Impact of Waste Water on The Physico-Chemical Quality of Water Sources In Bed of Oued Essaquia Elhamra In South of Morocco

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ABSTRACT

The springs of water in the bed of Oued Essaquia El Hamra object of our study, were chosen to illustrate impacts of entropic activities on the physico-chemical quality of these waters of springs. The analysis of the situation concerning spring, shows a rather important potential in quantity of water. However, the physico-chemical quality of the water is very low, characterized by very high mineralization and constituents at this state a source of degradation of the immediate environment, furthermore the results of the physicochemical parameters indicators of pollution: COD (chemical oxygen demand), BOD5 (biochemical oxygen demand over 5 days), dissolved oxygen (DO), nitrate (NO3), nitrite (NO2), ammonium (NH4+), Kjeldahl nitrogen NTK, phosphates (total P and orthophosphate PO42-), etc. stipulate that the waters in these sources are exposed to heavy pollution expressed by those parameters that exceed standards. In the absence of polluting industry in the city of Laayoune; it appears that this pollution is mainly due to domestic wastes, washing stations, hospitals and, climatic agents on sedimentary rocks is responsible for high concentrations of certain chemical elements such (Cl-, SO42-, B, Ca2+ ... ). The principal component analysis (PCA) was performed using average values for each parameter, results reveal the existence of a relatively marked temporal variation of these descriptors, showing four different stations in groups according to their physico-chemical quality and the level of contamination by sewage discharges.

Keywords: arid climate, water of springs, Oued Sakia El Hamra, physicochemical quality, wastewater.

1.INTRODUCTION

The hydric potentialities are key elements which determine any possibility of socio-economic development particularly in Saharan regions, this vital element can be a vector of potentially dangerous agents [1, 2]. The groundwater and the surface water are influenced by various pollutants discharges, agricultural, industrial, and / or domestic [3] [4]. In addition the potential of good quality hydric resources is exposed to extreme cyclical variations [5, 6]. Leaned in the desert, the city of Laayoune has water resources limited in quantity and quality [7]. Furthermore, the wastewater of the city are Dumped without treatment into Oued Essaquia El Hamra, which constitutes the main water course in the region of Laayoune. [7]. In addition the Runoff from water springs in the bed of Oued Essakia might alter the water quality of the latter. Because of physicochemical composition of spring water are linked to its underground routelikegeological composition, depth and the transit time[8]. Mineral waters and hot springs were the subject of several studies, hydrogeological, geothermal, geochemical and physicochemical, they have particular physicochemical...
properties that can certainly change the quality of receiving environments [9,12]. Faced with a lack of information on the composition and safety of water of sprigs at Oued Essaquia Elhamra, we conducted a study aimed to determining the physico-chemical quality of the water of springs. The objective of this work is determined to improve the water-level knowledge in the study area and within the perspective adequate proposal likely to better use of these resources and to evaluate the risk of contamination of the superficial groundwater of Fem Elwad situated downstream, which constitutes the principal hydrogeological unit in the region of Laayoune [13,14]. In order to know the real state, the quality of water and to determine the type and origin of the pollution of water spring. We measured the various physicochemical parameters during the months of January, May, July, November and December of the year 2015. For better understanding of the degradation process of the water quality, collected data interpretation was carried out by CPA.

2 Climate of the region

The climate of the region is arid, cold in winter, hot and dry in summer tempered by marine humidity over a coastal fringe not exceeding 50 km wide, and marked by the scarcity of rainfall that are random in nature short often stormy and can have catastrophic consequences, they generally grouped between October and March (Figure 2). During the study period, the highest rate was recorded during the month of November 2014 (79.5mm). The monthly average temperature ranges between 16.5 °C and 26.5 °C. The minimum and maximum average values are 11 and 31.5 °C, respectively. The region is characterized by the importance of daily and yearly discrepancies between them.

![Figure 1](image1.png)

**Figure 1:** (a) monthly average Rainfall of the periods 2011-2015, 2014 and 2015, and (b) Temperature minimal, medium, maximal and the year 2015.

Regarding the wind, it blows in the area throughout the year, the monthly average of the speeds of the wind varies between 15.4 to 19.2 m/s, to note that this characteristic can represent a major economic asset within the framework of a development of the exploitation of the wind energy in the region. However the wind is also the determining factor in the genesis of silting phenomenon that poses serious problems with deteriorating infrastructure (port, road network,...) and silting of homes which damages the built environment and the network sanitation causing the overflow of the last.

3- Study area

In this study we have identified eighteen springs spread over an area of 7 km length in the bed of Oued Essaquia Elhamra, the majority of which have a low flow. The springs labeled as S1, S2, S3, S4, S5, and S6. In the current state they are badly maintained and as a dumpster for house hold waste water located on the shore of Oued Essaquia Elhamra especially (S1, S2, S3) which are next to the locality of Douar Imkhaznia in Amon of study area, also S5 and S6 are located successively close to the Souk Ejjaj and Elfarah district in downstream. Regarding (S4) it is located on the right bank of Oued Essaquia Elhamra near the military barracks. (Figure 2)
3.1 Hydrogeological presentation of the groundwater Aquifer of Laayoune

Several authors have discussed the regional geology since 1934 especially in Tarfaya Laayoune basin [15, 18]. The superficial aquifers of the Laayoune correspond to the geological formations permeable Upper Miocene to Plio-Quaternary encouraging the transit of infiltrating water in high salt load. The aquifer of Laayoune is located around the city on either side of Oued SaquiaEl Hamra, covering an area of approximately 150 km² [13]. The aquifer of the rights banks extends NE of Laayoune, beyond the northern cliff of Saguia El Hamra. It is contained in the coquinalimestone of Pliocene limited to either side by marl elevations giving birth to a wide cuvette of 5 km and 10 km long, in continuity of coquina limestone groundwater flows in clayey sands (North, West and East) or in fossil dolomitic limestone marl little (West). Furthermore the aquifer of the left bank is limited to the north by the southern cliff of Oued Saquia Elhamra and extends south and south east it circulates in the coquina limestone resting on a marl substratum, which extend over 12 km long and 4 km wide [13]. The groundwater level regard to the ground increases from East to West and reaches its maximum in the center. The outputs of the aquifer at Laayoune comprise some water withdrawals for irrigation purposes and essentially the spring object of our studies.

Figure 2: Location of the study area extracted from the topographic map of Laayoune (modified)
4. Materials and methods

After identifying springs water, the samples were collected during the month when flow is high (in February 2015) and for those whose flow is low (May, July, November 2015), on eighteen springs, six of which the flow is quite important were studied, some parameters have been measured on site, while others have been preserved and transported to the laboratory for analysis according to standardized protocols in accordance with the standards of Rodier 2009 [19] and AFNOR in 1997 [20].

5. Results and discussion

Sources of water in the bed of Oued Essaquia El Hamra as shows in pictures taken during sampling was poorly maintained. The proximity of its springs to wastewater networks indicates a very high risk of contamination.
5.1 Flow of springs and piezometric level of superficial aquifer of Laayoune

Flow measurements have shown a rather important potential in water for S2; S3, S5, and S6 (Figure 5). The profile of the flow depends on the evolution of the recharging table following rainfall. It is very important after the exceptional rainfall of November 2014 and it was noted that reaches high values during the month of February and tends to decrease during the summer months and increased during the November. However, it decreases during the month of December due to the absence of rainfall (Figure: 1). This observation is associated with a decrease in piezometric level of groundwater controlled at several wells especially 646/120, 831/120 located, respectively located on the right and left bank of the Oued Essaquia Elhamra which depends on rainfall recorded.

![Figure 4: Photos of studied springs](image)

![Figure 5: Temporal evolution of the flow of springs and piezometric level of the superficial slick in Laayoune](image)

5.2 physicochemical parameters

The temporal variation of various physicochemical parameters of water of the six springs studied allowsto note the following:

Temperature

The temperature plays an important role in modifying biological and physicochemical property of water, in this study it ranges between 20 °C and 26 °C, which allows to classify the water of these springs among the hypothermal waters [8], the temporal variation of the water temperature is not significant during the year and remains linked to the study period, it does not show large variation between the different sources and is associated exclusively to the notion of time and not at the sampling station.
Figure 6: Temporal evolution of the temperature °C of springs (S1, S2, S3, S4, S5, and S6)

Water pH

The pH recorded during the study period did not show significant variations between different springs, pH values of water sources has varied from 6.91 to 7.67 (Figure 6). These pH values are admissible by WHO standards, which sets the pH of drinking water at values between 6.5 and 8.5. Less values found demonstrate the stability of the established balance between the different chemical elements, this situation could be attributed to buffer phenomenon of the waters facing the contribution of pollution [21].

Conductivity, Salinity and the concentration of Chloride ion

The conductivity measurement allows to quickly evaluate the global mineralization of the water and to follow its evolution[19]. It was noticed that, for the electrical conductivity of the water springs of all measured samples, ranged between 10.91 mS to 21.9 mS/cm (Figure 7), the values exceed the WHO standards, which is 1500µS/L. These very high values of conductivity can be related to the geological nature of the studied area[15, 18] when rainwater cross these formation they acquire a high mineralization [11], measuring salinity and chloride ion concentration shows that they follow the same pace as that of the conductivity varies respectively between 14.7 and 6.9 mg/L, 8042.5 and 3750 mg/L, well beyond the standards (200 mg/l for Cl) [6], and allows to classify these waters among the very low quality, the temporal profile of its three parameters is marked with an low decrease of values during the humid season for instance February compared to July and November. The increased mineralization in the summer would be favored by the decrease in water flow in favor of a high evaporation, the greatest value of the conductivity measured in the station S3 (21.9 ms/cm) located middle of the measuring station, which can be explained by the difference between the geological nature of the land crossed by the waters of different springs. These high values in conductivity, salinity and chloride ion concentration can also be explained either by leaching of evaporites (halite = NaCl) or by contamination from a salt wedge due to intense pumping in the study area [13].

The hardness

The water hardness (TH) is due to dissolved polyvalent metal ions. [18]. In this study TH varies between (31 mEq/L and 68 mEq/L). According to the classification of Lidwin et al., 1993 [22]. The analyzed waters are very hard these values are probably related to the nature lithology of aquifer and especially its composition of magnesium and calcium (Figure 7). Thus the concentration of calcium ions (Ca ²⁺) in the water source are very high exceed WHO standards, which is 70 mg/L [23]. These values are related to the dissolution of carbonates [18], or the dissolution of the sulphates such as gypsum.
Figure 7: Temporal evolution of the conductivity CE, salinity, total hardness TH, pH, chloride ion concentration Cl⁻ and calcium ions Ca²⁺ of the springs (S1, S2, S3, S4, S5 and S6)

Dissolved oxygen O₂
Dissolved oxygen participates in the majority of chemical and biological processes in aquatic environment and its average content into the unpolluted surface water is about 8.0 mg/L [19], [23]. In the studied waters, the oxygen concentration range between 3.5 mg/L and 1.3 mg/L (Figure 8). The evolution of dissolved oxygen values in all water of springs reflects a strong deterioration of its quality, S1 springs located upstream, present throughout this study the lowest values.

The complete alkalimetric title (TAC)

the temporal evolution of this parameter (Figure 8) is marked by lighter fluctuations as well during the periods of rainfall than the dry period, values oscillate between a minimum of 5 and a maximum of 8 (mEq/L) those values are very high, they demonstrate the greater load mainly bicarbonate ions and suggests the dissolution of carbonate gypsum. This observation is supported by the lithological nature of the formations of the basin [18].
Figure 8: Temporal evolution of complete alkalimetric title TAC, concentrations of nitrogen Kjeldahl NTK, nitrate $\text{NO}_3^-$, ammonium $\text{NH}_4^+$, nitrite $\text{NO}_2^-$ and dissolved oxygen $\text{O}_2$ of (S1, S2, S3, S4, S5, and S6)

Nitrate $\text{NO}_3^-$:

The concentration of nitrates most oxidized state of nitrogen is very important for S3, S6, S5, and S4, the values exceed WHO standards, which is 50 mg/L[23], testify considerable nitrification probably related to the oxygenation of the environment and contamination by wastewater, the temporal evolution of the nitrate content in S3 is characterized by the increase in the months of May and July this increase could be explained by the important contribution that has springs in wastewater during the summer period, regarding the other three springs it did not show the same pace, because of the wastewater discharge. For S1 and S2 the nitrate concentration does not show great variation over the study period with a slight increase.

The nitrite $\text{NO}_2^-$:

Nitrites constitute intermediate forms between nitrates and ammonia nitrogen, which explains the low concentrations found in aquatic environments. A concentration above 0.10 mg/L should not be exceeded in groundwater [19]. Measurements of concentration in the springs reveal that it exceeds the standards, except in S6 the concentration was lower. Agents reducing nitrite into nitrate such microorganisms may be responsible for its concentrations.
Ammonium $\text{NH}_4^+$

Ammonium is the final reduction product of nitrogenous organic substances, its presence generally show an incomplete degradation process of the organic matter [19]. Its concentration in natural waters is a good indicator of water pollution from urban effluent. Natural levels in groundwater and surface water are usually below 0.2 mg/l. Anaerobic groundwaters may contain up to 3 mg/l [23], in this study it is higher for S3 (3.2 mg/L), while other springs show low values compared to S3, the ammonium content undergoes a slight decrease during summer this observation can be related to the relative increase in the concentration of oxygen and that of nitrate during the same period.

Kjeldahl Nitrogen TKN

Kjeldahl Nitrogen is present in spring water at variable concentrations (Figure 8). Relatively quite low in the downstream spring S6, with an average of 0.8 mg/L. However in S3, the values recorded is averaging 3.07 mg/L. The origin of its concentrations may be discharges of wastewater or the presence of nitrate reduction agents. Regarding the orthophosphates concentration, the temporal evolution in spring water reveals low contents. An increase content was recorded during the months of May, July and November these values remains low considering the extent of pollution suffered by these springs.

COD and BOD 5

The high content of COD and BOD 5, are registered in May and July, they reach maximum and minimum values of 195.4 and 44.14 mg/L, respectively. These high value may possibly be linked to the added of organic matter by wastewater infiltration which increases during the hot season in addition to the proximity of these springs of sewerage networks, that is located in a deteriorated condition (Figure 4). The analysis results also shows that the springs S1, S2 and S3 are the most exposed to this pollution because in summer the significant decrease in the flow rate of springs associated with the predominance of wastewater and warming waters could be the origin high contents.

![Graphs and charts showing temporal evolution of various parameters](image-url)

Figure 9: Temporal Evolution of total phosphates $P_T$, orthophosphate $PO_4^{3-}$, chemical oxygen demand in 5 days $\text{DCO}_5$, and chemical oxygen demand $\text{DCO}_5$ of the sources (S1, S2, S3, S4, S5, et S6)
Boron

Naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicates [23]. The pH and salinity govern the speciation of boron in the water. It is reported that, under different conditions of pH and salinity, the species H$_3$BO$_3$ and B(OH)$_4$ coexist [24], the concentration of boron in the water of springs reaches very high values 6.3 mg/L for S6, the value exceed the standards WHO which is 2.4 mg/L [23]. Climatic agents on sedimentary rocks rich in clay may be responsible for these high levels particularly granitic and pegmatiterocks [25]. Human activity also releases boron in the environment, but at a lower proportion.

Sulfates

The temporal evolution of the concentration of sulfates in water of springs has for origin the different geochemical processes responsible for the dissolution of the species and the spatial evolution of their concentrations especially gypsum (CaSO$_4$) pyrite (FeS). In this study it reaches a maximum value of 1997.8 mg/L at the spring S3. The measured concentration in all springs exceed regulatory values recommended by WHO which is 250 mg/L [23], a slight increase was noticed in the during the summer. These high levels of sulfates in the waters of springs is essentially due to the sedimentary nature of the geological formation [16, 18].

6- Multivariate analysis ACP

In order to show a temporal structure allowing identify factors or the most determining phenomena in the dynamics of this system, we have practiced a principal components analysis ACP. It is generally used to reduce the number of these dimensions into a data matrix, which allow selecting the most determinant parameters, and studied the overall change in data. Analysis of the results reveals that most of the information is explained by the first two factorial axes F1xF2. The proper values of the two components F1 and F2 and their contribution to the total inertia are shown in Table 1. The two axes taken into account to describe the correlations between variables related to temporal structures to holds them alone 61.5% of the total information with 39.89% for axis 1 and 21.65% for axis 2 (Table 1). The first factor corresponds to the elements EC, salinity, TH, Ca$^{2+}$, Cl$^-$, PO$_4^{3-}$, SO$_4^{2-}$, NTK) that are associated with hardness, salinity, sulfate and orthophosphate kjeldal nitrogen, which have good correlations between them. The second factor, which represents 21.65% of the total variance corresponds to ions (NO$_2^-$, NO$_3^-$, BOD$_5$, COD and P$_i$), closely linked to organic pollution.
Figure 11: graphic approach of the ACP of physicochemical parameters in water according to plan (F1xF2): representation of the factorial card of variables; and the factorial card of the measuring station.

The typological structure generated by the factorial design, F1xF2 (Figure 10) shows the individualization of four different groups according to their physico-chemical quality:

**Group I:** formed by the station S1 and S2 characterized by significant mineralization and a very high vulnerability to organic pollution (COD, BOD5, NO2 and Pt), besides these parameters increase during the summer. Factorial map samples confirms that the water taken at the station S1 and S2 differ from other samples. They are the richest in various organic forms linked to pollution and inorganic chemistry related to geological formations.

**Group II:** formed by the statements of the third station S3 at which it is observed that the mineralization is very high, as S3 is very vulnerable to the parameter ((EC, NTK, Salinity, SO\(_4^{2-}\) and NH\(_4^+\)) in addition correlation, between conductivity and sulfates is important, this explains that the mineralization of the station S3 in addition to ion in water including calcium and chloride ion etc., the sulfate ion contributes to the increase in conductivity. The NH\(_4^+\) and NTK parameters are perfectly correlated, which are due to the pollutant reject and presence of reducing agent from other the pyrite.
Group III: formed by the S4 and S5 stations that are characterized by high mineralization and low organic load. This group distinction shows that the S4 and S5 are less exposed to domestic discharges view that these two stations are located successively under a building near souk Ejjaj and on the right bank of Oued Essaquia next to the Auxiliary Forces barracks less exposed to the domestic reject.

Group IV: formed by the measurements of the station S6 which is characterized by very high vulnerability to boron and nitrate, in addition mineralization is high. The spreading area of the city of Laayoune is not far from this spring allows saying that the nitrate concentration is mainly due to the infiltration of wastewater, and good oxygenation of the medium. However, the high value found in Bore in addition to domestic rejection could be due to the chemism of geological formation that have a sedimentary nature.

7. Conclusion
In conclusion, the results of this study allow us to establish an overview and bring out recommendations to contribute to controlling the problems related to these springs, the physicochemical analysis results show that, the quality of water sources in the bed of Oued Essaquia Elhamra is very low, they have a very high mineralization due to the impact of discharges of domestic wastewater causing water pollution in these springs. The Principal Component Analysis using the physico-chemical parameters allowed us to distinguish a zonation of the quality of water springs studied. The degree of contamination of these waters varies from one source to another according to the level of exposure to the domestic discharges, thus the CPA show that, the organic pollution gradient decreasing from upstream to downstream reflecting the impact of the domestic discharges, superficial groundwater of FEM el Oued located downstream of the study area is exposed to a serious risk of contamination following the infiltration of water with high mineral and organic load. In order to remedy this problem, it appears judicious of doing up these springs and exploiting the maximum water in irrigation, and taking into account the use of plants tolerant to salinity with well-controlled irrigation doses, because the flow and high saline load limit the exploitation of its springs, in fact the use of such waters for drinking is impossible requiring huge investment to be desalinated and purified.

References
[10]. karim El Mourabit and al hydrogéochimie des sources thermaux du couloir sud rifain (Maroc), Bultin d’hydrogéologie N 22(2008): 77-90

[14]. Zakaria ZGOURDAH, Driss BELGHYTI, Salah Eddine SAMRI et Khadija ELKHARRIM (Contribution à l’étude de la salinisation de la nappe côtière de Foum El Oued (Laayoune) au Maroc).


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