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Variation of the chemical composition of Grouz dam waters, Eastern Algeria

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ABSTRACT

The quality of surface water has been deteriorated in recent years, due to agricultural, urban and industrial development. The objective of this study is to evaluate the impact of agriculture, and industrial wastewater on water quality of the Grouz dam in Eastern Algeria. To achieve this, the dam water composition has been established in the period between January 2007 and June 2010. The long-term trends are analysed using the least squares method. The results show a low salinity and a substandard concentration of different elements. Generally, the water feature is bicarbonated- chlorinated- sodic to calcic in connection with the lithology. Carbonates are in precipitation phase, while evaporates are in equilibrium or in dissolution phase. Most items that are in conjunction with fertilizers and effluent, increased during this period: EC (72.36%), COD (63.33%), BOD_5 (32.08%) and NO_3^- (175%). The increase in nitrates is due to the contribution from fertilizers and nitrification of ammonium. The concentration of the other items (NO_2^-, NH_4^+ and PO_4^{3-}) decreased at the same time as that of dissolved oxygen (50%). The ammonium concentration decrease is related to nitrogen nitrification, while the orthophosphates concentration is related to its low mobility and to the different processes that can occur in the rivers. The increase in COD (27–145 mg/l O_2), BOD_5 (2.1–10 mg/l O_2) and the decrease in pH suggest a degradation of organic substance by micro-organisms that consume dissolved oxygen. A disturbing eutrophication of the reservoir appears seasonally after the spraying of fertilizers.

Keywords: Dam; Salinity; Nutrients; Precipitation; Dissolution; Eutrophication; Algeria

1. Introduction

The surface water quality has experienced a large deterioration in recent years, due to agricultural, urban and industrial development. Several studies in the world on the effects of agricultural, industrial and urban effluents on the quality of surface water are reported [1–10] and in Algeria [11–18].

In the East of Algeria, the watershed of Oued Rhumel in Oued Athmania, covers an area of agricultural land exceeding 900,000 ha. A big part of this land is irrigated near to the dam where fertilizers are more and more used. This river drains 2,500–3,500 m^3/d of wastewater from upstream agglomerations (Chelghoum Laid and Tadjenanet) which count 150,000 inhabitants. This situation has led to the deterioration of the quality of the Grouz dam waters which are intended for drinking water supply (DWS). This

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work is realized in connection with the dam waters of east Algeria where the pollution problem began to take a magnitude. It is intended to bring a contribution to a better understanding of this phenomenon.

2. Materials and methods

2.1. Characterization of dam water

The watershed of Oued Rhumel in Oued Atmania drains much of the southern watershed of the Tell of Setif (Fig. 1), and is part of the upstream area of the Kebir-Rhumel catchment. This subwatershed is controlled by the Grouz dam located at the southern edge of the village of Oued Athmania. Covering an area of 1,130 km^2, it is limited by ridges with summits ranging between 1,048 and 1,276 m. The plain, stepped between 970 m to the south-west and 920 m north-east, has a slope not exceeding 2%. A big part of this plain is covered by Mio-Plio-Quaternary sediments formed by clays, marls, silts, alluvium and limestone crust. This covering can reach a thickness of 500 m and contains levels of gypsum in some places [19]. It is also noticed, a presence of limestone of Eocene of Tellian layer and the Cenomanian of the neritic layer of Constantine sandstones and limestone of the Barremian of all southern Setif [20]. Most of the watershed (80%) is occupied by little sandy clays of low to medium permeability. The remaining (20%) is occupied by good permeability substances represented by limestones and lacustrine limestone. The Oued Rhumel River receives some major tributaries, among others, Oued El Mehri River on the right bank, Oued Boumrah and Oued Dekri Rivers on the left bank. The main river of Oued Rhumel flows only during rainfall and drains much of the wastewater in the region. The average annual rainfall recorded at the dam station reaches 372 or 342 mm and is taken up by evaporation and the rest is shared between infiltration (6 mm) and run-off (24 mm) [21].

2.2. Sampling and analytical methods

For 10 years, many hydrochemical data were acquired on the surface water of the catchment of Oued Rhumel River and of the Grouz dam [11,16,22]. These results have largely contributed to the understanding of the hydrochemical functioning of the hydrological system. In order to characterize the hydrochemical dynamism, many samples are analysed in order to understand the mechanisms of pollution of these waters. The sampling frequency adopted in the last observation period (January 2007–June 2010) was one sample per month. This strategy has enabled to collect 35 water samples in polyethylene bottles which were filled by subsurface water. The samples are stored at 4°C and are transported to the laboratory in a period not exceeding 4 h according to the recommendations of Rodier [23]. The pH, the electrical conductivity of water (EC in $\mu S\,cm^{-1}$) and the concentration of dissolved oxygen ($O_{2dis.}$) were measured *in situ* by means of a field multiparameter which is of the WTW category. The respective accuracies with which these parameters were measured are ±0.1, ±1 and ±0.1%. The concentrations of calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), sulphate (SO_4^{2-}), bicarbonate (HCO_3^-), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), orthophosphate (PO_4^{3-}), along with the chemical oxygen demand (COD) and the biochemical oxygen demand during 5 d (BOD_5) were determined in the laboratory of the National Agency for Water Resources (ANRH) situated in Constantine [24] using standard analysis techniques [23].

2.3. Trends method

All samplings done have helped in obtaining some time series forming a table of (35) lines and (16)

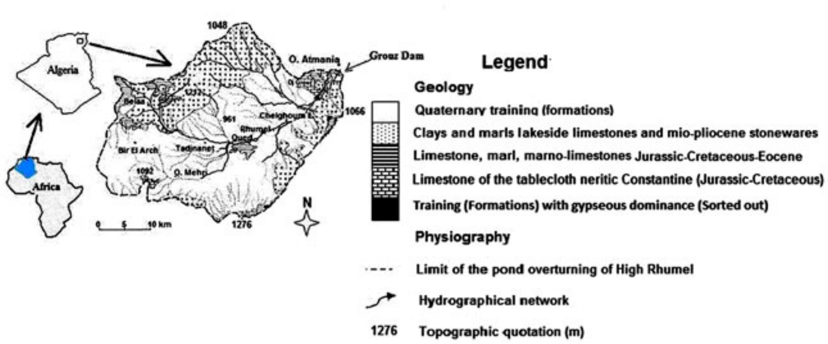

Fig. 1. Geographical and geological location of the Grouz dam.

columns. This type of data has a certain structure (univariate or multivariate linear or nonlinear) that has to be brought and studied efficiently. These series are treated by many numerical models [25], including that of Régnier [26], which is a model based on least squares equations having a linear trend, which allows the fitting of a chronological serial (Y_t) with the function $C(t) = a.t + b$. The least squares straight line ($Y = a.t + b$) (i.e. the trend line) is determined from the set of points (t; Y_t) that minimizes the distance $\Sigma[Y_t - (a.t + b)]^2$. This method allows a better fit of the trend line, but the presence of an outlier value in the serial limits its effectiveness. In most cases, the slope of the straight line which determines the trend differs from zero. If this slope is positive, it represents an increase in the concerned parameter, and is pointed at as a positive trend case, otherwise, it is a case of a negative trend. The use of this technique allows countering the "background noise" effects resulting from short-term variations and distinguishing the run-off effects and seasonal changes and thus, brings out the possible effects of pollution of anthropogenic origin in long term. This method helps also in detecting breaks in time series. In the case where several changes occur in the series, it is necessary to introduce techniques which enable to analyze different subseries of original signal separately [27]. Here, Excel 2010 is used to determine the trend straight line, based on the least squares method.

3. Results and discussion

3.1. Characterization of dam water

The results of this study are shown in Table 1, where the measured concentrations of the different elements are given. All these concentrations are below the WHO standards [28] and those of Algeria [29]. The diagram of Piper applied to these waters (Fig. 2) shows that the samples have bicarbonated- chlorinated- sodic to calcic features. This is in connection with the calcareous forming of Mesozoic and the saliferous formation of the Mio-Plio-Quaternary. This chemistry is acquired by interaction of water with carbonate rocks and terrigenous sediments. This mechanism has been studied using the saturation index (IS) of some evaporiteminerals (halite, anhydrite and gypsum), carbonate (aragonite, calcite and dolomite), and dissolved O_2 and CO_2. This simulation was made using the program Phreeqs [30] to calculate the IS defined by the (formula 1).

$$IS = \log\,(IAP/k) \quad (1)$$

where IAP is the ion activity and K is the constant of equilibrium. The equilibrium is reached when $IS = 0$. If $IS > 0$, water is supersaturated (the precipitation of minerals is needed to reach equilibrium) and if $IS < 0$, water is undersaturated (the dissolution of minerals is needed to reach equilibrium). The IS values of water samples were reported in Table 2. These values show that, in addition to halite, minerals are either close to equilibrium ($IS \neq 0$), in case of anhydrite and gypsum, or supersaturated ($IS > 0$), in case of carbonate minerals (calcite, aragonite and dolomite) indicating a time of contact with the rock, long enough to allow their dissolution. The positive values of carbonate minerals indicate that the water has undergone significant changes as a result of CO_2 degassing ($IS < 0$). According to Djidi et al. [31], this degassing usually occurs when charging karstic-aquifers or due to the rise in water temperature, generating the calcite precipitation. The second hypothesis is more plausible, in the case of Grouz dam waters subject to an ambient temperature which can reach 42°C in summer [21]. For halite, $IS < 0$ suggests that this mineral phase is in dissolution phase.

3.2. Origin of principal major elements

The origin of principal major elements (Ca^{2+}, Mg^{2+}, SO_4^{2-} and Na^+) which characterize water feature and its hydrochemical evolution is discussed using binary diagrams.

3.2.1. Calcium, magnesium and sulphates

The molar ratio Ca^{2+}/Mg^{2+} provides information on the origin of these elements from the dissolution of calcite and dolomite. If this ratio, Ca^{2+}/Mg^{2+} is less or equal to 1 (≤1), it is a dolomite dissolution. However, a higher ratio reflects calcite dissolution [32]. When it is greater than 2, it indicates the dissolution of silicate minerals [33]. In most cases, Grouz dam waters are characterized by ratios ranging between 1 and 2 (Fig. 3(a)), reflecting a calcite dissolution and secondarily dissolution of silicate, minerals and dolomite. The origin of these major elements was also raised with the diagram $Ca^{2+} + Mg^{2+} + SO_4^{2-} + HCO_3^-$. If the analytical points align around the straight line of slope 1, the dominant reactions are due to the dissolution of calcite, dolomite and gypsum. The base exchange tends to move the points downwardly due to excess of $SO_4^{2+} + HCO_3^-$ or upwardly due to excess of $Ca^{2+} + Mg^{2+}$ [34,35]. This process is done according to the following reaction.

$$2Na^+ + Ca^{2+}(Mg^{2+})\text{argile} \leftrightarrow Na - \text{argile} + Ca^{2+}(Mg^{2+}) \quad (2)$$

By examination of Fig. 3(b), it is noticed that the points are located below the equilibrium line which reflects a base exchange caused by an excess of SO_4^{2+} + HCO_3^- in the sediments of Mio-Plio-Quaternary. The presence of sulphates in large quantities in dam waters (192–328 mg/l) could also be attributed to the dissolution of anhydrite or pyrite according to the following formula proposed by Appelo and Postma [36].

$$FeS_2 + 4.75O_2 + 1.5H_2O + 4e^- \leftrightarrow Fe(OH)_3 + 2SO_4^{2-} \quad (3)$$

3.2.2. Chlorides and sodium

It is known that chlorine is a highly mobile chemical species, weakly interacting with the encasement. It is part of the conservative elements, frequently used as tracers to study the hydrological cycle. Acquiring of Na^+ and Cl^- content may result from the dissolution of halite or from a mixing with seawater. This second hypothesis is rejected because of the remoteness of the Mediterranean Sea (about 100 km). Analytical points of dam water samples, presented in a diagram Na^+/Cl^-, show a good distribution ($r = 0.45$ for $p < 0.01$ and $n = 35$) around a line of a slope equal to that of halite (Fig. 3(c)). In other words, the molar ratio Na^+/Cl^- of these samples is similar to that of the halite (Na^+/Cl^- halite = 1.00). This approach suggests that the presence of Na^+ and Cl^- is due to the dissolution of saliferous formations.

3.2.3. Salinity

Salinity can have two origins, either carbonate or saliferous. To make the difference, a graph for $Ca^{2+} + Mg^{2+}/Na^+ + Cl^- + SO_4^{2-}$-EC has been established (Fig. 3(d)). The dam water salinity appears to be changing in two ways, one in conjunction with the carbonates and the other in connection with the evaporites. This is related to the equilibrium state of these two mineral groups, carbonate minerals being in excess, while evaporites are generally close to equilibrium or in dissolvedphase. This had led to two straight lines which intersect for low values of the electrical conductivity.

Table 1
Summary of chemical analysis of the Grouz dam water: Max, mean, min, standard deviation (SD) and coefficient of variation (CV)

Parameters	pH	CE	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	NO_2^-	NH_4^+	PO_4^{3-}	N/P	COD	BOD_5	O_2-dis
Max	8.5	2370.0	121.4	47.0	273.0	8.0	480.0	328.0	262.3	34.0	2.0	3.0	0.41	500.0	145.0	10.0	13.0
Mn	7.90	1,761.71	89.86	36.72	164.89	4.72	302.85	262.0	187.14	7.69	0.54	0.84	0.22	52.78	61.16	5.98	8.09
Min	7.50	1,300.0	58.9	25.0	70.4	3.0	215.0	192.0	122.0	0.6	0.01	0.01	0.05	4.0	27.0	2.8	5.3
SD	0.22	300.95	14.47	7.09	36.15	1.23	66.10	42.99	34.17	7.27	0.48	0.76	0.10	83.13	27.28	2.02	2.04
CV	0.03	0.17	0.16	0.19	0.22	0.26	0.22	0.16	0.18	0.94	0.88	0.90	0.43	1.58	0.45	0.34	0.25

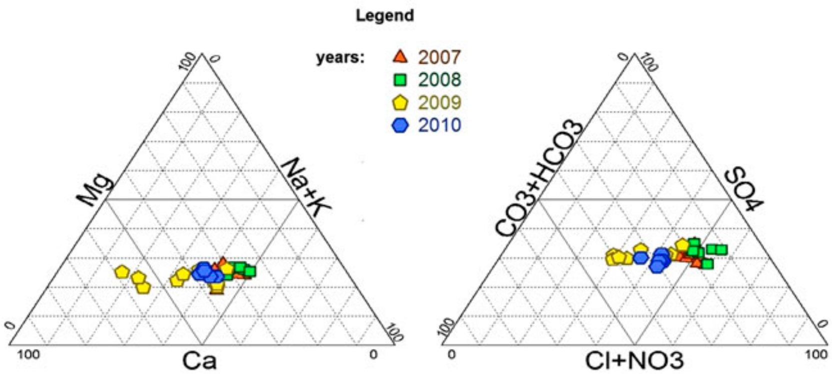

Fig. 2. Diagram of Piper applied to Grouz dam waters.

Table 2
Summary of stability indices of the Grouz dam water: Max, mean, min, standard deviation (SD) and coefficient of variation (CV)

Parameters	Aragonite	Calcite	Dolomite	Gypsum	Anhydrite	Halite	CO_2 (g)	O_2 (g)
Max	0.8	0.94	1.72	−1.10	−1.3	−5.53	−2.09	−34.05
Mn	0.26	0.41	0.69	−1.35	−1.59	−6.21	−2.68	−38.1
Min	0.04	0.0	0.03	−1.56	−1.78	−7.05	−3.39	−43.63
SD	0.31	0.31	0.64	0.11	0.11	0.35	0.27	2.92
CV	1.19	0.76	0.93	−0.08	−0.07	−0.06	−0.10	−0.08

3.3. Variation of chemical element

The Grouz dam is an important resource of DWS for which it is mainly used. It is therefore, imperative for the region to focus on the physicochemical water quality of this dam. This description has been made by investigating the trend of chemical parameters and nutrients. These water quality trends can be detected based on the average concentrations changes over a long period. Several studies on the quality of surface waters were conducted in eastern Algeria [11,12,15,17,18,37], but none of the authors has used this technique to study the quality of surface waters.

3.3.1. Major chemical elements

The linear trends were identified using the instantaneous concentrations. These are shown in Fig. 4. The mean initial and final values for the chosen period were used to calculate these variations. For most parameters, the slope significantly differs from zero (−133.3% –175%). Carbonate elements showed a negative trend ranging from −18.64% (Ca^{2+}) to 46.67% (Mg^{2+}) whereas, positive trends are recorded for saliferous elements (64% for SO_4^{2-}, 50% for Cl^-, 40.74% for Na^+ and 76.47% for K^+). These different trends are to be set in relation with the equilibrium state of different minerals in water. The precipitation of carbonate minerals causes a decrease in calcium and magnesium (negative slope), while the dissolution of some evaporiteminerals (halite and sylvite) and the use of potassium fertilizers, lead to an increase in Cl^-, Na^+ and K^+. The gypsum and anhydrite are in equilibrium with water, which have lead to a small increase in SO_4^{2-}. As shown in Fig. 5, these chemical changes caused an increase in the overall salinity (EC) of 72.36% and a decrease in pH of 3.87%.

3.3.2. Nitrogen

The presence of nitrogen (NO_3^-, NO_2^- and NH_4^+) in water depends on the nutrient supply of farmland (spreading, livestock waste and fertilizer) and wastewater discharge. In Oued Rhumel watershed, the most commonly used fertilizers are ammonium nitrate, urea of both phosphor and potassium, superphosphates, chloride of potassium and smaller quantities of sulphate of ammonium, sodium, nitrate of calcium and sulphate of potassium. The absence of reliable inventories does not allow a comprehensive analysis of this phenomenon. However, this pollution will be emphasized by the general trends and by the identification of possible relationships between these elements and

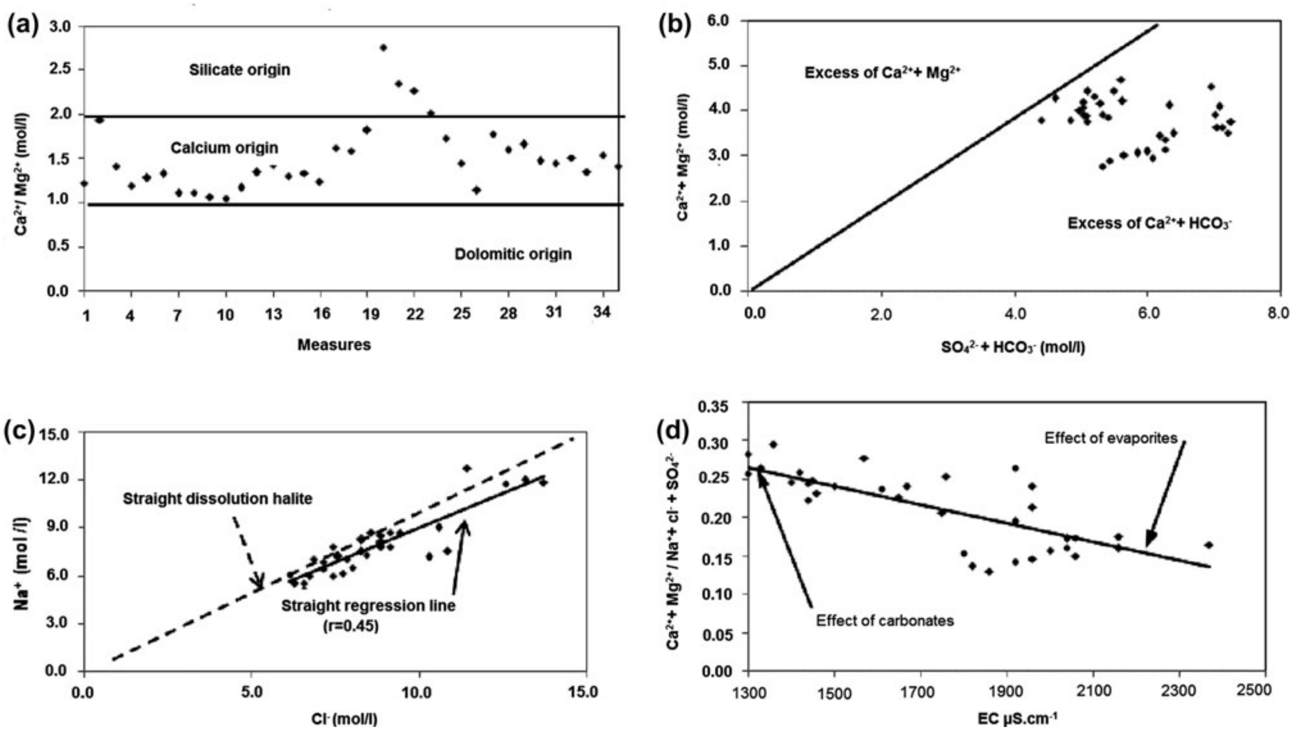

Fig. 3. Major principal elements origin of Grouz dam waters.

dissolved oxygen [38–41]. The analysis of the trends of these different parameters found (Fig. 6) that the largest increase was recorded for nitrates with 175%. On the other hand, nitrites and ammonium, recorded a decrease ranging between 133.33% for NO_2^- and 57.5% for NH_4^+. This decrease in nutrients is accompanied by a decrease in dissolved oxygen of 50%. The large increase in NO_3^- recorded in the dam waters is to be linked with: (i) the high percentage (80%) of agricultural land in the watershed and the irrigated land near the dam, (ii) the use of fertilizers on these agricultural lands, (iii) the wastewater discharge without any previous treatment, both in nature and in main stream and (iv) a change in the form of ammonium and nitrite (Fig. 7) in the presence of oxygen aerobically according to the following two reactions [42].

$$NH_4^+ + 3/2/O_2 + H_2O \rightarrow NO_2^- + 2H_3O^+ \quad (4)$$

$$NO_2^- + 1/2\ O_2 \rightarrow NO_3^- \quad (5)$$

3.3.3. Phosphates

The increase in NO_3^- is accompanied by a decrease of 47.37% in the concentration of PO_4^{3-} (Fig. 8). So, there is no increase in the concentration of PO_4^{3-} despite the use of phosphate fertilizers. This can be explained in two ways: (i) phosphorus is not very movable and is easily absorbed by soil colloids and thus, removed by mechanical erosion processes [43,44], (ii) phosphorus concentrations are regulated in river water by several biogeochemical processes such as precipitation in apatite form [$(PO_4)_3$(F,Cl and OH) Ca_5] [45] and the consumption by aquatic plants [46–49].

3.3.4. The organic material

The lack of organic material measurements does not allow an analysis of the variation of this parameter. However, the fluctuations of COD (+63.33%) and of BOD_5 (+32.08%) may be used to estimate the evolution of the total organic material in water [28]. The values of COD (27 to 145 mg/l O_2) show that the weight of material stored at the dam is considerable. The BOD_5 (2.8 to 10 mg/l O_2) increase can be explained by the creation of microorganism breakdown conditions of organic material (Fig. 8). This deterioration is accompanied by a decrease in dissolved oxygen of 50%. This is in agreement with the decrease in pH which may be related to the organic material oxidation according to reaction 6, shown below, or to the pressure increase of CO_2 which leads

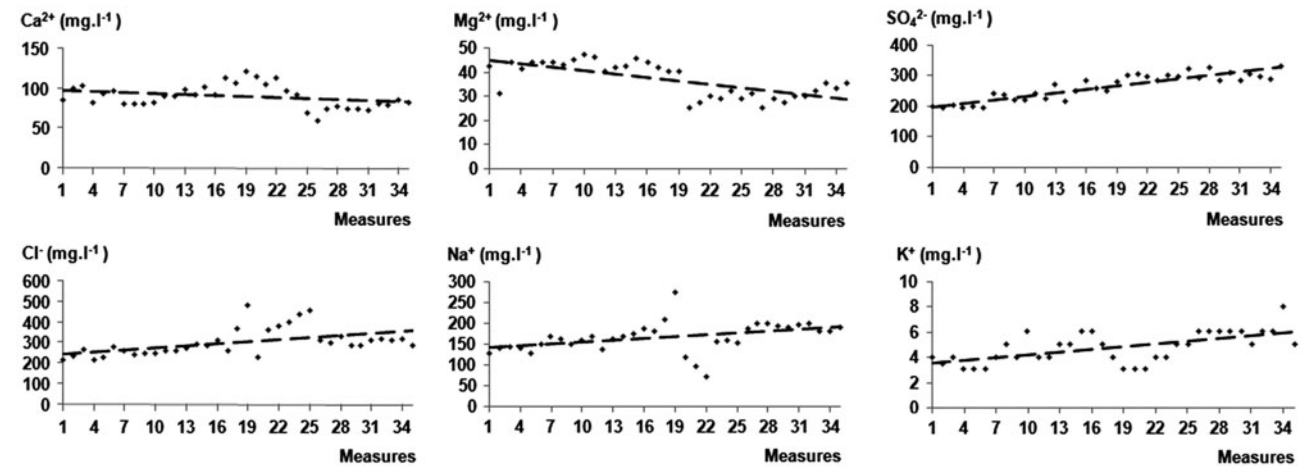

Fig. 4. Major principal elements variation of Grouz dam waters.

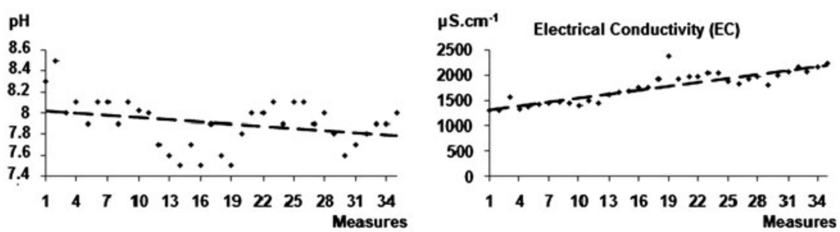

Fig. 5. Variation of pH and electrical conductivity of Grouz dam waters.

to a decrease in pH as showed in formula 7, given by Kempe [50].

$$CH_2O + O_2 \leftrightarrow CO_2 + H_2O \tag{6}$$

$$CO_2 + H_2O \leftrightarrow H_2CO_3^- \leftrightarrow H^+ + HCO_3^- \tag{7}$$

3.3.5. Eutrophication

The status of water eutrophication, indicated by N/P ratio values provides information on the likely presence of algae fixing atmospheric nitrogen for ratio values lower than 29 [51,52]. Indeed, the N/P ratios, computed during the entire monitoring are sometimes less than the value of 29 with probable occurrence of Cyanophyceae in Grouz water reservoir. 51.43% of the values of the N/P ratio are superior to the value 29. The phosphate supply contribution in late winter and spring confirms that the phosphorus acts as a limiting factor in water. As a consequence, the micro-organisms grow rapidly and can lead to an appearance of surface foam. Many stocks of Cyanophyceae have a capacity to produce dangerous toxins to both drinking and swimming waters [53]. An amount of 100,000 cyanobacteria/ml launches research on toxins and their dosage to ensure that the microcystin

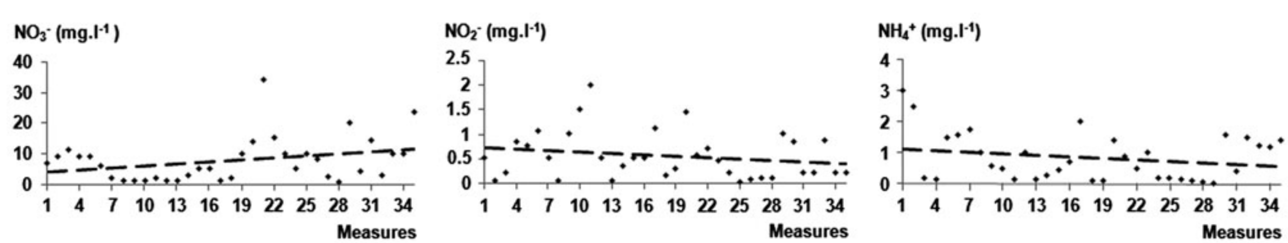

Fig. 6. Nitrogen variation of Grouz dam waters.

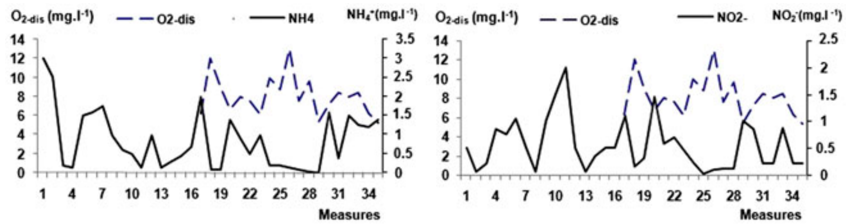

Fig. 7. Nitrogen-oxygen relationship of Grouz dam waters.

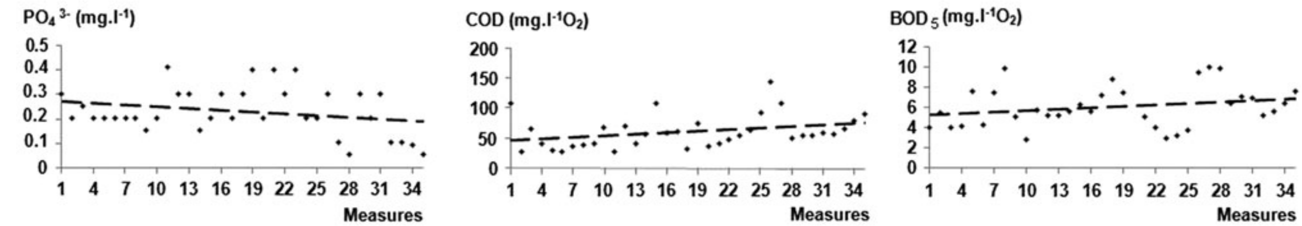

Fig. 8. Variation of phosphates, COD and biological oxygen demand of Grouz dam waters.

concentration does not exceed 1 μg/l as it was recommended by the World Health Organization [28].

4. Conclusion

In order to assess the effect of agricultural and industrial urban wastes on Grouz dam waters, the chemistry of these waters has been determined. The time evolution of some physicochemical parameters was carried for nearly four years. The obtained results show that the global salinity is low and that the different element concentrations are below the Algerian and the WHO standards. Generally, the water feature is bicarbonated- chlorinated- sodic to calcic in connection with the lithology**.** Calcium and magnesium are derived from carbonates dissolution, while chlorides and sodium come from saliferous terrigen formations. Carbonates are in precipitation phase while evaporites are in equilibrium or in dissolution phase. Most of elements and parameters that are linked to fertilizers and effluents have increased in dam water during this period: EC (72.36%), COD (63.33%), BOD_5 (32.08%) and NO_3^- (175%). This deterioration of water quality is due to the organic material decomposition, accompanied by a pH decrease of 3.87%. The increase in nitrates is due to the contribution of fertilizers and the nitrification of ammonium, accompanied by a decrease in dissolved oxygen of 50%. The decrease in phosphate content of 47.37% is due to its low mobility and to the various biogeochemical processes that may occur in the river waters such as the apatite precipitation form and the consumption by the dam aquatic plants. Grouz dam waters seem to become more and more polluted like most of surface waters in eastern Algeria.

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