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Water-Sediment Physicochemical Dynamics in a Large Reservoir in the Mediterranean Region under Multiple Stressors

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Abstract: Nowadays, the Mediterranean freshwater systems face the threat of water scarcity, along with multiple other stressors (e.g., organic and inorganic contamination, geomorphological alterations, invasive species), leading to the impairment of their ecosystem services. All these stressors have been speeding up, due to climate variability and land cover/land use changes, turning them into a big challenge for the water management plans. The present study analyses the physicochemical and phytoplankton biomass (chlorophyll-a) dynamics of a large reservoir, in the Mediterranean region (Alqueva reservoir, Southern Portugal), under diverse meteorological conditions and land cover/land use real scenarios (2017 and 2018). The most important stressors were identified and the necessary tools and information for a more effective management plan were provided. Changes in these parameters were further related to the observed variations in the meteorological conditions and in the land cover/land use. The increase in nutrients and ions in the water column, and of potentially toxic metals in the sediment, were more obvious in periods of severe drought. Further, the enhancement of nutrients concentrations, potentially caused by the intensification of agricultural activities, may indicate an increased risk of water eutrophication. The results highlight that a holistic approach is essential for a better water resources management strategy.

Keywords: Alqueva reservoir; climate variability; land cover/land uses; water-sediment dynamics

1. Introduction

Currently, water scarcity and its quality are the main challenges concerning water resources [1]. In addition to being a stressor on its own, water scarcity can drive the actions of other stressors, the increment of chemical and ecological effects of water degradation and water abstraction. In fact, freshwater systems are constantly affected by multiple stressors, including urban and agricultural activities, growing population, hydropower generation, and climate change. Understanding how stressors interfere in chemical and ecological status and in freshwater ecosystem services at a regional scale is essential for developing specific water management plans and shaping future environmental policies [2,3]. Currently, in Europe, the relevance of multiple stressors differs regionally [4]: in the north, the higher pressures are related to hydropower plants; in central Europe, the intensive agriculture and floods are the most important drivers of the hydromorphological pressures, whilst in the Mediterranean, the catchments are impaired mainly by water scarcity and intensive agriculture. Crosswise to all these pressures, the climate is changing globally, increasing the risk of floods and pollution in wet regions and droughts in water-scarce regions [5,6]. Current climate change models' projections indicate that the Mediterranean region will face a decrease in precipitation and an increase in temperatures, particularly in summer, leading to more severe extreme events, and promoting the decrease in the availability and quality of the water resources [6,7]. The Mediterranean is amongst the most vulnerable regions to climatic and anthropogenic changes and thus one of the world's water crisis hotspots [7]. Adding to these facts, the predictions for water demands indicate a global increase of about 20 to 30% by 2050 [8], inducing higher stress in arid and semi-arid regions already affected by water scarcity [5–7]. In Portugal, and despite being generally considered a low water stressor country, the southern region frequently suffers from water supply problems during summer [9]. In fact, the Alentejo region is already under hydrological stress with deficient water availability and is prone to meteorological extreme events, such as the severe droughts that occurred in 2003–2005, 2011–2012 and 2016–2017 [10]. The meteorological conditions impact the water quantity and quality, and may also lead to changes in Land use/ Land cover (LULC), such as the growth of irrigation crops and associated changes in management operations of reservoirs and water treatment plants.

In the south of Portugal, 10 to 30% of the freshwater systems are reservoirs, heavily modified water bodies (HMWB) [11], planned for water storage and mainly used for irrigation and water supply [12], with the largest one being the Alqueva Reservoir. These reservoirs are similar to natural lakes in some aspects, such as water storage and low flow [13]. Nevertheless, they differ in annual and inter-annual storage variability, management options and catchment areas, features that induce much larger fluctuations in the water level than in natural lakes [14]. For those reasons, they respond differently to climate change and to other stressors [15]. Several climate change scenarios foresee a decrease in water quality in reservoirs, mainly in semi-arid regions, due to the increase in pollutants concentration and sediments as a result of lower water levels [10,16]. This fact may be more evident in reservoirs located in intensive areas of agriculture and tourism, increasing abstraction and decreasing the ecological and chemical status. In this global change scenario, the sustainable management of reservoirs may be an important key issue, ensuring the water's quantity and quality, as well as the ecosystem's balance and services. To develop sustainable management strategies for a better balance between water abstraction and conservation, improving the ecological/ chemical status of reservoirs, it is essential to understand its dynamics and the main stressors of each system component. Although the impacts of multiple stressors on rivers and streams have been relatively well explored in the Mediterranean region [17–20], the specific consequences for reservoirs need further investigation. Most studies on reservoirs use modeling tools for the assessment of climate change impacts of on water quantity, in combination with socio-economic conditions, as well as changes in soils and water uses [15,16,21–23]. Few studies have linked the water-sediment dynamics with the ecosystem status in real conditions of climate change [24,25]. Studies developed in the Alqueva reservoir showed a nutrients increase and the presence of hazardous substances in water and sediments [26–28]. To help decision making about sustainable and specific management plans, considering the actual climate change scenario and intensive land use, it is important to link these results with those of the present study about the dynamics of the reservoir in different climate real conditions under several stressors.

Bearing in mind the above statements, the main aims of the present study were: (i) to assess the physicochemical and phytoplankton biomass dynamics in the water column and sediments of Alqueva reservoir, under diverse meteorological conditions and real land use scenarios; (ii) to correlate the changes of the analyzed parameters with variations in the meteorological conditions and in the land cover/land use; (iii) to identify the most important stressors, to improve the ecological and chemical status of the reservoir and its ecosystem services; (iv) to integrate the results obtained since 2006 in the Alqueva reservoir for a better understanding of the water body; (iv) to provide necessary tools and information to be used in a better and more specific management plan of the reservoir, which may be included in the upcoming River Basin Management Plans.

2. Materials and Methods

2.1. Study Area and Sampling Sites Characterization

The Alqueva reservoir is the largest artificial lake in Western Europe, with a surface area of 250 km^2, 85 km long, 4150 hm^3 maximum storage capacity with 3150 hm^3 useful capacity, and a catchment area of 55,000 km^2. Water stored in Alqueva reservoir allows multipurpose usages such as (i) public water supply, with the reinforcement of 5 dams that supply about 200,000 inhabitants; (ii) agriculture, with an irrigated area of about 120,000 ha and which will increase to 170,000 ha in the coming years; (iii) industry; (iv) clean energy production (520 MW); and (v) tourism [29]. It is located in the Guadiana basin in Alentejo, a semi-arid region in the south of Portugal, bordered by Spain in the east (see Figure 1). The Alqueva primary inflow is the river Guadiana, which flows north to south through the Portuguese territory. Guadiana flow has strong seasonal variations, typical wet season flows are of the order of 100 m^3/s, whereas dry season flows drop to values below 20 m^3/s. Smaller water input contributions come from other tributaries: Degebe, Álamo, Azevel, Lucefécit, and Asseca streams, along the reservoir west margin and the Zebro and Alcarrache streams, along the east margin [30]. The Guadiana catchment has a population of 1.9 million inhabitants, with a density of 28 inhabitants/km^2 in Spain and 114 inhabitants/km^2 in Portugal (https://ec.europa.eu/eurostat/home (accessed on 23 December 2020)).

The most representative types of soils are lithosols, litholic soils, Mediterranean brown soils, and podzols, primarily derived from shale, clay, and limestone [31]. Generally, the land was mainly used for olive trees growing, agroforestry of holm oaks (‘*montado*’), and annual rainfed crops (wheat, oats, and sunflowers). Extensive livestock production is the most important animal-farming activity in the catchment [32].

Four sampling sites were selected in the Alqueva reservoir: Álamos (Al; 38°33′84.46″ N, 7°57′34.41″ W), Mourão (Mr; 38°39′36.33″ N, 7°38′75.51″ W), Montante (Mn; 38°22′35.42″ N, 7°45′94.95″ W) and Lucefécit (Lf; 38°55′52.83″ N, 7°29′91.37″ W). These sampling points, with lentic conditions, have fixed platforms installed by the Portuguese Environmental Agency (APA) to monitor the water quality of the reservoir. Montante and Mourão platforms are located in clear cut surroundings and deep areas of the reservoir, with 60 m and 50 m depth, respectively; whilst Álamos and Lucefécit platforms are located in a forested surrounding and a ca. 20 m deep area [33].

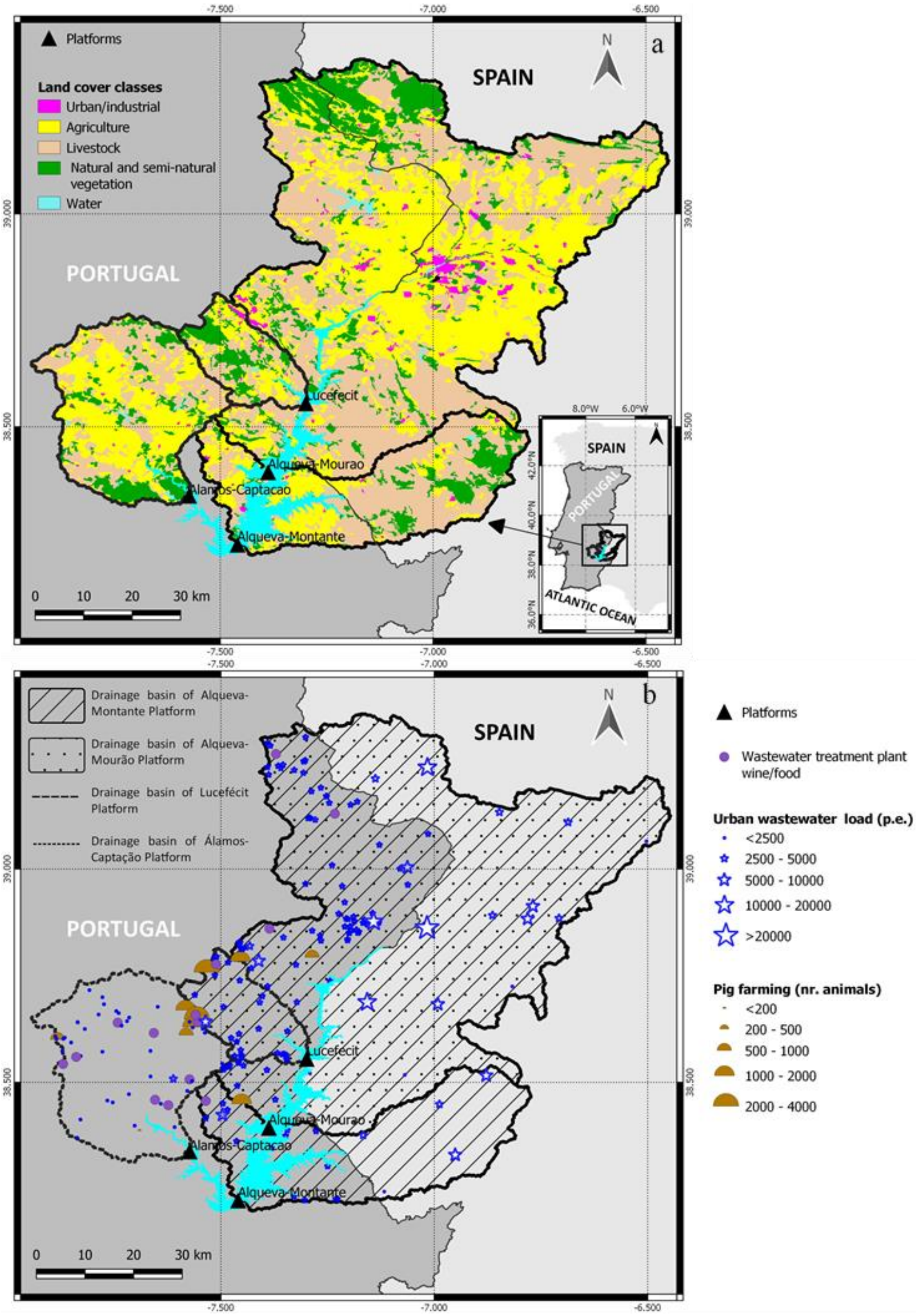


Figure 1. (**a**) Map of the study area located in Alentejo region. The black triangles indicate the platforms, from North to South: Lucefécit; Mourão; Álamos and Montante and the land cover classes are represented by the colors indicated in the legend. Bottom-right inset shows the study area location in the map of Portugal. (**b**) Map showing the location of the industrial wastewater treatment plants (wine and food related), the urban wastewater loads and the number of animals in pig farms distributed in the four drainage basins indicated in the legend.

2.2. Climatological and Land Use/Land Cover (LULC) Characterization

2.2.1. Climate Conditions

In general, the climate in the region is dry sub-humid to semi-arid, with Mediterranean characteristics (Csa in Köppen's classification), with hot summers, high level of insolation and evapotranspiration, and mild winters. The average annual temperature is about 16 °C, ranging from 9 °C to 23 °C. In the coldest month, January, the mean daily minimum temperature is lower than 6 °C, with frequent negative values, especially in the valleys.

In summer (July and August) the mean daily maximum temperature is above 30 °C, being frequent values close to 40 °C or higher. The precipitation regime is characterized by highly spatial and temporal irregular behavior, varying between abundant rainfall episodes (concentrated in only a few minutes or hours), and drought periods, that can last a few months. In the last Climatological normal, the average annual rainfall is less than 600 mm. The annual distribution of precipitation is extremely irregular, being less than 300 mm in dry years and rising to more than 900 mm in wet years [34]. Summer rainfall is very low and about 80% of annual precipitation occurs during the three winter months (December to February).

For the meteorological characterization of the study period (2017–2018), a weather station installed in the left margin of the reservoir, near the Montante platform, was used. This weather station measures and records the several meteorological variables, namely Air Temperature (Tair), Relative Humidity (RH), Precipitation (Prec), Wind Speed (Wins), and Shortwave Solar Radiation (Rad) [35].

2.2.2. Land Use/Land Cover (LULC) Patterns

Shuttle Radar Topography Mission (SRTM) elevation data at a resolution of 1 arc-second (30 m) were used to estimate the drainage basin areas associated with each platform (represented by the different black lines in Figure 1). The drainage basins of the platforms represent the appropriate areas to analyze and relate land cover to changes in the water column and sediments of the Alqueva reservoir since they collect and drain off the surface and groundwater, as well as precipitation into the control points. To note that Montante drainage basin encompasses Mourão and Lucefécit basins, Mourão includes the Lucefécit basin, and Álamos drainage basin does not overlap any of the other three basins.

Land Use/Land Cover (LULC) was obtained from the analysis of the 2018 CORINE Land Cover (CLC) inventory, retrieved from satellite imagery (Sentinel-2 and Landsat-8 for gap filling), available from Copernicus Land Monitoring Service (https://land.copernicus.eu/ (accessed on 23 December 2020)). Five main categories describing typical LULC types in the region were considered: urban/industrial (Urb/Ind); agriculture and pasture (Agr); livestock (Liv); natural and semi-natural vegetation (Nat); water (Wat). Figure 1 also shows the distribution of land cover types, with agriculture and livestock as the main activities around the Alqueva reservoir, followed by natural and semi-natural vegetation (including Montado landscape) more often found in the south-eastern regions. The pollution point sources information represented in Figure 1, such as the wastewater treatment plants (urban and industrial), and the pig farming, were courteously provided by the Administration of the Hydrographic Region of Alentejo (ARH Alentejo).

2.3. Sampling

Water and sediment samples were collected at the four selected platforms represented in Figure 1, Álamos (Al); Mourão (Mr), Montante (Mn); Lucefécit (Lf). The study comprised 12 sampling campaigns, from January 2017 to November 2018: in January (Jn), March (Mr), May (M), July (Jl), September (Sp), and November (Nv).

The wet period included the months of January, March, and November, and the dry period included the months of May, July, and September, as defined by the Portuguese Environmental Agency for the Alentejo region. This seasonal evaluation is justified by the importance of the variability of the tributaries' hydrologic regimes for the reservoir water quality, particularly in these semi-arid areas of Portugal, where the river discharges may range from zero in the dry period to high discharge rates during the wet period. These changes affect all the physical, chemical, and biologic parameters of the reservoir [32].

At each platform were collected: (i) surface water: 2 L for chlorophyll quantification and 2 L for chemical parameters analysis using a Van Dorn bottle; and (ii) 5 L of surface sediments (<10 cm), which were gathered using a stainless steel Van Veen grab of 0.05 m^2 with a maximum volume of 8 L. The water samples were stored in polyethylene bottles, and kept in the dark, and the sediment samples were packed in polyethylene bags. All samples were transported in a cooler at 4 °C to the laboratory, where they were conserved and stored following the requisites for water and sediments conservation for each parameter until the analyses were performed (maximum storage time: 1 week) [36,37].

In situ, vertical profiles of water temperature (T; °C), pH, electrical conductivity (EC; µS/cm) and dissolved oxygen (DO; mg/L), were measured using a multiparametric probe YSI 6820 MPS probe®. The transparency (Secchi depth (SD); m) was measured with a Secchi disk and used as an indicator of the suspended particles and solutes presence, allowing the determination of the euphotic zone (EuphZ; 2.5 × SD).

In a reservoir, the water level is constantly changing, and thus the surface elevation, the water volume, and the surface area present constant fluctuations. These parameters were monitored in every campaign and considered for this study: surface elevation, surface fluctuation, volume, and surface area (Table S1).

2.4. Physical, Chemical and Phytoplankton Biomass Characterization

2.4.1. Water Parameters

The water chemical parameters analyzed were: biochemical oxygen demand (BOD_5; mg/L; Respirometric method), total phosphorus (TP; mg/L; Molecular absorption spectrometry), Kjeldahl nitrogen (KN; mg/L; Kjeldahl method), nitrate (NO_3; mg/L; Ionic chromatography), nitrite (NO_2; mg/L; Ionic chromatography), ammonium (NH_4; mg/L; Molecular absorption spectrometry), chlorides (Cl; mg/L; Ionic chromatography), sulphates (SO_4; mg/L; Ionic chromatography), calcium (Ca; mg/L; Ionic chromatography) and sodium (Na; mg/L; Ionic chromatography) [36].

Total nitrogen (TN was determined, using the following equation [36]):

$$\text{TN (mg/L)} = 0.226 \times [\text{NO}_3;\ \text{mg/L}] + 0.304 \times [\text{NO}_2;\ \text{mg/L}] + [\text{KN};\ \text{mg/L}] \quad (1)$$

In general, chlorophyll-a (Chl-a) can be used to reflect the phytoplankton biomass and the trophic state of a reservoir, thus playing a key role in the eutrophication evaluation [38]. The determination of Chl-a was performed based on the Portuguese standard NP 4327 [39] and Standard Methods 10,200 H [36]. The pigment was extracted with 90% acetone after sample filtration in a glass fiber filter (GF/C Whatman).

2.4.2. Sediment Parameters

The sediments' pH ($pH_{pore\text{-}water}$) and the electrical conductivity ($EC_{pore\text{-}water}$; µS/cm) were analyzed in pore-water samples [37].

Sediment grain-size distribution was determined following the Portuguese Laboratory of Civil Engineering E196 method [40]. The chemical parameters determined were: organic matter content (OM; %; calcination at 500 °C; [37]); total nitrogen (TN; %; Kjeldahl method; [36]); total phosphorus (TP; %; molecular absorption spectrometry with molybdo-vanadate phosphoric acid; [36]).

2.5. Statistical Treatment of Data

The study assessed a total of 37 variables displayed by the following categories: (i) water and sediments physicochemical and biological parameters: (a) water: T_w; pH_w; EC_w; DO; BOD_5; TP; KN; TN; NO_2; NO_3; SO_4; NH_4; Cl; Na; Ca; Chl-a; (b) sediments: Sand; Silt; Clay; $pH_{pore\text{-}water}$; $EC_{pore\text{-}water}$; OM; TP_s; TN_s; (ii) drainage basin characteristics (LULC): Urb; Agr; Liv; Nat; Wat; (iii) climate conditions: T_{air}; RH; WinS; Prec; Rad; (iv) reservoir characteristics: EuphZ, surface elevation, surface fluctuation.

The variables were explored and described by descriptive statistics (mean ± standard deviation) and by multivariate statistical analysis (Principal component analysis and cluster analysis), based on two matrixes, one for water (48 samples × 19 physicochemical and biological parameters) and another for sediments (48 samples × 8 physicochemical parameters) integrating reservoir properties, LULC and climate conditions. Data were normalized (log x; x = mean value) prior to multivariate statistical analyses, avoiding misclassification due to differences in data dimensionality.

Spearman's rank correlation was used to analyze the strength of linear associations between water and sediments physicochemical parameters, drainage basin characteristics, reservoir properties, climate conditions, and years of the study (2017: drought and 2018: post-drought).

The multivariate statistical methodologies were used with the following aims: (i) principal component analysis (PCA): to assess the relationships and possible patterns between variables, determining the main climate and LULC parameters that account for the variability of the water body status,; (ii) cluster analysis (CA): to group the sampling locations according to their water characteristics. The CA groups were plot into clusters according to their similarities, using the Euclidean distance between samples. [41,42].

All statistical analyses were carried out using the STATISTICA 7.0 (Software™ Inc., Pottstown, PA, USA, 2007).

3. Results and Discussion

3.1. Meteorological and Land Use/Land Cover (LULC) Characterization

3.1.1. Meteorological Conditions

Figure 2 presents the temperature, precipitation, and wind speed data measured in 2017 and 2018. The temperature differences between years (1-minute temperature values represented by the grey dots) are clearly showing higher values in 2017 than in 2018, from April to November (Figure 2a). In contrast, the monthly accumulated precipitation (represented by the red bars) in 2017 is roughly half of the amount in 2018. The monthly mean temperature (blue line) shows that high temperatures were registered for a longer period in 2017 than in 2018, and the red bars confirm that after March 2017 the precipitation was scarce, which caused the severe drought conditions. The precipitation that occurred in March 2018 triggered a relief of the drought conditions, registered in 2017, a year that was classified as extremely warm and dry in comparison with the Climatological Normal of 1971–2000 (www.ipma.pt; last accessed on 25 September 2019). The year of 2018 did not present significant deviations from the climatological normal, with the mean annual temperature showing a slight deviation of +0.2 °C and the precipitation presenting a slightly higher annual value (112% of the climatological normal). Relative to solar radiation, 2017 was characterized by an accumulated global horizontal radiation of 6.84×106 kJ/m^2, higher than for the year 2018 (6.46×106 kJ/m^2). Regarding the wind speed (Figure 2b), grey dots present daily means and blue lines represent 15 days averages, the behavior along the year presents oscillations between calm and relative windy periods, frequently associated with the frontal precipitation events in the rainy period and to the summer Iberian thermal low and related sea breeze system [43].

3.1.2. LULC Characterization

The distribution of LULC was analyzed in terms of the percentages obtained for each class within the four drainage basins, corresponding to the following areas: Álamos: 1279 km^2; Montante: 7332 km^2; Mourão: 5912 km^2; Lucefécit: 425 km^2 (Figure 3). Notice that the agriculture class, as well as livestock, were the dominant classes in all the drainage basins, generally constituting 80% of the total LULC. Agriculture dominates in Álamos (46%) and livestock in Montante, Mourão and Lucefécit. Presently, the most representative crops in the Guadiana basin are olive and vineyard with an agriculture based in intensive cultural practices (irrigation, fertilization, and pesticides application). Pig farming is one of the most important livestock activities in the basin, which may constitute an important source of diffuse pollution, mainly by the transport of nutrients and organic matter to the reservoir (Figures 1 and 3). In the Portuguese territory of the Guadiana basin, the pig farms were mainly located at the drainage basins of Álamos (7028 animals) and Lucefécit (5300 animals), yielding 5.5 and 12.5 animals/km^2, respectively. In general, these effluents present high amounts of nutrients, particularly NH_4 from the animals urine, and metals such as Cu and Zn, used as supplements to increase animals´ growth and reproduction rates [44].

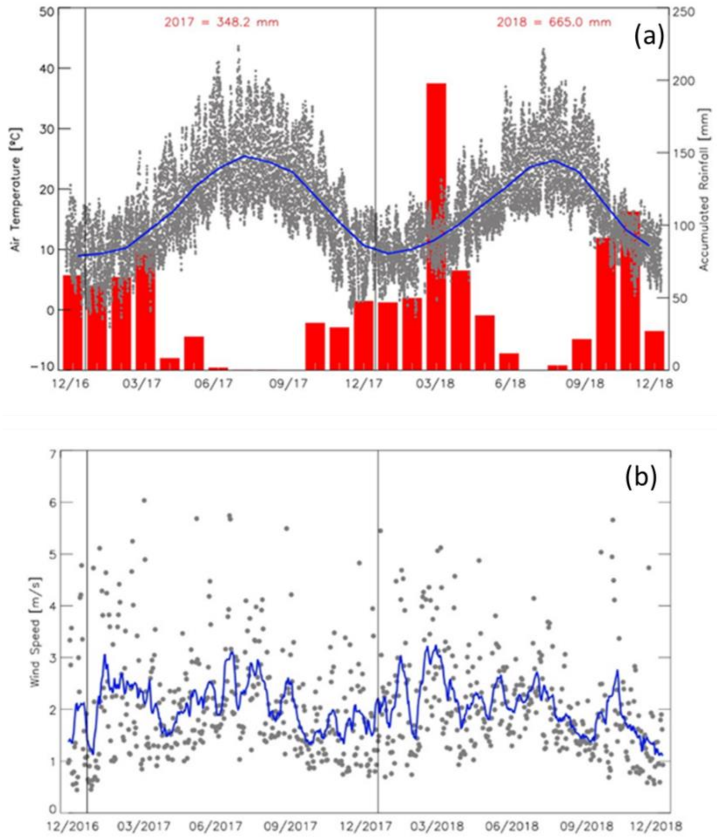


Figure 2. Meteorological charts from a station installed in the lower part of the Guadiana basin at the Alqueva reservoir shore in the period December 2016 to December 2018. (**a**) 1-min and monthly mean (grey dots and blue line) air temperature and monthly accumulated rainfall (red bars). The grey vertical line separates the years 2017 and 2018; (**b**) Daily and monthly mean wind speed (grey dots and blue line).

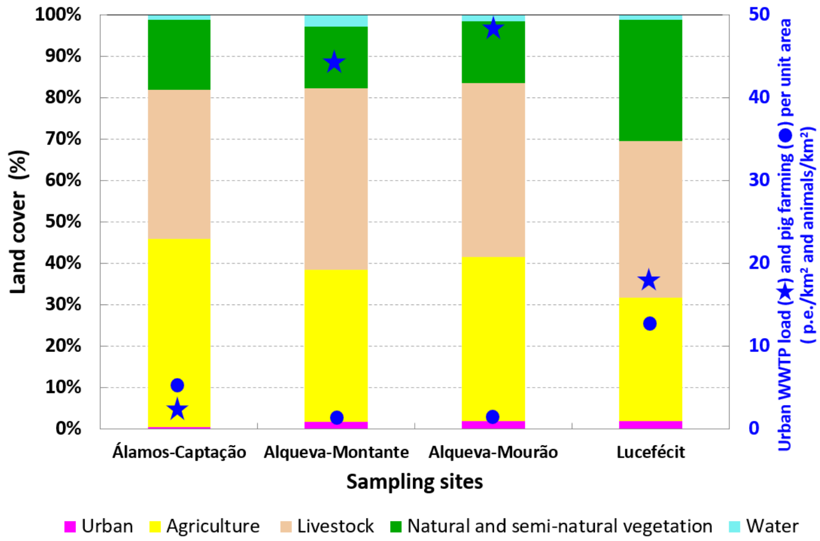


Figure 3. Percentages of the land use classes in the drainage basins of the sampling locations at Alqueva reservoir. Blue stars indicate the total urban wastewater treatment plants' (WWTP) load and blue circles illustrate the number of animals, both per unit area at each drainage basin.

Lucefécit had the highest percentage of natural and semi-natural vegetation (29%), mostly constituted by the Montado landscape (typical in the Mediterranean region), which may act as a buffer to the pollution processes [45]. The urban class has small expressivity in the generality of the drainage basins, which is justified by the low population density corresponding to dispersed small villages. The drainage basins of Mourão and Montante are the most influenced by urban wastewater treatment plants' (WWTP) discharges, with the highest WWTP loads per unit area (49 p.e./km^2 and 44 p.e./km^2, respectively) (Figures 1 and 3). The remaining point sources of pollution in the region were winery wastewater treatment plants with seasonal effluents, mainly produced during autumn-winter and characterized by high concentrations of nutrients and low pH values [46] (Figures 1 and 3).

3.2. Water Column Seasonal and Spatial Dynamics

3.2.1. Temperature and Dissolved Oxygen Profiles

Understanding hydrodynamics and thermal stratification are of great importance for the mixing patterns knowledge, constituting useful tools for the management of reservoirs [47]. The physical characteristics of the reservoir are influenced by meteorological conditions and have an impact on its chemical and biological dynamics, as observed by the obtained Spearman "*on ranks*" correlations (Table S2). The vertical temperature profiles (Figure 4) indicate that the reservoir is stratified once per year, generally from May to September, presenting a monomictic regime as reported elsewhere [27,48]. Nevertheless, at Montante the reservoir presented a larger stratification beginning in March/ April with the maintenance of the differences among epilimnion and hypolimnion until September. Lucefécit was the location where the thermal stratification period was shorter as already observed in other works [27].

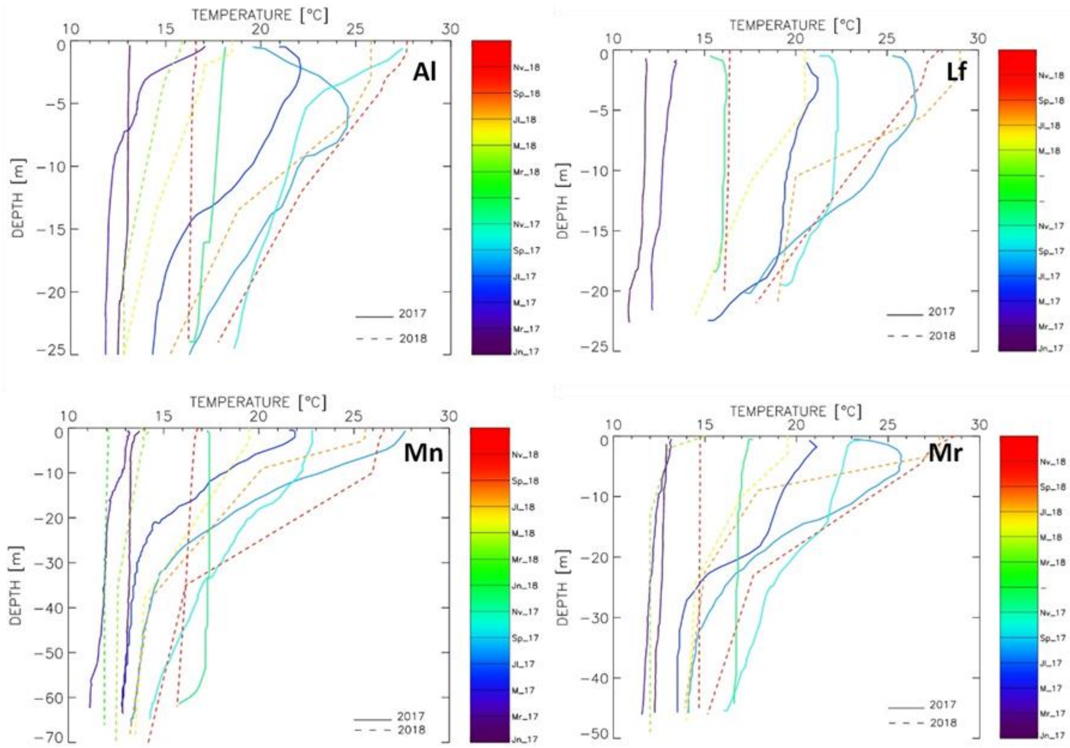


Figure 4. Temperature profiles, at the four sampling locations at Alqueva reservoir, in the months of January (Jn), March (Mr), May (M), July (Jl), September (Sp) and November (Nv), during 2017 (full lines) and 2018 (dashed lines). Al–Álamos, Lf–Lucefécit, Mn–Montante and Mr–Mourão.

These differences in the water mixing phases may be correlated with the wind regime, depth, and flow conditions (Table S1, Figure 2). Figure 5 shows the water temperature vertical profile for Montante (location with the highest depth of the reservoir (64–65 m)) where the development of the thermocline can be clearly seen on both years (black dots). In 2017, surface water temperatures ranged between 23 and 28 °C with bottom temperatures of 13–16 °C. The maintenance of moderate temperatures (17–20 °C) was observed at up to 40 m of depth, during July to September. Meanwhile, in 2018 surface water temperatures were around 24–25 °C and bottom temperatures were 14–15 °C, with moderate temperatures observed up to 20 m of depth, indicating a warming of the water column during the drought year. The progress of temperature in the reservoir was influenced by meteorological conditions, highlighted by the correlations obtained with the mean air temperature ($R = 0.92$; $p < 0.01$), precipitation ($R = -0.79$; $p < 0.01$) and global radiation ($R = 0.80$; $p < 0.01$) (Table S2). The records of the thermal cycle of the reservoir showed a warming tendency, with the progress of water temperature values at the wet period, of 9–10 °C in 2006 [32], 10–12 °C in 2012 [46], and 11–13 °C currently. In the dry period, the warming tendency at the surface is not so clear, probably due to the high influence of air temperature in the epilimnion. These results may indicate that in years characterized by the intensification of drought conditions, with the increase in air temperatures and the decrease in rainfall events, accentuated changes in the physical regime of reservoirs may occur, even in those of large dimensions, like the Alqueva reservoir, as reported elsewhere [49–51].

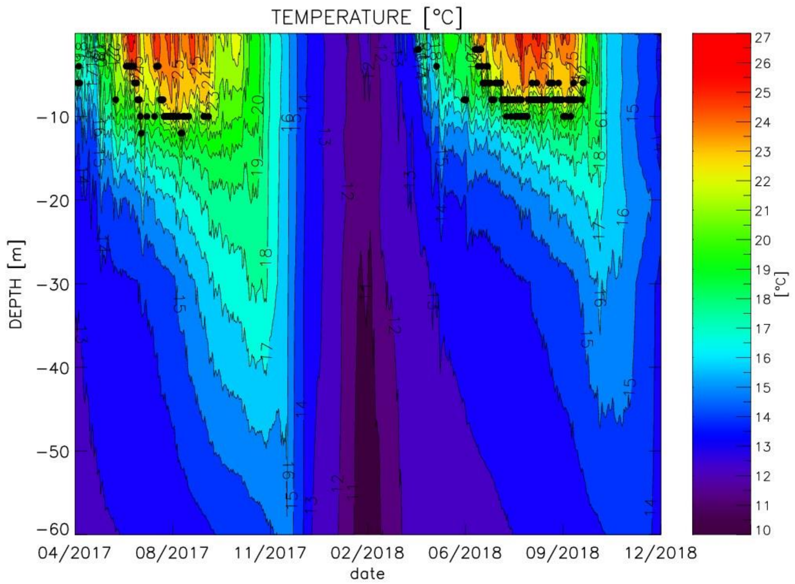


Figure 5. Vertical temperature profile and thermocline (black dots) over time in Montante during the period April 2017 to December 2018. The bottom of the graph (60 m) represents the bottom last thermistor depth and not the bottom of the reservoir.

The stratification period of the reservoir, in a large part of the year, is attended with a depletion of DO values in the hypolimnion as displayed in Figure 6, incrementing the differences in water chemical characteristics between the two layers. Dissolved oxygen values dropped sharply from the thermocline, leading to the development of anoxia during the dry period. This process was longer in 2017 (drought year) with DO values of 0–1% at the bottom, between May and September, correlated with the temperature water column stratification and with the settling and breakdown of organic material in the reservoir, as already reported by Naselli-Flores et al. [52]. During the wet period (November-January), the wind increase and the air temperature decrease ensure the complete mixing of the two phases, with DO values varying between 80 and 100%. The results highlight that DO percentages in surface water were positively correlated with the air temperature ($R = 0.39$; $p < 0.01$) and the water temperature ($R = 0.40$; $p < 0.01$), and negatively correlated with the rainfall ($R = -0.38$; $p < 0.01$) and the relative humidity ($R = -0.52$; $p < 0.01$), showing again the influence of the meteorological conditions on the physical status of the reservoir. Further, the increase in the DO levels was correlated with the increase in algae productivity (represented by the Chl-a in the present study) that occurred mainly during the dry period due to the atmospheric favorable conditions, ($R = 0.47$; $p < 0.01$)

(Table S2). The transparency, determined by the Secchi disk, showed small differences among the locations, generally with higher values in the wet period, as observed for other reservoirs [53,54]. Lucefécit was the location with the lowest transparency values, which may be explained by the proximity to the riparian zone, the lowest depth and the highest algae productivity (Table S1; Figure 1 and Figure 8) [53,54].

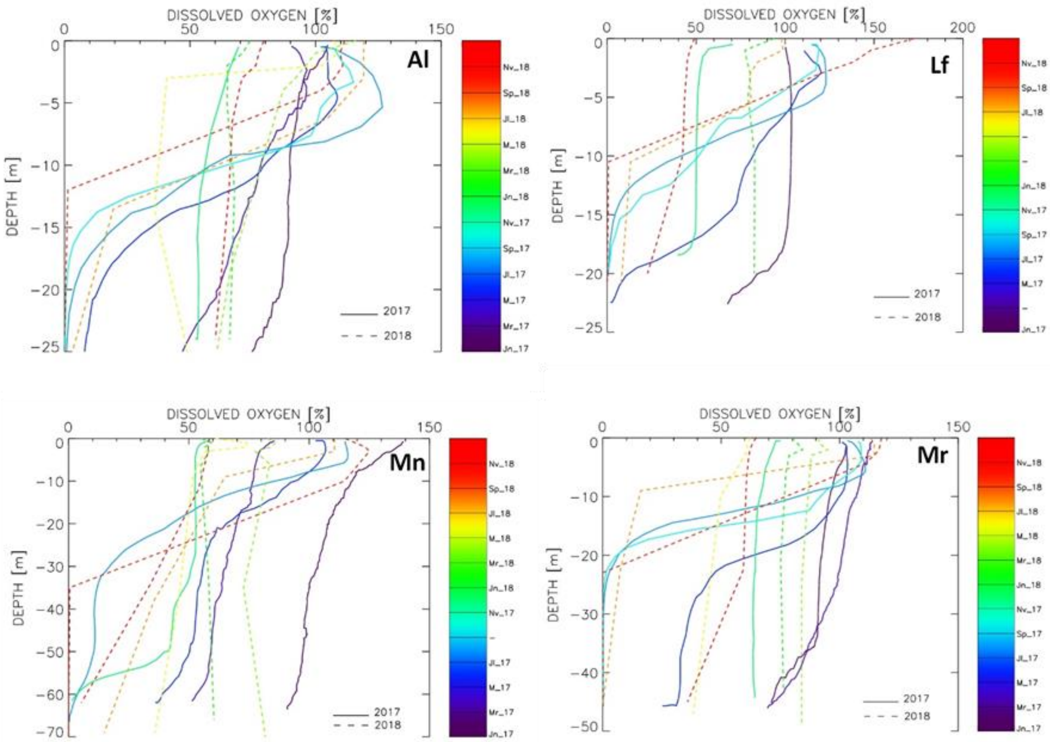


Figure 6. Dissolved oxygen profiles, at the four sampling locations at Alqueva reservoir, in the months of January (Jn), March (Mr), May (M); July (Jl); September (Sp) and November (Nv), during 2017 (full lines) and 2018 (dashed lines). Al: Álamos; Mn: Montante; Mr: Mourão; Lf: Lucefécit.

3.2.2. Chemical and Phytoplankton Biomass Patterns

Surface waters of the reservoir presented a slightly alkaline pH ranging from 7.51 to 9.44. Lucefécit showed the highest values of pH in the dry period 2018, surpassing sporadically the Water Framework Diretive (WFD) limit for the good ecological potential (pH < 9) [55] (Figure 7). Water EC ranged between 368 and 581 μS/cm, with the highest values observed at Mourão in September 2018 (581 μS/cm) (Figure 5). Both parameters were influenced by the meteorological conditions, increasing with T_{air} and dropping with precipitation (see Table S2). When the trends over the years were analyzed, a slight rise of the water pH and an obvious increase in the EC_w values (2006/2007 [28]; 2011/ 2012 [27]; and present), were observed. The trend of EC_w values was correlated with the rise of the concentrations of sodium, sulphate and chlorides over time, supported by the correlations observed among EC_w and these parameters (Table S2) [29,30]. Further, when we analyzed the concentrations of some cations (such as Na, Ca) with the conductivity values, and we verified similar patterns along the years [29,30]. These correlations have already been observed in other Mediterranean reservoirs [56].

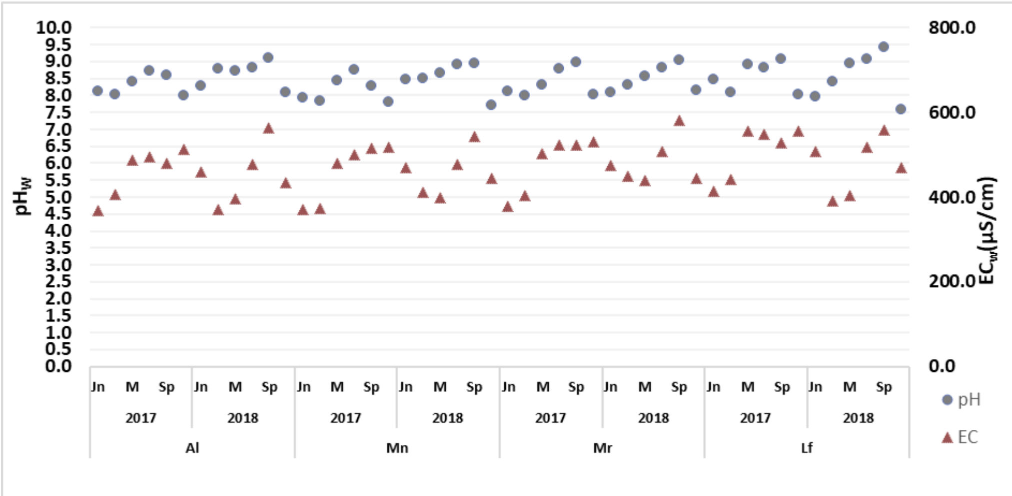


Figure 7. Values of pH$_W$ and electric conductivity (EC$_W$; µS/cm) measured in situ of each location (Al: Álamos; Mn: Montante; Mr: Mourão; Lf: Lucefécit), during the study.

Concerning organic descriptors, the BOD_5 ranges from 2 to 10 mg/L, presenting, at dry period, values higher than the WFD limit proposed for the good ecological potential (5 mg/L). Lucefécit was the location that exhibited the maximum BOD_5 concentrations in both years (Figure 8). Concentrations of $BOD_5 > 5$ mg/L are considered significant pressures for the systems, putting them at risk of failing the environmental objectives related to the good potential [57]. Agriculture and livestock classes may have contributed to the levels of this parameter, at Álamos and Lucefécit. Currently, the results do not reveal a clear significant correlation among LULC and BOD_5, however this kind of linkage has already been observed in other studies [27,58–60].

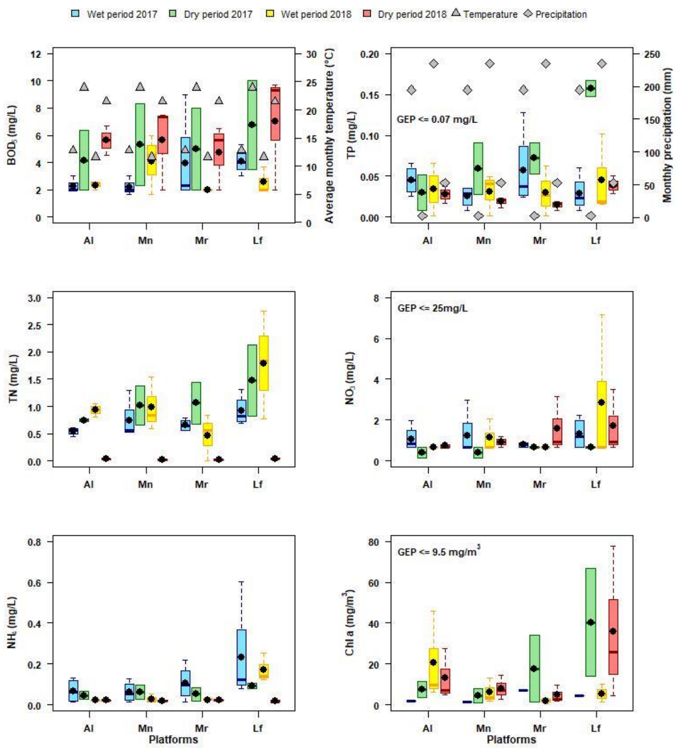


Figure 8. Spatial and temporal variation of the organic descriptors, nutrients, and Chl-a in the water samples during the period of the study. The black circles indicated the mean, the line across the box represents the median, and the bottom and top of the box show the standard error. Recommended guide levels for the good ecological potential (GEP) are indicated in the plot [55].

Nitrogen and phosphorus are the main factors leading to algae blooms, being important parameters for estimating reservoirs´ degrees of eutrophication, and ecological status [59]. Generally, algal blooms may occur when TP and TN concentrations in water reach 0.02 and 0.2 mg/L, respectively [55]. In the present work, TP and TN concentrations were above 0.02 and 0.2 mg/L, in most of the sampling campaigns (Figure 8), indicating the risk of algal blooms not only in the dry period but also in the wet one. The TN levels presented high spatial and temporal variability, ranging between 0.01 and 2.75 mg/L, Lucefécit being the location with the greater values detected. In fact, the highest values of TN, at the water column, occurred at Lucefécit in the wet period 2018, probably due to the runoff from agriculture practices and livestock activities, the LULC classes more representative in its drainage basin, as already observed in other Mediterranean reservoirs [60]. On the other hand, TP achieved the highest concentrations in the water column during the dry period 2017 at Lucefécit, surpassing the limit for the good ecological potential (TP $\leq$ 0.07 mg/L; [55]). This temporal pattern is not the most usual, once the greatest concentrations of TP generally occur during the wet period due to the increase in runoff, the decrease in algae productivity, and the overturn of the water. Nevertheless, it had already been observed in 2012 [29], a year also characterized by a severe drought [10]. This occurrence has been more evident in areas with low depth without external loading, making the internal loading an important driver for the increase in nutrient concentrations in the reservoir. A similar increase in nutrient concentrations due to higher internal loading had also been observed in other reservoirs during summer [61,62]. This internal source of nutrients results from the sediments under anoxic conditions during the stratification phase. In fact, Søndergaard et al. [62] suggested that during the mixed phase, the oxic conditions are maintained along the water column and phosphorus is adsorbed into iron (III) compounds, which partially inhibits the sediment´s phosphorus release. During the anoxic phase (stratification period), the iron (III) is reduced to iron (II) and subsequently both iron and phosphorus returned into the water solution. With the saturation of phosphorus in the lower phase of the water column, an upward transport occurred, from the deeper sediment to the oxic layers of the water. The observed decrease in TP concentrations in the Lucefécit sediment during the stratification period, achieving the lowest values in September 2017, supports the occurrence of this process (Figure 8).

The excess of organic matter and nutrients in water are a driving force for the increase in the algae productivity, supported by the positive correlations observed between Chl-a and BOD_5 (R = 0.46; p < 0.001), TP (R = 0.38; p < 0.05) and TN (R = 0.52; p < 0.001), as reported elsewhere [56]. Lucefécit presented the highest concentrations of Chl-a during the dry period, surpassing the limit for a good ecological potential (9.5 mg/m^3, for reservoirs of South Portugal [55]) in 56% of the total samples, and in 44% of the samples from Álamos. These locations, with the lowest depth and with considerable external sources of nutrients, as farming pigs and intensive agriculture activities, also showed the lowest euphotic zones. In fact, in a study carried out on 50 surface water bodies in Greece, the most impacted lakes by agricultural and urban classes had the lowest secchi depth [60]. The increase in phytoplankton also contributed to the lower levels of euphotic zone observed, supported by negative correlation between Chl-a and euphotic zone (R = $-$0.814; p < 0.01). Despite the similar patterns for the temporal and spatial variability of Chl-a observed, the concentrations in the Alqueva have been increasing over the years [63].

3.3. Sediments Seasonal and Spatial Dynamics

3.3.1. Granulometric Characteristics

The sediment particle size has a great influence on the distribution of natural and anthropogenic elements, as organic matter, nutrients and metals, showing usually high affinity to fine particles (<0.063 nm) [26,27,64]. These compounds may be released from the sediments to the bottom phase of the water column under specific limnological conditions. The granulometry analysis displayed spatial differences in the reservoir (Figure 9), with locations such as Álamos, Lucefécit and Montante mainly constituted by fine particles (clay and silt), and others as Mourão with a sand particles fraction higher than 50%. The sediments' granulometric fractions of Álamos, Lucefécit and Mourão were consistent with the results obtained in 2012, a factor that may indicate a low sedimentation rate, at the reservoir [26,27]. Higher proportions of sand particles were recorded at Mourão and Montante, both areas with a sharp depth and steeper slopes, located in the middle of the reservoir. Lowest water flows, such as at Álamos and Lucefécit (locations in the tributaries of the reservoir), induce a greater accumulation of fine-grained sediments, according to the general pattern observed for reservoirs [65]. Further, the results pointed to the association between grain size and LULC, with the linkage between sand and urban class ($R = 0.63$; $p < 0.001$), and clay with agricultural uses ($R = 0.40$; $p < 0.001$) (Table S2).

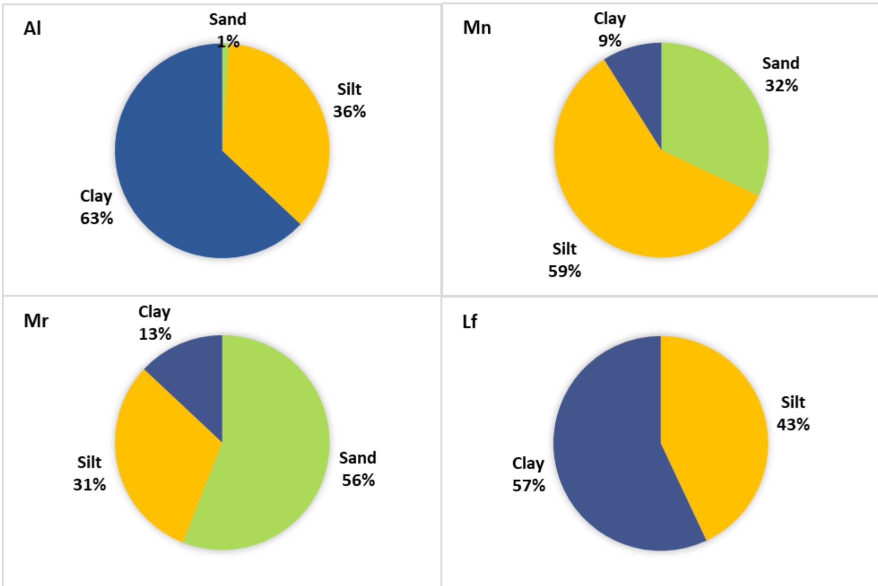


Figure 9. Sediments' granulometric fractions at each sampling location (Al: Álamos; Mn: Montante; Mr: Mourão; Lf: Lucefécit) in the Alqueva reservoir.

3.3.2. Chemical Patterns

The variability of the main chemical parameters of the Alqueva sediments is displayed in Figure 10a ($pH_{pore\text{-}water}$ and $EC_{pore\text{-}water}$) and Figure 10b (OM, TP, TN). The $pH_{pore\text{-}water}$ values ranged from slightly acid to slightly alkaline, with the sediments from Álamos having the lowest values during the dry period 2017. The $EC_{pore\text{-}water}$ values were greater than at surface water, ranging from 285 to 952 µS/cm (at Mourão_May 2018 and Montante_September 2018, respectively). The $EC_{pore\text{-}water}$ presented positive correlations with urban class ($R = 0.43$; $p < 0.001$) and livestock class ($R = 0.58$; $p < 0.001$), as already observed for the sediments of Alqueva tributaries at Guadiana Basin [66]. Generally, over the years, the sediments showed an acidification trend, with a slight decrease in $EC_{pore\text{-}water}$ [29]. The organic matter contents ranged from 5.1 to 13.1%, with the lowest values observed at Mourão (Figure 10b), a location mostly constituted by sand particles. Surface sediments of the Alqueva reservoir are mainly inorganic, with OM contents < 12% [67]. Despite the high variability of TPs concentrations, much influenced by oxic conditions, pH and iron forms [68], all the sediments presented concentrations of TPs higher than the severe effect level ($TP_{SEL} > 0.2\%$; [69]), classifying the sediments as heavily polluted, and likely to affect the health of sediment-dwelling organisms. Montante was the location with the highest concentrations of TP_s, achieving values of 17.5% in the wet period for both years. Notwithstanding the current TPs concentrations, an obvious decrease in TPs was observed since 2012, another fact that supports the hypothesis that the sediments of Alqueva constitute a significant internal sink and source of phosphorus of the reservoir. In general, the sediments presented TN_s concentrations higher than the SEL ($TN_{SEL} > 0.48\%$; [69]) during the wet period of 2017. Despite this scenario, the TNs concentrations have been presenting a slight rising trend over time, which can be linked with the intensification of agriculture practices, as reported elsewhere [60].

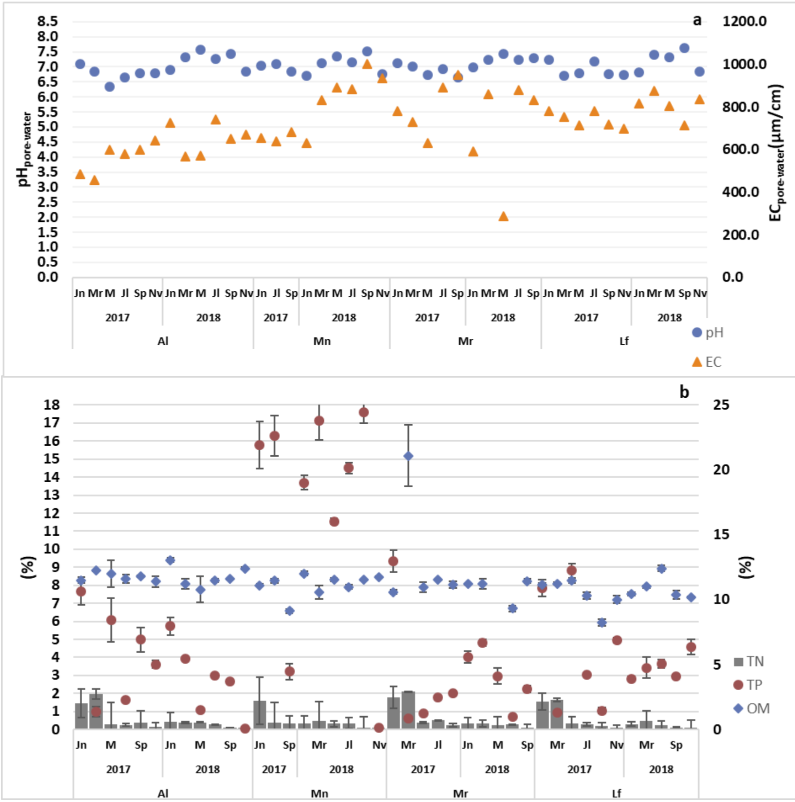


Figure 10. Dynamics of sediments' chemical characteristics: (**a**). $pH_{pore\text{-}water}$; electric conductivity ($EC_{pore\text{-}water}$) and (**b**). organic matter (OM); total phosphorus (TP_s); total nitrogen (TN_s), values represented by mean± standard deviation (n = 3), in the different sampling locations ((Álamos (Al), Montante (Mn), Mourão (Mr) and Lucefécit (Lf)).

3.4. Influence of Clime and LULC Patterns on Physic-Chemistry and Phytoplankton Biomass of the Reservoir

3.4.1. Drought and Post-Drought Periods

The annual dynamics of water chemistry showed that $pH_{pore\text{-}water}$, nutrients (TP, TN, NH_4, NO_3, TNs), and ions (Cl, Ca) were the parameters that presented the highest variability, being those that suffered a greater influence of the drought (2017) or the post-drought (2018) conditions (Table S2). Hence, TP, TN_s, Cl, Ca and NH_4 presented higher concentrations in the reservoir during 2017 (drought year). The opposite was observed for $pH_{pore\text{-}water}$, TN, and NO_3, that presented the highest values in the reservoir during 2018. The results showed that the effects of drought in the chemical parameters were not similar in the whole reservoir, revealing spatial differences that may be explained by variations in the hydro geomorphology and LULC of each drainage basin.

Several studies reported the effect of drought events on different water quality parameters, observing the increase in EC and ions concentrations (e.g., Cl, Na, Ca, SO_4), with the corresponding deterioration of water quality [50,51]. The increase in ions concentrations during the drought years may be justified by low flows, a decrease in runoff, and high evaporation rates, leading to a reduction in the reservoir water volume, as observed in the present study by the lower mean surface elevation (2017: 147.13m and 2018: 148.21m; Table S1) and the negative value of surface fluctuation mean (−0.72 m) during 2017. Contrarily, the results indicated that water EC was not related with the drought year. Some authors already reported that in agricultural and livestock areas, the drought effects on

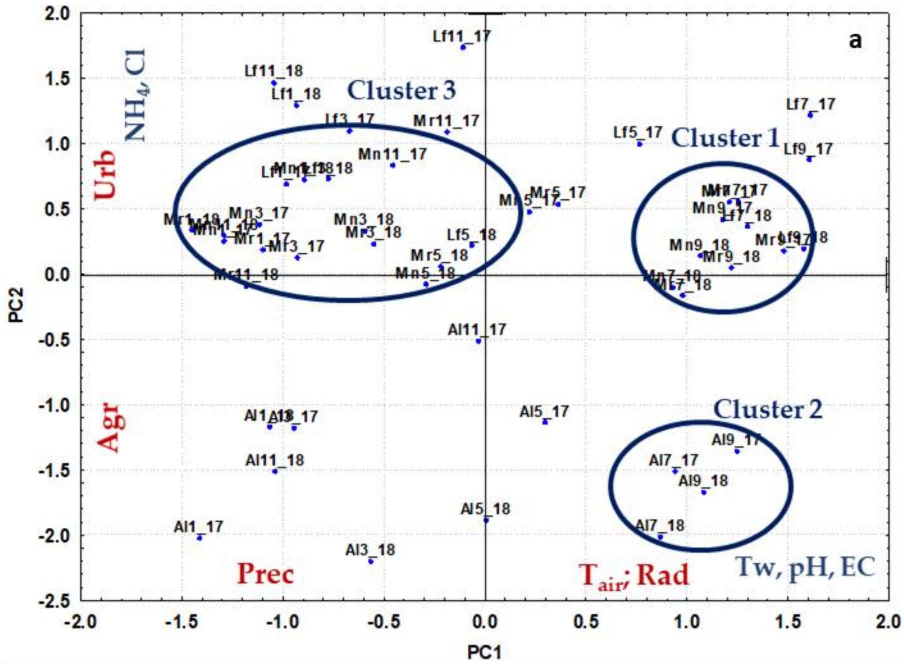
EC are unclear, suggesting the influence of other variables, such as the inflow of ions from agriculture practices, in the values of EC_w [51].

Nutrients presented mixed responses during the drought period, with the concentrations of TP and NH_4 more influenced by drought, opposite to TN and NO_3 with higher concentrations more evident in the post-drought period. These results may indicate that the main sources of phosphorus and nitrogen pollution are not the same. In fact, TP showed an increase in the drought year with high significance at Lucefécit, probably resulting from a reduction in water volume and an intensification of loads from point sources of pollution, such as effluents from urban areas and pig farming, on its drainage basin (Figure 3). In the case of TN, a rise of the concentrations was not observed in the drought period, probably because the most important sources of pollution are the intensive agricultural practices, for which the loads to the reservoir are markedly influenced by precipitation, as reported by Barros et al. [70] in the Roxo reservoir. Nevertheless, in addition to the various sources of pollution (diffuse and/or point), other mechanisms/ processes in the reservoir can also influence the nutrient´s dynamics, such as the stratification and the algae productivity [51].

The results for Chl-a were similar to those reported by most of the studies, with significant elevated biomass during the droughts, which has been attributed to more favorable hydrodynamic conditions for algal growth and changed nutrient dynamics [51].

3.4.2. Meteorological Conditions and LULC Patterns

The application of a Principal Component Analysis (PCA) allowed the establishment of correlations among water and sediments physicochemical parameters and the LULC classes in the drainage basins, under different climate conditions. The results highlighted the importance of the climate conditions on the description of the water variability in the reservoir. In fact, the first component (PC1) represented the influence of meteorological conditions (T_{air}, Prec, Rad) on the characteristics of water (see Figure 11a), generating 35% of the total variance. Indeed, these climate factors were those that presented greater variances among the drought (2017) and post-drought (2018) years. The water parameters most influenced by these explanatory factors were the pH, Tw and EC_w (with loadings ≥ 0.75), followed by the DO and BOD_5 (with loadings between 0.75–0.50), all these parameters with a positive participation in PC1, indicating that their increase in the water reservoir is influenced by the air temperature increase and the precipitation decrease. The second component (PC2) represents the LULC classes as an explanatory factor, with 19% of the total variance, with agriculture and urban classes being the most important. The parameters most influenced by LULC were NH_4 and Cl, their increase being observed with the rise of urban activities and precipitation on the drainage basins. There was an obvious distribution of the water samples in the PCA according to the sampling period and the meteorological conditions, the samples from the dry period being located in the positive quadrant of the PC1 more influenced by T_{air} and Rad, and the samples from wet period, displayed at the negative quadrant of PC1, more influenced by precipitation. The positive quadrant of PC1 integrated 55% of samples belonging to the drought year (2017). Furthermore, Hierarchical Cluster Analysis (HCA) was used to classify the samples according to their similar characteristics. Hence, the water samples were grouped in three clusters, the first one (cluster 1) located at the positive quadrant of both PCs' integrated dry samples from Montante and Mourão, with high pH and EC and very influenced by urban activities. Cluster 2 grouped dry samples from Álamos, more influenced by agriculture activities. Cluster 3 grouped the wet samples, influenced by precipitation and urban activities.



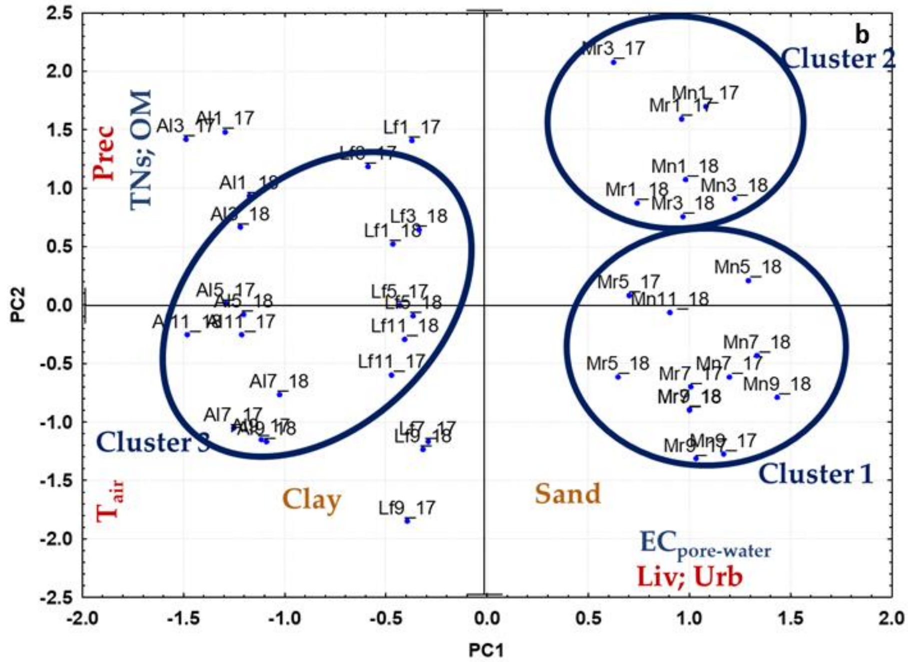


Figure 11. Principal Component Analysis (PCA) plot showing the distribution of the climate factors, Land use/ Land cover (LULC) factors and physicochemical parameters of the Alqueva reservoir water samples (**a**) and sediments samples (**b**) on the bidimensional plane defined by the first two principal components (PC). In the figure are displayed the samples' scores and the statistically significant clusters obtained through the Square Euclidean distance. Samples were collected at Al, Mn, Mr, Al, Lf, during the years of 2017 and 2018 in the months of January (1); March (3); May (5); July (7); September (9) and November (11).

Relatively to sediments, the PCA showed that the LULC classes (urban and livestock) and the sediments' granulometric fractions (clay and sand) presented higher importance on the distribution of the samples than meteorological conditions, explaining 33% of the total variance of the samples (Figure 10b). The $EC_{pore-water}$ was the parameter more influenced by LULC classes and occurred in higher values in samples constituted mostly by sand particles. The PC2 showed 22% of the total variance and was explained by meteorological parameters such as precipitation (positive quadrant) and T_{air} (negative quadrant). The parameters with a major influence on PC2 were TNs and OM (positive participation). As for the water samples, a clear display of the sediment samples on the PC associated with the sampling period was observed. The cluster analysis allowed the construction of three clusters. Cluster 1 (positive quadrant of PC1) integrated dry samples from Mourão and Montante, very influenced by urban and livestock classes and granulometry constituted mostly by sand particles. Cluster 2 located at the positive quadrant of both PC gathered wet samples from Mourão and Montante more influenced by precipitation and with higher amount of TN and OM. Cluster 3 integrated the samples with higher amounts of fine particles, all from Lucefécit and Álamos.

4. Conclusions

Reservoirs play an important role in water management, especially in Mediterranean areas like Alentejo (Southern Portugal), where water is typically scarce and is projected to become even scarcer under climate and LULC changing scenarios.

In the present study, the aim was to understand the effects/ impact of climate and LULC changes in the physicochemical and biological dynamics of the Alqueva reservoir. In fact, climate change and overexploitation due to the intensification of agriculture practices could contribute to water scarcity and the impairment of water quality, significant issues nowadays. This type of forecast or projection requires the development of studies that disclose how the reservoirs will react to drought conditions and to the rise of certain LULC classes, such as the intensification of agricultural activities, likely to happen in the Alqueva's irrigated area.

Hence, the results indicated that during drought conditions, the reservoir undergoes physical and limnological changes with the increase in water temperature along the water column, an increase in stratification periods and anoxic conditions, as well as sediments acidification, with different patterns along the reservoir mainly influenced by depth, flow and geological properties. The LULC changes have influenced the concentrations of nutrients and organic descriptors in the reservoir, with their increase over time. In fact, the intensification of the agricultural activities (increasing the irrigation and the use of fertilizers and pesticides) has promoted the increment of nutrients loads transfer to the water system.

The impact of LULC changes becomes more evident during drought periods, mainly due to the increase in air temperature, inducing a high evaporation rate and a reduction in water volume. Among the nutrients, phosphorus is the most problematic, with sediments highly contaminated by it and becoming an important internal source of pollution for the reservoir, during drought conditions. This process could stimulate the algae productivity that the drought conditions already support by itself. The increase in water nutrients and algae productivity has been observed over the years, with the possible speed-up of eutrophication at the reservoir. Furthermore, higher TP concentrations and algae might compromise the compliance of the environmental objectives defined on Water Framework Directive, which is already happening at Lucefécit zone (north of the reservoir).

The multivariate analysis showed the importance of drought conditions in the impact of LULC changes to the reservoir, as well as in its entire physicochemical dynamics, which is much worrying, since the climate projections indicate that the number of drought periods will most probably increase in this region.

The results provide information to the decision-makers, to build strategies on how to avoid a higher deterioration of the water quality in the Alqueva reservoir, induced by interacting and synergistic effects of climate change and LULC management. It is essential to promote the sustainability of LULC, with the control of agriculture areas in the basin and the implementation of sustainable environmental management practices. In fact, the adaptation solutions based on LULC changes would seem the most effective to address reservoir water quality issues, and therefore territorial planning can play an important role in adaptation and mitigation in this region. Finally, this work shows that studies of the vulnerability of reservoirs to climate and LULC changes should assess water/sediment dynamics and account for the reservoir's conditions (water volume stored; water demand; fluctuations of water levels). In that way, the water quality and its multiple uses within the watersheds can be preserved.

Further work is needed in this system during future drought scenarios, as in systems with similar LULC classes in the Mediterranean region, to derive scientific data for optimizing the water management sustainable policies in a climate changing World.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4441/13/5/707/s1, **Table S1.** Sampling date, Secchi depth, and platform depth for each sampling location, together with details of surface elevation, surface fluctuation, volume, and surface area for the twelve field campaigns, considering the total study area of the Alqueva reservoir; **Table S2.** Spearman correlation coefficients between the climate conditions, LULC classes, water and sediments physicochemical parameters in the Alqueva reservoir: (*) significant at $p < 0.05$; (**) significant at: $p < 0.001$.

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