JEE Journal of Ecological Engineering

Journal of Ecological Engineering 2021, 22(8), 92–102
https://doi.org/10.12911/22998993/140261
ISSN 2299-8993, License CC-BY 4.0

Received: 2021.06.16
Accepted: 2021.07.24
Published: 2021.08.06

Comparative Study of the Physico-Chemical and Metallic Quality of Waters and Sediments in the Larbaa Basin (Morocco) in the Dry and Wet Period

Rachida Afgane[1*], Faiza Benjelloun[1], Abderrahim Lahrach[1], Fatima Daide[1]

[1] Georesources and Environment Laboratory, Sidi Mohamed Ben Abdellah University, Fez, Morocco
* Corresponding author's email: rachida.afgane@gmail.com

ABSTRACT
The catchment area of Oued Larbaâ is located in the eastern prerif at the very eastern end of the large Innaouene basin, a stream of Oued Sebou [Lahrach. A et al., 1994]. The objective of the study was to establish a quality comparison of the watershed during the dry and wet seasons. Eight water and sediment samples were taken during the two seasons, all along the main channel of the Larbaa river, taking into account anthropogenic activities and the areas of confluence with its tributaries: Tarmasst, Taza, Larouireg, Defali and Jaouna. The physicochemical parameters (pH, EC, TDS, nitrates, sulfates, chlorides), as well as metal contamination (Al, Zn, Ni, Pb, Ag, Fe, Cd, Cr, Cu, Mg, Mn) were studied in summer. The results revealed the alkaline pH higher than 7, a significant electrical conductivity in several stations, but still conforming to the Moroccan standards. Laboratory analyses reflect that the waters of the basin have generally good quality, except for a few peaks that indicate metallic contamination in Fe and Al. In order to better assess whether there is an anthropogenic effect influencing these results, and to remove the relationships between the different parameters studied, a statistical analysis was carried out with the PCA tool. This analysis made it possible to indicate Cr, Ni and Al as indices of pollution in certain areas. Although the results obtained have been tolerant until now, it is necessary to put in place an action plan to control the areas at risk of contamination during the years.

Keywords: Larbaa Basin, surface water, physico-chemistry, pollution, heavy metals, surface water.

INTRODUCTION

The quality and availability of natural surface water has remained one of the world's major concerns. Natural, anthropogenic and economic constraints remain the main factors considered for the management of this quality. Indeed, the anthropogenic factor remains the main cause of the degradation of water sources, and one that needs to be controlled [Bouras et al., 2010]. Thus, metallic contamination of aquatic ecosystems can cause adverse effects on their components and affect their ecological balance. In this regard, the Larbaa basin located in the region of Taza was chosen to be the subject of a qualitative study of its water and sediments. The evaluation of the quality of the surface waters of Larbaa basin, has been conducted by several authors in the framework of research, but not the study of its sediments. This work consists in updating the results obtained in these studies, and interpreting them in a different way, through a statistical analysis (the Principal Component Analysis), as well as completing the study with the analysis of the basin sediments, which is very important to obtain more reliable results concerning the metallic contamination. The present study aimed to assess the quality of the water and sediments of Larbaa on the one hand, and to determine the location of points that may present a risk of pollution of the aquatic environment on the other hand. In order to carry out this work, physico-chemical analyses were realized in situ (pH, C.E, TDS, salinity), and in the laboratory (chlorides, nitrates, sulfates, Al, Zn, Ni, Pb, Ag, Fe, Cd, Cr, Cu, Mg, Mn). The relationships between the different physico-chemical and metallic parameters were determined by PCA to better assess the anthropogenic effect on water quality.

MATERIALS AND METHODS

Presentation of the study area

The Larbaâ watershed is part of the large Sebou basin. It falls within the Mediterranean domain, situated in the eastern prerif at the very eastern end of the Innaouene basin, a tributary of the Oued Sebou [Lahrach, 1994], between latitudes (34° 15 405, and 34° 30 N), and longitudes (3° 55' 622 and 4° 00' 645 E). The basin is limited by the watershed of Oued Lamssounau North, the sub-watersheds of Oued Larbaa in the South, the tributaries of Moulouya in the East, and the watershed of Lahdar in the West. The surface area of the basin studied is estimated at 775.59 km² and its main stream is the Oued Larbaa, which is about 70 km long.

Morphologically, the upstream parts of the basin show mountainous ridges characterized by high altitudes (1000 to 1500), steep slopes that often exceed 25% and a deep digging of the river. In the middle parts between Ain boukllal and the confluence with Bouljraf, the river crosses low mountains with slopes exceeding 15% [Sadiki et al., 2012]. Towards the South, the marly prerifaine hills dominate, offering an airy relief and less steep slopes [Tribak, 2000].

The basin is characterized by a semi-arid Mediterranean climate in the northern part, and humid in the southern part. The average annual rainfall at the Taza station is 660 mm in the southern part of the basin. It is only 394 mm at the station of Ain Boukallal, located in the center of the basin in a sheltered position. Rain storms are characterized by heavy rains in autumn, a slight decrease in winter, with a relative maximum in early spring. The most important rainy period is from October to May.

The average monthly temperatures are between 10 °C and 29 °C. July and August are the hottest months of the year, with highest temperatures between 32 °C and 34 °C. December, January and February are the coldest months of the year, with minima between 9 °C and 14 °C (Sebou Hydraulic Basin).

Geologically, the Larbaa Basin is part of the eastern prerif. It is part of a morphostructural context marked by the predominance of an essentially marly and marl-sandstone substratum of the Cretaceous and late Tertiary, soft and friable, which constitutes a preferred terrain for water erosion [Tribak, 2000]. Moreover, the intensity of fracturing and the presence of several tectonic accidents reinforce the fragility of the basin [Akdim et al., 2003].

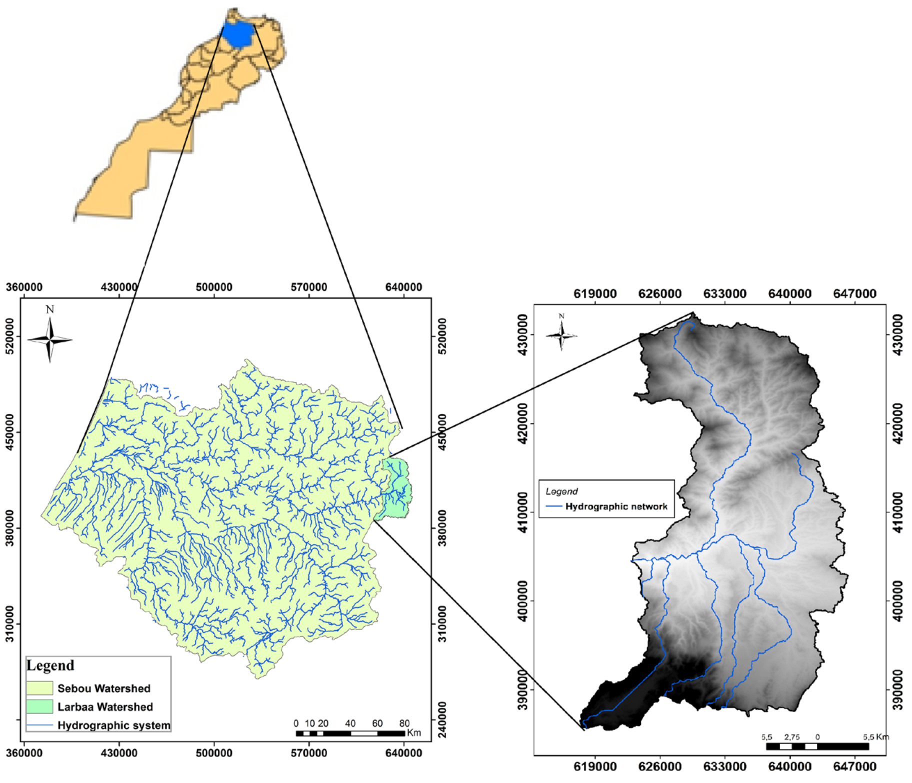

Figure 1. Map of the geographical location of the Larbaa basin

Sampling and experimental methods

Eight water and sediment samples were taken along the main river Larbaa, taking into account anthropogenic activities and the confluence zones with its tributaries: Tarmasst, Taza, Larouireg, Defali and Jaouna.

The water samples were transported to the laboratory in plastic bottles at 4°C and analyzed within 24 hours [Afnor, 1997].

The degree of water pollution (domestic, agricultural and industrial) was determined by measuring the physicochemical parameters: pH, electrical conductivity (EC), total dissolved solids (TDS) and salinity of each sample were measured *in situ* using a multiparameter meter, as well as chlorides (Cl-), sulfates (SO_4 ^{2}-), nitrates (NO^3-) and heavy metals for sediments.

These analyses were carried out in the laboratory of the Faculty of Science and Technology of Fez. The concentration of heavy metals in surface water and sediments concerned the elements Al, As, Cd, Cr, Cu, Fe, Mn, Ni and Pb, and were measured at the Regional University Centre of Interface (CURI) in Fez.

RESULTS

Physicochemical characteristics

The results of the analysis of the water of Larbaa for the year 2017, during the dry period and the wet period, are presented in the Table 1.

Hydrogen Potential

It is obviously an important parameter for water characterization. Low pH values indicate the possible presence of toxic ions in the water, and high pH values increase the concentrations of ammonia that are harmful to the growth and development of aquatic life. According to the Moroccan standard for surface water quality, the pH is generally between 6.5 and 8.5 in natural waters. In the study area, there is not much variation between dry and wet periods in all samples. The basic pH is higher than 7 due to the calcaro-marl soils crossed by the basin.

Electrical conductivity

It represents the ionic charge of the water, and therefore provides the information on the content

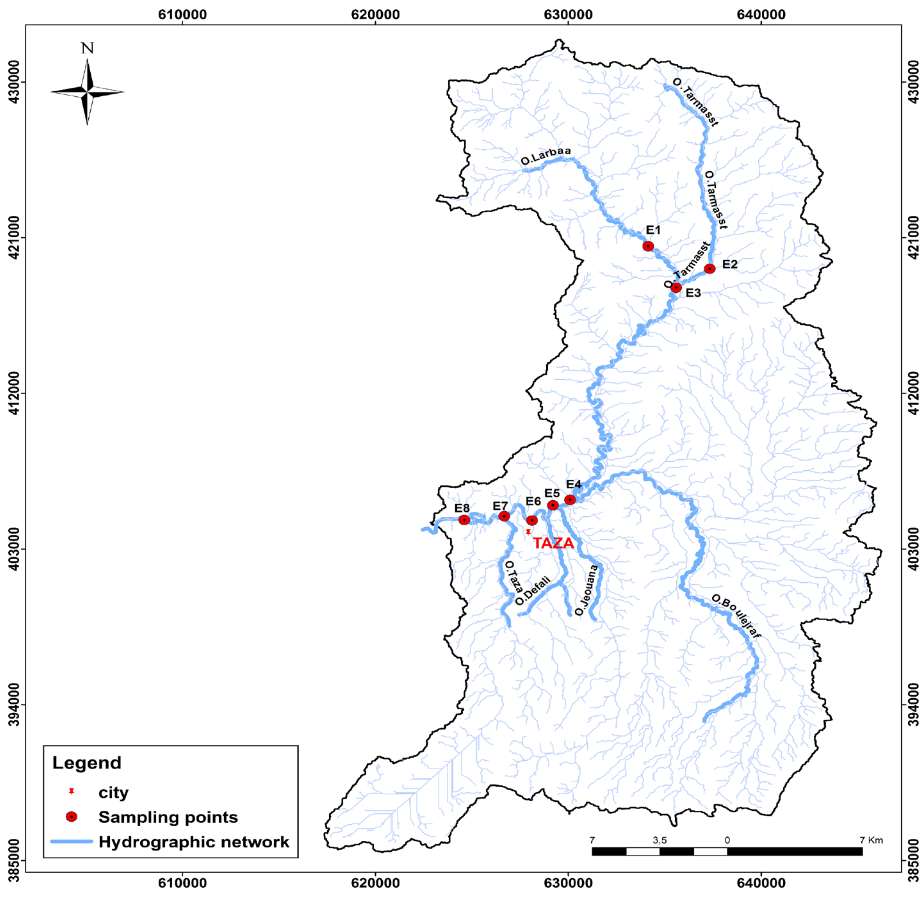

Figure 2. Location of sampling points

Table 1. Physico-chemical parameters of the waters

Sample	Dry period				Wet season			
	pH	EC	TDS	Salinity	pH	EC	TDS	Salinity
E1	8.86	6.54	0.12	0.1	7.68	197	1.28	0.1
E2	7.90	3.7	1.12	0.1	7.41	165	1.82	0.1
E3	8.29	4.86	3.72	0.21	7.65	138	2.03	1.13
E4	8.97	244	1.33	0.1	7.82	842	3.18	0.6
E5	7.60	410	3.04	0.3	7.38	932	5.12	0.5
E6	7.62	567	3.70	0.2	7.80	1096	4.01	0.5
E7	7.65	410	2.23	0.2	7.74	842	4.59	0.4
E8	7.93	509	2.78	0.23	7.75	560	3.48	0.3

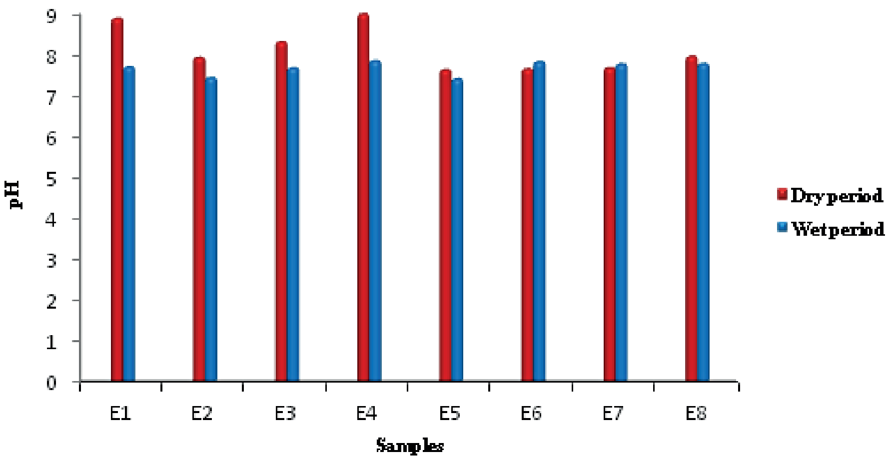

Figure 3. Variation in Hydrogen Potential

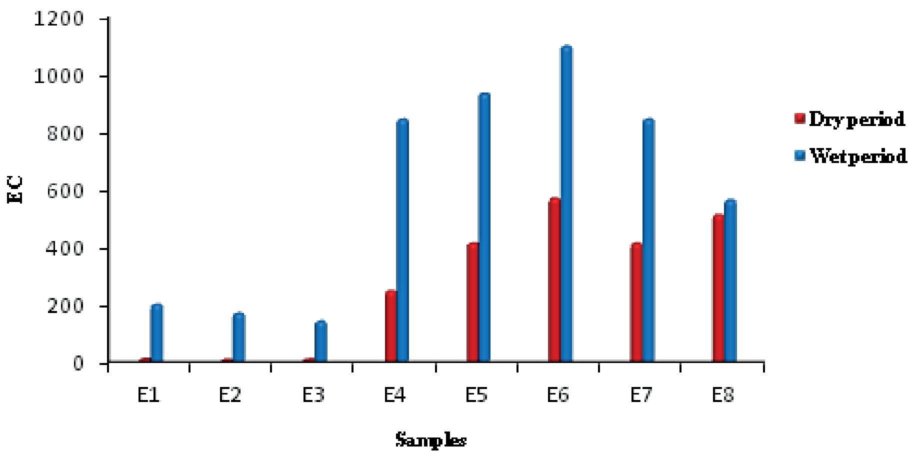

Figure 4. Variation in electrical conductivity

of total dissolved solids in the water. Conductivity is generally dominated by magnesium, calcium, and sodium cations as well as the sulfate, chloride, and bicarbonate anions. The results obtained for the considered samples show high conductivity values in the wet period compared to the dry period. This variation is explained by the dissolution of the ions present in the river caused by precipitation in winter. In spite of this rise, the values are still acceptable and respect the Moroccan standard which requires a value of 2700 µs/cm for surface water.

Chlorides

Chlorides are inorganic ions, which are found in all waters at varying concentrations. Chlorides are often found as salts and the most

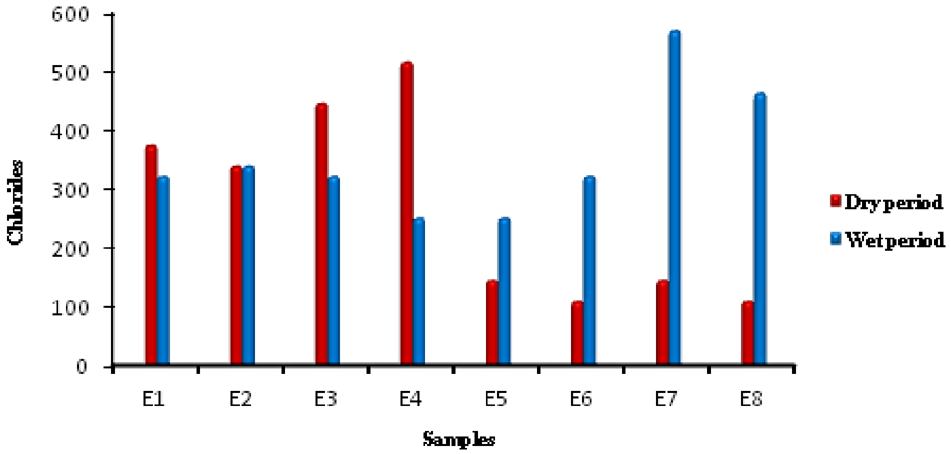

Figure 5. Variation of chlorides

common are NaCl, KCl, and $MgCl_2$. Once dissociated, they remain in ionic form in water. They are often used as a pollution index. The chloride values vary between 106.5 mg/l (ECH8) and 514.7 mg/l (ECH4) during the wet period, as well as between 248.5 mg/l (ECH5) and 568 mg/l (ECH7) during the dry period. It can be noted that in the upstream part of the catchment area (samples 1 to 4), the chloride concentrations during the dry season are higher than those recorded during the wet season. On the other hand, in the downstream part (samples 5 to 8), very high chloride values were noted during the wet season compared to the dry season. This increase in the downstream part of the basin is explained by the cumulative chloride values. However, the values recorded throughout the basin do not exceed the Moroccan standards set at 750 mg/l [Arrêté conjoint..., 2002]. These waters are classified in the average grid of surface waters.

Nitrates

Nitrates result from the nitrification of nitrogen, and represent the highest form of oxidation in soil and water, in the form of highly soluble and mobile mineral salts. Their concentrations in natural waters are between 1 and 10 mg/l.

The nitrate values along the Larbaa basin do not exceed the Moroccan standards set at 50mg/l. These low values are linked to the fact that the land is not very well fertilized. Despite this, during the wet season, downstream of the basin, and near the public dump of the city of Taza (ECH 6 and ECH7), the nitrate levels become high. This is due to the decomposition of the organic and mineral matter contained in the leachate.

Sulfates

Sulfates are naturally present in various minerals. Calcium sulfate is the most prevalent form present in water, and is not soluble

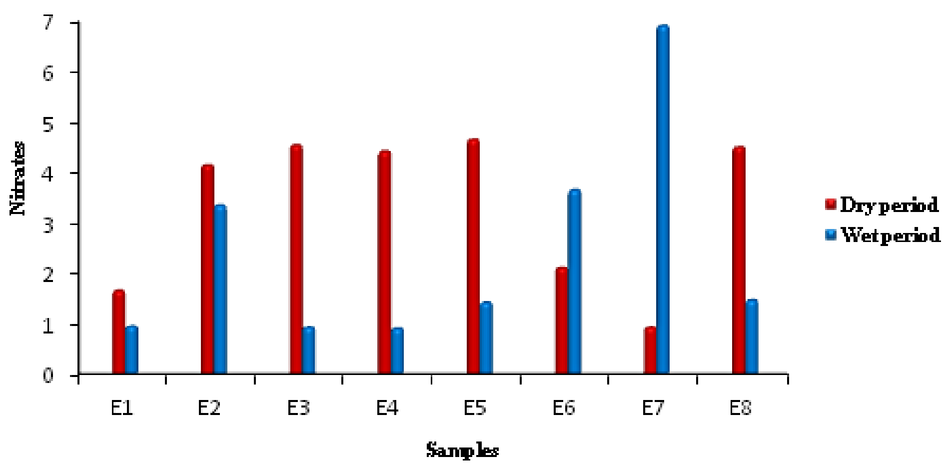

Figure 6. Variation of nitrates

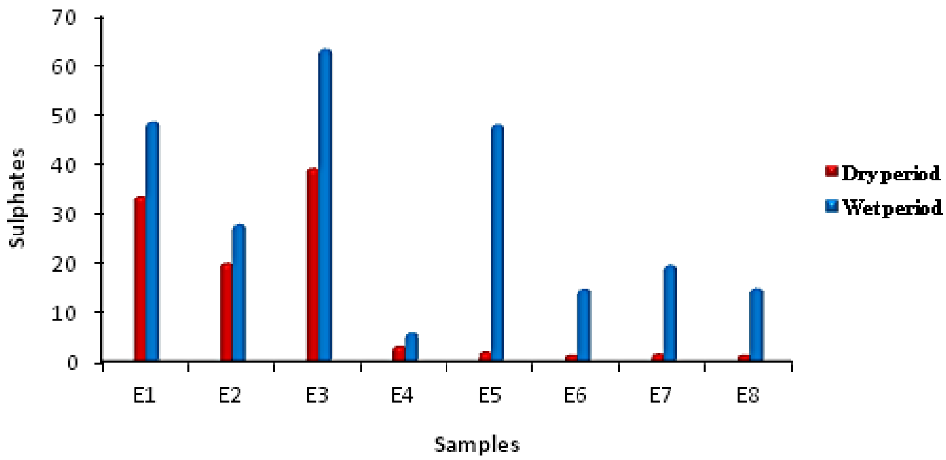

Figure 7. Variation of sulfates

in water. The threshold established in the Grid of Surface Water Quality in Morocco requires a concentration lower than 100 mg/l for excellent quality. The results obtained show significant sulfate values during the wet season, compared to the dry season. This is due to the dissolution of gypsum which is the sulfate mineral present in the basin. However, the values recorded do not exceed the Moroccan standards.

Sediments

Heavy metals

The water is flowing, which makes its composition unstable and therefore leads to inaccurate metal analysis. However, sediments may contain the non-soluble fraction of metals, and therefore, allow for more reliable results regarding metal contamination in rivers. For these reasons, their concentrations have been determined in sediments where it is no longer appropriate to speak of "heavy metals", but "trace metal elements" which refer to mineral compounds present in very low concentrations. The elements most studied in Moroccan surface waters are (Al, Zn, Ni, Pb, Ag, Fe, Cd, Cr, Cu, Mg, Mn).

The heavy metals measured showed metallic pollution at some sampling sites in the study area, compared to the Moroccan drinking standard. The lead concentration at sites S6, S7 and S8 is high in wet periods. On the other hand, during the dry period these concentrations are very negligible, which means that there is precipitation of the insoluble fraction of lead in the underground layers. The high concentrations in the sampling sites are explained by the discharge of wastewater from the city of Taza into the river, as well as the leachate from the landfill set up next to sites S6 and S7.

The iron and aluminum concentrations are clearly elevated at all stations during both wet and dry periods. These values are primarily explained by the lithological formation of the basin which is composed of clay minerals, mainly silicates and phyllosilicates containing iron and aluminum. It was noticed that these values increase downstream of the basin compared to upstream, which is explained by the influence of Taza city by its wastewater discharges and the leachate from the landfill.

Industrial activity is generally the main source of these metals polluting Moroccan surface waters. The study area registers the presence of textile and food-processing industrial zones [Ben Abbou et al. 2014], which are responsible for the effluents containing mainly salts, detergents, organic acids, and organic matter containing micropollutants. This explains the low levels recorded for most metals.

Principal Component Analysis (PCA)

Principal component analysis is a descriptive statistical analysis method, which will allow evaluating the different links between physicochemical and metallic parameters, as well as the effect of anthropogenic activities on the quality of Larbaa basin [Philippeau, 1986]. The data introduced are 14 variables: EC, TDS, Al, As, Cd, Cr, Cu, Fe, Mn, Na, Ni and quantitative Pb for 8 units (individuals). Table 2 and Figure 9 give the correlations between variables and factors and the projection of the variables in the axes F1 and F2, respectively.

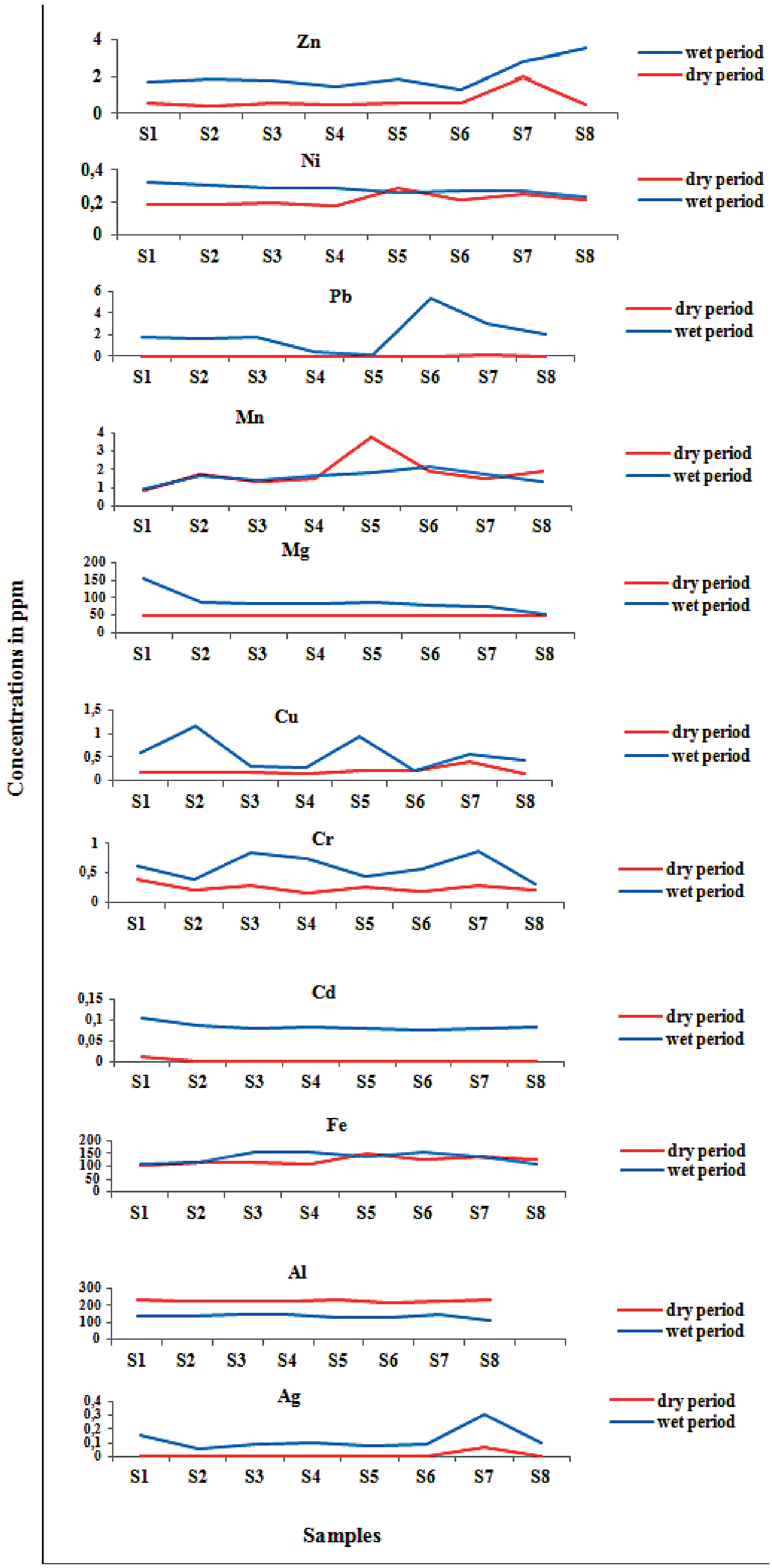

Figure 8. Spatial variation of heavy metals

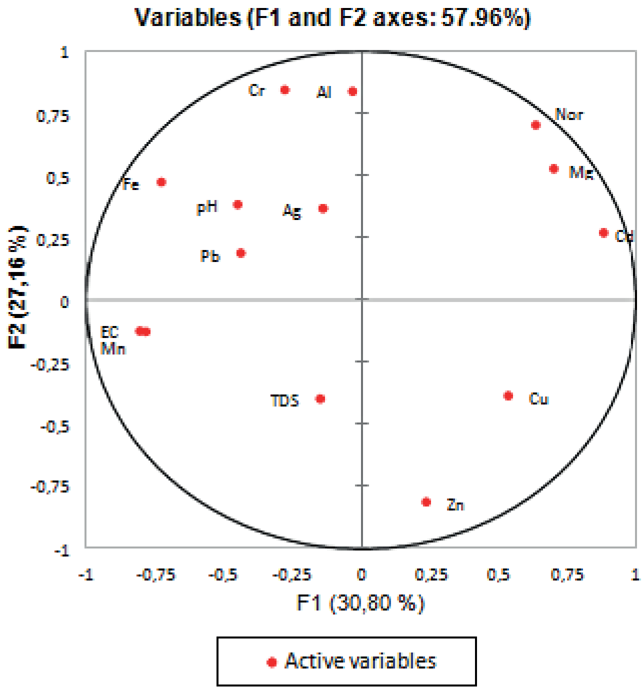

Figure 9. Distribution of physico-chemical parameters and metals according to the F1xF2 plan

The two dimensions of PCA F1 and F2 express 57.96% of all information. The F1 axis has a variance of 30.80% and consists of electrical conductivity, pH, Pb, Mn, Mg, Cu and Cd. It shows the following correlations: Cu & pH (-0.904), Mn & CE (0.748), Cd & Mg (0.867) Mg & Ni (0.769) and Cd & Mn (-0.816). The F2 axis has a variance of 27.16% and consists of Al, Ag, Zn, Cr and TDS. It presents the following correlations between them: Zn & Al(-0.770) Al & Cr(0.778).

The distribution of the physico-chemical and metallic parameters according to the different sampling stations at the level of the Larbaa basin reveals that it contains two main varieties of water:

- The first (G1) presented by stations 3, 4, 5, and 6 linked to axis F2 and located downstream of the Larbaa wadi, with the exception of station 3 located upstream. This water is characterized by an alkaline pH, which is likely to decrease. This variety is loaded in terms of mineralization (Cr, Al, Fe, Ag, Pb). It is located in the positive part of the F2 axis, which shows that it presents signs of contamination, mainly by Cr, Al, Fe, Mg and Ni.
- The second (G2) presented by the two stations 7 and 8 are located on the negative side of the F2 axis. This shows that it does not present any danger of contamination from the point of view of heavy metals. This variety shows a high mineralization and high TDS which explains the high electrical conductivity value. The simple reason for the high TDS is the accumulation of mineralization at the two stations, due to their extremely downstream location in the basin.
- Stations 1 and 2 do not belong to any group. Both are located on the positive side of the F1 axis, with slightly low levels of Mg, Cu and Cd that can threaten the water quality if they exceed standards.

Table 2. Correlation between Variables and Factors

Variables	F1	F2
pH	-0.450	0.384
EC	-0.806	-0.125
TDS	-0.150	-0.395
Zn	0.234	-0.810
Nor	0.633	0.704
Pb	-0.439	0.189
Mn	-0.784	-0.127
Mg	0.698	0.528
Cu	0.533	-0.383
Cr	-0.279	0.845
Cd	0.880	0.271
Fe	-0.728	0.475
Al	-0.034	0.839
Ag	-0.141	0.368

Table 3. Correlation between variables

Variables	pH	CE	TDS	Zn	Ni	Pb	Mn	Mg	Cu	Cr	Cd	Fe	Al	Ag
pH	1													
CE	0.298	1												
TDS	-0.274	0.275	1											
Zn	-0.064	-0.263	0.230	1										
Ni	-0.138	-0.596	-0.448	-0.502	1									
Pb	0.474	0.291	-0.584	-0.220	-0.171	1								
Mn	-0.053	0.748	0.043	-0.356	-0.424	0.373	1							
Mg	-0.144	-0.401	-0.332	-0.406	0.769	-0.150	-0.564	1						
Cu	-0.904	-0.276	0.295	0.104	0.217	-0.416	0.002	0.176	1					
Cr	0.451	0.007	0.018	-0.650	0.343	0.089	-0.059	0.154	-0.501	1				
Cd	-0.059	-0.610	-0.315	0.036	0.686	-0.208	-0.816	0.867	0.199	-0.077	1			
Fe	0.291	0.491	-0.012	-0.633	-0.084	0.112	0.579	-0.254	-0.514	0.620	-0.620	1		
Al	0.061	-0.165	-0.142	-0.770	0.692	-0.108	0.074	0.268	-0.069	0.778	0.017	0.557	1	
Ag	0.356	0.169	0.360	-0.265	0.016	0.222	-0.147	0.104	-0.147	0.574	0.072	-0.036	0.206	1

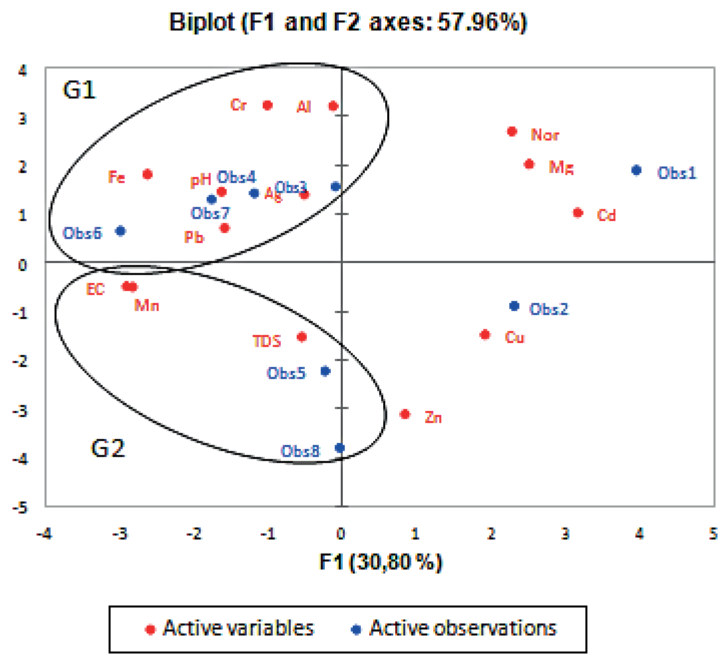

Figure 10. Distribution of variables and individuals as a function of the F1 and F2 axes

The pollution detected by PCA is related to axis F2 (Fig. 10). It is presented mainly by the Cr, Al, and Ni metals. This pollution is related to the stations downstream of the watershed, where the agglomeration of Taza city is located and which is responsible for the discharge of domestic waste into the waters of the river, as well as the leachate from the public landfill in this area which percolates into the waters.

The study with the PCA tool allowed the authors to simplify the interpretation of the results obtained during the study, through tables and graphs. The authors visualized through the different relationships between variables and individuals, which enabled to create a second model of only three variables which are Cr, Ni, and Al from an initial model of eight variables.

CONCLUSIONS

The study carried out in the catchment area of the Larbaa river, allowed a comparison between the physicochemical and metallic quality of the water and sediments during a dry season and another wet season.

The river water have a basic pH higher than 7, due to the calcaro-marly soils of the basin, an important electrical conductivity in the wet season but which remains acceptable, caused by the dissolution of the different salts in the water. The chlorides increase downstream of the basin in the wet season by accumulation, but do not exceed the standard set at 570 mg/l.

The nitrate values do not exceed the Moroccan standard (50 mg/l), but peaks were recorded in samples 6 and 7 near the public dump, which is explained by the decomposition of organic and mineral matter in the waste. The high sulfate values during the wet season, compared to the dry season, are due to the dissolution of gypsum encountered at the basin. However, the values recorded do not exceed the Moroccan standard. The sediments were analyzed to provide more reliable results concerning the metallic contamination of the rivers. Heavy metals (Al^{3+}, As^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Pb^{2+}), in the Larbaa basin have the values in accordance with Moroccan and European health standards [WHO, 1984 and MATEE, 2002], with the exception of Pb, which is high at sites S6 and S7, and Fe and Al, which are very high at all sampling points. These high concentrations are explained by the mineralogical formations in the basin, the discharge of wastewater from the town of Taza into the river, as well as the leachate from the landfill set up next to sites S6 and S7.

In order to better visualize these results and establish the relationships between sampling sites and physicochemical analysis results, the PCR tool was used to highlight the following heavy metals: Cr, Al, and Ni in the downstream part of the basin (confluences of Larbaa basin with Taza river, Defali river and Boulejraf river). The levels of these metals have been acceptable until now, but may increase and prove to be very harmful. The study area registers the presence of textile and food-processing industrial zones, which are responsible for effluents containing mainly salts, detergents, organic acids and organic matter with micropollutants. This explains the low levels recorded for most metals. However, it is necessary to reduce and better manage pollutants and discharges at Taza city and its landfill to control the tolerance of these results, which seem to increase over the years when comparing this study with the study of Ben Abbou et al. [2014].

Acknowledgements

It is important to remember that this work would not have succeeded without the participation and support of many people. I would like to express my deepest gratitude to them. First of all, I would like to express my sincere thanks to the the laboratory of Functional Ecology and Environmental Engineering at the Université Sidi Mohamed Ben Abdellah, and to its Director Lahsen El Ghadraoui, for his help in all aspects of the laboratory work.

I would like to sincerely thank Dr. Faiza Benjelloun, as the supervisor of this work has always shown listening and very available to help me throughout the realization of this work, as well as for the time she has devoted to me.

I would like to thank Mr. Mustapha Ijjaali, Dean of the Faculty of Science and Technology, who has always encouraged the researchers to carry out their work in the best conditions.

I would like to express my gratitude to Dr. Lahrach Abderrahim who participated in the drafting of this work and its correction, as well as his remarks and relevant suggestions that allowed me to improve the quality of this manuscript.

A big thank you goes to my colleague Fatima Daide, who also participated in the writing of this article and who was available to work all the time and in all conditions, with full responsibility and enthusiasm.

A big thank you is also addressed to all the people of the laboratory of Functional Ecology and Environmental Engineering with whom I strongly interacted during my thesis. I also thank my friends Zineb Moumen, Soumaya Nabih, Abdessamad Jalouni and Rachid Motei for their kindness and sympathy.

I would like to thank especially my parents, my sisters and my brothers, who during all these years have always given me their trust, their encouragement and their support at all times

REFERENCES

1. Afnor, 1997. Qualité de l’eau. Recueil des normes françaises environnement (en français). Vol. 1, 2, 3 and 4, pp. 1372.
2. Akdim B., Laaouane M., Taous A. and Obda K. 2003. Risques hydrologiques dans la région de Taza (Maroc): Genèse, conséquences et problèmes d’aménagement (en français). Geomaghreb, 14, 47–60.
3. Arrêté conjoint n° 1275–01 du 17 octobre 2002 définissant la grille de qualité des eaux de surface (en français) - B.O n° 5062 du 5 décembre 2002.

4. Ben Abbou M., El Haji M., Zemzami M., Bougarne L. and Fadil L. 2014. Dégradation de la qualité des eaux de la nappe alluviale de l'Oued Larbaa par les déchets de la ville de Taza (Maroc) (en français). International Journal of Innovation and Scientific Research, 10(2), 282–294.
5. Bouras S., Maatoug M., Hellal B. and Ayad N. 2010. Quantification de la pollution des sols par le plomb et le zinc émis par le trafic routier (cas de la ville de Sidi Bel Abbès, Algérie occidentale) (en français). Les technologies de laboratoire, 2, 5(20), 17.
6. Lahrach A. 1994. Potentialités hydrogéothermiques du Maroc oriental (en français). Thesis of Doctorate of Specialty, National School of Engineers of Sfax, Tunisia.
7. Philippeau G. 1986. Comment interpréter les résultats d'une analyse en composante principales (en français), ITCF: Paris, pp. 63.
8. Sadiki A., Mesrar H., Faleh A. and Chaaouan J. 2012. Modélisation et cartographie des risques de l'érosion hydrique: cas du bassin versant de l'oued Larbaa (Maroc) (en français). Papeles de Geografía, 11(55–56), 179–188.
9. Tribak A. 2000. L'érosion hydrique en moyenne montagne du Prérif oriental (Maroc): étude des agents et des processus d'érosion dans une zone de marnes tertiaires (en français). Thesis of State Doctorate, University Chouaib Doukkali, El Jadida.