

Impact assessment of groundwater contamination near a solid waste landfill and recovery center, case of Oum Azza (Rabat, Morocco): Water quality assessment study

Evaluation de l'impact de la contamination des eaux souterraines à proximité d'un centre d'enfouissement et de valorisation des déchets solides, cas d'Oum Azza (Rabat- Maroc): Etude d'évaluation de la qualité de l'eau

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Abstract. This work aims to evaluate the potential impact of the solid waste landfill and recovery center (CEV) of Oum Azza (Rabat, Morocco) on the quality of the groundwater. The hydro-chemical quality of these waters for the supply of the rural population in this region was studied through the spatio-temporal monitoring of a certain number of physical and chemical parameters. In fact, the 21-well water was collected during both winter and summer seasons of 2017. The results of this study show that the groundwater of the Oum Azza water table is highly mineralized and very hard. Some wells also indicate a contamination of human origin in particular, organic, nitrogen phosphorus, and metallic and it also emerges from the various physicochemical and statistical analyzes using Principal Component Analysis (PCA), that pollution in summer is more pronounced than in winter. Moreover, the correlations observed between the various mineral and organic parameters analyzed so that the analysis in PAC makes it possible to highlight a strong organic and metallic anthropogenic contamination at the level of some wells downstream of the CEV.

Keywords : groundwater, hydrochemistry, contamination, mineralization, CEV Oum Azza, Morocco.

Résumé. Ce travail a pour objectif l'évaluation de l'impact potentiel du centre d'enfouissement et de valorisation des déchets solides (CEV) d'Oum Azza (Rabat, Maroc) sur la qualité des eaux souterraines. La qualité hydro-chimique de ces eaux qui servent à l'approvisionnement de la population rurale, de cette région a été étudiée à travers le suivi spatio-temporel d'un certain nombre de paramètres physiques, chimiques et métalliques. En effet, l'eau de 21 puits a été collectée pendant les saisons d'hiver et d'été de 2017. Les résultats de cette étude montrent que les eaux souterraines de la nappe phréatique d'Oum Azza sont fortement minéralisées et très dures. Certains puits indiquent également une contamination d'origine humaine, notamment organique, azotée, phosphorée et métallique. Il ressort également des diverses analyses physicochimiques et statistiques réalisées à l'aide de l'analyse en composantes principales (ACP), que la pollution estivale est plus prononcée qu'en hiver. Par ailleurs, les corrélations observées entre les différents paramètres physiques minérales et organiques analysés ainsi que l'analyse d'ACP permet de mettre en évidence une contamination anthropogénique organique et métallique très prononcée en particulier au niveau de quelques puits en aval du CEV.

Mots Clés : Eaux souterraines, hydrochimie, contamination, minéralisation, CEV Oum Azza, Maroc.

INTRODUCTION

Groundwater is of a strategic nature and plays a very important role in Morocco's socio-economic development, but it faces overexploitation that exceeds its capacity for renewal and deteriorates its quality.

About one-third of the world's population draws groundwater for drinking (Nickson *et al.* 2005). Considered the most drinkable, these waters are also the source of drinking water for the rural population, 36 % of resources used in Moroccan cities come from groundwater and 70% are used by the population, according to the State Secretariat for Water (SEE), hence the need to preserve it and ensure its quality.

However, one of the major problems in managing the quality of this commodity is its pollution. In addition to natural pollution due to the critical deterioration of the mineralogical quality of some aquifers because of their geological contexts, there is also agricultural pollution, and urban and rural household pollution caused by household waste which in

the absence of reliable sanitation devices, contaminate this resource with leachates.

The work we present is to study and evaluate the impact of the Oum Azza landfill and waste recovery center (CEV; Fig. 1a) on the quality of this resource from the point of view of potability through the measurement of major ions, metallic elements and organic materials, namely Nitrogen, Phosphorus and Biological and Chemical Oxygen demand. Thus, the hydro chemical approach and the multivariate analysis were used to process the data of these investigations.

Area's simplified geology

Oum Azza belongs to the plateau of Ain Aouda (Rabat, Morocco; Fig. 1a), whose study area is attached to the coastal Meseta area (Piqué 1979). Paleozoic shales, sandstones and limestones (Ordovician, Silurian, Devonian or Carboniferous; Fig. 1b) are very widely represented (Piqué 1979, EL Hassani 1990, SAM 2009). In intercalations in shales, there are lot of (Ordovician and/or Carboniferous) quartzites and or sandstone

bancs whose thickness varies from a few meters to a few tens of meters (Combe *et al.* 1975, Piqué 1979, EL Hassani 1990, SAM2009; Fig. 1a-b). Paleozoic rocks are strongly tectonized and metamorphosed (caledonian and variscan phases; Piqué

1979, EL Hassani 1990) and are uncomfortably surmounted by the Miocene and Plio-Quaternary marls, limestones and conglomerates (Millies Lacroix 1974, Akil 1990, Sitel & Akil 1996; Fig. 1b).

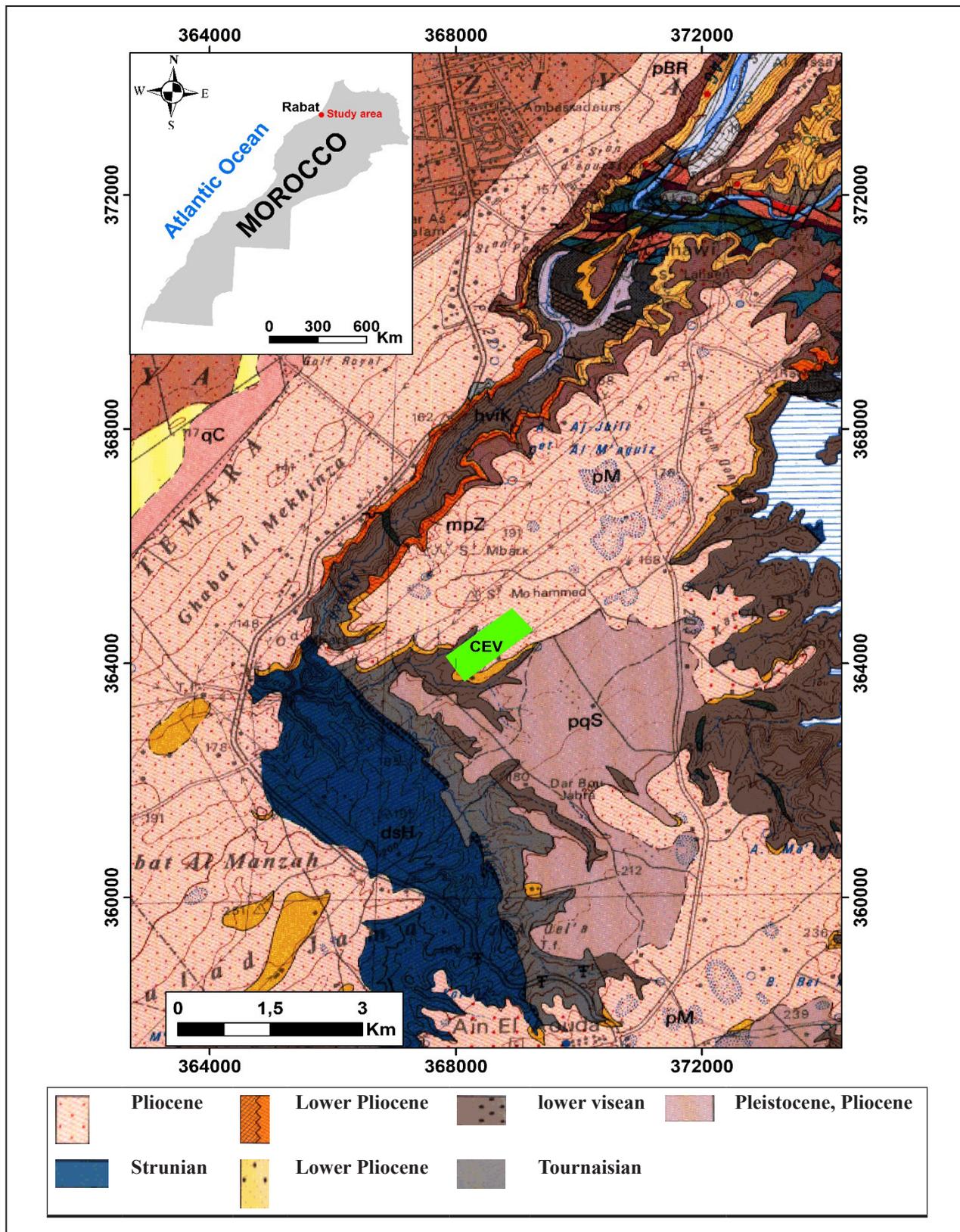


Figure 1a. Extracted geological map of the studied areas (For a complete legend see the geological map of Morocco 1/100000, sheet of Rommani, Vidal 1989). In green the Oum Azza landfill (CEV) localization.

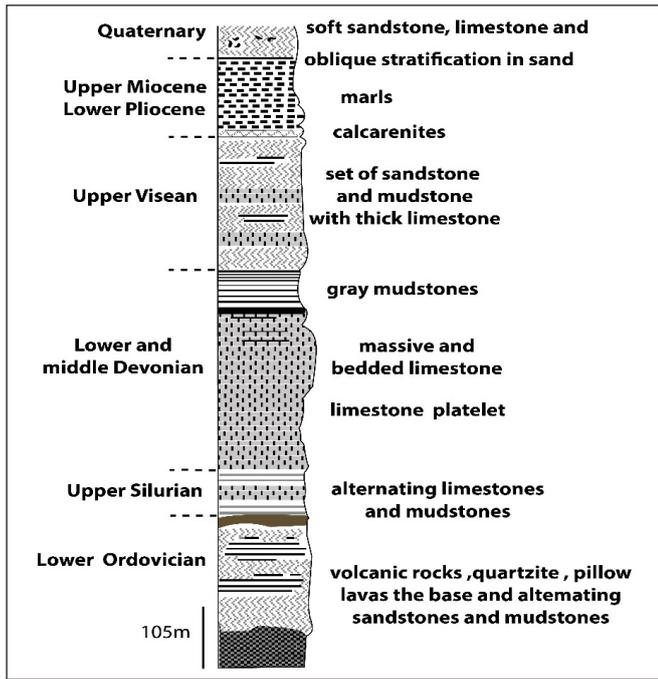


Figure 1b. Synthetic stratigraphic column of the Akrach area (in Morarech *et al.* 2015, modified).

Area's hydrogeology and climate

On the hydrogeological level, an aquifer system is developed at the interface of the fractured and altered basement of the Neogene and Quaternary plateau formations. According to the Hydraulic Basin Agency of Bouregreg and Chaouia (ABHBC) report (ABHBC 2011), this free table covering an area of about 350 km² flows in a SE-NW direction (Amraoui 1999) and it is well defined hydrogeologically by the Bouregreg river in the North, Akrach river in the East and Ykem river toward the South, whose deep valleys cut up to the substratum (paleozoic shales)

isolate it from any external underground supply. The Paleozoic formations of the area are uncomfortably surmounted by Miocene deposits and plio-quaternary formations (Millies Lacroix 1974). The bedrocks consists of Paleozoic shales in the South-West and Miocene marls in the North-East (Combe *et al.* 1975, SAM 2009).

According to data from the General Direction of Local Authorities (DGCL) (DGCL 2015) the climate area is semi-arid Mediterranean type with a mild, moderate maritime influence and rainy in winter. In summer, it becomes humid and temperate with days of Chergui (hot wind blowing from the East) (DGCL 2015). The average rainfall is around 500 mm per year, the annual average temperature is 18 °C with a thermal amplitude of about 20 °C (ABHBC 2016).

The piezometric measurements carried out during this study show that the depth of the piezometric surface, with respect to the ground, is very variable in space and time. It varies between 1.5 and 27 m during high water and between 4 and 44 m during low water periods in 2015, whereas it varies between 3.3 and 31.2 m during high water and between 2.6 and 41.8 m in low water period in 2017. However, according to the hydrogeological studies of the Hydraulic Basin Agency of Bouregreg and Chaouia ABHBC (2016) for the Oum Azza - Ain El Aouda sector, classes of depths of water inflows have been defined, and are generally between 5 and 33 m, thus exploiting the water tables most superficial water.

MATERIAL AND METHODS

Sampling and methodology

In order to evaluate and quantify the physicochemical characteristics of the groundwater surrounding the CEV of Oum Azza, the area explored was chosen in relation to the location of the CEV and in relation to the flow direction of the groundwater. Thus, 21 wells were selected and were the subject of this study. Their Cartesian coordinates are given in (Tab. 1) and their geodesic locations are displayed in (Fig. 2).

Table 1. Lambert coordinates of sampled well waters.

Wells	X	Y	Wells	X	Y	Wells	X	Y
P1	366501	363270	P8	369129	365116	P15	369284	363982
P2	366824	364186	P9	369380	365216	P16	368986	363918
P3	367157	364136	P10	369833	365830	P17	368489	363506
P4	367406	363960	P11	369701	364938	P18	371453	363674
P5	367458	363766	P12	369381	365088	P19	371578	364594
P6	368261	365560	P13	369931	364644	P20	371600	362272
P7	368351	365168	P14	369368	364202	P21	367975	357456

Well water samples were collected during the wet and dry seasons (April-August 2017). 42 samples were taken manually and the water samples were conditioned then transported in a cooler container at 4 °C to the Laboratory. Measurements, in situ, performed to characterize the physicochemical quality of the well water of the concerned several parameters: temperature, pH, dissolved Oxygen and

conductivity while physicochemical parameters were measured in the National Laboratory for Pollution Monitoring and Studies (LNEPS) of the State Secretariat for Sustainable Development, and the metallic parameters in the Laboratory of the Technical Support Unit for Scientific Research (UATRS) under the National Technical Scientific Research Center (CNRST; Rabat), according to standardized analysis methods (Table 2).

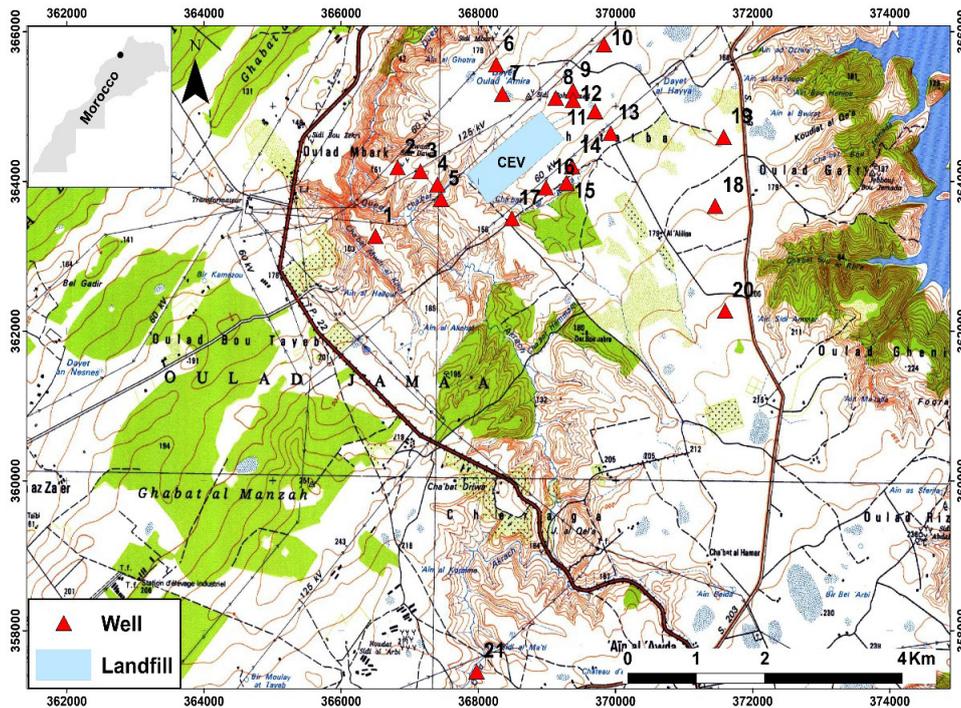


Figure 2. Sample map extract from the topographic map of Morocco at 1/50000, sheet of Temara.

Table 2. Physico-chemical parameters analyzed and the methods used.

Parameter	Abbreviation	unit	Reference method	Moroccan standard NM 03.7.001
Potential hydrogen	pH	-	ISO 10523-2008	pH < 8,5 > 6,5
Electrical conductivity	CE	$\mu\text{S}/\text{cm}$	ISO 7888-1985	2700
Temperature	T	$^{\circ}\text{C}$	ISO 7888-1985	
Biological Oxygen demand	BOD	$\text{mg O}_2/\text{l}$	DIN 38409T51	5
Chemical Oxygen demand	COD	$\text{mg O}_2/\text{l}$	ISO 6060-1989	
Total Nitrogen Kjeldhal	NTK	$\text{mg (N)}/\text{l}$	ISO 5663-1984	
Nitrite ion	NO_2^-	mg/l	ISO 6777-1984	0.50
Nitrate ion	NO_3^-	mg/l	DIN 38405-D9-2	50
Ortho-Phosphate	PO_4	mg/l	ISO 6878/1-1986	-
Total phosphorus	P_{total}	mg/l	ISO 6878/1-1986	-
Chloride ion	Cl^-	mg/l	DIN 38405-D1-1	750
Sulfate ion	SO_4^{2-}	mg/l	NF T90-040 (néphéométrique)	400
Ammonium ion	NH_4^+	mg/l	ISO/DIS 7150	0.5
Turbidity NTU	Tur	NTU	ISO 7027	5
Alkalimetric title	AT	$\text{mg CaCO}_3/\text{l}$		-
Full alkalimetric title	TAC	$\text{mg CaCO}_3/\text{l}$	(ISO 9963-1 (1996)	-
Total hardness	TH	fH°	NF T 90-003	-
Calcium ion	Ca^{2+}		ISO 6059:1984	-
Magnesium ion	Mg^{2+}	mg/l		-
Sodium ion	Na^+		ICP-AES :	-
Arsenic	As		Spectrométrie d'Emission Atomique	10
Cadmium	Cd		(avec plasma couplé par induction)	3
Chromium	Cr			50
Manganese	Mn	$\mu\text{g}/\text{l}$		500
Nickel	Ni			20
Lead	Pb			10

RESULTS

Hydrochemistry of groundwater

The different physicochemical parameters of groundwater have been measured and analyzed statistically and are subsequently compared to Moroccan standards : Norme

Marocaine : NM 03.7.001 (2006) in terms of the quality of water intended for human consumption. These results are reported in (Tab. 3).

The pH of the wet season varies between 6.84 and 7.96 while that of the dry season varies between 6.8 and 8.05. The obtained pH values are fairly close to neutrality with a

Table 3. Descriptive statistics for wet and dry seasons 2017(CE: $\mu\text{s}/\text{cm}$; Turb: NTU; TH: $^{\circ}\text{F}$; ETM: $\mu\text{g}/\text{l}$, the rest of the parameters mg/l).

Wet season				Dry season			
Variable	Minimum	Maximum	Average	Variable	Minimum	Maximum	Average
pH	6.84	7.96	7.25	pH	6.80	8.05	7.25
T $^{\circ}\text{C}$	20.00	37.40	22.22	T $^{\circ}\text{C}$	20.70	37.10	22.79
CE	610	8250	2174	CE	640	7510	2100
O $_2$	3.84	13.29	9.67	O $_2$	1.50	9.25	5.88
Turb	0.04	33.24	3.35	Turb	0.06	578.00	35.92
BOD	1.00	7.00	3.15	BOD	1.00	9.00	3.23
COD	1.00	38.40	10.07	COD	1.00	153.6	17.37
NTK	0.42	74.49	12.53	NTK	2,37	112.56	30.23
NH $_4^+$	0.02	97.00	5.49	NH $_4^+$	0.01	91.37	4.67
NO $_2^-$	0.14	1.09	0.54	NO $_2^-$	0.02	1.79	0.22
NO $_3^-$	1.43	98.50	17.49	NO $_3^-$	6.10	446.00	60.77
PO $_4^{3-}$	0.29	0.97	0.66	PO $_4^{3-}$	0.88	1.14	1.01
P $_{\text{total}}$	0.9	1.2	1.05	P $_{\text{total}}$	0.06	1.34	0.39
Cl $^-$	85.08	2368.06	597.33	Cl $^-$	70.90	2141.18	449.1
SO $_4^{2-}$	51.00	510.00	121.3	SO $_4^{2-}$	17.00	355.00	72.8
HCO $_3^-$	91.00	627	265.65	HCO $_3^-$	50.00	250.00	127
TH	16.00	208.00	60.7	TH	20.00	204.00	61.2
Ca $^{2+}$	49.70	400.78	170.81	Ca $^{2+}$	56.11	649.26	178.3
Mg $^{2+}$	13.00	330.00	66.6	Mg $^{2+}$	5.00	234.00	46.07
Na $^+$	48.00	686.00	182.1	Na $^+$	0.04	689.99	210.0
K $^+$	1.200	135.00	20.76	K $^+$	0.10	124.19	14.74
As	<DL	221.00	81.10	As	<DL	130.00	6.50
Cd	27.00	59.00	44.90	Cd	<DL	20.00	7.00
Cr	<DL	4.00	1.80	Cr	20.000	40.00	22.00
Mn	<DL	514.00	47.25	Mn	<DL	720.00	99.00
Ni	<DL	<DL	<DL	Ni	<DL	20.00	2.00
Pb	13.00	48.00	32.80	Pb	<DL	280.00	117.50

slight tendency towards basicity. These values comply with the Moroccan standard (NM 2006) for the quality of water intended for human consumption. With regard to dissolved Oxygen, the values obtained are very heterogeneous and the respective average levels recorded during the wet and dry seasons are 9.67 mg/l and 5.88 mg/l . Indeed, the lowest content is obtained during the dry season at the P5 well which is of the order of 1.5 mg/l while the maximum value is 13.3 mg/l recorded in the well P21 during the wet season. It is noted that only 28% of the wells explored comply with the Moroccan standard. The water temperatures of the studied wells are homogeneous, the averages displayed for the sampling campaigns, in wet and dry weather, are of the order of 22 $^{\circ}\text{C}$. Nevertheless, well P14 records the highest

temperature values of about 37 $^{\circ}\text{C}$, for both wet and dry seasons. These high temperature values are probably due to the influence of the close proximity of said CEV, especially since vapors emanate from this well probably caused by this rise in temperature. For the turbidity of the studied wells, the average values obtained are 3.35 NTU and 35.92 NTU respectively during the wet and dry seasons. In fact, the high levels of particulate matter are detected in the P14 well with maximum concentrations of 33.24 and 578 NTU respectively in wet and dry season. This particular well (P14) is located about ten meters, in the vicinity of the CEV just below the locker and which can be considered as the most impacted by the CEV as well as by road traffic (trucks and skips). It should be noted that 60% and 75% of the analyzed wells in this study

comply with the standard recommended respectively in wet and dry season. In addition, the values of the Biochemical Oxygen Demand (BOD) range from 1 to 7 mg (O₂)/l and from 1 to 9 mg (O₂)/l in wet and dry periods respectively, which correspond to average concentrations of 3.15 and 3.23 mg (O₂)/l. The highest BOD values for both wet and dry seasons are detected in samples taken from P14 and P16 wells. While the chemical Oxygen demand (COD) values range from 1 to 38 mg (O₂)/l and from 1 to 153 mg (O₂)/l with respective averages of 10.07 mg (O₂)/l and 17.37 mg (O₂)/l respectively in wet and dry periods, and the highest levels are detected in wells P14, P15 and P18. Note that the COD/BOD ratio is 5.5 for the P14 well in winter and this quadruple value in summer, which confirms that the origin of this non-biodegradable pollution and probably due to contamination by leachate infiltration of the CEV, whereas for the P16 well, it seems that the contamination is more accentuated in the winter rainy season.

The burial of moisture-rich solid waste under anaerobic conditions contributes to the fermentation of organic materials that percolate in the shallow aquifer (Morarech *et al.* 2015) and contaminate groundwater nearby. Kjeldhal Nitrogen (NTK) and ammonium ions (NH₄⁺) have mean values of 12.53 and 5.49 mg/l respectively in the wet period and 30.23 and 4.67 mg/l in the dry period. Well P14 records the highest NTK value in wet season which is 74.5 mg/l. While the P9 and P14 wells have the highest respective values in the dry season which are of the order of 112.5 and 110.3 mg/l. Well P14 has NH₄⁺ contents of 97 mg/l and 91.37 mg/l in wet and dry periods respectively. All these results show that 10% of the wells studied do not comply with the standards in force for both campaigns. Concerning nitrates (NO₃⁻) and nitrites (NO₂⁻), the respective average levels are 17.49 and 0.54 mg/l in wet period and 60.77 mg/l and 0.22 mg/l in period dried. The P15 well records the highest levels of NO₃⁻ and NO₂⁻ at 98.5 and 1.09 mg/l, respectively, in the wet period, while exceeding the standard in force. However, in the dry period the wells P10, P11, P15 and P20 record values that exceed the Moroccan standard (50 mg/l for NO₃⁻); while the P14 well exceeds the norm for NO₂⁻.

For the contents of phosphates (Ptotal) and ortho-phosphates (PO₄³⁻), they have mean concentrations of 1.05 and 0.66 mg/l respectively in the wet period and 0.39 mg/l and 1.01 mg/l in dry season. In the wet period, the P4 well has the highest Ptotal content of 1.2 mg/l and the P4 and P9 wells have PO₄³⁻ contents of 0.97 and 0.73 mg/l respectively. However, in the dry period, the P4 and P9 wells record respective P_{total}/PO₄³⁻ values of (1.34 and 1.4 mg/l) and (0.88 and 0.88 mg/l). The total hardness has an average value of 60.7 °fH in humid period and 61.2 °fH in dry period. These waters are very charged with Calcium and Magnesium ions, which classifies them in the category of "very hard water". The average conductivity measured during the wet seasons is 2174 µS/cm whereas it is 2100 µS/cm in the dry period, the maximum values recorded are 8250 and 7510 µS/cm obtained at the level of the P18 well, respectively during wet and dry periods. For wells P1, P14, P15, P16 and P18 the values of the conductivities exceed the recommended standard (≥ 2700 µS/cm). This strong mineralization is also linked to the presence of other elements; especially:

- Chlorides with averages of 597.33 and 449,13 mg/l for the wet and dry periods, respectively, the majority of the studied wells 75 % remains in conformity with the standard (750 mg/l) except well water P1, P14, P15, P17 and P18 taken

during the wet period and the wells P1 and P18 in the dry period, however 67 % of the well water analyzed exceeded the French standard (NF) (250 mg/l). Sodium with respective averages of 182.1 and 210.0 mg/l for the wet and dry seasons, wells P1, P4, P14, P15, P19 and P20 show contents that exceed the NF (200 mg/l) in the wet period while the wells P1, P4, P14, P15, P16, P17 and P20 exceed it in the dry period.

- Alkalinity (HCO₃⁻) with respective averages of 265.65 and 127.0 mg/l in the wet and dry season, all the wells analyzed have significant levels.

It should be noted that the results of the analyzes carried out on the waters of well P3 are not taken into account in the statistical analysis nor hydro-chemical because it is an abandoned well filled with waste and birds excrements and its study remains a case apart.

With regard to heavy metals, the arsenic content in wet season varies between a value below the limit of detection and 221 µg/l with an average of 81 µg/l and a maximum concentration at the P14 well located just a few steps away from the CEV. However, during the dry season, the Arsenic is present at the P14 well at a concentration of 130 µg/l. The arsenic content repaired in the analyzed waters exceed the Moroccan and WHO standard which is of 10 µg/l during the two seasons.

The average concentration of cadmium varies between 7 and 44.90 µg/l respectively in wet and dry season. In fact, the majority of wells are cadmium-free in the dry period except for wells P5, P8, P11, P17, P18, P19 and P20 which have a concentration of 20 µg/l, thus exceeding the recommended standard. However, the P12 well records the maximum cadmium content (59 µg/l) in the wet season with all wells exceeding the recommended standard. During the wet period the average Manganese varies between a value below the limit of detection and 47.25 µg/l in the wet season while in the dry season the Manganese varies between a value below the limit of detection and 99 µg/l. Manganese is present only in wells P14, P15, P16 during the wet season but it is present in all wells in the dry season. The maximum manganese content recorded at well P14 is 514 and 720 µg/l respectively in wet and dry periods. The P14 well is the only one that exceeds the standard in force during both periods. All wells waters analyzed record a chromium concentration lower than the recommended standard 50 µg/l for both wet and dry periods. Otherwise, all the analyzed waters are free of Nickel in the dry season while in the wet season only the P14 and P20 wells register a concentration of 20 µg/l which coincides with to the maximum value allowed by the Moroccan and WHO standard. The average concentration of lead is 32.80 and 117.50 µg/l respectively in wet and dry season. In the wet and dry seasons, the maximum level respective recorded is 48 µg/l at the P11 well and 280 µg/l at P17 well, with an exceedance of the recommended standard of 10 µg/l for all the waters analyzed.

Statistical analysis

All the results obtained in this study were analyzed statistically using the Principal Component Analysis (PCA) via the XLstat software (Addinsoft 2016)

Correlation between variables for the two realized campaigns

The correlation coefficient between variables is commonly used to estimate the relationship between two variables. Examination of the correlation matrix allowed to establish some significant correlations between the different elements during the two sampling campaigns.

The correlation matrix of the wet season highlights different links and correlations existing between the studied parameters. Very significant positive correlations in this matrix are observed between electrical conductivity, Chlorides and Calcium ions, hydrotimetric titer and Magnesium ion and a lower correlation with Potassium ion, all negatively correlated with lead, which reflects the participation of these elements in the acquisition of saline load of water. Moreover, other positive and strong correlations are observed between turbidity, temperature, COD, NTK, NH_4^+ , Potassium ion, bicarbonates, Arsenic, Manganese and less correlation with BOD. This group is negatively correlated with dissolved Oxygen. It should also be noted that nitrates, nitrites, COD and Calcium ion are positively correlated. Potassium ion is positively correlated with temperature, COD, NTK and NH_4^+ , all negatively correlated with dissolved Oxygen. Likewise, it should be noted that Cadmium and Chromium show no correlation.

As for the correlation matrix of the dry period, it displays very significant positive correlations between the electrical conductivity and the chlorides, the Calcium ion, the hydrotimetric titer, the Magnesium ion already existing in humid period in addition to the sulphates, Sodium ion and COD. Furthermore, there is a very significant positive correlation between turbidity, NH_4^+ , NO_3^- , temperature, Arsenic, Manganese, K^+ and significant correlation with NTK and Nickel. In addition, there is a very significant positive correlation between nitrites, Potassium and Ammonium ions, temperature, turbidity, Arsenic, Manganese and Nickel. However, chromium is correlated with nickel whereas Lead is significantly correlated with nitrate ion. It emerges from these correlation values that the groups of correlated variables have a common origin. They evolve in the same direction and are produced by identical phenomena.

Principal Component Analysis (PCA)

In order to evaluate the impact of the Oum Azza landfill and waste recovery center on groundwater, a Principal Component Analysis (PCA) supported with the correlation matrix, was performed on a data matrix formed by the results obtained from during the two campaigns carried out in 2017. This analysis makes it possible to highlight the different trends, possible correlation and to have an idea on the hydrochemical behavior and the points having undergone possible contaminations.

Principal component analysis (PCA), is a statistical method descriptive multidimensional, a powerful identification tool, which is mainly used in important research fields. Indeed, the use of PCA for the interpretation of the data seems an interesting solution for a better understanding of water quality as in our case (El Morhit *et al.* 2008). PCA generates new variables by linear combination of original data. The principal components (F_x) are orthogonal and uncorrelated variables obtained by applying the actual variables, consequently the axis F_x can be visualized graphically and offer information for the majority of significant variables after the reduction in dimensionality of the data without loss of the actual information (Giri & Singh 2014).

1. Wet period

For the Wet period the projection of individuals on factorial F1-F2 and F1-F3 maps represents 67.74 % of total inertia. The PCA determines the individualization of the groups corresponding to the different qualities of water.

The most important factor (F1), explaining 32.29 % of the total variance, had high loading values with organic matter, nitrogenous matter, turbidity, Potassium ion, bicarbonates,

Arsenic and Manganese. It is defined as pollution axis negatively correlated with dissolved Oxygen. The second most important factor (F2), explaining 20.09 % of the total variance, had high positive correlation coefficients with the electrical conductivity, the Chlorides, the Calcium and Magnesium ions, and the hardness all correlate negatively with Lead defining the mineralization of the waters studied. Similarly, factor F3, explaining 10.36 % of the total variance, had a strong relationship with nitrites and nitrates indicating a certain anthropic activity. It can be seen that the dominance of the organic pollution represented by the F1 axis in the wet period can be explained by the possible contamination by a direct contact of the groundwater with the leachates, due to a rise of the phreatic level or its overflowing storage tanks or rejection in the natural environment following the heavy rains according to what residents report.

In the space of individuals, three main groups are identified (Fig. 3): Group 1: it contains the majority of wells. This group located at the intersection of axis F1 and F2 is characterized by a low to medium mineralization and well P14 located at the end of axis F1 because of a pronounced pollution in organic and nitrogenous matter, in particular NTK and NH_4^+ and metallic elements in particular Arsenic and Manganese. Group 2: characterized by strong mineralization, particularly the P1, and P18 wells. Group 3: located on the positive side of the F3 axis, it contains the wells P4 and P15 which are characterized by a pollution of the nitrous nitrogen and the phosphatic -matter

2. Dry period

For the dry period the projection of individuals on factorial F1-F2 and F1-F3 maps represents 66.15 % of total inertia. The most important factor (F1), explaining 31.31 % of the total variance. The F1 axis is defined by pollution parameters, it is very significantly correlated with turbidity, temperature, Ammonium and Potassium ions, nitrites, COD and metallic elements in particular Arsenic, Manganese and Nickel.

The F2 axis explaining 24.73 % of the total variance, is considered to be an axis of mineralization is closely correlated with Chlorides, Calcium, Magnesium and Sodium ions, hydrotimetric titer, and COD which is negatively correlated with dissolved Oxygen. The strong correlation between Chloride and Sodium ions could be related to the dissolution of halite (Appelo & Postma 2005), which is considered to be a major process contributing to salinization of groundwater. Similarly, strong correlations between Cl^- and Ca_2^+ (0.86), Cl^- and Na^+ (0.93) and between hardness and Na^+ (0.87) are due to the ion exchange processes between Sodium and Calcium ions while the significant correlation between Sodium and Calcium (0.79) and Magnesium ions (0.73) supports this hypothesis. The strong correlation between Potassium, Ammonium ions and nitrite ion is indicative of human activity. While the F3 axis explaining 10.11 % of the total variance, is correlated positively with total phosphates and BOD and negatively with dissolved Oxygen.

The chemical parameters defining the factorial plane F1-F2 and F1-F3 (Fig. 4) make it possible to distribute the studied wells sampled in the space of the individuals in three groups according to their mineral and organic load.

Group 1: On the F1-F2 plane of the individuals, the majority of the analyzed samples gather in the center, they are characterized by medium to strong mineral and organic pollution, which is attributed to the COD, the matter nitrogen, the Manganese and Arsenic. Indeed, the well P14 located on the extreme negative side of the

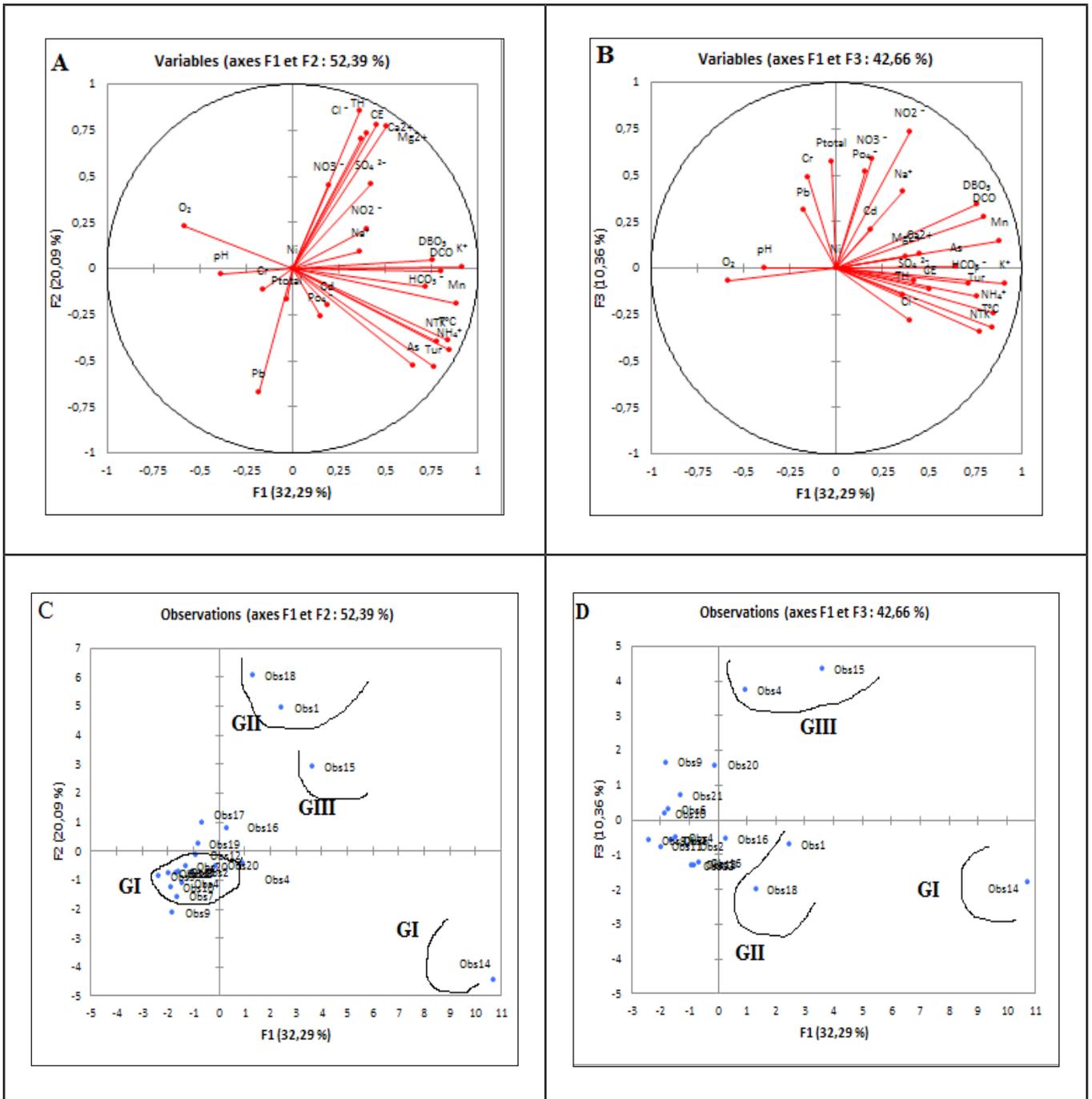


Figure3. Graphical approach according to factorial design F1-F2 and F1-F3 of the groundwater of the Wet campaign. A: Correlation circle of variables F1-F2. B: Correlation circle of variables F1-F3. C: Projection of sampled water points F1-F2. D: Projection of sampled water points F1-F3.

F1 axis is identified by an excessive load of organic and metallic matter mentioned above.

Group 2: located on the positive side of the F2 axis, it encloses the P1 and P18 wells characterized by a strong to very strong mineralization.

Group 3: this group is characterized by a phosphate pollution, it is located on the positive side of the axis F3 is composed of wells P4 and P9, .

The grouping of bicarbonate, Magnesium and Calcium ions along the F2 axis indicates that they have the same origin and mechanism of mineralization. In fact, the bicarbonate, Magnesium and Calcium ions appear in the water after a stay and prolonged contact with the surrounding rocks.

Hydro geochemistry

The hydro geochemical study makes it possible to determine the chemical facies of the water of the sampled wells. The Piper diagram was established to know the impact

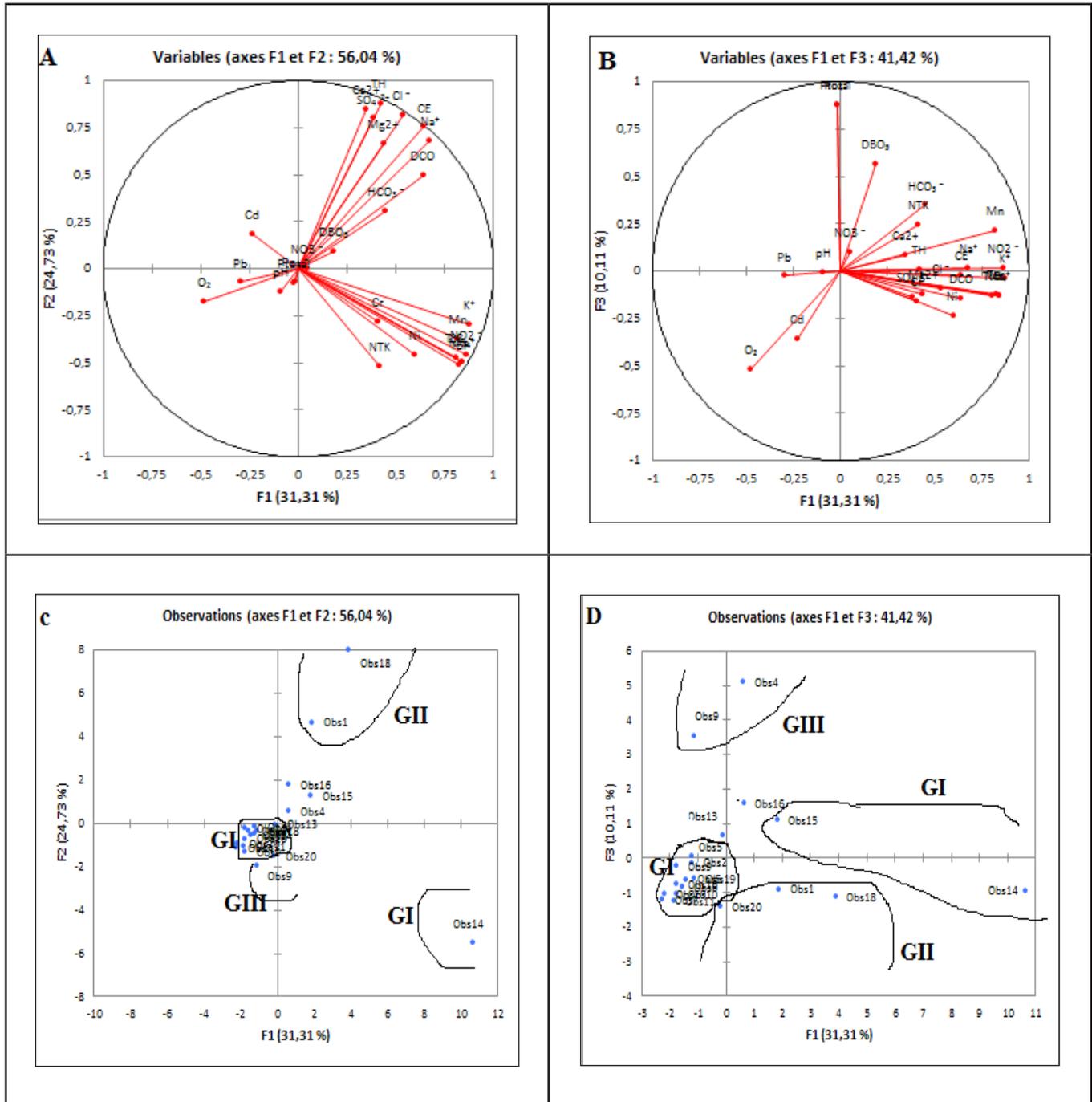


Figure 4. Graphical approach according to factorial design F1-F2 and F1-F3 of the groundwater of the dry season A: Correlation circle of variables F1-F2 B: Correlation circle of variables F1-F3. C: Projection of sampled water points F1-F2. D: Projection of sampled water points F1-F3.

of geology on water quality and also to illustrate the evolution of chemical facies aquifers

- For the Piper diagram in the wet season (2017) there are three facies, the most dominant is that of calcium and magnesium chloride. The sodium-potassium chloride facies characterizes the P19, P12, P14 and P8 wells and that of the sodium bicarbonate characterizes the P20 well (Fig. 5).

- For the Piper diagram in the dry season (2017), two facies are distinguished, the dominant one being calcium - magnesium chloride. Chloride - sodium and potassium facies characterize wells P19, P12, P14, P20 and P8. From (Fig. 5) it can be seen

that the P20 well changes from sodium bicarbonate facies in the wet period to sodium chlorides in the dry period, which clearly explains the high concentration of chloride ions in the samples analyzed. This indicates that the groundwater composition is unstable and is likely to change as a result of ion exchange reactions (Appelo & Postma 2005).

DISCUSSION

The hydrochemical facies of Oum Azza's groundwater shown in the Piper diagram (Fig. 5) that these facies differ from one sampling campaign to another, so we have a calcium-

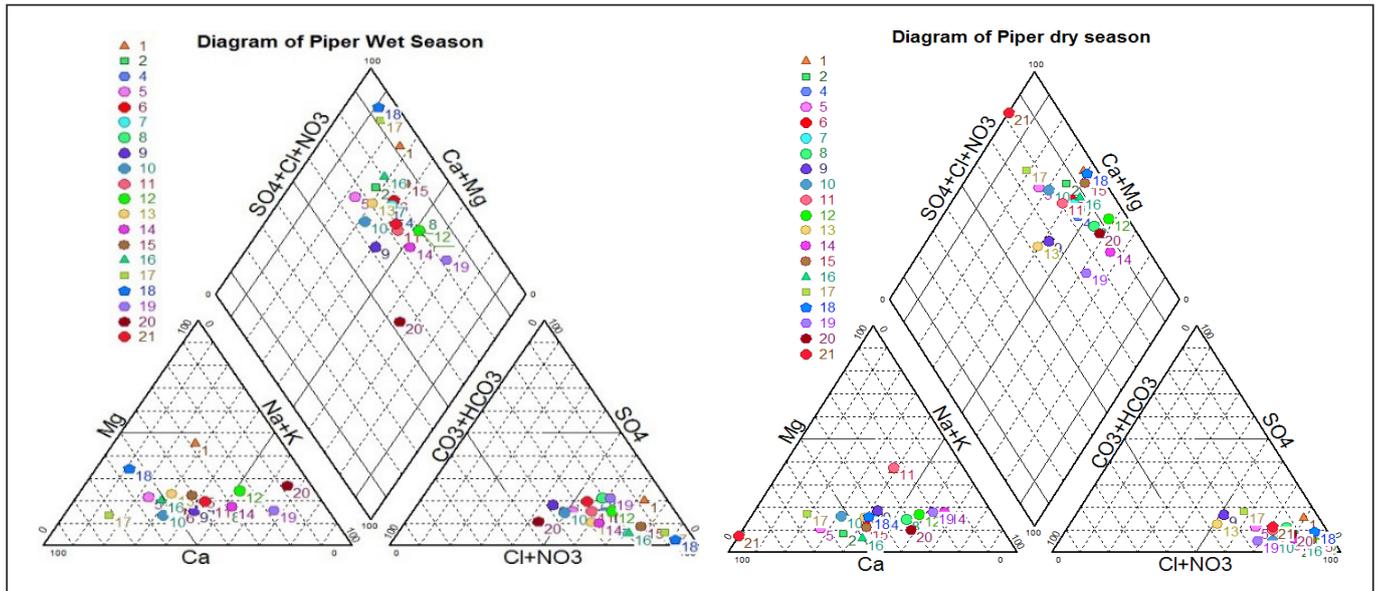


Figure 5. Piper diagram of the wet and dry seasons.

magnesium chloride facies, sodium chloride - potassium and that of sodium bicarbonate.

The dominance of the chlorinated-calcified facies identified is probably related to the geological formations of the study area where calcites, dolomites, and limestone rocks are found. It is also noted that during the two sampling periods, the Ca^{2+} content is higher than the Mg^{2+} content, this is related to the dominance of the calcium chloride facies in the study area. However, the high nitrate levels of well P15 (98 mg/l) during wet period, wells P10 (76 mg/l), P11 (69 mg/l), P15 (446 mg/l), P20 (77 mg/l) and P21 (93 mg/l) in the dry period exceeding the standard in force (50 mg/l) may imply contamination of these wells in particular by the CEV, septic tanks and the use of fertilizers in agriculture (Güler *et al.* 2012). In addition, nitrate has revealed only one correlation with lead during the dry season, which implies contamination by chemical fertilizers, but the existence of lead in almost the majority of the wells during the two seasons argues for other sources of emission, notably road and rail traffic and the atmospheric transport of metallic trace elements, to the extent that several studies have traced it. Moreover, nitrate concentration above 10 mg/l has been shown to have adverse health effects on pregnant women and infants (Groen *et al.* 1988). The presence of nitrite in the wells P15 (1.09 mg/l) during the wet season and in the P14 (1.79 mg/l) in the summer season, all of which are located downstream of the CEV, and which exceed the standard recommended (0.50 mg/l); (NM 2006), has shown a quasi-renewable contamination caused by the infiltration of wastewater and by a lack of Oxygen in the medium (Hakoo 2001); particularly in the dry period, which is confirmed by the low dissolved Oxygen content in the P14 well (3.4 mg/l). The strong correlation between the nitrites and the Ammonium ion (0.96), Potassium ion (0.93), Manganese (0.94), Arsenic (0.96) and Nickel (0.64), in the dry period, indicate that they have a common origin (same source) which can be linked to infiltration of leachates which are in turn rich in Ammonium ion (2030 mg/l), Potassium ion (2430 mg/l), Arsenic (400 $\mu\text{g/l}$) Manganese (1018 $\mu\text{g/l}$) and Nickel (319 $\mu\text{g/l}$). As for the Ammonium ions, Arsenic and Manganese respectively are present in a large quantity at the well P14 during the two periods wet (97 mg/l, 221 $\mu\text{g/l}$ and 514 $\mu\text{g/l}$) and dry (91.37 mg/l, 130 $\mu\text{g/l}$ and 720 $\mu\text{g/l}$). The measured concentrations far exceed the recommended

standard (0.5 mg/l, 10 $\mu\text{g/l}$ and 500 $\mu\text{g/l}$); according (NM 2006), they are certainly at the origin of anthropogenic pollution. Ions such as NH_4^+ , NO_2^- , NO_3^- are considered as indicators of anthropogenic pollution (Jalali 2007, Navarro & Carbonel 2007).

Correlations observed between conductivity and mineral elements could be related to the geological nature of the substrate. Indeed, the Calcium nature ion of the bedrock of our study area justifies it.

However, the existence of a correlation between conductivity and COD during the summer season implies that part of this strong mineralization can be attributed to human activity: wastewater discharges and/or leachate releases discharge (Hakoo 2001, Kattabi 2002). For organic matter, particularly BOD and COD, the high values recorded at the P14 and P15 wells in the wet season and at the P14 and P18 wells in dry season coincide with the low dissolved Oxygen values that are of the order $\approx 3,4$ mg/l. This deficit of dissolved Oxygen is the result of the degradation of organic matter; which subsequently causes the generation of NO_2^- and NH_4^+ (Nicolardot 2000). In addition, the groundwater analyzed in the wet and dry season is very hard, since TH is above 18 $^\circ\text{fH}$ according to the (Durfur & Becker 1964) classification. These high levels are related to the lithological nature of the aquifer formation and in particular to its Magnesium and Calcium ions composition and to the fact that the groundwater studied has a calcareous substrate, which is proved by strong correlations between the hardness and Calcium ion (≈ 0.9) and between hardness and Magnesium ion (≈ 0.8) during the wet and dry period. However, for the groundwater studied during the summer period, the significant correlated values of 0.94 and 0.65, respectively, between hardness and chloride ions and between hardness and COD, suggest that the strong hardness has two probable origins: the nature of the underlying geological matrix (calcite, dolomite) and the anthropogenic impact that seems to be related to the impact of the CEV of the study area.

Considering the relationship between pH and bicarbonates established by the carbon balance, there is a low correlation between pH and bicarbonates during the two sampling campaigns (0.07 wet period) and (0.22 dry period), implies that gaseous exchanges, notably with CO_2 , occur only

slightly in the high concentrations of bicarbonates recorded in the analyzed waters (50 -627mg/l) (Benabbou *et al.* 2014). However, the good correlation of bicarbonates with almost all the indicator elements pollution claims for anthropogenic contamination either by the leachates generated by the CEV of Oum Azza (50 000 mg/l) or by the fertilizers of agricultural activity in the area corroborate with study indicated that high HCO_3^- originates from the degradation and oxidation of organic materials (Huq *et al.* 2019). And, the elevated HCO_3^- plays a key role in hydrochemical evolution and metal mobilization in aquifers. Furthermore, during wet period one raises good affinities of Arsenics with organic materials and with bicarbonate (0.53) as well as Manganese with bicarbonate (0.58), according to Bourg (1988) carbonates can incorporate metallic cations in their crystal lattice. Besides, the existence of a correlation between the organic materials, NTK and HCO_3^- , allows to deduce that elements trapped in the organic materials is due to likely contamination from CEV leachate infiltration. Moreover, the temperature in the presence of organic materials can increase its degradation, which can produce acidic and complexing substances (Lions 2004), which corroborates with our results in particular the good correlation between Arsenics and T°C (0.92) and the BOD and T°C (0.84) and by recording temperatures reaching 37°C at the P14 well during the winter period (EL Bayoudi *et al.* 2019). We also note that Arsenic has a high affinity with Manganese (0.84), which suggests that they have the same origin, in particular CEV leachate. Nickel is significantly correlated to Arsenic (0.69) also to pollution indicator especially NH_4^+ (0.69) and NO_2^- (0.64), in addition, Nickel and chromium (0.85) are strongly correlated too, which allows to deduce that their origin is anthropogenic. In the case of Cadmium, no correlation is observed for both periods of analysis, hence its exogenous origin.

CONCLUSION

At the end of this study, several important results have been obtained, the ground waters of the Oum Azza zone being prospected are characterized by a hardness and pronounced alkalinity that exceed the Moroccan norms. The quality of the groundwater studied is dependent on a preponderant mineralization gradient that persists from the period of precipitation in winter to the dry period in summer and are characterized by the dominance of sodium chloride facies probably due to the geological formation of the study area. Moreover, this study, based on physicochemical and PCA analyzes, shows that pollution in summer is more pronounced than in winter, probably because of the phenomenon of evaporation. The analyzed waters recovered downstream of the CEV are the most contaminated and this phenomenon is even more accentuated in the summer period compared to the winter period, in particular the waters of the P14 well which are loaded with various organic and inorganic pollutants (NTK, NH_4^+ and NO_2^- , COD, Mn, As, Cd, Pb ...) whereas the P15 well indicates pollution mainly of the nitrous nitrogen type and the P4 and P9 wells indicate a phosphate type pollution. Pollution could be attributed to poor well hygiene and to the impact of the landfill and waste recovery center CEV. These excessively loaded water in organic matter and in particular micropollutant minerals exceeding the standards in force, at certain points, could involve great health risks to residents, hence the need to treat and continuously monitor the groundwater in this area. It should be noted that other work on heavy metals and on bacteriological analysis have been carried out and their interpretations are in progress in order to detect other possible metal and/or bacteriological

pollution. However, a systematic follow-up of the evolutions of the water quality during all the seasons of the year is indispensable on the one hand and we plan to carry out an isotopic study of the groundwater of the region in order to understand the hydrological and geochemical mechanism and behaviors, of the aquifer on the other hand.

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