

Assessment of surface water quality in the Beni Haroun dam Algeria using X-ray fluorescence spectrometry after preconcentration

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Abstract

X-ray fluorescence spectrometry after preconcentration of the water of Beni Haroun dam (BHD), Mila, Algeria. Has carried out with two different methods which yielded the contents as following Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Mo, Cd, Ba and Pb. The first method is preconcentration t evaporation temperature (PET), this method based on the recovery of limestone, and it is simple and cheaper. Whereas the second preconcentration method is based on the absorption of cations on Amberlite XAD -7 resin (AXAD-7R). The effect of certain parameters such as pH, temperature, conductivity, Nitrate dosage, chemical oxygen demand (COD) and limit of detection has been studied. The detection limits were reached for Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Zn, As, Br, Sr, Zr, In and Ba, during the four seasons of the year 2018. In this Water, the X-ray diffraction analysis showed the existence of the following phases: Calcium Carbonate Hydrate: $\text{CaCO}_3 \cdot \text{H}_2\text{O}$, Sodium Chloride NaCl and silicon dioxide SiO_2 . The principal component analysis (PCA) has been studied. The matrix of correlation between trace element and the PCA indicates that they come from similar sources. This explains the anthropogenic contributions of agricultural pollution by runoff water, discharges of domestic water and soil erosion. Regular monitoring of heavy metals in Beni Haroun dam water has recommended avoiding any risk of excessive accumulation.

Keywords: trace elements; Beni Haroun dam; X-Ray Fluorescence (XRF); Limestone; Amembrlite XAD -7resin; principal component analysis (PCA).

1. Introduction

Trace elements investigation in dam water of Beni Haroun using X-ray fluorescence (XRF) after preconcentration, has been our concern to preserve this strategic resource from any risk of contamination. We must spend all the efforts to obtain drinking water that is as healthy as possible [1]. The Beni Haroun dam is located in the north east of Algeria, at 36°33'19" North and 6°16'11" East; it contains the greatest artificial reserve. In February 2012 and December 2014, its reserve reached 1 billion m³ of water[2] it is equipped with a large strategic hydraulic transfer complex including a pumping station with a flow of 21 m³/s over 700 m vertical drop, which feeds five cities in the East (Mila, Constantine, Oum El Bouaghi, Batna and Khenchela) [3].

As well as the heavy metal-containing materials to aqueous samples is one of the most dangerous types of pollution in aquatic systems. Heavy metal contaminants can accumulate in the water easily. Trace elements are present in all compartments of the environment, and multiple anthropogenic activities favor their dispersion [4]. Aquatic systems contamination by toxic substances, in particular trace elements, from point and diffuse sources

(drainage water, sewage, industrial and agricultural effluents) [5]. The physicochemical parameters of waters determine the mobility and bioavailability of heavy metals by affecting their speciation and therefore their behavior[6]. Tailings are directly discharged into natural depressions, including onsite wetlands resulting in elevated concentrations [7]. The potential for exposure and toxicity, of all metals, according to the Environmental Protection Agency of the United States, chromium (Cr) has been designated and its compounds as one of the 17 chemicals posing the greatest threats to human health [8]. As well as the high concentration of iron and other elements in the water used in the industry can be harmful. Example, iron in water can cause coloring of laundry and porcelain [9]. Moreover, the deterioration of water quality is the result of heavy use of chemical fertilizers and fertilizers in agriculture. Thus, the degradation of the quality of surface and underground water by nitrogen, phosphorus and metal elements, induced by agricultural activity, has been widely verified in the world [10]. Livestock has also participated in a remarkable way in water pollution [11-12-13]. As well as the geological site of the dam showing rocky units, are from upstream to downstream: Eocene marls,

strongly deformed and altered, an Eocene limestone bar (Ypresian), and finally, black marls of Paleocene constituted of marl, located immediately downstream of the dam [14-15-16]. The analysis of water samples is a key step in the characterization process of contaminated water. It allows the identification of contaminants and the determination of the extent and degree of contamination in a given water. The performance of the analytical methods used is therefore essential to ensure a good evaluation and subsequently to choose an adequate remediation strategy. Trace element analysis techniques has prompted researchers quickly developed these techniques in response to the growing need for accurate measurements at very low amount of content in various matrices [17]. Among these techniques, X-ray fluorescence spectrometry (XRF) is an elemental analysis method widely used in science and industry for the detection and quantification of elements present in liquid, solid or powder samples, without particle preparation. X-ray fluorescence (XRF) is based on the principle of excitation of individual atoms, by an external energy source, emit X-ray photons of a wavelength or characteristic energy. It has the advantage of being non-destructive, multi-element, fast and cheaper compared to other techniques [18]. The need for preconcentration of trace elements or ions in aqueous results from the fact that instrumental analytical methods often do not have the necessary selectivity, sensitivity, or freedom from matrix interferences. The chemical techniques used in preconcentration can provide, in many cases, analyte isolation, as well as enrichment factors. There are several methods of trace elements separation and preconcentration by coprecipitation, flotation, solvent extraction, ion exchange (of specific or non-specific resins) and sorption [19]. In the present work, we used preconcentration on Amberlite XAD-7 resin and preconcentration at evaporation temperature (PET). The (PET) is based on the recovery of limestone, to determine the trace elements in the surface water of Beni Haroun dam, Algeria. This method has shown its effectiveness.

Other physicochemical parameters has been done such as conductivity, chemical oxygen demand (COD) and nitrate determination and pH shift between 7,15 and 8,11, as well as the X-ray diffraction analysis to see the different phases in our samples.

The main objective of this study is the assessment of water Beni Haroun dam quality that will be based on the oligo-elements concentration (C_{Oli-e}). Through a research for the factors associated with the pollution phenomenon including a number of potential explanatory variables, namely, preconcentration technique, stations, seasons and oligo-elements. This work leads us to show which isbest performing technique, the season's effect, the most polluting station and the most focus elements. Our database consists of five characters, four of them are qualitative and one of them is quantitative variables, described as below:

- Stations: 2 -level factor: S1 and S2.

- Seasons: 4-level factor: winter, spring, summer, autumn.
- Preconcentration: 2-level factor: PET (limestone), Amberlite XAD -7 resin.
- Oligo-elements (C_{Oli-e}): eleven-level factor: Na, Mg, Al, Si, S, Cl, K, Ca, Fe, Zn and In.

To evaluate water of Beni Haroun dam and the best performing technique, a binary interest factor ('Colig-e', 'Non Colig-e'), based on concentration of oligo elements (Colig-e). The data analysis technique adopted to achieve this work is the principal component analysis (PCA).

2. Materials and Methods

2.1. Sampling, preconcentration techniques and analysis

The choice of the S1 station near the wall of the dam (GPS coordinates 36°56 55 N 6°27 61 E) and the station S2, drinking water pumping station (GPS coordinates 36°49 44 N 6°31 12 E).As well as the two methods of preconcentration were primarily provided information makers of (metallic element traces) in the water of Beni Haroun dam and the choice of the method. They allow spatio-temporal monitoring of oligo-elements concentrations at the dam.

Characterization of most present trace elements in the water of Beni Haroun dam was performed using X-ray fluorescence spectroscopy. This technique enables us to identify all the elements of Periodic Table except for hydrogen, lithium and beryllium. The analysis of the light elements (boron, carbon, nitrogen and oxygen) is tricky. As for the quantification of nitrogen and carbon, nitrate nitrogen was measured by JENWAY brand UV-Vis spectroscopy, carbon by a DCO-meter of a Hach brand model 45600, conductivity by conductivity meter JENWAY 4510 and the acidity was measured with a brand JENWAY 3505 PH-meter.

The analysis was performed by Panalytical Epsilon 3 spectrometry of 9 watts power. Epsilon 3 is an energy dispersive X-ray fluorescence spectrophotometer for the elemental analysis range from Na to Am and concentration range from ppm to 100 %. The device connected to the computer equipped with analysis software OMNIAN. During all analysis, the samples are fitted under helium flux. The X-ray tube, which is made with metal-ceramic to ensures a better stability of the X-rays than the traditional glass tubes, its role is selecting optimal excitation conditions.

The preconcentration at evaporation temperature method was used for samples S1 and S2 at a temperature of 80°C. A powder (limestone) buffer 2.5 mm in diameter and 2.5 grams in weight was produced under a pressure of 8 tons for the use ofthe analysis by X-ray fluorescence which was recovered by evaporation of 10 liters of water of the dam which gives 250 mg/l. While forthe Amberlite XAD-7 resin method of samples S1 and S2 and after drying at room temperature, a weight of 2.5 grams of each sample was used for X-ray fluorescence analysis.

The range of X-ray fluorescence was recorded under different excitation conditions, for the Beni Haroun limestone (S1 and S2) at 80°C, and the Amberlite XAD-7 resin of the S1 and S2 samples. The X-ray fluorescence range were recorded six times under different excitation conditions. The peaks are strongly attenuated under such conditions. The first (Omnian) was realized with silver filter of 100 μm thickness, a 30.00 keV ddp and a 300 μA current. The second (Omnian1) was realized with aluminum filter of 200 μm thickness, a 20.00 keV ddp and a 450 μA current. The third (Omnian2) was realized with aluminum filter of 50 μm thickness, a 12.00 keV ddp and a 750 μA current. The fourth (Omnian3) was performed without a filter, a ddp of 5.00 keV and a 667 μA current. It allows us exploring the energy domain up to about 26 keV. The use of a silver filter allows us exploring the spectrum domain stretching between 1 and 26 keV, but the use of an aluminum filter makes it possible to explore the domain of the spectrum between 1 and 20 keV.

The diffractometer was realized with an X'pert-PRO analytical powder diffractometer. The data recording was achieved out within an angle range from 10° to 90° with a 0.013°/read for a 560 s step time. The voltage and current of the tube were 45 kV and 40 mA, respectively. The device uses a 0.154060 nm wavelength radiation with a tube made of copper (Cu) anode. The diffraction data were analyzed with a PANalytical X'Pert High Score Plus software program. The crystalline phases were

determined compared to registered models of the PDF2 data base.

The COD determination have carried out by oxidation of the organic matter in sulfochromic medium at 150°C. The decrease in the oxidant concentration (potassium dichromate) isproportional to the amount of organic matter contained in the sample. A spectrometric length of 345 nm determines the decrease. It isproportional to the amount of oxygen necessary for the oxidation of the organic matter present in the sample. However, the use of sodium salicylate results in the appearance of sodium paranitro salicylate, which makes it possible to determine the concentration of nitrates at a spectrometric measurement of 420 nm.

2.2. Statistical analysis

For the processing of the results, we used a principal component analysis PCA, which is an exploratory and descriptive method [20]. Its purpose is to replace the p initial variables strongly correlated with each other in p variables called principal components not correlated with each other, and of gradually decreasing variance. We aim to study the effect of the factors 'limestone', 'Resin' 'Stations', 'Seasons' and 'Trace elements' on the best performing technique and the presence of pollution. Relations between the analyzed elements were examined using test student (T test) to compare two variances with a statistical significance fixed at p-value <0.05. PCA was performed using R (4.3.2) software.

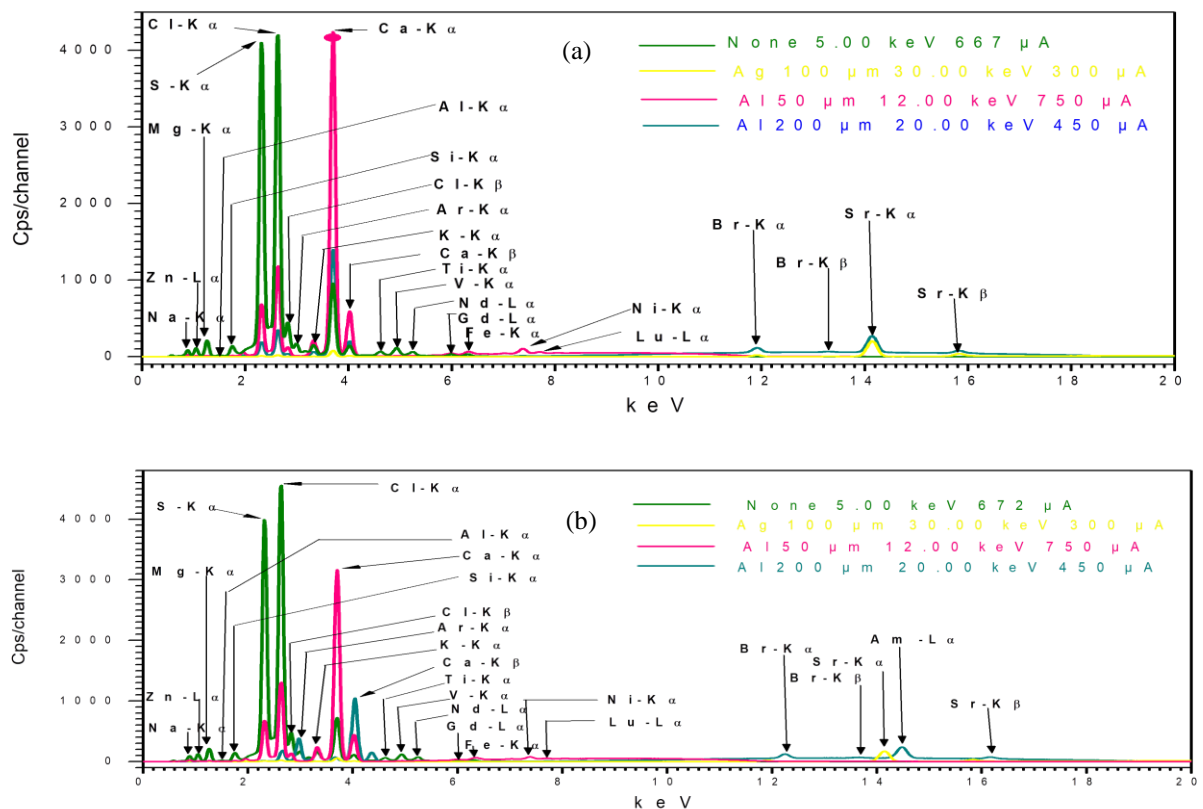


Figure 1. XRF spectra of limestone from BeniHaroun dam using (PET) method (a) sample S1 (b) (sample S2)

3. Results and discussion

3.1. X-ray fluorescence

The results obtained by the spectroscopic analysis of the X-ray fluorescence under different conditions are presented in (Figure 1 (a), (b)) and (Figure 2(a), (b)) successively for the limestone and Amberlite XAD-7 resin, samples S1 and S2 of the Beni Haroun dam. A metallic composition has explained by the position of

pics in spectrum. The information of spectra indicate the presence in the limestone as well as with XAD-7 resin of Beni Haroun dam the following elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Zn, As, Br, Sr, Zr, In and Ba. The total mass of the preceding elements represent 99,52% and 98,8% of the total mass successively of the water evaporated by the preconcentration method at the evaporation temperature (PET) and the mass by the preconcentration method of Amberlite XAD-7 resin.

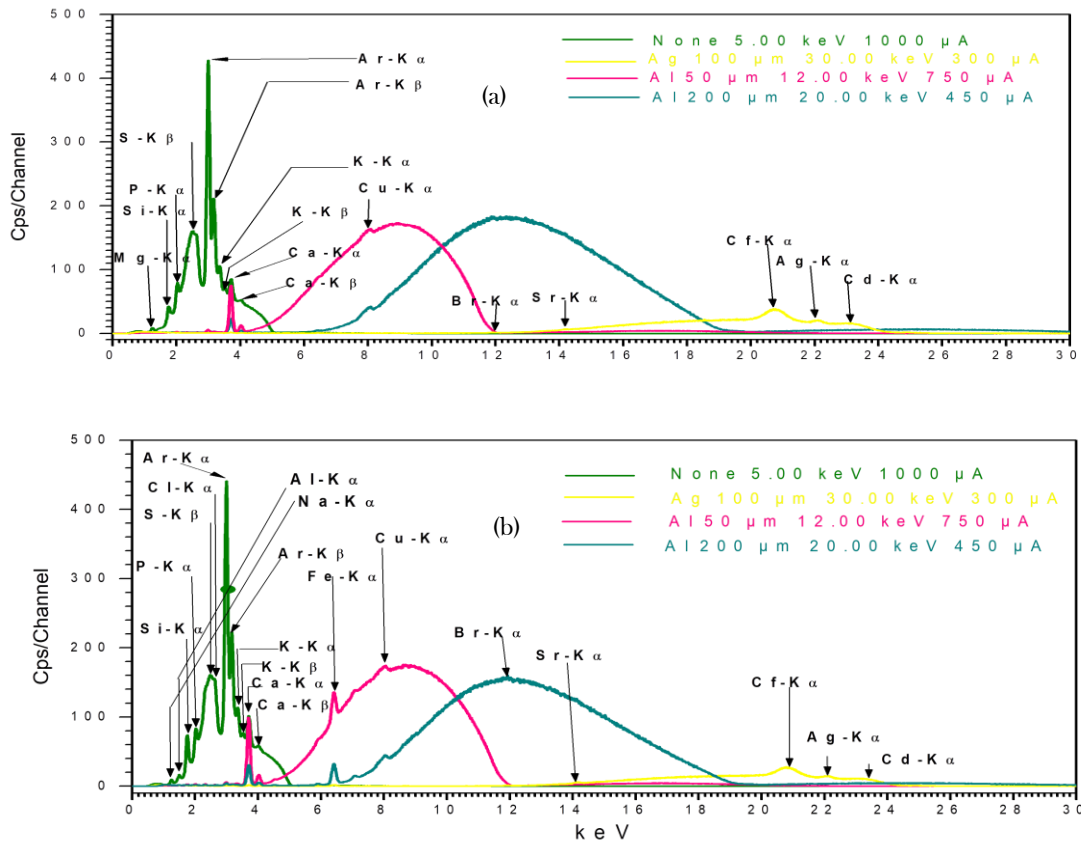


Figure 2. XRF spectra of water from BeniHaroun dam using the Amberlite XAD-7 resin method. (a) sample S1 (b) (sample S2)

Spectra of energy dispersive X-ray fluorescence (ED XRF) using the XAD-7 resin (Figure 2 (a), (b)) and limestone methods (Figure 1 (a), (b)) of the water of BeniHaroun dam, achieved with different filters has shown that several rays were measured for most of the elements, these rays are:

- Kα and Kβ of the light elements Na, Na, Mg, Al, Si, P, S, Cl and K, for an energy between 5.00 keV (667 μA), and 12.00 KeV (750 μA).
- Kα, Kβ, Lα and Lβ of the medium and heavy elements Ca, Ti, Mn, Fe, Zn, As, Br, Sr, Zr, In and Ba, for an energy between 12 keV (750 and 450 μA), and 30.00 keV (300 μA).

The area of the peaks is proportional at concentration percentage of trace elements.

The X-ray fluorescence does not determine the form in which the elements are linked, and the linked elements

are generally light and therefore not measurable. Consequently, to find a solution to this problem, we resort to the use of the X-ray diffraction analysis (XRD)(Figure 3).

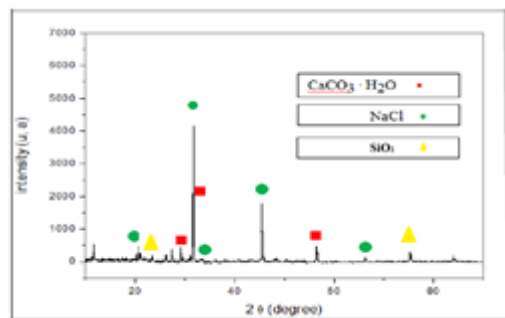


Figure 3. XRD specter of the limestone of BeniHaroun dam.

The X-ray diffraction analysis of the specter of the limestone from BeniHaroun dam showed the existence of the following phases: Sodium Chloride NaCl (PDF number 00-001-0994), Calcium Carbonate Hydrate: $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (PDF number 00-015-0020) and silicon dioxide SiO_2 (PDF number 01-085-1054).

3.2. Statistical analysis methods

3.2.1. Descriptive statistics

The statistical data of the physicochemical characteristics and the trace elements of the water of BeniHaroun dam are summarized in the (Table 1).

Table 1: Descriptive statistics of physicochemicals properties and trace elements.

Variable	Min	Max	Moy	Ecart-type
pH	7.15	8.23	7.66	0.288
Cond($\mu\text{S}/\text{cm}$)	721.00	844.00	747.19	39.336
NO_3 (mg/l)	6.204	8.361	6.892	0.788
COD(mg/l)	18.372	21.383	19.923	0.828
Na %	6.645	10.078	8.484	1.694
Al %	0.058	0.077	0.070	0.008
Cl %	18.986	21.917	20.382	1.328
Mn %	0.009	0.012	0.010	0.001
Fe %	0.015	0.021	0.018	0.003
Zn %	0.005	0.022	0.015	0.007
As %	0.003	0.004	0.004	0.001
Ba %	0.009	0.015	0.012	0.003
Mg %	4.433	7.697	6.305	1.455
Ca %	0.030	0.070	0.048	0.017

The pH of the water dam BeniHaroun of two stations S1 and S2 shows a slight variation, It fluctuates between 7,15 and 8,23 with an average of 7,66. The dam waters have a pH close to neutral with an alkaline character. This alkaline character could be attributed to the photosynthetic activity of phytoplankton, including cyanobacteria, and / or to high concentrations of bicarbonate in the medium[21-22].

The Ecart type which represents the most common dispersion characteristic. The values of the conductivity of the dam water fluctuate during the 48 campaigns between (700 <Cond <900 $\mu\text{S}/\text{cm}$), these values of the current work remain below the values of conductivity recorded in other dams [23-24].

Nitrates are essential nutrients for aquatic plants and seasonal fluctuations can be caused by plant growth and decomposition. Nitrate concentrations and river flows have the same annual trend, with the lowest values during summer and the highest values in winter [25]. While the Chemical Oxygen Demand (COD) quantifies the chemically degradable pollution by hot oxidation. Normally the COD content of surface water is low. However, conductivity, nitrates and COD values are high in humid periods [26].

The tests of evaluating the content of nitrate and COD successively in the water of the dam is in average of 6.892 and 19.923 mg/l, are in below standards recommended by the World Health Organization (WHO). The total concentration of trace elements measured in water samples from the Beni Haroun dam after pre-concentration (limestone) in the both stations, has shown a results which indicate irregular fluctuations in the both stations and during the four seasons (Figure 4).

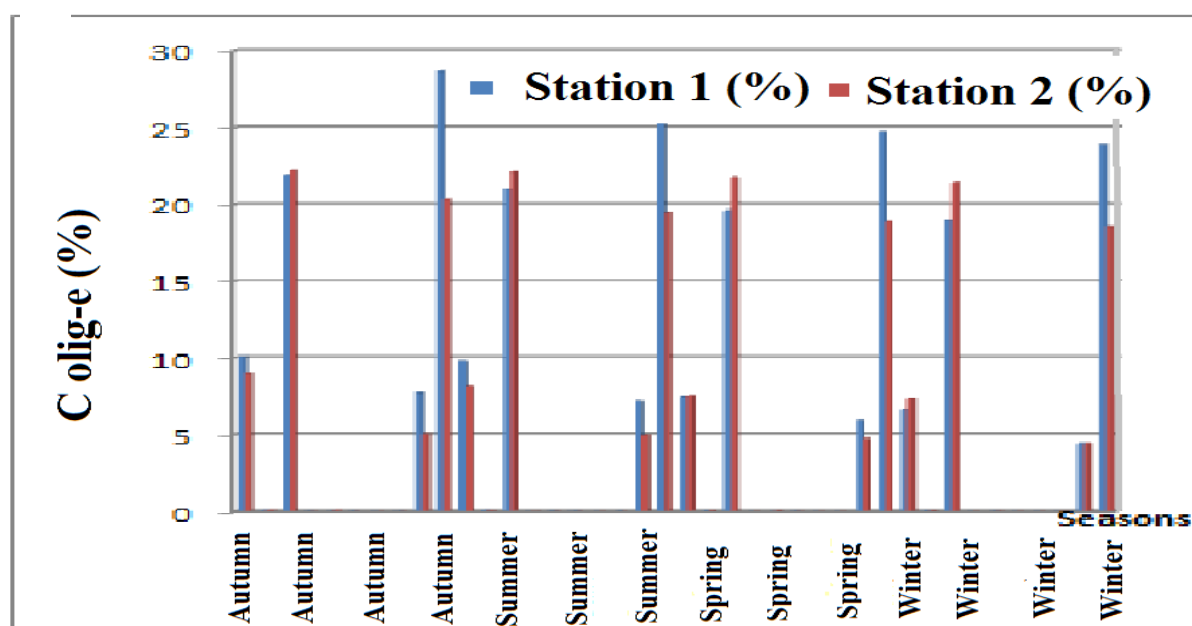


Figure 4. Spatio-temporal variation of trace elements concentration from the water of Beni Haroun dam.

Indeed the physicochemical conditions and the seasonal effects play an important role to change the concentrations of trace elements. In the rainy season, the enrichment in trace elements is mainly due to the increase in metallic pollutant loads in runoff from the first floods [27]. Which shows trace elements very high in sediment. While in the surface waters of the dam, a high concentration of trace elements observed in station 1 compared to station 2 and in the dry seasons but much more in autumn, which can be explained by the diffusion of each element in the dissolved phase. While the low concentrations during the rainy season could certainly be explained by the dilution phenomena.

In order to check the water of the dam contamination status, the contamination index (CI) is calculated. The raw results of the metallic contents constitute an instrument for assessing the degree or index of metallic pollution and the spatio-temporal trends associated with it [28-29]. CI is defined for a given metal as the ratio of the measured content at a given station to the optimum natural content set as a reference by the World Health Organization (WHO). The CI have expressed by the following formula: $CI = C_{\text{Oligo}} / C_{\text{ref}}$

Tableau 2: Means contamination indices (MCI) of trace elements

Trace element	Unit	C_{Oligo} Station S1	(MCI) Station S1	C_{Oligo} Station S2	(MCI) Station S2
Na	mg/l	25.195	0.126	22.800	0.114
Mg	mg/l	21.743	0.145	21.231	0.142
Al	µg/l	193.5	0.968	182.6	0.913
Cl	mg/l	57.293	0.229	54.25	0.217
Mn	µg/l	0.03	0.0003	0.05	0.0005
Fe	µg/l	302.5	0.605	293.5	0.587
Zn	µg/l	0.055	0.011	0.25	0.05
As	µg/l	10	1	10	1
Ba	µg/l	37.5	0.375	39.8	0.398
Ca	mg/l	74.163	0.370	80.2	0.401

We calculate means contamination indices (MCI) of Na, Mg, Al, Cl, Mn, Fe, Zn, As, Ba and Ca. Based on guidelines of (WHO 2011) standard for each element (Tableau 2).

The conditions of contamination or non-contamination:

- If CI close to 1, we consider that the site is not or little contaminated.
- If CI beyond 2, the site is subject to the start of contamination.
- If CI is less than 1, it is either a dilution or an analytical error [30].

It is known that the mineral salts contained in water (Na, Cl, Ca, Mg, K etc.) have effects on the soil, plants and human beings. In addition, according to (Person, 1978) salts cause changes in the structure of the soil and the consumption of these waters can cause chronic diseases. However the contamination index of trace elements such as Na, Mg, Cl are less than 1, consider not contaminate, we can explain these results due to dilution.

Metals are found naturally in organisms through the food and water. Metals such as copper, selenium and zinc are essential metabolic components at low concentrations. However, metals tend to bioaccumulate in tissues [31]. While metals such as Aluminum, Iron and Arsenic have shown an average contamination index close to 1 for Aluminum and Iron, while for Arsenic equal to 1. These metals are mainly found in the drinking water [32-33]. Arsenic is a semi-metallic element found naturally in certain surface and underground waters, can cause cancer in people exposed to excessive concentrations by drinking water. Heavy, industry and mining can result in higher concentrations than would be found naturally [34]. The average contamination index of the trace elements determined by X-ray fluorescence in the surface waters of the Beni Haroun dam, have values within or below the tolerance limit, indicating the absence of contamination during the sampling period.

Table 3: Comparative study of the physico-chemical parameters and the contamination of trace elements, between Beni Haroun dam and other hydro systems in the world.

Parameters	BeniHaroun (present study)	OuedChélif (Algeria, 2018)	Nil Egypt, (2010)	Rhône (France, 2011)	Litani (Lebanon, 2014)	Sebou (Maroc, 2015)
Cond (mS.cm ⁻¹)	0,72-0,85	0,9-80,0	0,4-7,3	/	0,6-0,8	0,7-2,4
NO ₃ ⁻ (mg.L ⁻¹)	6,20-8,36	0,5-15,7	/	0,1-12,4	0,2-39,0	10,0-490,0
DCO (mgO ₂ .L ⁻¹)	18,37-1,383	28,8-3160,8	1,0-30,9	/	20,0-53,0	/
Cl (mg.L ⁻¹)	54,25-7,293	165,7-1287,0	117,8-218,6	3,5-21,2	31,0-800,0	46,0-490,0
Al (µg.L ⁻¹)	182,6-193,5	0,0-1563,8	0,0-0,4	/	0,0-0,1	3,1-310,0
Zn (µg.L ⁻¹)	0,25-0,055	0,6-270,1	0,0-0,4	0,-8,4	0,0-0,3	1,2-210,0
Fe (µg.L ⁻¹)	293,5-302,5	0,0-1073,0	0,0-0,3	/	0,1-4,2	5,9-270,0
As (µg.L ⁻¹)	9,6-10	0,0-5,3	0,0-0,1	1,2-4,7	/	0,5-3,0

The results obtained in the Beni Haroun dam surface waters of the present work are compared with other hydro systems in the world in order to estimate the level of contamination (Tableau 3). Concerning these conductivities, values remain well below the values recorded in other dams but close to that of Litani, Lebanon [35]. While nitrates and chemical oxygen demand (COD) are within the standards set by the World Health Organization (WHO) and close to that of the Nile, Egypt [36]. Nevertheless, the trace elements show a low concentration, but the Cl⁻ is stronger than in Rhone, France [37]. The concentration of Arsenic element (As) in the present study is very high compared to other systems as hytrosebou, Morocco and OuedChélif [38-39]. These elements are indicative of industrial activity, wastewater discharges and natural erosion processes.

3.2.2. Test student (Test t)

We use the student test (Test t) to compare two variances between the preconcentration methods and the two stations (S1 and S2) which are summarized in the table 4.

Tableau 4: Test student (Test t) for the preconcentration methods and the two stations (S1 and S2)

methods	stations	variances	T student	df	P-value
Limston	S1	2.79882	0.3853	150	0.7006
	S2	1.88538			
XAD-7 resin	S1	4.41854	0.4490	78	0.6546
	S2	2.79199			
Limston	S1	6.59908	2.2208	114	0.0283*
		0.37661			
XAD-7 resin	S2	8.68457	4.3455	60.738	0.000054*
		3.21048			

* $P \leq \alpha = 0.05$: there is a significant correlation

We observed that the student test showed a significant correlation ($P\text{-value} \leq \alpha = 0.028$ and $P\text{-value} \leq \alpha = 0.000054$) for the method of preconcentration by temperature evaporation (PET) "limestone" and the method of resin XAD -7 Amberlite "Resin" from station S1 and S2 successively.

3.2.3. Principal component analysis (PCA)

A principal component analysis (PCA) made from data obtained allows to know enrichment of dam water with trace elements and the different physicochemical parameters for 14 variables. The latter is performed on a data matrix consisting of 48 samples (Figure 5(a),(b)).

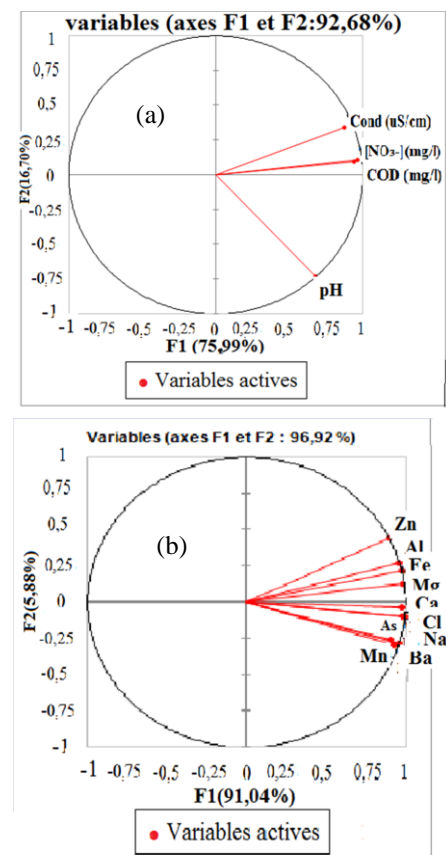


Figure 5. Representation of principal component analysis (PCA) results of the water Beni Haroun dam: Projection of variables (a) physico-chemical properties (b) Trace elements.

(Figure 5(a)) presents the distribution of the physico-chemical parameters measured. According to the two main axes (F1 and F2), explaining 92.68% of the total variance. The contributions are as follows: F1 (16.70%) and F2 (75.99%). The pH is negatively correlated with conductivity (Cond), NO₃⁻ and COD; which confirms the important role which plays in the increase these parameters and its monitoring of the trace element contents.

(Figure 5(b)) presents the distribution of the trace elements analyzed (Zn, Al, Fe, Mg, Ca, Cl, Na, As, Ba and Mn) according to the two main axes (F1 and F2), explaining 96.92% of the total variance. The contributions are as follows: F1 (5.88%) and F2 (91.04%).

The analysis of the trace elements shows that the Zn, Al, Fe, Mg are positively correlated with the Ca, Cl, Na, As, Ba and Mn which means that several previous studies have indicated that the discharge of industrial and domestic activities are responsible for the high concentrations of trace elements in aquatic environments, [42].

4. Conclusion

The Beni Haroun dam is part of the Oued EL Kebir drainage basin, which feeds five cities in the northeast of Algeria of drinking water. The results of X-Ray Fluorescence analysis with two different methods (XAD-7 resin and limestone) and the physicochemical analyzes, conducted in this study, showed that reliability and profitability of limestone in the determination of trace elements with low contents of trace elements, good oxygenation of the superficial waters, the reservoir never reached an anoxic stage during the period of study, the alkaline pH and conductivity are standard. The raw results of the trace elements contents and the physicochemical parameters were an instrument to assess the degree or the contamination index of the trace elements and the spatio-temporal trends associated with it. A principal component analysis (PCA) made from data obtained has allowed to know enrichment of dam water with trace elements and the different physicochemical parameters. Generally, the water quality of the Beni Haroun dam seems to be suitable despite to some recognized disturbances in some sections, which are essentially linked to alterations by trace element and some physicochemical parameters, which influence the quality of the surveyed dam.

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References

- [1] World Health Organization (WHO), Guidelines for Drinking Water Quality, Recommendations, (2011) 4th ed. Switzerland.
- [2] National Agency for Dams and Transfer, Mila. Algeria, (2017) 1.
- [3] S. Boulahbel, A. Mebarki, 5th International Resources Symposium, ENSH Blida, (2013) 749-754.
- [4] K. Swarnalatha, A.G. Nair, Research and Management, 22 (2017) 65-73.
- [5] N. Dahri, A. Atoui, M. Ellouze, H. Abida, Journal of African Earth Sciences. 140 (2018) 29-41.
- [6] K. Singh, N.B. Singh, Int. J. Chem. Sci. 12 (1) (2014) 191-198.
- [7] P.S. Devolder, S.L. Brown, D. Hesterberg, K. Pandya, K Journal of environmental Quality, 32 (3) (2003) 851-864.
- [8] Environmental Protection Agency (EPA) 745-R-99-001, 33/50 Program, March (1999).
- [9] Y. Yamini, N. Amiri, J. AOAC Int. (2001) 84-713.
- [10] R. Trabelsi, M. Zairi, H. Ben Dhia, *Hydrogeol. J.*, 15 (2007) 1341-1355.
- [11] I. G. Krapac, W. S. Dey, W.R. Roy, C.A. Smyth, S. L. Sargent, J. D. Steele, *Environ. Pollut.*, 120 (2002) 475-492.
- [12] M. S. Hamaidi, F. Hmaid, A. Zoubiri, F. Bouaklil, Y. Dhan, *Eur. J. Sci. Res.* 32 (2009) 369-380.
- [13] M. K. Aouati, H. Bougherara, H. Ouled-Haddar, M. Sifour, S. Aissaoui, B. Kebabi. *J. Mater. Environ. Sci.*, 9 (3) (2018) 804-810.
- [14] A. Mebarki State doctoral thesis, Geography and Land Use Planning, Hydrology option, (2005) 288-295.
- [15] Tractebel, Engineering, Transfer of Beni Haroun, Synthesis Report, Algiers, A.N.B, 1 (1999).
- [16] F. Grecu, I. Zavinu, L. Zahria, L. Comanescu, *Physio-Géo - Géographie Physique et Environnement*, 1 (2007) 79-93.
- [17] J. C. B. Richard, M. J. T. Milton, *TrAC Trends in Analytical Chemistry*, 24 (3) (2005) 266-274.
- [18] J. Koen, N. WoutDe, D. S. GeertVan, V. Laszlo, V. Bart, T. Roberto, F. E. Brenker, *TrAC Trends in Analytical Chemistry*, 29 (6) (2010) 464-478.
- [19] K. Terada, *Analytical sciences* (1994) pp 108-144.
- [20] R. Palm, *Notes stat. Inform. (Gembloux)* 98 (2) (1998) 33.
- [21] F. R. Pick, D. R. S. Lean, *J. Mar. Freshwat. Res.*, 21 (1987) 425-434.
- [22] Bougarne et al., *JMES*, 8 (7) (2017) 2296-2301.
- [23] M. Hamzeh, B. Ouddane, M. Daye, J. Halwani, *Water Air Soil Pollut.* 225 (2014) 1878-1892.
- [24] N. Dahri, A. Atoui, M. Ellouze, H. Abida, *Journal of African Earth Sciences*. 140 (2018) 29-41.
- [25] E. Baurès, I. Delpla, I. S. Merel, M. F. Thomas, A. V. Jung, O. Thomas, *Journal of Hydrology*, 477 (2013) 86-93.
- [26] B. Benkaddour. Doctoral thesis in cotutelle of the University of Perpignan, Uni. Mostaganem. (2018) pp 65-74.
- [27] M. Melghit, Magister's thesis in Ecology, Mentouri University of Constantine (2012) pp 175.
- [28] A. Rosso M. Lafont, A. Exinger, *International Journal of Limnology*, 29(3) (1993) 295-305.
- [29] M. El Morhit, M. Fekhaoui, P. Élie, P. Girard, A. Yahyaoui, A. El Abidi, M. Jbilou, *Cybiu*, 33 (3) (2009) 219-228.
- [30] D. Boust, J. M. Jouanneau, C. Latouche, *Bull. Inst. Geol. Bassin Aquitaine*, 30 (1981) 71-86.
- [31] C. A. Harguinteguy, A. F. Cirelli, M. L. Pignata, *Microchemical Journal* 114 (2014) 111-118.
- [32] N. T. Hieu, B. K. Lee, *J. Atmospheric Research*, 98 (2010) 2-4.

- [33] I. Boudraa et al, Journal of New Technology and Materials, 07, 01 (2017) 64-68.
- [34] M. L. Alonso Castillo, I. Sánchez Trujillo, E. Vereda Alonso, A. García de Torres, J. M. Cano Pavón, Marine Pollution Bulletin, 76 (1-2) (2013) 427-434.
- [35] N. Nehme, Thèse de Doctorat. Université de Lorraine, (2014) 359.
- [36] H. H. Elewa, The Open Hydrology Journal 4(2010) 1-13.
- [37] P. Ollivier, O. Radakovitch, B. Hamelin, Chemical Geology, 285 (2011) 15-31.
- [38] H. Hayzoun, C. Garnier, G. Durrieu, et al. Science of the Total Environment, 502 (2015) 296-308.
- [39] B. Benkaddour. Thèse de doctorat Perpignan en cotutelle avec l'Université Abdelhamid Ibn Badis (Mostaganem, Algérie), (2018) 81-82.
- [40] K. Anazawa, H. Ohmori, H. Tpmiyasu, H. Sakamoto, Geochimica et cosmochimica Acta. 67 (18S) (2003) 17.
- [41] L. Belkhiri, A. Boudoukha, L. Mouni, Int. J. Environ. Res., 5 (2) (2011) 537-544.
- [42] H. Yin, J. Deng, S. Shao, et al. Environmental Monitoring and Assessment, 179 (2011) 431-442.