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Contribution to the study of water chemistry and quality of Ziz River upstream of Hassan Addakhil Dam «High Atlas-Morocco»

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Abstract

Morocco is a Mediterranean country subject to water scarcity and pollution. This phenomenon is more present in his oriental and southern borders. The water quality is an essential condition for the establishment of a management system that will help ensure water supplies in the future. The Hassan Addakhil dam located in the north of Errachidia city, is an outlet for the waters from the Ziz River. It guarantees permanent water supply to all the cities and agglomerations (almost 240 000 inhabitant according RGH 2014) downstream the dam and in addition the drained waters from the dam to allow the irrigation of farmland in the Ziz Valley (4500 ha) and the plain of Tafilalet (22400 ha). The objective of this work is to identify and quantify pollution along the Ziz River upstream of the dam Hassan Addakhil from its major source of Sidi Hamza until the dam. This study investigates the spatial water quality pattern of eight stations located along the Ziz River. It has included the physicochemical analysis to characterize the environment and highlighted the parameters that determine the water quality namely: The conductivity, temperature, pH, major ionic components cations (calcium, magnesium, potassium and sodium), anions (chloride, sulfate, nitrate and bicarbonate), and a set of some trace elements (Iron, manganese, fluoride ...) This work is a fundamental step in the development of protection perimeters around the dam Hassan Addakhil. The study highlighted two water families: Sulfated calcic, and Chloride Sodium. The waters are usually well oxygenated; pH, temperature, and the nitrates and sulfates are considered eligible. An increase in certain trace elements is stored, in particular for arsenic and barium upstream towards downstream, and fluctuations in the levels of iron due to leaching by sediments along the Ziz River. The domestic liquid wastes contribute to the increase of traces elements in the waters.

Keywords: Dam of Hassan Addakhil, physicochemical quality, trace elements, liquid wastes.

1. Introduction

The water resources, both surface and groundwater, are becoming increasingly rare and affected by various sources of pollution. Human activities are the main reasons behind the deterioration of water. Thus, it is necessary to take all actions to guarantee and protect the quality of water intended for drinking supply and irrigation, which involve the need to protected water source perimeters catchments including deductions dams.

The Ziz basin in the southeastern Morocco is an example of a vulnerable water resource in arid areas. Both climatic models and actual trends in rainfall amounts collected in the region have projected a significant decrease in precipitation in Atlas Mountains, which provides the major source of water in southern Morocco [1].

The dam of Hassan Addakhil located in the southern piedmont of the High Atlas Centro-oriental is considered as an important unit in the region of Errachidia. It collects the waters of the high basin of Ziz, it also helps in controlling flooding and ensure regularized volume of 100 million m³ of water per year [2]. It covers the needs for drinking water and irrigation in the region, collects Ziz water catchment with average annual rainfall of about 124 mm [3]. And it ensures the irrigation of the Ziz Valley (4500 ha) and the plain of Tafilalet (22400 ha).

The Works in the study area have worn both on the hydrological and hydrogeological flow modeling of surface water [4-5], and groundwater of Ziz basin [6] and also on water quality of the dam [2].

Currently, the water of Ziz River, which feeds the dam Hassan Addakhil is subject to anthropogenic and agricultural action, which could cause deterioration of its water quality [3].

The objective of this work is to value the quality of water and to quantify the pollution along the Ziz River upstream of the dam, from the source of Sidi Hamza until the dam. This study presents a fundamental step in the delimitation of protected areas around the dam Hassan Addakhil. The conducted physicochemical analysis is planned to determine the water quality of the Ziz River feeding the dam.

2. Presentation of the study area and Ziz basin

2.1 Location of the study area

In the Ziz Basin, located in arid areas in southeastern Morocco, and which belongs to the great Basin Ziz-Rheris, surface waters are scarce. The dam Hassan Addakhil located 15 km north of Errachidia is used to collect surface water from the River Ziz and ensures the irrigation of farmland in the Ziz Valley, the plain of Tafilalet downstream and watering livestock (Figures 1-2-3).



Figure 1: Location Map of Ziz basin and study area

2.2 Geological framework

The Ziz basin extends from the High Atlas in the north to Anti-Atlas in the south. The central part contains the pre-African furrow, the fore deep located between the High Atlas and Anti-Atlas and contains the Cretaceous basin of Errachidia (Figures 1-3). The study area extends from the extreme east of the Central High Atlas to the western part of the Oriental High Atlas. It is limited to the North by the High Moulouya (Eastern Meseta) and to the south by the Oriental Anti-Atlas (Figures 1-3).

The geology of the Errachidia basin includes distinct structural domains that span from the Mesozoic until the Quaternary [7] (Figure 2).

The Trias is constituted of detrital deposits, doleritic basalt with evaporite levels, in angular unconformably above the deformed Paleozoic basement and structured by several tectonic phases [8-9-10]. The Jurassic series rest conformably on the red formations Triassic-Lower Lias. Their lithology consists essentially of dolomite, limestone, calcareous marl alternations, and silico-clastic detritus [9-11-12-13].

The Quaternary has a great lithological heterogeneity with deposits consisting mainly of conglomerates, gravels, pebbles, silts, of fluvio-lacustrine elements, sandstone, and marls sometimes. Their thickness does not exceed 50 m. the bedrock of quaternary deposits varies greatly in space; those are (Figure 3):

- Paleozoic substratum in the regions of Tinjdad, Tafilalt, Todgha, Ferkla ...;
- Cretaceous levels in the regions of Goulmima and the Ziz Valley;
- Jurassic horizons in areas of the Rich (High Atlas Ziz basin).



2.3 Hydrogeological frame

The water resources in the province of Errachidia consist of a share of aquifers located along the valleys and characterized by their small size and their direct dependence on weather conditions and secondly, deep aquifers of which are subdivided from north to south in three well separated hydrogeological units: high Atlas, the Cretaceous basin Boudnib- Errachidia-Tinghir and the Anti-Atlas [14-15-16-17] (Figure 3).



Figure.3: Main hydrogeologicals units in the Ziz-Rheris-Guir and Maider Basins [18]

The High Atlas contains a set of interconnected hydrogeological units (Lias and Dogger): The Lias is forming a relatively continuous system and Aalenien and Dogger aquifers form networks, fragmented into separate basins in each synclinal basin and usually without communication, sometimes with multiple aquifer levels. The waterproof series Toarcian-Aalenian separates between aquifers sets of lower Lias-Domerian and those of the Aalenien-Dogger. Communications between aquifers are only possible across the holes [18].

The water depth, according to the survey conducted in February 2014 at twenty water points, varies from a few meters to more than sixty meters. Productivity can exceed 100 l/s in the fractured Liassic formations in the areas of FourmTillicht, Tazmamert, Kheng, etc., with TDS typically less than 2 g / 1 [19]. The values of electric conductivity oscillate between 360 and 13000 μ S / cm [17].

These aquifers give birth to several sources; the most important are those of Zaouia Sidi Hamza, Tahamdount, Aghbaloun'Kerdous and Toudgha [18].

2.3 Climate and Surface water

The Hassan Addakhil dam is located in a semi-desert bioclimatic stage. Temperatures have significant seasonal variations with a very hot summer and a very cold winter. The annual rainfall regime is characterized by the existence of two rainy seasons: autumn and spring [2].



Figure 4: Distribution of rainfall map of the Ziz basin [20]

The distribution of rainfall map in the Ziz basin, obtained by isohyets method [20], based on the rainfall data of the hydrological basin agency Ziz-Rheris is presented in the figure 4.

The watershed of Ziz is formed mainly by semi-permeable and permeable grounds that occupy almost the entire area of the basin, which favors the infiltration of surface water.

The hydrographic system is rich by important valleys, but low development and sustainable way. The Ziz River presents regime a Saharan tendency, the main stream comprises an upper direction over 122km east-west becoming north-south of the village of kerrando. This course drains the basin upstream Ziz which is limited to the south by the Hassan Addakhil dam [21].

The Ziz River and its tributaries intersect the major structure axes of the High Atlas, forming the transverse valleys called "Foum" .The main tributaries are issued from Atlas: Outerbat River, Nsala River, Talsast River and Sidi Hamza River (Figures 1-3-5). On the right bank of Ziz (intermediate basin), several tributaries reach the Ziz in times of heavy flooding, while on the left bank, the Ziz receives two important tributaries: the River Meski formed by the confluence of several small Rivers and Aoufous whose tributaries are Boubarnous River and Rahma and sources of Aoufous which confer the steady state.

3. Sampling and analysis

Water resources in the Ziz basin are facing problems of shortage that continue to worsen and also presented vulnerability to pollution.

As part of this qualitative study of the Ziz River on the upstream of the dam Hassan Addakhil, a monitoring of the quality of these waters from upstream to downstream of the dam in April 2013 and all the basin Ziz-Rhéris in 2012 have been performed [22]. Seven sampling points (Table.1) are selected based on the River system (Figure 6), their locations relative to household pollution (traffic, factories, towns ...) and according to their importance in relation to the assessment of the quality of surface water.

The water analyses were performed at the UATRS platforms which are a set of technological unit that offers to the Moroccan universities and industry expertise, and different type of analysis. The University of Mohammed V, has gently covered the fees for the analysis.

The electrical conductivity, temperature, pH, alkalinity, dissolved oxygen and the redox potential were measured at the sampling point. At the laboratory, the anions (chloride, sulfate, nitrate and bicarbonate) were measured by ionic chromatography and analysis of calcium, magnesium, potassium, sodium and Silicon were made by ICP-AES. A set of some heavy and trace element (iron, manganese, fluoride ...) were analysed by ICP-AES (Ultima 2 - JobinYvon). The collection, transportation and storage of water samples refer to the protocol and procedures defined [23].



Figure 5: Location Map of sampling points

4. Results and Discussion

4.1Physical parameters (in situ analysis)

The temperatures recorded in this study vary between 18, 3 °C and 19, 7 °C; the data recorded in the four stations upstream of the reservoir does not have large significant differences between stations.

The thermal springs (Hamat), which belong to the large fault system Tizi'n' First, their temperature is between 40 °C in the Hamat Moulay Ali Chrif (S5) and 27°C in the Hamat Moulay Hachem (S6) and Aghbalou N'larbaa (S7) (Figure 6a).

The study area of surface water has a pH of between 6.8 and 8.5 (Figure 6b).

Conductivity of surface waters is less than 750 μ S / cm. The stations S3 shows a value of 1350 μ S/cm, where at the dam it is 785 μ S / cm (Figure 6c). However the conductivity of the waters of the Ziz River recorded an increase during the summer months due to intense evaporation and indicates strong mineralized salt water. For the thermal springs there was a fairly high conductivity.

468.07

512.92

648.77

434.96

S. Hamza

up Rich

bothmane

dam

19.7

18.3

19.6

19

8.5

7.54

8.05

8

66.31

59.51

66.52

46.33

Table.1. Results of physicoenemical analysis measured in 2015													
Sample	pН	Т	redox	Cond	O2	Alkalinity	Cl	SO4	NO_3	Mg	Ca	k	Na
Unit		°C	mv	μS / cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Hamat Mly Ali chrif	6.80	40.40		4000.00	2.50	210	5420.40	1821.60	0.10	77.85	575.60	23.05	2219.70
Hamat Mly Hachem	8.10	27.00	-0.90	2425.00	2.78	171	626.48	85.14	6.81	23.53	85.00	2.89	294.67
Aghbalou n'larbaa	8.00	30.30	0.80	2432.00	3.24	900	597.56	86.68	7.14	23.72	74.84	3.18	294.53
Sample	TI	DS	Τ°	pH	(Ca Cond	d Mg	Na	K	HCO ₃	Cl	SO4	NO ₃
Unit	Unit mg/l		°C	mg/l m		$\mu S / cr$	n mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l

732

750

1350

785

36.94

28.02

29.76

22.89

27.7

45.37

86.37

49.5

4.76

5.76

7.16

6.88

150

186

198

152

52.55

78.91

130.15

78.07

120.16

101.19

124.4

78.08

9.65

8.16

6.41

1.21

Table.1: Results of physicochemical analysis measured in 2013



Figure 6: Spatial evolution of Temperature (**a**) pH (**b**), and conductivity (**c**) of waters of the Ziz River measured in 2013

The dissolved Oxygen values range from 4.5mg/l to 5.6mg/l, which corresponds to average quality water and the waters of the River Ziz are well oxygenated. However, for water Hamat, dissolved O_2 is between 2 and 3 mg/l indicating a poor water quality. The annual curve concentrations of O_2 dissolved in the water of the River Ziz is of sinusoidal shape, with lower values in summer than winter [8]. This is due to the decreased solubility of that element when the temperature is increased.

4.2 Global mineralization

The concentrations of nitrates recorded during the study ranged from 1 mg/l and 9.65 mg/l; the levels of chlorides and sulfates of these waters are much lower compared to the standard limits (350 mg/l for chlorides and 250 mg/l for sulfates) [24], this corresponds to a water of good to excellent quality (Figure 8).

The presence of the ions is necessarily linked to the dissolution of minerals, the elements Ca^{2+} , Mg^{2+} and HCO_3^{-} are related to the dissolution of carbonate formations in the High Atlas Mountains.

The three sources, they have very high values in particular the chloride with a concentration of 5420 mg/l at Mly Ali Cherif source (Figure 6).

In the water of Ziz River, Nitrate concentrations are less than 10 mg/l (Figure 8). The concentrations of both, chloride and sulfate, show values below 200 mg/l (Figure 8), this corresponds to a water of good to excellent quality. On the other hand, the presence of the ions is necessarily linked to the dissolution of minerals; in fact the results of concentrations the elements Ca^{2+} , Mg^{2+} and HCO_3^- are related to the limestone dissolution in the High Atlas Mountains (Figure 8).

These waters have a sodium-potassium and chloride facies, and they are also in equilibrium with respect to calcite, dolomite and aragonite



Figure 7a: Spatial evolution of cationic major anionic component in the waters across of the Ziz River



Figure 7b: Spatial evolution of anionic major in the waters across of the Ziz River



Figure 8: Spatial evolution of Nitrates in the waters across of the Ziz River

The projection of water analysis on 2013 samples results on the Piper diagram reveals the following facies (Figures 9a-9b):

-Sulfated calcic and Magnesium (Ca-SO4) (Mg)-Type, for surface water upstream of the dam Hassan Addakhil, and showing enrichment on NaCl while moving from the Sidi Hamza spring upstream of the River Ziz into the Hassan Addakhil where the waters have a mixed facies (Figure 9a) .Mineralization is regulated by calcium and magnesium for cations and by sulfates for anions.



Figure 9a: Piper plot showing the surface water distribution of ZizRiver

-Chloride Sodium and potassium or sodium sulfated Na (K) Cl (SO4), for three sources (Figure 9b). In this case the mineralization is governed by Sodium and Potassium for cations, and anions for chlorides. They are also in equilibrium with respect to the calcite, dolomite and aragonite. The spatial distribution of those facies chemical depends on the lithological nature.



Figure 9b: Piper plot showing the water thermal distribution

4.3. Saturation index SI

It is the ratio of ion activity IPA the product of solubility at a given temperature. This index indicates the phase trends to dissolve or precipitate, and can track the geochemical evolution of water, resulting different reactions processes related to the water rock interaction. When it is positive (SI), it means that the solution is saturated or supersaturated with respect to the mineral that tends to precipitation. By cons, when (SI) is negative, the solution is sub saturated screw mineral screw which tends to dissolution [25].

In this study the saturation index is calculated through the PHREEQC is a computer program used to perform a variety of low-temperature aqueous geochemical reactions. The results obtained are summarized in the table 2 below:

The waters are predominantly under-saturated and minerals, this means that these elements still have a tendency to dissociate. About calcite, aragonite and dolomite, we can say that the water is more or less saturated to supersaturate with these minerals.

Mi	neral	SATURATION INDEX SI							
	Formula	Sample 1	Sample 2	Sample 3	Sample 4				
Anhydrite	$CaSO_4$	-1,83	-1,95	-1,84	-2,12				
Aragonite	CaCO ₃	-0,84	0,77	-0,12	0,18				
Calcite	CaCO ₃	-0,68	0,92	0,03	0,32				
Dolomite	CaMg (CO ₃) ₂	-1,64	1,79	-0,03	0,62				
Gypsum	Ca SO ₄ .2H ₂ 0	-1,57	-1,79	-1,6	-1,88				
Halite	NaCl	-7,39	-7,02	-6,53	-6,98				

Table 2: Values of the saturation index for different water samples

4.4Trace elements

Heavy metals are natural constituents in rocks and in mineral deposits. The natural presence of these elements is the geochemical background to assess the impact of a heavy metal into the environment, presence alone is not sufficient. This impact is given potential if the metal is present at levels abnormally high concentrations compared to the geochemical background [26].

A set of trace elements and heavy metals were performed and show a good water quality across of the Ziz River section until it reaches the Hassan Adakhil dam, however a trend of increasing levels of some elements appears. In fact, it concerns Arsenic and Barium. A Further study will be performed to understand their origin, including new sample analysis and a geochemical speciation to prospect the origin of those two elements.

Indeed the human impact on the surface water when they reach the city of Rich (Figure 10), here the input of the liquid wastes from the city contributes to the dilution of the trace elements and heavy metals except for Arsenic.



Figure 10: Variation of some trace elements and heavy metals across of Ziz River

The fluctuation and the high levels of Iron since the Sidi Hamza source until the dam (Figure10) is due to its leaching from the soil, sediments and rocks from the bed of Ziz River.

The three thermal sources have higher levels of those elements, and it also appears the Hamat Moulay Ali chrif contributes to the increasing of those elements in the waters.

sample	Al	Fe	As	Со	Mn	Ni	Pb	Sr	Zn	Ва	Si
Unit	mg/l										
S. Hamza	0.29	0.3	0.06	0.58	0.11	0.02	0.02	3.52	0.02	0.11	5.17
Up Rich	0.19	0.01	0.08	1.46	0.11	0.41	0.03	2.49	0.02	0.1	3.56
Aitothmane	0.05	0.06	0.18	0.11	0.1	0.02	0.04	2.7	0.02	0.13	3.34
Dam	0.3	0.4	0.28	0.73	0.11	0.04	0.03	1.69	0.02	0.14	2.65

Table 3: Results of traces elements and heavy metals analysis

Conclusion

The hydrochemical study of surface waters of the Ziz basin upstream of the dam Hassan Addakhil showed that the waters are moderately to highly mineralized. Piper diagram highlights two types of chemical facies: The sulfated calcic, and chloride sodium.

The conductivity of the thermal water is generally high and reaches 2432μ S/cm for the sources, which can affect seriously the chemistry of the Ziz River during the dry season and change at the end the mineral equilibrium in the HassanAddakhil Dam. The salinity of the water is controlled mainly by chlorides and sodium.

The presence of heavy and trace elements in this water contributes to deteriorate their quality (Pb, Zn, Ba and As) in particular for Arsenic and Barium from the upstream towards downstream of the Ziz River. The domestic liquid wastes contribute in the increase of traces elements in the waters, and shows a fluctuation in the levels of iron due to leaching by sediments along the Ziz River. It also appears that the thermal sources are the cause of the presence of those elements in the waters, especially Hamat Moulay Ali Cherif.

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References

- 1. Chaponniere A. And Smakhtin V., Work.pap. 110, Dro.Ser. 8 Coll.Srilanka, Int.wat. Mangt. Instit. ISBN 92-9090-635-9 (2006).
- 2. Ouhmidou M., Chahlaoui A., Kharroubi A., Chahboune M., J. Mater. Environ. Sci. 6 (2015)1663-1671
- 3. Drif K., Kacimi I., Hilali M., Kassou N., Bahaj T., Morarech M., Mor. J. Chem. 2-5(2014) 434-437.
- 4. Margat J., Ress. en eau du Maroc, (1977) 310-380.
- 5. Ait Boughrous A., Thèse de Doct. , Fac. Sci. Semlalia, Marrakech. (2007) 207.
- 6. El Jaafari A., Morin G., Belkhadir R., El Jaafari S., 3^{ème} J. Int .des Géosci.de l'Env.Abstr. Conf.El Jadida (2005) 08-10 Juin.
- 7. Michard A., Not. et Mém. Serv. Geol. Maroc, N°252. (1976) 408.
- 8. Charrière A., Thèse Doct. Etat, Toulouse, (1990) 589.
- 9. Hinaje S., Thèse de 3ème cycle, Fac. Sci. Rabat. (1995) 238.
- 10. Chafiki D., El Hariri A., Souhel A., Lachka N., Sarih S., Dommergues J., J. Afr. Earth Sci., V 49, (2007) 90–102.
- 11. Sadki D., Elmi S., & Amhoud H., Le 1^{er} Coll. Nat. Sur le Jur. Marocain, (1999) 122-123.
- 12. Piqué A., Charroud, M., Laville, E., & Amrha, M., Mém .du Mus. Nat. d'hist. Natur., V182 (2000) 93-106.
- 13. Igmoullan B., Sadki D., Fedan B., et Chellai E. H., Bull. de l'Inst. Sci.de Rabat, Sect. Sc. de la Terre 23 (2001) 47-54.
- 14. Margat J., Not.et Mem. du Serv.Géol. du Maroc N°97, Rabat (1952)
- 15. Margat J., Des tombes J., et Hollard H., Not.et Mem .du Serv. Géol. du Maroc ,150bis (1962) Rabat.
- 16. DRH GRZ, Rapp.de la miss. II, Unpublished (2009).
- 17. Nouayti N., Khattach D., Hilali M., J. Mater. Environ. Sci. 6 (4) (2015) 1068-1081

- 18. ABH GZR, Et .Syn.Hydrog .Haut Atlas, Unpublished (2009)15-16.
- 19. Hilali M., Boualoul M., Sahbi H., Benamara A., 2^{ème} Coll. Inter. sur la Gest. et la Présrv.des Ress. en Eau (CIGPRE 2). Meknès, les 10 11-12 mai 2012.
- 20. Nouayti. N., Hilali. M., Khattach. D., Mezraoui. M , Coll. Syst.Nat.d'Inf. d'Eau, 02,03 et 04 déc. N'WIS (2014), Rabat.
- 21. Drif K., Kacimi I., Hilali M., Kassou N., Bahaj T., Morarech M., Act. Coll. des 19^{eme} J. Tech. du CMH. de l'AIH (2013) 273-280, Bordeaux.
- 22. Bahaj T., Kacimi I., Hilali M., Kassou N., Mahboub A., Proc. Earth and Plan. Sci., (WRI 14), 7(2013)44 48.
- 23. ONEP, Direct.Contr. Qualité des eaux, Maroc (2007).
- 24. SEEE, Normes de Qualité B.O.2002, Secrétariat d'Etat auprès du Ministère de l'Energie, des Mines, de l'Eau et de l'Environnement (MEMEE), chargé de l'Eau et de l'Environnement, (2007) Maroc.
- 25. Ammary B., Thèse d'état, Fac. des Sci. de Rabat. (2007).
- 26. Alloway B.J. et Ayres D.C., Blackie Acad. Prof., Chapman and Hall, London, (1997)394.

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