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STUDY AND EVALUATION OF THE PHYSICO CHEMICAL GROUNDWATER QUALITY OF AN AGRICULTURAL REGION AROUND BENI MELLAL CITY

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ABSTRACT

An attempt was made to find whether or not the quality of ground water in the areas of study suitable for human consumption. Ground water samples were collected from wells in different locations within a radius of 25 km of Beni mellal city. These water samples taken from 10 sampling points in each one of 4 areas were analyzed for their physicochemical characteristics. The results show that the conductivity in the four areas is an average of about 1138 μScm^{-1} that is far exceeds the national standard and WHO regulatory limit of about 500 μScm^{-1} . The pH is in the range of values that was found usually in the groundwater. The turbidity in some samples recorded 4.74 NTU which is strictly achieved maximum limit 5 NTU for WHO norms of acceptable water for human consumption that it must be below 1NTU. The high values of turbidity are due to high soil erosion. The values of chlorides have recorded 550 and 750 mg l^{-1} in some sample in the 4 areas, which are higher than the permissible safe limit of about 250 mg l^{-1} . This could give water an aggressive (corrosive) character and can so free the constituent metals of the pipelines, which are toxic for human. The values of the total hardness of the water (TH) ranges between 159.2 mg l^{-1} of CaCo_3 (15.9 $^\circ\text{F}$) and 308.8 mg l^{-1} of CaCo_3 (30.8 $^\circ\text{F}$) in 4 areas. This value is also within the hard level. The Complete Alkalimetric Title CAT in many samples presents an average of about 329.2 mg l^{-1} , which is above the prescribed limit 250 mg l^{-1} . Magnesium and calcium are slightly overcoming the desirable limit of 100 mg l^{-1} , but remain below permissible limit of about 150 and 200 mg l^{-1} . The average value of nitrate NO_3^- of about 60.3 mg l^{-1} is higher than permissible limits in order of 50 mg l^{-1} , sometimes the value has overcome 133 mg l^{-1} . However, the contents in nitrites, and ammonia are very lower than all the standards. The same thing for sulphates SO_4^{2-} has not overcome permissible limit. The parameter DO or dissolved oxygen of these waters are good. The results of these analyses were treated by multivariate statistical methods including Principal Component Analysis normalized (PCA) and cluster analysis. The application of Principal Component Analysis normed to these results shows that there is a close relationship between all chemical and physical parameters of the groundwater. The analysis of the plan factorial F1 and F2 shows that more of 49 % are well expressed. The analysis in this plan shows that all parameters are expressed and represented well. A meaningful interrelationship has been demonstrated between the electric conductivity and the chloride ($r=0.86$), Calcium ($r=0.8$) *et also* with the nitrate ($r=0.77$). There is also a good interrelationship between chloride and calcium ($r=0.68$) and magnesium ($r=0.6$). From these results, this study shows that the water resources of the studied areas are strongly influenced by human activities regarding nitrate and this is probably due to an agricultural contamination by nitrogen fertilizers, and/or to infiltration of wastewater to waters underground. So, groundwater in region requires precautionary measures before to drinking them so as to prevent adverse health effects on human beings. As well as, it should awareness of the local population on the importance of protecting water quality and to establish strategies for exploiting their natural water resources.

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INTRODUCTION

Water, an element necessary for any survival on Earth provides a basis for human development. Indeed, the establishment and expansion of human settlements, the installation of many industries and the intensification of agriculture are closely linked to the presence in sufficient quantity of this natural source. However, on Earth quantitative distribution of water is not uniform.

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Indeed, under the influence of their types of climate, some areas of the globe, receive only a small amount of this irreplaceable treasure (Saad, 2011). Groundwater is of critical importance in most parts of the world. However, this resource was once good, is currently threatened by a variety of point and diffuses sources of contamination (Amadou, 2014). Water can also be a source of disease because of its contamination with household waste, industrial, agricultural and other organic wastes (OMS, 2003). The chemical composition of water from the natural environment is highly variable. It depends on the geological nature of the soil where it came from, as well as the reactive substances that would meet it when flowing. So the

quantitative and qualitative composition of the groundwater suspended solids and dissolved, inorganic or organic nature indicate its quality (Jain *et al.*, 2005). This quality can be impaired when external substances come into contact with the aquifer. Such it is the case of toxic or undesirable substances that make groundwater unsuitable and toxic for various uses including its use as drinking water. The intensive use of natural resources and increasing human activities has caused serious problems on groundwater quality (Foster, 1995). In Morocco, the region of Beni Mellal Tadla perimeter is one of the most important agricultural regions in Morocco. The resources in agriculture and drinking water are provided by the karstic massif of the Atlas and the shallow and deep aquifers in the Tadla plain (Bouchaou *et al.* 1997). These sources, of course with good quality water, are very vulnerable to any kind of pollution due to human actions and the influence of climate variability (Saad, 2011). In the aim, to contribute in the control of quality of groundwater for drinking and irrigation in this agricultural region, we made a study that focuses on the evaluation of the physico-chemical quality of water on several samples from different sites. These results were compared to local and international standards for water potability. As well as, statistical methods has been used to deduce the relationship between the all of parameters.

Study Area

Situated at 200 km from the SE of Casablanca, to a middle altitude of 400 m, it is limited in the North by the Tray Central and dominated to the Sud by the summits of the Middle Atlas (jbel R'Nim: 2404 m and Tassemit jbel: 2247 m, in the S and to the SE of Beni Mellal, respectively). The Middle Atlas, is much reduced in width, is tangent to the High Atlas, of which it is only separated by a set of enough narrow synclinaux that makes continuation, toward the West, to the valley of the Moulouya. To the Est, the depression of the Tadla comes to end in corner, between the tray of Zem wadi and the retom-agape atlasique. It continues, beyond the wadi El Abid (Massoni and Missante 1967). The zone studied Ouled Ali is among the most important agricultural zones that produce Niora red pepper, it is to 15 Km of the city of Beni Mellal.

Climatology

The survey of the climatic data is necessary for understanding of the mechanisms of feeding and circulation of the superficial and underground waters. They permit to approach the elements of balance that are the precipitations and the evapo-transpiration. The morphology shows a terracing between 500 m (piedmont named Dir) and 2400 m (mountain). The region receives a height of yearly middle rain going from 400 mm (plain and piémont) 700 mm (in mountain). The yearly middle temperature is the order of 19°C, the seasonal variations are important and the daily gap can reach 20°C. The yearly efficient rain is the order of 100 mm on the plain and the Dir and of 300 mm on the Atlas (Bouchaou *et al.*, 1997).

Hydrography

The resources of underground waters of the survey zone come essentially from the complex aquifer composed of the mio-plioquaternaire tablecloth of the Tadla plain subdivided hydraulically in two independent tablecloths situated on both sides of the wadi Oum Er Rbia. The groundwater of Beni Amir to the North (right strand of the wadi Oum Er Rbia) and the

tablecloth of Beni Moussa at the South (left strand of the wadi Oum Er Rbia) (EAC 2010).

Beni Amir

The groundwater circulates in the lacustrine limestones that rest (40 -50 m of depth) on impervious clays. It is nourished naturally by very weak contributions, this groundwater was therefore enough deep (30 to 40 m). But the setting in water of the perimeter of Beni Amir, equipped with channels in earth that are dragging a fast remontie of the level until less than 2 m on vast surfaces. The importance of these ascents also explains itself by the presence, to the downstream, of the perimeter, of a clayey doorstep that slows down the out-flow strongly toward the SW of the tablecloth (Massoni and Missante, 1967).

Beni Moussa

The lands in which circulate the groundwater are extremely heterogeneous: chalky, marno-chalky and clays more or less permeable. The passages, lateral and vertical, of some to the other are being very rapid. The groundwater of Beni Moussa is therefore very complex. Its natural food is assured by rains, relatively important on the north face of the Atlas, and by the rise of the water spraying on the piedmont. Since some years, adding to the losses of irrigation water. There was ascents of the level, but less important and less general than in Béni Amir. On the whole, the out-flow of waters makes itself toward the N-NW, the slope varying strongly (Massoni and Missante, 1967).

The Salinity

The mineralogical quality of the waters of the groundwater is globally much damaged. The comparison of the relative electric conductivities to the campaigns of August 1978 and November 1995 shows a spectacular increase of the mineralization that puts a serious risk because of the extent of the problem (Faouzi, and Larabi, 2001). Beni Moussa: The gradient of saltiness increases toward the west (of the upstream toward the hydraulic downstream). The average of the saltiness varies from 1.18 dSm⁻¹ in Beni Moussa of the East to 3.98 dSm⁻¹ in Béni Moussa of the west. Beni Amir: The groundwater is salted more than the one of Beni Moussa, the middle saltiness varies of 3.27 upstream to 5.8 dS m⁻¹ hydraulic downstream (Saaf, 2009).

MATERIALS AND METHODS

The 20 sampling (on 4 sites) have been done every 8 day, from the borings and the wells of the studied area. The analyses immediately took place after sampling in the laboratory of the analyses physicochemical of ONEP (National Office of drinking water) to Beni Mellal. The studied physicochemical parameters are: the temperature, the pH, the conductivity, the turbidity, TH, TAC, the chlorides, calcium, magnesium, the oxydability, the dissolved oxygen, ammonium, nitrate, nitrite and sulfates. The methods used are those adopted by the ONEP in conformity with the Moroccan norm (03.7.001) and the instructions of WHO (1993) for determination of Quality of drinking water. The pH and the temperature have been determined by one pH-meter provided with a probe measuring the temperature. The conductivity has been measured by a conductivimeter. The chlorides are measured by the volumetric method to the mercuric nitrate. The ions calcium

and magnesium are measured out by complexometry with the help of a solution of ethylene di-amine tetra acetic acid (EDTA) (Rodier 1996). The complete alkalimetric title (CAT) has been analyzed by volumetric dosage with the HCl 0.1N. The dissolved oxygen is determined by the thiosulfate of sodium. The oxydability has been determined by oxidization to hot in acidic environment. The ions ammonium, the sulfates, the nitrates and the nitrites are analyzed by colorimetric methods with the help of an UV-visible molecular spectrophotometer. The ions ammoniums are determined by method to the bruise of indophenols and the measure was made to a wave length of 630 nm. The ions sulfates are precipitate in the hydrochloric acid containing barium and then are measured to a length of wave of 630 nm. The nitrates are reducing in nitrites by the method of Column reduction, and then measured to a length of wave of 540 nm. The nitrites are determined in acidic environment in presence of NED: N - (1 Naphthyl) ethylene diamine) and has been measured to a length of wave of 540 nm.

Principal component and cluster analysis

Comparison of the averages was carried out by ANOVA test post-hoc Tukey. Principal components analysis (PCA) and cluster analysis were carried out between different parameters. The PCA has for objective to present one maximum of information graphically in a picture of data, on the basis of the principle of the double projection on the factorial axis. This statistical method permits to transform the initial quantitative variables; all are more or less in relationship to each other, to new quantitative variables, non correlated, which are named principal components. The interrelationship between the factors and variable and the projection of the variables in the space, the F1 and F2 axes and the matrixes of intermediate interrelationships have been gotten with software XLSTAT 2014.

RESULTS AND DISCUSSIONS

The aim of the present study is to determine the extent of ground water contamination under antropic and agricultural area. The physicochemical parameters examined for each of the water points within 4 areas are presented in the table 1. The comparison of the values has been made against national norms (03.7.001) for water suitable for human consumption and WHO standards (1993). The results indicated that the quality of water considerably varies from location to other location. These parameters are discussed below:

Temperature

Temperature is one of the most important factors in aquatic environment (Singh *et al.*, 2005). Temperature affects solubility of oxygen in water, the solubility of oxygen in water increases with decreasing temperature (Joshi *et al.*, 2001). It plays one a role in the solubility of gases, in the dissociation of salts dissolved and so on variability of pH, it also acts on the density, the viscosity, as well as on the chemical and the biochemical reactions, on development and the growth of living organisms in water and in particular the micro-organisms (WHO, 1993). Indeed, even moderate changes in water temperatures can have serious impacts on change of those physicochemical parameters and on aquatic life, including bacteria, algae, invertebrates, etc (Choudhary *et al.* 2011). So it is important to know the temperature of water constantly. In studied samples, water temperatures fluctuate

naturally both daily and seasonally. The water samples were collected and analyzed between March to July. The temperature of water ranged from 21- 25°C. According to the norms of drinking water fixed by the WHO (1993), water is excellent when the temperature varies between 20 and 22°C; tolerable when the temperature oscillates in the interval of 22 - 25°C; middling when it is understood between 25 and 30°C.

The potential of hydrogen (pH)

The acidity of water doesn't pose in itself any problem opposite the consumer's health. However, the acidic water distributed by a network of pipelines can constitute a threat indirectly for the health of the ill-informed or imprudent consumer. The acidic water is indeed aggressive (corrosive) and can free the constituent metals of the pipelines (in interior to the dwellings), to know iron, the copper, lead, the nickel, the chromium and zinc (Hanon and Rouelle 2011). In the literature, the values of the potential Hydrogen are located between 6 and 8.5 in the natural waters (Chapman *et al.*, 1996). The values of pH of our samples are acceptable (7.0 to 8.5) compared to the norm of WHO (6.5-8.5) (Table 1).

The turbidity

The turbidity is an optical parameter that express the optic properties of a water to absorb or / and to distribute light. It is due to the presence of matters in finely divided suspension as like clays, silts. The suspension of particles in water that is interfering with passage of light is called turbidity. Turbidity is caused by wide variety of Suspended particles. Turbidity can be measured either by its effect on the transmission of light which is termed as Turbidimetry or by its effect on the scattering of light which is termed as Nephelometry (Arya *et al.* 2014). The recorded values within our samples are acceptable between 0.14 and 4.74 NTU according to the Moroccan norm (Table 1). The World Health Organization establishes that the turbidity of drinking water should not be more than 5 NTU, and should ideally be below 1 NTU.

The conductivity

The conductivity represents one of the means to validate the physicochemical analyses of water, indeed measured contrasts of conductivity on an environment allow to put in evidence of the pollutions, of the zones of mixture or an infiltration, etc. In fact, according to Rodier (2009), the conductivity allows to appreciate the degree of water mineralization in so far as most matters dissolved in water are electrically as loaded ions. The conductivity is also function of the water temperature, it is more important when the temperature increases. The values recorded during the analyses of our samples are important, it varies between 851 and 1585 $\mu\text{S}/\text{cm}$, the average in the four areas is of about 1138 $\mu\text{S}/\text{cm}$. These values far exceed the WHO regulatory limit of 500 $\mu\text{S}/\text{cm}$ indicating relatively the high salt contents and the high amount of dissolved inorganic substances in ionized form. This shows that the waters of this region are relatively strong, and this is may be in relation with the anthropogenic activities as like as high agricultural activity or contamination by the garbage and the sewage in the agglomerations neighbor due to lack of purification system.

The chlorides

The chlorides are are widely distributed in nature as salts of sodium (NaCl), potassium (KCl), and calcium (CaCl₂). Their

content in waters is very variable and related mainly to the nature of the lands crossed. The recorded values in our samples oscillate between 88, 216, 550, 750 mg l⁻¹ in the 4 areas with a mean of 148,3 mg l⁻¹. These values are sometime higher than the WHO permissible safe limit of 250 mg l⁻¹. However, they are in conformity with the local norm of the drinking water, where the chlorides must have content lower to 750 mg l⁻¹ in the waters of human consumption (Norm Moroccan 1991). According to (Amoako *et al.*, 2011), the levels at these measurements may decrease the drinking quality of water due to the taste, as well as they lead to the corrosion of metals. Janardhana *et al.* (2013) have reported that chloride a major anion in potable and industrial water has no adverse effect on health, but imparts bad taste to drinking water. People accustomed to higher chloride in water are subjected to laxative effects.

less than 61 mg l⁻¹ is considered soft; 61-120 mg l⁻¹, moderately hard; 121-180 mg l⁻¹, hard; and more than 180 mg l⁻¹, very hard. In our study, the values of the total hardness of the water (TH) is ranges between 159.2 mg l⁻¹ of CaCO₃ (15.9 F °) and 308.8 mg l⁻¹ of CaCO₃ (30.8 F °) in the 4 areas. This value is within the hard level. However, none of the samples has crossed the maximum permissible limits of 500 mg l⁻¹ (WHO standards) as well as of national norms (600 mg l⁻¹ of CaCO₃). The undesirable effects that are especially of order organoleptic or aesthetic resulting from the presence of the calcium in the drinking water can come of its contribution to the toughness (AWWA, 1990). Generally, the water containing excess hardness is not desirable for drinking. The taste threshold for the calcium ion is in the range of 100–300 mg l⁻¹, depending on the associated anion, and the taste

Table 1. Water quality parameters for four areas around Beni Mellal city

Parameters	Units	Minimum	Maximum	Average	Standard deviation	Standard and WHO permissible limit
pH		6.81	7.37	7.14	0.13	6.9-9.2
Température	°C	21.2	25.00	23.44	1.13	
conductivity	µScm ⁻¹	851.0	1585	1138.3	244.4	300-500
turbidity	NTU	0.14	4.74	1.4	1.43	1-5
TH	mg l ⁻¹	159.2	308.8	217.4	47.94	100-500
CAT	mg l ⁻¹	189.1	390	329	47.9	250
Cl ⁻	mg l ⁻¹	88.75	216.5	148	37.0	200-600
SO ₄ ²⁻	mg l ⁻¹	16.79	73.5	40.42	15.44	200-400
NO ₃ ⁻	mg l ⁻¹	9.96	133	60.2	31.5	40-50
NO ₂ ⁻	mg l ⁻¹	0.002	0.050	0.014	0.013	0.5-3
NH ₄ ⁺	mg l ⁻¹	0.014	0.241	0.043	0.048	0.3-1.2
Ca ²⁺	mg l ⁻¹	84.8	192	140	33.2	100-300
Mg ²⁺	mg l ⁻¹	38.4	132	74.2	25.4	30-150
Oxygen Dissolves	mg l ⁻¹	5.08	7.84	6.41	0.79	-
Oxydability	mg l ⁻¹	0.40	2.26	0.90	0.44	-

They reported also that the chloride concentration serves as an indicator of pollution by sewage. Chloride concentration in water indicates presence of organic waste particularly of animal origin. Increase in chloride concentration in discharge of municipal and industrial waste has been reported (Priyanka *et al.*, 2010). As well as, the high chloride levels may be attributed to natural geochemical activities. Many of the major aquifers yield a calcium bicarbonate type water in and near outcrop areas. Also, these high concentrations could be due to greater amounts of evaporite minerals, such as anhydrite and gypsum, available for dissolution (Naus *et al.*, 2001). So, the dissolution of evaporite minerals and long residence time also are possible explanations for the occurrence of this water type (Naus *et al.*, 2001). The chlorides ions may react with the water producing hydrochloric acid which leads locally to a decrease of pH of waters. This acidity presents the inconvenience of corrosion in case of contact with copper pipe when the content in chlorides is upper to 150 mg l⁻¹ (Hanon and Rouelle 2011). In some samples, the values exceed this threshold value and present also another risk, that a high content can lead to the formation of organohalogene compounds that can lead to mutagenic and carcinogenic effects (Guergazi and Achour, 2005).

Total hardness

Total hardness of water is not pollution parameter but indicates water quality mainly in terms of Ca²⁺ and Mg²⁺ expressed as CaCO₃ (De, 2006). The calcium is generally the dominant element of the drinking waters and its content varies essentially following the nature of the lands crossed (chalky or gypsies land) (Rodier *et al.*, 2009). Water that has a hardness

threshold for magnesium is probably lower than that for calcium. In some instances, consumers tolerate water hardness in excess of 500 mg l⁻¹. Depending also, of the interaction of other factors, such as pH *et* alkalinity, water with hardness above approximately 200 mg l⁻¹ may cause scale deposition in the treatment works, in distribution system and in the pipework and in the tanks within buildings. It will also result in excessive soap consumption and subsequent "scum" formation (Mostafa *et al.* 2013). On heating, hard waters form deposits of calcium carbonate scale. Soft water, with a hardness of less than 100 mg l⁻¹, may, on the other hand, have a low buffering capacity and so be more corrosive for water pipes (Remia and Logaswamy, 2010).

CAT (Complete Alkalimetric Title)

The alkalimetric total title corresponds to water content in free alkaline, carbonates and hydrogen carbonates which originally comes from the limestone bedrock of the watershed that gives water its bicarbonate nature. The Complete Alkalimetric Title of samples varied from 189.1 mg l⁻¹ to 390.4 mg l⁻¹, with average of about 329.2 mg l⁻¹. The highest desirable limit prescribed by WHO is 250 mg l⁻¹ for drinking purposes. So, the alkalinity is in many samples above the prescribed limit. However, the alkalinity characteristic has been demonstrated contribute in the stability of water by control its aggressiveness to the pipes and appliance (WHO, 2006). In fact, for some metals, alkalinity (carbonate and bicarbonate) and calcium (hardness) also affect corrosion rates. Successful control of iron corrosion has been achieved by adjusting the pH to the range 6.8–7.3, hardness *et* alkalinity to at least than 40 mg l⁻¹ (as calcium carbonate). In the case of the lower values, the

application of lime and carbon dioxide to soft waters could be used to increase both the calcium concentration and the alkalinity as calcium carbonate.

Table 2. Values and percentages expressed for the main axes

	F1	F2
Clean Valeur	4.757	2.105
Variability (%)	33.976	15.036
% cumulated	33.976	49.013

Table 3. Correlation between the variables and the factors

	F1	F2
pH	-0.611	0.238
Température	-0.099	0.734
Conductivity	0.956	0.140
Turbidity	-0.084	-0.544
TAC	0.606	0.078
Cl ⁻	0.801	-0.155
SO ₄ ²⁻	0.521	-0.580
NO ₃ ⁻	0.779	0.249
NO ₂ ⁻	0.573	0.248
NH ₄ ⁺	0.176	-0.250
Ca ²⁺	0.718	0.325
Mg ²⁺	0.721	-0.290
dissolved oxygen	0.214	0.661
Oxydability	0.354	-0.116

Calcium and Magnesium

Determination of calcium hardness indicates that the value ranges from 84.8 to 192.0 mg l⁻¹. WHO prescribed desirable limit for calcium concentration as 100 mg l⁻¹ and permissible limit as 300 mg l⁻¹ (WHO, 2011). So the values of our samples are in this range and show that calcium content has no injurious effect on human consumption. For Magnesium, it is usually occurs in lesser concentration than calcium due to the fact that the dissolution of magnesium rich minerals is slow process and that of calcium is more abundant in the earth's crust (Geetha *et al.* 2008). In the present study, all the ten samples have shown magnesium values ranges from 38.4 to 132.0 mg l⁻¹ with average of about 74.16 mg l⁻¹. The values are often within the permissible limit of about 100 mg l⁻¹ (WHO, 2011). So, the magnesium and calcium have slightly overcome the desirable limit of 100 mg l⁻¹, but remain below permissible limit of about 150 and 200 mg l⁻¹.

Dissolved oxygen

The dissolved oxygen measures the concentration of the dioxygen dissolved in water (Rodier 1984) he participates in the majority of the chemical and biologic processes in aquatic environment. Dissolved oxygen is an important parameter in water quality assessment and biological processes prevailing in the water. The DO values indicate the degree of pollution in the water bodies. The presence of dissolved oxygen (DO) enhances the quality of water (Janardhana *et al.* 2013).

An ideal DO value is of 5.0 mg l⁻¹ that present the standard for drinking water (Bhanja and Ajoy, 2000). Dissolved oxygen (DO) of water samples in the four studied areas determined in the present investigation ranged between from 5.08- 7.84 mg l⁻¹. The middle content in the waters of the survey region is the order of 6.41 mg l⁻¹ (Table 1). These waters can be so classified in the category of the good quality waters concerning its oxygen contents NM 03.07.001 /1991). Oxygen is supplied to ground water through recharge and by movement of air through unsaturated material above the water table.

Maheshwari *et al.* (2011) reported that the value of DO increases in winter due to circulation of cold water as well as the high solubility of oxygen at low temperature.

Nitrogenous compounds

Nitrate

Concerning the nitrogenous compounds, the nitrate NO₃⁻ of which the contents in the water, especially subterranean water, is of a major importance to determine also the quality of the water and the related sanitary risks (Janardhana *et al.* 2013). The high nitrogen content is an indicator of organic pollution. It results from the added nitrogenous fertilizers, decay of dead plants and animals, animal urines and feces, etc. They are the product of the organic nitrogen oxidization by the microorganisms in soil or water. The sources of nitrates in the underground waters consist of the animal and plant matters in decomposition, the agricultural manures, manure, the domestic worn-out waters and the geological formations containing soluble nitrogenous compounds or also of industrial origin (chemical industries, manure, nitrogenous, factory of ice, textile industries...) (Kanmani and Gandhimathi, 2013). The increase in one or all the above factors is responsible for the increase of nitrate content (Rahman, 2002). In the present study, the NO₃⁻ has registered values in the range of the 9.96 - 133.0 mg l⁻¹ with the average of 60.3 mg l⁻¹ (> the WHO standard 50 mg l⁻¹) (Table 1). So, the main reason of the presence of nitrates in subterranean waters could be due to the agricultural practices in the sampling fields, and which are originated from abundant use of industrial fertilizers strongly charged in nitrate. The latter reaches subterranean waters by the land- infiltration (Najih *et al.* 2014).

This contamination could be also coming from others anthropic origins such as excessive use of manures and the pesticides, or domestic by the worn-out waters: detergents, soaps and housekeeping products and (the septic tanks) and poor sanitation. While, the excessive presence of nitrate can provoke an important problem of public health such as the methemoglobinemia of the infant (syndrome of the blue baby), as well as a risk of cancer (USEPA, 2004). So, although that this risk of reduction of the capacities of transportation of the oxygen by the hemoglobin of blood, for the adult, is weak. At the time of exhibitions repeated on the long term, the nitrates participate in the formation of nitrosamines, molecules whose carcinogenic character is established (Pontius, 1993; Ward, 1996). Sutton *et al.* (2011) have reported that more than 10 millions of European are exposed to rates of nitrates in the drinking water that overcome the authorized doorsteps with a risk of cancer increased if they drink them regularly. Moreover, the high nitrate level in drinking water may adversely affect the central nervous system (Chern *et al.*, 2005). Prasad and Ramesh (1997) explained that the high nitrates level is the indicative of high pollution load. Mason (1991) has observed the increased levels of nitrates by intrusion of sewage and industrial effluents into the natural water.

Nitrite

Nitrites are also veritable indication of biological pollution in natural waters (Addo *et al.*, 2013). The presence of nitrites in elevated concentrations is also an indication of organic pollution in the water body.

Table 4. Correlation Matrix of the various water quality parameters

Variables	pH	T°	Condu.	Turbi.	TAC	Cl ⁻	SO ₄ ⁻²	NO ₃ ⁻	NO ₂ ⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	dissolved oxygen	Oxydability
ph	1													
Température	0.006	1												
conductivity	-0.515	0.012	1											
turbidity	-0.048	-0.250	-0.125	1										
TAC	-0.336	-0.084	0.462	-0.232	1									
Cl ⁻	-0.510	-0.080	0.861	0.183	0.246	1								
SO ₄ ⁻²	-0.287	-0.475	0.366	0.102	0.265	0.395	1							
NO ₃ ⁻	-0.342	0.043	0.775	-0.069	0.477	0.542	0.128	1						
NO ₂ ⁻	-0.222	-0.124	0.504	-0.211	0.298	0.249	0.297	0.428	1					
NH ₄ ⁺	-0.188	-0.048	0.131	0.431	0.077	0.168	0.149	0.014	0.100	1				
Ca ²⁺	-0.317	0.142	0.806	-0.162	0.451	0.688	0.142	0.486	0.456	0.058	1			
Mg ²⁺	-0.554	-0.278	0.664	-0.023	0.334	0.600	0.442	0.625	0.184	0.080	0.145	1		
dissolved oxygen	0.170	0.419	0.271	-0.117	0.074	-0.004	-0.137	0.364	0.403	0.151	0.178	0.042	1	
Oxydability	-0.076	0.043	0.211	-0.149	0.374	0.029	0.650	0.175	0.199	-0.022	0.116	0.204	0.034	1

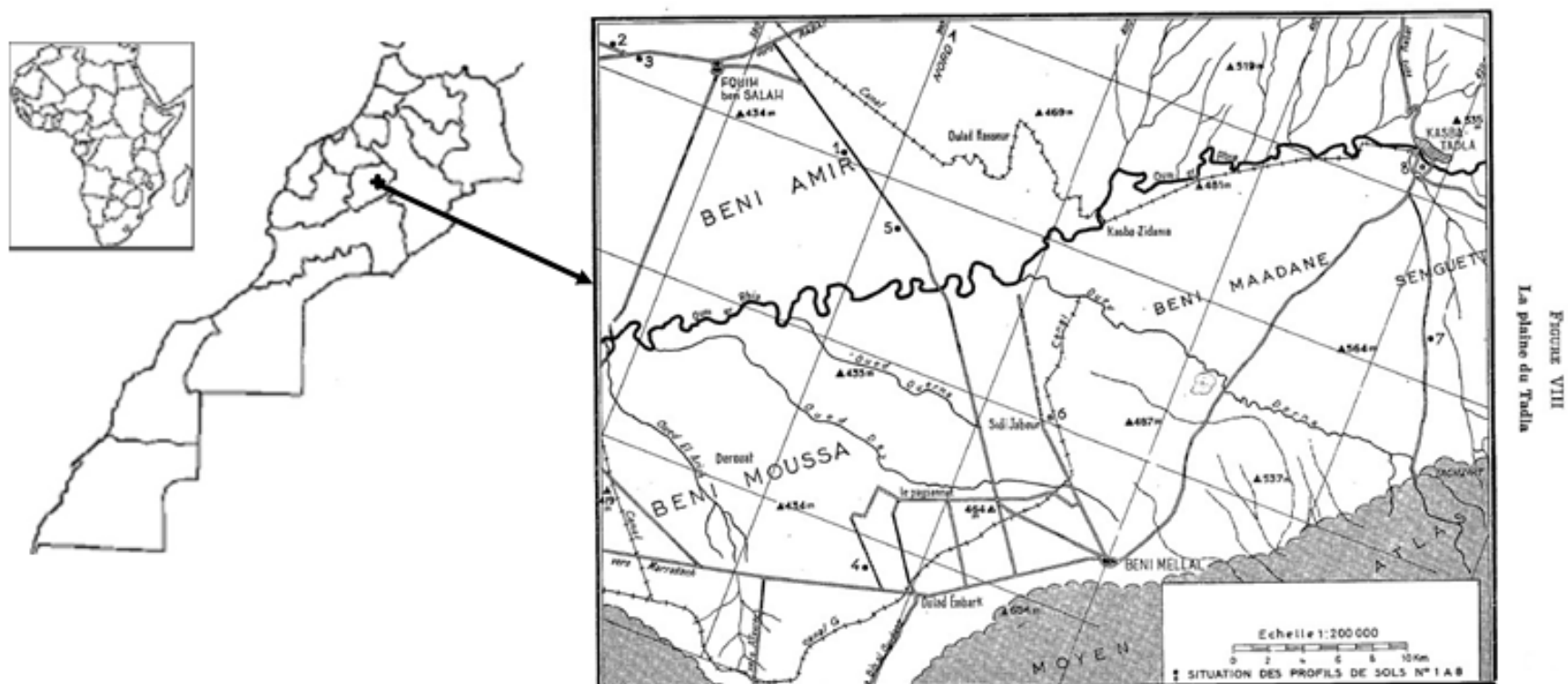


Figure 1. The map of the plain of Tadla (Massoni and Missante, 1967)

Some authors have reported that the presence of the nitrite in waters is a sign of anthropic contamination, resulting of the infiltration of the worn-out waters and a beginning of deficit of the medium in oxygen (Aghzar *et al.*, 2002; Sinan 2000). Pontius (1993) reported that reduction of nitrate to nitrite could be a risk to adults deficient in glucose phosphate dehydrogenase. Ward (1996) reported nitrite could react with secondary amines or amides in water or food to form N-nitroso compounds that are potential animal carcinogens. In the present investigation, the contents of sample groundwater in nitrites ($0.002-0.05 \text{ mg l}^{-1}$), have probably, no risk as far as they are very lower than the standard of the WHO fixed to 3 mg l^{-1} (Table 1) (WHO, 2011). The results of the analyses gotten are also in accordance with the Moroccan norm (03.7.001) that is fixed to 0.5 mg l^{-1} . The Environmental Protection Agency (EPA) has since adopted the 10 mg l^{-1} as standard of the maximum contaminant level (MCL) for nitrate-nitrogen and 1 mg l^{-1} for nitrite-nitrogen for regulated public water systems.

underground waters are poor in nitrogen ammoniacal except of the waters descended of soils rich in organic matter or rich ammonia contents. Rodier, (2009) reported that nitrogen ammoniacal is met in waters, it is usually translated a process of incomplete deterioration of the organic matter in connection with the lack of available oxygen, it shows a contamination of human or industrial origin. In our study ammonia presents the little values of about 0.014 to 0.241 mg.l^{-1} with average of about $0,043 \text{ mg.l}^{-1}$, which are strictly below the norm 0.3 mg.l^{-1} (WHO standard).

Sulphates

Sulfur is 14th the most abundant element in the crust of the earth. Sulfate is produced in the environment from the oxidization of the elementary sulfur, sulphurized minerals, or of organic sulfur. Sulphate is found in small quantities in ground water. The origins natural of the sulfates are the rainwater and the setting in solution of evaporative

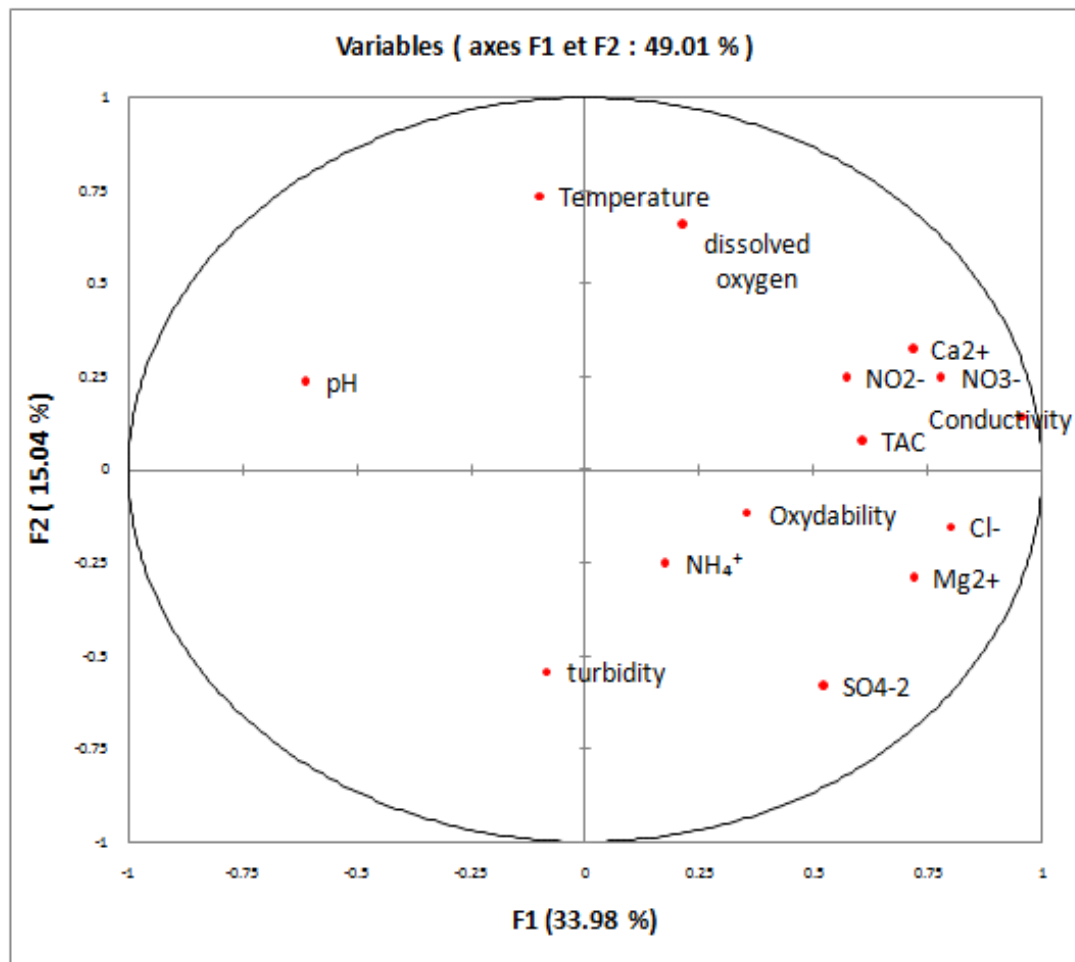


Figure 2. The square cosines for all variables in components F1 and F2 obtained from the Principal Components Analysis PCA

Ammonia

Ammonia are designated under the term ammonia of the shapes ionized (ion ammonium, NH_4^+) and non ionized (NH_3). Some deep waters can be charged of ammonia by reduction of the nitrates under the action of bacteria or by sands that contain the minerals containing iron (for example, glauconie). The high ammonia content was considered originated from the anaerobic conditions which contributing to nitrate reduction towards ammonia gas phase (Fatta *et al.*, 1998). Usually, the

sedimentary rocks, notably gypsum (CaSO_4), but also of the pyrites (FeS) and more rarely of magmatic rocks (galena, blende, pyrites). Sulphate may come into ground water by industrial or anthropogenic additions in the form of Sulphate fertilizer (Janardhana *et al.* 2013). The anthropic origins are the combustion of coal and oil that entails a production important of sulphides (that one recovers in rains), as well as it is originated from the use of chemical manure and laundry. Sirajudeen *et al.* (2013) report also that discharge of industrial

wastes and domestic sewage tends to increase its concentration. Sulphates of well water in the study area ranged from 16.7 to 73.54 mg l⁻¹ with average of about 40.42 mg l⁻¹. The sulphate values of the samples for all stations lie within the permissible limits of WHO (250 mg l⁻¹) (WHO, 1993). The ions sulfate (SO₄²⁻) to concentrations superior to the value guide in the drinking water can provoke some diarrheas at the human (CDC-EPA, 1999).

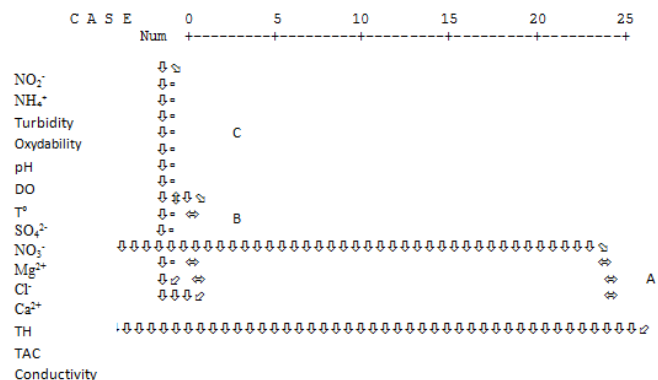


Figure 3. A dendrogram obtained by application of the Ward's method for water quality parameters

According to Amoako *et al* (2011), chloride and sulphate have similar health-based guidelines, but may cause concern due to taste if found at higher concentration. However, evidence relating to chronic human health effects to specific drinking water contamination is very limited. In the absence of exact scientific information, scientists predict the likely adverse effects of chemicals in drinking water using laboratory animal studies and, or when available, human data from clinical reports and epidemiological studies (Nkansah and Ephraim, 2009). The standard development process were assumptions for protection of public health in that they tend to err on the side of caution in assessing potential health risk (Nkansah and Ephraim, 2009).

Heavy metals

On the other hand, it is important to supply the human body the essential metallic nutrients. Despite this importance, the high concentration of heavy metals in the water could lead to adverse effect and influence the beneficial use of the water. The potential risk of chemicals is important because it is too difficult to treat them in water *et also* there is no metabolically degradation of them in human body. Most of developing countries have no means of chemical treatment due to limited financial ability. The analysis of heavy metals of all stations surveyed, shows that Cu, Zn, Pb and Cd (Table 2) are less than the guideline value of consumption in the Moroccan and international standards. These results indicate that the study area is free of any natural source of metal pollution (mineral deposit) or also anthropogenic mining activity that can affect the water resources.

Statistical analysis

Principal Component Analysis (PCA)

Multivariate methods were found to be suitable for deducing the water quality parameters and the determination of relationships among them, *et also* for the samples clustering, as well. These techniques can be helpful for assessors to obtain

a global view on the water quality in any urban or other geographical territory when analysing large data sets without a priori knowledge about them (Vialle, 2011, Pathak, 2012). A starting data matrix, with columns representing the different samplings (observations) corresponding to the measured parameters (variables), was constructed. A total of observations were further analysed with Principal Component Analysis (PCA). In PCA, the number of components is equal to the number of variables. A component, however, is comprised not only of a single variable but all of the variables used in the study. The PCA analysis showed that of the 14 components, the first component (F1) accounted for about 33.98 % of the total variance, the second component (F2) accounted for about 15.04 % of the total variance of the dataset Table 2. Table 3 gives the loadings for the two first principal components and square cosines are presented in Figure 2. A variable is increasingly well represented by a component as the corresponding value of the square cosine approaches the unit. Several variables are well represented by the two first components. The variables that primarily contributed to the first eigenvector were conductivity (0.956), Cl⁻ (0.801), NO₃⁻ (0.779), Mg²⁺ (0.721), Ca²⁺ (0.718), TAC (0.606) (Table 3). Thus, the first principal component can be interpreted as an ionic component. The second eigenvector was mainly related to organic and mineral suspended load, with the most significant variables being temperature (0.734), dissolved oxygen (0.661), turbidity (-0.544), SO₄²⁻ (-0.580). The same results of PCA statistical analysis were reported by Pathak (2012) which have suggested that regarding the physicochemical properties and hygienic importance of these parameters, some of them could be used primarily for the frequent water quality monitoring: Conductivity, nitrate NO₃⁻, chloride Cl⁻. These parameters were identified as more important in judging the quality of waters. These parameters indicate that groundwater was contaminated from nitrate fertilizers and manures used in agriculture or because of its contamination with sewage or household waste leachate, industrial, and other organic wastes.

Hierarchical cluster analysis

To confirm the associations between the variables in the total dataset, Cluster analysis CA was performed on the measured chemical variables. The search for natural groupings among variables was a complementary way to study the latent structure of the data and permitted the comparison of the results of CA to those provided by the PCA. When CA was applied, the dendrogram (Figure 3) showed three different clusters identified as A, B and C. The variable conductivity presented by the cluster (A) is strongly related to the variables in cluster (B) as NO₃⁻, Mg₂⁺, Cl⁻, Ca₂⁺, TH and TAC. Indeed, there is adequate agreement between results obtained by unsupervised PCA and CA to confirm the conclusions that of importance of these parameters to judging the quality of water. But all other are presented in separated cluster C such as SO₄⁴⁻, NO₂⁻, NH₄⁺, Oxydability, turbidity, pH, DO, T°.

Correlation among physical and chemical parameters of water quality

The correlation relationship demonstrated that high correlation coefficients was recorded between conductivity and the ions Cl⁻ 0.861, NO₃⁻ 0.775, Ca₂⁺ 0.806, Mg₂⁺ 0.664. As well as between Cl⁻ and Ca₂⁺ 0.688, Mg₂⁺ 0.600 and between NO₃⁻ and

Mg_2^+ 0.625. This confirms the mineral rock solubilisation due to presence of chloride. Similar results was found by Yadav *et al.* (2012) which have shown high correlation between conductivity and Cl⁻. A significant correlation was also demonstrated between SO_4^{2-} and oxydability 0.650. This indicates anaerobic state due probably to water contamination by the organic load. Accordingly, this study indicated that some physico-chemical parameters are out of the highest desirable limit or maximum permissible limit. Hence, these water samples of well cannot be absolutely fit for directly drinking. Some essential treatments are needed to convert them drinkable water. From the results of the present study it may be said that the people in these rural areas are therefore exposed to higher potential risk.

Conclusion

The study was undertaken to assess the quality of ground water samples of Beni Mellal region. It has shown that values of some physical and chemical parameters in the well water samples were within the permissible limit such as pH, dissolved oxygen DO, Magnesium and calcium, nitrites, ammonia. However, the others didn't comply with national and WHO standards such as physical characteristics like turbidity in addition to the chemical ones such as conductivity, total hardness, Complete Alkalimetric Title, and chemical components as chloride, nitrate, sulphates, all of them have contributed to the non-potability of these well water. The observed total hardness suggest that the ground water is fairly hard. Hardness is not suitable for drinking and others uses. The hard water may cause severe health troubles like cardiovascular disorder and kidney problems. Similarly, the high chlorides content is probably due to the presence of chemicals and to the application of acidic fertilizers. Consequently, the high chloride content and total hardness could exert after an intense chemical aggressiveness to the metallic pipes and filters of drinking waters. As well as, this could explain the high turbidity due to desegregation of the surrounding rocks.

The important saltiness of the underground waters presented by the data could be originated from the excessive use of manures and pesticides *et all* the phytosanitary products. Others causes are the contamination of the underground waters by domestic worn-out waters since the regions don't have the network of sewage purification except of the septic tanks. As well as, it must be added other factor such as the possibility of irrigation by the surface water that is saline contaminated by industrial garbage or dismissals household wastes leachates. The water of the studied area is not absolutely fit for directly drinking purpose. But, it needs treatments to minimize the contamination. It is recommended that water analysis should be carried out from time to time to monitor the rate and kind of contamination. It should also to expand awareness among the people to maintain the cleanness of water at their highest quality and purity levels to achieve a healthy life.

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