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State of nitric pollution of the Mnasra aquifer, Coastal zone of the Gharb plain (Morocco)

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Abstract

Water pollution by nitrate has become increasingly a serious problem in coastal countries. Agricultural activities are probably the most significant anthropogenic sources of nitrate contamination in groundwater. Mnasra is the largest agriculture irrigated zone in the plain of Gharb, well known for its intensive agricultural activities. The excessive use of fertilizers and manure under gravity irrigation system especially for sandy-loam soils similar to those of the area. The present study was the evaluation of nitrate concentration in groundwater, and know the probable origins of this contamination, for this purpose, A physicochemical characterization was carried out following the sampling of 63 wells and 7 boreholes. The results show high concentrations of nitrates, 85% of the wells taken will exceed the potability standard (50 mg / L). The analysis of temporal trends in nitrate concentrations observed over 23 years showed a significant degradation of the water quality of wells between 1993 and 2017 with excessive levels reaching five to six limits the potability limit. This is confirmed by the coarse nature and sandy soil texture that can promote nitrate leaching, the low piezometric level in this region, the type of irrigation and the massive use of soil and fertilizers.

Keywords: *Agricultural pollution, Aquifer, Groundwater, Mnasra, Morocco, Nitrate.*

1. Introduction

On the global scale, nitrate is the chemical pollutant that exhibits the largest distribution in groundwater. Recently, a significant increase in nitrate-nitrogen content has been detected in many aquifers, in particular those in developing countries that underlie intense agricultural production [1, 2, 3]. Te resulting nitrate concentration in groundwater depends on (i) net precipitation and nitrate leaching from land use, (ii) redox conditions and nitrate reduction in the groundwater system [4,5], (iii) hydrogeological conditions and residence time in the groundwater system [6] and (iiii) Poor fertilizer application, surface spreading of animal manure, and improper on-site sanitation systems [7]. Long-term effects of N losses from agricultural land on groundwater nitrate content have been reported from all over the globe [8, 9]. The region of Mnasra is the most agricultural area of the Gharb plain dominated by vegetable and industrial crops. The aquifer is a very productive, easily accessible, and intensively exploited for irrigation by private pumping [10]. The number of wells drilled in the aquifer, exceeding 20,000. The high permeability of the soil and the subsoil and the shallow depth of the aquifer lead to the presence of a large amount of nitric nitrogen, in the soil which is subsequently transmitted by drainage by irrigation water [11]. Multiple efforts have been devoted to improve agricultural practices so nitrogen leaching due to fertilization is minimized [12,13] , to track its movement through the unsaturated zone and its migration beneath the water table [14,15,16], to analyze biogeochemical processes so denitrification rates can be identified and induced aquifer clean-up be subsequently applied to remove nitrate from groundwater [17,18]. Moreover, so these efforts did not take into consideration, using elevated nitrate content in drinking water can commonly cause public health risk and environmental pollution. It acutely causes health effect of methaemoglobinaemia or infantile cyanosis known as “blue baby syndrome”, in which blood lacks the ability to carry adequate oxygen to the individual body cells. In addition, long term exposure to excessive nitrate amount has been found in many literatures to be a risk cancers for older people , esophageal and stomach cancer, diabetes, and thyroid hypertrophy [19, 20, 21].

2. Materials and methods

*2.1**Study area***

The Mnasra region covers an area of 488 km^2 between the city of Kenitra in the south, the Oued Sebou extended by the parallel line passing through Sidi Allal Tazi in the east, Merja Zerga near Moulay Bouselham in the north. The geological building is composed of schists and quartzites, located at a depth of more than 2500 m in the center of the plain. A powerful marl series “blue marls” of up to 2000 m constitutes the impermeable floor of the Gharb aquifer system. From the Peliocen onwards, sedimentation became regressive, consisting of lumachelles, sandstone and conglomerates. On these formations are deposited over a thickness of 200m, Peliocen sediments of marine origin. They are located in the coastal zone and are made up of sands, sandstones and calcareous sandstones, in which thin clayey-silt levels are interspersed. These formations constitute a major aquifer reservoir (Fig. 1). The aquifer system of the Gharb coastal zone can be presented by free aquifer consisting of essentially sand-sandy formations surmounting the "blue marls" [23], stored in the Mio-Pliocene and Quaternary fillings of the Gharb plain, part of which is of fluvial origin ; deposited by the main river in the plain represented by the Sebou wadi [24]. The soil of the region is occupied by heavy soils (vertisols and fluvisols). The sandy soils of the coastal zone cover about 39,000 ha or 15% of the area of the Gharb plain [25]. The climate is Mediterranean with oceanic influence. It receives an average annual rainfall of about 566, 4 mm. The rainfall period extends from October to the end of April, with a maximum for November, December and January. Mean temperatures range from 12°C in winter to 23°C in summer. Potential evaporation exceeds 150 mm during the dry months of June to September and is less than 80 mm during the months of December to February [26].

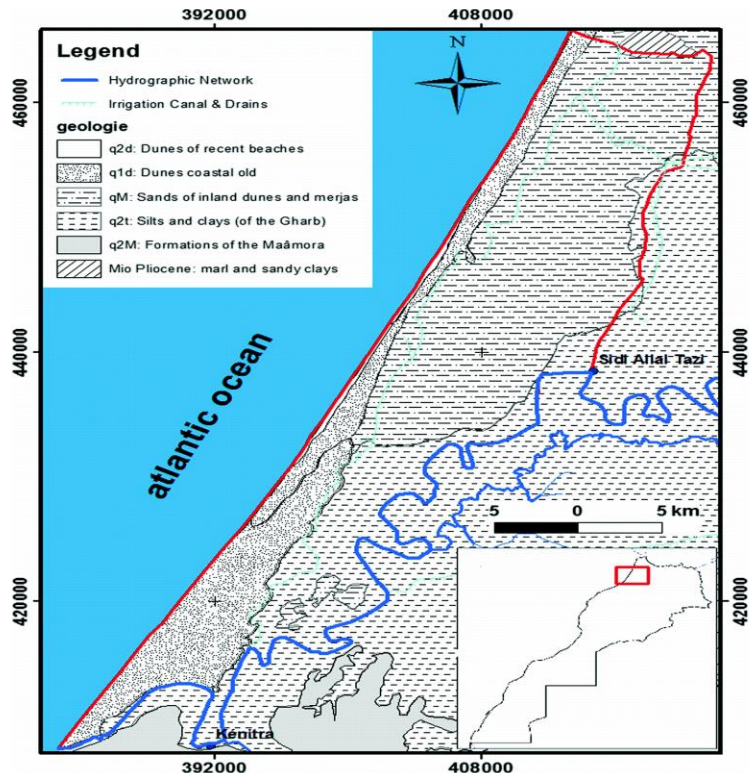

Figure 1. Geological location of the area under study [22]

*2.2**Sampling and analysis***

Field investigation and groundwater sampling were carried out on 63 wells and 7 boreholes. The wells investigated had depths ranging from 10 to 60 m, and were fully screened. The choice of these wells was essentially based on two criteria: the intensification of the crops and the depth of the aquifer. The depth to water table was assumed to be correlated with well depth, and, based on this assumption, wells were classified based on the depth as shallow wells (depth < 20 m), intermediate wells (20 m < depth < 40 m), and deep wells (depth > 40 m). According to personal interviews with well owners, the studied wells were used as drinking water sources on a daily basis, irrigation and animal feeding (Fig.2). The selected well is located in the region of Mnasra adjacent to agricultural lands. It has a maximum and minimum pumping rates of 3350 and 440 m3 /d, over the scenario period. Physical parameters i.e. temperature, pH and electrical conductivity (EC) of the samples have been measured immediately in situ by using the Jenway 3510 pH-meter. Nitrates (NO_3^-) and ammonium (NH_4^+) were determined using Jasco V-530 UV/VIS spectrophotometer. Soil samples are taken from the same areas in a depth of 20 cm where groundwater samples have already been taken. Soil texture component (clay, sand, and silt) percentages were calculated using the Robinson pipette method [27]. Those measurements were performed according to the AFNOR standards [28] and performed in the laboratory of the National Institute of Agronomic Research (INRA), Rabat.

*2.1**Regionalization of results***

The mapping of the physico-chemical parameters was performed using the ArcGIS software (ESRI), version 9.3. The distribution maps were generated using the Inverse Distance Weighting (IDW) interpolation method [29, 30].

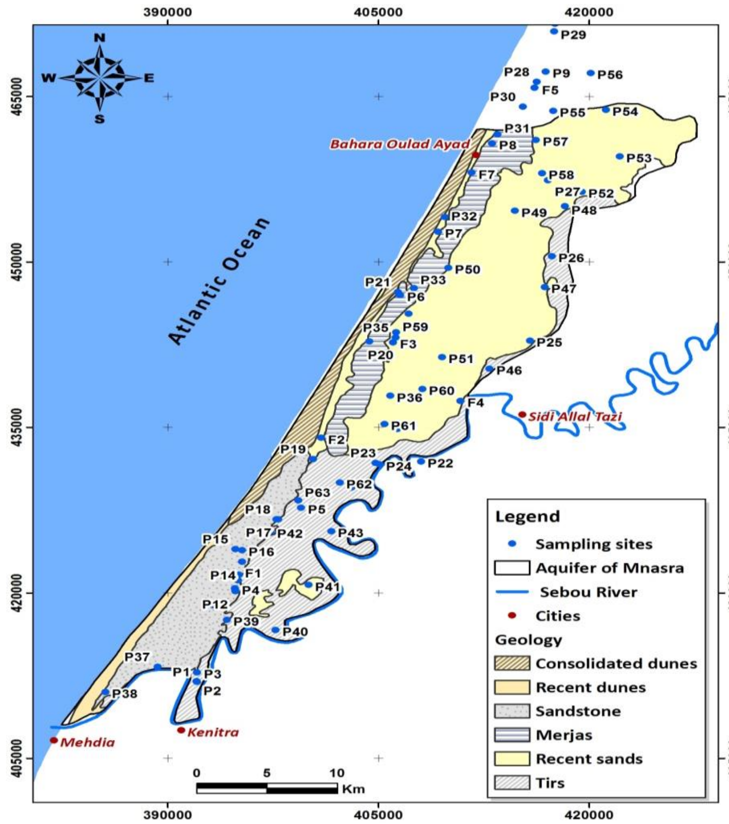

Figure 2. Map of the Mnasra zone with the sampling sites

3. Results and discussions

*3.1**Current situation of nitric pollution of Mnasra***

The results of this study obtained show that the temperature fluctuates between 19 and 25 ° C with an average of 21° C. For pH, the results obtained showed that the values varies between 6, 91(P_{14}) and 8, 65 F_6. These pH values thus measured for the study are safe for the consumer. Electrical conductivity is used to evaluate the rate of mineralization of the environment. The higher the conductivity, the more water is strongly mineralized. The values are between 267µS/cm (P_{15}) and 9870 µS/cm (P_{40}).

Nitrates and nitrites are not carcinogenic if they do not exceed WHO standards. These last stipulate that the nitrate content of drinking water should not exceed the concentration of 50 mg / L [31]. The nitrate and ammonium values found in the groundwater were classified and summarized in Table 1.

Table 1. Simplified grid for assessing the overall quality of groundwater [31]

Quality	parameters			
	Nitrates (mg/L)	% of analyzed wells	Ammonium (mg/L)	% of analyzed wells
Excellent	<5	0	< 0 ,1	0
Good	5-25	7,15	0,1- 0,5	0
Medium	25-50	11,42	0,5-2	2,85
Bad	50-100	32,85	2-8	55,71
Very bad	>100	48,58	> 8	41,44

The distribution of nitrate contents in the Mnasra region is linked to the polluting factors previously mentioned, and in particular to agricultural activity and the lithological nature of the surface layer. Nitrate ions quickly infiltrate and maximum levels are recorded in the North and Northeast part where the water table is very close to the surface (3 to

10 m). The low values are recorded at the level of the dune cord where the water table is fairly deep (30 to 50 m) (Fig. 3).

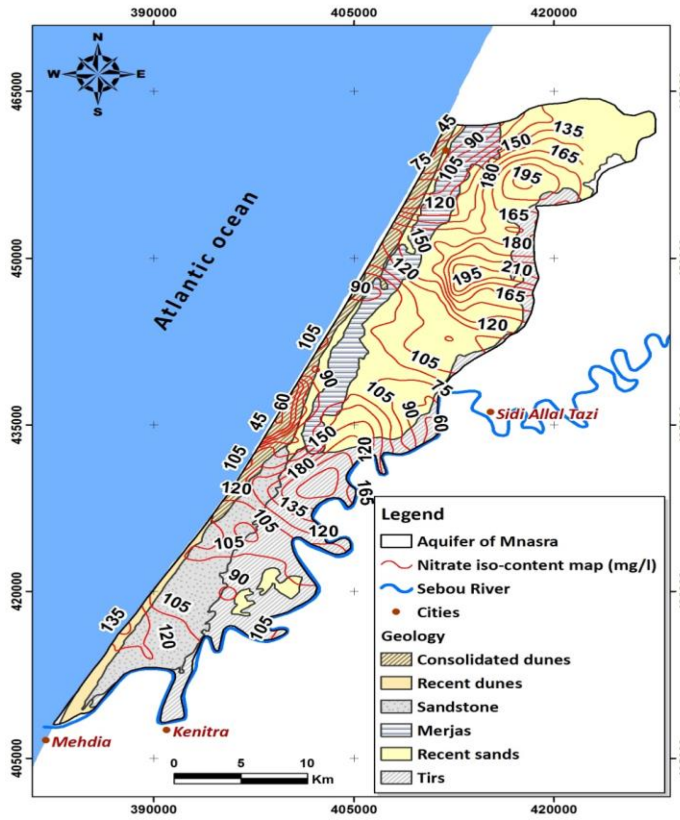

Figure 3. Iso - nitrates map

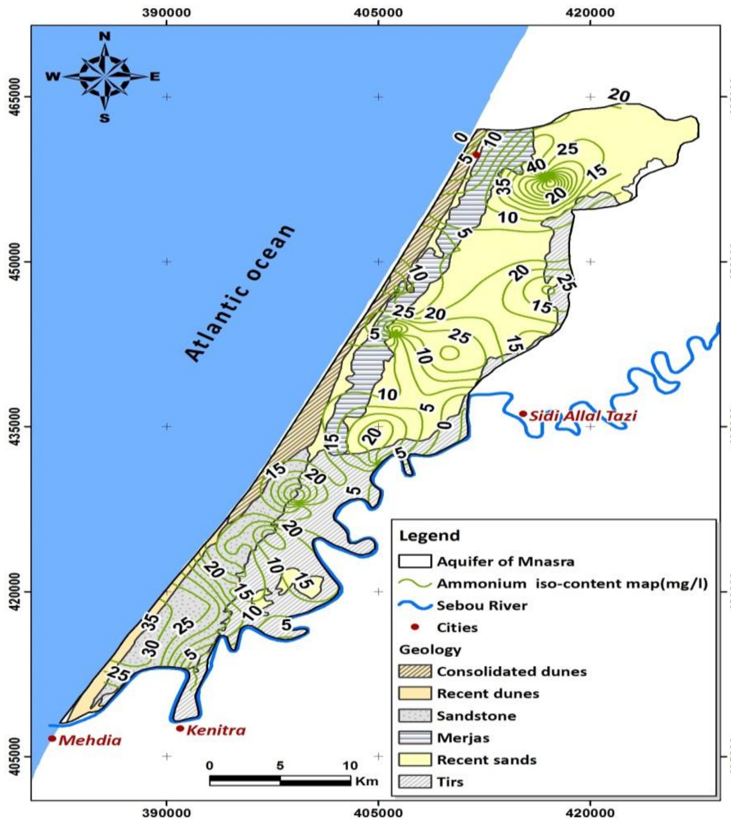

Figure 4. Iso - ammonium map

The high nitrate values are reported by other authors who have worked on the Mnasra aquifer. Indeed Marouane and al. [32] found a maximum value of nitrates of 400 mg / L? this is due to the massive use of nitrogenous fertilizers, to breeding, to the sandy loam nature of the soil and to the mode of widespread gravity irrigation in the region. The distribution of ammonium contents shows that the contents are very high. This is due to a reduction in nitrogenous forms (nitrates and nitrites) under reduced conditions and which are linked to the supply of nitrogenous agricultural fertilizers. Its presence in high rate indicates recent pollution, and low levels indicate old pollution [33] (Fig. 4)

3.2Possible origins of nitric contamination

*3.2.1 **Nitrate - depth relationship***

Many studies have linked nitrate content to well depth [34]. Figure 5 clearly shows that wells that are less than 20 m deep (shallow groundwater) exceed 50 mg / L with the exception of 12 wells. Surface water may contain higher nitrate concentrations than deep water due to autotrophic metabolisms under redox conditions [35].

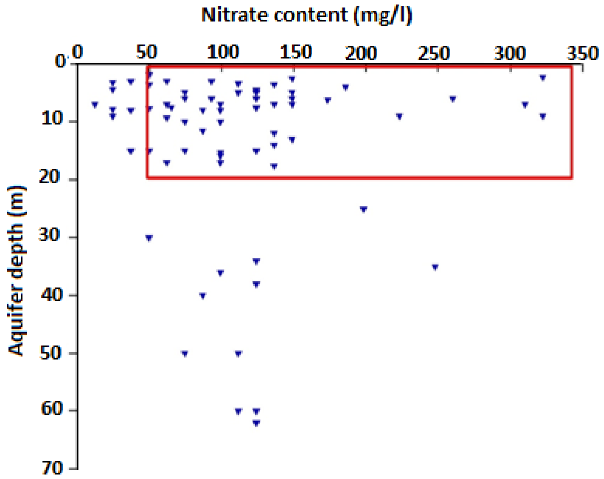

Figure 5. Nitrate - depth correlation curve

*3.2.2 **Nitrate - fertilizer relationship***

In order to reveal the effect of agricultural activities on the presence of nitrates, we carried out analyzes on samples taken from cultivated soil (sampling soils near wells). The comparison of the concentrations of nitrogen in the soil with those of the nitrates contained in the water of the aquifer of Mnasra shows a good correlation (Fig. 6), however we point out the presence of some points where the concentration of nitrates is very high compared to that of nitrogen, this is probably due to another origin other than fertilizers. Figure 7 summarizes the main figures revealed by our survey related to different cultivation encountered in terms of production. Actually, this region is well known by industrial crops: such as sugar beet, sugar cane, in addition to conventional crops such as cereals, and vegetables due to the appropriate climate and soil properties (Fig.7).

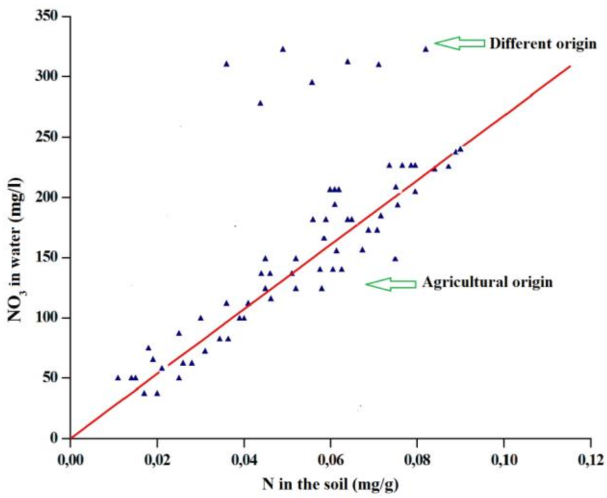

Figure 6. Correlation of the concentration of nitrates with nitrogen in the soil

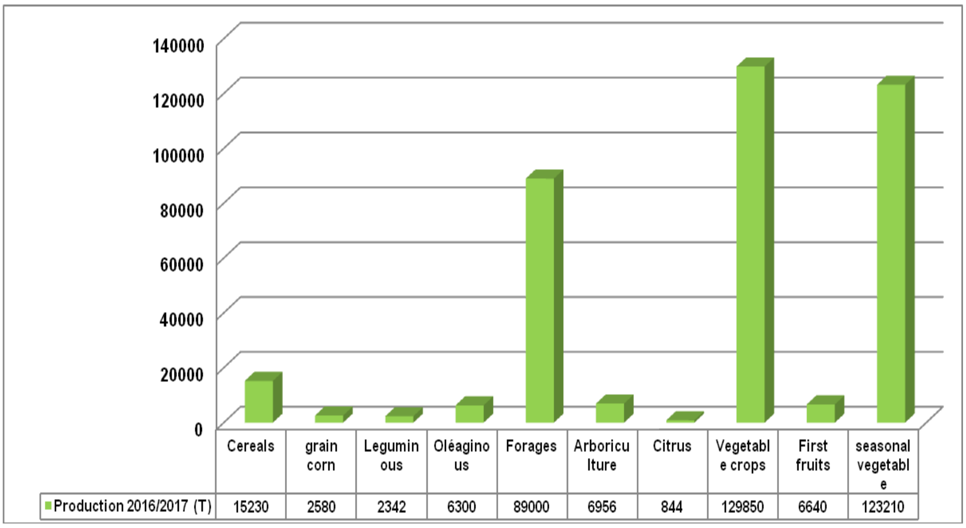

Figure 7. Different crops established in the region and their production

Most fertilizers used in surveyed farms are Ammonitrate 33, 5%, NPK, urea (24 N Kg/ha/application), further livestock manure used (cattle and poultry) amounted to 33 tons/ha/year. The following table gives the main crops and the doses of fertilizer applied nationwide [36]. A study by Wang et al. [37] shows that a reduction in fertilizer application would not lead to a rapid decrease of nitrate concentrations in groundwater. Because nitrate accumulation is the premise of leaching, a substantial amount of nitrate must have accumulated in the soil in the prior experiments. Then, the infiltration flow provides a carrier for the accumulated NO_3^-–N in the soil profiles to move down, finally presenting the possibility of contaminating the groundwater [38].

3.2.3 ***Nitrate – livestock relationship***

Another source of nitrates is manure from intensive farming, which can cause nitric contamination of water. In the study by Laftouhi et al. [39] on the pollution of groundwater in the Essaouira basin by nitrates, he was able to estimate the quantity of nitrates from cattle in this region. He reported that a herd of 40,470 sheep and 4,270 cattle generates an average amount of nitrates in the order of 1,770 and 1,345 tonnes / year respectively. Marouane et al. [40] shows that farmers in the Mnasra region apply manure purchased or obtained from their farm. The most commonly used are manure from chickens (droppings) or cows (Table 3).

Table 2. *Applied Fertilizer Doses for Main Crops*

Crops	Area (Ha)	Quantity of fertilizer (Kg/Ha)			Frequency (%) *	Total fertilizer quantity (Tonne)		
		N	P_2O_5	K_2O		N	P_2O_5	K_2O
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	50-2500	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

Table 3.Number of livestock in the study area

Mnasra	**Number of livestock**						
Year	Cattle				sheep	goats	Modern beehives
	Purebred	cross breed	Local breed	Total			
2017	4924	7256	777	12957	20966	403	300

3.2.4 ***Nitrate - climatic condition relationship***

Several studies have shown a positive correlation between nitrate concentration and seasonal change; the highest nitric concentration is observed during the rainy period [41].These authors have shown that spring precipitation can transport pollutants from the surface to the deep layers of the soil and subsequently to the water table. In summer, evapotranspiration and high temperature create favorable conditions for transforming N-ammonia into N-nitric.

In our study, the samples are taken in June and July 2017 where we observe that 97% of the samples had a concentration greater than 50 mg / L. The precipitation and temperatures measured at the regional level are summarized in Table 4: A study by Marouane et al [41] carried out in the same region show that in 2011, 84% of samples revealed high amount of nitrates, and only 16% respected the critical limit. In 2012, 90% of samples presented values above the guideline value. From December to February 2012. The results demonstrated that nitrate concentration was high during the spring and summer periods.

Table 4.Temperatures and precipitation calculated in the sampling year [42]

Pluviometry in mm		**Temperature in °C**	
2016-2017 campaign	average 30 years	**2016-2017 campaign**	average 30 years
668,2	566,4	Min : 20,5	Min: 12,0
		Max:28,7	Max: 23,0
		Medium: 24,6	Medium:17,5

*3.2.5 **Nitrate - Irrigation relationship***

The survey of the Mnasra region also revealed that 27,000 ha of the area were irrigated by gravity irrigation and 3,770 ha drip [43]. All the farms surveyed were equipped with a drip irrigation system. The volume of irrigation depends on the climate. In winter, the average volume is 0.5 L / hour at 10 cm distance between the drippers for 2 hours per day, while in summer; the volume is 1 L / hour for every 10 cm for 2 hours per day. Table 5 shows the relationship between soil types with doses and numbers of irrigation where in our study it was found that high concentrations of nitrate are present in sandy soils where in these soils permeability and infiltration pollutants are high.

Table5.*characteristics of the different types of soil in the study area [44]*

Soil types	units	Sandy	Toug	Dehs light	Heavy soils
Irrigation dose	m^3/ha	100 à 200	500 à 700	500	600 à 700
Number of irrigation	-	11 à 16	2 à 3	2 à 3	2 à 3

*3.2.6 **Nitrate - Soil texture relationship***

Depending on the type of soil, intensive and repeated use of manure and fertilizers can increase the risk of nitrate contamination of groundwater. Our results show that the lowest contents, in sites with fine texture. The average grades were noted at the sites with a sandy-clay texture. On the other hand, the highest concentrations were recorded in the coarse-textured sites. These present more than 60% of the soils of Mnasra which are sandy in nature (Fig. 8) therefore have a large macroporosity which allows to release more dissolved elements such as nitrates which will be housed in the aquifer.

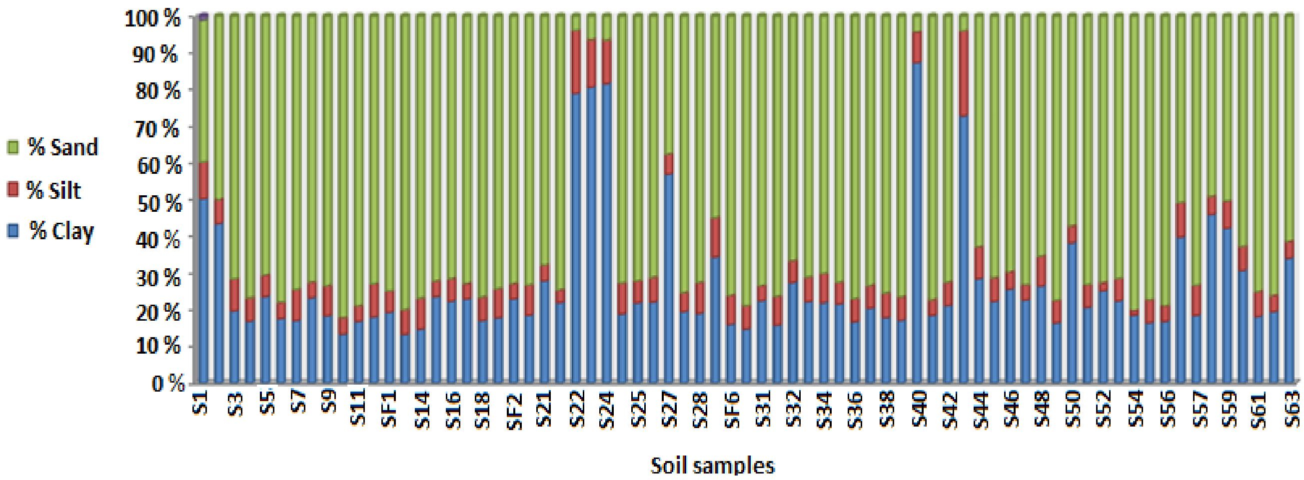

Figure 8. Granulometry of Mnasra soils

*3.2.7 **Nitrate - type of surface soil relationship***

Mnasra soils have different infiltration rates depending on the type of soil [45] (Tabl. 6):

- Rmel soils with a very sandy texture with an infiltration speed greater than 20 cm / h (very permeable);
- Toug soils (black fatty sands) with a heterogeneous silty-sandy to silty-clayey texture with an infiltration speed generally between 6 and 12 cm / h (permeable to slightly permeable);
- Dehs soils with a silty to silty-clay texture with an infiltration speed of the order of 2 to 6 cm / h (not very permeable);
- Tirs and hydromorphic soils with a very clayey texture and an infiltration speed between 0 and 2 cm / h (very little permeability).

***Table 6.**Physical characteristics of the different types of soil [44]*

Soil types	Units	Sandy	Toug	Dehs light	Heavy soils
Vertical permeability	cm/ hour	30 à 100	2 à 10	< 2	< 1
Horizontal permeability (1)	cm/ day	high	medium	medium	low
Horizontal permeability (2)	cm/ day	high	high	medium	very weak
Apparent density	-	1,60	1,65	1,45	1,55
Equivalent humidity	%	4	14	22	30
Useful reserve	mm	15	62	86	125

Figure 9 shows the spatial distribution of the infiltration rates of the different soils in the Mnasra region. These coefficients were estimated from a pedological study by ORMVAG (1996) [44] and are calculated on the basis, on the one hand, of the pedological nature and on the other hand, the areas of the different types of soil.

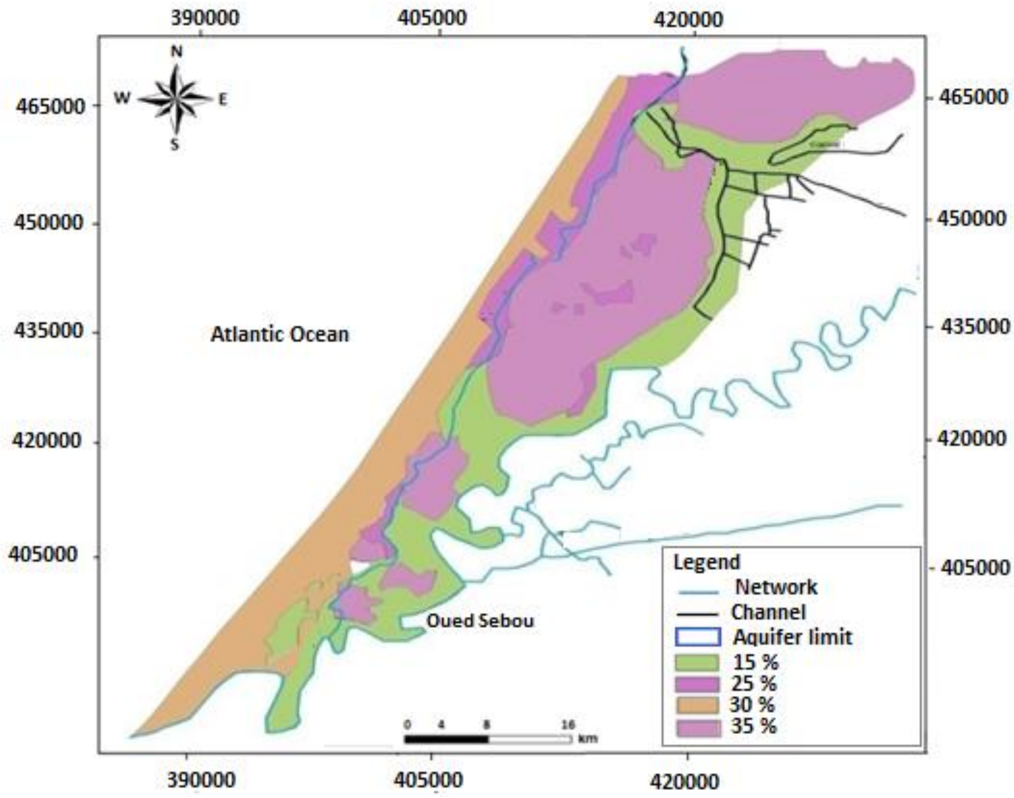

Figure 9. Infiltration map of the Mnasra area [44]

3.2.8 Nitrate - thickness of the unsaturated zone relationship

The measurements made to determine the thickness of the unsaturated zone show water depths from the ground ranging from 1, 2 m to 60 m. The highest thicknesses (20 to 60 m) of the unsaturated zone are found mainly along the dune cordon of the littoral edge and in the southern zone of Mnasra. The interior dunes have much smaller thicknesses between 5 and 10 m. everywhere else, the aquifer is located at depths less than 5m [46](Fig.10).

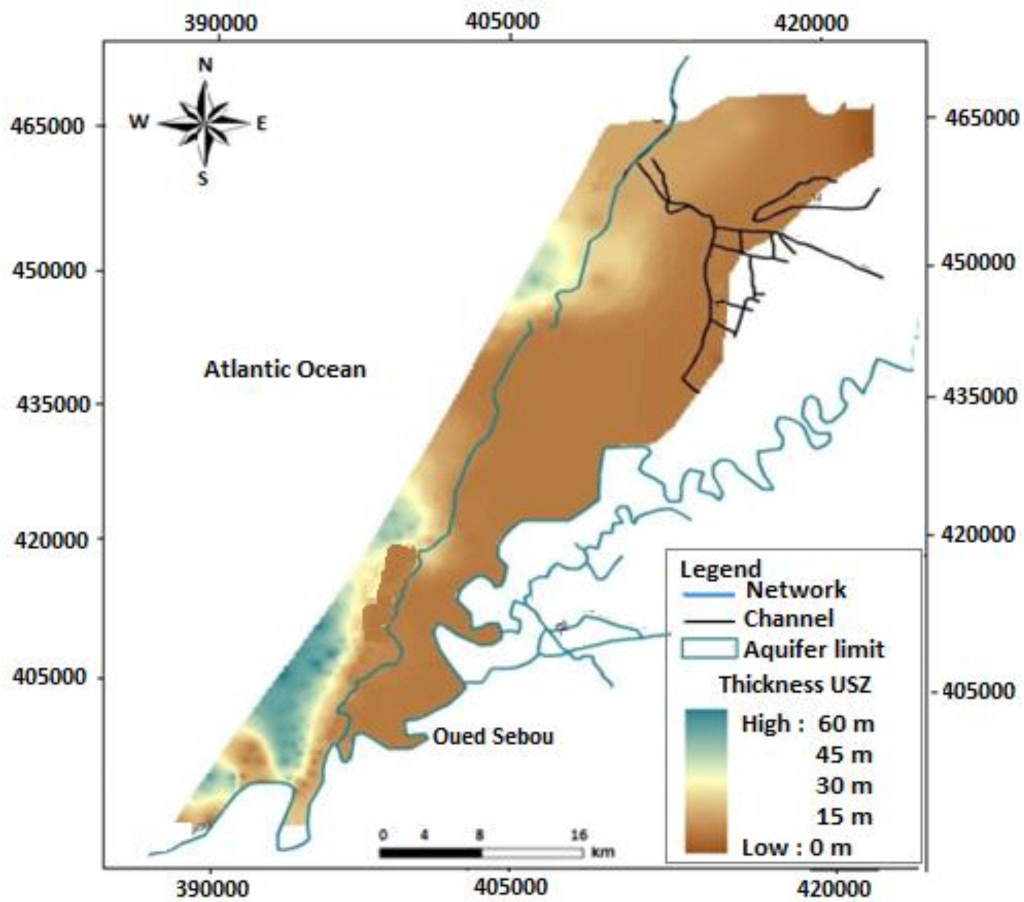

Figure 10. Thickness of the unsaturated zone [46]

A study by Sanchez pérez et al. [44] shows that the unsaturated zone travel time, complex root zone processes, including denitrification, N mineralization, N uptake into soil organic matter may vary widely within the agricultural regions with similar climatic and hydrogeologic conditions. Unsaturated zone travel time may be particularly long in (semi-)arid regions with highly efficient irrigation systems, minimal annual recharge rates much smaller than 300 mm, and in regions with deep vadose zones (> 20 m) [48].

3. Comparison of nitric pollution from wells between 1993, 2003, 2007 and 2017

Nitric pollution of groundwater in the coastal area of the Gharb of Morocco has been noted since 1993 by the Regional Office for Agricultural Development of the Gharb by a measurement of 159 wells for the companion periods of 1994, 2003 and 2007.

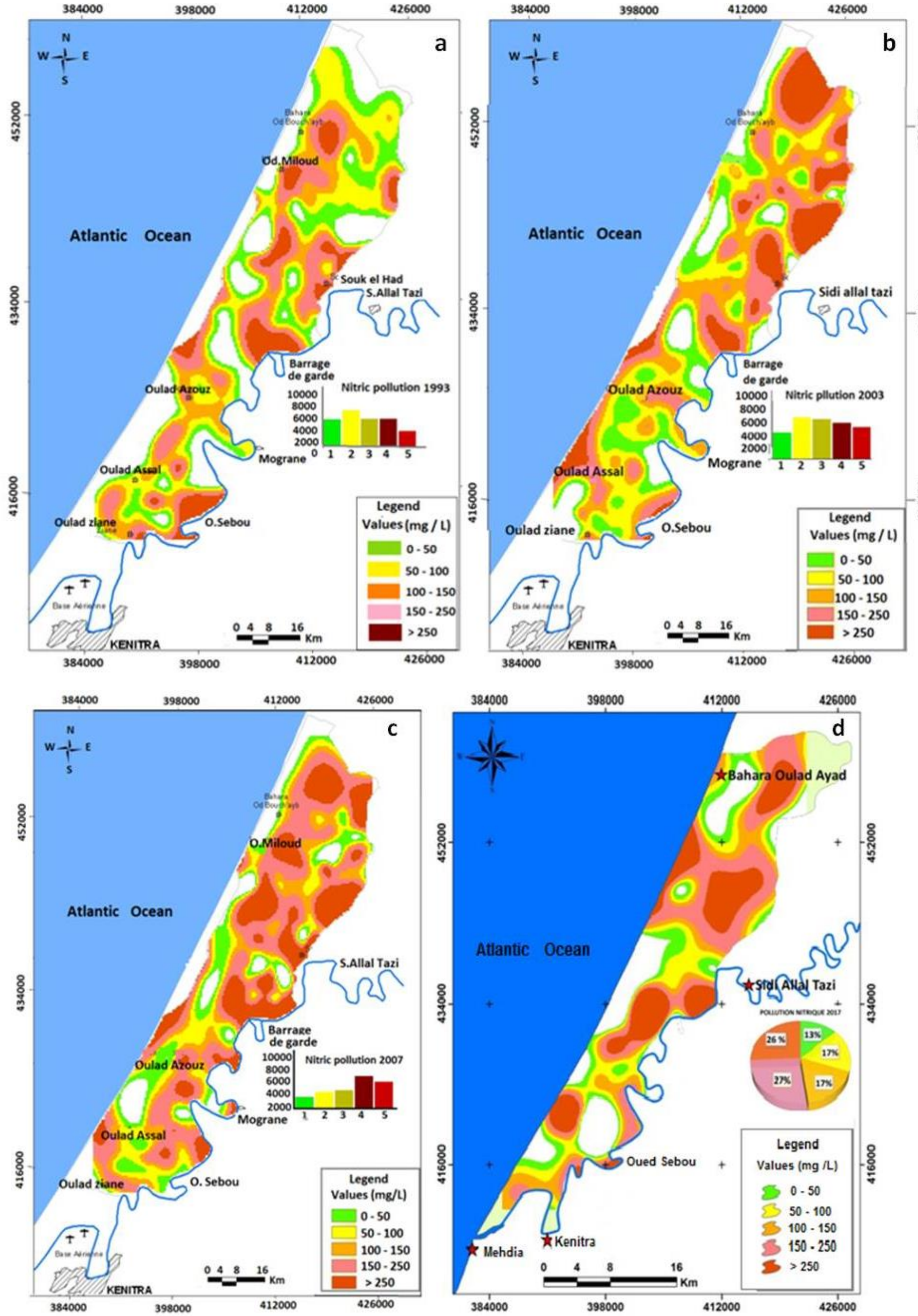

Figure 11. Spatial distribution of nitric pollution, (a): 1993; (b): 2003; (c): 2003; (d): 2017

- For the situation in 1993, shows that only 21% of the measurement points had acceptable values vis-à-vis the drinking water standards relating to nitrates, and that more than 10% of the measured points had more than 5 times the drinking standard (50 mg / l). It should be noted that at the time, agricultural intensification in the area was only in its beginning (Fig. 11a).
- For the 2003 situation, the map shows that the zones of the aquifer not exceeding the drinking standards no longer occupied less than 16% of surface area (21% in 1993) and knowing that this zone has values exceeding 5 times (250 mg / l) the potability standard occupied respectively 18.4% in 2003 (Fig.11b).
- For the situation in 2007, shows that only 11.5% of the measurement points had acceptable values vis-à-vis the drinking water standards for nitrates and values exceeding 5 times (250 mg / l) the standard of drinking water occupied 22.2% respectively in 2007(Fig.11c).

For the situation in 2017, shows that only 13% of the measurement points had acceptable values vis-à-vis the drinking water standards for nitrates and values exceeding 5 times (250 mg / l) the drinking water standard occupied 26% respectively (Fig.11d).

A classification into five classes has been established according to the nitrate content of the water and summarized in Table 7. There is a slight increase in the area occupied by class C5, the other classes C1, C2, C3 and C4 have experienced a different variation in the year 2017 may be due to the sampling period, the number of wells as well as the mapping method used.

Table 7. *Percentage of land occupied by each class of wells out of the total land mapped in 1993, 2003, 2007 and 2017*

Classes	**Nitrates content (mg/l)**	**Quality**	**Years**			
			1993	2003	2007	2017
			Surface occupied by class / total surface * 100			
C1	$V \leq 50$	Excellent	20 %	15 %	11 %	13 %
C2	$50 < V \leq 100$	Good	27 %	24 %	16 %	17 %
C3	$100 < V \leq 150$	Medium	20 %	21 %	31 %	17 %
C4	$150 < V \leq 250$	Bad	20 %	21 %	31 %	27 %
C5	$V > 250$	Very bad	**12 %**	**18 %**	**25 %**	**26 %**

The analysis of the degradation of the nitric quality of the Mnasra aquifer is mainly observed in the North than in the South. This can be explained by two main causes:

- Increased intensification of greenhouse crops (Fig. 12, 13) in the northern part (≈ 74%) than in the southern part (≈26%);

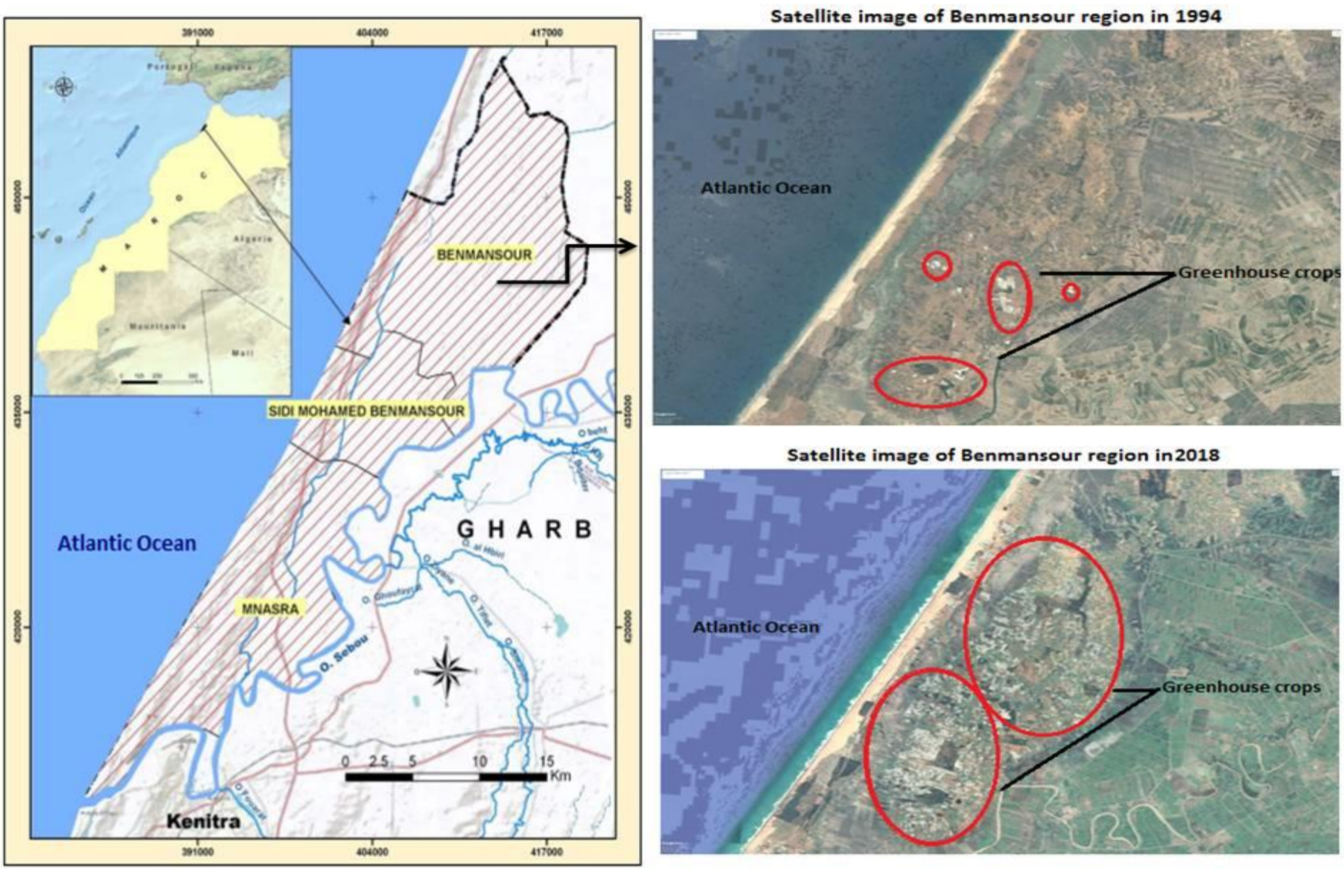

Figure 12. Evolution of greenhouse crops in Benmansour region between 1994 and 2018

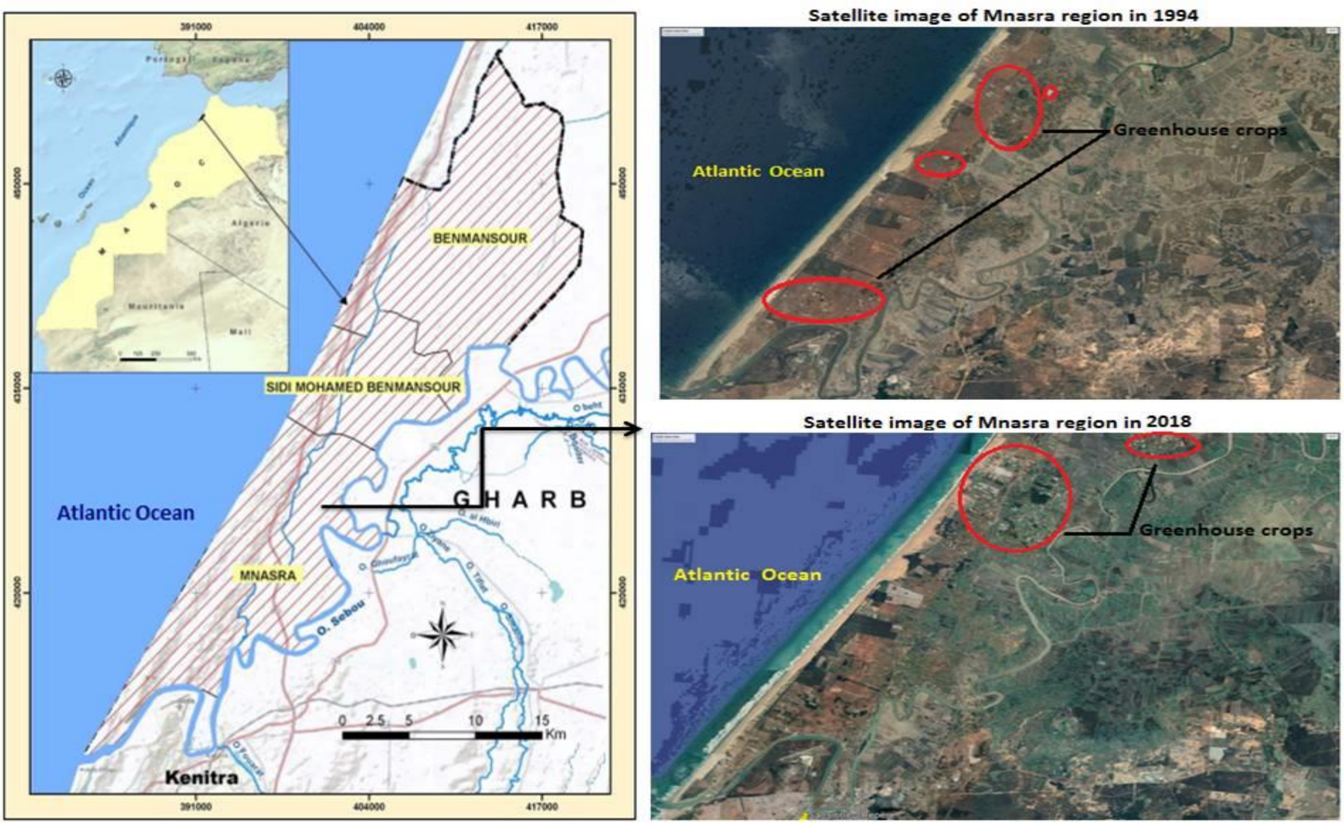

Figure 13. Evolution of greenhouse crops in Mnasra region between 1994 and 2018

➢ In the northern part, the piezometric curves form a bulge whose N-S axis corresponds to a dividing line of water to two directions of flow, one towards the ocean and the other towards Wadi Sebou. The watershed is governed by the crest line of the piezometric surface to the right of the internal dune sector. In the West, the flow takes place in the direction of the Ocean. In addition, it is in the North zone where we meet the dunes and the interior dune flats with not very hectic relief, high from 5 to 20 m above sea level. Thus, they correspond to the widest area of the sandy domain and whose water table is very close to the surface (3 to 13 m), which explains the current intensive exploitation. Consequently, this study raised nitric pollution more accentuated in the North than in the South of the Mnasra zone (Fig.14).

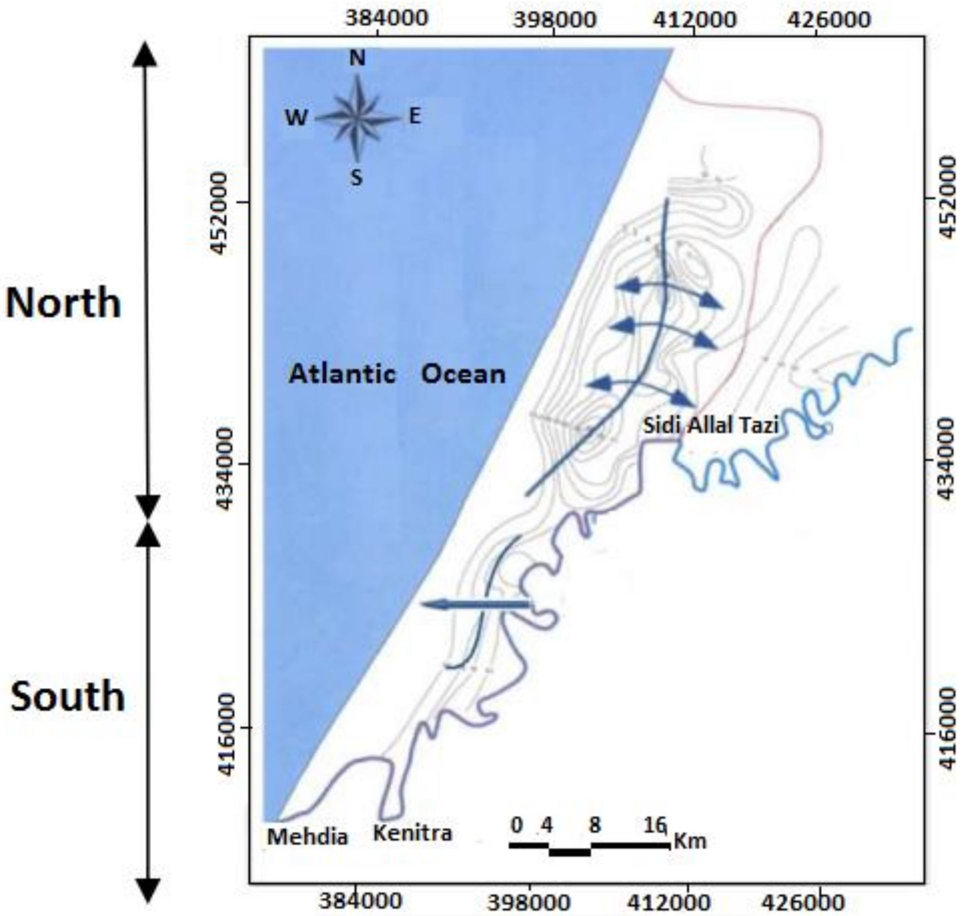

Figure 14. Piezometric map showing the directions of underground flow in the North and South zone of the Mnasra Aquifer

4. Conclusion

Although nitrates are naturally present in some groundwater, high concentrations are generally the indirect result of human activities, the impact of which can be felt in the long term. Analysis of the temporal trends in nitric concentrations observed over 23 years showed a sharp deterioration in the quality of well water between 1993 and 2017 with excessive levels reaching in some cases; values five to six times the potability limit. The observed trends can be attributed to variations in the rate of agricultural intensification linked to the socio-economic factors of the region. Added to this are the poor agricultural management practices adopted by farmers with the predominance of gravity irrigation and the spreading of large quantities of fertilizer for better yield. These practices are far removed

from conservative and preservative measures of already scarce resources. The impact of the soil texture could be highlighted. The sandy nature of the soil can promote the leaching of nitrates and accentuate the pollution process.

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