Comparative Study of Groundwater Pollution of M'nasra and Sfafaa zones (Gharb, Morocco) by Nitrates

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Abstract. The quality of water resources in Morocco is degraded by pollution from agriculture, industry and urbanization. In this work we have realized a comparative study of two groundwater pollution zones: M'nasra (Kenitra) and Sfafaa (Sidi Slimane). In general, the results of this study showed that most water wells are strongly mineralized as the conductivity far exceeds the standard of drinking water. Sodium chloride (NaCl) concentration is between 33.9 and 1184.6 mg / l and shows some of the wells are loaded with salts. The pH is generally basic in all wells. Pollution by nitrates two regions showed that the ground water is strongly affected M'nasra zone terms of the permeability of the soil of the city. The concentration of nitrate can reach high values compared to the results obtained on the ground water at Sfafaa zone whose nitrate concentrations around 20 mg/l. Further pollution of groundwater in the two regions of the shows values of organic matters that go far beyond the standards of drinking.

1 Introduction

Groundwater contamination by nitrates (NO₃) represents a massive environmental problem. From today, NO₃ is the most ubiquitous groundwater contaminant in the world and agricultural activities are mainly blamed for these problems. Groundwater is a strategic water source for human activities. In addition to being often of large volumes, they generally provide better quality water than surface water. These waters constitute 23% of the planet's freshwater resources [1] which must be conserved and protected from all kinds of pollution.

In fact, the natural levels of nitrates in groundwater are generally very low (typically less than 10 mg/l), but their concentrations increase with human activity such as agriculture (nitrogen fertilizers), domestic effluents, leachates from landfills, etc. This increase is the main cause of degradation of groundwater quality and mainly of more vulnerable water tables.

In general, nitrates move relatively slowly in soil and groundwater: there is a lag time of approximately 20 years between pollution activity and detecting the pollutant in groundwater. For this reason, it is anticipated that routine pollution activities will continue to affect nitrate concentrations for several decades. However, if the pressure in the aquifer is high, transport can be very fast in the saturation zone.

In the Gharb region of Morocco, nitrate concentration in some wells reach 130 mg/l due to intensive agricultural practices [2]. Vulnerable aquifers are frequently located in zones of high water demand, such as coastal areas (Algeria, Italy, France, Morocco, Tunisia, etc). Besides, irrigated farming accounts for a large share of total water withdrawals: 83% in Greece, 68% in Spain, 57% in Italy, and 52% in Portugal [3]. The drip irrigation system is more and more encouraged by the Moroccan government via 80% of subvention. The mismanagement of irrigation can result in water misuse and also in strong negative impacts on the environment, such as nitrate pollution and eutrophication.

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The objective of this work is to evaluate and compare the groundwater pollution of two zones of M'nasra and Sfafaa (plain of Gharb) by nitrates. This study will subsequently raise the awareness of leaders to implement a plan of action to minimize the vulnerability of groundwater in Morocco.

Description of the study area

Geographic location

The surface area of the Gharb region is 600 Km². The region of M'nasra is dominated by sandy and clayey soils. The climate is Mediterranean with annual precipitations ranging between 480 and 600 mm, and the average temperature is 27°C in summer and 13°C in winter (Office Régional de Mise en Valeur Agricole du Gharb, 2017). Eighteen water samples were collected from 18 wells (less than 50 m depth) installed in 19 sites located on the coastal zone of M'nasra in Gharb region, Northwest of Morocco (Figure. 1). The levy has been carried out in the periods the summer during 2017.

The Sfafaa zone belongs to the Province of Sidi Slimane, located around the geographic coordinates 34° 15′0″ and 6° 9′36″. It is limited to the North by the Province of Sidi Kacem, in the South-east by the rural commune of Boumaiz (Province of Sidi Slimane), and to the West by the rural commune of Kecybia (Province of Sidi Slimane). The zone of Sfafaa extends over approximately 197km². The samples of water wells were collected during the summer2014. The mean

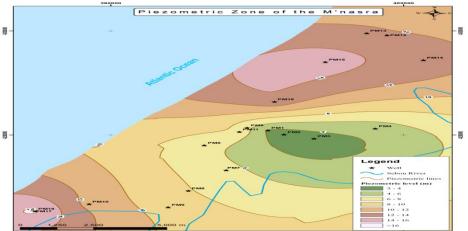
Water samples were collected in 11 clean plastic bottles and stored in the freezer (-10°C) until their analysis.

Geology

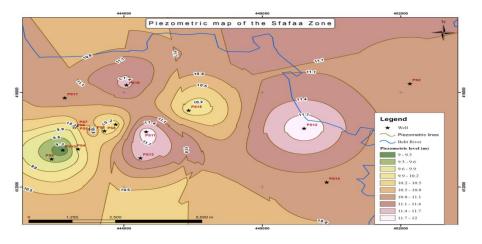
Concerning the pedo-landscape, our study zone is a part of the Vertisol domain of the Gharb region, with alluvial deposits from the Quaternary, mainly of the Late Pleistocene and Holocene.

In general, the Gharb plain is a depression between two major structural domains: the Primary Meseta to the South and the Rif mountains to the North and the East. This plain is mainly marked by geological subsidence of the Middle and Late Miocene. The Gharb load is contemporary to the Rif mountains uprising, which caused enormous landslides. The East of the Gharb plain, corresponding to our area of study, is an accumulation zone of Quaternary continental sediments, alternately coarse (cobble and gravel) and fine (silts and clays), following climate cycles. The distribution of these deposits is very heterogeneous both laterally and vertically.

annual precipitation of 386.4 mm. We have prospected 17 wells, belonging to the Sfafaa zone.



(a) Piezometric map of the M'nasra zone.



(b) Piezometric map of the Sfafaa zone.

Fig. 1. Piezometric maps of the two regions chosen for the study.

The main crops groun in the study area are field crops, vegetable crops (potatoes, tomatoes, etc) wheat etc (M'nasra and Sfafaa).

Table 1 summarizes the main crops and fertilizer doses applied at the national level [4].

Table 1. Applied Fertilizer Doses for Main Crops

Crops	Area (Ha)	Quantity of fertilizer (Kg/Ha)			Frequency	Total fertilizer quantity (Tonne)		
		N	P2O5	K2O	(%) *	N	P2O5	K2O
IRRIGATED	33.423					5.853,82	2.949,87	3.274,3
* Sugar Crops	7.400							
+ Sugar Cane	5.200	175-200	55	35-102	100	910-1.040	286	182-530,5
+ Sugar Beet	2.200	155	126	63	-	341	277,2	138,6
* Cereals	5.556	67-97	42-56	21-28	-	372,2-539	233,4-311,1	116,6-155,7
* Vegetable	8.265							
+ Industrial tomato	1.417	153-400	200-250	288-440	100	216,8-556,8	283,4-396,7	428-623,5
+Potato	2.719	296-600	50-255	110-350	-	805-1.631,4	136-693,3	293-951,6
+ Strawberry	1.624	160-400	100-140	70-155	-	259,8-641,6	162,4-227,4	113,7-251,7
+Melon -Watermelon	1.650	60	28	14	-	99	46,2	23
+ Niora	8.55	130-160	114-225	180-220	-	111,2-138,8	97,5-192,4	153,9-188,1
*Peanut	10.283	115-180	0-80	0-85	-	1.263,1-1.977,1	878,7	933,6
* Citrus	1.919	54-132	45-54	94-96	-	103,6-253,3	86,35-103,6	180,4-184,2
RAINFED	99.252					3.227,4	1.841,64	907,24
* Sugar Crops	2.075	155	126	63	100	321,6	261,45	130,72
* Cereals	59.067	60-67	28-42	14-21	60	2.126,4-2.374,5	992,3-1.488,5	496,2-744,2
* Leguminous	7.744	14	28	14	10	10,85	21,7	10,85
* Forages	9.376	60	28	14	30	168	78,4	39,2
* Vegetable (Melon)	6.092	60	28	14	60	219,3	102,34	51,17
* Sunflower	6.847	60	28	14	60	246	114,8	57,4
* Olive tree	8.051	14	28	14	10	11,2	22,54	11,2
Total Area	132.675					9.131,22	4.791,51	4.181,54

(%)*: Frequency of use by farmers.

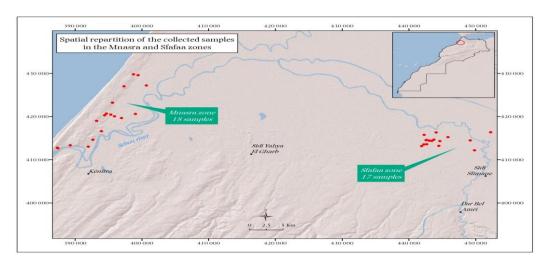
2 Material and Methods

2.1 Characteristics of groundwater sampling points

The present study is conducted on a network of 35 stations spread over two regions in the Gharb Plain M'nasra (Kenitra) and Sfafaa (Sidi slimane) (Figure 2). The stations were chosen according to their representativity in relation to the urban perimeter of the two cities, agricultural zones (M'nasra and Sfafaa) and their proximity to the sources of pollution (industrial zones or Ouled Berjal waste discharge). The geographical distribution is as follows:

- -PM1, PM2, PM3, PM4, PM5, PM6, PM11 and PM16 stations located between the Sebou River and the Atlantic Ocean.
- Stations PM7, PM8, PM9, PM10, PM11, PM17, PM18 located after the public landfills (Ouled Berjal).

- PM12, PM13, PM14 and PM15 stations located in the North East of the M'nasra zone (upstream of Sebou).
- PS1, PS2, PS3, PS4, PS5, PS6, PS7, PS8, PS9, PS10 and PS11 stations located in the center of the Sfafaa zone.
- PS12, PS13 and PS14 stations located upstream of Oued Bhet (Sidi Slimane).
- PS15, PS16 and PS17 stations located downstream of Oued Bhet (Sidi Slimane).



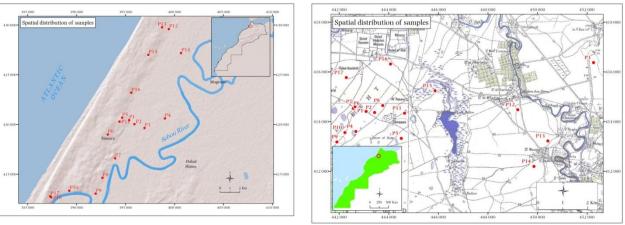


Fig. 2. Map of the M'nasra and Sfafaa zones with the sampling points.

2.2 Sampling and laboratory analysis

The measurement of electrical conductivity (EC) and hydrogen ion concentration (pH) were performed in situ using the Jenway 3510 pH-meter. Chloride (Cl⁻) was measured by the titrimetric method. Nitrates (NO₃⁻) was determined using Jasco V-530 UV/VIS spectrophotometer. Sodium (Na⁺) was determined using the Jenway Clinical PFP 7 flame photometer and oxidizability by KMnO₄. Those measurements were performed according to the AFNOR standards [5].

2.3 Statistical analysis

First of all, a matrix of Pearson correlation coefficients between any two variables was computed and the coefficients were tested for their statistical significance. We then used Principal Component Analysis [6], a multivariate analysis technique that provides an excellent means for gaining useful information from data sets with many variables [7]. In particular, PCA can aid in the compression and classification of data. The purpose is to reduce the dimensionality of a data set by finding a new set of variables, smaller than the original set of variables, which nonetheless retains most of the sample's variance. Success relies on the presence of correlations among at least some of the original variables; otherwise, the number of new variables will be almost the same as the number of original variables. The new variables, called principal components, are uncorrelated, and are ordered by the fraction of the total variance each

retains. The PCA was performed in this study using SPSS 20.

3 Results and discussion

3.1 Parameters Physicochemical

Human activities exercise much polluting pressures on surface water, then deferred to the water table. This deterioration in the quality of certain nitrate wells in the aquifer could be attributed to point and dispersal releases of livestock products and wastewater that has not been previously treated. Certain factors seem to favor this contamination such as the shallow depth, the permeability of the soil, the speed of infiltration, the proximity of public landfills, industrial zones, etc. Deep aquifers indirectly bound to the soil surface are therefore better protected against nitrate leaching, in contrast to shallow aquifers, which are more vulnerable because of their shallow depth which facilitates contact between leached nitrates and groundwater [8]. Contamination of the water table could cause many diseases in the population using groundwater as a source of drinking water. The effects on human health of acute poisoning by nitrates are now known, which is not the case of long-term effects.

The results obtained showed that the pH varies between 7.4 and 8.1 for the aquifer of the M'nasra zone, whereas for the 17 wells in the Sfafaa zone, the pH admits a minimum value of 6.6 and 7.4 as the maximum value. The pH values thus measured for the two zones chosen for the study are safe for the consumer (Figure 3).

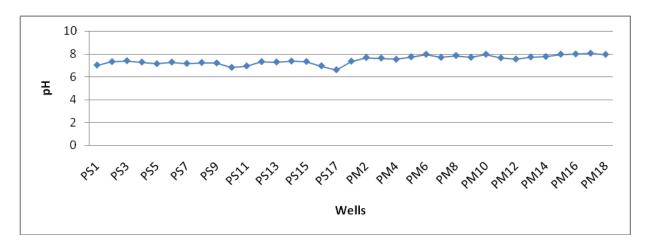


Fig. 3. Variation of pH values.

Electrical conductivity is used to evaluate the rate of mineralization of the environment. The higher the conductivity, the more water is strongly mineralized. The results of this study show that some wells in the Sfafaa zone (PS16, PS15 and PS12) are highly mineralized. The values are

between 370 and 6110 μS / cm. In addition, the groundwater conductivity at the M'nasra zone shows a maximum value of 1269.5 μS / cm. At the Sfafaa zone, well water is mainly used for irrigation in the region. This is accompanied by a high salinity, in particular the PS16 well which has a

concentration of 1184.62 mg / l in NaCl (Figure 4) while the other wells have concentrations varying between 33.93 and 477.95 mg / l. In addition, the salinity for the wells in the M'nasra zone varies between 53.31 and 319.4 mg / l.

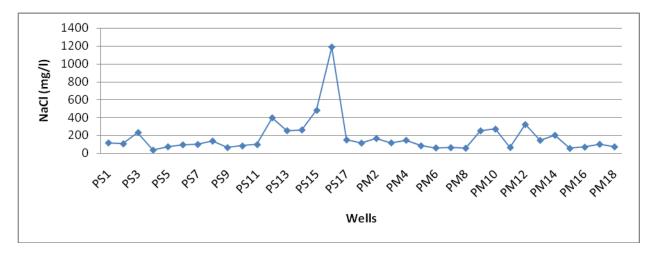


Fig. 4. Variation in the concentration of NaCl.

3.2 Nitrate pollution

Domestic and urban discharges contribute locally to nitrate contamination of aquifers, but fertilization by the application of chemical or organic nitrogen fertilizers and intensive animal husbandry (animal waste) constitute the main cause.

Excess nitrates in soil are driven every year a little deeper, mainly by winter rains. The rate of migration of nitrates to the aquifers is slow, on average 1 to 2 m / year, but varies according to the nature of the subsoil. The excess of nitrogen spread on the surface therefore takes on average 10 to 20 years to reach a water table 20 m deep [9]. On the surface of the soil, organic and mineral elements alter cycles of water, carbon and nitrogen on a global scale. These transformations involve multiple risks to human health, aquatic spaces, biodiversity and agricultural productivity. The challenge for agriculture is therefore to produce more respectfully less using water resources, with respect for biodiversity and greenhouse gas emissions [10].

Nitrates and nitrites are not carcinogenic if they do not exceed WHO standards, but their possible transformation into N-nitroso compounds in water or food before ingestion, or in the body after ingestion, could increase the risk of cancer and fetal malformation (teratogenicity) in humans [10-11]. The results obtained for the nitrate analysis for the two study zones showed that the concentrations for 18 sampling points in the M'nasra vary between 49.6 and 198.4 mg / 1 whereas those detected at the wells of the Sfafaa zone range from 0 to 40.9 mg / 1 (Figure 5).

For the M'nasra zone, it is noted that the wells near the Ouled Berjal landfill and the Kenitra industrial zone are loaded with nitrates with values that go well beyond drinking water standards. However, all the wells in the Sfafaa zone, far from pollution sources, have nitrate concentrations that are below the WHO standard (50 mg / 1) [10].

However, in the highly fissured geological formations, the rains reach the aquifer in a few hours to a few months, this is the case of the M'nasra zone whose soil has cracks, whereas in the less permeable formations it is will take several tens or even hundreds of years.

Nitrogen inputs, if they are higher than plant exports, represent surpluses likely to flow to rivers and aquifers. In 2010, nitrogen surpluses ranged from 5 to 145 kg / ha of utilized agricultural area (UAA), with an average of 32 kg / ha [4]. In addition, it has been shown that the risk of pollution of the Tadla water table is aggravated, for vegetable crops, by the regular application of manure at doses up to 80 T / ha [12]. This shows that the mismanagement of fertilizer products can

contribute to the increase in groundwater pollution and subsequently the infiltration of soluble substances not retained by vegetation: excess cases in relation to its needs. The regions most affected by nitrogen pollution were those of intensive farming with a high load of organic nitrogen due to animal effluents, those of heavily fertilized field crops and those with shallow water resources (basement areas with low permeability basements, alluvial aquifers, karst aquifers) [13].

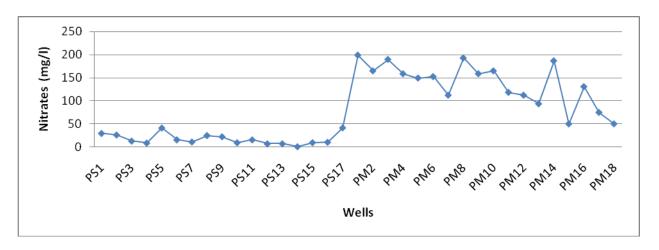


Fig. 5. Variation of nitrate concentration.

Although, the water table in the M'nasra zone has higher levels compared to the Sfafaa zone, the nitrate pollution is high this may be due to contamination by the largely developed industrial activities in the city of Kenitra, but also by leachates from the city's uncontrolled Ouled Berjal landfill[14].

The vulnerability of groundwater depends mainly on the countries and regions because in reality the essential variable to be considered is the renewable resource and, that is to say the volume that recharges the groundwater each year [15]. In addition, the results of the physicochemical analysis in the leachate of several discharges have shown a high contamination of organic salts and heavy metals at Egypt [16]. In addition, it has been shown that in Romania landfills can represent potential sources of pollution for surface water and groundwater [17, 18]. It is for this reason that the development of new disposal areas is of utmost importance. Leachate percolation from landfill waste is a source of pollution of groundwater resources by infiltration, thus constituting a threat as important as that related to the increasing water deficit. The city of Larache landfill is a typical model of deterioration of water resources through a leachate contamination from the landfill and agricultural practices [19].

The results obtained on the pollution of the water table of the city of Taza showed a more or less strong degradation especially downstream of the city discharge [20]. The analysis of ground and surface waters revealed that nitrate ions have a mean concentration of less than 50 mg / 1 with temporal variations of remarkable amplitude (standard suggested by WHO) [14,21].

Organic matter by oxidizability by KMnO₄

This parameter is used to evaluate the organic matter content in the well water. In fact, the organic matter present in the wells varies considerably from one well to another. In the well waters of M'nasra zone, it varies between 2.2 and 10.6 mg/l whereas those in the Sfafaa zone have a minimum of 0 mg/l and a maximum of 9.9 (Figure 6). However, these values show that 57.1% of well water cannot be used as a source of drinking water.

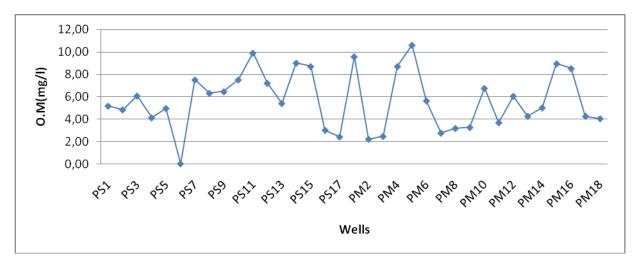


Fig. 6. Variation of Organic Matter.

3.3 Multivariate statistical analysis of physicochemical parameters

Physicochemical parameters (variables) and water points (individuals) were projected separately in the factorial plane (PC1xPC2) of the principal component analysis (PCA) to better understand their representative distributions with respect to the factorial axes. The interpretation of the statistical analysis by the PCA has been done only on two

axes PC1 and PC2 because they alone contain more than 70% of the information. PC1 axis presents 47.8% and the PC2 axis presents 23.4% of the total inertia (Figure 7). The PCA allowed us to characterize 2 groups of chemical elements each corresponding to a set of groundwater samples with the same characteristics.

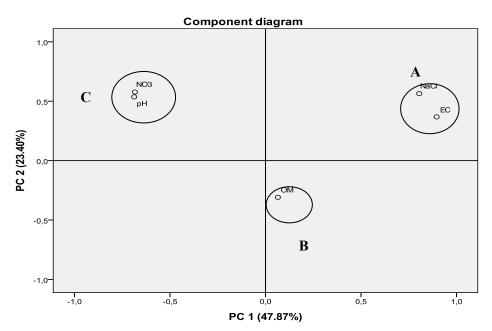


Fig. 7 .Loading plot for the principal component analysis: groundwater properties in the PC1–PC2 plan.

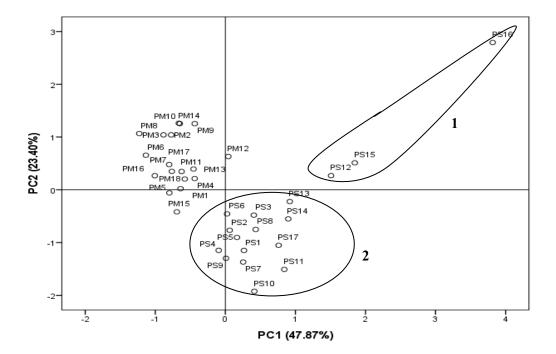
Groups A: This group consists essentially of NaCl and the electrical conductivity (EC) opposed to pH and nitrate along the PC1 axis. These parameters

correspond to the set of wells consisting of PS12, PS15 and PS16 (Group 1) and which has a very

high conductivity and salinity and very low pH, nitrates (Figure 7).

Groups B:

This group is formed by organic matter. It is placed in negative position on the PC2 axis. This setting characterizes the PS1, PS2, PS3, PS4, PS5, PS6, PS7, PS8, PS9, PS10, PS11, PS13, PS14, and PS17 wells (Group 2).



 $\textbf{Fig. 8} \ . \ Score \ plot \ for \ the \ principal \ component \ analysis: \ water \ samples \ in \ the \ PC1-PC2 \ plan.$

4. Conclusion

The results obtained have shown that parameters such as salinity, conductivity, and nitrates far exceed drinking water standards. The concentration of nitrates in the well waters of the M'nasra zone varies around 150 mg / l whereas those detected in the wells of the Sfafaa zone are close to 20 mg / l.

Groundwater in the M'nasra zone is more contaminated with nitrates than Sfafaa. This pollution detected at the level of the wells is mainly due to their situations in relation to the landfill and also in relation to the industry. In addition, the waters of the Sfafaa zone are more saline compared to the waters of M'nasra, especially the PS16 point which is downstream of Oued Beht. To avoid pollution of the water table, it is necessary to strike a balance between the misuse of nitrates sources and the total prohibition of them. With regard to organic matter determined by KMnO₄ oxidability, 57.1% of well water cannot be used as a source of drinking water.

In order to avoid ecological and health problems, it is necessary to take concrete measures to limit the pollution of the Gharb water table (M'nasra) and to protect the health of the population in rural areas.

Based on investigations and analysis, some suggestions for solving the problem, such as best management practices for nitrogen fertiliser and improving environmental awareness, are discussed.

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