

Study of the Physicochemical and Bacteriological Quality of the Groundwater of Martil

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Abstract

The Martil aquifer is one of the most important aquifers of the Mediterranean coastal basins that is located in the northern region of Morocco. This groundwater is easily exploitable by the population. This requires an evaluation of the water quality of the aquifer, the fundamental purpose of which is to contribute to the hydrogeological, hydrogeochemical and bacteriological knowledge of the water resources of the Martil aquifer. 16 sampling points were studied. The water samples were taken during the winter months of 2015 and 2016 and analyzed. The parameters determined are: T° , pH, CE, Cl^{-} , SO_4^{2-} , NO_3^{-} , NO_2^{-} , HCO_3^{-} , Na^{+} , K^{+} , Mg^{2+} , Ca^{2+} , MO, TA, TAC and TH and the biological parameters (CT, CF and SF). The application of the Principal Component Analysis (PCA) method has made it possible to identify the parameters that most contribute to the determination of the quality of these groundwaters; to show their spatial variability; to group the water sampling points into homogeneous groups allowing spatiotemporal analysis of the water quality of the water table. The temperature does not present large spatial and temporal variations. The pH is relatively neutral to slightly alkaline. The electrical conductivity exceeds the values recommended by the standard in 37.5% of the points in 2015 and 31.25% of the points in 2016. A correlation exists between the Electrical Conductivity (EC) and the ions Cl^{-} , Ca^{2+} , Mg^{2+} , SO_4^{2-} and HCO_3^{-} . The ion concentrations (Ca^{2+} , Mg^{2+} , K^{+}) were all below the guideline value of the Moroccan standard. The concentration of Cl^{-} ions was high in 31.25% of the points in 2015 and in 25% in 2016. These waters are soft and of low alkalinity mainly due to bicarbonate ions (HCO_3^{-}). The concentrations of nitrates, the Organic Matter content (OM) and the concentrations of biological parameters are all lower than the guideline values of the Moroccan standard.

The parameters determining the water quality classification of the Martil aquifer are electrical conductivity and chloride ions.

Keywords: Chlorides; Electrical Conductivity; Groundwater of Martil; PCA; Physicochemical and Bacteriological Quality

The challenge facing all regions of Morocco is the protection of the quality of water resources [2,3].

Introduction

Water is a natural element essential to the life of humanity, its economic and social development and the ecological balance of its living environment. The quantity and quality of available water resources are becoming increasingly complex and difficult to solve. Morocco is characterized by a semi-arid Mediterranean climate in most of its territory and by limited and irregular water resources in time and space. Indeed, Morocco is characterized by a scarcity of water resources and a fragility of hydraulic systems due to their exposure to numerous natural and anthropogenic aggression [1].

The Mediterranean Coastal Basin, in particular the Martil water table which is located in the northern region of Morocco is the subject of our study. This region is experiencing significant economic and social development generating a high water demand of 550 million m^3 / year. This population growth and the increase in economic, agricultural and industrial activities resulted in a large exploitation of the water resources of the region. The Martil water table is easily exploited by the population (FORUM URBAIN MOROCCO, 2006). The shallow depth and the ease of exploitation of the underground water of the commune pushed the local population to exploit the water of the water table by traditional

wells of depth between 1 and 4 m. This phenomenon exposes the sustainability of resources and therefore the entire economy of the region to a serious risk. Indeed, the exploitation of water requires a detailed knowledge of the aquifers concerned [4,5], whose fundamental aim is the contribution to the hydrogeological, hydrogeochemical and bacteriological knowledge of the water resources the groundwater of Martil.

Material and Methods

Study Area: groundwater of Martil

The Martil aquifer is part of the Mediterranean coastal basins that extend from the Oued Rhiss-Nekor basin to the Oued Fnidek basin and occupy an area of nearly 7,775 km², their average altitude is 550m. The region is drained by numerous rivers (Oued Martil, Laou, Amsa, Smir) which, at their mouths, form

very narrow valleys with the exception of those of Oued Laou and Martil which is subject to our study. Groundwater is stored in a set of free aquifers located in the pluvial-quaternary plains (clay marls, sands, conglomerates, gravel) and in the carbonate massifs of the Triassic and Lias [6-8]. Aquifers are distinguished from the limestone chain of the Rif and the aquifers with open water from the alluvial plains [8,9].

Sampling points

16 control points located along the Oued Martil upstream (Tétouan-Tangier and Dar Benkarrech road) green downstream (the sea coast) were chosen. The sampling points are designated by numbers M1 to M16 going from the upstream to the dimension. The codes as well as the data relating to the location of these sampling points are summarized in Table 1.

Codes	Désignation	Nature du point de prélèvement	X	Y	Province	Cercle	Commune	Nom de carte	N° de carte	Echelle
996/2	M1	Forage	4,97,360	5,50,000	Tétouan	Tétouan	El Azhar	Tétouan	NI30194a	1/50000
992/2	M2	Forage	4,99,700	5,50,900	Tétouan	Jbala	Dar Ben Karrich	Tétouan	NI30194a	1/50000
120/2	M3	Piézomètre	5,02,660	5,51,050	Tétouan	Tétouan	Sidi Mandri	Tétouan	NI30194a	1/50000
150/2	M4	Puit	5,05,430	5,60,560	Tétouan	Tétouan	El Mallaliyine	Tétouan	NI30194a	1/50000
621/2	M5	Puit	5,05,590	5,52,440	Tétouan	Jbala	Azla	Tétouan	NI30194a	1/50000
1284/2	M6	Puit	5,05,895	5,59,800	Tétouan	Tétouan	Martil	Tétouan	NI30194a	1/50000
49/2	M7	Puit	5,07,230	5,56,320	Tétouan	Tétouan	Martil	Tétouan	NI30194a	1/50000
638/2	M8	Puit	5,07,450	5,54,070	Tétouan	Tétouan	Martil	Tétouan	NI30194a	1/50000
1283/2	M9	Puit	5,07,750	5,59,650	Tétouan	Jbala	Martil	Tétouan	NI30194a	1/50000
344/2	M10	Puit	5,08,825	6,61,650	Tétouan	Jbala	Azla	Tétouan	NI30194a	1/50000
10/2	M11	Puit	5,09,150	5,53,200	Tétouan	Tétouan	Sidi Mandri	Tétouan	NI30194a	1/50000
1282/2	M12	Puit	5,09,550	5,59,000	Tétouan	Jbala	Azla	Tétouan	NI30194a	1/50000
76/2	M13	Puit	5,09,600	5,56,250	Tétouan	Tétouan	Martil	Tétouan	NI30194a	1/50000
512/2	M14	Puit	5,11,000	5,53,070	Tétouan	Jbala	Azla	Tétouan	NI30194a	1/50000
1281/2	M15	Puit	5,11,150	5,57,550	Tétouan	Jbala	Azla	Tétouan	NI30194a	1/50000
360/2	M16	Puit	5,12,020	5,54,110	Tétouan	Jbala	Azla	Tétouan	NI30194a	1/50000

Table 1: Geographical location and Characteristics of the points studied in the Martil river system.

Sampling method

The samples were taken during the winter periods (from October to March) of the years 2015 and 2016. The water is taken at about 50 cm from the free surface of the water, and it is the third lifting of the water which is retained as analysis water. For wells with a pumping system, the samples are taken after pumping for 10 minutes to take deep water from the wells. All precautions are taken to avoid possible contamination. For physicochemical analyzes, water samples are taken from 1.5l bottles. For bacteriological analysis, samples are taken in sterile 0.5L flasks. At each sampling we measured in situ the water temperature, the electrical conductivity and the pH. After these measurements, the water samples are conditioned and conveyed according to the

Afnor NT 90-100 standard.

Methods of analysis

The study of the water quality sampled at the different points of the Martil aquifer concerned the main physical, chemical and bacteriological parameters such as: Temperature (T°), hydrogen potential (pH), conductivity (CE), chlorides (Cl^{-}), sulphates (SO_4^{2-}), nitrates (NO_3^{-}), nitrites (NO_2^{-}), sodium (Na^{+}), potassium (K^{+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), bicarbonates (HCO_3^{-}), Organic Matter (OM), Alkalimetric Titer (TA), Total Alkalimetric Titer (TAC) and Hardness (TH), Total Coliforms (TC), Faecal Coliforms (CF)) and faecal streptococci. The techniques used to determine these parameters are summarized in Table 2.

Parameters	Unit	Techniques
Temperature	$^{\circ}C$	In situ measurement using a mercury thermometer
pH		In situ measurement by potentiometric method using pH meter
Conductivite Electrique (CE)	$\mu S/cm$	In situ measurement using conductivimeter
Chlorures	mg/l	Assay by Mohr method to silver nitrate reagent.
Sulfates	mg/l	Determination by spectrophotometric method with hydrochloric acid and barium chloride reagents
Nitrates	mg/l	Determination by spectrophotometric method with sodium salicylate reagent.
Nitrites	mg/l	Determination by spectrophotometric method with diazotization reagent
Bicarbonates	mg/l	Acidimetric determination with sulfuric acid
Alkalinity	$^{\circ}F$	Dosage by the titrimetric method
Hardness	$^{\circ}F$	Determination by titrimetric method with EDTA
Calcium	mg/l	Titrimetric titration with EDTA
Magnesium	mg/l	Calculated by the difference in total hardness and Calcium
Sodium and Potassium	mg/l	Determination by the flame spectrophotometry method.
MO	mg/l	Determination by Mohr's method with silver sulphate and mercury sulphate.
Fecal coliform	CF/100ml	Membrane filtration. Culture on medium Tergitol 7 Agar with TTC
Total coliforms	CT/100ml	Membrane filtration. Culture on medium Tergitol 7 Agar with TTC
Fecal streptococci	SF/100ml	Membrane filtration. Culture on Slanetz Bartle medium

Table 2: Methods for analyzing physicochemical and microbiological parameters used for the typology and assessment of water quality.

Assessment of the physicochemical and bacteriological quality of water

The assessment of groundwater quality was made on the basis of a grid comprising five indicators of physicochemical, organic, nitrogen, and bacterial pollution. These parameters are: Conductivity, chloride ions, nitrates, NH_4^+ , KMnO_4 oxidizable materials and Faecal coliforms (Table 3) [10].

Quality parameter	Conductivity ($\mu\text{S}/\text{cm}$)	Cl^- (mg/l)	NO_3^- (mg/l)	NH_4^+ (mg/l)	MO (mg/l)	CF (100ml)
Excellent	< 400	< 200	< 5	< 0,1	< 3	< 20
Good	400 - 1300	200 - 300	May-25	0,1 - 0,5	03-May	20-2000
Average	1300 - 2700	300 - 750	25 - 50	0.5-2	05-Aug	2000-20000
Bad	2700 - 3000	750 - 1000	50 - 100	02-Aug	>8	>20000
T. Bad	> 3000	> 1000	> 100	>8	-	-

Table 3: Simplified grid for assessing the overall quality of groundwater [10].

Statistical analysis

A Principal Component Analysis (PCA) of a matrix of 16 sampling points and the aforementioned physicochemical variables was performed to analyze the water typology of the Martil aquifer. For this analysis we used the XLSTAT 2019 software.

Results and Discussions

Spatiotemporal evaluation of the alterations of the water quality parameters of the Martil water table for the two years 2015/2016

Physical parameters

The spatiotemporal analysis of the physical parameters measured in the different water sampling points of the Martil aquifer shows that the degree of temperature does not present large spatial and temporal variations. The observed temperature values are consistent with what is reported in the literature that groundwater is less sensitive to temperature variations than surface water [11,12]. The pH values of the waters of the Martil water table vary between 7.78 and 8.8 in 2015 and between 6.3 and 8.8 in 2016;

they comply with the WHO standard. In general, the pH of natural waters is between 6 and 8.5 [12-17]. The electrical conductivity of the waters of the Martil aquifer shows heterogeneity in all sampled points of the aquifer (Table 4). It is generally between 950 $\mu\text{S}/\text{cm}$ (M2) and 6310 $\mu\text{S}/\text{cm}$ (M16) measured in the year 2015 and between 857 $\mu\text{S}/\text{cm}$ (M2) and 4260 $\mu\text{S}/\text{cm}$ in the year 2016. Values exceeding the limit of the Moroccan groundwater standard are recorded at sampling points M4, M6, M9, M13, M14 and M16. These points are located downstream of the Martil aquifer and in areas characterized by the presence of septic tanks added to the industrial activity and calcaire-dolomitic nature of the geological substratum. The electrical conductivity depends on the endogenous and exogenous organic matter charges, generating salts after decomposition and mineralization and also with the evaporation phenomenon which concentrates these salts in water, it also varies according to the geological substrate crossed [17]. The values of the electrical conductivity allow according to the Moroccan standard to classify the waters of the points of sampling of the groundwater of Martil between good to very bad for the two years 2015 and 2016.

	Year 2015			Year 2016		
	T°C eau	pH	CE (µS/cm)	T° Eau (°C)	pH	CE (µS/cm)
M1	12,7	7,8	1320	21,5	7,3	1410
M2	24,8	7,8	950	19,2	7,78	857
M3	16,5	7,57	1640	17	6,3	1594
M4	15,8	8,2	2840	18,5	7,65	2980
M5	17,9	7,76	1420	18	7,05	1304
M6	17,8	7,76	3260	18	8,7	3100
M7	18,1	7,9	1030	17	7,66	980
M8	17,7	8,26	1736	17,8	8,25	1590
M9	17,2	7,8	3980	18,5	7,4	4020
M10	19	7,21	1050	18,3	7,4	2080
M11	17	7,68	2030	18	6,6	1975
M12	16,5	7,64	1680	20,4	7,6	1740
M13	15,1	8,2	3760	18,3	8,4	2480
M14	16,6	7,5	2900	17,6	6,9	2960
M15	16,3	8,69	975	20,1	8,8	1880
M16	16,9	8,6	6310	16,4	8,65	4250

Table 4: Physical parameters measured in the waters of the Martil water table for the years 2015 and 2016.

Chemical parameters

In space, the different concentrations of these elements are heterogeneous and have a positive trend going from upstream to downstream of the basin, in particular the sampling points located in Azla and rural Martil. Over time, these concentrations have an increasing positive trend, which reflects an increase in the content of these elements in accordance with electrical conductivity (Table 5 and Table 6). The continuous contribution in these elements is in connection with the geological environment and the anthropic action.

Spatiotemporal evolution of cations

Calcium: Calcium concentrations are below the limit set by WHO in all points in the year 2015 and show a slight increase in the year 2016 at points M3, M6, M12 and M16. This increase in concentrations can be explained by the drought experienced in 2016. However, the measured values cannot qualify the water of these wells of good or bad quality since the Moroccan standard does not designate any maximum value. acceptable (VMA) for calcium in water. Even international standards do not recommend a standard for calcium. According to the Federal-Provincial-Territorial Committee on Health and the Environment in Canada, there is no evidence that calcium in drinking water is harmful (SANTE CANADA 2012). On the other hand, the nappe zone is mainly composed of raw limestone, dolomitic limestone and dolomite, a zone of flyschs which consists of various terrains ranging from Cenozoic to intercalation of calcareous sandstones and calcareous microbricks [18,19]. The lithological and rocky constitution of this zone could, however, have an influence on the concentration of this parameter in groundwater.

	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	MO	TH	TA	TAC
M1	122,6	7,5	475	0,57	409	14,2	3,12	6,7	0	6,7
M2	70,5	8,3	71	4,72	238	220,3	1,12	4,2	0	3,9

M3	193,2	9,7	291	6,09	519	250,2	3,84	10,4	0	8,5
M4	91,4	69,5	986	5,54	439	483,4	5,9	10,3	0,8	7,2
M5	110,6	5,8	469	0	805,2	19,5	5,36	6	0	13,2
M6	118,2	7,8	986	0,98	415	45,6	6,88	6,5	0	6,8
M7	86,6	19,7	447	0,16	317	14,2	2,88	5,94	0	5,2
M8	111,8	11,7	631	0,98	573	31,2	3,92	6,5	0	9,4
M9	111	5,6	1312	0,82	427	21,9	5,84	6	0	7
M10	28,9	16	553	8,13	244	68,5	6	2,8	0	4
M11	156,3	8,3	723	1,62	732	168,5	5,68	8,5	0	12
M12	128,3	80,7	390	13,19	354	343,9	1,52	13	0	5,8
M13	160,3	145,8	1227	5,32	317	391,4	2,64	20	0,3	5,2
M14	153,1	14,1	674	4,74	537	184,6	6,88	8,8	0	8,8
M15	40,9	40,8	482	1,85	329	80	2,88	5,4	0,6	5,4
M16	157,1	24,3	2411	1,01	384	104,9	2,48	9,8	1,2	6,3

Table 5: Values of the chemical parameters measured in the waters of the Martil water table in the year 2015.

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	MO	TH	TA	TAC
M1	1030	6	124,2	9,72	354,5	2,67	213,5	529,9	1,52	7	0	3,50
M2	220	2	76,15	6,8	106,35	3,99	152,5	79,9	1,2	4,36	0	2,50
M3	900	0	216,43	25,27	389,95	3,19	494,1	769,43	1,67	12,88	0	8,10
M4	16800	8	104,21	70,96	553,02	3,23	292,8	458,95	2,99	10,32	0	4,80
M5	1360	0	96,19	16,10	389,95	0	549	147,04	6,11	6,12	0	9
M6	2500	5	211,62	23,33	758,63	11,42	518,5	492,76	4,15	12,48	0,23	8,50
M7	800	5	62,52	26,24	1488,9	3,16	524,6	124,19	1,63	5,28	0	8,60
M8	1500	0	137,87	13,61	581,38	481,9	30,50	525,62	3,89	8,00	0,5	7,90
M9	3460	0	196,39	167,67	1063,5	0	561,2	532,76	4,58	16,36	0	9,20
M10	2100	3	152,3	6,8	882,44	22,70	317,2	268	2,71	8,16	0	5,20
M11	1850	0	136,27	14,58	673,55	0	67,1	408	3,95	8,00	0	1,10
M12	1110	51	245,29	31,30	538,84	32,96	439,2	729,9	3,19	14,80	0	7,20
M13	1770	2	76,95	27,22	709	1,55	519,72	246,1	1,99	6,80	0,18	8,52

M14	2780	0	168,34	14,58	886,25	3,26	506,3	602,29	4,37	9,6	0	8,30
M15	1440	1	68,14	41,8	460,85	34,33	451,4	492,76	2,79	6,84	0,22	7,4
M16	3600	0	224,25	24,30	1488,9	3,51	494,1	423,71	3,4	13,2	0,5	8,10
NB : Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ et Mo en mg/l ; TA, TAC, TH en °F.												

Table6: Values of the chemical parameters measured in the waters of the Martil water table in the year 2016.

Magnesium: Magnesium levels are generally below the WHO standard for magnesium of 50 mg / l, except for M4 (69 mg / l), M12 (81 mg / l) and M13 (145 mg / l) in the year 2015 and M4 (71 mg / l) and M9 (167 mg/l) in 2016. These high concentrations can be explained by the drought that characterized the year 2016 and the Coastal and rocky structure of the region because magnesium is found in limestone, marl-limestone and triassic formations (gypsum) [17].

Total Hardness (TH): The Total Hardness of water (TH) or Hydrotimetric Titer (TH) is mainly related to the amount of calcium and magnesium in the water. The spatiotemporal evolution of the total hardness (TH) at the level of the prospected wells show that the waters of the Martil aquifer are relatively very soft to moderately hard according to the Durfor and Becker classification [20]. Hardness values range from 2.8 °F to 20 °F in 2015 and from 4.36 °F to 16.36 °F in 2016. They do not exceed the standard (35 °F). These results are consistent with the concentrations of calcium and magnesium ions recorded in groundwater for both years. This fact is probably related to the lithological nature of the geological formation of the water table of Martil, and in particular to its composition in magnesium and calcium [15,21].

Sodium and potassium: Sodium is in very high concentrations that far exceed the limit value recommended by the WHO being 150 mg / l in all sampling points for the year 2016. When potassium, values presented by the waters of the sampling points are all below the WHO recommended limit value of 12 mg / l with the exception of M12 (51 mg / l) at Azla. The unique value of 51 mg / L remains paradoxical. The results are interpreted by making the link with the climate, particularly the dry period of 2016 when the water level in the wells decreases and the salt concentration increases. In terms of quality, the sodium level exceeds the required standards, attesting to the poor quality of the waters of the well of the groundwater of Martil for this parameter in the year 2016.

Spatiotemporal evolution of anions

Chlorides: The concentrations of chloride ions measured in waters of the Martil aquifer range between 71 mg / l (M2) and 2411mg / l (M16) in 2015 and between 106.35 mg / l (M2) and 1488, 9 mg / l (M16). the recorded levels do not exceed the Moroccan

standards set at 750 mg / l (N.M, 2002) in the majority of sampling points, ie 68.75%; result in agreement with a previous study of El Morabiti on the same area of Martil. This study found chloride ion concentrations that did not exceed the norm in 60% of the sampled points [22]. The minimum values of the chlorides were recorded in the upstream part of the aquifer. The high values are observed at sampling points M4, M6, M9, M13 and M16 in 2015 and at points M7, M9, M10 and M16 in 2016. These points are located downstream of the groundwater. They have the highest concentrations of chlorides due to their geographical location close to the mother whose spray is responsible for it. Indeed, the presence of marine intrusion, a chemical industry added to the use of agricultural fertilizers could generate a significant presence of this element in these points. These high chloride values could also be related to the dissolution of salt minerals and the infiltration of irrigation water [23-25]. On the other hand, the concentrations of chloride measured in water in the year 2016 are generally very high compared to those measured in 2015. This can be interpreted by the dry climate experienced in 2016.

Sulphates: The values of sulphates recorded in the waters studied vary widely in time and space. In 2016, sulphate levels were well above the value set by the Moroccan standard (NM 03.7.001) (400 mg / l) in 69% of sampling points. These values vary between 79.9 mg / l (M2) and 769.43 mg / l (M3). Sulphates (SO₄²⁻) come from runoff or seepage into gypsum soils. They also result from the activity of certain bacteria (chlorothiobacteria, rhodothiobacteria, etc.). This activity can oxidize sulphuretted hydrogen sulphide (H₂S) to sulphate [13,17]. In 2015, sulphate concentrations ranged from 14.2 mg / l (M1) to 483.4 mg / l (M4). They were below the norm except for the M4 sampling point at Elmalaleynne. The elevation of the concentration of SO₄²⁻ in the M4 point could be due to the bacterial oxidation of hydrogen sulphide (H₂S) from septic tanks and waste from the dairy industry.

Bicarbonates: The content of bicarbonates in groundwater depends mainly on the presence of carbonate minerals in the soil and aquifer, as well as the CO₂ content of air and soil in the catchment [26]. The bicarbonate content of groundwater not subject to anthropogenic influences varies between 50 and 400 mg / l [26]. The median values of bicarbonate contents are around 302 mg / L in the usual

area of unpolluted groundwater [26]. The bicarbonate content of the points studied varies overall from a low of 238 mg / l in 2015 to 67.1 mg / l in 2016 and a high of 805.2 mg / l and 561.2 mg / l in 2016. High values are probably due to the circulation of these waters in the aquifer reservoir of calcareo-dolomitic nature [27].

Nitrates

The nitrate contents measured in the 16 sampling points of the Martil stage remain well below the value allowed by the Moroccan standard which is 50 mg / l with the exception of point M8 (481.9 mg / l) in 2016. Low nitrate values indicate that the waters studied are not subject to nitrate pollution risk, but these values indicate wastewater discharges. The study did not reveal any significant influence of the temporal effect on the nitrate concentrations in the analyzed points. The different variations between the sectors studied are probably due to the different sources of pollution, their locations and their distances from the wells surveyed. Results in agreement with the previous study carried out on the Martil aquifer [28].

Organic Matter (OM)

The concentrations of the organic matter measured are lower than the limit set by the Moroccan standard in all the waters of the sampling points in the year 2015 and the year 2016. The measured values make it possible to qualify the water of the Martil aquifer in excellent to medium quality organic matter.

Spatiotemporal variation of biological parameters in the groundwater of Martil

From a bacteriological point of view, the analysis of the values obtained from the three faecal pollution indicator parameters (total coliforms, faecal coliforms and faecal streptococci) did not reveal bacterial contamination of human and / or animal origin.

The results obtained make it possible to classify the waters of the Martil aquifer in good to excellent quality according to the Moroccan classification of groundwater [29]. The results did not show significant differences over time (2015/2016) (Table 7). The low load of water in bacteria indicative of pollution is due to the fact that the survival of the bacteria and their displacement are influenced by the hydrodynamic characteristics of the aquifer, the physicochemical characteristics of the water table, the anatomic state and physiological germs [30-32].

The aquifer texture of the Martil aquifer is silty clay sand with sandy silts and may contribute to the filtration and adsorption of microorganisms. According to Schoeller, in areas with permeability of interstices such as sands, pollution is only transmitted at a very low speed; the size of the surface of the solid particles allows a significant retention, especially if there are clay particles [33]. The two years of study, are characterized by a reduction of the rainfall with a severe drought in 2016 this which decreases the flow rates of the water and the flow velocity of the water table. According to Jean Ghislain Tabué Youmbi, the maximum distance traveled by microorganisms is essentially determined by the speed of flow of the water table and the extension of bacterial pollution depends on the life span of microorganisms in the water. aquifer. The largest reductions in seed numbers are obtained for low flow rates [34]. In addition, studies on the propagation of bacteria in the saturated zone have shown that as soon as the microorganisms penetrate a saturated zone, they are largely retained at the upper interface of this zone and undergo very little lateral dispersion [34]. While the sodium content determined for all of our samples indicates a high sodium concentration that exceeds the standard in 2016. This one, when it is contained in the water, is likely to lead to an increase in soil alkalinity, to reduce its permeability, especially at the surface, despite possible leaching [35,36].

	Year 2015			Year 2016		
	CT /100 ml	CF/100 ml	SF /100ml	CT/100 ml	CF/100ml	SF /100ml
M1	144	64	320	36	16	18
M2	0	0	0	48	12	24
M3	336	8	148	560	396	88
M4	960	28	96	120	110	24
M5	960	4	188	560	440	8
M6	104	48	0	164	110	36
M7	140	56	112	240	160	40
M8	104	72	72	960	880	48

M9	88	20	32	180	120	20
M10	1360	256	0	30	20	44
M11	900	8	48	560	480	16
M12	800	48	48	100	64	32
M13	600	40	20	190	160	300
M14	424	0	256	816	740	8
M15	860	64	80	50	20	36
M16	860	12	168	280	260	8

Table 7: Biological parameters measured in the waters of the Martil aquifer for the years 2015 and 2016.

Typology of waters of the groundwater of Martil

A Principal Component Analysis (PCA) was performed on samples taken from 16 wells collecting the Martil water table for the two years 2015 and 2016. The analysis carried out is a reduced centered PCA which was performed on a table of 14 variables (pH, CE, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Cl^- , HCO_3^- , NO_3^- , TH, TA, TAC et MO). The interpretation of this ACP will be according to the order of appearance of the results given by the software. The first result of the PCA that appears is the correlation coefficient that is commonly used to estimate the relationship between two variables. It is a simple statistical tool to show the degree of connection between two variables. The correlation matrices for the variables were presented in (Table 8) for 2015 and (Table 9) for 2016. Kaiser's criterion [37] was applied to determine the total number of significant factors. According to this criterion, only factors with an eigenvalue greater than or equal to 1 will be accepted as possible sources of variance in the data. Two main components (CPs) were selected and the results show that the two CPs represent more than 45.92% of the total variance. Factor 1 (axis F1) represents 25.70% of the variance and is determined by the pH, CE, Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^- , TH, TAC et TA. The factor 2 of the PCA (axis F2) is determined by HCO_3^- , NO_3^- and MO. It represents 20.22% of the variables.

Variables	PH	CE	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	TH	TAC	TA	MO
pH	1											
CE	0,375	1										
Ca^{2+}	-0,052	0,481	1									
Mg^{2+}	0,316	0,216	0,131	1								
Cl^-	0,482	0,955	0,312	0,194	1							
NO_3^-	-0,379	-0,166	-0,001	0,483	-0,260	1						
HCO_3^-	-0,116	-0,004	0,450	-0,328	-0,040	-0,359	1					
SO_4^{2-}	0,056	0,138	0,269	0,727	0,016	0,670	-0,157	1				
TH	0,215	0,427	0,641	0,845	0,319	0,374	-0,009	0,709	1			

TAC	-0,115	-0,004	0,450	-0,328	-0,039	-0,359	1,000	-0,157	-0,009	1		
TA	0,759	0,605	0,003	0,317	0,706	-0,088	-0,195	0,288	0,247	-0,194	1	
MO	-0,393	0,137	0,018	-0,334	0,111	-0,210	0,459	-0,171	-0,246	0,459	-0,185	1

Table 8: Pearson correlation matrix between the physical variables and the concentrations of the major elements of the Martil water table for the year 2015.

Variables	PH	CE	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	HCO ₃ ⁻	SO ₄ ²⁻	TH	TA	TAC	MO
pH	1													
CE	0,278	1												
Na ⁺	0,050	0,428	1											
K ⁺	0,019	-0,139	0,002	1										
Ca ²⁺	-0,134	0,514	-0,047	0,383	1									
Mg ²⁺	0,015	0,554	0,365	-0,013	0,177	1								
Cl ⁻	0,213	0,736	0,047	-0,121	0,214	0,240	1							
NO ₃ ⁻	0,246	-0,173	-0,097	-0,056	-0,011	-0,138	-0,101	1						
HCO ₃ ⁻	0,105	0,380	-0,044	0,065	0,225	0,335	0,416	-0,518	1					
SO ₄ ²⁻	-0,185	0,306	0,096	0,356	0,710	0,216	-0,107	0,154	0,065	1				
TH	-0,041	0,690	0,212	0,362	0,887	0,577	0,281	-0,092	0,378	0,716	1			
TA	-0,717	0,338	-0,063	-0,203	0,152	-0,140	0,279	0,607	-0,106	0,082	0,095	1		
TAC	0,278	0,325	-0,112	-0,006	0,244	0,297	0,421	0,127	0,781	0,170	0,365	0,318	1	
MO	-0,067	-0,391	0,106	-0,072	0,270	0,250	0,125	0,141	0,208	0,093	0,301	0,130	0,353	1

Table 9: Pearson correlation matrix between the physical variables and the concentrations of the major elements of the Martil water table for the year 2016.

The analysis of PCA variables in factorial F1-F2 reveals two large groupings of the parameters studied in the groundwater of the Martil water table for the two years of study 2015 and 2016 (Figures 1, 2). respectively). The first grouping around the factorial axis F1 and which takes into account pH, CE, Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻, TH, TAC and TA, shows a mineralization of the water by the phenomenon of dissolution of the rock. The factor F1 thus defines an axis of global mineralization of the water. However, the groupings on either side of this axis show that these elements come from two different dissolution mechanisms. Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻ arise from rock weathering after a long water-rock contact time and acid hydrolysis of minerals. The low correlation of pH with CE, TH, Na⁺, K⁺, Mg²⁺, SO₄²⁻, Cl⁻ and Ca²⁺ (Tables 8, 9) shows that the redox mechanism predominates over that of acid hydrolysis [38]. The factor F1 is therefore an axis of global mineralization of the water by the phenomenon of dissolution of the rock following a long water-rock contact time (mineralization residence time by acid hydrolysis of the minerals) and the oxidation-reduction which is the dominant mechanism in the acquisition of ions in the groundwater of the region. Common sources of chlorides (Cl⁻) are halite (NaCl) and minerals related to evaporite deposits. They are also found in marine sediments and in coastal environments [39]. The second grouping around the F2 axis and takes into account HCO₃⁻, NO₃⁻ and MO. This factor is therefore an axis of mineralization by anthropic action.

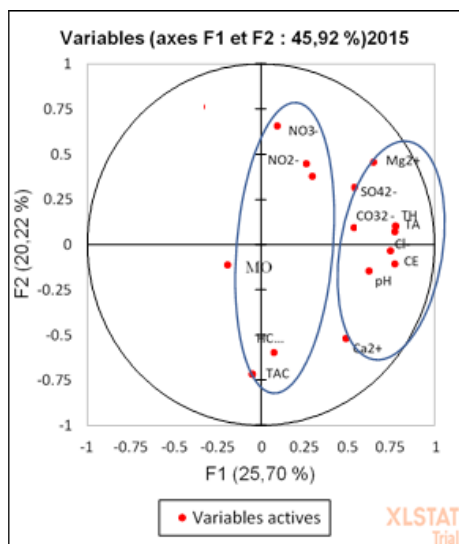


Figure 1: Correlation Between Variables and Factors 2015.

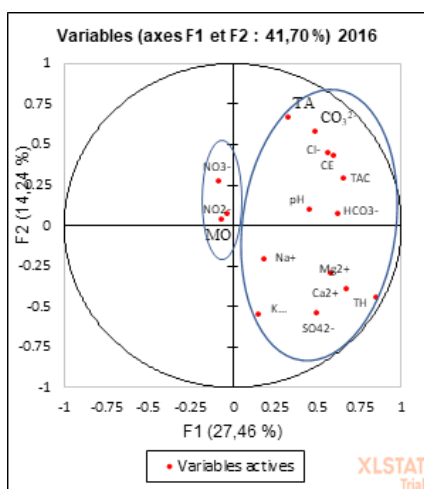


Figure 2: Correlation Between Variables and Factors 2016.

The graphical representation of the variables and sampling points shows, overall, according to the physicochemical quality of their waters, four groups in 2015 (Figure 3) and three groups in 2016 (Figure 4):

In 2015: Group1: Water marked by high levels of electrical conductivity and high levels of minerals especially chlorides. These are sampling points M4, M13 and M16. Overall, they are the most heavily loaded with dissolved inorganic materials and reflect a pollutant load contained in domestic, industrial and agricultural leaching water from the upstream basin. These points represent poorly maintained wells located in an area characterized by major anthropogenic pollution caused mainly by the total absence of a liquid sanitation system, the existence of unstandardized and

overloaded septic tanks, the existence of the polluted dead arm of Martil, the dilapidated and mediocre management of household waste.

Group 2: these are the points represented by the F2 axis positively correlated with the nitrates M12 (NO_3^- : 13.19mg / l and M15 (NO_3^- : 1.85mg / l). These measured concentrations remain below the limit set by the Moroccan standard This can be explained by the phenomenon of self-purification [27,40]. However, the chloride-nitrate combination (M12: Cl $^-$: 390 mg / l and M15: 482mg / l) indicates that the origin of these two elements comes from animal husbandry, amendments and / or wastewater [41]. These wells are located in the Jbala sector characterized by the total absence of liquid sanitation network and the existence of unstandardized septic tanks in addition to agricultural and livestock activities. While the number of people living in this sector is small, human activity remains water is average.

Group 3: These points are correlated with HCO_3^- ions. This is the water taken at points M6 and M9 located at Martil and M14 located in Azla (Jbala). HCO_3^- ions can come from the dissolution of dolomitic limestone and dolomite which makes up the ground of the aquifer. [18,25,27,42], as they can come from the reduction of nitrates by anaerobic bacteria using nitrates as a source of O_2 according to the reaction:



These points reflect water from bad to very bad quality. This result is explained by the situation of these points in the extreme downstream of the aquifer. They receive the pollutants brought from the upstream basin. In addition, the sector is characterized by the complete absence of liquid sanitation and the existence of non-standardized septic tanks and high residential density in addition to agricultural activity.

Previous studies have shown that groundwater quality in the Loukkos, Tangier and Mediterranean Coastal basins, located in northern Morocco, remains a function of anthropogenic actions and that quality is very poor at the level of Martil aquifers [44].

Group 4: These waters are characterized by the lowest levels of chemical variables. They are taken at the M1, M2, M3 and M11 wells located in the city of Tetouan and points M5, M7 and M8 located in the city of Martil. These points are located in areas where the sources of urban pollution are minimal through the installation of the sewage network and sewage treatment plants. These points reflect waters of good to medium quality.

The sampling point M10 located at Azla (Jbala) is not represented by any correlation axis. It has a value of the electrical conductivity (CE: 1050 $\mu\text{S} / \text{cm}$) according to the Moroccan standard (CE <2700 $\mu\text{S} / \text{cm}$). So the water from this sampling point has low levels of minerals.

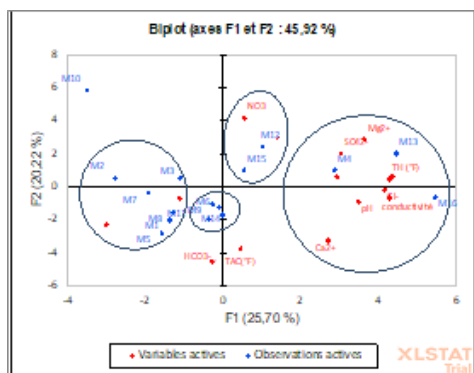


Figure 3: Projection of the sampling points on the F1 and F2 plan for the year 2015.

In 2016:

PCR analysis of the physicochemical parameters made it possible to group the sampling points into 3 groups according to their correlation with the F1 and F2 axes (Figures 3, 4). This grouping reflects the same water quality results studied as in 2015. In fact, the sampling points located downstream of the water table and the points located in the sectors characterized by the total absence of liquid sewerage network and the existence of unstandardized septic tanks and high residential density present poor to very poor quality water. The points located in areas where the sources of urban pollution are minimal through the installation of the sewage system reflect good to medium quality water. An exception is observed at points M7 and M10 which have experienced a rise in conductivity levels and the water quality at these points has deteriorated. This increase in conductivity can be explained by increases in the concentrations of minerals in the water due to the severe drought that marked the year 2016. The concentrations during the dry period are higher than during the wet period; This can be explained by the decrease in the level of the water table during the dry period and the influx of rainwater which leads to a dilution resulting in the decrease of the levels in different elements [35].

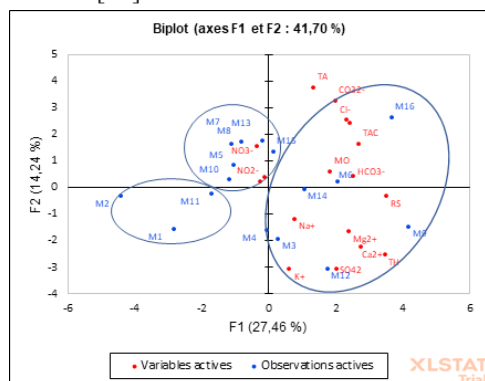


Figure 4: Projection of the sampling points on the F1 and F2 plan for the year 2016.

Conclusion

This study has shown that the waters of the Martil aquifer are classified as good to very bad by going from the upstream to the sea coast. The electrical conductivity and the chloride ions are responsible for the classification of the waters of the aquifer in poor quality, to very bad. The concentrations of the other parameters remain below the values recommended by the Moroccan standard. the waters of the Martil aquifer are relatively very mild to moderately hard and of low alkalinity mainly due to bicarbonate ions (HCO_3^-).

The low load of water in bacteria indicative of pollution arises from the fact that the texture of the aquifer of the Martil aquifer is of silty-clay sand with sandy silts can contribute to the filtration and adsorption of microorganisms. Principal component analysis revealed mineralization of water by the phenomenon of rock dissolution following a long water-rock contact time and oxidation-reduction. The low correlation of pH with CE and the main minerals (Na^+ , K^+ , Mg^{2+} , SO_4^{2-} , Cl^- and Ca^{2+}) shows that the oxidation-reduction mechanism is dominant in the acquisition of ions in the groundwater of the region.

The ACP grouped the water sampling points into homogeneous groups according to their mineral content, their geographical location and their approximation to the sources of pollution. Overall, the results did not show a significant difference between the two years of study 2015 and 2016.

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