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RESEARCH ARTICLE

Analyzing eutrophication and harmful algal bloom dynamics in a deep Mediterranean hypereutrophic reservoir

Mohamad Abbas[1] · Sara Dia[1,2] · Eliza S. Deutsch[3] · Ibrahim Alameddine[1]

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Abstract

Excessive point and non-point nutrient loadings accompanied with elevated temperatures have increased the prevalence of harmful algal bloom (HAB). HABs pose significant environmental and public health concerns, particularly for inland freshwater systems. In this study, the eutrophication and HAB dynamics in the Qaraoun Reservoir, a hypereutrophic deep monomictic reservoir suffering from poor water quality, were assessed. The reservoir was mostly phosphorus limited, and large algal particulates dominated light attenuation in the water column. During bloom events, surface chlorophyll-a concentrations increased up to 961.3 µg/L, while surface concentrations of ammonia and ortho-phosphate were rapidly depleted; surface dissolved oxygen reached supersaturation levels and surface pH levels were up to 3 units higher than those measured in the hypolimnion. Meanwhile, measured Microcystin-LR toxin concentrations in the reservoir exceeded the World Health Organization 1 µg/L provisional guideline 45% of the times. Yet, the results showed that most of the toxins were intra-cellular, suggesting that they decayed rapidly when released into the reservoir. Results from a random forests ensemble model indicated that tracking the changes in surface dissolved oxygen levels, ammonium, ortho-phosphate, and pH can be an effective program towards predicting the reservoir's trophic state and algae blooms.

Keywords Eutrophication · Lakes · Harmful algal blooms · Microcystin-LR · Trophic state · Qaraoun Reservoir · Random forests · Mediterranean

Introduction

Anthropogenic water quality pollution affects many important aquatic systems, causing turbid waters with high algal biomass, leading to the deterioration of affected ecosystems (Long et al. 2020; Scheffer 1997; Schindler 1974; Schindler et al. 2016; Zhang et al. 2020). Globally, freshwater systems are increasingly turning eutrophic. The percentage of eutrophic lakes has increased from 41% to more than 61% between the late 1970s and the early 2000s (Gibson et al. 2000; Li et al. 2021). It has been estimated that more than 40% of the lakes in North and South America and more than 50% of the lakes in Asia and Europe suffer from eutrophication (ILEC 1993). In a recent study aiming to assess the trophic state of 2,058 large inland water bodies, Wang et al. (2018) reported that more than 63% of them were eutrophic.

Excessive nutrient loading along with rising global temperatures have favored the proliferation of harmful algal blooms (HABs) (Li et al. 2020; Paerl and Huisman 2008; Zu et al. 2020). HABs include blooms caused by toxic cyanobacteria, which pose serious environmental and public health concerns for inland lakes and reservoirs (Beaulieu et al. 2013; Carmichael 2001; Chen et al. 2020; Paerl and Huisman 2008). Cyanobacterial blooms have been shown to produce toxins that cause serious and sometimes fatal liver, digestive, neurological, and skin diseases (Bartram and Chorus 1999; Carmichael and Boyer 2016). HABs are also responsible for significant socio-economic damages, resulting from recreational losses and the depreciation of surrounding real estate (Dodds et al. 2009). One of the most widespread and studied toxic algae genera in the world is Microcystis (Huisman et al. 2005; Zhang et al. 2020).

Responsible Editor: Lotfi Aleya

✉ Ibrahim Alameddine
ia04@aub.edu.lb

[1] Department of Civil and Environmental Engineering, American University of Beirut, Beirut, Lebanon

[2] Emlyon Business School, Lyon, France

[3] Department of Ecology and Evolutionary Biology, University of Toronto, Toronto, Canada

Microcystis generates a wide variety of cyanotoxins, including Microcystin-LR (MC-LR) that can cause a direct risk on human health (IARC 2010; Lone et al. 2015; Otten et al. 2012). As a result, the World Health Organization (WHO) has defined 1 µg/L as a provisional guideline for MC-LR in drinking water (Michalak et al. 2013; WHO 1996).

Many interacting environmental factors affect the growth of cyanobacterial species under eutrophic conditions. One of the main factors is elevated water temperatures, whereby high temperatures boost the growth, photosynthesis, and metabolic processes of cyanobacteria (Carey et al. 2012; Wei et al. 2020). In particular, Microcystis has a high optimum growth temperature (between 25 and 32 °C) (Jiang et al. 2008; Liu et al. 2011). Changes in the thermal stratification structure of a water body has also been suggested to be an important forcing function that can affect cyanobacterial growth and species composition. Another factor affecting algal blooms in freshwater systems is nutrient availability. Lakes and reservoirs are subject to external nutrient loading from rivers, domestic and industrial wastewater outlets, and agricultural runoff from heavily fertilized farm fields (Dolan and Chapra 2012; Muhammetoglu et al. 2005). Additionally, internal nutrient loading from sediments is an important source for HAB proliferation across many freshwater systems (Søndergaard et al. 2003; Wetzel 2001). Several problematic cyanobacteria are able to regulate their buoyancy and thus benefit from light at the surface during the day and from access to inorganic nutrients in the lower sections of the water column at night (O'neil et al. 2012; Visser et al. 2016; Wagner and Adrian 2009).

Although phosphorus is well recognized as the most important limiting nutrient promoting eutrophication in freshwater systems, other researchers have identified nitrogen as a co-limiting nutrient for algal growth in some systems (Conley et al. 2009; Lewis Jr and Wurtsbaugh 2008; Spivak et al. 2011; Sterner 2008). As a result, the need to manage and regulate phosphorus or nitrogen loads alone or concomitantly as a control measure for eutrophication in freshwater systems remains an active area of research (Wurtsbaugh et al. 2019). Cyanobacteria grow in environments with varying nutrient levels (Davis et al. 2009; Elliott 2012; Paerl and Otten 2013). For example, Microcystis is able to internally store phosphorus and thus are able to double three or four times without the need for a supplemental phosphorus source (Reynolds 2006).

In the Mediterranean region, HABs remain understudied and underreported even though they have become a frequent phenomenon, partly due to the prevailing natural warm climatic conditions (Vardaka et al. 2005). Several assessments conducted on lakes and reservoirs in the Mediterranean basin have reported cyanobacterial impairments in lakes and reservoirs across Greece (Moustaka-Gouni 1993; Tryfon et al. 1997; Vardaka et al. 2000), Spain (Romo et al. 2012, Villena and Romo 2003), Turkey (Albay et al. 2003; Köker et al. 2017; Sömek et al. 2008), and Lebanon (Atoui et al. 2013; Deutsch 2020; Fadel et al. 2014; Slim et al. 2014).

The main aim of this study is to expand our limited understanding of HAB dynamics in semi-arid Mediterranean freshwater systems and to showcase the potential of random forests (RF) models to identify the main environmental factors associated with algal blooms. This is illustrated by modeling and assessing the dynamics of algal blooms over a period of 7 years (summer of 2013–summer of 2019) in the Qaraoun Reservoir, a hypereutrophic, deep, and monomictic reservoir located along the semi-arid eastern Mediterranean basin. This study also quantifies for the first time the MC-LR toxin levels in the reservoir over two growing seasons.

Material and methods

Study site

Qaraoun Reservoir (33° 34′ N, 35° 42′ E, altitude = 840 m) is the largest freshwater body in Lebanon (Fig. 1). The surface area of the reservoir fluctuates between 4 and 10 km^2, depending on seasonal precipitation, river flows, and dam releases. The maximum depth of the reservoir exceeds 40 m near the dam. The dam was constructed in 1959; it was intended to supply water for irrigation, domestic water, recreational purposes, and hydroelectric power production. The reservoir is located in an area that is characterized by hot dry summers and moderately cold wet winters-typical of the Mediterranean region. Annual precipitation rates in the area range between 250 and 750 mm, with an average of 600 mm per year, mostly falling between December and March (Deutsch et al. 2018; Geara-Matta et al. 2010). The reservoir is subject to point and non-point pollutant loads that reach it from agricultural, industrial, and domestic wastewater discharges. These discharges have severely deteriorated the reservoir's water quality, limiting its ability to meet its designated uses (BAMAS 2005; Darwish et al. 2021; Deutsch et al. 2018; ELARD 2011; Fadel et al. 2021; Fadel et al. 2019; Jurdi et al. 2002; Shaban and Hamzé 2018; Sharaf et al. 2019). Given that the reservoir is located in a semi-arid hot climate, it has a high propensity to suffer from algal blooms (Shaban and Hamzé 2018). Cyanobacteria blooms were first reported in 2009 and have since become frequent and persistent (Atoui et al. 2013; Deutsch et al. 2020; Dia et al. 2019; Fadel et al. 2021, 2014; Slim et al. 2014). Microcystis and Aphanizomenon were identified as the major cyanobacterial genus in the reservoir, with blooms lasting from May to December (Atoui et al. 2013; Deutsch et al. 2020).

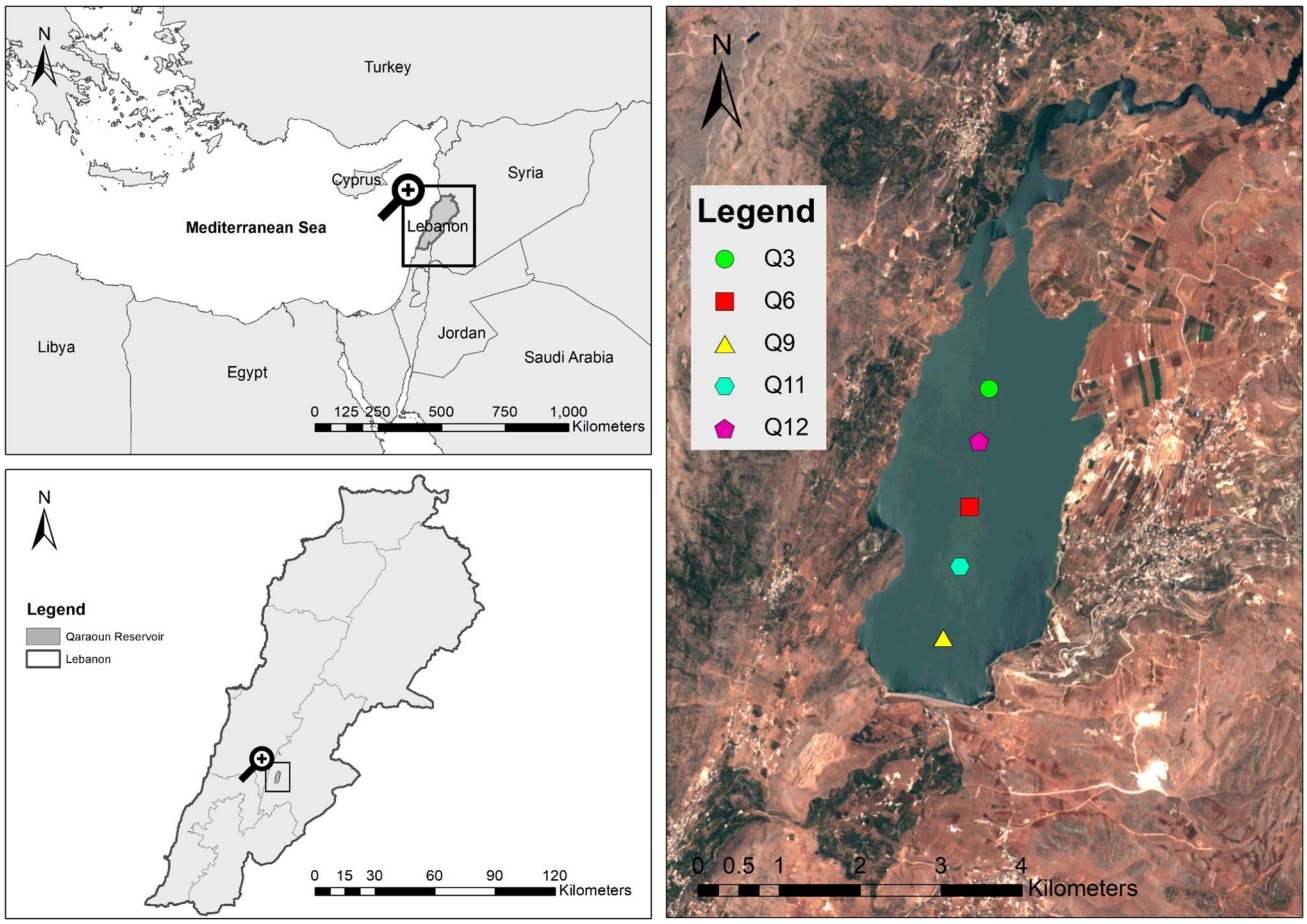

Fig. 1 Location of reservoir and sampling locations.Q3 (median depth = 15 m), Q12 (median depth = 13 m), Q6 — "middle" (median depth = 20 m), Q11 (median depth = 15 m), andQ9 — "deep" (median depth = 32 m)

Water sampling and analysis

Water samples were collected on a regular basis between July 2013 and October 2019 at five sampling-stations that extend along the reservoir's centerline, starting from the river inlet up to the dam outlet (Fig. 1). Sampling in the winter months was occasionally interrupted due to poor weather conditions. Water samples were taken at two depths (surface and bottom) and analyzed for a wide variety of physicochemical parameters, in addition to surface chlorophyll-a (Chl-a) and MC-LR concentrations. Secchi disk depth (SDD) was measured in the field using a 20-cm diameter disk to assess water transparency. Additionally, a YSI-EXO2 sonde was deployed to generate continuous vertical profiles of pH, DO, temperature, Chl-a, phycocyanin, and turbidity. Water samples were collected at ~ 10 cm below the surface and at 4 m above the bottom of the reservoir using a Van Dorn sampler. Water samples were stored on ice in 500 ml glass bottles. The water samples were subsequently analyzed in the lab for pH, total dissolved solids (TDS), conductivity, ammonium (NH_4^+), nitrate (NO_3^-), orthophosphate (PO_4^{-3}), total suspended solids (TSS), and Chl-a. Total dissolved solids (TDS) and conductivity were both measured using a Cole-Palmer TD/Conductivity meter. Nutrient analyses were conducted colorimetrically using a HACH DR-3900 Spectrophotometer. All laboratory procedures were carried out based on the Standard Methods for the Examination of Water and Wastewater (APHA et al. 2012) (refer to Supplementary Material; Table S1). Additionally, microscopic analysis were conducted to identify the different algae up to the genus level and their abundance was assessed through a Bio-Rad TC10 Automated Cell Counter (adapted from APHA et al. 2012) (refer to Supplementary Material Table; S1). While there is no agreed upon definition of what constitutes an algal bloom event (German et al. 2020; Shen et al. 2019), elevated levels of Chl-a have been widely adopted as a proxy of blooms (Gons et al. 2008; Papenfus et al. 2020; Soomets et al. 2020). Many studies report an algal bloom event when surface Chl-a concentrations exceed the 40 µg/L limit (Balali et al. 2013; Havens 1994; Stanley et al. 2003). In this study, that threshold was adopted.

MC-LR levels in the reservoir were measured during the growing season for the years 2018 and 2019. In 2018, MC-LR levels were determined semi-quantitatively, using the ENVIROLOGIX QualiTube kits for Microcystin (PN ET 022). The QualiTube kits are able to distinguish between low levels of MC-LR (< 0.5 µg/L), medium levels (0.5 to 3 µg/L), and high levels (> 3 µg/L). The QualiTube kits for Microcystin operate based on a competitive enzyme linked immunosorbent assay (ELISA) method. The limit of detection of the EnviroLogix Microcystin Tube Kit is 0.3 ppb (EnviroLogix 2015). In 2019, MC-LR levels in the reservoir were assessed quantitatively using the ELISA technique (Lürling et al. 2014) that has been approved by the USEPA (USEPA Method 546). ELISA kits were procured from Eurofins Abraxis, INC (Part Number 520011OH). The water samples were divided into two subsamples. The first subsample was filtered through a glass microfiber filter paper (GF/C filter, Whatman, UK) and directly analyzed to obtain the extracellular Microcystin levels. The second subsample underwent three freeze–thaw cycles to lyse the cells; measured MC-LR levels represent the total concentrations (i.e., the intracellular and the extracellular). Both total and extracellular MC-LR concentrations were computed by fitting a semi-log curve of $\%B_o$(i.e., $100 \times B/B_o$) versus MC-LR concentrations, where B is the mean absorbance value for a given MC-LR standard and B_o is the mean absorbance value for the zero MC-LR standard. Following the procedure developed by Eurofins Abraxis, INC, six MC-LR standards ranging in concentration between 0.0 ppb and 5 ppb were used to develop the semi-log curve calibration.

Trophic state assessment

Chl-A concentrations (µg/L) and SDD measurements (m) were used to compute the reservoir's Carlson's Trophic State Index (CTSI) over the study period (Eqs. 1 and 2) (Carlson 1977). Furthermore, the trophic state of the reservoir was evaluated based on the trophic state boundaries defined based on the Chl-a levels (µg/L) for tropical/subtropical reservoirs (Cunha et al. 2013). Deviations between the SDD-based and Chl-a based trophic state indices were also assessed.

$$CTSI(Chl-a) = 10 \times \left[6 - \left(\frac{2.04 - 0.68 \times \ln(Chl-a)}{\ln(2)}\right)\right] \quad (1)$$

$$CTSI(SDD) = 10 \times \left[6 - \left(\frac{\ln(SDD)}{\ln(2)}\right)\right] \quad (2)$$

Note that based on the Chl-a concentrations, temperate freshwater systems are classified as oligotrophic (Chl-a less than 2.6 µg/L), mesotrophic (Chl-a between 2.6 and 6.4 µg/L), eutrophic (Chl-a between 6.4 and 56 µg/L), or hypereutrophic (Chl-a greater than 56 µg/L). For tropical/subtropical reservoirs, they are classified as oligotrophic (Chl-a less than 3.9 µg/L), mesotrophic (Chl-a between 3.9 and 10 µg/L), eutrophic (Chl-a between 10 and 27.1 µg/L), or hypereutrophic (Chl-a greater than 27.1 µg/L).

Statistical analysis

In an effort to better understand eutrophication and cyanobacterial bloom dynamics in the reservoir, various statistical analysis techniques were used. Paired *t*-tests from the "stats" package in the software R (R Core Team 2013) were used to compare differences in the concentrations of the physicochemical parameters between surface and bottom samples, as well as between shallower and deeper sections of the reservoir. Repeated measures ANOVA from the "rstatix" package in the software R (Kassambara 2020) was used to compare the means of the concentrations measured across the 5 sampling stations. The repeated measures ANOVA allows us to block the effects of temporal variability when comparing different sections of the lake.

The random forests machine learning technique, from the "randomForest" (Breiman et al. 2018) and the "ranger" (Wright et al. 2018) packages in R, was used to model the relationship between the Chl-a-based Carlson trophic state index (Eq. 1), an indicator of algal blooms, and measured physicochemical parameters. The random forests technique aggregates a large number of decision trees in order to obtain an enhanced prediction of the response variable from various predictors (Breiman 2001). Aiming to reduce the correlation between the different decision trees, the method applies the split-variable randomization, whereby at each split in every decision tree, the algorithm selects a split variable from a random subset of the predicting variables. Random forests are able to handle numerous correlated variables without a decrease in prediction accuracy, while also identifying the most important variables correlated to the response variable. The method has been previously applied for water quality modeling and for the assessment of the trophic status of lakes across the USA (Hollister et al. 2016). Note that the random forests models need to be tuned to obtain optimal results. The tuning parameters used were the number of variables tried at each split and the bootstrap sampling size. The latter is the resampled percentage of the data set used for each decision tree; we tested different percentages ranging from 55 to 80%. For the number of variables tried at each split, we assessed values ranging between 2 and the total number of variables. All statistical analyses were conducted using the R software (R Core Team 2015).

Results

Algal blooms and toxin levels

Chlorophyll-a and phytoplankton community

During the study period, measured surface Chl-a concentrations were highly variable, ranging from 0.01 to 961.3 µg/L, with an average value of 92.9 µg/L (Fig. 2). Chl-a levels dropped over depth; yet concentrations remained elevated all along the epilimnion indicating that cyanobacteria were able to adjust their buoyancy within that zone (Supplementary Material; Figure SM8). As expected, Chl-a levels were highest during the summer months. Blooms tended to occur over the majority of the growing seasons across the seven years. Interestingly, blooms also occurred in the non-growing season, particularly when water temperatures were above 17 °C and/or when surface nutrient concentrations peaked following turnover and/or increased external loading caused by the first flush that follows the end of the dry summer season (Fig. 2). Microscopic analysis of collected surface water samples showed that the phytoplankton community was primarily dominated by cyanobacteria species found in the reservoir which were *Microcystis aeruginosa* and *Aphanizomenon flos-aquae*. Microcystis and, to a lesser extent, Aphanizomenon, dominated the algae community in all but the winter months, suppressing eukaryotic growth in the growing season. Microcystis experienced monospecific blooms across all summers during the study period. Aphanizomenon tended to bloom in conjunction with Microcystis in spring and fall. Microcystis appeared to limit the growth of Aphanizomenon biomass when temperatures were highest. Similar results were previously reported by other studies on the Qaraoun Reservoir (Fadel et al. 2015, 2016).

Surface Chl-a levels were found to be highly correlated with surface TSS levels (Spearman $r = 0.6$, p-value $< 2.2 \times 10^{-16}$) and negatively correlated with SDD (Spearman $r = -0.67$, p-value $< 2.2 \times 10^{-16}$). This indicates that most of the Qaraoun's turbidity is a direct result of excessive algal growth. Moreover, the positive correlation between surface Chl-a and surface temperature (Spearman $r = 0.26$, p-value $= 2.77 \times 10^{-6}$) highlights the importance of the latter in promoting cyanobacterial growth (Blottière et al. 2014; Wu et al. 2016).

MC-LR levels

Thirty-three surface samples were collected and assessed for their Microcystin-LR levels between July and October 2018 using the ENVIROLOGIX QualiTube semi-quantitative kits. More than 80% of the collected samples had toxin levels exceeding the 0.5 µg/L level. Moreover, 15% of the collected samples had concentrations in excess of the 3 µg/L threshold (Fig. 3). Overall, MC-LR levels were positively correlated with the surface Chl-a concentrations measured in the lake (Spearman $r = 0.57$, p-value $= 1.46 \times 10^{-4}$). In 2019, total MC-LR levels at the surface ranged between 0.054 and 15.57 µg/L ($n = 69$, median = 0.88 µg/L, mean = 1.78 µg/L), while the intracellular MC-LR levels had a median value of 0.66 µg/L ($n = 69$, range = 0.002–14.94 µg/L, mean = 1.55 µg/L). Overall, 45% of the total MC-LR levels measured in the lake exceeded the WHO 1 µg/L provisional guideline for drinking water (Fig. 3). The total MC-LR levels were found to be highly correlated with the intracellular MC-LR (Spearman $r = 0.956$, p-value $< 2.2 \times 10^{-16}$). This indicates that while the total toxin levels were high, the extracellular toxin levels appear to be low. This could be

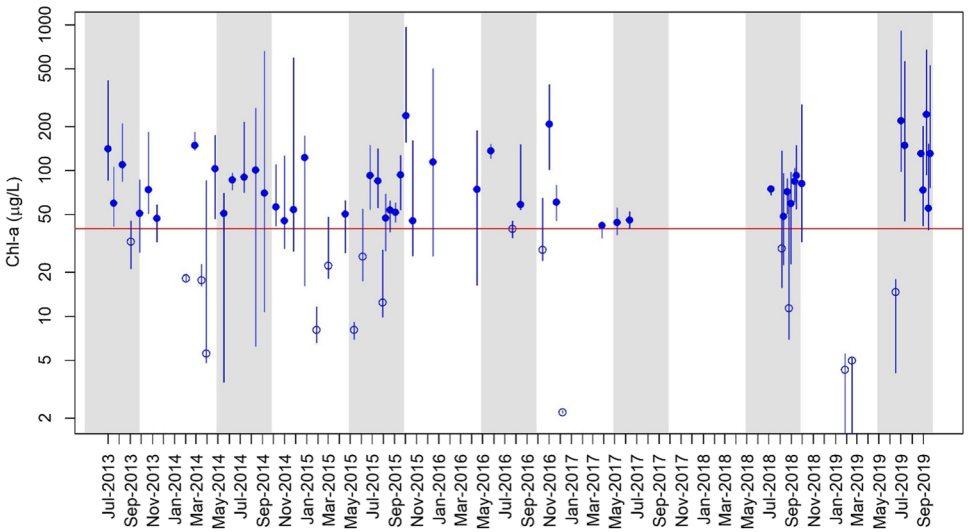

Fig. 2 Temporal variability of surface Chl-a levels in the Qaraoun Reservoir across the study area. The solid blue circles represent the median surface Chl-a levels when a bloom event was recorded. The open blue circles represent the median surface Chl-a concentrations in the absence of a bloom. The vertical lines show the minimum and maximum Chl-a observed across the 5 monitoring stations. The red horizontal line signifies the 40 µg/L limit, which was used to define a bloom event. The grey-shaded areas represent the growing season (May to September)

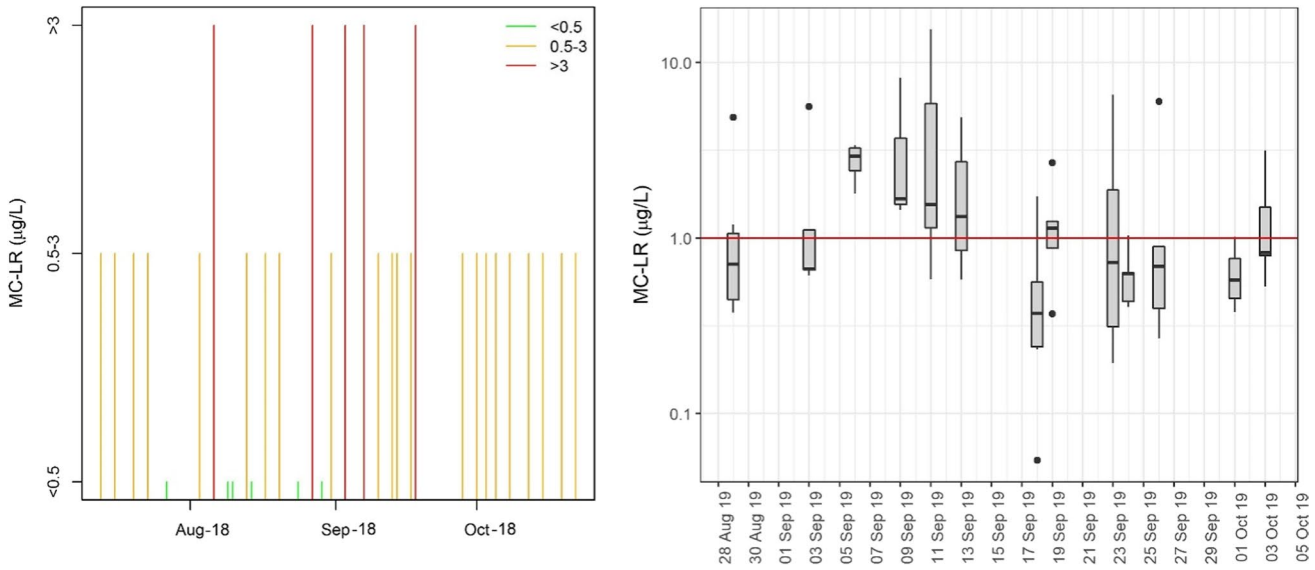

Fig. 3 Total MC-LR levels between July and October 2018 (left) and between August 2019 and October 2019 (right)

a due to the possible rapid degradation of the extracellular toxin in the lake. Naturally occurring indigenous microbial flora, particularly the gram-negative phylum of Proteobacteria that tend to be common in freshwater systems, have been shown to be effective in degrading MC-LR in lakes (Best et al. 2002; Dziga et al. 2013).

Physical parameters

Over the study period, the lake experienced significant seasonal as well as interannual variability in its annual volume as a result of changes in river inflow, precipitation, water discharge from the dam, and to a lesser extent the temporal variability in evaporation and infiltration. The reservoir's volume fluctuated between a maximum of 200.6 MCM and a minimum of 17.5 MCM (91.3% change) between 2013 and 2019, with a mean of 88.8 MCM (Supplementary Material; Figure SM1). The year 2014 was the driest year across the 7-year study period. During that year, the reservoir's volume never exceeded 56.6 MCM.

As a result of high algal concentrations in the reservoir, SDD levels were generally low. They varied between 0.18 and 4.2 m, with a median value of 1.15 m. SDD was highest during the winter and early spring months (refer to the Supplementary Material; Figure SM2). Meanwhile, the lowest SDD levels were recorded during the summer season. Overall, the range of surface TDS in the reservoir was between 94 and 681 ppm and surface TSS concentrations ranged from 0.01 to 177 mg/L. TSS showed a clear seasonal pattern, with the highest concentrations occurring between late spring and early fall, concurrent with periods of high algae growth (refer to the Supplementary Material; Figure SM 3). As expected, TSS concentrations was negatively correlated with SDD (Spearman $r = -0.65$, p-value $< 2.2 \times 10^{-16}$).

The reservoir experienced significant fluctuations in its surface and bottom temperatures both within a given year as well as between years (Fig. 4). On average, surface temperatures ranged between 7 and 30 °C, while bottom temperatures fluctuated between 5 and 25 °C. Differences in surface temperatures across the lake were statistically insignificant throughout the year. In the growing season (May till September), surface water temperatures exceeded 25 °C more than 45% of the times. These high temperatures represent optimum growth temperatures for Microcystis; the probability of observing a bloom when surface water temperatures exceeded 25 °C was close to 80%. Bottom temperatures across the five sampling locations were found to be statistically different during the growing season (repeated measures ANOVA, p-value $= 4.69 \times 10^{-6}$). Temperatures in the deep stations tended to remain significantly cooler than those measured in shallower sections as a result of stratification. Vertical temperature profiles in the lake were recorded at Q6 (depth varied between 6 and > 34 m, median = 20 m) and Q9 (depth varies between 14 and 34 m, median = 32 m) (Fig. 1). At Q6, the thermal stratification extended between May and September in wet years (2015, 2016, 2017, and 2019); weaker stratification was observed in dry years. In the deeper sections of the reservoir (Q9), strong vertical temperature stratification extended between April/May and October. Vertical temperature differences during stratification reached up to 15 °C.

Surface DO (mg/L) levels ranged between 0.8 and 18.5 mg/L. They were highest in early summer, reaching super saturation levels during the growing season, when

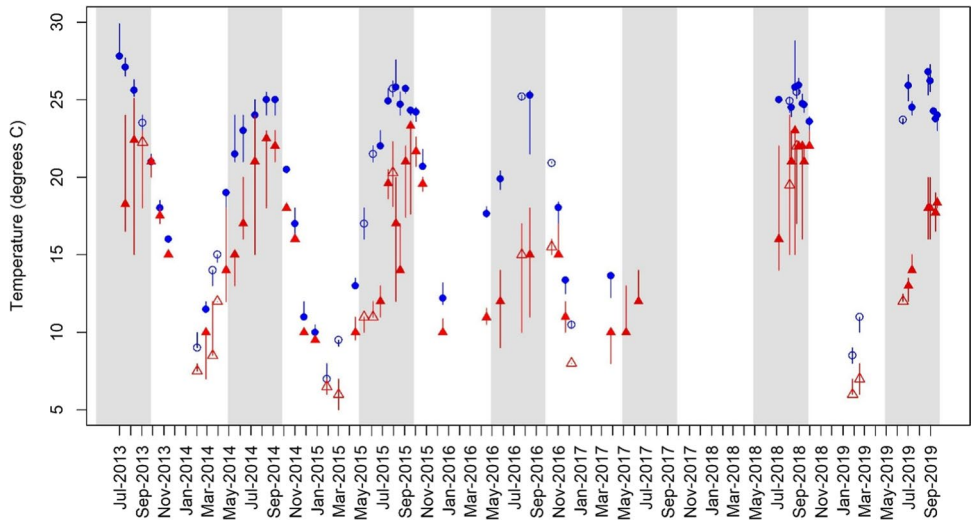

Fig. 4 Temporal variability of water temperature in the Qaraoun Reservoir. The solid blue circles represent the median surface temperatures when a bloom event was recorded. The open blue circles represent the median surface temperatures in the absence of a bloom. The red solid triangles represent the median bottom temperatures when a bloom was recorded, while the open red triangles represent the median bottom temperatures in the absence of a bloom. The vertical lines show the minimum and maximum temperature observed across the 5 monitoring stations. The red horizontal line signifies the 40 µg/L limit, which was used to define a bloom event. The grey-shaded areas represent the growing season (May to September)

cyanobacterial blooms dominated (refer to Supplementary Material; Figure SM2). Meanwhile, bottom DO concentrations (range = 0.18–11.6 mg/L) were progressively depleted over the summer. Between May and September, 67% of the bottom DO samples were below the 3 mg/L limit defined for hypoxic conditions. Overall, the deep section (Q9) of the reservoir remained hypoxic for more than 93% of the time between May and September; meanwhile, hypoxia was observed 75% of the time in the middle section (Q6) of the lake over the same period.

Surface pH levels ranged between 6.8 and 10.7. They were generally highest during the summer and fall months; pH levels peaked during bloom events. The difference between top and bottom pH levels reached 3 units when the

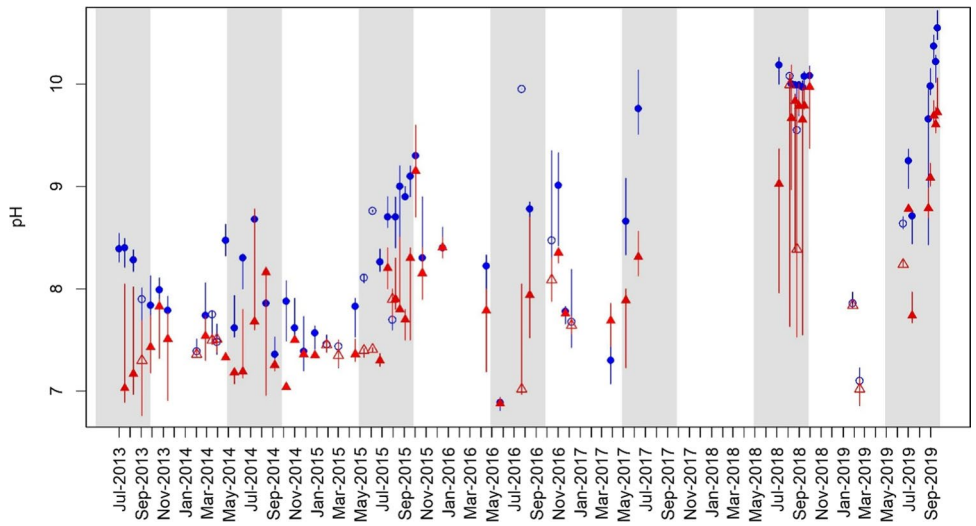

Fig. 5 Temporal variability of water temperature in the Qaraoun Reservoir. The solid blue circles represent the median surface pH levels when a bloom event was recorded. The open blue circles represent the median surface pH levels in the absence of a bloom. The red solid triangles represent the median bottom pH levels when a bloom was recorded, while open red triangles represent the median bottom pH levels in the absence of a bloom. The vertical lines show the minimum and maximum pH across the 5 monitoring stations. The red horizontal line signifies the 40 µg/L limit, which was used to define a bloom event. The grey-shaded areas represent the growing season (May to September)

lake was stratified and experiencing an algal bloom (Fig. 5). High surface pH values observed during the growing season were due to accelerated photosynthesis and the uptake of dissolved carbon dioxide in the water column as a result of the large algal biomass. As expected, there was a statistically significant positive correlation between Chl-a and surface pH values (Spearman $r = 0.33$, p-value $= 2.86 \times 10^{-10}$). Following the reservoir's turnover at the end of the growing season (months 10–11), surface pH levels dropped significantly. Interestingly, the surface pH of the reservoir during the growing season consistently increased throughout the study period at a rate of 0.26 units of pH per year.

Nutrients

The mean surface PO_4^{-3} concentration in the reservoir between 2013 and 2019 was 0.27 mg/L (range = 0.01–5.2 mg/L), with peaks occurring during the winter due to external river loading and at the end of summer following the end of stratification and the mixing with the nutrient rich hypolimnatic waters (Fig. 6). In the growing season, surface PO_4^{-3} levels decreased significantly, as orthophosphate was assimilated and stored by cyanobacteria. This was confirmed by the significant negative correlation between Chl-a and surface orthophosphate levels (Spearman $r = -0.26$, p-value $= 1.329 \times 10^{-6}$). Bottom PO_4^{-3} concentrations over the entire study period (range = 0.01–5.6 mg/L) had an average concentration of 0.54 mg/L. They were generally elevated during the summer period, when stratification was strong and when internal loading from the anoxic sediments became an important pathway. When the reservoir turned over (October–November), bottom PO_4^{-3} levels decreased significantly as a result of mixing. Bottom PO_4^{-3} concentrations measured at the 5 stations during the growing season were statistically higher than their corresponding surface levels (paired t-test, p-value $= 3.398 \times 10^{-8}$); no statistical difference was found between surface and bottom levels during the winter months, when the reservoir was well mixed (paired t-test, p-value = 0.06). During the non-growing season, no statistical differences in surface and bottom PO_4^{-3} concentrations were found across the 5 stations (repeated measures ANOVA for surface, p-value = 0.901; repeated measures ANOVA for bottom, p-value = 0.392). Nevertheless, a significant spatial difference was observed for bottom PO_4^{-3} concentrations during the growing season (repeated measures ANOVA, p-value = 0.037), with the highest levels recorded at Q9, the deepest sampling location with the strongest and most stable stratification. Meanwhile, surface levels remained largely homogenous across all stations (repeated measures ANOVA, p-value = 0.259).

Surface ammonium concentrations ranged between 0.01 and 4.3 mg/L as N, while those measured at the bottom ranged between 0.01 and 7.8 mg/L as N. Differences between surface and bottom ammonium concentrations was largest during the summer season due to the release of ammonium from sediment under anoxic conditions. Similar to orthophosphate, surface NH_4^+ levels dropped considerably and consistently during the algal growing season, with algae depleting the available ammonium in the epilimnion. This can be seen in the negative

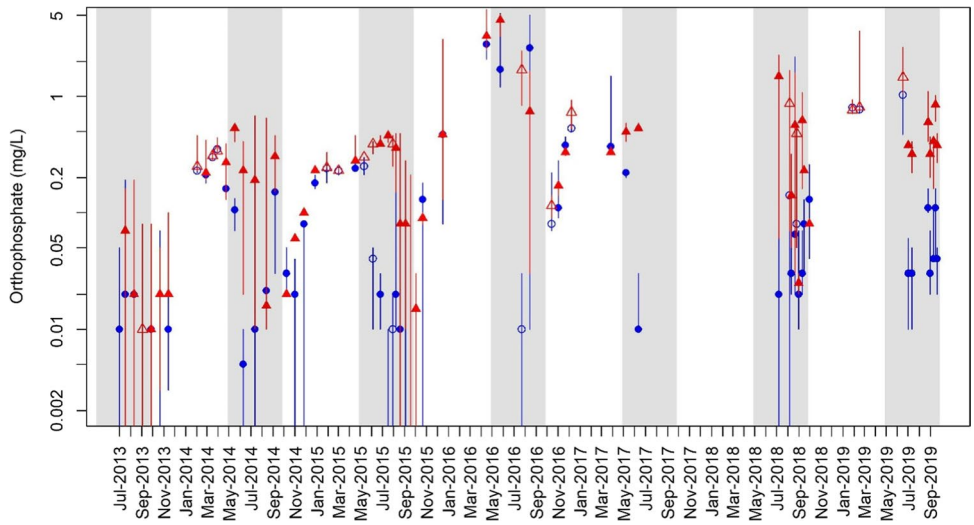

Fig. 6 Temporal variability of PO_4^{-3} concentrations in the Qaraoun Reservoir. The solid blue circles represent the median PO_4^{-3} levels when a bloom event was recorded. The open blue circles represent the median surface PO_4^{-3} levels in the absence of a bloom. The red solid triangles represent the median bottom PO_4^{-3} levels when a bloom was recorded, while the open red triangles represent the median bottom PO_4^{-3} levels in the absence of a bloom. The vertical lines show the minimum and maximum PO_4^{-3} across the 5 monitoring stations. The red horizontal line signifies the 40 µg/L limit, which was used to define a bloom event. The grey-shaded areas represent the growing season (May to September)

correlation between Chl-a and surface NH_4^+ (Spearman $r = -0.31$, p-value $= 4.597 \times 10^{-8}$). Differences between surface and bottom concentrations decreased in the non-growing season, even though the mean bottom levels remained slightly higher than mean surface concentrations (refer to Supplementary Material; Figure S5). Overall, there was little spatial variability in the surface and bottom ammonium levels across stations for both surface and bottom samples (repeated measures ANOVA p-value $= 0.253$ for surface samples; repeated measures ANOVA p-value $= 0.131$ for bottom measurements). Surface nitrate (NO_3^-) levels ranged between 0.01 and 11.6 mg/L, while bottom concentrations ranged between 0.01 and 10.4 mg/L. Unlike ammonium and orthophosphate, there were little differences between surface and bottom concentrations across seasons. The highest concentrations of NO_3^- were observed in the winter as a result of high external loadings (river inflow and runoff), while the lowest NO_3^- concentrations occurred during the summer season following cyanobacterial blooms (refer to Supplementary Material Figure S10).

Nutrient limitation in the reservoir was determined based on the surface DIN:orthophosphate ratio. The optimal DIN:orthophosphate ratio (N:P ratio) for phytoplankton growth is 16:1 based on molar concentrations (7.23 based on mass concentration) (Ærtebjerg et al. 2003; Redfield 1934; Tett et al. 1985). In freshwater systems, phosphorus is expected to play a more critical role than nitrogen in limiting algal growth. In the Qaraoun Reservoir, the system was mostly phosphorus limited (75% of sample points showed DIN:orthophosphate ratios higher than the Redfield ratio, versus 25% of the samples showed minor N-limitations).

Lake trophic state

The surface Chl-a based CTSI index was found to be higher than that based on SDD 92% of the times (Fig. 7). All of those cases were observed during bloom events. This indicates that algae, in particular large algal particulates, dominate the attenuation of light in the water column (Carlson and Simpson 1996). Moreover, when comparing the temperate surface Chl-a based trophic state (Carlson 1977; Carlson and Simpson 1996) to that proposed for tropical and sub-tropical reservoirs (Cunha et al. 2013), significant differences were observed between the two indices. Based on the Carlson's classification, the reservoir was considered hypereutrophic 52% of the times (68% of which were in the growing season), 43% eutrophic (55% of which were in the growing season), and 3% mesotrophic (85% of which were in the non-growing season), and 2% oligotrophic (100% in the non-growing season) (Fig. 8). Based on the Chl-a based classification proposed for tropical/subtropical reservoirs, the reservoir was considered hypereutrophic 80% (65% of which were in the growing season), 11% eutrophic (52% of which were in the growing season), 7% mesotrophic (76% of which were in the non-growing season), and 2% oligotrophic (100% happening in the non-growing season) (Fig. 8).

The developed RF model that was able to identify the most significant relationships linking surface Chl-a-based Carlson trophic state index (CTSI) to the measured physicochemical parameters. It had a root-mean-square error (RMSE) of 3.6 and an R^2 of 86%. The best model was achieved when the number of variables tried at each split was set to 7 and when the bootstrap sampling size was set to 80%. The model had an out-of-bag (OOB) RMSE of 7.3 and an OOB R^2 of 45%. The final predictive variables used in the model included several physio-chemical factors, whose relative importance are shown in (Fig. 9). As can be seen, the most important predictor of

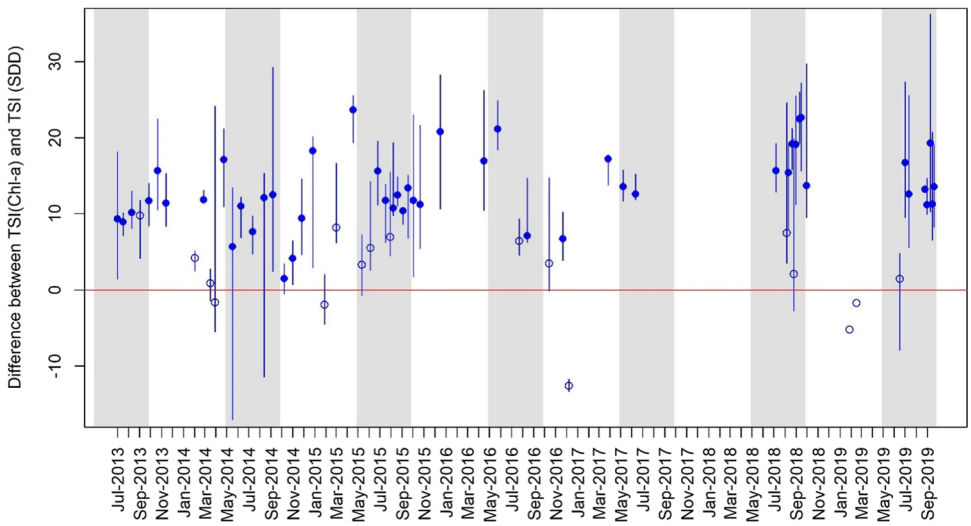

Fig. 7 Temporal variability of the difference between CTSI(Chl-a) and CTSI(SDD) in the Qaraoun Reservoir across the study area. The open circles represent the median difference. The vertical lines show the minimum and maximum difference ranges observed across the 5 monitoring stations. The grey-shaded areas represent the growing season (May to September)

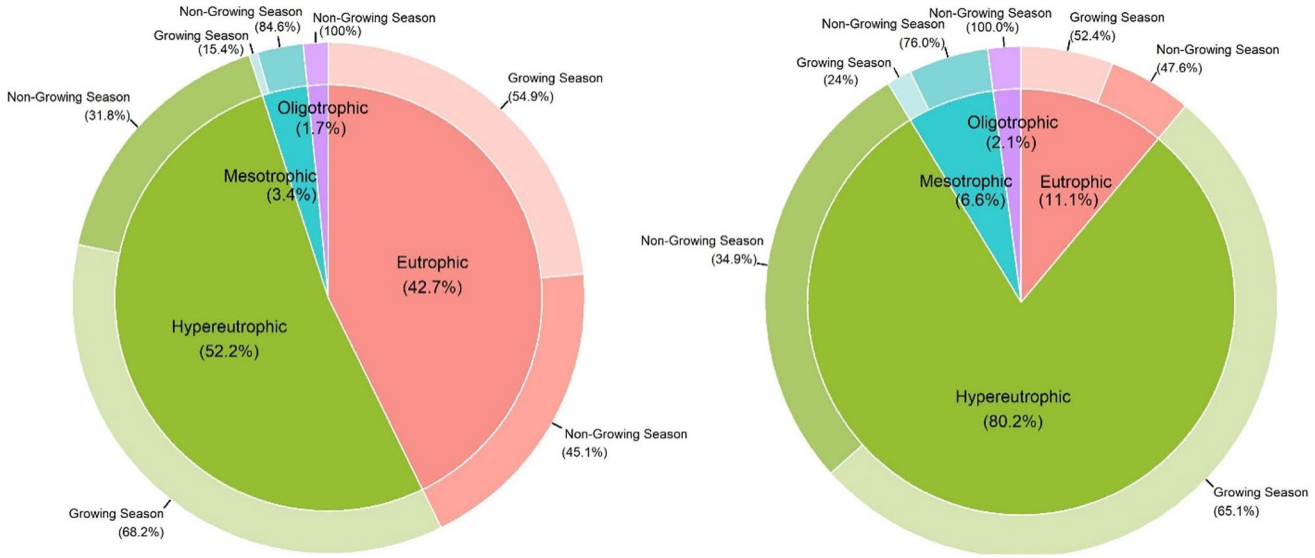

Fig. 8 Pie chart of the trophic classes of the Qaraoun Reservoir based on the temperate water bodies classification (left) and the tropical/subtropical reservoirs classification (right)

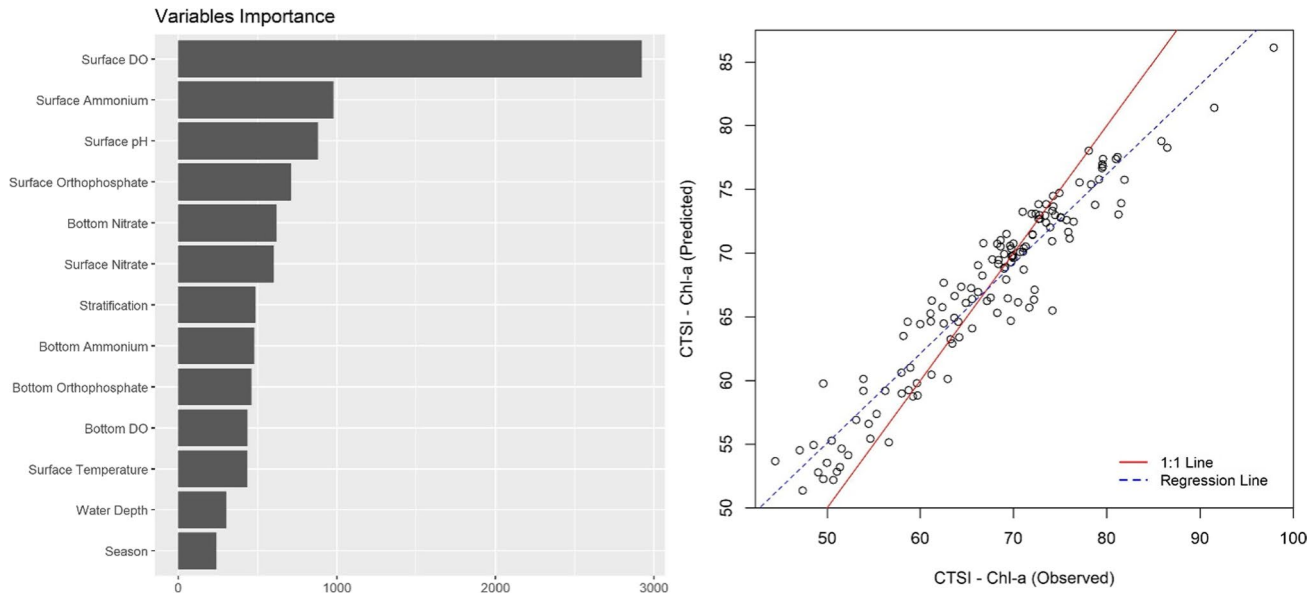

Fig. 9 Results of the tuned random forest model for the Chl-a based trophic state index (CTSI–Chl-a). The variables importance (left) and the predicted versus observed plot (right)

the Chl-a based CTSI was surface DO. This was followed by surface nutrient levels (ammonium and orthophosphate) and surface pH. Bottom concentrations of nutrients and DO were comparatively less important than their surface levels.

Discussion

The Qaraoun Reservoir is characterized by a semi-arid hot climate, making it naturally prone to cyanobacterial growth (Shaban and Hamzé 2018). Moreover, excessive nutrient loadings have fueled extreme HAB events that were consistently observed over the 7 years spanned by this study (between 2013 and 2019). In the reservoir, the HABs were mainly dominated by Microcystis. In this study, we found that the reservoir encountered considerable seasonal and interannual fluctuations in its water level and volume. Additionally, surface and bottom water temperatures in the reservoir significantly fluctuated interannually and within a given year. The importance of temperature on cyanobacterial growth has been reported by various studies (Blottière et al. 2014; Carey et al. 2012; Kosten et al. 2012). Higher temperatures are known to promote algal growth, photosynthetic, and metabolic processes, and improve nutrient uptake abilities (Davis et al. 2009). The Qaraoun Reservoir had high surface temperatures that exceeded 25 °C throughout the growing season (June, July, August, and September). High lake temperatures have been reported previously by Fadel et al. (2021) and Deutsch et al. (2020). These elevated temperatures promote cyanobacterial bloom events, in particular Microcystis that has an optimum growth temperature ranging between 25 and 32 °C (Deutsch 2020, Jiang et al. 2008; Liu et al. 2011). Note that lake temperature also indirectly effected cyanobacterial growth, as strong thermal stratification hinders the mobility of released nutrients from the hypolimnion into the epilimnion. In Qaraoun's deep sections, strong thermal stratification was observed starting from April/May and lasting until turnover in September or even October. The turnover often triggered a HAB event due to the mixing of the nutrient rich bottom waters with the surface as previously reported by Wagner and Adrian (2009). During the growing season, the surface DO measurements in the Qaraoun reached super saturation levels as a result of the cyanobacterial photosynthetic activity. Concurrently, the reservoir's hypolimnion experienced hypoxic conditions that extended longer in the deep section of the reservoir as compared to the middle and shallow sections due to stronger thermal stratification. Furthermore, surface pH values peaked during cyanobacterial blooms and dropped following the reservoir's turnover. This is the result of algal photosynthetic growth that contributes to the loss of carbon dioxide in the water (Kosten et al. 2012). Additionally, changes in the pH levels in the bottom waters can affect the release of phosphorus from the sediments that can also trigger algal growth (Huang et al. 2005).

During the study period, the Qaraoun Reservoir experienced high external nutrients loading during the rainy winter season that led to high surface orthophosphate and ammonium concentrations. When algal bloom events occurred, surface PO_4^{-3} and NH_4^+ dropped significantly as a result of the assimilation and storage of these nutrients by algae. This was confirmed by the negative relationship between Chl-a and these two parameters. Concomitantly, bottom PO_4^{-3} and NH_4^+ concentrations were elevated during the summer season due to nutrients release from the anoxic sediments under stratified conditions. Following the reservoir's turnover at the end of the growing season, bottom orthophosphate and ammonium levels decreased considerably due to the lake's internal mixing. Moreover, the DIN:orthophosphate ratio showed that the reservoir was mostly phosphorus limited. Given that Microcystis are able to internally store phosphorus and modify their buoyancy to reach the nutrient-rich hypolimnion under stratified conditions, they were able to bloom even when the surface nutrient concentrations in the lake were low (Carey et al. 2012; Chung et al. 2014; Molot et al. 2014). The lowest SDD levels and the highest TSS concentrations were recorded during the summer growing season, concurrent with massive cyanobacterial bloom events. Our comparison of the trophic state indices computed based on Chl-a and SDD showed that the Qaraoun Reservoir was classified as hypereutrophic most of the times based on both classifications. Nevertheless, the fact that the Chl-a based TSI values were higher than those based on SDD indicates that algae, in particular, large algal particulates, dominated the attenuation of light in the reservoir's water column (Carlson and Simpson 1996). This confirms that most of the Qaraoun's turbidity is a direct result of excessive algal growth, as previously reported by Deutsch et al. (2018) and Fadel et al. (2016).

The random forests model fared well in predicting the trophic state in Qaraoun Reservoir. Monitoring the trophic state of a lake provides a rapid assessment of its biological productivity and thus can allow for the identification of unusually high productivity that is often associated with harmful blooms (Hollister et al. 2016). The random forests model indicated that the Chl-a-based Carlson trophic state index showed strong relationships with measured physicochemical parameters in the lake. Regarding the physical parameters, the model showed the relative importance of surface DO and pH levels in predicting the trophic state. This is expected given that during cyanobacterial blooms, surface DO concentrations reached super saturation levels, while pH levels increased above neutrality due to the dissolved carbon dioxide depletion in the water column (Kosten et al. 2012; Liu et al. 2011). Consequently, surface DO and pH levels were good indicators of an algal bloom event. While DO and pH are not a cause of eutrophication but a manifestation of the process, the results from the random forests model indicate that these two easy to-measure and low-cost metrics can form the basis of an affordable HAB monitoring system.

Moreover, the model showed that the overall surface nutrient concentrations had a higher importance as compared to bottom nutrient levels, with the exception of nitrates that showed similar importance for both surface and bottom samples. The high importance of surface orthophosphate and ammonium levels as predictors of trophic state is expected as both levels drop sharply during a cyanobacterial bloom event. This was clearly seen by the strong negative relationship between Chl-a on the one hand and orthophosphate and ammonium on the other.

This study has for the first time assessed cyanotoxin levels in the reservoir, by quantifying the intra, extra, and total Microcystin-LR (MC-LR) levels. Measured levels were alarming, as 45% of the total MC-LR levels exceeded the WHO 1 µg/L provisional guideline for MC-LR in drinking water. This highlights that the reservoir's water quality will require advanced treatment before it can be used for potable purposes. This is particularly important given that there are plans to use part of the water stored in the reservoir to provide domestic water for the largest urban area in Lebanon. The incident that happened in Toledo, USA, in the summer of 2014, where the Ohio Environmental Protection Agency ordered a short-term tap water ban in the city after high levels of Microcystin were detected in Toledo's water supply following a HAB event in Lake Erie (Wilson 2014), serves as a reminder of the risks that Microcystis has on future water projects planned for Qaraoun and the rest of arid and semi-arid Mediterranean basin. Interestingly, several eutrophic Mediterranean lakes have also reported equally high toxin levels, reaching up to 19.5 µg/L in Lake Pamvotis, Greece (Naselli-Flores et al. 2007; Vareli et al. 2009). In the Qaraoun Reservoir, most of the toxin concentrations were found to be intracellular rather than extracellular, which may indicate that the toxins were effectively broken down naturally after release. Yet, the risks associated with cell lysing that may be caused by conventional water treatment is a serious concern that should not be overlooked.

Overall, this study highlights the deteriorated state of the Qaraoun Reservoir and underscored the importance of managing the ever-increasing cyanobacterial blooms. Given that future ambient temperatures in the region are projected to increase as is the probability of extended periods of temperatures above 25 °C (Fayad 2013), Microcystin HAB events are expected to worsen. From a management perspective, the focus should be on limiting external nutrient loads that promote the growth of cyanobacteria as well as adopting sediment treatment to reduce internal nutrient loads. Reducing external nutrient loads requires controlling both point and non-point pollution sources. This includes restricting the discharge of untreated municipal and industrial wastewater into the Litani river and reducing the use of fertilizers in the basin. This also involves raising awareness among the residents of the Litani river watershed, particularly on the hazards associated with the use of nutrient-rich detergents and fertilizers. Yet the public needs to be made aware that based on previous eutrophication remediation efforts, the recovery of lakes and reservoirs is often slow (Wurtsbaugh et al. 2019). McCrackin et al. (2017) analyzed 89 studies worldwide, in an effort to assess the response of aquatic systems to eutrophication management measures. They reported that after the complete cessation of nutrient discharge, response variables recovered 34% of their baseline conditions over a median of 13 years. Accordingly, managing nutrient loads at the watershed level should not be expected to have an instant effect on the reservoir's water quality, particularly due to the existing high sediment nutrient stores (Chen et al. 2018; Deutsch et al. 2020).

Conclusion

This study presents a relatively long-term assessment of the eutrophication status of the most important freshwater system in Lebanon and describes the dynamics of the recurrent HABs. The study highlighted the large spatio-temporal variabilities in the reservoir's physical and chemical parameters and discusses their direct and indirect impacts on HAB events. The elevated temperature levels during the growing season were found to be optimal for supporting the growth of Microcystis. Surface DO and pH levels were found to be strong indicators of cyanobacterial growth. Surface DO levels were found to reach super saturation during algal bloom events, while surface pH levels rose above neutrality. TSS and SDD showed high correlations with Chl-a concentrations, which indicated that most of the reservoir's turbidity was a result of excessive algal growth. Elevated nutrient levels were found to be strong promoters of HABs. Surface orthophosphate and ammonium levels were completely depleted during the algal growing season, while bottom concentrations were high due to nutrient sediment release promoted by the anoxic stratified conditions in the reservoir. Also, this study quantified for the first time the MC-LR levels in Qaraoun and underscored the health and environmental risks associated with their high levels. Finally, this study concluded that the reservoir was hypereutrophic over most of the study period and is in need of implanting an urgent basin-level management strategy to control cyanobacterial blooms.

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Author contribution All authors contributed to the study conception and design. Material preparation and data collection were performed by Mohamad Abbas, Sara Dia, and Eliza S. Deutsch. Data analysis and interpretation were conducted by Ibrahim Alameddine and Mohamad Abbas. The whole research was supervised by Ibrahim Alameddine. All authors read and approved the final manuscript.

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Data availability The data that support the findings of this study are available from the corresponding author, Alameddine, I., upon reasonable request.

Declarations

Ethics approval All authors confirm that this manuscript conforms to the ethical standards and requirements of the journal.

Consent to participate This research paper did not utilize any animal testing or human participants.

Consent for publication This does not involve any individual's data. All authors have consented to publish this work.

Competing interests The authors declare no competing interests.

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