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Nitrogen Retention Effects under Reservoir Regulation at Multiple Time Scales in a Subtropical River Basin

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Abstract: Reservoirs are an important nitrogen sink as a result of their retention effect, but their retention performance may vary with hydrologic conditions with time-varying characteristics, which also change them from being a sink to source over time. This study uses a coupled modelling system (Soil and Water Assessment Tool (SWAT) and a two-dimensional hydrodynamic and water quality model (CE-QUAL-W2) to analyze the nitrogen retention effect and influential factors at annual, monthly, and daily scales in Shanmei Reservoir in southeast China. The results showed that there was a positive retention effect of total nitrogen (TN), nitrate-nitrogen (NO₃-N) and ammonia nitrogen (NH₄-N) in most years, with average retention rates up to 12.7%, 7.83% and 26.17%, respectively. The reservoir serves mainly as a nitrogen sink at an annual scale. The monthly retention performances of TN and NO₃-N were observed during the wet season (April-October) with higher water temperature and lower velocity, while a release effect occurred during the dry season (November–March). For NH₄-N, which is prone to nitrification, the retention effect lasted longer, from May to December. The daily nitrogen retention process changed more dramatically, with the retention rate varying from -292.49 to 58.17%. During the period of dispatch, the regulated discharge was the primary factor of daily retention performance, while the hydraulic residence time, velocity and water level were all significantly correlated with nitrogen retention during the period without dispatch.

Keywords: nitrogen retention; release effect; reservoir regulation; multiple time scales; hydrodynamic factors

1. Introduction

A large number of water conservation projects have been instigated worldwide to retain river water behind dams, and these have significantly changed hydrological characteristics, physical transformations, nutrient transfers, and transport flux of rivers [1,2]. Nutrients in reservoirs are primarily removed from water by certain processes that include sediment burial, temporary storage in biomass, and denitrification [3–5]. This may reduce the amounts of nutrients transported downstream. Nitrogen is the material basis of the biogeochemical cycle and the main element of eutrophication. The impacts of reservoirs on nitrogen retention within watersheds may include the reduction of the nitrogen transported downstream and the slowing of the trend of eutrophication in estuarine waters [6]. Estimating the nitrogen retention effect in a reservoir is of great importance for controlling eutrophication and improving the aquatic environment.



Many recent studies have focused on nitrogen retention in reservoirs. In most studies, nitrogen nutrients are supposed to be retained by river damming, with retention rates ranging from 5% to 90%, with the reservoir acting as a nitrogen sink [7-9]. Other studies have concluded that nitrogen retention might have positive or negative effects in different periods. During the period of low inflow, the reservoir may release nitrogen in its role as a nitrogen source [10]. The retention effects may change according to the time scale, with the role of the reservoir shifting from a source to sink. The nitrogen retention in the reservoir may be influenced by the inflow, nutrient load, water residence time, temperature, and mean depth [3,11]. These factors have time-variation characteristics, leading to temporal-scale differences in nitrogen retention at different time scales [12]. In recent years, most studies into nutrient retention in reservoirs have been concerned with an evaluation of the retention flux at longer time scales (e.g., monthly, annual, or longer). There is little research into the effects of the characteristics of watershed runoff and reservoir outflow at shorter time scales; e.g., daily [7,13]. Apart from modifying the natural flow regime, the residence time of the water, and the seasonal fluctuations of water temperature and dissolved oxygen content [14,15], the daily operation of a reservoir also has a great influence on the decomposition, mineralization, and transformation of nutrients [16]. However, systematic studies on the effects of various factors on the retention efficiency of nutrients at different time scales are relatively rare.

Large reservoirs usually have multiple functions of use; i.e., flood control, irrigation, municipal/industrial water supplies, and power production [17,18]. The way in which a dam is used to regulate runoff alters the seasonal fluctuations of hydrological factors and also has a direct impact on the nitrogen retention process [19]. The proper regulation of reservoir inflow, outflow and water level are expected to increase the water velocity, which enhance the hydrodynamic conditions and reduce the nutrient concentrations and the growth of phytoplankton in the reservoir [20]. However, there are few studies on the distinction of the effects of key factors on nitrogen retention with or without reservoir regulation, which is significant in providing guidance for the implementation of appropriate management to improve water quality and control potential eutrophication in the reservoir, downstream and estuary.

Shanmei Reservoir, the most important water source of Quanzhou City, is located in southeast China. Rapid population growth and socioeconomic and agricultural development in the Shanmei Reservoir watershed have substantially increased the pollutant loads delivered to the reservoir. High total nitrogen concentrations have caused a serious deterioration of the water quality with regard to irrigation and water supply. To investigate the non-point source pollution in the upland watershed and nitrogen retention in the reservoir, a coupled watershed–reservoir modeling system consisting of a watershed distributed model (Soil and Water Assessment Tool (SWAT)) and a two-dimensional laterally averaged water quality model (CE-QUAL-W2) was applied. In this study, we applied this coupled modeling system to simulate the nitrogen retention effects among TN, NO₃-N, and NH₄-N at annual, monthly, and daily scales, and (2) to evaluate the influence of reservoir regulation on nitrogen retention at different time scales.

2. Study Area and Methods

2.1. Study Area

The Shanmei Reservoir is a multi-year regulated storage reservoir located in southeastern China. It is a large multipurpose reservoir with power generation, irrigation, and water supply functions, which supplies drinking water for Quanzhou City, which has more than four million residents downstream of the reservoir. It has a drainage area of 1023 km², with an average annual runoff of 14×10^8 m³. The watershed is drained by inter-basin water transfer and two rivers, the Taoxi and Huyangxi rivers. The amount of water diversion from Longmentan Reservoir is 4.17×10^8 m³. These rivers feed into the Shanmei Reservoir (Figure 1).

The Shanmei Reservoir has a surface area of 26 km², with a length of 12 km, a maximum width of 7 km, and a maximum depth of 50 m (Figure 2). The reservoir has a total storage capacity of 6.55×10^8 m³ and an effective storage of 4.72×10^8 m³, with the normal high-water level reaching 96.48 m. The mean annual precipitation is 1600 mm, but there is great inter-annual variability. The precipitation in the dry years is less than half of that in the wet years. The seasonal variations within the year are also very distinct due to the subtropical monsoon climate, with precipitation in the dry season (November–March) only accounts for 16%.



Figure 1. Shanmei Reservoir watershed stream networks.



Figure 2. (a) Segmentation and (b) vertical computational grids of the Shanmei Reservoir.

2.2. Coupled Modeling System

In our previous study, we conducted a coupled watershed–reservoir modeling system consisting of a watershed distributed model (SWAT) and a two-dimensional laterally averaged water quality model (CE-QUAL-W2) [21]. The watershed model (SWAT) is a dynamic, semi-distributed, and physically-based model. It was first developed by the USDA Agricultural Research Service (ARS) to simulate hydrological processes in uplands and streams and generates quantitative information regarding water yield, sediment yield, and nutrient loadings [22–24]. The spatial data used in SWAT include a digital elevation model (DEM), the land cover and soil maps. The topography is represented by a 30 × 30 m elevation raster, which was obtained from the International Scientific Data Platform of the Chinese Academy of Sciences (http://datamiffor.csdb.cn/admin/datademMain/jsp). The soil information map (1:500,000) from the Soil Fertilizer Laboratory of Fujian Province was used to identify ten soil types in the watershed. The land cover data of 2006 was obtained from an interpretation of the Landsat Thematic Mapper (TM) remote-sensing images, which were classified into eight types including rice, rainfed cropland, forest, orchard, grassland, medium density residential, water body and bare land. In addition, the daily precipitation and climate data for 1990–2010 were obtained from 16 precipitation stations and two weather stations. In the study, the Shanmei Reservoir watershed was divided into 38 sub-basins and 297 hydrology response units (HRUs), shown in Figure 1.

The characteristics of the hydrological and thermal properties and of the biogeochemical processes in the Shanmei Reservoir were simulated using a two-dimensional (longitudinal/vertical) hydrodynamics and water quality model named CE-QUAL-W2, which was developed by the US Army Corps of Engineers and has been applied widely [25–27]. In this study, Shanmei Reservoir was divided into two branches, with a total of 18 segments, covering the area of sub-basins 36, 37, and 38 in the SWAT model. The main body of the reservoir from Masi County to the Shanmei Dam section was designated Branch 1, with a length of 9.6 km and consisting of 11 segments (2 to 12). The other riverine section, from Jiudu Town to the middle of the reservoir, was designated Branch 2, with a length of 2.4 km and consisting of 3 segments (15 to 17) (Figure 2a). There are 28–38 computational vertical layers, each 1.5 m thick, resulting in 463 grids in total (Figure 2b). The orientation of each segment relative to geographic north was determined based on the average stream centerline in that segment.

To couple the two models, the daily flows and nitrogen concentrations from sub-basins 36 and 37 simulated by SWAT served as the inflow boundary conditions of Branch 1 and 2 for the CE-QUAL-W2 model. The overland flow from sub-basins 36, 37, and 38 simulated by SWAT were adopted as evenly distributed tributary inflows into the reservoir. The associated concentrations of water constituents were also used as inputs.

We evaluated the performance of the daily runoff simulated by SWAT using a five-year period (2001–2005) for calibration and another five-year period (2006–2010) for validation. Due to the issue of data availability, sediment calibration was based on data during the period from 1995 to 1997. Daily water quality data were used for calibration over a two-year period (2008–2009) and for validation over a one-year period (2010). As shown in Table 1, the simulated runoff performed well with a Nash–Sutcliffe efficiency (E_{NS}) of 0.88 for calibration and 0.87 for the validation period. The daily and monthly E_{NS} values of the sediment were 0.58 and 0.77, respectively, which are acceptable for this modeling accuracy. On the basis of the SWAT simulation, we calibrated CE-QUAL-W2. The absolute mean error (AME) and root mean square error (RMSE) of water level, temperature, dissolved oxygen (DO), NO₃-N, TN, and NH₄-N were rather small, and the normalized objective function (NOF) was always between zero and one, which is still within the range of acceptable accuracy. Therefore, the coupled model reasonably reflected the hydrodynamic processes and water quality in the Shanmei Reservoir and its watershed. Specific calibration details of the coupled model were given in [21].

Table 1. Calibration and validation results of the hydrological and water quality indexes for the Soil and Water Assessment Tool (SWAT) model and the two-dimensional hydrodynamic and water quality model (CE-QUAL-W2).

Index	ENS		AME		RMSE		NOF	
macx	Calibration	Validation	Calibration	Validation	Calibration	Validation	Calibration	Validation
Runoff (m ³ ·s ⁻¹)	0.88	0.87	-	-	-	-	-	-
Sediment (t)	0.58	0.51	-	-	-	-	-	-
Water level (m)	-	-	0.28	1.81	0.35	1.83	0.00	0.02
Water temperature (°C)	-	-	0.93	1.87	1.09	2.36	0.05	0.10
$DO(mg \cdot L^{-1})$	-	-	0.73	1.03	0.89	1.07	0.11	0.11
NO_3-N (mg·L ⁻¹)	-	-	0.38	0.39	0.56	0.59	0.27	0.32
TN (mg·L ^{-1})	-	-	0.61	0.13	0.82	0.14	0.34	0.06
NH_4 -N (mg·L ⁻¹)	-	-	0.03	0.03	0.04	0.04	0.59	0.35

The E_{NS} values of daily runoff and sediment were applied to evaluate the performance of SWAT model; the absolute mean error (AME), root mean square error (RMSE) and normalized objective function (NOF) of water level, water temperature, DO, NO₃-N, TN and NH₄-N were calculated to assess the performance of CE-QUAL-W2 model.

2.3. Nitrogen Retention Calculation and Influential Factor Analysis

Applying the coupled modeling system, the daily runoff and TN concentrations of inlet and outlet segments of the reservoir were simulated during the period 1991–2010. Based on the calculation of input and output nitrogen flux at annual, monthly, and daily time scales, the nitrogen retention effect in the reservoir was evaluated using the nitrogen retention flux (N_{ret}) and nitrogen retention rate (R_N) using the following equations [13]:

$$N_{\rm ret} = N_{in} - N_{out} \tag{1}$$

$$R_N = \frac{(N_{in} - N_{out})}{N_{in}} \times 100\%$$
 (2)

$$N = \frac{\sum_{i=1}^{n} C_i Q_i}{n}$$
(3)

where N_{in} is that portion of the nitrogen flux simulated as entering the reservoir daily (t N·day⁻¹) and N_{out} is the portion of the nitrogen flux simulated as exiting the reservoir daily (t N·day⁻¹). Here, Q_i is the instantaneous flow of the reservoir (m³·s⁻¹), C_i is the simulated nitrogen concentration (mg·L⁻¹), and *n* is the number of days with concentration and flow data (d). When the values of N_{ret} and R_N were positive, a retention effect of nitrogen in the reservoir was shown; otherwise, the negative values showed a release effect.

Nitrogen retention performance is determined by a number of factors, including hydrological and hydrodynamic conditions (inflow runoff, hydraulic residence time (HRT), velocity, and water level), nitrogen load, and water temperature in some studies, mostly using continuous monitoring data [9,28,29]. However, it is not feasible to conduct the analysis of the nitrogen retention effect and influential factors at multiple time scales due to the lack of long-term data in the area, while the coupled use of the upland watershed hydrological model (SWAT) and downstream waterbodies model (CE-QUAL-W2) was able to overcome the disadvantages mentioned above. Based on the coupled modeling system, our previous studies have found that the nitrogen load of Shanmei Reservoir is significantly related to rainfall and runoff from the upland watershed [21]. The TN retention effect in the reservoir was determined to be positive in the wet season and negative in the dry season, while the influential factors were not quantitatively analyzed, and neither was the retention effect of other nitrogen forms. Therefore, this study was focused on the analysis of the hydrological and hydrodynamic conditions of the reservoir, and six factors were selected as the subjects of interest: inflow runoff $(m^3 \cdot s^{-1})$, regulated discharge difference $(m^3 \cdot s^{-1})$, hydraulic residence time (s), velocity $(m \cdot s^{-1})$, temperature (°C), and water level (m) at annual, monthly, and daily scales. Here, the inflow runoff and velocity came from the values simulated by the coupled model system. The outflow, temperature, and water level came from data measured in the reservoir. The hydraulic residence time was calculated here as the reservoir volume divided by the outflow, the reservoir volume was calculated with the water level–volume relationship, and the regulated discharge difference is the difference between the inflow and the outflow. Due to the reservoir management, the hydrodynamic conditions with or without regulation may have different influences on the nitrogen retention effect. Therefore, the nitrogen retention effect under reservoir regulation was determined based on the temporal variations of the regulated discharge difference. Here, we divided the daily regulation into two cases, dispatching and non-dispatching, according to the existing time series of regulated discharge differences and real regulation records. Based on the amount of statistical data and the actual conditions of reservoir regulation, the absolute value of discharge difference less than 2 m³·s⁻¹ during 1991–2010 is defined as a non-dispatch case. Other difference (i.e., higher than 2 m³·s⁻¹) conditions were treated as dispatch cases.

Furthermore, we calculated the correlation between each factor and the retention flux and retention rate at annual, monthly, and daily time scales with or without dispatch by multivariate linear correlation analysis to determine the time-scale differences of the retention characteristics and influencing factors of different forms of nitrogen nutrients (TN, NO₃-N, and NH₄-N) in the reservoir.

3. Results

3.1. Nitrogen Retention Effect at Multiple Time Scales

3.1.1. Annual Retention Effect

Influenced by the subtropical monsoon climate and reservoir operation, the inflow and outflow discharge of Shanmei Reservoir showed significant interannual variation. The mean annual inflow was estimated to be from 25.5 to 62.1 m³·s⁻¹, while the mean annual outflow was estimated to be from 22.89 to 61.58 m³·s⁻¹. As shown in Figure 3a, the regulated discharge difference between inflow and outflow varied from -1.01 to 15.01 m³·s⁻¹, with most values being positive, except during the years 1999 and 2009, which had negative values close to zero. The inter-annual change of the nitrogen concentrations in the reservoir were small (Figure 3b), where mean values for TN, NO₃-N, and NH₄-N concentrations in the inflow and outflow equaled 2.67 and 2.42 mg·L⁻¹, 1.86 and 1.68 mg·L⁻¹, and 0.19 and 0.13 mg·L⁻¹, respectively.

Influenced by the differences of discharge and concentration, the inflow nitrogen flux mostly exceeded the outflow flux in Shanmei Reservoir. It appeared that am annual TN retention flux of -206.5 to 1334.69 t and retention rates of -9.35% to 34.81% are feasible on an annual basis, with retention varying yearly (Figure 3c,d). A total of 17 years showed a retention effect, while small release effects occurred in 1991, 1999, and 2009. Mean values for the NO₃ retention flux varied from -322.82 to 903.85 t, whereas the values for retention rates varied from -24.52 to 35.43%. Only a small release effect appeared in 1991, 1999, 2001, 2005, 2008, and 2009, while the other 14 years all showed a retention effect. The mean values for NH₄-N retention flux varied from 2.61 to 139.33 t, whereas the retention rates varied from 2.21 to 47.12%, with all years presenting retention effects.



Figure 3. Annual variation of hydrological condition and nitrogen retention effects in Shanmei Reservoir. (a) Discharge of inflow and outflow; (b) nitrogen concentration of inflow and outflow; (c) retention rates of TN, NO₃-N, and NH₄-N; (d) retention flux of TN, NO₃-N, and NH₄-N.

3.1.2. Monthly Retention Effect on Nitrogen Concentration

The monthly inflow of the reservoir, expressed as watershed water yield, was variable, varying from 12.4 to 92.62 m³·s⁻¹. As shown in Figure 4a, the fluctuation of outflow discharge was gentler, ranging from 23.39 to 59.25 m³·s⁻¹, and the discharge difference varied in the range -11.54 to 33.37 m³·s⁻¹. It appeared that due to the regulation, the outflow was lower than inflow during the wet season (April–October) to contain the flood, while it was higher during the dry season (November–March) to maintain the downstream water supply. The trend of the change in the inflow was in accordance with the discharge difference, with the two reaching their peak values in June and August, respectively.

Seasonal fluctuation in nitrogen retention was also noted in Shanmei Reservoir. As shown in Figure 4c,d, TN and NO₃-N exhibited a retention effect mostly during the wet season. The highest values of TN and NO₃-N retention flux and retention rates occurred in August (83.94 and 81.56 t; 32.41 and 30.54%, respectively), which was consistent with other studies [28]. In contrast, the release effect occurred during the dry season (November–March), whereas the least-negative values of retention flux and rates occurred in January (-83.94 and -81.56 t; -81.56 and -100.92%, respectively). In the case of NH₄-N, a release effect was present in January, March, and April, and a retention effect occurred in other months. The greatest amount (15.52 t) of NH₄-N retention flux occurred in August, with retention

rates up to 40.48%, whereas the highest values of release flux occurred in April, with a net export flux of 4.61 t, accounting for 60.35% of the total incoming load. This also showed the reservoir in its roles as a sink and source for NH_4 -N over the course of the year.



Figure 4. Monthly variation of hydrological condition and nitrogen retention effects in Shanmei Reservoir. (a) Discharge of inflow and outflow; (b) nitrogen concentration of inflow and outflow; (c) retention flux of TN, NO₃-N, and NH₄-N; (d) retention rates of TN, NO₃-N, and NH₄-N.

3.1.3. Daily Retention Effect

The daily inflow fluctuates more remarkably, ranging from 11.2 to 167.47 m³·s⁻¹. The outflow fluctuates less intensely due to flow regulation in the range 16.35 to 70.5 m³·s⁻¹, and the fluctuations in the nitrogen flux tend to be smoother. According to Figure 5a, during the wet season, the reservoir was in a state of impoundment due to the greater inflow than outflow. The daily retention flux processes of TN and NO₃-N resulted in a retention effect in the wet season, with the values of TN flux ranging from –1.6 to 21.87 t and NO₃-N ranging from –0.6 to 13.88 t (Figure 5c). The retention rates fluctuated much more dramatically, with the values of TN changing from –66.43 to 40.02% and NO₃-N changing from –76.49 to 36.51% (Figure 5d). In contrast, the output flux was greater than the input flux during the dry season. This induced release effects for TN and NO₃-N, with values of at least –192.56 and –198.29%, respectively. For NH₄-N, the characteristics of the retention effect varied more dramatically, with retention rates ranging from –242.22 to 58.17%, while the retention flux varied from 0.42 to 1.48 t.



Figure 5. Daily variation of hydrological condition and nitrogen retention effects in Shanmei Reservoir. (a) Discharge of inflow and outflow; (b) velocity; (c) retention flux of TN, NO₃-N, and NH₄-N; (d) retention rates of TN, NO₃-N, and NH₄-N.

3.2. Influential Factors Affecting Nitrogen Retention at Multiple Time Scales

Nitrogen retention and the removal efficiency were highly variable in response to many influential factors, the impact of which differed dramatically and caused different retention effects for TN, NO₃-N, and NH₄-N at annual, monthly and daily scales.

As shown in Table 2, at the annual scale, the reservoir inflow was significantly correlated with TN and NO₃-N retention flux and retention rates (p < 0.05), while it was not related to NH₄-N. There are significant (p < 0.01) relationships between the regulated discharge difference and the retention flux and rates of TN, NO₃-N, and NH₄-N. Statistically significant (p < 0.01) negative relationships were obtained between flow velocity and the retention rate of TN, NO₃-N, and NH₄-N (correlation coefficients of -0.729, -0.668, and -0.654, respectively).

As with the annual scale, the monthly inflow and regulated discharge difference were dramatically related to the retention flux of nitrogen (Table 2), resulting in greater nitrogen retention in the wet season than in the dry season. Temperature was also significantly related to the retention flux of TN, NO₃-N, and NH₄-N (p < 0.01), with correlation coefficients of 0.937, 0.950, and 0.735, respectively. This showed that there is seasonal variation of nitrogen retention, with a greater retention effect in summer than in winter. Furthermore, both the hydraulic residence time and velocity showed significant (p < 0.01) negative relationships with the retention flux of TN and NO₃-N, while there was no relationship with NH₄-N.

In the case of daily dispatch, inflow runoff, regulated discharge difference, velocity, temperature, and water level were significantly correlated with the retention flux and rates of TN, NO₃-N, and NH₄-N (p < 0.01). However, the hydraulic residence time was only closely related to retention rate (p < 0.01),

not with retention flux. In the case of non-dispatch, inflow and discharge differences had little effect on the retention flux and rates of TN, NO_3 -N, and NH_4 -N. Hydrodynamic factors such as residence time, flow velocity, and water level still had notable effects, especially on the retention rate, and the relation coefficients were higher than those of the dispatching period. Nevertheless, the relative influence of water temperature decreased and no longer influenced the retention effect of NH_4 -N, while the correlations of TN and NO_3 -N were still remarkable.

Table 2. Correlations between influential factors and nitrogen retention at annual, monthly and daily scales.

			Inflow	Regulated Discharge Difference	Residence Time	Velocity	Temperature	Water Level
Annual	TN	N _{ret}	0.539 *	0.969 **	0.16	-0.759 **	-0.288	0.488 *
		R _N	0.450 *	0.937 **	0.216	-0.729 **	-0.315	0.412
	NO ₃ -N	N _{ret}	0.517 *	0.920 **	0.121	-0.717 **	-0.262	0.442
		R _N	0.501 *	0.878 **	0.089	-0.668 **	-0.271	0.391
	NH ₄ -N	Nret	0.397	0.677 **	0.116	-0.559 *	-0.095	0.4
		R _N	0.192	0.749 **	0.413	-0.654 **	-0.163	0.333
Monthly	TN	N _{ret}	0.973 **	0.986 **	-0.711 **	-0.759 **	0.937 **	0.3
		R _N	0.838 **	0.847 **	-0.543	-0.899 **	0.919 **	0.453
	NO ₃ -N	N _{ret}	0.942 **	0.946 **	-0.764 **	-0.811 **	0.950 **	0.257
		R _N	0.822 **	0.824 **	-0.624 *	-0.920 **	0.925 **	0.358
	NH ₄ -N	N _{ret}	0.852 **	0.881 **	-0.499	-0.55	0.735 **	0.335
		R _N	0.325	0.343	0.178	-0.443	0.308	0.425
Daily with dispatch	TN	N _{ret}	0.937 **	0.977 **	-0.006	-0.617 **	0.785 **	0.268 **
		R_N	0.694 **	0.681 **	0.219 **	-0.783 **	0.803 **	0.493 **
	NO ₃ -N	N _{ret}	0.921 **	0.939 **	0.005	-0.673 **	0.823 **	0.268 **
		R _N	0.624 **	0.610 **	0.223 **	-0.763 **	0.751 **	0.493 **
	NH ₄ -N	N _{ret}	0.741 **	0.792 **	-0.113 *	-0.426 **	0.545 **	0.205 **
		R _N	0.206 **	0.240 **	0.167 **	-0.315 **	0.183 **	0.686 **
Daily with non-dispatch	TN	N _{ret}	0.273	0.111	0.626 **	-0.865 **	0.591 **	0.695 **
		R_N	0.323	-0.01	0.618 **	-0.827 **	0.601 **	0.776 **
	NO ₃ -N	N _{ret}	0.154	0.283	0.23	-0.628 **	0.468 *	0.168
		R _N	0.263	0.189	0.461 *	-0.810 **	0.572 **	0.498 *
	NH ₄ -N	N _{ret}	0.057	-0.104	0.252	-0.031	0.096	0.406
		RN	0.046	-0.119	0.665 **	-0.465 *	0.144	0.808 **

 N_{ret} and R_N stand for the nitrogen retention flux and retention rate. ** p < 0.01; * p < 0.05; others represent "no significant correlation". The daily correlations were divided into two cases of dispatch and non-dispatch in the reservoir.

4. Discussion

4.1. Comparison of Different Forms of Nitrogen Retention Effects

Nitrate is the main form of total nitrogen in Shanmei Reservoir and presents characteristics of retention similar to those of TN at different time scales, while NH₄-N is more unstable and its retention effects are more different.

Based on 20 years of statistics, it is concluded that the reservoir mostly played the role of a sink at the annual scale, retaining different forms of nitrogen in the reservoir. Over the year, the nitrogen retention differed with the hydrological seasons. For TN and NO₃-N, during the wet season (April–October), the reservoir played the role of a nitrogen sink with nitrogen retention, while during the dry season (November–March), it acted as a source with nitrogen release. The observed seasonal fluctuation in nitrogen retention confirmed the conclusions of earlier research [30–32].

In quantitative terms, denitrification dependent on temperature is considered the main mechanism of nitrate retention in waters [31,33]. Generally, temperate-zone denitrification is observed above 5 °C, being optimal in the range 25–30 °C [31]. The low DO observed in summer (warm) water may stimulate denitrification and reduce the nitrate mass, thus increasing the contribution of nitrogen

retention. Furthermore, the high retention rate noted in August also pointed to the phenomena caused by biochemical processes connected with temperature and the growth of organisms, as well as the sedimentation of matter originating during spring and early summer [31]. In addition, the rise of water level in the flood season was also conducive to the sedimentation and interception of organic nitrogen [12,34], which retains more nutrients than in the dry season. From November to March in the next year, due to the effects of aquatic plant assimilation and water flow dilution, the output nitrogen concentration was always lower than the input concentration. For TN and NO₃-N, the influence of the regulated discharge difference exceeded that of the reduction of concentration in discharged water, causing the nitrogen flux transported downstream to increase. This conclusion is in good agreement with previous studies [10] who showed that there was typically a release of TN during low-flow conditions.

NH₄-N is the form of nitrogen preferred as a nutrient by most aquatic plant species, and some loss of nitrogen may occur via plant uptake. It is also prone to nitrification, which also results in concentration reduction [33,35]. Thus, much more NH₄-N was removed in the Shanmei Reservoir and the retention effect lasted for eight months, from May to December. In the early stage of the dry season (November and December), the effect of the decrease in the NH₄-N concentration exceeded that of the increase of outflow, resulting in less output than input. The release effect occurred from winter to spring (January to April). This is mainly due to the gradual rise of the temperature, which accelerates the growth of the plants and decreases the DO concentration, weakening nitrification. Then, the outflow concentration of NH₄-N began to exceed the inflow concentration, resulting in the release effect. Furthermore, the NH₄-N regeneration at the reservoir bottom (sediment–water interface) in winter and spring is an important process supplying nitrogen to the overlying water [36]. The upward resuspension of NH₄-N from the benthic loading results in the nitrogen release effect [37,38].

4.2. Influence of Reservoir Regulation on Nitrogen Retention

Reservoir regulation changes the characteristics of certain parts of the water body from "river" to "lake", altering the annual and seasonal fluctuations of the streamflow, velocity, water level and residence time of the water [5,39]. In the relationship analysis shown in this paper, the regulated discharge difference was the most significant factor, with extremely significant correlation at annual, monthly and daily scales with dispatch. Velocity showed the closest relationship, while the relative degrees of influence of residence time and water level on the nitrogen retention varied from irrelevance to partial correlation, then to extremely significant correlation at annual, monthly and daily scale. In hydrological phenomena, the characteristics of hydrological processes may differ greatly in different periods. The short duration of the daily scale may cause a great deal of randomness relative to longer timescales such as yearly and monthly scale. Comprehensive effects of daily hydrological processes and reservoir regulation will affect the biogeochemical cycling of nutrients in reservoirs and lead to complex changes of nitrogen retention in the reservoir [40]. Therefore, some factors have little influence on the annual scale, while they have a significant influence on the daily scale.

Many studies have suggested that years with high inflow had large nitrogen flux and resulted in a mass retention [16,41]. However, some studies reported that more nitrate was removed in dry years than in an average year [8,42]. We found that a distinct relationship was present between inflow and the retention flux of TN and NO₃-N, but not with NH₄-N. A large amount of NH₄-N input loading does not necessarily infer high mass-retention in the reservoir. In contrast, there were a distinct relationship between regulated discharge difference and different forms of nitrogen retention. This is mainly because the retention flux was determined by input and output flux, and the influence of the regulated discharge difference should be considered simultaneously. Davi et al. showed that the retention may thus be underestimated, as other streams may contribute to increasing nutrient and solid concentrations in the water [12]. Therefore, the difference in discharge upstream vs downstream could be more important than inflow when analyzing nutrient and sediment retention. However, the regulated discharge difference was not always significantly correlated with nitrogen retention in daily processes. In the case of non-dispatch, when inflow equaled outflow, nitrogen retention was no longer affected by the inflow and the regulated discharge difference, while other hydraulic factors such as velocity, residence time and water level still had notable effects on the nitrogen retention, no matter whether there was dispatch or non-dispatch in the reservoir.

The effect of residence time on nitrogen retention in Shanmei Reservoir was more complex than that of other factors, and the calculated correlation coefficient could be positive or negative with time. On an annual scale, residence time was not related to nitrogen retention flux or retention rate; on a monthly scale, it was negatively correlated with TN and NO₃-N retention flux, but not with NH₄-N. On the daily scale, it was positively correlated with TN, NO₃-N, and NH₄-N retention rate, and partially correlated with retention flux. There are different opinions regarding the effect of residence time on the nutrient retention effect. The predominant opinion is that nitrogen retention in lakes and reservoirs is directly proportional to hydraulic residence time [3,43]. A longer residence time allows for more interaction of nitrate-rich water with benthic sediment, which is conducive to denitrification [40]. This causes high levels of nitrogen retention. Nevertheless, some other studies have found that some reservoirs with a short residence time showed a greater capacity to retain nitrogen [44], especially when they were loaded with substantial amounts of nitrogen [45]. It is concluded that the retention mechanism is not governed completely by residence time. With the comprehensive effect of nitrogen loading, regulated discharge, and some other factors, the nitrogen retention process showed complex characteristics at different time scales.

It is known that the flow velocity and associated turbulence affects the biogeochemical dynamics process, such as the growth rates of benthic algae and the uptake rates of nutrients [46,47]. Some studies performed on the relationship between flow conditions and denitrification reported that increasing velocity could inhibit denitrification, which is the main mechanism of nitrogen removal [29,48]. In our research, whether at annual, monthly, or daily scales, with or without dispatch, the flow velocity was always the key factor affecting nitrogen retention in Shanmei Reservoir. The velocity is an important parameter of hydrodynamic conditions: high velocity incurs strong hydraulic disturbance, which is beneficial to the diffusion and degradation of nitrogen and accelerates the vertical movement of nitrogen on its way to the exit of the reservoir [47]. On the other hand, it also hinders the deposition of nitrogen, causing the reduction of nitrogen retention in the reservoir. During the dry season, Shanmei Reservoir shows a discharge state with the greater outflow. The velocity was quite rapid with a mean value of 0.03 m s⁻¹ and a maximum value of 0.056 m s⁻¹ occurring in January (Figure 5b). This made it easy for nutrients to be carried downstream to the estuary. On the contrary, during the wet season with the state of impoundment, the flow velocity slowed to approximately 0.01 m s^{-1} , and the lowest value of 0 m s⁻¹ occurred in October. This indicated that the flow tends to be stationary, and the nitrogen is likely to accumulate in the sediments or be retained in the reservoir by plant uptake.

To a certain extent, the water level reflected reservoir operation directly, which rose from April and peaked in October due to flood retention and then dropped from November to March. The water level mainly affects the daily process of nitrogen retention. A high water level with low velocity indicates the impoundment of a reservoir with large inflow, so that there is abundant time for sedimentation and nitrogen retention. Conversely, a low water level with high velocity reflects a discharge state, when the nitrogen release effect occurs in the reservoir.

Nitrogen retention in reservoirs is of great significance to the control of water eutrophication. It can be concluded from this study that the hydrodynamic conditions in the reservoir have a significant impact on nitrogen retention. Reasonable reservoir dispatching measures can be taken to change the hydrological and hydrodynamic conditions, thereby affecting the process of nitrogen migration, transformation and retention in the reservoir. It is considered that, because of the management of reservoirs, the locations of outlet and discharged water volumes will also affect the residence time of the water body and nutrient retention [49]. Reservoirs with power production are mostly discharged from the bottom, with a short water residence time and strong water self-purification ability. These are not conducive to the growth of plankton and algae [50]. Reservoirs with irrigation or drinking source

functions discharge from their surface, which provides a long residence time and slight fluctuation of the water level. This is conducive to the growth of algae and accelerates the eutrophication process [51]. Therefore, according to the multiple functions of large reservoirs, further discussion is needed regarding the implementation of reasonable operations to regulate the effect of hydraulic factors on nitrogen nutrient retention in the reservoir area.

5. Conclusions

An assessment of nitrogen retention effect under reservoir regulation at multiple time scales in Shanmei Reservoir in southeast China has been performed with a coupled modeling system of SWAT and CE-QUAL-W2. It was found that the reservoir switched its roles as a nitrogen sink and source at different time scales. The reservoir acted as a nitrogen sink at the annual scale, with TN, NO₃-N and NH₄-N mostly showing a positive retention effect. TN and NO₃-N exhibited a retention effect during the wet season (April–October) and release effect during the dry season (November–March), while NH₄-N showed a longer positive retention effect lasting from May to December. The nitrogen retention process fluctuated dramatically at the daily scale, with the retention rate varying from -292.49to 58.17%.

The relative degree of influence of hydrodynamic factors affected by reservoir regulation on nitrogen retention differed, with the trend having the greatest effect at the daily scale and least at annual scale. The regulated discharge difference was the most significant factor, with extremely significant correlation at annual, monthly and daily scales with dispatch, while it had little effect at daily scales without dispatch. However, residence time, flow velocity and water level had notable effects on the daily nitrogen retention, no matter whether there was dispatch or non-dispatch in the reservoir. Considering the multiple functions of large reservoirs, further investigation is needed regarding the implementation of reasonable operations to regulate the effect of hydrodynamic factors on nitrogen retention in the reservoir.

Author Contributions: L.M.B. designed the framework of the study, conducted the simulation and analyzed data. C.X.W. and C.Y. coordinated the analysis of nitrogen retention effects. G.L. and D.H.J. revised the statistical analysis. All authors discussed the results and commented on the manuscript.

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