High frequency data provide new insights into evaluating and modeling nitrogen retention in reservoirs

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Abstract

Freshwater ecosystems including lakes and reservoirs are hot spots for retention of excess nitrogen (N) from anthropogenic sources, providing valuable ecological services for downstream and coastal ecosystems. Despite previous investigations, current quantitative understanding on the influential factors and underlying mechanisms of N retention in lentic freshwater systems is insufficient due to data paucity and limitation of modeling techniques. Our ability to reliably predict N retention for these systems therefore remains uncertain. Emerging high frequency monitoring techniques and well-developed ecosystem modeling shed light on this issue. In the present study, we explored the retention of $\text{NO}_3\text{-N}$ during a five-year period (2013-2017) in both annual and weekly scales in a highly flushed reservoir in Germany. We found that annual-averaged $\text{NO}_3\text{-N}$ retention efficiency could be up to 17% with an overall retention efficiency of ~4% in such a system characterized by a water residence time (WRT) of ~4 days. On the weekly scale, the reservoir displayed negative retention in winter (i.e. a source of $\text{NO}_3\text{-N}$) and high positive retention in summer (i.e. a sink for $\text{NO}_3\text{-N}$). We further identified the critical role of Chl-a concentration together with the well-recognized effects from WRT in dictating $\text{NO}_3\text{-N}$ retention efficiency, implying the significance of biological processes including phytoplankton dynamics in driving $\text{NO}_3\text{-N}$ retention. Furthermore, our modeling approach showed that an established process-based ecosystem model (PCLake) accounted for 58.0% of the variance in $\text{NO}_3\text{-N}$ retention efficiency, whereas statistical models obtained a lower value (40.5%). This finding exemplified the superior predictive power of process-based models over statistical models whenever ecological processes were at play. Overall, our study highlights the importance of high frequency data in providing new insights into evaluating and modeling N retention in reservoirs.

- 36 **Keywords:** Nitrogen removal; Reservoir; High frequency monitoring; Statistical modeling;
- 37 Ecosystem modeling

1. Introduction

The drastically disrupted nitrogen (N) cycling by human activities has become one of the planetary systems exceeding its boundary and thereby stands out of the ‘safe operating space’ (Rockström et al. 2009). It is estimated that anthropogenically created N amounted to 187 Tg in 2005 (equivalent to total fixed N from natural processes), which originated mostly from Haber-Bosch industrial production, agricultural fertilization, land use change, and fossil fuel combustion (Canfield et al. 2010, Galloway et al. 2008). One third of the excess N, however, is ultimately transferred from the land into the ocean, deteriorating estuaries, coastal and offshore areas with severe eutrophication and hypoxia (Galloway et al. 2004, Harrison et al. 2009, Seitzinger et al. 2006, Vitousek et al. 1997, Yu et al. 2019).

Lakes and reservoirs are important inland aquatic systems providing valuable ecological services for downstream waters, including N removal via denitrification, whenever hypoxic or anoxic conditions prevail, and to a lesser extent by burial in sediment (Harrison et al. 2009, Saunders and Kalff 2001). It is estimated that on a global scale, overall retention capacity of lakes and reservoirs is ten times higher than that of terrestrial systems, and approximately 20% of total denitrification occurs in freshwater systems including lakes and reservoirs (Seitzinger et al. 2006). The disproportional important role of small lentic systems in removing nutrients has also been gradually recognized (Cheng and Basu 2017, Harrison et al. 2009). In addition, increasing number of reservoirs around the globe (Lehner et al. 2011) demonstrates the importance to better understand the role of reservoirs in N cycling in the landscape.

Nonetheless, to reliably predict N removal capacity for a given inland aquatic system remains challenging. N retention efficiency of aquatic systems varies from around 10% in the catchment of Upper Mississippi River (Loken et al. 2018) to almost 90% in Waikato Basin

(Alexander et al. 2002). The huge variability and its underlying causes may have large impacts on management, as the retention capacity of these systems can determine the strategy against nutrient pollution by either emphasizing on upstream control or relying on the downstream elimination in aquatic systems. The controversy may be reconciled by better resolved monitoring data and more mechanistic aquatic ecosystem models that enable to link N removal to the underlying mechanisms and their controlling environmental factors.

It has been demonstrated that influential factors driving N retention in lakes and reservoirs include N loading, water residence time (WRT), water depth, water temperature and total phosphorus (TP) concentrations (David et al. 2006, Finlay et al. 2013, Harrison et al. 2009, Saunders and Kalff 2001, Tong et al. 2019, Windolf et al. 1996). However, these studies on N retention in lakes or reservoirs were mostly based on an inter-annual budget, whereas few studies paid attention to intra-annual patterns including seasonal or even finer temporary scales. Relevant biological processes such as phytoplankton growth that are strongly interactive with nutrient dynamics have been overlooked in general. We argue that in inter-annual investigations, the effects of biological processes that undergo strong seasonal variations on N retention are simply not resolvable. High-frequency monitoring (Porter et al. 2012) allow to investigate the effects of biological processes on the N budget of aquatic systems at intra-annual temporary scales. Ultimately, the urgent need for iterative near-term ecological forecasting (Dietze et al. 2018) calls for the prediction of water quality issues such as nutrient retention on a much shorter temporal scale. This is also relevant because key characteristics like WRT, water temperature or N loading can display considerable intra-annual variations.

Current understanding of N retention in lakes and reservoirs is hampered not only by observational data but also by modeling techniques. While the statistical modeling based on

regional or global datasets have demonstrated their capacity in predicting N retention in lakes and reservoirs on the basis of annual budgets, they cannot link to the underlying processes and are unable to dynamically predict N retention at sub-annual timescales. Process-based ecosystem models, on the other hand, generate dynamic nutrient budgets and predict nutrient retention by explicitly addressing the processes and mechanisms underlying (Janssen et al. 2019). Therefore, we expect a superior performance of process-based ecosystem model over statistical model in projecting N retention in lentic ecosystems such as reservoirs.

Taken together, we aim to address the following research questions in the present study: Can high frequency data provide new insights into N retention in reservoir at both long (annual) and short (weekly) temporal scales? Can we resolve the impact of seasonal ecosystem dynamics on N retention and link retention to specific ecological processes? Can we take advantage of the recent advancements in aquatic ecosystem modeling to predict N retention in a dynamic framework? To this end, the specific goals of this study are as follows: 1) to investigate N retention on different temporal scales (annual and weekly) in a reservoir system (Königshütte Reservoir, Central Germany) with a 5-year data set from high-frequency monitoring; 2) to adjust existing statistical models addressing the combined effects of both hydrological and biological factors on N retention in this reservoir; 3) to investigate whether process-based ecosystem models have better predictive abilities for N retention than statistical models; and 4) to provide new insights and implications on lake and reservoir management for mitigation of excess N.

2. Materials and methods

2.1 Study site

Königshütte Reservoir is one of six reservoirs in the Rappbode Reservoir system in

Harz Mountains, Germany (Fig. 1), located at a crest elevation of 423.3 m a.s.l. (Rinke et al. 2013). The reservoir has a mean depth of 4.9 m (maximum 13.0 m), a maximum surface area of 28.5 ha, and a maximum water volume of $1.4 \times 10^6 \text{ m}^3$. The average WRT is very short (within 4.3 days) so that the reservoir is a highly flushed system. The catchment area is 154.2 km^2 , with forest and grassland (meadow) as the main land use types (approximately 90%). The reservoir receives water from two riverine inflows (Kalte Bode and Warme Bode). The outlets are discharging either into the downstream river Bode towards Wendefurth Reservoir (gauge Hirtenstieg) or into a water transfer gallery towards Rappbode Reservoir. The water gallery delivers approximately one third of the annual inflow into Rappbode Reservoir, which is the largest drinking water reservoir in Germany in terms of volume, providing drinking water to more than one million people (Wentzky et al. 2018a).

2.2 Water budget

Hydrological data, including water level (m a.s.l.), water volume (10^6 m^3), precipitation (mm) and water discharges for the two inflows and the two outflows ($\text{m}^3 \cdot \text{s}^{-1}$) from January 1st, 2013 to December 31st, 2017, were provided on a daily basis by the reservoir authority of the state Saxony-Anhalt, Germany (Talsperrenbetrieb Sachsen-Anhalt). Diffusive inflow from the shore of the reservoir is estimated as 7.5% of the inflow of Warme Bode based on the ratio of surface areas. Groundwater input, output and evaporation loss were considered negligible and not included. Water surface area was derived from water level changes and the hypsographic curve of the reservoir linking water level to surface area (Fig. S1). The water budget is fully balanced during the five years of investigation by slightly adjusting the inflow of Warme Bode, based on the fact that the flow measurement in Warme Bode is most likely to be biased due to channel dynamics, while the water flow

measurements in other locations are more reliable due to stable artificial channel.

2.3 High frequency monitoring data

Data from the high frequency monitoring in Königshütte Reservoir are part of the Rappbode Reservoir Observatory (Rinke et al. 2013), which belongs to the TERENO project (<http://www.tereno.net>). There are three sampling sites equipped with probes, namely, YBK (Kalte Bode), YBW (Warme Bode) and YKB (Königshütte Reservoir, at the dam) (Fig. 1). These probes include optical sensors (ProPS, TRIOS, Germany) measuring light extinction in the UV spectrum (190-360 nm) providing continuous and automatic measurements on concentrations of NO₃-N, and a multi-parameter probe (YSI6800, YSI, USA) measuring water temperature and chlorophyll a. The data measured on-site are automatically transferred to a central server via a GSM module and stored in a database, from which we collected the data for the three sample sites during January 1st, 2013 and December 31st, 2017. NO₃-N concentrations (mg·L⁻¹) and water temperature (°C) were measured at all stations in a time step of 10 min. Chl-a concentrations were measured at the same frequency only at YKB because the inflows contained no suspended algae given their rather short channel lengths through forested, mountainous areas. The data were pre-processed to eliminate outliers using Grubbs' test (Grubbs 1950) with the null hypothesis that no outliers exist in a normally distributed data set. The missing values (outliers or functional failure of the instruments) in the time series for NO₃-N and water temperature (fraction ranged 0.1-1.9%) were replaced by linear interpolation (not for Chl-a due to a larger missing fraction of 11.8%) (Table S1).

In addition to the high frequency monitoring, there was also a regular field sampling program (biweekly) from January 2016 to December 2017 at the same three sites. Water samples were collected and transported back to the laboratory for wet chemical analysis of

TN, NO₃-N, NH₄-N, TP, and SRP, as outlined by Friese et al. (2014).

2.4 Nitrate budget calculation

Since inorganic N in the inflows and reservoir is mostly present in form of nitrate, ammonia is not important in the system (e.g. NO₃-N: 0.77±0.28 mg·L⁻¹, NH₄-N: 0.02±0.02 mg·L⁻¹ in both inflows from 2016 to 2017). Therefore, we established a dynamic NO₃-N budget for Königshütte Reservoir during 2013 and 2017 on both annual and weekly scales. We quantified riverine NO₃-N inflow and outflow loads based on both discharges and NO₃-N concentrations. NO₃-N inputs include riverine input from Kalte and Warme Bode plus atmospheric deposition onto the water surface of the reservoir. The atmospheric deposition, including both dry and wet, was estimated to be 5.5 g ha⁻¹ d⁻¹ for central Germany (Boltersdorf et al. 2014). Königshütte Reservoir has a mesotrophic state (Carlson 1977) with an average TP concentration of 0.020 (0.008-0.053) mg·L⁻¹ at YKB during 2016 and 2017. Water bodies with low productivity usually have low input of N from bacterial fixation, which was on average estimated to be 0.3% of the external input (Finlay et al. 2013). Therefore, biological N fixation was not included in the budget. Total outputs include riverine outflow towards Hirtenstieg and the water gallery. Other output processes such as fish production and groundwater were not considered due to their minor contributions.

We calculated annual NO₃-N retention rate ($N_{ret,rate}$; Mg N·year⁻¹) and retention efficiency ($N_{ret,\%}$; %) during 2013-2017 following the equations below. All components have the same unit of Mg N per day.

$$N_{ret,rate} = \sum I_r + \sum D_{at} - \sum O_{r,d} \quad (\text{eq. 1})$$

$$N_{ret,\%} = (\sum I_r + \sum D_{at} - \sum O_{r,d}) / (\sum I_r + \sum D_{at}) \quad (\text{eq. 2})$$

where I_r represents the total riverine NO₃-N inputs; D_{at} represents the total atmospheric NO₃-

N deposition; $O_{r,d}$ represents the total riverine $\text{NO}_3\text{-N}$ outputs. Likewise, weekly $\text{NO}_3\text{-N}$ retention was calculated based on weekly instead of annual data. Note that $\text{NO}_3\text{-N}$ retention is composed of both $\text{NO}_3\text{-N}$ being removed (removal) and $\text{NO}_3\text{-N}$ being stored within the reservoir water (see SI text for detailed description), while the change in $\text{NO}_3\text{-N}$ transitory storage is negligible in comparison to the total input or removal.

2.5 Statistical modeling on the annual scale

We utilized several statistical models for predicting N retention efficiency on the annual-scale (Table 1). These models include SPARROW, NiRReLa, RivR-N and those proposed by Windolf et al. (1996) and David et al. (2006), all of which have been developed and tested by other field data. We compared the estimations from these models to the calculated annual $\text{NO}_3\text{-N}$ retention efficiency in Königshütte Reservoir in each of the five years being investigated.

2.6 Statistical modeling on the weekly scale

To analyze the combined effects of different biological and hydrological factors on $N_{ret,\%}$ (and also $N_{ret,rate}$), a stepwise selection using linear regression models was applied. Calculated $N_{ret,\%}$ (and also $N_{ret,rate}$) on a weekly basis were considered as the response variables. We performed the Farrar-Glauber (FG) test to check for multicollinearity among the explanatory variables, using functions ‘omcdiag’ and ‘imcdiag’ for overall and individual diagnose, respectively, from the ‘mctest’ package in R (Imdadullah et al. 2016). After multicollinearity was eliminated, we used autoregressive model (‘acf’ (autocorrelation function) and ‘pacf’ (partial autocorrelation function) in R (R Core Team 2018)) to identify the existence and order of autocorrelation in the time series. We further performed Durbin-

Watson (DW) test by 'dwtest' in R package 'lmtest' (Zeileis and Hothorn 2002) to check for the first-order autocorrelation in the residuals of ordinary least squares (OLS) models (if any), which would overestimate the model performance (Shultz et al. 2018). In case of significant results from DW test, we applied the generalized least squares (GLS) model by 'gls' in R package 'nlme' (Pinheiro et al. 2012), which is a modified OLS model to deal with autocorrelation in the model residuals. Bayesian information criterion (BIC) was used as criterion for model selection during the stepwise procedure, while we also referred to RMSE (root mean squared error), AIC_c (Akaike's information criterion corrected for small sample sizes) and adjusted r^2 (r^2 adjusted for the number of terms included in the model). All analysis were performed using R statistics program version 3.4.3 (R Core Team 2018).

2.7 Predictions from process-based ecosystem modeling

PCLake model is an ecosystem model for temperate shallow non-stratified lakes. The model is composed of a mixed water column and a sediment surface layer (Janse 2005). Biogeochemical cycling of C, N and P is highly resolved in this model including relevant processes like denitrification, algal uptake and sedimentation. We assumed that PCLake is applicable to Königshütte Reservoir because stratification hardly occurs except short episodes during high summer temperature when stratification is restricted to a small spot in front of the dam. During these episodes, the hypolimnion contributes only a very low fraction (<10%) to the overall volume and its contribution to N processing can therefore be neglected. The input data of PCLake included water discharge (inflow and outflow), TN and TP loading, and lake water temperature, which were prepared based on the high-frequency dataset described above. According to the laboratory data during 2016 and 2017 in the inflows, TN concentration was approximately 1.6 times of NO₃-N concentration, NH₄-N concentration

was approximately 2.4% of $\text{NO}_3\text{-N}$ concentration, and TP concentration was about 2% of TN concentration (all provided as median values). We estimated TN and TP loading based on nitrate loading, and fractions of $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ in the TN loading were also applied to the model accordingly. In addition, given that PCLake was developed for temperate shallow lakes, we applied the default settings for daily light intensity and day length from the model (Janse 2005). Model simulation starts from Jan. 1st, 2013 to Dec. 31st, 2017 at a time step of one day. Initial condition of the model was derived from the clear lake state setting calibrated from over 40 Dutch lakes (Janse et al. 2010) but with relatively low macrophytes density ($1 \text{ g}\cdot\text{m}^{-2}$) because there was hardly macrophytes in the reservoir. To eliminate the effect from the initial conditions, we added a ‘burn-in’ period of five-year before the simulation with the same external condition in 2013, following other modeling approaches with PCLake (Kong et al. 2017a, Kuiper et al. 2015). This procedure allows the model to start the simulation at equilibrium. Model outputs were validated by data for various water quality variables in the reservoir.

3. Results

3.1 Total $\text{NO}_3\text{-N}$ budget for 2013-2017

High frequency data of $\text{NO}_3\text{-N}$ concentrations, Chl-a concentrations (YKB only) and water temperature at the three sampling sites from 2013 to 2017 provide between 232,542 and 269,300 data points per station (Fig. 2 and Table S1). The high frequency data of $\text{NO}_3\text{-N}$ concentrations are reliable based on the comparison with those measured in laboratory at the same time (see Fig. S2 and descriptions in the SI text for more details). Total riverine input and output of $\text{NO}_3\text{-N}$ during the five years were 440.76 Mg and 423.16 Mg, respectively (Fig. 3). Warne Bode (YBW) accounted for the dominant fraction of the $\text{NO}_3\text{-N}$ input (76.9%). The

outputs, on the other hand, were equally distributed between Hirtenstieg (50.2%) and the gallery (49.8%). Atmospheric deposition of $\text{NO}_3\text{-N}$ was 0.25 Mg, providing a marginal contribution to the total budget. Similarly, the change in $\text{NO}_3\text{-N}$ storage amounted to only 0.45 Mg. Over the five years, total amount of $\text{NO}_3\text{-N}$ being removed from and retained in the reservoir amounted to 17.85 Mg, corresponding to a total retention efficiency of 4.05%.

3.2 $\text{NO}_3\text{-N}$ retention on the annual scale

On the annual scale, $\text{NO}_3\text{-N}$ retention efficiency varied and ranged from -2.89% (2017) to 16.53% (2014) in Königshütte Reservoir (Fig. 4), while $\text{NO}_3\text{-N}$ retention rate varied from $-32.43 \text{ mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (2017) to $124.87 \text{ mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (2014). We found much higher $\text{NO}_3\text{-N}$ retention in 2014 compared to the other years. Statistical models predicted the inter-annual variations of $\text{NO}_3\text{-N}$ retention efficiency during 2013 to 2017 with distinct performances (Fig. 4). For the three models (RivR-N, David et al. and Windolf et al.) that only require hydraulic load (Q_s), predictions were mostly inconsistent with observations, with a tendency to underestimate the higher values (2014) and overestimate the other lower ones. On the other hand, for the other two models (SPARROW and NiRReLa) incorporating both Q_s and settling velocity (v_s), predictions were consistent with most of the observations except for the negative value in 2017, only when v_s was calibrated for each year separately. Our results indicate that $\text{NO}_3\text{-N}$ retention efficiency cannot be properly predicted by variability in Q_s only.

3.3 $\text{NO}_3\text{-N}$ retention on the weekly scale

The weekly N-retention showed considerable variation over the seasons that exceeded the inter-annual variance markedly, while weekly retention efficiencies ranged from -66.58%

to 99.05%, and the inter-annual retention efficiency varied between -3% to 17% (compare Fig. 4 and 5). We observed a significant seasonal pattern of weekly $\text{NO}_3\text{-N}$ retention efficiency with values generally highest in summer and lowest during late winter and early spring. For $\text{NO}_3\text{-N}$ retention rate (ranged from $-694.9 \text{ mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ to $857.1 \text{ mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$), a less significant seasonal patterns was observed, but we found lower variance in summer than in other seasons (Fig. S3). On the other hand, characteristic seasonal variations in $\text{NO}_3\text{-N}$ loading, $\text{NO}_3\text{-N}$ concentration, Q_s , WRT, water depth, water temperature and Chl-a concentrations were observed (Fig. S4). We found significant correlations between $\text{NO}_3\text{-N}$ retention efficiency (as well as retention rate) and all the seven factors above (Fig. S5). The correlation analysis suggested negative effects from $\text{NO}_3\text{-N}$ loading, $\text{NO}_3\text{-N}$ concentration, and Q_s , whereas positive effects from WRT, water temperature and Chl-a concentration on $\text{NO}_3\text{-N}$ retention were detected (Fig. 5 and Fig. S3). We therefore proceeded to establish multiple linear regression models to quantify the contributions of different factors on $\text{NO}_3\text{-N}$ retention efficiency and rate.

3.4 Statistical modeling of weekly $\text{NO}_3\text{-N}$ retention

On a weekly scale, we first considered Q_s , WRT, $\text{NO}_3\text{-N}$ loading, $\text{NO}_3\text{-N}$ concentration, water depth, water temperature and Chl-a concentration as the seven potential explanatory variables for the response variables of $\text{NO}_3\text{-N}$ retention efficiency and rate. We removed all the observations (weeks) without valid Chl-a data (29 out of 261). FG test implied the presence of multicollinearity among the seven explanatory variables (Chi-square test statistic 1442.36). The multicollinearity in the model primarily attributed to Q_s (variance inflation factor (VIF)=22.59), $\text{NO}_3\text{-N}$ loading (VIF=20.33) and $\text{NO}_3\text{-N}$ concentration (VIF=4.25), as the theoretical threshold value of VIF at 5% level of significance would be

2.14 for a degree of freedom of (6, 225). Q_s and $\text{NO}_3\text{-N}$ loading exhibited a strong correlation to WRT (Fig. S5). Given that hydraulic load Q_s and WRT are both scaling with the inflow discharge, and the strong correlation between $\text{NO}_3\text{-N}$ loading and WRT, Q_s and $\text{NO}_3\text{-N}$ loading were both discarded in the following model analyses. Collinearity was subsequently lower, whereas VIF of water temperature (3.62) and $\text{NO}_3\text{-N}$ concentration (3.00) were still high. We further removed these two variables, resulting in the explanatory variables including WRT, water depth and Chl-a concentration without multicollinearity. Initial results of multilinear regression modeling using OLS suggested the significant positive effects of WRT and Chl-a concentration ($p < 0.001$) on $\text{NO}_3\text{-N}$ retention. However, we found a significant spike at a lag of 1 (week) in the time series of response variables (retention rate, retention efficiency) and explanatory variables (WRT and Chl-a concentrations), implying first-order autocorrelation in the dataset (Fig. S6 and S7). The DW statistics were 1.0052 ($p < 0.01$) and 1.1786 ($p < 0.01$) for the models of retention efficiency and rate, respectively, both suggesting significant positive autocorrelation in model residuals. We concluded that the autocorrelation in model residuals needs to be accounted by using the GLS model. We selected the correlation structure of first-order autoregressive process (AR(1)). The best statistical model with explanatory variables including WRT and Chl-a explained 40.5% of total variability in weekly $\text{NO}_3\text{-N}$ retention efficiency (Table 2) with normally distributed residuals (Fig. S8). For $\text{NO}_3\text{-N}$ retention rate, the best model included WRT and Chl-a concentration as the explanatory variables, accounting for only 9.6% of the total variability (Table S2). We concluded that weekly $\text{NO}_3\text{-N}$ retention rate overall cannot be properly predicted by statistical modeling in Königshütte Reservoir. Water depth is not a significant explanatory variable in both models.

3.5 Process-based ecosystem modeling for NO₃-N retention

Without calibration, the process-based ecosystem model PCLake performed well in predicting the dynamics of NO₃-N and Chl-a concentrations in Königshütte Reservoir from 2013 to 2017 (NO₃-N: $R^2 = 0.859$, RMSE = 0.193; Chl-a: $R^2 = 0.702$, RMSE = 3.225; Fig. 6A and B). In addition, PCLake model prediction for TN, ammonia, organic N and TP were consistent with observations (Fig. S9 and Table S3). This result implied that the chance of overparameterization was low in the mechanistic model. Intriguingly, PCLake showed a higher prediction power for NO₃-N retention efficiency than the statistical model (Fig. 6C), such that PCLake accounted for 58.0% of the variability in NO₃-N retention efficiency, while statistical models with explanatory variables of WRT and Chl-a concentration obtained a lower value (40.5%). One reason for the superior power of PCLake was its ability to predict negative NO₃-N retention efficiency that usually occurred during winter and spring times, whereas the statistical model could hardly predict negative retention efficiencies (Fig. 6C). The regression line from PCLake-derived N retention is close to the 1:1 line while the regression line from the statistical model is strongly deviating from the 1:1 line and had a much lower slope.

4. Discussion

In this study, high frequency monitoring data facilitated the investigation of NO₃-N retention in a small, heavily flushed reservoir over short and long temporal scales, and allowed us to compare statistical and process-based ecosystem models regarding their capability in predicting N retention in this complex lentic water system.

4.1 Annual scale N retention: the role of settling velocity

Our statistical-based estimation of $\text{NO}_3\text{-N}$ retention in Königshütte Reservoir on annual scale was comparable to other studies. During 2013 to 2017, annual $\text{NO}_3\text{-N}$ retention efficiency was up to 17% with a WRT ranging from 2.96 to 4.69 d, while the retention rate ranged from -32 to 125 $\text{mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. In comparison, an investigation on 16 Danish lakes (WRT = 14.6-251.6 d) reported that $\text{NO}_3\text{-N}$ retention efficiency ranged from 11 to 72%, and the corresponding rate ranged from 47-234 $\text{mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (Windolf et al. 1996). In addition, a study in a small lake in Illinois, USA (WRT = 5-32 d) suggested a $\text{NO}_3\text{-N}$ retention efficiency of 37% and a rate of 91.23 $\text{mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ (Kovacic et al. 2000). Our findings were in line with the previous studies, indicating a potential of N retention in small reservoirs that has been overlooked as an important sink of nutrient in inland ecosystems (Cheng and Basu 2017).

We supported our findings for the importance of v_s by recalculating the N retention in another system (Lake Shelbyville) reported by David et al. (2006). Field observations in Lake Shelbyville suggested an averaged N retention efficiency of 58% (31-91%) over 23 years. David et al. (2006) applied RivR-N model (Seitzinger et al. 2002) with the observed Q_s (ranged 5.27-27.93 $\text{m}\cdot\text{yr}^{-1}$) for Lake Shelbyville, which resulted in a underestimated efficiency (ranged 26-48% with a mean of 32%). Alternatively, we used the SPARROW model with the reported v_s based on denitrification rate (21.02-94.60 $\text{m}\cdot\text{yr}^{-1}$) (David et al. 2006) and obtained an efficiency of 42.9-94.7%, which fitted much better to the field observations. David et al. (2006) argued that the RivR-N model was developed based on a dataset from lakes with low N concentrations; therefore, the model underestimated the N retention with increasing WRT. They proposed a modified RivR-N model (Table 1), which fitted better to the data for Lake Shelbyville. However, we found that the modified RivR-N model could not accurately predict N retention in Königshütte Reservoir, primarily because

Q_s in Königshütte Reservoir (258.8-436.1 $\text{m}\cdot\text{yr}^{-1}$) was much higher than that in Lake Shelbyville, which was out of the calibration domain of the model. Overall, our reanalysis highlights the necessity of v_s -inclusive modeling in predicting $\text{NO}_3\text{-N}$ retention in reservoirs on the annual scale in addition to hydrological factor (e.g. Q_s).

Our statistical modeling of annual N retention efficiency only worked out if v_s was used as a free parameter, i.e. changed annually, which highlights the importance of settling. However, from a mechanistic point of view, settling in models for N retention can be misleading because N is not really settling unless being absorbed by phytoplankton that is subject to sedimentation. In addition, denitrification as an important N elimination process is completely different from settling. To reconcile this contradiction, we argue that in the simplified, annual scale N retention models (Table 1), the parameter v_s effectively captures a suite of N cycling processes. Specifically, v_s basically scales the rate of N removal in lentic systems and includes both settling of organic N (which finally burial within sediments) and denitrification. In addition, other factors including the Fickian diffusion from the sediments and/or ammonification may indirectly link to v_s and in turn affect N retention. Overall, v_s represents all biogeochemical processes that are related to N retention, thereby providing a critical predictor to N retention in addition to Q_s .

We found the calibrated v_s for Königshütte Reservoir were 25, 45, 1, 15, and 1 $\text{m}\cdot\text{yr}^{-1}$ for 2013 to 2017, respectively (Fig. 4). The values were highly variable between years that might be driven by multiple processes aforementioned. In addition, for a system at mesotrophic state, we did not expect such high v_s values, as a study on nitrogen retention suggested that on a global scale, reservoirs and lakes have averaged v_s of 13.66 and 6.83 $\text{m}\cdot\text{yr}^{-1}$, respectively (Harrison et al. 2009). Highest v_s in our study (45.0 $\text{m}\cdot\text{yr}^{-1}$ in 2014) was even in the same magnitude of that in Lake 227 (73.3 $\text{m}\cdot\text{yr}^{-1}$), which was a highly eutrophic

experimental lake (Ruan et al. 2014, Schindler et al. 2008). Meanwhile, v_s was found up to 94.6 m·yr⁻¹ in Lake Shelbyville located in an agriculture region (David et al. 2006). One explanation could be the growth and temporal dominance of diatom in the reservoir. Diatoms could contribute to a high settling velocity of N due to their siliceous frustules and slow mineralization (Wentzky et al. 2018b), which in turn led to elevated flux of NO₃-N sedimentation from the water column into sediment surface.

The addition of v_s in modeling approaches increases the difficulty towards a general-applicable predictive model, because accurate estimation of settling velocity becomes mandatory for one specific system in one individual year. Ultimately, the application of an annual scale settling velocity appears to be oversimplified because our study demonstrated that N retention shows a strong seasonal pattern and this feature is fully ignored when applying a certain elimination rate on an annual scale. This calls for a better strategy using process-based modeling (see below).

4.2 Weekly scale modeling: new insights into NO₃-N retention in reservoirs

The weekly scale statistical modeling allowed us to investigate NO₃-N retention at shorter, i.e. intra-annual time scales. First, our analysis highlighted the importance of biological process, i.e. algal growth (represented by Chl-a concentration), on NO₃-N retention efficiency in the reservoir, which were usually overlooked by the existing statistical models. We found higher NO₃-N retention efficiency in summer than in other seasons (Fig. 5), which followed the pattern of Chl-a concentration (Fig. S4). Intensified algae growth in summer contributed to NO₃-N retention via a three-step process: 1) N uptake by algae; 2) proliferation of algal cells; and 3) sedimentation of dead algae with N that would be either denitrified or buried in sediment. We performed an additional assessment on the factors determining the

phytoplankton assemblage in the reservoir (Fig. S10). We found that phytoplankton assemblage was predominantly driven by P (see SI text for more details). Based on either data analysis (Finlay et al. 2013, Tong et al. 2019) or whole-ecosystem experiments (Kaste and Lyche-Solheim 2005), importance of P in dictating N cycling of freshwater ecosystems had previously been well-recognized. Besides, we showed that due to low ammonia concentrations, phytoplankton used the abundant nitrate as the alternative N source, which in turn imposed a profound effect on the $\text{NO}_3\text{-N}$ retention in Königshütte Reservoir. The critical role of algae in $\text{NO}_3\text{-N}$ retention identified in this study therefore holds a consistency to the contribution from P, because it had been proved that the sedimentation of N from water column to anoxic sediment served as the underlying mechanisms for the impact of P on N cycling (Small et al. 2014). Second, our model supported the previous finding that WRT was a positive determinant of $\text{NO}_3\text{-N}$ retention efficiency in lakes and reservoirs (Finlay et al. 2013, Tong et al. 2019), because longer WRT simply allowed for longer time for more intensive N removal processes within the water column and sediment. Overall, we found an interesting combination of both hydrological (WRT) and biological factors (Chl-a) that determined the weekly scale $\text{NO}_3\text{-N}$ retention. Although this is in line with the annual scale statistical modeling suggesting the joint contributions from both Q_s and v_s , it is also pointing out clearly that annually averaged retention efficiencies are misleading because the underlying processes undergo strong seasonal change and therefore call for investigation on sub-annual time scales.

Other potential influential factors were discarded by either collinearity analysis or stepwise regression modeling. Due to its significant negative correlation (Fig. S5), $\text{NO}_3\text{-N}$ concentration (or $\text{NO}_3\text{-N}$ pool) in the reservoir was considered as the consequence rather than the driver of $\text{NO}_3\text{-N}$ retention, and therefore was excluded from the statistical model. This

was against previous findings (Windolf et al. 1996), where $\text{NO}_3\text{-N}$ concentration was modeled as a positive explanatory variable for retention. We argue that in a small time scale (such as weekly), the general assumption that higher $\text{NO}_3\text{-N}$ concentration would lead to higher denitrification rate (Pina-Ochoa and Álvarez-Cobelas 2006) and in turn higher $\text{NO}_3\text{-N}$ retention efficiency (David et al. 2006, Windolf et al. 1996) does not apply, whereas negative relation between $\text{NO}_3\text{-N}$ concentration and retention were found. The lower $\text{NO}_3\text{-N}$ concentration in summer was attributed to the lower $\text{NO}_3\text{-N}$ loading and high retention efficiency (Fig. S4). This was because on a weekly scale, $\text{NO}_3\text{-N}$ concentrations in reservoir were positively related to Q_s (Fig. S5), which was a constraint on $\text{NO}_3\text{-N}$ retention. Furthermore, the relative low $\text{NO}_3\text{-N}$ concentration in Königshütte Reservoir (0.050-2.099 $\text{mg}\cdot\text{L}^{-1}$) might have limited the sediment denitrification (Wall et al. 2005). The total $\text{NO}_3\text{-N}$ retention rate ranged from 42.74 to 175.09 $\text{mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$, over 80% of which could be attributed to denitrification based on estimations in other systems (Garnier et al. 2010). However, this was much lower than the value observed in other systems (e.g. 169.9-616.4 $\text{mgN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ in Lake Shelbyville) (David et al. 2006). As a result, the positive relation between $\text{NO}_3\text{-N}$ concentration and retention might be confounded.

We found no effect of water temperature on $\text{NO}_3\text{-N}$ retention efficiency, which was against our assumption inferred from the similar seasonal patterns between $\text{NO}_3\text{-N}$ retention efficiency and water temperature (Fig. 5 and Fig. S4). Previous studies had not reached a consensus on the effects of temperature on denitrification rates in aquatic system, as positive (Seitzinger 1988), negative (Sørensen et al. 1979) and no relations (Cavaliere and Baulch 2018, Harrison et al. 2009, Pina-Ochoa and Álvarez-Cobelas 2006) were reported. Despite the insignificant contribution of temperature to our model, we argue that on a seasonal scale, temperature should have a positive effect on $\text{NO}_3\text{-N}$ retention efficiency, which however

could have been masked due to potential linkage between temperature and other factors (such as WRT and Chl-a concentration) and therefore remained difficult to be isolated. The same could apply to water depth. In fact, water depth can be related to water-sediment interactions that affects profoundly the processes driving NO₃-N removal (Windolf et al. 1996).

Overall, our statistical modeling on a weekly scale unraveled the critical role of Chl-a, which was well supported by the interactions of N and P cycling in aquatic systems. Therefore, our findings provided new insights in our understanding of N retention in reservoirs, and highlighted the necessity to zoom into seasonal variations in the hydrological and biological dynamics in order to identify the underlying mechanisms in N retention in freshwater ecosystems that were masked in annual scale investigations.

4.3 Process-based ecosystem modeling

The comparative modeling approach demonstrates the advantages and disadvantages of process-based relative to statistical modeling. We showed that predictions of N retention with process-based modeling (PCLake) without parameter calibration were more accurate than statistical models (Fig. 6). Our results exemplify the advantages of process-based models, which rely on the explicitly mechanistic description on N cycling. This allows for the direct prediction on NO₃-N concentrations in the reservoir with high accuracy based on external conditions and in turn for the precise calculation of retention efficiency. On the contrary, statistical models are limited in many aspects, such as a lack of mechanistic understanding, difficulty in addressing nonlinear relationships in ecosystems, and limited transferability when applied to conditions beyond their calibration domain (Janssen et al. 2019). Our results demonstrate how these limitations could constrain the prediction power on the annual scale NO₃-N retention efficiency (Fig. 4), and that only ~40% of the variation in

NO₃-N retention efficiency on a weekly scale could be explained (Table 2). On the other hand, statistical models are simple and powerful tools that have been widely used in analyzing nutrient retention (Finlay et al. 2013), and they allow upscaling to the global level (Harrison et al. 2009), for which mechanistic models are inadequate due to higher demand for parameterization and computation. This is indeed the advantages of statistical models. Our study demonstrates that the final statistical models are fairly simple with limited number of variables. By contrast, process-based model (PCLake) is relatively complex comprising a multitude of state variables and processes. Consequently, it would be essential to reconcile the higher likelihood of overparameterization, which requires more effort in modeling evaluation. However, PCLake model has been parameterized based on data from over 40 temperate shallow lakes (Janse et al. 2010), and our study demonstrates that this parameter set is capable of representing the general patterns in other temperate lake/reservoir systems. Additionally, recent studies have nicely illustrated the possibility to overcome the disadvantages of process-based models such that mechanistic models at intermediate complexity could be also used for regional- or global-scale investigation (Bruce et al. 2018, Janssen et al. 2014). Overall, we advocate that both model types have their application domains and the combination of both would be powerful in projecting NO₃-N retention efficiency in reservoirs and potentially other systems such as natural lakes.

4.4 Merits and limitations of high frequency monitoring

As far as we know, this is the first study to make an extensive use of high frequency data for N retention evaluation in a small, heavily flushed reservoir. The small reservoir system with relatively simple hydrological features allowed us to establish high-frequency monitoring networks and N budget over five years, with which we performed in-depth

analysis of N retention patterns across different temporal (annual and weekly) scales and unraveled hidden mechanisms. We found apparent intra-annual patterns (weekly) and highlighted the role of biological factors, which was not resolvable using dataset with less temporal frequency. The extremely rich dataset was subsequently used to parameterize both statistical models along with a well-developed process-based model to 1) shed light on their predictive abilities for N retention and 2) offer insights and implications for lake and reservoir management of excess N. In addition, compared to previous studies with datasets from multiple lakes and temporally coarse sampling, studying N retention in one specific system with high frequency data has the advantage that confounding factors due to differences among lakes play no role (Kong et al. 2017b). Overall, we presented new research questions and also a novel methodological framework, which could be applicable to other similar systems and investigations.

We found uncertainty embedded in the nutrient budget and retention based on data from monthly or biweekly monitoring. We resampled in our high frequency monitoring dataset to mimic both biweekly and monthly monitoring schemes. In the biweekly scheme, NO₃-N concentration data in all inflows and outflows were selected from the high frequency data starting from one of the 14 days between Jan. 1st-14th, 2013, and then collected biweekly onwards. We therefore obtained 14 scenarios of biweekly sampling schemes for each year from 2013 to 2017. For monthly scheme, the starting time was one of the 30 days between Jan. 1st-30th, 2013, and then collected every 30 days onwards. We calculated NO₃-N retention efficiency and rate using these 14 (or 30) subsets of data, while we linearly interpolated the NO₃-N concentrations between sampling dates as the common practice. We compared these results to the values based on high frequency data that was considered as the real retention (Fig. 7). Both NO₃-N retention efficiency and rate can deviated enormously from the real

data, implying that the calculated NO₃-N retention from biweekly and monthly sampling data can be largely under- or over-estimated.

Nonetheless, there was a tradeoff of benefits gained by monitoring a greater number of water quality variables with reasonable temporal frequency and by focusing on a smaller subset of variables with the fine granularity. High frequency data were limited by the measurable water quality variables. In our study, only nitrate could be directly measured at high frequency, while other nitrogen species (e.g. ammonia and organic N) and also other chemicals (e.g. P and silica) were missing, which would be critical in understanding the characteristics of the aquatic systems. In addition, high frequency monitoring is subject to issues such as the reliability due to occasional functional failure in situ. Our study highlights the importance of high frequency data in improving the N retention evaluation in reservoirs, which would be more powerful when combined with regular monitoring programs.

5. Conclusions

Our study supports the critical role of small lentic aquatic systems in contributing to the nutrient retention in inland waters. Annual-averaged NO₃-N retention efficiency of a small reservoir in central Germany could be up to 17% with a five-year averaged retention efficiency of ~4% in such a system characterized by a water residence time (WRT) of ~4 days. While average annual N retention in this highly flushed system remains rather small, effective N retention on shorter time scales (weekly) can substantially deviate from this annual mean and in our study ranged from -67% to 99%. The reservoir often displayed negative retention in winter (i.e. it was a source of N due to mineralization processes) and high positive retention in summer (i.e. acting as a sink for N), which has implications for management of downstream waters. Beyond the morphological and hydrological features, our

study unravels the critical role of phytoplankton dynamics as a biological factor in determining N retention in reservoirs, which makes a step towards a comprehensive understanding on the mechanisms of nutrient retention in inland freshwater systems. We attribute our findings to the availability of the high frequency monitoring data, which has shown the large potential in identifying new mechanisms that cannot be easily realized by biweekly/monthly sampling routine. In addition, our results exemplify the superior prediction capacity of process-based ecosystem models over statistical models on N retention. We therefore advocate taking advantage of the emerging high frequency data and advancements in process-based ecosystem models in evaluation of nutrient retention in lakes and reservoirs.

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Notes

The authors declare no conflict of interest.

589

590 **Appendix A. Supplementary materials**

591 Additional Information include: SI Text for difference between N retention and
592 removal, a brief description on the high frequency data, and an assessment on the factors that
593 determine the phytoplankton assemblage. SI Figures S1-S10. SI Tables S1-S3.

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Fig. 1. Location of Königshütte Reservoir in central Germany. (A) Elevation of the catchment (denoted by the white polygon) and the surrounding area. Locations of the major tributaries (Kalte Bode, Warme Bode), and the two outflows (Hirtenstieg and water gallery) as well as the main Rappbode Reservoir are shown. (B) Land use type distribution of the catchment. Locations of the three sample sites (YBK: Kalte Bode; YBW: Warme Bode; YKB: in reservoir) are highlighted.

Fig. 2. Time series of high frequency monitoring data in Königshütte Reservoir during 2013 to 2017. (A) Hydrological variables including total water inflow and outflow ($\text{m}^3 \cdot \text{s}^{-1}$), net water flux ($\text{m}^3 \cdot \text{s}^{-1}$) and water level (m a.s.l.). **(B)** $\text{NO}_3\text{-N}$ concentration ($\text{mg} \cdot \text{L}^{-1}$) in three sampling sites. **(C)** Water temperature ($^{\circ}\text{C}$) in three sampling sites and Chl-a concentration ($\mu\text{g} \cdot \text{L}^{-1}$) in the reservoir.

Fig. 3. Total NO₃-N budget in Königshütte Reservoir from 2013 to 2017. The box in the middle represents the reservoir. The line thickness is proportional to the NO₃-N fluxes in the unit of Mg (=10⁶ gram).

Fig. 4. Annual NO₃-N retention efficiency and statistical modeling results. (A) Observed annual NO₃-N retention efficiency during 2013-2017 in Königshütte Reservoir, together with predictions from five statistical models listed in Table 1. **(B)** Other limnology variables (annual average) during 2013-2017 in Königshütte Reservoir. *N_load*: NO₃-N loading (gN·m⁻²·d⁻¹); *WRT*: water residence time (d); *Qs*: the areal hydraulic loading (m·d⁻¹); *vs_calibrated*: calibrated apparent settling velocity (m·yr⁻¹); *Chla*: Chlorophyll a concentration (µg·L⁻¹); *Temperature*: water temperature (°C).

Fig. 5. Weekly $\text{NO}_3\text{-N}$ retention efficiency and relationship with other factors in the reservoir. (A) Weekly $\text{NO}_3\text{-N}$ retention efficiency during 2013-2017. (B) Weekly $\text{NO}_3\text{-N}$ retention efficiency against $\text{NO}_3\text{-N}$ loading ($\text{gN}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$) and the areal hydraulic loading (Q_s ; $\text{m}\cdot\text{d}^{-1}$). (C) $\text{NO}_3\text{-N}$ concentration ($\text{mg}\cdot\text{L}^{-1}$) and water residence time (WRT; d). (D) Weekly $\text{NO}_3\text{-N}$ retention efficiency against water temperature ($^{\circ}\text{C}$) and Chlorophyll-a concentration (Chl-a ; $\mu\text{g}\cdot\text{L}^{-1}$). The red line in each panel is the smoother line using ‘geom_smooth’ with either ‘lm’ or ‘loess’ method selected by the program automatically in the R package ‘ggplot2’ (Wickham 2016). The grey area is the confidence interval.

Fig. 6. Observed against modelled data for Königshütte Reservoir from 2013 to 2017. (A and B) Probe and PCLake simulated NO₃-N and Chl-a concentrations on a daily scale (NO₃-N: $R^2 = 0.859$, RMSE = 0.193; Chl-a: $R^2 = 0.702$, RMSE = 3.225). (C) NO₃-N retention efficiency. Modelled values include both predictions from statistical model (Table 2) and process-based ecosystem model (PCLake). Red and blue solid lines are best fits from linear regression for statistical model predictions ($y = 0.39x + 8.08$, $R^2 = 0.405$, $n = 232$, $p < 0.001$) and PCLake predictions ($y = 0.88x + 0.77$, $R^2 = 0.580$, $n = 232$, $p < 0.001$) to observations, respectively. The grey area is the confidence intervals (95%). Solid black line is the 1:1 line representing a perfect prediction to the observed data.

Figure 7. Comparison of NO₃-N retention calculated by both high frequency monitoring and the biweekly/monthly monitoring data. The biweekly/monthly scheme is mimicked from the resampling in the high frequency data during 2013 to 2017. **(A)** NO₃-N retention rate and **(B)** NO₃-N retention efficiency. Variability of the biweekly/monthly random sampling data is represented by medians (P50), and the 5th (P5), 25th (P25), 75th (P75), and 95th (P95) percentiles.

799 **Table 1.** Overview of the statistical models for N retention efficiency ($N_{ret,\%}$) in lakes or
800 reservoirs on an annual scale. Q_s ($\text{m}\cdot\text{yr}^{-1}$) is the areal hydraulic loading. v_s ($\text{m}\cdot\text{yr}^{-1}$) is the
801 apparent settling velocity. Z (m) is the water depth.

Model name	Equation	References
SPARROW	$N_{ret,\%} = \frac{1}{1 + v_s(Q_s)^{-1}}$	(Alexander et al. 2002)
NiRReLa	$N_{ret,\%} = 1 - \exp \frac{-v_s}{Q_s}$	(Harrison et al. 2009)
RivR-N	$N_{ret,\%} = 88.45 \cdot Q_s^{-0.3677}$	(Seitzinger et al. 2002)
David et al.	$N_{ret,\%} = 243.00 \cdot Q_s^{-0.5632}$	(David et al. 2006)
Windolf et al.	$N_{ret,\%} = 96 \cdot Q_s^{-0.48} \cdot Z^{0.34}$	(Windolf et al. 1996)

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Table 2. Statistical modeling results for weekly NO₃-N retention efficiency using stepwise multivariable linear regression with generalized least squares (GLS). r^2 is the coefficient of determination. $Adj.r^2$ is the r^2 adjusted for the number of explanatory variables. $RMSE$ is the root mean squared error. AIC_c is the Akaike's information criterion corrected for small sample sizes. BIC is the Bayesian information criterion.

<i>Retention efficiency</i> (<i>n=232</i>)	r^2	$Adj.r^2$	$RMSE$	AIC_c	BIC	F <i>statistic</i>	P <i>value</i>
<i>Explanatory variables</i>							
<i>WRT, Chl-a</i> (best model)	0.4098	0.4046	22.01	2031.83	2048.99	79.91	<0.001
<i>WRT</i>	0.3265	0.3236	23.65	2042.66	2056.41	111.5	<0.001

<i>Explanatory variables</i>	<i>Coefficients</i>	<i>Std. Error</i>	<i>t ratio</i>	<i>P value</i>
(<i>Intercept</i>)	-18.013	4.4227	-4.07	<0.001
<i>WRT</i>	3.096	0.4058	7.63	<0.001
<i>Chl-a</i>	1.801	0.4842	3.72	<0.001