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Original Research

Diel Variation of Water Inorganic Nitrogen and Phosphorus during Algal Blooms

Jinzhi Wang[1, 2], Binghui Zheng[2], Xiaoming Kang[1], Hui Yu[2], Da Li[2], Xia Jiang[2]*

[1]Beijing Key Laboratory of Wetland Services and Restoration, Institute of Wetland Research, Chinese Academy of Forestry, Beijing, China
[2]State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, China

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Abstract

Water nitrogen and phosphorus may exhibit pronounced diel changes as affected by diel temperature and DO fluctuations due to algal productivity (photosynthesis and respiration) in eutrophic lakes. Here, we used a laboratory experiment to evaluate the diel dynamics of water ammonium (NH_4^+), nitrate (NO_3^-), and soluble reactive phosphorus (SRP) in different periods of algal bloom in the highly polluted region of Taihu Lake, China. Results showed that diel changes of water NH_4^+, NO_3^-, and SRP depended on the different periods of algal bloom. Diel variations of NH_4^+, NO_3^-, and SRP showed increased trends during algal decomposition, and decreased trends at the beginning of algal growth, suggesting that their diel variations were mainly controlled by algae self through nutrients released by decomposing algae or algal assimilation. However, water NH_4^+, NO_3^-, and SRP decreased from predawn maxima to afternoon minima and subsequently increased when Chl-a was high, which might be governed by the combined effects of algal assimilation and geochemical processes (e.g., nitrification, denitrification, and Fe-bound P cycles). Overall, the diel biogeochemical cycles of inorganic nitrogen and SRP have important implications for the accuracy of pollution assessment and provide important support for the control and management of eutrophic lakes.

Keywords: diel variation, ammonium, nitrate, soluble reactive phosphorus, algal bloom

Introduction

Aquatic ecosystems worldwide have been negatively affected by eutrophication that results in undesirable algal blooms. Phosphorus (P) and nitrogen (N) are the critical elements controlling algae production, and their migration and transformation are largely controlled by temperature, oxygen content, redox condition, and pH [1-2]. In general, the higher the temperature, the higher the P and N released from sediments. Under aerobic conditions, P is sorbed to Fe oxides, which are insoluble, while in anaerobic conditions parts of the insoluble Fe oxides are reduced to their soluble Fe^{2+} forms, resulting in sediment P release into the surrounding water [1, 3]. Meanwhile, N transformations are also heavily dependent on ambient oxygen conditions. Nitrification, the microbially mediated oxidation of ammonium

*e-mail: jiangxia@craes.org.cn

(NH_4^+) to nitrate (NO_3^-), can only occur in the presence of oxygen. Conversely, denitrification, the microbially mediated reduction of NO_3^- to N_2, is favored under anoxic conditions [4].

Bio-geochemical processes affecting water quality may occur on a diel timescale in response to the solar photo cycle. The amplitude of some of these diel processes can be as large as the changes occurring on annual and seasonal timescales [5]. Diel cycles of dissolved oxygen (DO) are dominated by photosynthesis and respiration of aquatic plants, algae, and other microbes, thereby affect the transformations of N, P, and Fe in aquatic ecosystems [6]. For example, Cohen et al. [7] showed highly regular diel cycles of DO, NO_3^-, and soluble reactive phosphorus (SRP), and the diel SRP change was strongly correlated with DO variation in a large spring-fed river, suggesting photosynthetic control directly via assimilation, and/or indirectly via geochemical reactions. Harrison et al. [8] observed a decrease in DO, followed by a decrease in NO_3^- in a subtropical stream with the cessation of photosynthesis in the evening, while NH_4^+ concentration increased with the onset of night and anoxic conditions when phytoplankton N uptake and nitrification were inhibited [4, 9]. Roberts and Mulholland [10] demonstrated that the high spring gross primary production (GPP) in a forested stream corresponded to daily decreases in NO_3^- over the illuminated hours, resulting in high diel NO_3^- fluctuation amplitude, which dampened as the canopy closed. Chittoor et al. [11]found that the amplitudes of the diel changes of DO, NO_3^-, and DOC showed significant seasonal variability, and NO_3^- concentration varied from a daytime minimum to a nighttime maximum, which was attributed to nitrification during the day in autumn.

Taihu Lake, with an area of 2,338 km^2, is the third largest freshwater lake in China, and is located in the Yangtze River delta – the most rapidly developing region in China. Over the past three decades, excessive nutrient inputs have led to the appearance and persistence of massive blooms of toxin-producing cyanobacteria, which have seriously degraded water quality and adversely impacted human use of the lake [12]. To reveal the biogeochemical cycle of N and P for further eutrophication control, previous studies did much research on N and P exchange at the sediment-water interface in a eutrophic lake, which indicated that both algae and associated water environmental variables could explain the dynamics of N and P during algal blooms [13-16]. However, many researchers ignore the diel variations of water N and P, and its driving mechanism in the different periods of algal bloom in a eutrophic lake. Moreover, water bodies with high productivity are apt to show diel changes of O_2, phosphate, and nitrogenous species [17], which is essential not only for guiding the collection and interpretation of water quality data but also for the early warning and emergency disposal of water bloom disasters. Therefore, the objective of our study was to determine the diel variations of water NH_4^+, NO_3^-, and SRP concentrations in the different periods of an algal bloom, and the reasons for their diel dynamics in Meiliang Bay, a highly polluted region of Taihu Lake [18].

Materials and Methods

Experimental Design

The surface sediments and water were collected from Meiliang Bay, where large numbers of algae have accumulated due to the southeast monsoon winds in summer [19]. Surface sediment samples (upper 10 cm layer) were collected using a grab sampler. After homogenization, all the samples were transported to the laboratory for the experiment. Upon return to the laboratory, plant residues and shell fragments were removed from the fresh sediment. The general characteristics of the lake water are summarized in Wang et al. [15]. Algal scum, 91.9% of which was accounted for by *Microcystis* spp. [20], was collected from the Mengwan Channel to the west of Meiliang Bay, Taihu Lake.

The experiment included two treatments: sediment + water + algae (Algae), and sediment + water as the control (Control). All treatments were replicated three times, giving a total of 6 experimental units. Approximate 16 L homogenized sediments were placed into each of 6 barrels with 45 cm in diameter and 70 cm in height, producing a sample 10 cm thick. The barrels were filled with 80 L of lake water collected in situ, producing a water column of 55 cm high, and let stand for around 24 hours. Three barrels were chosen randomly and transferred algae, the rates of application of algae were referred to the chlorophyll a (Chl-a) concentration ranged 78.5-978.3 μg L^{-1} during the algal bloom of Taihu in 2007 [12]. The experiment was conducted outside in Dafunan Village on the lakeshore of Meiliang Bay, Taihu Lake, and was run for 20 days (September 2013).

Water samples were daily collected from 0.3 m below surface water to determine NH_4^+, NO_3^-, SRP, and Chl-a at around 10:00. For our daily or diel observations, water DO and ORP were sampled daily every 2 hours using a YSI 6600 multi-parameter water quality sonde (YSI Incorporated, Yellow Springs, USA). Subsequently, water was collected every 2 hours to measure NH_4^+, NO_3^-, and SRP concentrations from 06:00 to the next day at 04:00 on September 4-5, September 10-11, September 17-18, and September 22-23. Air temperature and photosynthetically active radiation (PAR) were measured every half-hour by a meteorological data collector CR1000 (Campbell, USA) in an automatic weather station nearby.

Chemical Analysis

Water NH_4^+, NO_3^-, and SRP concentrations were determined according to [21]. Water samples were filtered through a glass microfiber filter (GF/C, Whatman, Brentford, UK). The concentrations of NH_4^+, NO_3^-, and SRP in filtered water were determined using Nessler's reagent spectrophotometry method, the ultraviolet spectrophotometry method, and the molybdenum blue method, respectively.

Statistical Analyses

Effects of algal bloom on the physico-chemical characteristics of overlying water were analyzed by the repeated measures analysis of variance (ANOVA). Statistical tests were considered significant at the $P<0.05$ level. When treatment effect was significant, least significant difference (LSD) tests were used to check for quantitative differences between treatments. For all ANOVA's, the assumption of normality was checked with Kolmogorov-Smirnov tests, and the assumptions of homogeneity of variance were checked using Levene's test. If the assumptions were not met, data were log-transformed prior to analysis. Statistical analyses were performed using SAS procedure (SAS Version 8.1, SAS Institute Inc., Cary, NC, USA).

Results

Temporal Dynamics of Water Quality Variables

Algal bloom significantly increased water NH_4^+, NO_3^-, and SRP concentrations (Fig. 1). In the Algae treatment, during the first 7 days NH_4^+, NO_3^-, and SRP concentrations increased, and decreased in the following September 10-12, subsequently the concentrations of NH_4^+, NO_3^-, and SRP showed different trends. For example, NO_3^- concentration remained at a low level, while SRP concentration dramatically increased, NH_4^+ concentration increased until September 18. Chl-a concentration as a good indicator of phytoplankton biomass can be roughly divided into three phases: Chl-a concentration decreased to a minimum value of 73.8 μg L^{-1} on September 10 and subsequently began to dramatically increase and reached the maximum during September 13-18. Afterword Chl-a concentration decreased again. The Chl-a concentration in the algae-free control treatment averaged 21.4 μg L^{-1} and remained constant during the whole incubation. Algal bloom significantly decreased water ORP and DO concentration ($P<0.001$), during the first 7 days ORP in the algae treatment decreased to the minimum value and thereafter increased, and water DO concentration in the algae treatment was less than 0.5 mg L^{-1} prior to September 19 and increased thereafter (Fig. 2).

Diel Dynamics of Environmental Variables

The PAR showed a marked diel trend, with the maximum at noon and minimum at night, the range of PAR cycle was greatest on September 4-5, and was lowest on September 22-23, which indicated the intermittent cloud cover (especially during the afternoon with light rain) (Fig. 3). The air temperature cycle typically lagged PAR by 1 to 3 hours, and peak temperatures were observed at 14:00 on September 4-5, at 14:30 on September 10-11, at 15:30 on September 17-18, and at 12:30 on September

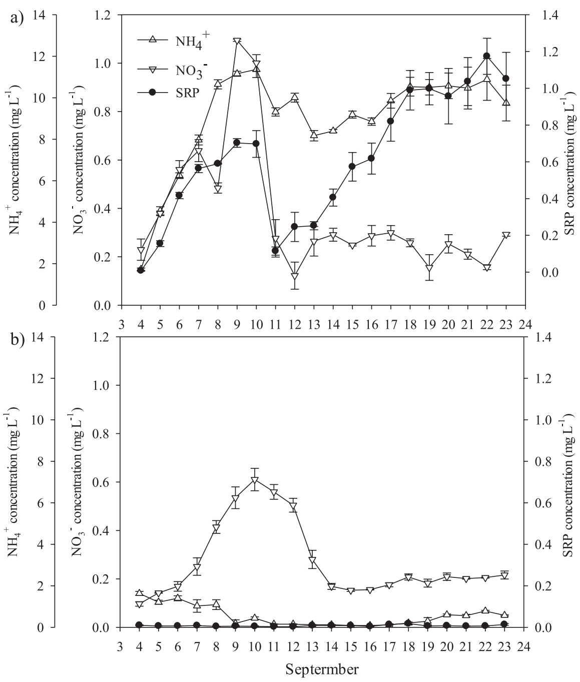

Fig. 1. Dynamics of water ammonium (NH_4^+), nitrate (NO_3^-), and soluble reactive phosphorus (SRP) in the Algae a) and Control b) treatments (data are mean ±SE).

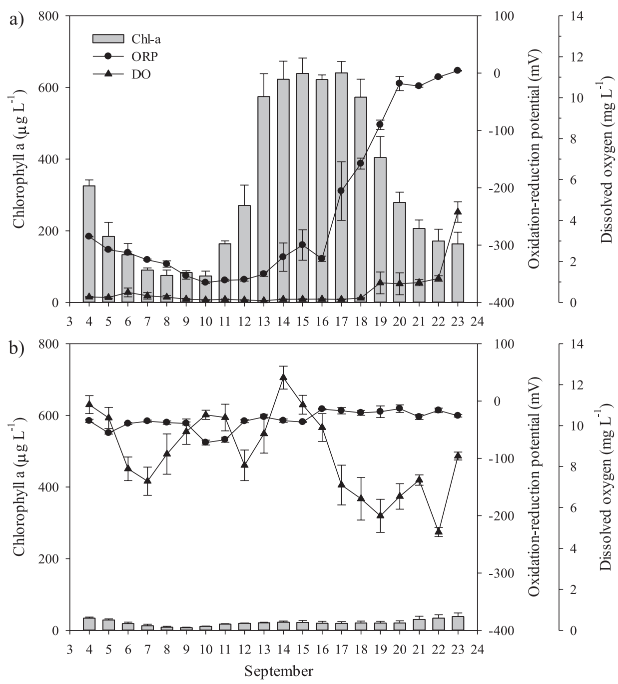

Fig. 2. Dynamics of water chlorophyll a (Chl-a), oxidation-reduction potential (ORP), and dissolved oxygen (DO) in the Algae a) and Control b) treatments (data are mean ±SE).

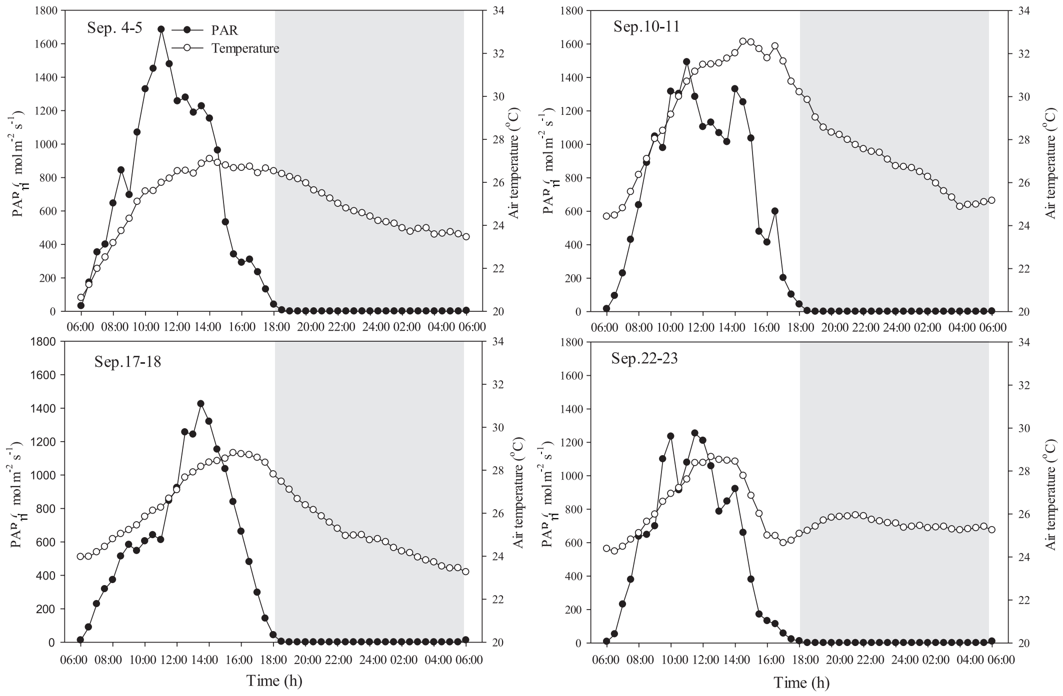

Fig. 3. Diel dynamics of photosynthetically active radiation (PAR) and air temperature on September 4-5, September 10-11, September 17-18, and September 22-23 (shaded areas represent the nocturnal period).

22-23. In the algae treatment no distinct diel patterns were found for water DO and ORP on a 24-h timescale on September 4-5 and September 10-11, while DO a nd ORP separately reached the maximum at ca. 16:00 on September 17-18 and at ca. 12:00 on September 22-23. In the Control treatment water DO showed a rapid increase from predawn minima to afternoon maxima and afterward decreased (Figs 4-5).

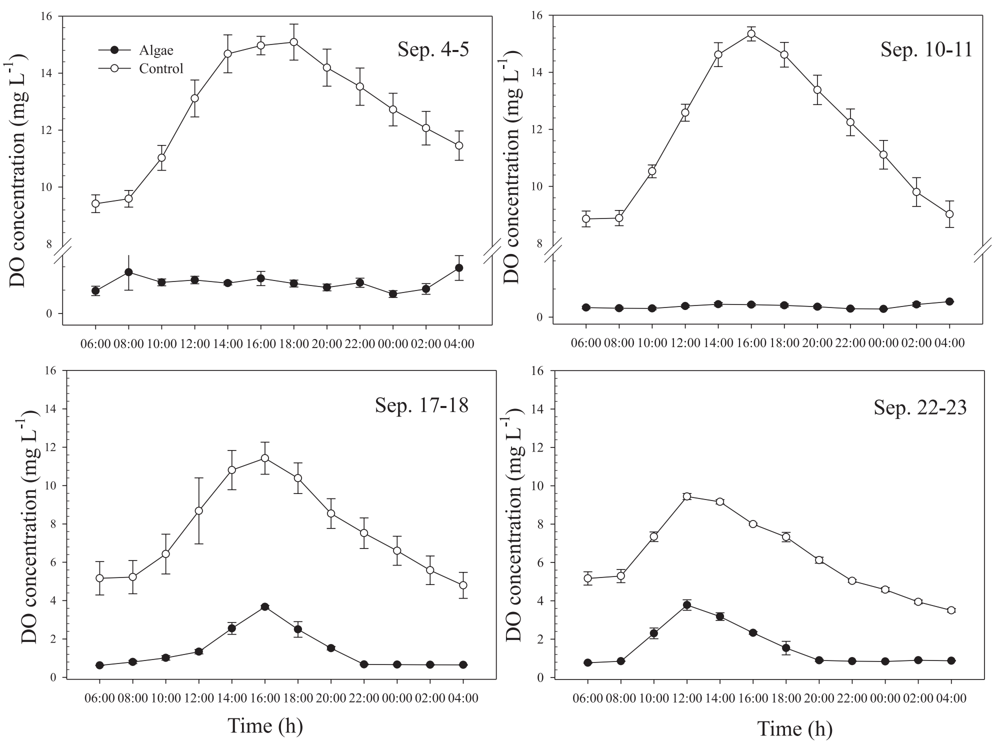

Fig. 4. Diel dynamics of water-dissolved oxygen (DO) on September 4-5, September 10-11, September 17-18, and September 22-23 in the Algae and Control treatments (data are mean ±SE).

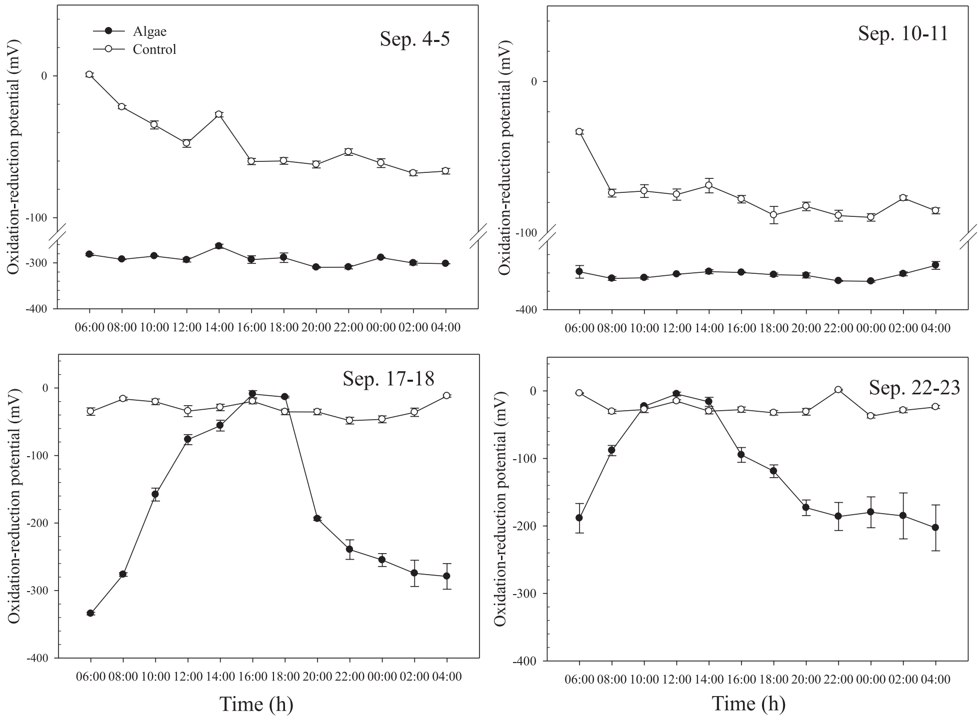

Fig. 5. Diel dynamics of water oxidation-reduction potential (ORP) on September 4-5, September 10-11, September 17-18, and September 22-23 in the Algae and Control treatments (data are mean ±SE).

Diel Dynamics of Inorganic Nitrogen and Phosphorus

The diel dynamics of NH_4^+ and NO_3^- concentrations depended on the presence of algae and different periods of algal bloom (Table 1). For example, in the algae treatment NH_4^+ and NO_3^- concentrations increased on September 4-5, while significantly decreasing in the daytime (from predawn to dusk) on September 10. The NH_4^+ and SRP concentrations on September 17-18 and September 22-23 showed marked diel variations, with the minimum in the afternoon and maximum at dawn (Figs 6 and 8). The amplitudes of diel NH_4^+ and SRP fluctuations in Algae treatment on September 17-18 were 14.9% and 18.6%, respectively, which were higher than their corresponding values on September 22-23. Similar to diel fluctuations of NH_4^+ and SRP, water NO_3^- concentration on September 17-18 decreased in the daytime, increased, and reached the maximum at dawn. In contrast, NO_3^- on September 22-23 showed an opposite diel trend (Fig. 7). The concentrations of NH_4^+, NO_3^-, and SRP in Control treatment did not show consistent day-night variation (Figs 6-8).

Discussions

In this study diel cycles of nutrients depended on the nutrient species (e.g., NH_4^+, NO_3^-, and SRP) and the sampling periods of algal blooms. Based on Chl-a and algal appearance, September 3-10 was characterized as a period of algal decomposition in this study. The effects of algal decomposition on water SRP concentration are demonstrated in different respects. Firstly, during algal decomposition 40-65% of P in algae was released into water [22] and dramatically increased water P level [13, 15-16]. Secondly, algal decomposition depressed DO and decreased pH at the sediment-water interface, upon which water P was increased due to the increased P release from sediments [16, 20]. Therefore, in this study

Table 1. Results (*F*-values) from repeated ANOVA measurements for the effects of algal bloom (Algae) and sampling days (Time) as fixed factors on water environmental variables and water NH_4^+, NO_3^-, and SRP concentrations during the experiment.

Treatments	NH_4^+	NO_3^-	SRP	DO	ORP	pH
Algae	1229.9^{***}	76.4^{***}	617.5^{***}	1558.8^{***}	2487.8^{***}	1138.0^{***}
Time	1.3^{ns}	173.85^{***}	105.9^{***}	38.4^{***}	280.4^{***}	9.9^{**}
Algae×Time	74.1^{***}	3.2^{ns}	103.9^{***}	47.5^{***}	121.9^{***}	49.1^{***}

*, **, ***: Statistically significant at P<0.05, 0.01, 0.001, respectively; ns: not statistically significant

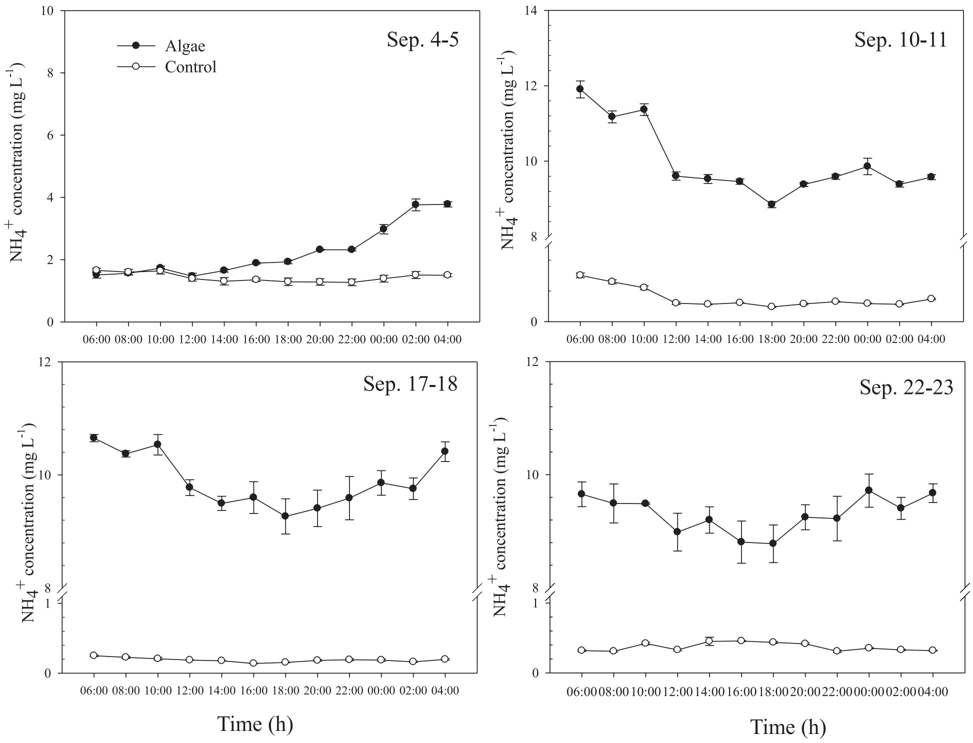

Fig. 6. Diel dynamics of water ammonium (NH_4^+) concentrations on September 4-5, September 10-11, September 17-18, and September 22-23 in the Algae and Control treatments (data are mean ±SE).

the diel increased water SRP concentration on September 4-5 might result from P release from decomposing algae and sediments. However, Wang et al. [15] analyzed the dynamics of different P species in water and sediments, as well as the relationships between water P concentrations and related environmental variables

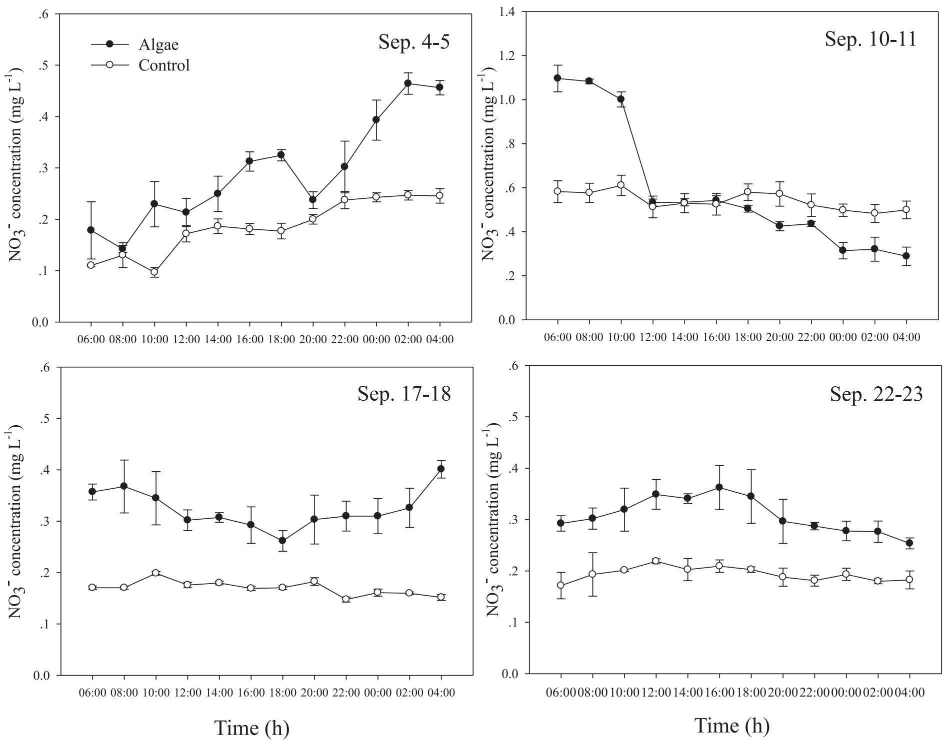

Fig. 7. Diel dynamics of water nitrate (NO_3^-) concentrations on September 4-5, September 10-11, September 17-18, and September 22-23 in the Algae and Control treatments (data are mean ±SE).

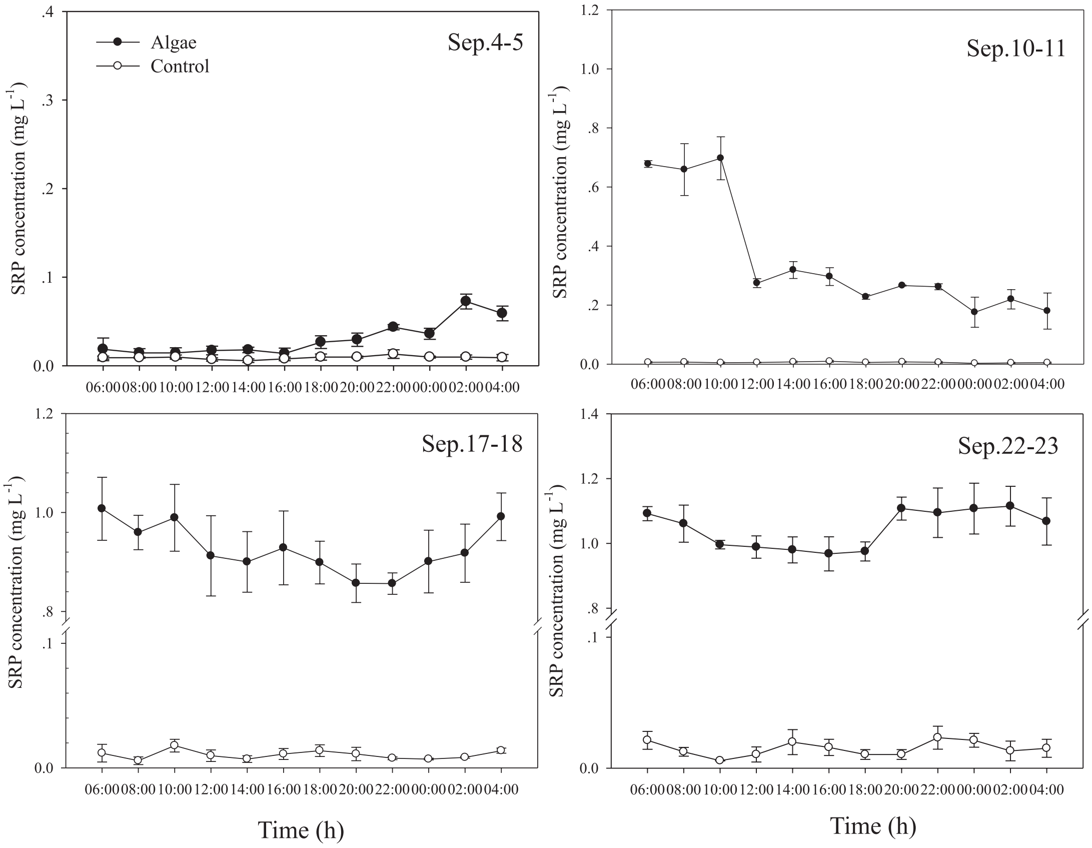

Fig. 8. Diel dynamics of water-soluble reactive phosphorus (SRP) on September 4-5, September 10-11, September 17-18, and September 22-23 in the Algae and Control treatments (data are mean ±SE).

(e.g., Chl-a, DO, ORP, NO_3^-, and pH), and concluded that the increased total P, dissolved total P, and SRP concentration during algal decomposition might mainly result from the release of decomposing algae instead of sediment P release. Therefore, in our study the diel-increased SRP concentrations on September 4-5 might mainly result from the decomposing algae release. In addition, under anaerobic conditions the sediment denitrifying process was promoted by small molecular compounds such as volatile fatty acids, which were released from algal decomposition [23], and the N loss through denitrification was offset by the N release from algal decomposition, thereby increased inorganic N concentration on September 4-5.

After September 10, the color of partial algae changed to green, Chl-a concentration began to dramatically increase and then reached the maximum, which indicated that algal growth became the dominant process [24]. At the beginning of algal growth water NH_4^+, NO_3^-, and SRP concentrations in the algae treatment dramatically decreased in the daytime (from 06:00 to 18:00) on September 10, when water DO and ORP were kept constant, and Chl-a concentration dramatically increased by 90 µg L^{-1} from September 10 to September 11. The decreased NH_4^+, NO_3^-, and SRP concentrations might mainly result from nutrients assimilation by algae in the daytime of September 10, when GPP was high at the beginning of algal growth. Jauzein et al. [25] studied the N uptake by dinoflagellate using the ^{15}N-labelling technique and found that it preferred uptake for NH_4^+ relative to NO_3^-. On September 10 water NO_3^- concentration continually decreased at night, which indicated that the diel-decreased NO_3^- concentration on September 10-11 might result from the combined algae uptake in the daytime and denitrification process under anaerobic conditions [4]. The diel dynamics of NH_4^+, NO_3^-, and SRP concentrations on September 4-5 and September 10-11 suggested that their diel cycles during algal decomposition and subsequently the beginning of algal growth were affected more by the algae itself through nutrients released from decomposing algae and algal assimilation than other biogeochemical processes (e.g., denitrification and Fe-bound P release).

In contrast, on September 17-18 and September 22-23, SRP concentrations in the algae treatment reached the minimum in the afternoon and maximum at dawn. The diel minima of SRP lagged the maximum of water DO and ORP by 4 to 6 h. The diel cycle for water SRP concentration might result from the combined effects of P assimilation by algae and P exchange at the sediment-water interface. Sediment P mobility was largely controlled by the sorption of P forms to Fe oxides, which was controlled by the DO concentration [1-2, 26]. At noon/afternoon DO and ORP in this study reached their maximum values, water-soluble Fe^{2+} concentrations were kept at the lowest value [6, 8], which favored the sorption of P to Fe oxides that is insoluble [1]. The diel variation of SRP on September 17-18 and on September 22-23 was consistent with previous findings that conditions more from oxic conditions during the light hours to hypoxic conditions (defined as < 2 mg O_2 L^{-1}) [27] at night explained the elevated SRP in a barrier-lagoon complex during the periods of high productivity in summer [28]. The aforementioned results could explain why in our study water SRP concentration was lowest in the afternoon on September 17-18 and September 22-23.

On September 17-18 diel cycle of water NO_3^- in algae treatment typically had the lowest concentration in the late afternoon and the highest concentration in the early morning, which was consistent with previous studies in streams [7, 29]. Assimilation of NO_3^- by primary producers is the main cause of diel NO_3^- cycles [6, 10], and the amplitude of diel NO_3^- fluctuation depends on light conditions, temperature, and the relative rates of autotrophic and heterotrophic activities [10, 30]. Scholefield et al. [29] found that NO_3^- concentrations were negatively correlated to water temperature. In contrast, NO_3^- concentration on September 22-23 showed a rapid increase from predawn minima to late afternoon maxima and gradual decreases after sunset, which might indicate that diel cycles of inorganic N might be dominated more by NH_4^+ oxidation (i.e., nitrification) or NO_3^- reduction (i.e., denitrification) than by biological assimilation of inorganic N when algal biomass was at a relatively low level. Gammons et al. [17] found that nitrification rates were significantly faster during the day than at night due to a combination of higher temperature and higher DO concentration. Thus, water NO_3^- concentration increased during the day while NH_4^+ concentration decreased on the 24-h timescale of September 22-23 in this study. The diel cycle of NO_3^- can be amplified by nighttime consumption of NO_3^- by denitrifying bacteria residing in sediments [31]. A contradiction of previous studies showed the absence of diel NH_4^+ concentrations in more pristine streams [10], and we observed diel changes in NH_4^+ concentrations on both September 17-18 and September 22-23. The minima of NH_4^+ concentrations in the late afternoon might not be assimilated by algae, when Chl-a was relatively low, while NH_3 emissions [17] and the nitrification process were the likely explanations for decreases in NH_4^+ concentration during the day with higher temperature, pH, and DO. According to Azov and Goldman [32], NH_3 concentration increases 10 fold for a 10°C temperature increase or a one-unit pH increase. Algae and other organisms contributed to the rise in pH with the onset of daytime photosynthesis, while in the evening the lowest pH resulted from the absence of photosynthesis and the ongoing respiration.

Conclusions

In this study, we demonstrated that the diel variations of water NH_4^+, NO_3^-, and SRP depended on the different periods of algal bloom. Diel NH_4^+, NO_3^-, and SRP showed increased trends during algal decomposition, and decreased trends at the beginning of algal growth, suggesting that these diel variations were mainly driven by biological process (e.g., algal assimilation and decomposition). When Chl-a was high and stable, water SRP, NH_4^+, and NO_3^- concentration decreased from predawn maxima to afternoon minima, which might be governed by the combined biological and geochemical processes. During algal deposition, geochemical processes were the major drivers of these diel cycles. Overall, our results indicated that the trends and amplitudes of water NH_4^+, NO_3^-, and SRP in eutrophic lake differed in different periods of algal bloom, which were driven by different mechanisms. The diel cycles of water quality parameters in this study will lead to better predictions of how lake ecosystems might react to changing environments, which provide important support for algae control and management of eutrophic lakes.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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