Original article

Assessment of the seasonal variations in hydrochemistry of Oued Fodda dam, Algeria

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ABSTRACT

This study was carried out on the surface water of Oued Fodda dam in western Algeria, and aimed to evaluate the seasonal variations of chemical characteristics with the aim to define the processes controlling the mineralization of surface water in this dam. The results showed significant variations in the majority of parameters during the study period from 2009 to 2013, indicating slightly alkaline water, and a SO₄-Cl-Ca-Mg water type. Principal component analysis (PCA) and cluster analysis (CA) were used to explain the correlations between the parameters analysed, and the probable sources of surface water contamination. The calculation of saturation indices (SI) of water indicated undersaturated water with respect to halite (NaCl), and equilibrium with respect to the other minerals. While, the temporal variation of physico-chemical parameters such as EC, TDS, SO₄²⁻, Cl⁻, Ca²⁺, Mg²⁺ indicated a reverse adjustment between physico-chemical parameters and water volumes (WV) in this dam, which can be explained by the weathering of silicate and carbonate minerals, these were justified by the use of ionic ratios, diagrams and scatter plots and multivariate statistical techniques. Conversely, evaluation of the organic water pollution level in this dam showed a water quality from moderately to severely polluted.

KEY WORDS: surface water quality, multivariate statistics, silicate and carbonate weathering, organic water pollution, Oued Fodda dam

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1. Introduction

The dilemma of water is the most challenge in worldwide, whether in terms of quantity or quality. The chemical composition of water resources are mainly governed by factors related to both anthropogenic activities and the natural conditions. In arid and semi-arid areas, in under developed contries, surface water (lakes, dams and rivers) is vulnerable to all kinds of pollution which pose problems of water quality deterioration, due to the influence of uncontrolled public discharges, untreated solid and liquid wastes, intensive use of agricultural fertilizers, overexploitation of water, evaportaion, erosion and sediment silting, which generate abnormal change to the watershed ecosystem (AL KUISI ET AL., 2009; KUMARI & RAI, 2020). All debris comes from living organisms which

develop an ecosystem, but sometimes can contribute to the deterioration of water quality of lakes and reservoirs, by increasing organic matter and algal proliferation, which leads to an increase in eutrophication and a decrease in oxygen concentration during the decomposition of organic substances (WU & CHEN, 2013; RAMESH & ELANGO, 2012; KÜKRER & MUTLU, 2019). Surface water is used generally for agricultural uses, so its quality should be evaluated to preserve public health and to guarantee high agricultural yields (SETIA ET AL., 2020; GUENFOUD ET AL., 2021). Water quality monitoring is also helpful to ensure the efficient management of water resources and the protection of aquatic life (BOUDERBALA, 2015; ETTEIEB ET AL., 2017). Several studies in the literature which examined surface water hydrochemistry, found that natural conditions contribute considerably

to the hydrochemical processes of water bodies and to the development of outbreaks of waterborne diseases which are linked mostly to the effect of human activities near to rivers or lakes (WAKAWA ET AL., 2008; ABDALLA & SCHEYTT, 2012; BOUDERBALA ET AL., 2016; VADDE ET AL., 2018; RAVISH ET AL., 2020).

In Algeria, like most developing countries, the deterioration of surface water quality is of growing concern. Many studies have been conducted to define the problems of water quality degradation in lakes and dams, particularly at spatiotemporal scales (BOUGUERNE ET AL., 2017; MEBARKIA ET AL., 2017; BAHROUN & CHAIB, 2017; HAMIL ET AL., 2018; BIDHURI & KHAN, 2020; BOUDERBALA, 2021). Among the methods used for the determination of accurate information concerning hydrochemical water quality, we mention the use of multivariate statistical techniques, such as Cluster Analysis (CA) and Principal Component Analysis (PCA), which have been applied to characterize water quality and to determine the temporal variation caused by external factors, and also helped to identify the possible factors that influence water quality (SHRESTHA & KAZAMA, 2007; GARIZI ET AL., 2011).

Dams in Algeria provide many benefits in terms of drinking water supply, irrigation of agricultural land and industrial water supply, but these hydraulic reservoirs face many problems. Currently, Algeria has more than 80 big dams, with a total storage capacity of about 9 billion m³. The water volumes of these dams are facing a decline in storage volumes and the deterioration of quality, in addition to problems associated with silting (from sediment deposits), evaporation from the water bodies, and water losses through banks and foundations. The significant increase of erosion phenomena in some catchments during the last decades, decreases the water volume of dams by more than 0.5 % per year for each dam or reservoir, and some dams are completely silted (REMINI ET AL., 2015; BOUDERBALA, 2017). One of the principal tasks of the Water Resources Ministry in Algeria is to ensure the qualitative and quantitative preservation of water resources.

The surface water of Oued Fodda dam, in the study area, is under the effects of both natural conditions (silting, evaporation, loss through banks) and anthropogenic activities (solid and liquid waste, fertilizers), and it is used for the irrigation of agricultural lands, in this region, by 70% of farmers. The aim of this work was to evaluate the hydrochemistry of surface water in this dam, and to reveal the factors influencing the chemistry and in controlling water mineralization. Also, to determine the impact of natural conditions and anthropogenic activities on the water quality.

2. Materials and methods

2.1. Study area

The dam of Oued Fodda is located in the north west of Algeria (36°02'44" N and 01°48'42" E) about 155 km south west of the capital Algiers, and 28 km to the south east of Chlef city. It was built on the River Oued Fodda, in 1928 and put into service in 1932. It is a concrete gravity dam, with a high water level of 85 m. It is characterized by an upstream catchment area of 800 km², an average runoff coefficient of 22%, with a maximum altitude of 1985 m, a minimum altitude of 280 m and an average altitude of 836 m. The initial capacity of this dam was 228 Cubic Hectometer (Hm³), but in 2013 after fast filling with mud (silting) the capacity was reduced to half (114 Hm³). This dam has experienced a significant decrease of its water reserve over the two last decades due to a decrease in precipitation, which has had a consequence on the degradation of water quality and on agricultural soils. Thus, there is a significant need to assess the surface water quality for each month to better understand the interaction between water volume (water inputs) and water quality.

The deforestation of this elongated catchment is near to 30%, mainly the trees and bushes located on the Cretaceous lands, which have a direct impact on the natural erosion and bedload transport processes. Over the last five decades, the water of this dam has been released for irrigation of the agricultural middle Cheliff plain area (with an average volume of 20 Hm³), for a total irrigated area of 11000 ha, but now the irrigated lands from this dam have been reduced considerably.

The middle Cheliff catchment is characterized by a semi-arid climate with hot summers and cold winters despite its proximity to the sea, with an average rainfall near to 450 mm/year and an average temperature of more than 18°C (BOUDERBALA, 2019). The dam, which is the subject of this study, has been used for the drinking water of some cities and for the irrigation of some parts of the cultivated lands in this catchment. The dominant soil textures in the middle Cheliff Plain are loamy and clayey. Part of the soil of the Plain is saline, which has had an impact on agricultural yields and economic growth in this area, and it is also important to mention the need to add additional irrigation doses to leach the accumulated salts in the soil. This area has an agricultural vocation, and the local people are dependent on agricultural activities. The main cultivated crops in this Plain are cereals (30%), distributed between wheat (90%) and barley (10%), which are concentrated

in the foothills. Arboriculture (35%), which is distributed mainly between lemon, orange and olive trees. While, the vegetable crops (35%) are particularly potatoes, carrots, cabbages, cauliflowers, fennel, swedes, lettuces, and artichokes.

2.2. Geology and hydrogeology

From a geological point of view, the catchment of the Middle Cheliff corresponds to a sedimentary basin, with an east-west orientation. These detrital sediments age from the Jurassic to the Quaternary formations (Fig. 1). In this catchment, the recent layers are formed by alluvial deposits (coarse alluvium, gravels, sands, clays, and silts), which are observed mainly in the Plain and in the large streams.

Based on the detailed geological map, we observe the Cretaceous layers to have a thickness of more than 1000 m, over all the upstream of the catchment,

which is mainly formed by Cenomanian, Albian, Aptian, and Neocomian ages. They are principally formed of clay schist and quartzite schist layers, in which some banks of sandstone and dolomitic limestone are observed. In addition to that, we can also find marl limestones or limestone marls in the Cretaceous.

The dam of Oued Fodda was constructed in the Jurassic formations, specifically, the Callovian-Oxfordian, Doggar and Lias ages, and mainly formed of compact limestone, which is generally crystalline and dolomitic, combined with strips of marl. The dam of Oued Fodda has not experienced any difficulties with regards to geotechnical stability, or geological problems; however, the real problem that this dam experiences is silting, due to the absence of an effective management system for the watershed area of this dam.

Fig. 1. Geological map of study area (Extract from the geological map of Ech-Chlef 1/200000, modified by the author)

2.3. Sample collection and chemical analysis

Water sampling was carried out monthly (one sampling session per month was undertaken from the surface layer of water) for a period of 5 years (from 2009 to 2013) in the dam of Oued Fodda, to assess temporal variation in the water quality.

The water samples were preserved in pre-rinsed polypropylene bottles of 1.5 L at 4°C in darkness and transported to the laboratory for same day analysis (within 24h). During the in-field water sampling, some parameters were measured *in situ* such as temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) by using a multiparameter

(Multi 340i/SET WTW). The analysis methods used in the laboratory of the National Agency of Water Resources (ANRH) are those described by APHA (2005). Nitrate, nitrite, and phosphate were measured by molecular absorption spectrometry, the sulphates were done by the spectrophotometric method, the concentrations of calcium, magnesium, bicarbonates and chlorides were determined by the volumetric titration method. Sodium and potassium were analysed by flame spectrophotometry (Corning 410). The organic parameters of biochemical oxygen demand after 5 days (BOD₅), organic matter (OM), and suspended matter (SM) were analysed according to the standard methods as suggested by the American Public Health Association (APHA, 2005). While, the monthly volume inputs of water in the dam for the period from January 2009 to December 2013 was available from the National Agency for Dams and Transfers (ANBT).

The accuracy of the chemical analysis was verified by calculating the ionic balance errors, which are generally between $\pm 5\%$. Water ion chemistry, bivariate plots, and geochemical modelling (PHREEQC) were used to identify the ion exchange and to understand the mineral dissolution and the mineral saturation of surface water in this dam.

2.4. Statistical methods

Two different multivariate statistical analyses were used to examine the surface water data of Oued Fodda dam. These were principal component analysis (PCA) and cluster analysis (CA). Statistical analysis was carried out using the IBM SPSS statistics 25.0 software. PCA is a technique used to emphasize variation and bring out strong patterns in a dataset, while still retaining the inherent dependencies that exist in the data. It extracts factors

with eigenvalues > 1 which explain the total variation in the data set. Only components (factors) with eigenvalues > 1 were retained and later subjected to varimax rotation before being used for interpretation (VEGA ET AL., 1998; JIANQIN ET AL., 2010; USMAN ET AL., 2014).

Cluster analysis (CA) is a statistical technique that classifies water sample quality parameters into clusters whereby samples/variables within a particular cluster are similar to each other but dissimilar to other clusters. CA was performed based on agglomerative scheduling using a combination of Ward's linkage method and squared Euclidean distances as a measure of similarity between samples and/or parameters (ZHANG ET AL., 2014; SUNDARAY, 2010; GANIYU ET AL., 2018).

3. Results and discussion

3.1. Water quality characteristics

Physical parameters of the field samples such as pH, temperature and electrical conductivity (EC) showed pH values from 6.5 to 8.1, with an average of 7.5, indicating slightly alkaline water, while the temperature and EC values ranged from 9.2 to 33.5°C and from 825 to 2667 $\mu\text{S}/\text{cm}$ respectively. The EC was within the permissible standards recommended by FAO ($\text{EC} < 3000 \mu\text{S}/\text{cm}$). The total dissolved solids (TDS) values were between 528 and 1707 mg/l, indicating slight to moderate water quality, which was within the permissible level of TDS for irrigation water, of 2000 mg/l (AYERS & WESTCOT, 1985). The TDS values were negatively correlated with water volume (WV) ($r = -0.62$), that means when water volumes were low in this dam the TDS had high values and vice versa (Table 1).

Table 1. Correlation matrix between variables

Variables	WV	T°C	pH	TDS	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
WV	1											
T°C	0.02	1										
pH	0.13	0.24	1									
TDS	-0.62	0.07	-0.18	1								
Ca ²⁺	-0.34	0.03	-0.22	0.77	1							
Mg ²⁺	-0.45	0.02	-0.18	0.86	0.70	1						
Na ⁺	-0.45	0.09	-0.05	0.64	0.19	0.40	1					
K ⁺	0.10	0.31	0.11	-0.30	-0.26	-0.36	-0.15	1				
HCO ₃ ⁻	0.17	-0.29	0.01	-0.05	-0.18	-0.10	0.37	-0.11	1			
Cl ⁻	-0.56	0.06	-0.19	0.93	0.66	0.86	0.69	-0.32	-0.05	1		
SO ₄ ²⁻	-0.56	0.13	-0.17	0.93	0.88	0.86	0.47	-0.25	-0.20	0.84	1	
NO ₃ ⁻	0.23	0.10	0.31	0.02	-0.01	0.02	0.20	-0.20	0.17	0.13	-0.04	1

According to the chemical analysis results for the major ions, we observed that the most abundant cations were $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, indicating that the high concentrations of Ca^{2+} and Na^+ are related to the ionic exchange process between sodium and calcium elements, which leads to the precipitation of CaCO_3 in the soil profile. The temporal variation of major cations from January 2009 to December 2013 shows a big variation of these cations mainly in the first two years 2009 and 2010 due to the interaction between muddy deposits and the water of this dam (in the dead storage volume), mainly in the periods of low water inputs, which were accompanied by the effect of evaporation and the arrival of wastewater discharge from the urban agglomerations located upstream of the Oued Fodda dam. In 2011, we observed a considerable water flow which contributed to the increase of water volume in this dam, we observed a stabilization in the concentration of major cations from 2011 to 2013 (Fig. 2a). The order abundance of the major anions are $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^-$, indicating that sulphates and chlorides were the dominant anions in the surface water, which is related to the water-rock interaction process, the climate (proximity to

the sea), dissolution of gypsum, and may be related to the influence of anthropogenic activities. The temporal variation of major anions from January 2009 to December 2013 shows an irregularity of these anions mostly in the years 2009 and 2010 due probably to the interaction between muddy deposits and the water of this dam. In this period of low water volumes, the concentrations of major anions were enriched mainly by human activities and natural processes such as the effect of evaporation and the arrival of wastewater discharge from the urban agglomerations located upstream of the Oued Fodda dam. From the beginning of 2011, considerable water flows came into the dam, which generated small decreases of anion concentrations, indicating a dilution of water (Fig. 2b).

A CHADHA diagram (1999) was used to identify the hydrochemical facies. It shows that the content of alkaline earth metal ions are higher than the alkali metal ions, and the content of strong acid roots are higher than that of weak acid roots. Thus, a reverse ion exchange is established, and the water has for all the period from 2009 to 2013 a category of $\text{SO}_4\text{-Cl-Ca-Mg}$ water type (Fig. 3).

Fig. 2. Temporal variation of WV (Hm^3) versus, (a) cations and (b) anions in Oued Fodda dam

Fig. 3. Chadha diagram

The suitability of surface water of this dam for irrigation was assessed by using the sodium adsorption ratio (SAR) proposed by RICHARDS (1954) and defined as:

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}}$$

The values of SAR range from 1.0 to 4.6, which indicated that more than 92% of the water samples had permissible water quality for irrigation, except 8% of samples, which were in the field of doubtful water quality for irrigation (Fig. 4). The samples of poor quality were observed in the months of September, October and November for the years 2009 and 2010, when the water volume in the dam was very low.

Fig. 4. Classification of irrigation water using Wilcox's diagram

3.2. Statistical analyses

A correlation matrix was used to find the relationship between the physico-chemical elements as shown in Table 1. TDS is strongly correlated with calcium ($r = 0.77$), magnesium ($r = 0.86$), sodium ($r = 0.64$), chlorides ($r = 0.93$), and sulphates ($r = 0.93$). These good correlations can be explained by the contribution of these elements to surface water mineralization. The strong relationships between Na-Cl ($r = 0.69$), Cl-Ca ($r = 0.66$), Cl-Mg ($r = 0.86$) and Cl-SO₄ ($r = 0.84$) suggest dissolution of chloride minerals and pollution leaching, which contribute to the water dam mineralization. The significant correlations between SO₄-Ca ($r = 0.88$), SO₄-Mg ($r = 0.86$) indicate the contributions of sulphate minerals to the water composition, and suggest that the source of sulphates may come from dissolution of gypsum. However, the negative correlation between HCO₃⁻ versus Ca²⁺ ($r = -0.18$) and Mg²⁺ ($r = -0.10$) indicate the low contribution of carbonate minerals to water mineralization. However, anthropogenic activities observed upstream of this dam, such as, the use of fertilizers by farmers and the discharge of solid and liquid matter (untreated wastewater) contribute considerably to the water mineralization.

Principal component analysis (PCA). PC analysis identified three principal components accounting for 78.4% of the total variation of surface water quality in Oued Fodda dam for the studied period from 2009 to 2013 (Table 2 & Fig. 5). PC1 (Factor 1) accounts for 51.33% of the total variance indicating a strong positive loading of TDS, SO₄²⁻, Cl⁻, Ca²⁺ and Mg²⁺, which may be related to the influence

of anthropogenic pollution from liquid and solid waste, and due also to the probable dissolution of some minerals. The negative loading of SO_4^{2-} and Cl^- with water volume (WV) may be interpreted by the influence of the decrease of water volume (in the dam) on the increase in the concentration of these two parameters, under the effect of several phenomena linked mainly to the interaction between solid mud and water, evaporation, and mineral precipitation. PC2 (Factor 2) accounted for 15.83% of the total variance, showing a strong positive loading of HCO_3^- and Na^+ . The negative correlation between these ions can be explained by different types of ions sources in which come from. The bicarbonate may be derived from limestone of the Cretaceous, while the sodium may be derived from halite dissolution, but can also indicate organic pollution from non-point sources. PC3 (factor 3) accounted for 11.26% of the total variance, showing positive loading of NO_3^- which may be an indication of agricultural fertilizers and municipal solid and liquid wastes, while the negative loading of K^+ may be explained by the weathering of soils rich in potassium.

Table 2. Factor loading and eigenvalues of extracted components for the period from 2009 to 2013

Variables	Components		
	1	2	3
TDS	0.967	0.168	0.026
SO_4^{2-}	0.967	- 0.059	0.026
Cl^-	0.919	0.232	0.110
Mg^{2+}	0.898	- 0.020	0.160
Ca^{2+}	0.824	- 0.262	0.166
WV	- 0.661	- 0.179	0.457
HCO_3^-	- 0.198	0.787	0.216
Na^+	0.526	0.778	- 0.009
NO_3^-	- 0.053	0.255	0.758
K^+	- 0.327	0.009	- 0.645

Cluster analysis (CA). Cluster analysis of samples resulted in the dendrogram for water samples of the period from 2009 to 2013, and shows two statistical cluster groups (Fig. 6). The first cluster is observed for the months of October and November for the year 2009, and the months of September, October and November for the year 2010, corresponding to highly contaminated water ($\text{EC} > 2500 \mu\text{S}/\text{cm}$), where probably the dam received high leaching of domestic wastewater and agricultural fertilizers. This cluster characterises the samples of doubtful water quality for irrigation. While, the second cluster corresponds to water samples with low EC ($\text{EC} < 2000 \mu\text{S}/\text{cm}$). It seems that these water

samples from these periods of time were uncontaminated by pollutants or are slightly polluted, which is related to high water volumes in the dam, with low evaporation, and low leaching of mineral salts.

Fig. 5. PCA in 3D scatterplots of sampling water during the period from 2009 to 2013

Fig. 6. Dendrogram of cluster analysis for sampling water during the period from 2009 to 2013

3.3. Hydrogeochemical processes and mineral saturation

The hydrochemical processes caused by natural conditions and human factors can be explained with some diagrams, by using chemical analyses. Scatter plots based on the measured water parameters (major cations/anions), were used to determine some basic information about carbonate & silicate weathering of rocks, as well as evaporation dissolution which can be also identified.

$(Ca^{2+} + Mg^{2+})$ Vs $(SO_4^{2-} + HCO_3^-)$ and (HCO_3^-) Vs (Na^+) are generally used to determine the water environment domination, which can come from the dissolution of calcite, dolomite, or gypsum (NAGARAJU ET AL., 2006). Figure 7a shows the scatter plot of $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^-)$ and indicates that 95 % of the plotted points lie below the equiline of 1:1, with a strong correlation between $(Ca^{2+} + Mg^{2+})$ and $(SO_4^{2-} + HCO_3^-)$ indicating silicate weathering, except for samples from the months of September and October 2009 which show carbonate weathering and reverse ion exchange. Figure 7b shows the relationship between (HCO_3^-) versus (Na^+) and indicates that 90 % of the samples lie below the equiline of 1: 1, suggesting silicate weathering.

Other plots were also used to confirm the silicate weathering process as a source of some chemical elements. The plots of HCO_3^-/Na^+ versus Ca^{2+}/Na^+ and

Mg^{2+}/Na^+ versus Ca^{2+}/Na^+ relating to evaporation dissolution, silicate and carbonate mineral weathering processes highlight the silicate mineral phases in the hydrochemistry of water in this dam for all the months of water sampling from 2009 to 2013 (Fig. 8a, b).

Saturation indices measure deviations from thermodynamic equilibrium of a solution with respect to a mineral. The saturation index (SI) for a particular mineral, generally indicates whether the water is undersaturated ($SI < -0.5$), supersaturated ($SI > +0.5$), or at equilibrium ($-0.5 < SI < +0.5$), with respect to that particular mineral. The interval for the mineral equilibrium has been taken from -0.5 to +0.5 instead of $SI=0$ to take into account any uncertainties in the field measurements of pH or in the laboratory analysed concentrations. The geochemical program PHREEQC (SIMLER, 2014) was used to calculate the saturation indices of the following minerals in surface water: calcite, dolomite, anhydrite, gypsum and halite for all samples for the period from 2009 to 2013. The calculations of SI values showed that water in this dam is greatly undersaturated with respect to halite (NaCl), and slightly unsaturated with respect to gypsum and anhydrite (XIAO ET AL., 2015). However, water in this dam is generally in equilibrium with respect to calcite and to dolomite (Table 3 and Fig. 9).

Fig. 7. Scatter diagram of relation parameters of dam water: a – Relation between $(Ca^{2+} + Mg^{2+})$ Vs $(SO_4^{2-} + HCO_3^-)$ and b – (HCO_3^-) Vs (Na^+)

Fig. 8. Plot of (a) HCO_3^-/Na^+ versus Ca^{2+}/Na^+ and (b) Mg^{2+}/Na^+ versus Ca^{2+}/Na^+ relating to silicate and carbonate weathering

Table 3. Saturation index of calcite, dolomite and halite for the period from 2009 to 2013

Year	Calcite	Dolomite	Halite	Vol. (HM ³)	Year	Calcite	Dolomite	Halite	Vol. (HM ³)
01/01/2009	-0.46	-1.34	-6.41	2.1067	01/07/2011	0.23	0.2	-6.81	13.376
01/02/2009	0.61	1.05	-6.33	2.5282	01/08/2011	0.01	-0.05	-6.73	8.495
01/03/2009	0.26	0.28	-6.56	3.2145	01/09/2011	-0.28	-0.85	-6.62	0.778
01/04/2009	0.64	1.11	-6.38	3.4457	01/10/2011	0.44	0.69	-6.56	1.129
01/05/2009	0.53	1.03	-6.32	3.5187	01/11/2011	-0.23	-0.57	-6.53	1.149
01/06/2009	0.27	0.44	-6.41	3.545	01/12/2011	0.18	0.29	-6.49	1.19
01/07/2009	0.14	0.4	-6.48	2.7202	01/01/2012	-0.34	-0.66	-6.39	1.503
01/08/2009	0.08	0.21	-6.62	1.94	01/02/2012	-0.28	-0.8	-6.43	1.555
01/09/2009	0.13	0.36	-6.34	1.3	01/03/2012	0.18	0.29	-6.54	2.567
01/10/2009	-0.41	-1.08	-6.17	0.782	01/04/2012	0.17	-0.05	-6.55	6.063
01/11/2009	0.31	0.55	-6.19	0.789	01/05/2012	0.24	0.31	-6.92	11.614
01/12/2009	-0.04	-0.46	-6.31	0.782	01/06/2012	0.17	0.15	-6.58	11.722
01/01/2010	-0.59	-1.26	-6.56	2.1	01/07/2012	0.56	1.05	-6.74	11.295
01/02/2010	-1.24	-2.42	-6.35	3.679	01/08/2012	0.51	0.95	-6.55	2.402
01/03/2010	-0.33	-0.79	-6.82	4.979	01/09/2012	0.19	0.37	-6.5	0.761
01/04/2010	0.12	0.11	-6.53	5.319	01/10/2012	0.37	0.4	-6.59	1.734
01/05/2010	-0.08	-0.15	-6.42	3.554	01/11/2012	-0.02	-0.07	-6.47	2.567
01/06/2010	-0.14	-0.21	-6.19	3.259	01/12/2012	0.4	0.74	-6.5	4.946
01/07/2010	0.24	0.61	-6.27	1.002	01/01/2013	-0.17	-0.63	-6.39	5.811
01/08/2010	0.26	0.6	-6.02	0.8	01/02/2013	-0.25	-0.98	-6.53	6.512
01/09/2010	-0.06	-0.06	-5.8	0.231	01/03/2013	-0.43	-1.07	-6.39	6.858
01/10/2010	0.36	0.88	-5.74	0.124	01/04/2013	-0.09	-0.5	-6.36	7.457
01/11/2010	0.28	0.56	-5.54	0.108	01/05/2013	-0.31	-0.83	-6.39	7.549
01/12/2010	0.29	0.47	-6.05	0.276	01/06/2013	-0.2	-0.5	-6.47	7.735
01/01/2011	0.19	0.05	-6.19	0.727	01/07/2013	0.04	0.14	-6.46	7.214
01/02/2011	0.24	0.11	-6.74	4.146	01/08/2013	0.22	0.59	-6.29	0.653
01/03/2011	0.44	0.57	-6.88	12.965	01/09/2013	0.34	0.75	-6.14	0.31
01/04/2011	0.39	0.54	-6.85	14.674	01/10/2013	-0.23	-0.49	-6.08	0.525
01/05/2011	0.33	0.54	-6.84	19.905	01/11/2013	-0.51	-1.18	-6.27	1.486
01/06/2011	-0.15	-0.25	-6.87	18.706	01/12/2013	-0.28	-0.8	-6.45	5.049

Fig. 9. Saturation indices of some minerals in Oued Fodda water dam

3.4. Organic pollution

Organic pollution parameters. The organic parameters of the water samples from this dam show nitrate levels less than 4 mg/l, within the norm for unpolluted surface water by nitrates (Table 4), this is due to the low contents of dissolved oxygen (O₂). 75% of samples from 2009 to 2013 indicate values of O₂ lower than 8 mg/l (standard recommended in natural water), which prevents the development of algae in this dam. The nitrites (NO₂⁻) and phosphates (PO₄³⁻) show variations from 0 to 0.09 mg/l for both anions, with averages of 0.02 mg/l and 0.03 mg/l for NO₂⁻ and PO₄³⁻, respectively, which indicates surface water of poor quality to excessively polluted. The biochemical oxygen demand (BOD₅) expresses the quantity of oxygen necessary for the degradation of biodegradable organic matter in water by the

development of microorganisms. All values are lower than the standard recommended for surface water. The chemical oxygen demand (COD) expresses the quantity of oxygen necessary to oxidize the organic matter of water using an oxidant, and 3% of the samples exceeded this standard. However, the values for suspended matter indicate that more than 44% of the samples exceeded this standard (SM = 35 mg/l), which is due to the leaching of solid matter particles and organic matter from upstream of this dam into the dam. The high values for these parameters are mainly due to climatic and biological factors, as well as, other anthropogenic factors, such as, the discharge of domestic wastewater containing detergents, and the phosphate fertilizers used in agriculture. They are basically observed on the period of water flow (winter and spring) confirming the leaching source of these mineral salts.

Table 4. Standards values of the used parameters (Milijašević et al. 2011)

Parameter	Measurement unit	Quality standard	Min.	Max.	Average	% exceed standard
pH	-	8.5	6.5	8.1	7.5	0
O ₂	mg/l O ₂	8	3.6	10.2	7.2	75 %
Suspended matter (SM)	mg/l	35	4	170	50	44 %
BOD (biological oxygen demand)	mg/l O ₂	30	0.5	3.8	2	0
COD (chemical oxygen demand)	mg/l	80	19	95	44	3 %
Phosphates	mg/l	0.005	0	0.09	0.03	75 %
Sulfates	mg/l	250	177	888	349	80 %
Nitrate	mg/l	50	0	4	1.1	0
Nitrite	mg/l	0.03	0	0.09	0.02	22 %

Pollution index. The obtained physico-chemical and organic parameters were used for the evaluation of the extent of water pollution according to the water pollution index (WPI). The WPI represents the sum of the ratio between the observed parameters and the standard values:

$$WPI = \frac{1}{n} \sum_{i=1}^n \frac{C_i}{C_s}$$

Where: C_i, is the concentration of the analysed parameter obtained for dam water quality; C_s, is the standard values of the parameter *i*; n, is the number of parameters used for the evaluation of WPI.

The following parameters were used for the estimation of WPI: dissolved oxygen O₂, pH, suspended matter (SM), BOD₅, COD, nitrites, orthophosphates and sulphates. Several authors have classified the WPI into different classes (MILIJAŠEVIĆ ET AL., 2011; POPOVIC ET AL., 2016). If the value of WPI ≤ 1.0, the water is considered to

be very pure to pure, if 1.1 < WPI ≤ 2.0 the water is moderately polluted, if 2.1 < WPI ≤ 4.0 the water is polluted, if 4.1 < WPI ≤ 6.0 the water belongs to the group of impure waters, and if WPI > 6.1 the water belongs to the group of heavily impure waters. In order to assess the level of pollution of the water of Oued Fodda dam, and the relationship between organic water pollution and water volume in the reservoir, a graph (Fig. 10) was used for the studied period from 01/01/2009 to 31/12/2013. It mainly shows that the water quality of this dam can be either moderately polluted or more polluted, for the majority of samples. It also shows an inverse proportionality correlation between the water volume in the dam and the degree of organic pollution, which can be explained by the phenomena of leaching, accumulation and interaction between water, soils and pollutants from upstream of the dam. The WPI indices also show a general trend of organic pollution in this dam from one period to another.

Fig. 10. Variation of the WPI in the dam of Oued Fodda from 2009 to 2013

4. Conclusions

The surface water quality of Oued Fodda dam indicates a slight to moderate alkaline water quality. According to the chemical analysis results of the major ions of the dam water, we observed the abundance of Ca^{2+} and Na^+ cations, which probably come from CaCO_3 soils, and the abundance SO_4^{2-} and Cl^- anions, which can be related to the water-rock interaction process and to anthropogenic activities. The hydrogeochemical study showed that one single aspect of surface water, is "Ca- SO_4 water type" for all samples of the study period from 2009 to 2013.

Principal component analysis (PCA) identified three major components accounting for 78.4% of the total variance in water quality variables for this period. It highlighted the interrelationships between variables that influence water quality, which are mainly linked to mineral dissolution, water-solid interaction, weathering processes and anthropogenic activities. Cluster analysis (CA) was used to classify the water samples with similar properties, where the results distinguished two groups. Highly polluted water quality, characterised samples for months of low water volumes in the dam, and water quality of slightly, or low pollution, which marked the majority of samples for the rest of the study period. The analysis also showed that the majority of water samples were suitable for irrigation, except in some months in 2009 and 2010, when water volumes in this dam were very low, and was unsuitable for irrigation ($\text{EC} > 2500 \mu\text{S}/\text{cm}$). The mineralization of water in this dam is principally controlled by several processes, such as carbonate and silicate weathering, evaporation, and human activities (solid and liquid waste discharge, agricultural fertilizer use).

The calculated SI values were ranked in the order dolomite > calcite > gypsum > Anhydrite >

halite. The SI values for dolomite and calcite for most of water samples were greater than zero. Thus, water were oversaturated with respect to these minerals, indicating potential precipitation of calcite and dolomite during their transportation into different environments from high terrain to lower terrain due to change in water temperature and decreasing concentrations of CO_2 . All the SI values for gypsum, anhydrite and halite were less than zero, indicating that they remained under-saturated (potential dissolution).

The degree of pollution of the water in this dam varied from one period to another, depending on the concentrations of pollutants, which can be explained by the impact of leaching of soluble salts and minerals during rainy periods from the upstream area into the dam. It is a serious environmental problem due to untreated wastewater discharges and the excessive use of fertilizers in agriculture within the catchment area.

We also indicate that the organic matter contents (especially NO_3^-) of surface water in this dam are not yet alarming, but the situation can worsen, as shown by the WPI trend increase. Thus, the monitoring of water quality, the awareness of farmers of their use of fertilizers in agriculture, and the treatment of wastewater before its discharge need to be improved to preserve the quality of surface water resources in this area.

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