J. Appl. Environ. Biol. Sci., 7(8)1-10, 2017

ISSN: 2090-4274
Journal of Applied Environmental and Biological Sciences
www.textroad.com

Assessment of the Trophic State and Hydrochemical Characterization of Zerdaza Reservoir (North-East of Algeria)

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Received: March 21, 2017
Accepted: June 3, 2017

ABSTRACT

From January to December 2013, a monthly investigation was carried out in order to assess the water quality of the Zerdaza reservoir located in the North-East of Algeria. The evaluation of the trophic status was made according to the Carlson's Trophic State Index (CTSI). The hydrochemical facies was determined by using the Piper diagram and by the comparison of some water parameters values with the Algerian Environmental Quality Standards for Surface Waters. The results of the CTSI showed a very slight variation indicating that this reservoir water is eutrophic. The water is characterized by the predominance of Chlorinated-Sulphated Sodium–Calcium facies. Statistical analysis of the Standard Deviation (StD) indicated two categories of parameters. The first category was characterized by a very low variation and concerned the values of the Secchi depth (Sd), water Temperature (Temp), pH, Cl-, Total Nitrogen (TN), Mg+2, NO3-, K+ and Ca+2. The second one was characterized by a moderate to a high variation including the values of Chlorophyll a (Chl a), SO4-2, HCO3-, Total Phosphorus (TP) and Na+. The mean comparison of these parameters with the Algerian Standard Values for raw waters intended for human consumption showed that the waters of the Zerdaza reservoir were consistent with these standards for the period of investigation.
KEYWORDS: Zerdaza reservoir, Trophic state, Hydrochemical facies, Algerian standards.

1. INTRODUCTION

The stagnant waters are very valuable water reservoirs widely exploited by men for domestic, industrial and recreational needs. However, owing to the anthropic activities such environments are constantly deteriorating throughout the world as indicated in the literature [1,2,3,4,5,6,7,8,9,10,11,12,13], and particularly in Algeria where various studies [14,15,16,17,18,19,20,21,22] reported the negative effects of the agricultural, industrial and urban effluents on the quality of surface waters that may call into question the use of the water resource.
The International Lake Environment Committee (ILEC) mentions the major risks that may affect the lakes and reservoirs of the planet: sedimentation, reduced volumes of water, contamination by toxic substances (pesticides, chemicals from industrial, heavy metals, etc.), acidification, and the destruction of the ecosystems and the endemic species [23]. Among these risks, the eutrophication of water-supply reservoirs is one of the most prevalent environmental problems responsible for the degradation of water quality worldwide [24,25,26].
The causes of eutrophication are closely related to the nutrients (mainly Phosphorus and Nitrogen compounds) [25]. The nutrients may enter into the lakes as agricultural runoff, sewage or waste waters and also by cattle ranching. This causes over-enrichment of nutrients in the water bodies [27], inducing various environmental and human health problems (**Tab.1**).

Table 1: Impact of eutrophication on the waters of lakes and reservoirs [28].

. Reduction of the concentration of dissolved O2 throughout the water's body, particularly at depth; **. Deterioration in the organoleptic characteristics of drinking water;**
. Fish kills due to the deficiency of dissolved O_2; **. Development of algae bloom in summer;** **. Presence of toxins in the water produced by the high density of toxigenic algae;**
. Higher cost of drinking water treatment; **. Water clarity reduction;** **. Degradation of landscape appearance of the water surface.**

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The anthropogenic influence on the water quality and the ecological functioning of rivers, lakes and reservoirs are reflected by the trophic state, which is an important property of the aquatic ecosystems [29]. Its monitoring is an important part of assessing and managing the aquatic ecosystems.
Traditional methods to assess the water quality, and by the same way, the trophic state is to compare the experimentally determined such parameter values with the existing local normative. However, the comprehensive index can provide a global vision on the spatial and temporal trends in the overall water quality [28]. The most used method to evaluate the productivity of the water bodies is the biomass related trophic state index developed by Carlson [30]. The Carlson's Trophic State Index (CTSI) is a common method for characterizing a lake trophic state or overall health. It has been frequently used by researchers and government institutions to indirectly estimate the algal biomass and to indicate the eutrophication degree of lentic systems [29].
The aim of this study was to evaluate the trophic state of the Zerdaza reservoir and to monitor during a one-year investigation the evolution of some physicochemical parameters in order to determine the chemical trends of these waters by using the Piper diagram.

2. MATERIALS AND METHODS

2.1. Area of study and sampling sites

Located nearby Zerdaza village, the Zerdaza reservoir provides drinking water to the local urban areas (Zerdaza, El-Harrouch, Ain Bouziane, Mzedj Edchich) as well as to the industrial zone of Skikda. It represents a protection device of the Safsaf valley against flooding and ensuring the supply of irrigation waters to more than 1800 hectares of agricultural fields. With an initially estimated capacity of 32 million m3, its current volume reaches only 18 million m3 owing to siltation events. This reservoir is connected to two affluent wadis, Bouajeb and Khemakem, whose hydrological regimes allow distinguishing a dry and a wet season. In general, the area is characterized by a sub-humid Mediterranean climate with a rainy season from mid-October until April and a hot and dry summer for the rest of the year. The annual means of temperature and precipitation are respectively 18ºC and 667 mm. From January to December 2013, samplings were monthly collected from three stations (Fig.1):

- Station 1: 36° 35' 10.36" N ; 6° 54' 00.17" E
- Station 2: 36° 34' 59.75" N ; 6° 54' 14.63" E
- Station 3: 36° 34' 53.95" N ; 6° 54' 20.12" E

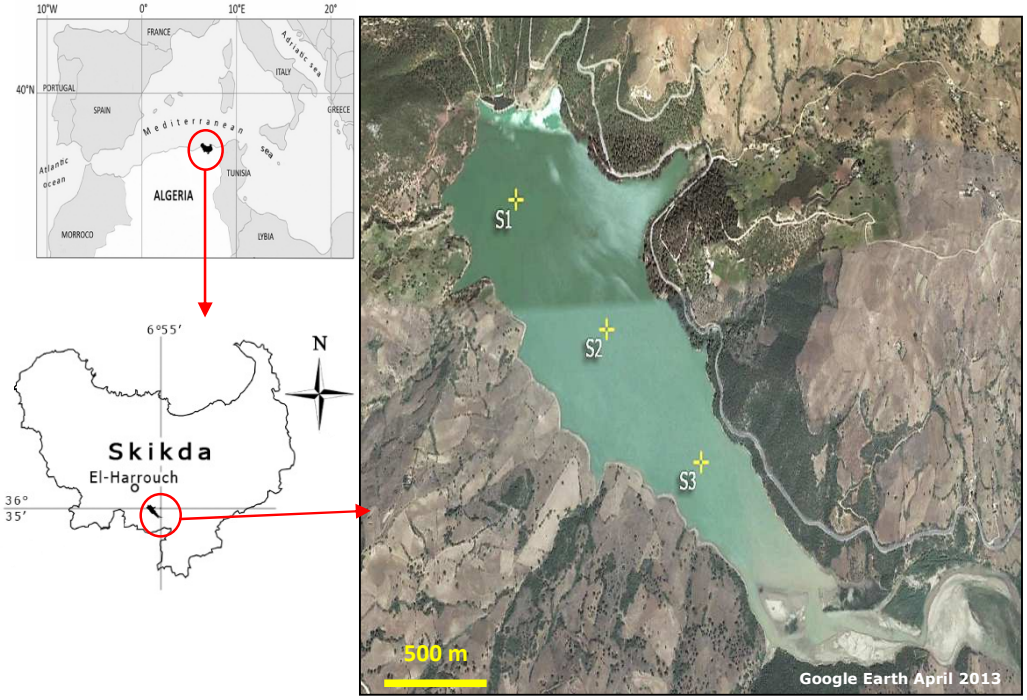

Figure 1: Geographic location of Zerdaza reservoir [31] and sampling stations.

2.2. Physicochemical analysis of the waters

At each station, samples of water were collected at -0.1 to -0.5m below the water surface using 1 L polyethylene bottles. These bottles were previously presoaked overnight in 10% (v/v) Nitric acid, then rinsed thoroughly with distilled water and left to dry. Before filling, the bottles were rinsed twice with the reservoir water. Labelled sampling bottles were in a kept in a coolbox and transferred within the same day to the laboratory and stored at 4°C until further analysis. For each station, the transparency of water was measured with a Secchi's disc.

In order to evaluate the trophic state of the water reservoir, analysis of the physicochemical elements concerned the Total Phosphorus and the Total Dissolved Nitrogen. The concentration of Chlorophyll a was determined by filtration of the water samples through a GF/F (0.45µm porosity) filter of 4.7cm, and the extraction was performed overnight in 10 ml of 95% ethanol. The concentrations were determined by spectrophotometry with phaeopigment and Chlorophyll b correction [32].

The trophic state was determined on the basis of the Carlson's Trophic State Indices (CTSI) using a logarithmic transformation of the mean values of the four variables, namely: Chlorophyll a concentration (Chl a), Secchi depth (Sd) and Total Phosphorus (TP) [30], as well as the Total Nitrogen concentration (TN) [33]. The equations are as follows:

$$\text{TSI (TN)} = 54.45 + 14.43 \ln(\text{TN}) \text{ (using a GF/C filter)}$$
$$\text{TSI (TP)} = 4.15 + 14.42 \ln(\text{TP})$$
$$\text{TSI (Sd)} = 60 - 14.42 \ln(\text{Sd})$$
$$\text{TSI (Chl } a\text{)} = 30.6 + 9.81 \ln(\text{Chl } a)$$
$$\text{CTSI} = [\ \text{TSI(TN)} + \text{TSI(TP)} + \text{TSI(Sd)} + \text{TSI(Chl a)}\ ] / 4$$

The waters with CTSI less than 40 are grouped into the Chl a oligotrophic state. The CTSI ranging from 40 to 50 are distinguished from a mesotrophic state. If the CTSI values range from 50 to 70, the waters belong to the eutrophic state, whereas for CTSI values higher than 70, the waters belong to the hypertrophic state [33].

The reservoir water facies was determined by the establishment of the Piper diagram, and by the measurements of K+, Na+, SO4-2, HCO3-, Mg+2, NO3- and Cl-. All nutrients were measured through the colorimetric methods. Sodium and Potassium concentrations were measured using the atomic absorption spectrometry. Calcium, Magnesium, and Chloride were determined by titrimetry, while SO4-2 was measured by the gravimetric method [34].

2.3. Statistical analysis

The independent t-test and one-way ANOVA were used to compare the means of the parameters generated from the different stations of the reservoir. The Spearman linear correlation was used to investigate the relationships among the various physicochemical parameters. The statistical analyses were performed using the software Statistic Package for Social Science (SPSS Ver.11.0).

3. RESULTS AND DISCUSSIONS

3.1 Variations of the water parameters

From January to December 2013, the ranging values of the physicochemical parameters of the waters of Zerdaza reservoir are presented in Table 2. The statistical analysis shows that the mean and median values are very close. This indicated the representativeness of the mean as well as the symmetrical distribution of the samples.

Depending on the value of StD, it can be seen two categories of parameters (Tab.2). The first category concerned the parameters Sd, Temp, pH, Cl-, TN, Mg+2, NO3-, K+ and Ca+2 having a very low range of variation and therefore are characterized by a low StD value (≤10). The second category concerned the parameters Chl a, SO4-2, HCO3-, TP and Na+ showing a moderate variation with StD ≥10. The StD of the electrical conductivity was 138.13 translating the variation within a wide range of values. The high conductivity may rise through natural weathering of certain sedimentary rocks or may have an anthropogenic source, e.g. industrial and sewage effluent [35].

The Coefficient of Variation (CV %) was used to evaluate the variation of values related to each parameter, and compared to the corresponding average. The parameters pH, Cl- and Ca+2 are characterized by a variation, not more than 10% if compared to their respective average. The parameters Cond., SO4-2, HCO3-, Mg+2, K+, and TP have a CV between 10% and 30%. The rest of the parameters

showed a CV greater than 30% indicating a significant variation of these parameters during the period of investigation.

The comparison of the means of the various parameters (Temp, Cond., Cl-, SO4-2, NO3, Na+, K+, and Ca+2) with the Algerian Standards Values (ASV) for raw water intended for human consumption (Tab.2), shows that the waters of Zerdaza reservoir were consistent with these standards during this investigation period.

Table 2: Physicochemical parameters of the waters of Zerdaza reservoir (Jan-Dec 2013).

Parameter	Range	OM	Med.	StD	CV%	ASV
Chl-a (µg/l)	7.45 - 35.52	19.21	17.842	10.26	53.44	/
DS (m)	0.56 - 1.54	0.96	0.8	0.31	32.57	/
T° C	10.13 - 26.01	17.59	16.83	5.29	30.1	25.00
pH	7.64 - 8.04	7.82	7.82285	0.09	1.21	/
Cond µs/cm	884 - 1257.5	1050.79	1052.25	138.13	13.15	2800.00
Cl^- (mg/l)	38.17 - 63.58	50.95	50.31	4.04	7.94	500.00
SO_4^{-2} (mg/l)	56.83 - 125.99	95.27	94.99	12.7	13.33	400.00
HCO_3^- (mg/l)	108.25 - 202.78	156.88	161.805	21.07	13.43	/
Mg^{+2} (mg/l)	11.85 - 21.84	17.41	17.7	1.74	10.01	/
NO_3^- mg/l	1.63 - 14	3.79	3.429	2.13	56.27	50.00
Total N (mg/l)	1.22 - 19.3	8.36	7.595	5.39	64.53	/
Total P (µg/l)	42 - 150	80.17	74	20.45	25.51	/
Na^+ (mg/l)	22.74 - 80.23	56.69	55.74	13.01	22.96	200.00
K^+ (mg/l)	2.89 - 10.18	4.95	4.218	1.65	33.3	12.00
Ca^{+2} (mg/l)	29.24 - 51.2	38.74	38.34056	3.72	9.6	200.00

OM: Overall Mean; Med: Median; StD: Standard Deviation; CV%: Coefficient of variation;
ASV: Algerian Standard Values.

The correlation matrix (Tab.3) shows that almost all the mineral elements display the same variations during the whole period of investigation as it is indicated by the positive correlation coefficient (significant or highly significant for Cl-, Na+, NO3-, Na+, Mg+2, TN, Cond and TP). This mineralization translated by the electrical conductivity parameter had a correlation of -0758 with the measured temperature with a high level of significance. This indicates a reverse change between these two parameters, probably because of the fact that the major part of the minerals comes from the earth leachate catchment during the rainy and cold season.

It also can be noted a positive and very highly significant correlation (0.809**, P = 0.001≤0.001) between SD and Temperature, but the change of this parameter was inversely proportional to the overall mineralization. It indicates that the attenuation phenomenon of light measured by the SD parameter is not due to suspended mineral materials, but rather to organic suspended matters. This finding is reinforced by the following results found in this study on the deviations of TSI as developed below.

Table 3: Pearson correlation matrix of the physicochemical data of Zerdaza reservoir waters.

	Chl *a*	SD	Temp	pH	Cond.	Cl^-	SO_4^{-2}	HCO_3^-	Mg^{+2}	NO_3^-	Total N	Total P	Na^+	K^+	Ca^{+2}
Chl *a*	1,000														
SD	0,078	1,000													
Temp	0,332	0,809**	1,000												
pH	-0,298	-0,399	-0,210	1,000											
Cond.	-0,551	-0,572	-0,758**	0,006	1,000										
Cl^-	0,281	0,543	0,681*	-0,288	-0,493	1,000									
SO_4^{-2}	0,289	-0,401	-0,111	-0,229	0,214	0,052	1,000								
HCO_3^-	0,267	0,830**	0,801**	-0,414	-0,526	0,445	0,084	1,000							
Mg^{+2}	-0,139	0,617*	0,428	-0,153	-0,145	0,055	0,021	0,792**	1,000						
NO_3^-	-0,492	-0,125	-0,305	0,274	0,480	-0,422	-0,156	-0,219	0,288	1,000					
Total N	-0,283	0,290	0,067	-0,274	0,154	-0,164	0,292	0,465	0,750**	0,523	1,000				
Total P	0,590*	0,108	0,496	-0,048	-0,702*	0,500	0,319	0,189	-0,138	-0,308	-0,069	1,000			
Na^+	0,293	0,768**	0,698*	-0,378	-0,478	0,654	-0,094	0,814**	0,543	-0,473	0,020	0,045	1,000		
K^+	0,410	0,458	0,406	0,075	-0,600*	-0,065	-0,379	0,509	0,321	-0,317	-0,107	-0,024	0,472	1,000	
Ca^{+2}	-0,202	-0,648*	-0,548	0,059	0,456	-0,446	0,313	-0,641*	-0,525	0,372	0,115	0,071	-0,897**	-0,564	1,000

3.2. The Hydrochemical facies

After conversion (from mg/L to mEq/L) of the values of the various minerals, the hydrochemical facies were determined using the Piper diagram as indicated in the literature [36,37,38]. If considering the water classification diagram of Back and Hanshaw [37], the waters of Zerdaza reservoir are characterized by the predominance of Chlorinated-Sulphated, Sodium-Calcium facies, with Sulfates, Chlorides, and Sodium originating from wastewater [2] (Fig.2,3).

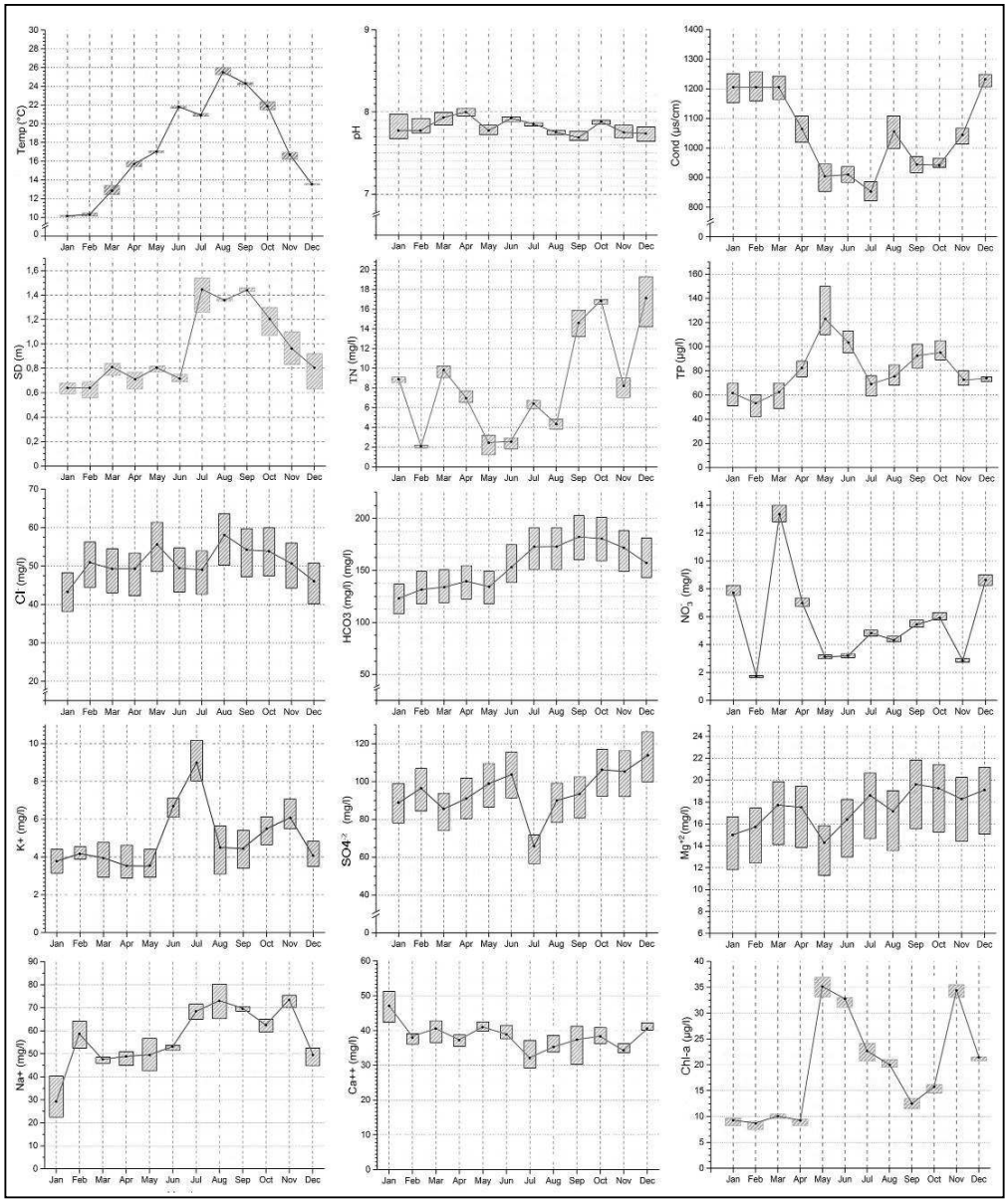

Figure 2: Developing trends of the physicochemical parameter, SD and Chl a from January to December 2013. The points represent the average values obtained from the 3 sampling sites. The upper and lower limits of the rectangles represent, respectively, the maximum and minimum values of each parameter measured throughout the period of investigation.

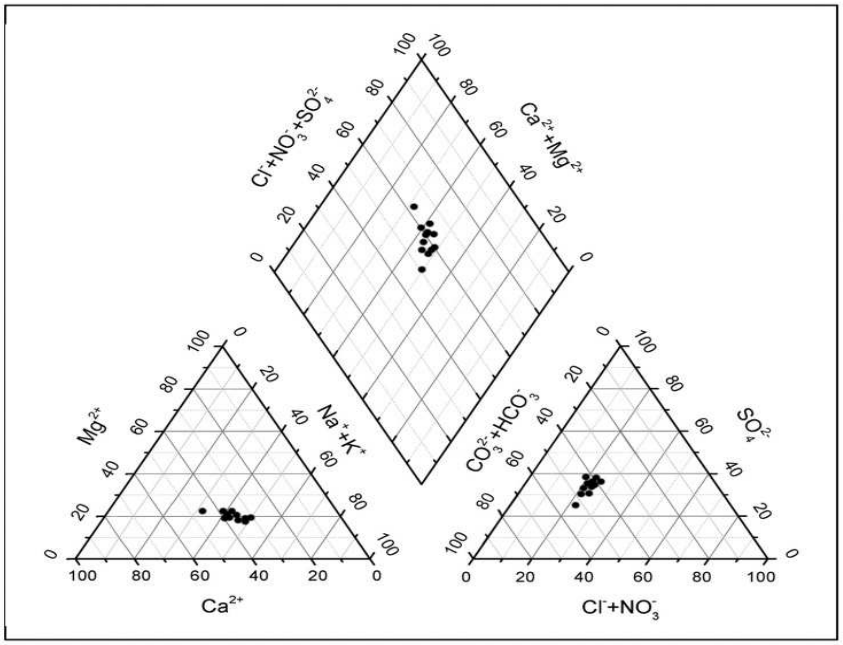

Figure 3: Piper diagram showing the major ion chemistry in Zerdaza reservoir.

According to the literature, Calcium can originate from nitrogen fertilizer inputs involved in the dissolution of carbonates according to the equations 1 and 2 [39,40].

Eq. 1: $NH_4^+ + 2O_2$ --------> $NO_3^- + 2H^+ + H_2O$

Eq. 2: $CaCO_3 + H^+$ --------> $Ca^{+2} + HCO_3^-$

The overall equation **Eq. 3** can be written as follows:

Eq. 3: $NH_4^+ + 2O_2 + 2CaCO_3$ --------> $NO_3^- + 2Ca^{+2} + 2HCO_3^- + H_2O$

According to Eq. 3, the molar ratio of Ca+2 and HCO3- during nitrification is equal to 1, while for Eq. 4, the molar ratio of Ca+2 / HCO3- is equal to 2 when the dissolution of carbonates is in association with the atmospheric CO2.

Eq. 4: $CaCO_3 + H_20 + C0_2$ --------> $2HCO3^- + Ca^{+2}$

The waters of Zerdaza reservoir show a Ca+2 / HCO3- molar ratio exceeding the value of 2. The increase of Ca+2 is due to the dissolution of carbonates from the atmospheric CO2 and optionally, due to the combination of this factor with the contribution of nitrogen fertilizers as it has been reported by Belhadj et al. [22].

3.3 Assessment of the trophic state

The values of the CTSI (Fig.4) show a very slight variation during the period of investigation with a minimum 60.98 recorded in February. From February to the end of the year, the CTSI values increase until reaching a maximum of 71.32 in December. This raise is the result of the long dry season recorded during 2013, and of the high photosynthetic activity of the phytoplankton.

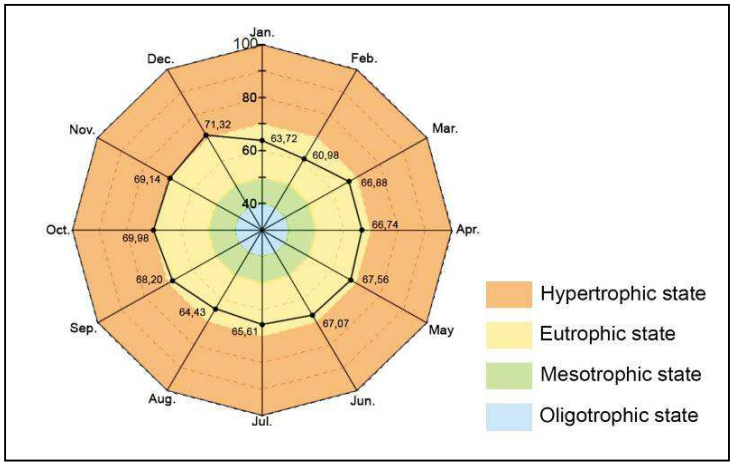

Figure 4: Radar diagram of Carlson's trophic state index of Zerdaza reservoir (Jan. to Dec. 2013).

The CTSI average value 66.80 was recorded during 2013, and if taking into account this value and the trophic state classification established by Kratzer and Brezonik [33], the waters of the Zerdaza reservoir should be considered as a eutrophic water category characterized by a moderate to a high productivity. According to Carlson [30], if TSI (Chl a) is greater or equal to TSI (SD) it indicates that the phytoplankton dominates the light attenuation in the water. When TSI (Chl a) is lower than TSI (SD), it indicates that the none algal suspended particles are responsible for the light attenuation. When TSI (Chl a) is greater or equal to TSI (TP) or TSI (TN) that means that the Phosphorus or Nitrogen is limiting the algal growth [24,41,42,43].

The values of the TSI (Chl a) (Fig.5) were largely higher than those of the TSI (SD) from January to April, while during the rest of the months of 2013 there was no significant difference between these two indexes. This suggests that the light attenuation and overall water turbidity of the Zerdaza reservoir are mainly due to a significant biomass of phytoplankton suspended in the waters but not related to the organic or mineral particulate matter. Indeed, the values of the two indexes TSI (TN) and TSI (TP) are significantly higher if compared to those recorded for the TSI (Chl a). This indicates that both Phosphorus and Nitrogen elements are in excess in the dam waters and do not constitute a limiting factor for the growth of phytoplankton. Therefore, depending on these elements, the phytoplankton biomass may be greater than recorded, and this lead us to suppose that there may be other factors that limit algal growth factor such as the zooplankton grazing.

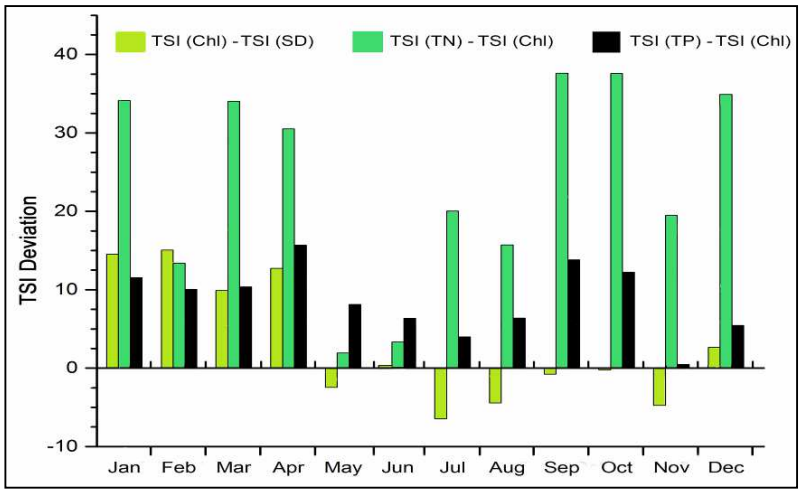

Figure 5: Deviations of the values of TSI (Chl *a*)-TSI (SD), TSI(TN)-TSI(Chl *a*) and TSI(TP)-TSI(Chl *a*) in Zerdaza reservoir from January to December 2013.

In lakes and reservoirs, significant empirical relationships have identified between Phosphorus concentration and the various indicators of the algal growth (Chlorophyll a, transparency, hypolimnetic oxygen depletion rate) [44,45] leading to the dominance of Cyanobacteria [45,46,47] that deeply influences the water turbidity [48].
On the other hand, a reverse trend to the conventional assumption of Cyanobacteria growth under conditions of high TN/TP with low TP concentration has been reported, implicating other factors (zooplankton grazing, sedimentation) involved in the complex relationship between the availability of both TN and TP and the Cyanobacterial blooms [48,49].
In tropical climates, eutrophic waters are generally N limited while oligotrophic waters are mostly P-limited [50]. The N limitation in polluted tropical waters is due to the sewage discharge (low N/P), denitrification (N lost from the bottom of the lake) and P release from the sediment (internal fertilization, with consequent decrease of TN/TP). On the other hand, further processes, such as nutrient excretion by zooplankton and algal/bacterial metabolism, can significantly change the TN/TP behavior [50].
The statistical analysis of the values of the measured parameters show variations over the time according to two different modalities; a category of parameters that varied very slowly throughout the year 2013, whereas the other one underwent rapid concentration changes during the same period. The water transparency in Zerdaza reservoir is strongly influenced by the phytoplankton growth, and the algal population is not limited by the availability of nitrogen and phosphorus elements in the waters as they were, in fact, present in excess.
Despite the eutrophic state indicated by the Carlson's trophic state index, the comparison of the obtained values of the physicochemical parameters with the Algerian standard values confirms that the waters of Zerdaza reservoir are in accordance with the requirements of the Algerian authorities to serve as irrigation water as well as drinking water after appropriate treatment.

Acknowledgements: The authors would like to thank Assoc. Prof. Dr Abderrafik Meddour (Aquaculture & Pathology Research Laboratory) for the English translation and revision of the earlier and present versions of this manuscript. The authors would like to thank the anonymous referees for their helpful comments and suggestions. The authors declare that they have no conflict of interest.

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