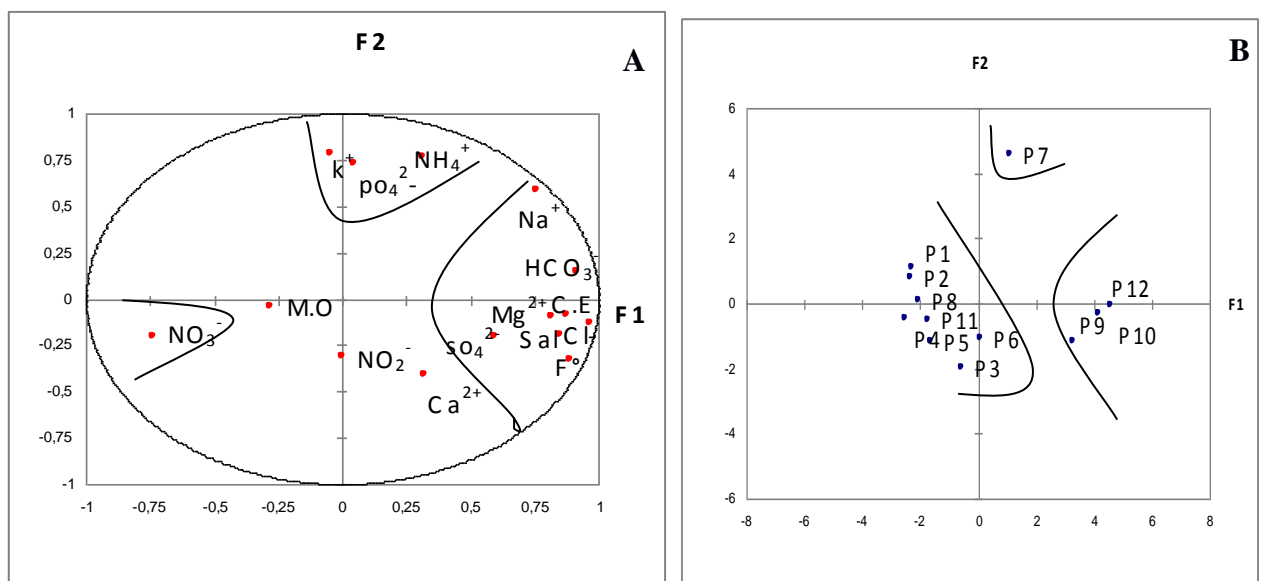


Fig.5a. Position of the variables and water points sampled on the (F1, F2) factorial plain of wet period. A: circle of correlation. B: Projected water points sampled.

The analysis of different trends obtained in the plane (F1xF2) during the dry period shows the individualization of three groups (Fig. 5a):

Group 1: contains the well 2, 4, 5 and 8. Characterized by low mineralization, this group is located on negative side of the F1 axis, which also presents high organic charge especially, nitrates.

Group 2: occupies a middle position on the axis F2, it includes wells W1, W3 and W11 characterized by hydrochemical conditions of medium quality except wells W3 and W6 are presenting higher NO_3^- , NO_2^- concentration; reflecting advanced pollution.

Group 3: characterized by strong mineralization, associated to the large presence of major elements such as magnesium, chloride, bicarbonate and calcium on one hand, and by pronounced hardness on the other hand. It is defined by the wells; W7, W9, W10, W12.

For the rainy period (Fig.5b), the multivariate analysis indicated a different situation from the dry season. In fact dilution affected some points that are charged with organic matter and nitrates, particularly wells W2, W4, W5 and W8. However, the situation remains the same for the W10 and W12 wells except well P7 which indicates a certain load of potassium and orthophosphates

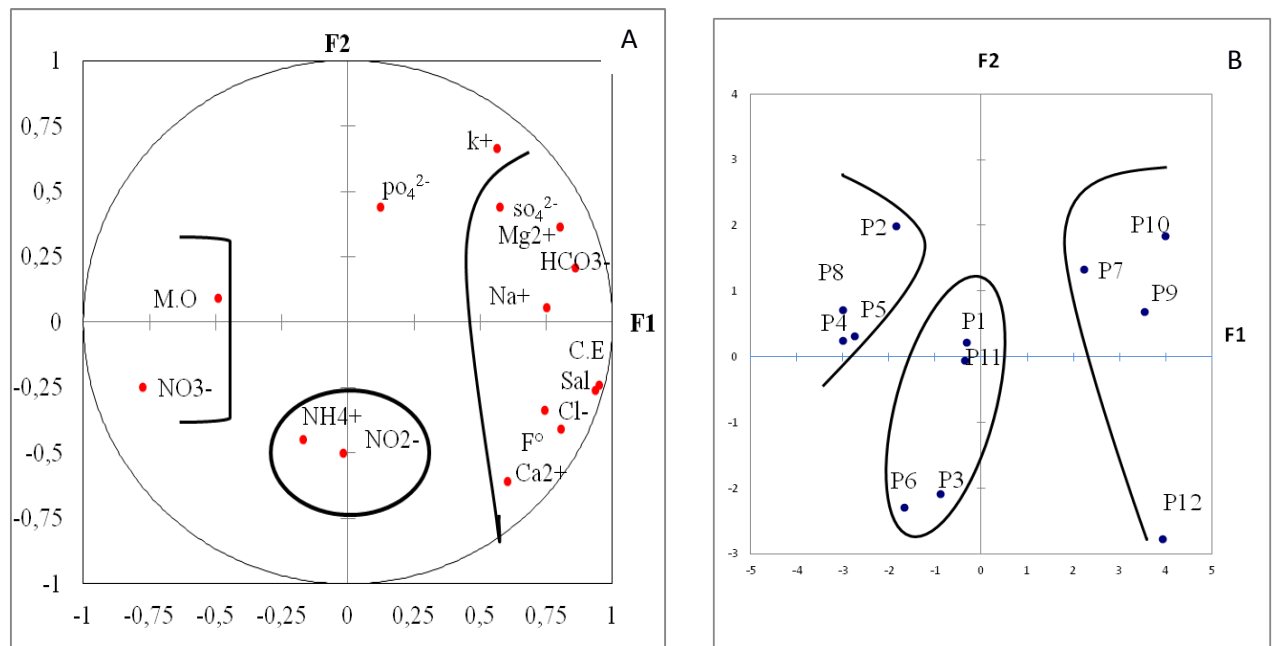


Fig.5b. Position of the variables and water points sampled on the (F1, F2) factorial plain of dry period. A: circle of correlation. B: Projected water samples.

Discussion:

Nitrate is produced during the final stage of decomposition of organic matter [8] and is the most prevalent form of nitrogen in groundwater [9].

The Samples taken from wells during dry and wet season have respectively averages of 20.41 mg\L and 19.37 mg\L respectively. The nitrate evolution shows (Tab. I and II) dissimilarity to the nitrite and ammonium, because these three ions have two opposed forms of nitrogen: the oxidized (nitrate) and the reduced (nitrites and ammonium). Those values are generally within the Moroccan and French recommended standard (50mg\L). However, our results are above the American standards (10mg\L). Groen et al. [10] indicate that nitrate concentration higher than 10mg\L is dangerous to the health of pregnant women and infants, because of its potential to cause methaemoglobinaemia [11]. In dry season, the greatest amount of nitrate concentration in well 6 (60mg\L) could be attributed to the proximity of the controlled landfill Oum Azza.

Ammonium contents have a relatively higher presence in well W6 (3.96mg\L). Which is due to the fact that contaminated land, contribute a significant quantity of nitrogen to groundwater. Hence, landfills are considered a major source of pollutants. During the last four decades, their impacts on groundwater quality have been extensively reported in many studies [3].The present work, shows a higher nitrate concentration in alluvial Sebou (Morocco) in comparison with domestic studies as Darwich et al. [12] ,who find that nitrate level is varying from 0.55mg\L to 6.5mg\L.

Also in dry period, the higher value of nitrites (0.32mg\L) is identified in well 3 located downstream of waste treatment centers. The greatest amount of nitrite could indicate a recent contamination [3] .This value exceed the international standards limits (0.1mg\L), the average contents (0.45mg\L) are also higher in studied wells as compared to those in rural groundwater supplies in Marrakesh area; Morocco by Lamrani et al [13].This effect may be an indication of the impact of waste treatment center Oum Azza. Indeed, the elements NH₄, NO₂ and NO₃, are considered indicators of anthropogenic pollution [14-15]. Comparison of concentrations values of chemical parameters in the different shows that wells situated upstream waste treatment center Oum Azza (W9, W10, W12) contained lower concentrations of nitrate, nitrite, than those situated downstream (W1, W2, W3, W4, W5, W6) in both wet and dry period.

For organic matter, the higher contents in wells W4 (9 mg/L) and W5 (8 mg/L) coincides with the low values of dissolved oxygen, which are in dry and wet season; values range from 2.67 mg / L to 3.02 mg and from 3.64 mg / L to 3.22 mg / L, respectively. This lack of dissolved oxygen is the result of the degradation of organic matter by chemical oxidation, or by biological oxidation causing the release of NO_2^- and NH_4^+ [16].

Chloride is usually a major indicator of the impact of waste on the physico-chemical quality of groundwater [3-17]. Indeed, waste contains great amounts in chloride [18]. High chloride concentration can also result from dissolution of soil and rock minerals. Based on the data and local geology, it can be said that high chloride concentration is more likely the result of sewage waste; which is could be confirmed by the correlation between chloride and nitrate (0.58) on one hand; on the other hand, a party of the chloride is bounded to local geology in study area.

The bicarbonate concentration in groundwater depends mainly on the presence of carbonate minerals in the soil and aquifer. According to Matthes [19]; the bicarbonate content about 302 mg/L in groundwater not subject to anthropogenic influences. In this study, the well water is rich in bicarbonates with values exceeding 600 mg / l during the dry period. There is no correlation between pH and bicarbonate ($r^2 = 0.005$ for the wet season and $r^2 = 0.005$ for the dry period), implying that the gas exchanges, including the CO_2 does not occur in high concentrations of bicarbonates recorded in the waters analyzed, contrary to what was found by Akoteoyon et al [20] in the aquifer of the coastal plain of Lagos (southwest Niger). A positive correlation exists between bicarbonate and sodium (0.74) in both rural low water and high water, would be in favor of a common origin of these elements, namely the dissolution of the complex HCO_3Na . Nevertheless its correlation with nitrate (0.60) and chloride ($r^2=0.73$ during the period dry, 0.61 during the wet period) reflects that a portion results of bicarbonates to presence of organic matter in the groundwater; which is oxidized, which in turn promotes dissolution of minerals.

Hardness in water is mainly linked to concentration of calcium and magnesium content [11], the hardness of water it reflects the nature of the geological formations with which it has been in contact. There is no limitation of water hardness by Moroccan Standards, but the WHO gives a value of 50°F as the maximum value for water hardness [6]. In this study, the majority hardness value is exceeding 18°F, which classified this studied water in "very hard" category [21]. The average values in wet and dry season of hardness are 15°F and 43.70°F respectively. In fact, this strong concentration could be related to aquifer lithology of the limestone (Visean (Primary)).

The spatial hydrochemical zonation of the groundwater in study area is defined by multivariate statistical methods. The flow direction SE- NW reveal the influential gradient of the processing waste center Oum azza on the quality of studied wells. In fact, wells upstream of waste treatment center Oum Azza (W9, W10, and W12) are under the dependence of the natural conditions. While, the wells downstream are directly influenced by the processing; particularly at wells (W3, W4, W5, W6) closest to the waste treatment center. Based on the data and local geology, highlighted two dominant processes that control water chemistry: the first endogenous, including natural background due to natural water-rocks interactions, which are observed calcites, dolomites, and limestone. While the second is due to anthropogenic source, connected to the closeness of the waste processing center Oum Azza.

Conclusion:

A hydrochemical and geochemical study conducted in Oum azza groundwater, showed the wells water were greatly hard, alkalized. Also, the monitoring of physicochemical parameters and major elements during the wet and dry period (2010) indicated that; in dry period revealed highest concentration of ion major than wet season. This could be due to the reduction of meteoric inputs and evaporation is responsible increasing concentration of dissolved ions. The statistical approaches was carried out in order to analyze groundwater quality; it revealed the hydro-system characterized by a dominant mineralization gradient; that persists even after passing from wet period to dry season. This passage is characterized by the dominance of facies Cl-Ca and nitrogen pollution. In fact, the origin of water quality is double; natural background related to the water-rock interaction, and anthropogenic influences, related to the presence of indicators of pollution. Resulting from the greatly degradation of organic matter presence as NH_4 , NO_2 -and NO_3 . The results could be attributed to waste treatment center Oum Azza closeness. People using this water without any treatment for their daily needs could be exposed to a serious health risks. It is then appropriate to carry out an epidemiological study in the area to determine the health risks associated with the presence of the Oum Azza center.

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