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Release characteristics of inorganic nitrogen in different water layers and its impact on overlying water from Liaohe River, China

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Abstract
Migration and release of sediment pollutants has become one of the important causes of water pollution, but the contribution of different forms of nitrogen in different water layers to the water quality of the overlying water is unclear. In this study, the main stream of Liaohe River with heavy nitrogen pollution was taken as an example. The static simulation method and related analysis techniques were used to explore the release characteristics of different forms of inorganic nitrogen and its effect on TN and Chla in overlying water from the different water layers. The results showed that the release rates of TN, NH_4^+-N and NO_3^--N from upstream, midstream and downstream sections were different, but the release characteristics of them in different water layers were the same basically. Generally, the inorganic nitrogen in the pore water of the sediment was released to the water body rapidly in the early 0–8 days. The contribution rate of NH_4^+-N and NO_3^--N to the change of TN_o was 76.85% for the upstream section, and the contribution rate of NO_3^--N to the change of TN_o was 65.02% for the midstream section. NH_4^+-N and NO_3^--N in the different water layers from downstream did not showed a significant correlation with TN of overlying water. NO_3^--N in sediments was the main contributor of TN and Chla changes in the overlying water and its content can reflect the nitrogen pollution trend of the water body to a certain extent. When the water retention time was 4–16 days, the TLI in the water body was relatively high. After effective control of exogenous pollution, the release of endogenous nutrients in Liaohe River should be paid more attention.

Keywords Liaohe River · nitrogen release · overlying water · Chla · TLI

Introduction

With the application of artificial nitrogen fertilizers (Galloway et al. 2008), industrial wastewater discharge (Gibson et al. 2012) and the increase of specific domestic water (Braga et al. 2000), a large amount of nitrogen is released into the natural water system (Zhu et al. 2019). N-containing compounds are essential nutrients for all life forms, but when too much N nutrients enter the aquatic environment, it will cause a series of ecological problems, such as eutrophication, hypoxia events, acidification of freshwater ecosystems, and poisoning of benthic organisms and fish etc. (Camargo and Alonso 2006; Bhatnagar and Sillanpää 2011). Eutrophication is usually caused by excessive discharge of nitrogen and phosphorus compounds, which leads to the proliferation of algae and other phytoplankton and the decline of water quality (Yang et al. 2015). It is the most important problem facing lake ecosystems. As a necessary nutrient for the primary production of aquatic ecosystems, the supply of nitrogen significantly affects the growth of algae in freshwater ecosystems (Nyenje et al. 2010; Xu et al. 2012; Pedro et al. 2013). The external nutrients load and the release and retention of nitrogen in the sediment are the main factors affecting the nitrogen content in the water body (Havens et al. 2001; Chong et al. 2012; Wang et al. 2014). When the external pollution source of the lake is controlled, the existence and release of nutrients in the sediments makes eutrophication still possible (Hu et al. 2007; Spears et al. 2008). Sediment plays a vital role in the transportation of nutrients and the surface water quality (Hasegawa et al. 2010; Wu et al. 2001) in freshwater ecosystems (Wang et al. 2003; Beutel

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2006; Lu et al. 2012; Antunes et al. 2013). Therefore, understanding the nutrient concentration and distribution in different water layers and sediment gaps will help to better understand the nutrient exchange process at the interface between sediment and water(Ye et al. 2014), quantify the impact of sediment nutrient loading, and improve water quality especially important (Havens et al. 2001).

Sediment is the main storage and accumulation place of nutrients and pollutants in lake water bodies. During the cycle of N and P nutrients in water bodies, sediments can be both release sources and storage sinks (Daniel et al. 1990), and play an important role in regulating the nutrient content in the water body. The nutrients accumulated in the interstitial water of the sediment can be exchanged with the overlying water through physical adsorption, chemical adsorption and cationic bridging (Rex and Petticrew 2010; Yang et al. 2015). Therefore, under certain conditions, nutrients will be released with changes of environmental conditions (Domagalski et al. 2007; Nyenje et al. 2010). It is known that the release of nutrients from sediments is affected by many factors such as pH, dissolved oxygen, water temperature, salinity, redox potential, and hydraulic disturbance (Zhang et al. 2012; Pedro et al. 2013). Studies have shown that when the input of exogenous nutrients is effectively controlled, the endogenous release of sediments often becomes an important reason for the deterioration of water quality and failure to recover (Hu et al. 2001). Therefore, in recent years, the endogenous release characteristics and potential of eutrophic lake sediments have received extensive attention (Perkins Underwood 2001; Rozan et al. 2002). Previous studies have shown that accelerated nitrogen application may pose a threat to eutrophication of downstream estuaries and coastal ecosystems (Xie et al. 2007). However, previous studies have paid more attention to lake eutrophication, while less attention has been paid to nitrogen pollution in rivers. At present, the research on the release characteristics of nitrogen at the interface between sediment and water mainly focuses on the diffusion flux of nitrogen form in the sediment and the induced attenuation seepage (Trimmer and Nedwell 1998; Carrey et al. 2014a, b), but there are few studies on the migration and release in different water layers. The effect of different forms of nitrogen in different water layers on the quality of overlying water is still unclear.

Liaohe River plays an important role in the ecological regulation, industry, agriculture, fisheries and other developments of Liaoning Province. It has been reported that TN and TP in the Daliao River are seriously exceeding the standard, all of which reach the inferior V water quality (China National Water Quality Standard) (Ma et al. 2015). The concentration of TN in Daliaohe River was 4.80–7.59 mg/L (Zhou 2013; Chen et al. 2019). In the current study, the main stream of Liaohe River with heavy nitrogen pollution was taken as an example. The static simulation method and related analysis techniques were used to study the release characteristics and its effect on TN and Chla in overlying water from different forms of nitrogen at the sediment-water interface under different water layers. The release, correlation and contribution of total nitrogen (TN), nitrate nitrogen (NO_3^--N), ammonium nitrogen (NH_4^+-N) in sediments to water quality and nutrient status of overlying water were analyzed, so as to provide a scientific basis for pollution control and management of river basin.

Materials and methods

Study area and sampling sites

The Liaohe River Basin is a southern river in Northeast China. It originated in Hebei Province and flows through Hebei Province, Inner Mongolia, Jilin Province and Liaoning Province. The Liaohe River has two water sources, the East Liaohe River and the West Liaohe River. The two sources met in Fudedian, Changtu County, Liaoning Province. The main stream of the Liaohe River leads to the cities of Tieling, Xinmin, Liaozhong and Panjin in Liaoning Province. The total length of the Liaohe River is 1345 km, and the drainage area is 219,000 km^2. It is injected into the Bohai Sea with the Shuangtaizi River at the intersection of the Shuangtaizi District in Panjin. In this study, the Fudedian (1), Yubaotai Bridge (2) and the estuary (3) in the upstream, midstream and downstream of the Liaohe River were selected as sampling sections (Fig. 1). In-situ samples of sediment and overlying water were collected and returned to the laboratory in October 2016 to determine the nitrogen release characteristics of the sediment. Water temperature (T), conductivity (EC), pH, dissolved oxygen (DO), total suspended solids (TSS), chemical oxygen demand (COD), total phosphorus (TP), TN, NH_4^+-N and other basic water quality index information are listed in Table 1.

Study methods

(1) Release characteristics of nitrogen in different water layers

The river sediments were placed into the three plexiglass columns with a diameter of 15 cm to a height of 15 cm, and then stabilized them for a week. The situ water was injected into each of the plexiglass columns to a height of 30 cm (Fig. 2). In order to prevent disturbance between

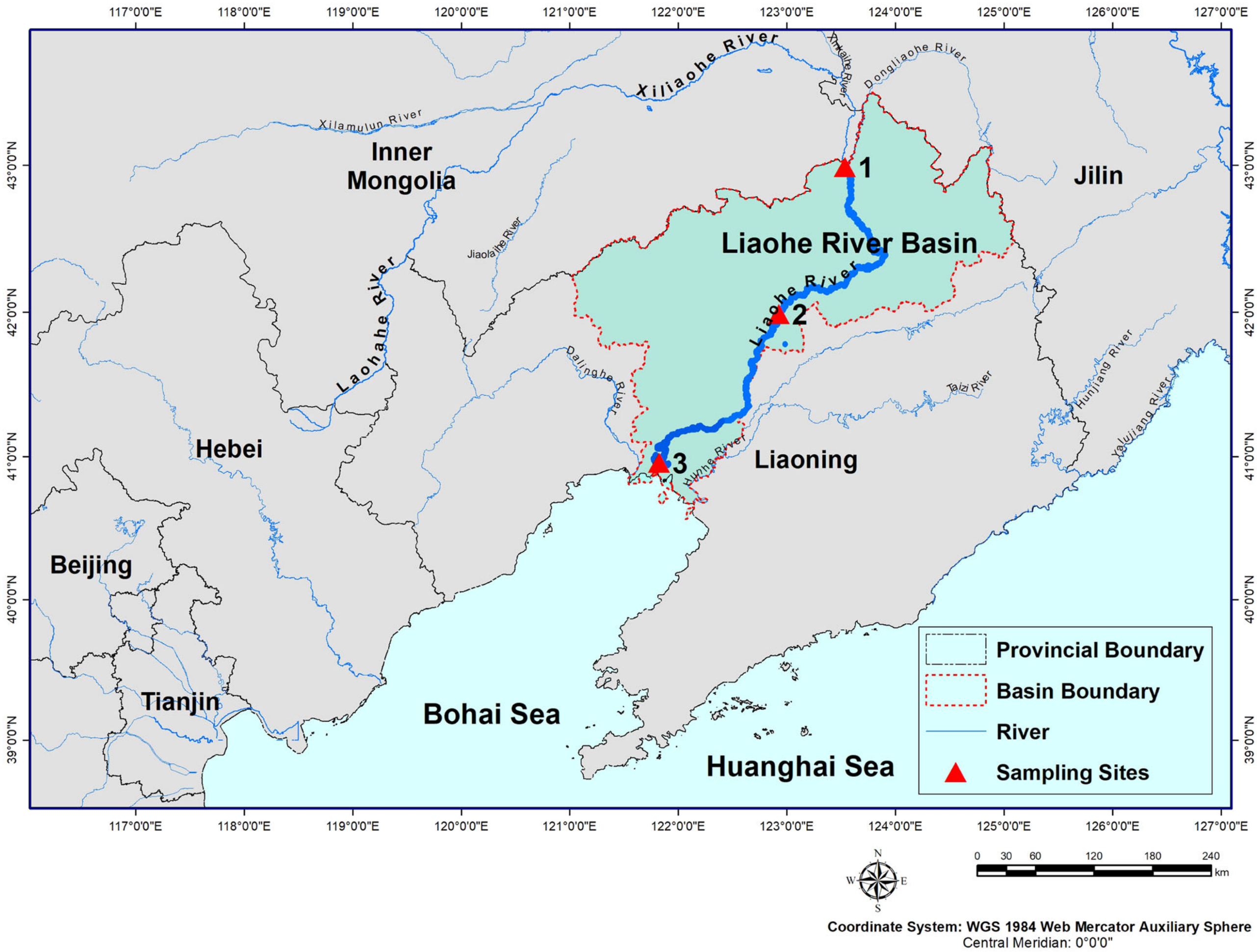

Fig. 1 Location of sampling section of sediments and overlying water in Liaohe River. The area within the red dotted line is the Liaohe River Basin; the bold blue line is the main stream of the Liaohe River; the red triangle is the sampling sites. 1, 2, and 3 represent the upstream, midstream and downstream from the main stream of Liaohe River, respectively

Table 1 Basic water quality index information of the three sections

Sampling site	T (°C)	EC (ms/cm)	pH	DO (mg/L)	TSS (mg/L)	COD (mg/L)	TP (mg/L)	TN (mg/L)	NH_4^+-N (mg/L)
1	3.8	0.302	6.97	8.47	22	17	0.02	1.1	0.42
2	3.6	0.542	7.18	8.73	94	4	0.11	1.0	0.24
3	9.8	2.850	7.31	9.13	262	5	0.47	3.2	0.48

water and sediment, water was injected slowly along the glass column wall. The sediment and the overlying water were subjected to the original column-temperature-controlled culture. The first sampling was collected after standing for 2 days, and the time interval was from short to long until the 65th day. At different times, take overlying water (about 3–5 cm from the water surface), surface water (about 5 cm from the sediment) and pore water (the surface sediment was centrifuged to take the supernatant), and the water sample corresponding to the sampling site was added to the original scale. The water samples were immediately filtered and DO, pH, TN, NH_4^+-N, NO_3^--N and chlorophyll a (Chla) in the water were determined (ORION-AQ3700). TN in the overlying water, surface water and pore water were represented by TNo, TNs, TNp, respectively. NH_4^+-N in the overlying water, surface water and pore water were represented by $NH4_o$, $NH4_s$, $NH4_p$, respectively. NO_3^--N in the overlying water, surface water and pore water were represented by $NO3_o$, $NO3_s$, $NO3_p$, respectively. The release rate (r) was calculated according to Eqs. (1) and (2), and the release kinetic curve was plotted. In this

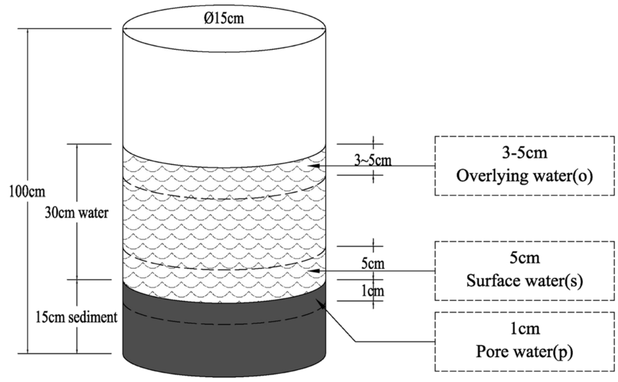

Fig. 2 Experimental simulation device for static release. Device is 100 cm high and 15 cm in diameter, in which 30 cm water and 15 cm sediment were injected. Gray parts represent sediments and wavy parts represent water

study, we collectively refer to the nitrogen migration rate between water media and the nitrogen release rate in the sediment as the release rate. The determination of different forms of nitrogen referred to the national standard method (CSEPA 2012). Soluble TN in the sediment was determined by potassium persulfate oxidation-UV spectrophotometry, NH_4^+-N was determined by Nessler's reagent spectrophotometry, and NO_3^--N was determined by phenol disulfonic acid colorimetry.

$$R = V[C_n - C_0] + \sum_{j=1}^{n} V_{j-1}\left(C_{j-1} - C_a\right) \tag{1}$$

$$r = (R_i - R_{i-1})/(s \times t) \tag{2}$$

Where R is the cumulative release amount, mg; V is the overlying water volume, L; C_0, C_n and C_{j-1} are the starting, nth and j-1th sampling contaminant concentrations, mg/L; C_a is the pollutants concentration of the added water sample, mg/L; V_{j-1} is the j-1th sampling volume, L; r is the release rate, mg/(m^2·d); R_i and R_{i-1} are the cumulative release of the i-th and i-1th samples, mg; s is the contact area of sediment-water interface, m^2; t is the release time, d.

(2) Characterization of nutritional status under different water layers

The evaluation method of the nutritional status of the river water in this study referred to that method for eutrophication of lakes in China (Jin et al. 1995). Comprehensive trophic level index (TLI) was developed on the basis of the Carlson Index (TSI). This method generally selects the five main indicators such as chlorophyll a (Chla), TP, TN, SD, and CODMn, which reflect the degree of nutrition of the water body. The calculation formulas for the nutritional status index of each parameter and TLI are as follows:

$$TLI(chla) = 10(2.5 + 1.086 \ln chla) \tag{3}$$

$$TLI(P) = 10(9.436 + 1.624 \ln TP) \tag{4}$$

$$TLI(N) = 10(5.453 + 1.694 \ln TN) \tag{5}$$

$$TLI(SD) = 10(5.118 - 1.94 \ln SD) \tag{6}$$

$$TLI(COD_{Mn}) = 10(0.109 + 2.66 \ln COD_{Mn}) \tag{7}$$

$$W_j = \frac{r_{ij}^2}{\sum_{j=1}^{m} r_{ij}^2} \tag{8}$$

$$TLI = \sum_{j=1}^{m} W_j \times TLI_j \tag{9}$$

In the formula, TLI_j is the nutritional status index of the j-th parameter, and W_j is the weight of the nutritional status index of the j-th parameter. With Chla as the reference parameter, the normalized correlation weight was calculated according to the formula (8). r_{ij} is the correlation coefficient between the jth parameter and the benchmark parameter (Chla), and m is the number of evaluation parameters. Referenced Li and Zhang's method Li Zhang (1993), the nutritional status of the lake was graded according to the TLI. The evaluation criteria are: $TLI \le 30$ is poor nutrition, $30 < TLI \le 50$ is medium nutrition, $50 < TLI \le 60$ is slight eutrophication, $60 < TLI \le 70$ is moderate eutrophication, $TLI > 70$ is heavily eutrophic.

(3) Contribution analysis

PCA was used to check the correlation between multiple variables (Zhu and Chen 2011). SPSS software was used to analyze the correlation between different forms of nitrogen and Chla, and to explore the migration and release of different forms of nitrogen in different water layers. Through Spearman correlation analysis, the correlation between impact factors and overlying water TN was determined. After removing the factors that were not related to the total nitrogen in the upper water, dimensionality reduction and factor analysis were carried out in turn, and basic statistical data and related parameter information were output. After the main factors were extracted through principal component analysis (PCA), the characteristic parameters were divided into some main components, and the influence and contribution of the main factors to the total nitrogen of the overlying water were identified and quantified. The whole process was carried out by using SPSS 20.0 software.

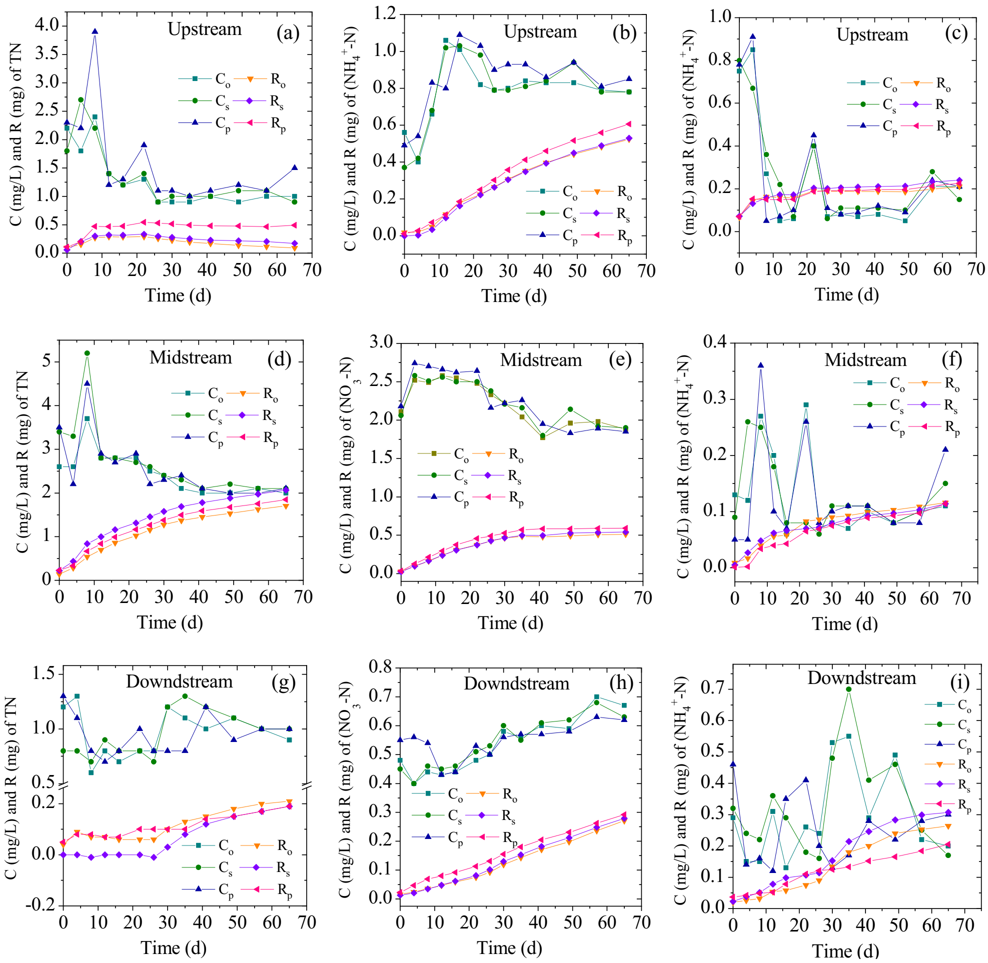

Fig. 3 Release kinetics of NH_4^+-N, NO_3^--N and TN from the different water layer. C_o, C_s and C_p represent the concentrations of the different forms nitrogen in the overlying water, surface water and pore water. R_o, R_s and R_p represent the cumulative release amount of the different forms nitrogen in the overlying water, surface water and pore water

Results and discussions

Release characteristics of nitrogen from different water layers

Release amount

The release dynamics process of TN, NO_3^--N and NH_4^+-N from different water layers was shown in Fig. 3. For upstream and midstream, the contents of TN, NO_3^--N and NH_4^+-N in different water layers gradually increase, reach the maximum at about 8th days, and then gradually decrease and stabilize (Fig. 3a, b). In the early stage of the experiment, the oxygen content in the water is sufficient, the aerobic microorganisms grow rapidly, and the organic matter released from the sediment is quickly decomposed to NH_3 and CO_2 (Beutel 2006). There is a concentration difference at the interface between the water and the sediment, which makes NO_2^--N, NO_3^--N and inorganic salt nitrogen in the sediment are gradually released into the water body, so that the TN concentration in the water body increases rapidly (Zhu et al. 2019). Except for NO_3^--N in the midstream, the content of NH_4^+-N in water and sediments decreased, while NO_3^--N increased, which may be related to the nitration of NH_4^+-N (Bowden 1986).

For upstream, the contents of NO_3^--N and NH_4^+-N in pore water were the highest, and that was almost the same in surface water and overlying water. The maximum cumulative release amount of TN in overlying water (R_o), surface water (R_s) and pore water (R_p) were 0.292 mg, 0.332 mg and 0.542 mg, the R_o, R_s and R_p of NO_3^--N were 0.523, 0.529, and 0.606 mg, and the R_o, R_s and R_p of NH_4^+-N were 0.211, 0.240, and 0.226 mg, respectively (Fig. 3a-c). The cumulative release of TN and NH_4^+-N stabilized after 10 days, while NO_3^--N was always increased. For midstream, the contents of NO_3^--N in pore water were the highest, and the NO_3^--N content and change trend of surface water and overlying water are basically the same. The R_o, R_s and R_p of TN were 1.706, 2.066 and 1.846 mg, the R_o, R_s and R_p of TN were 1.706, 2.066 and 1.846 mg, and

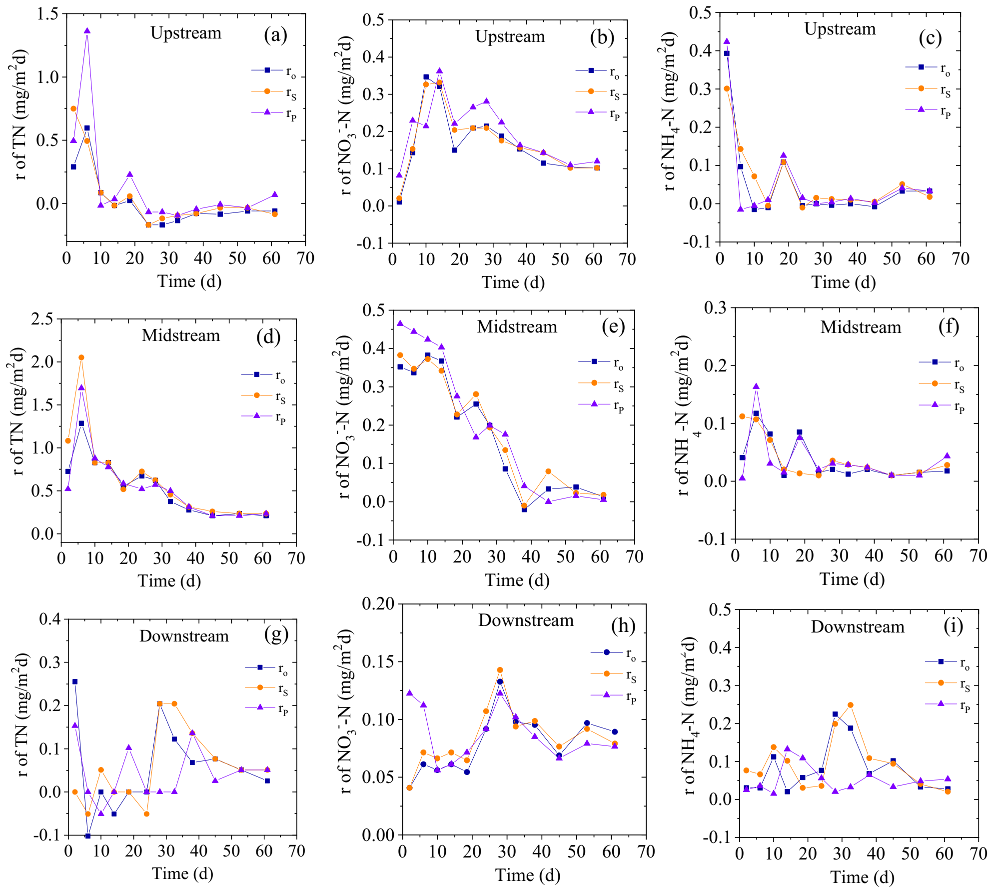

Fig. 4 Release rate (r) of TN, NO_3^--N and NH_4^+-N from the different water layer. r_o, r_s and r_p represent the release rates of the different forms nitrogen in the overlying water, surface water and pore water

the R_o, R_s and R_p of NH_4^+-N were 0.116, 0.114 and 0.114 mg, respectively (Fig. 3d-f). The cumulative release of NO_3^--N stabilized after 30 days, while TN and NH_4^+-N were always increased slowly. For the downstream, the R_o, R_s and R_p of TN were 0.21, 0.19 and 0.19 mg, the R_o, R_s and R_p of NO_3^--N were 0.271, 0.279 and 0.292 mg, and the R_o, R_s and R_p of NH_4^+-N were 0.264, 0.307 and 0.205 mg, respectively (Fig. 3g-i). TN and NO_3^--N in the sediment pore water were released to the water body during the first 10 days generally (Fig. 3h).

On the whole, it can be seen that the release of pore water was the largest, followed by surface water and overlying water, which indicating that NO_3^--N was gradually released from the sediment. The cumulative release amounts of TN, NO_3^--N and NH_4^+-N in the middle and upper streams were higher than that in the downstream, which may be related to the different physical and chemical properties of sediments in different sections. In general, the starting contents of TN, NO_3^--N and NH_4^+-N in the different sampling sites were different. Among them, the concentration in sediments and overlying water in the upstream and midstream sampling sites was relative higher, which may be affected by nearby human activities, especially agricultural non-point sources (Wang et al. 2018). The sediments at the downstream sampling site and the water body TN were relatively low, which may be related to the relatively weak human interference, nitrogen form composition of the sediment, the geological condition, and the physical and chemical properties of the water environment itself.

Release rate

Release rate of TN, NO_3^--N and NH_4^+-N from different water layer were listed in Fig. 4. For upstream and midstream, the release rate of TN, NO_3^--N and NH_4^+-N were reached the highest at 5 to 10 d basically. After that, the rate gradually slowed down (Fig. 4a-f). On the whole, the release rates of TN, NO_3^--N and NH_4^+-N from the upstream and midstream section were higher than that from the downstream sections. Among them, the maximum release rates of TN in the overlying water (r_o), surface water (r_s) and pore water (r_p) were 1.29, 2.05 and 1.69 mg/(m^2·d), respectively, and the release rate was larger at 5-8th days. During the 20th to 40th days, the release rate showed a negative value (Fig. 4a), which may be due to the sediment began to adsorb nitrogen from the water after the release reached equilibrium, which increased the sediment nitrogen concentration. At the beginning, NO_3^--N from upstream and downstream was in the absorption state, and the content increased. From the 20th day, it decreased and became release gradually. After that, the absorption and release were alternated, and the release rate decreased gradually. The sediments exhibited "negative release" of nitrate nitrogen in the water body when studying the dynamics of nutrient exchange at the sediment-water interface (Fan Morihiro 1997). It shows that nitrogen also tend to be absorbed by sediments under specific environmental conditions. The maximum release rates of NO_3^--N in the overlying water (r_o), surface water (r_s) and pore water (r_p) were 0.383, 0.383 and 0.464 mg/(m^2·d) from midstream, respectively, and the release rate was larger at 0–15 days. NH_4^+-N from the pore water in the sediment was released in the first 5 days generally, and the release rates occurred increase again in all sampling sections (Fig. 4c, f, i) after 20th days. At the same time, the increasing contents were all observed in Fig. 3c, f and i. The overall trend of the release rate of overlying water, surface water and pore water was about the same. This indicates that there may be a cycle between adsorption and release for NH_4^+-N in about 30 days. One form of N can be converted into another through various microbial processes. Unionized ammonia ($NH_3·H_2O$), ammonium (NH_4^+), and hydroxide ions (OH^-) are generally in equilibrium. $NH_3·H_2O$ is an unstable form of N and the $NH_3·H_2O$ concentration is related to the NH_4^+-N concentration, pH, and temperature. The equilibrium between $NH_3·H_2O$, NH_4^+, and OH^- can be expressed in its simplest form as the equation $NH_3 + H_2O \leftrightarrow NH_3·H_2O \leftrightarrow NH_4{}^+ + OH^-$ or NH_4OH (Zhu et al. 2019). Taking the midstream sample as an example, the release rate of NH_4^+-N increased rapidly in the previous week. On the 7th day, the release rate (r_p) of pore water reached a maximum of 0.163 mg/ (m^2·d), and then decreased with time. It stabilized at 25th day with the rate about 0.02 mg/ (m^2·d). Similar to NH_4^+-N, the release rate of TN increased sharply at the beginning, and reached the maximum value of 1.69 mg/(m^2·d) on the 6th day (r_p). After that, it gradually decreased to reach the dynamic equilibrium, and stabilized at 37th day with the release rate about 0.3 mg/ (m^2·d). The release rate of NO_2^--N gradually decreased, and the rate dropped to 0 at 45th day, and was no longer released. In general, the release rate of nitrogen at different sampling sites was different, which was related to nitrogen morphological characteristics, physical and chemical properties of sediment, microbial activities and external environmental factors (Domagalski et al. 2007; Yang et al. 2015). The release rates of TN and NO_3^--N were higher in the upstream and midstream sections, and the release rate of NH_4^+-N in the downstream samples was higher.

Effects of different forms of nitrogen on TN of overlying water

The nitrogen content, composition distribution and morphological characteristics of the sediments are closely related to the nitrogen content in the water, which can indirectly reflect the nitrogen pollution in the water (Antunes et al. 2013). Therefore, the law of water quality change can be predicted by studying the corresponding relationship among the different forms nitrogen from sediment, overlying water and surface water. Correlation analysis was carried out between different forms of nitrogen content and Chla content at different water layers (Fig. 5). The results showed that there was a significant correlation among the same forms of nitrogen in different water layers. Especially in the upstream and midstream sections, the performance was more obvious. Whether upstream or midstream section, $NO3_o$ was positively correlated with $NO3_s$ and $NO3_p$ ($p < 0.01$), and TN_o was positively

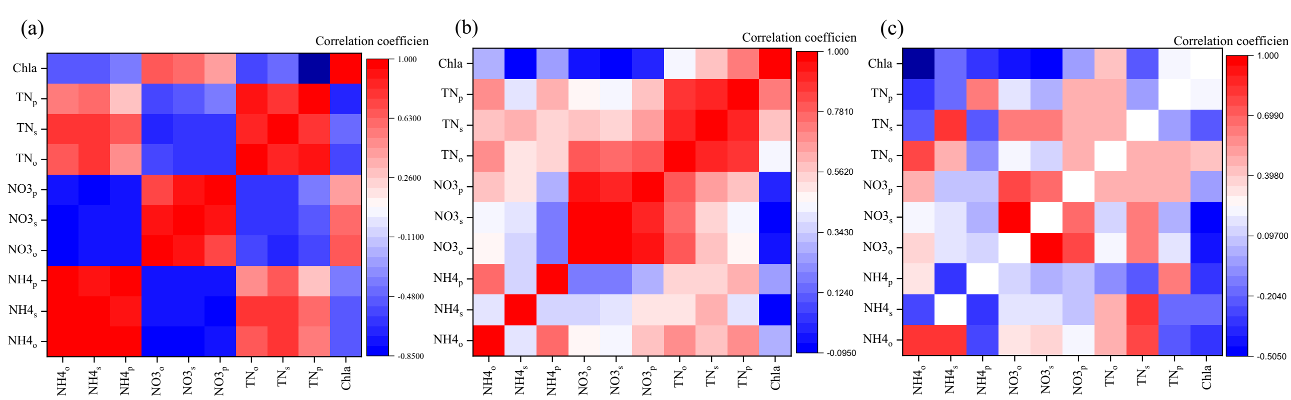

Fig. 5 Correlation of the different forms of nitrogen in in pore water (**a**), surface water (**b**) and overlying water (**c**). $NH4_o$, $NH4_s$, $NH4_p$, $NO3_o$, $NO3_s$, $NO3_p$, TN_o, TN_s and TN_p represent the NH_4^+-N, NO_3^--N and TN in the overlying water, surface water and pore water, respectively, and the following has the same meaning as here

correlated with TN_o and TN_p ($p < 0.01$). This indicated that nitrogen was released from pore water to upper layer and overlying water, which release the same as the migration process. Moreover, there was also a significant correlation among the different forms of the same water layer. For example, $NO3_o$ and $NH4_o$, $NO3_s$ and $NH4_s$, and $NO3_p$ and $NH4_p$ were showed significantly negatively correlated, and the correlation coefficients were -0.848, -0.780, and -0.747, respectively. This is also related to the conversion of NH_4^+-N into NO_3^--N due to nitrification (Bowden 1986). Furthermore, there were also some correlations among the different forms of nitrogen in different water layers. There was a positive correlation between TN_o and $NH4_o$ ($p <$ 0.05), TN_s and $NH4_s$ ($p < 0.01$), and the correlation coefficients were 0.680 and 0.793, respectively. For TN_o, the study found that with the exception of $NH4_p$ and $NH4_s$, all other forms of nitrogen were significantly correlated with TN_o in the upstream and midstream. Therefore, there was a significant positive correlation between nitrogen content from pore water, surface water and overlying water especially for NO_3^--N, and the correlation between pore water and overlying water was gradually enhanced. NO_3^--N and NH_4^+-N was negatively correlated from the upstream, probably due to the nitrification of NH_4^+-N gradually to NO_3^--N. There was a positive correlation between TN release and NO_3^--N and NH_4^+-N release in the midstream and downstream. Thus, there was a certain correlation between different forms of nitrogen in the water and different forms of nitrogen in the sediment, indicating that the nitrogen content in the sediment can reflect the nitrogen concentration and potential release capacity in the water to some extent.

With TN_o as the response variable, principal component analysis was used to identify the main influencing factors of different forms of nitrogen related to TN_o. The correlation between different forms of nitrogen and TN_o was significant in the upstream and midstream sections, but not significant in the downstream. After the main parameters were extracted by PCA, the characteristic parameters were divided into two main components (PC1 and PC2). From Fig. 6a, it can be known that for the upstream section, the correlation coefficients of ammonium nitrogen and nitrate nitrogen with the common factor of PC1 are relatively highest (between 0.813-0.925), and the explanation rate of the total variance is 76.85%, which contributes to PC1. TN contributed a lot to PC2 (R^2 is between 0.757 and 0.960). The explanation rate of the total variance of the variance was 11.93%, which was the main component of PC2. From Fig. 6b, it can be known that for the midstream section, the correlation coefficient of NO_3-N with the common factor in PC1 was relatively the highest (between 0.909-0.967), and the explanation rate of the total variance is 65.02%, which contributes the most to PC1. NH_4-N has a larger contribution to PC2 (R^2 is between 0.819 and 0.900), and the interpretation rate of the total variance is 21.53%, which was the main component of PC2. Therefore, in the upper and midstream sections, $NO3_p$ showed a significant correlation with TN in overlying water, which contributed a lot to TN pollution in overlying water. This showed that nitrogen pollution in the upper and middle reaches of the Liaohe River was likely caused by sediment release and migration to water bodies. Through further analysis of the reliability of PCA (Fig. 6c), it was found that the common factor variance extraction ratio of the parameters in PC1 and PC2 exceeds 50%, and the factor extraction has higher reliability. Based on the results of PCA, it was shown that NO_3-N in water and sediment were the main sources of TN in overlying water. Soluble nitrogen in the interstitial water of sediments passes through the sediment-water interface and is transported upwards, which is an important way to release nitrogen in sediments (Wang et al. 2002). Surface sediments are more susceptible to external influences due to direct contact with water bodies, and the distribution characteristics of pollutants in interstitial water are directly related to the internal load of lakes (Fan et al. 2002). Studies have reported that the nitrogen forms released from interstitial water to overlying water are mainly NH_4-N, followed by NO_3-N, and most of this nitrogen released from sediments is due to the degradation of organic matter (Dimitrios et al. 2007; Beutel 2006). However, for the upstream Liaohe section, the contribution rate of NH_4-N and NO_3-N to the change of TN_o was 76.85%. For the midstream section, the contribution rate of NO_3-N to the TN_o change was 65.02%. This showed that NO_3-N was the main supply form of TN in water. In general, the nitrogen in the main stream of the Liaohe River migrated and diffused to the water body in the form of NO_3-N, and the process of NO_3-N release to overlying water may be the nutrition supply mechanism of overlying water from the sediment. With the implementation of water pollution control measures, internal sources may be a major cause. This research focuses on the impact of internal sources on the overlying water. As for the source of nitrogen pollution in the water body, it is still caused by both internal and external sources (surrounding industrial pollution, agricultural non-point source, etc.) together.

Effects of different forms of nitrogen on Chla of overlying water

In this study, the correlation between Chla in overlying water and various nitrogen forms was analyzed. The results showed that Chla in the upstream and midstream sections was significantly related to some forms of nitrogen, while Chla in the downstream section was not related to all forms of nitrogen. For the upstream section, Chla showed a

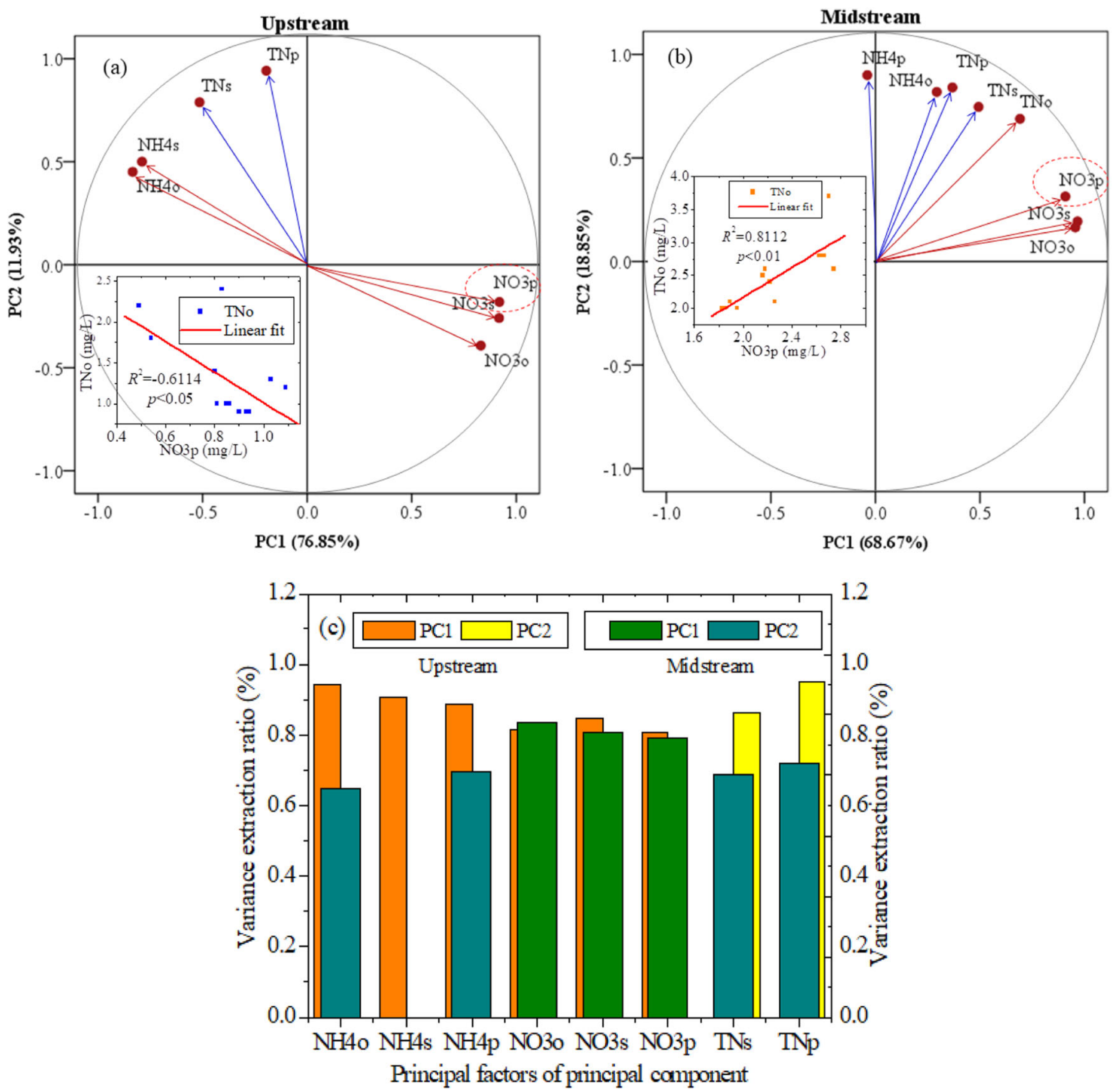

Fig. 6 Contributions of main components of nitrogen in different sections. (**a**) and (**b**) are the principal component loading diagrams of factors related to the TN_o in the different nitrogen indicators. The length of the arrow represents the correlation between the indicator and the common factor, red is the indicators of PC1, and blue is the indicators of PC2. (**c**) is the extraction ratios of common factor variance of the different forms nitrogen indicators to principal component

significant positive correlation with $NO3_o$ and $NO3_s$, and a significant negative correlation with TN_o and TN_p. Among them, the correlation coefficient between Chla and TN_p was -0.6941 ($p < 0.01$) (Fig. 7a). On the one hand, $NO3_s$ may be a nutrient supply source for Chla in overlying water. On another hand, TN_p was related to the TN_o and $NO3_o$, which indicates that the nitrogen in the sediment may migrate and release to the overlying water to promote the algae growth. For the midstream section, Chla was significantly positively correlated with TNs and TN_p. Among them, the correlation coefficient between Chla and TN_p was 0.718 ($p < 0.01$) (Fig. 7b). This indicates that the sediment TN_p was reduced and the overlying water Chla was also reduced. Meanwhile, TN_o showed a positively correlated with TN_p. Therefore, as the TN_p decreases, TN_o also decreases, which may cause the growth of algae in overlying water to be inhibited and thus reduce Chla. Thus, TN_p and $NO3_s$ may be the nutrient supply source for Chla in overlying water.

The changes of water body Chla and TLI during static simulation were shown in Fig. 7a-d. Under static simulation conditions, the content of Chla in the upstream and downstream was higher at 10–45 days, and the water body has different degrees of eutrophication. The contents of Chla in the upstream midstream and downstream were 0.001–0.067 mg/L, 0.001–0.032 mg/L and 0.001–1.664 mg/L, and the average contents were 0.033, 0.010 and 0.183 mg/L, respectively. It can be seen from Fig. 7d that the comprehensive nutrient status of the water body from the upstream was the medium nutrient state ($30 \leq TLI \leq 50$) in the two periods from the 12th to the 16th days and

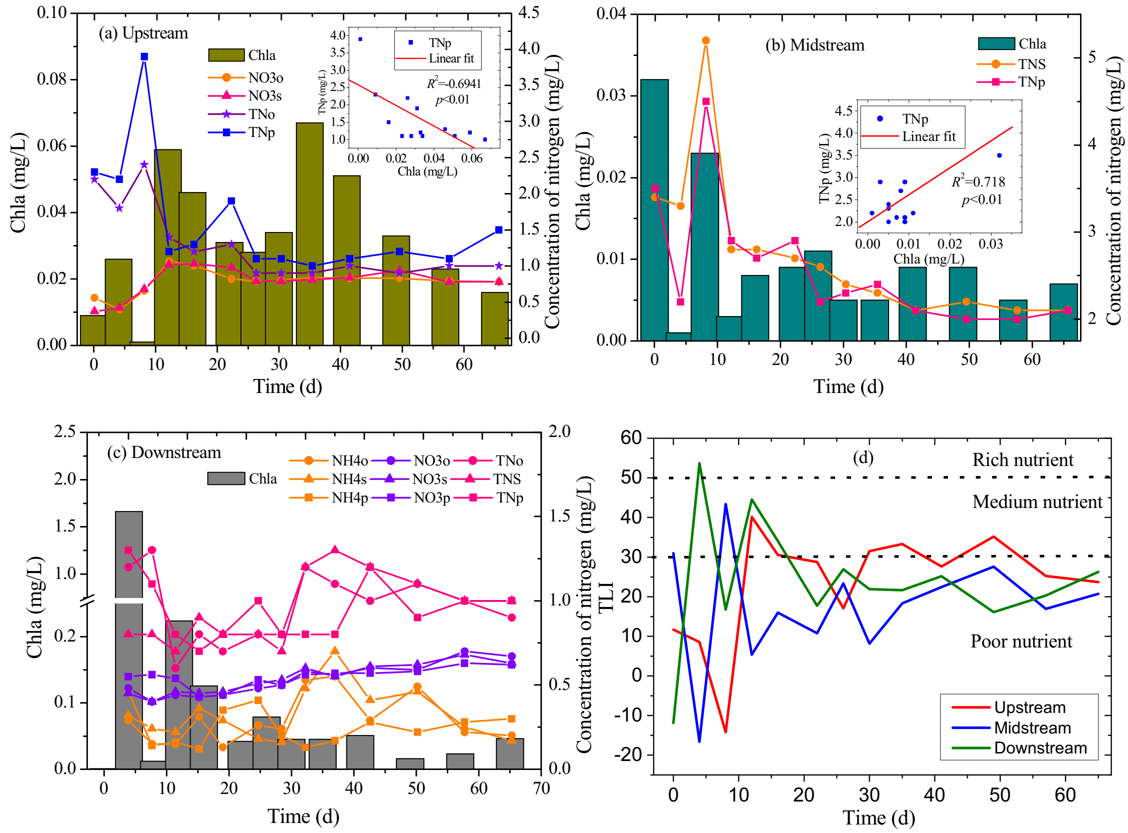

Fig. 7 Changes of Chla and *TLI* in overlying water during the static simulation. (**a**) and (**b**) are the changes of Chla and related forms nitrogen in overlying water from the upstream and the midstream; (**c**) is the changes of Chla and all different forms nitrogen in overlying water from the downstream; (**d**) is the changes of TLI in overlying water from the three sections

30–49 days. TLI in the rest time period was less than 30, which was in a state of poor nutrition and meant a lower risk of eutrophication. The collected water sampling from the midstream was in the middle nutrient state on the 8th day (TLI = 45.4), and the rest time belonged to the poor nutrition state. The collected water sampling from the downstream reached the rich nutrient state on the 4th with the comprehensive trophic level index as high as 53.7, and it was slight eutrophic. It was in the middle nutrient state during 12–16 days, and the rest time was in a poor nutrition state. In general, the TLI was low in the water bodies of the three sampling sections of the Liaohe River. When the water retention time is 4–16 days, the TLI in the water body was relatively high.

Conclusions

Through laboratory simulation experiments, the dynamic changes of nitrogen in the different layer and its effect on the quality of overlying water were studied. The nitrogen release rates of sediments in upstream, midstream and downstream were different. The release rates of TN and NO_3^--N in the midstream were higher, and the release rate of NH_4^+-N in the upstream was higher. Among them, the release time of NO_3^--N and TN was shorter, generally the release rate was faster at 4–10 days, the cumulative release amount was increasing, and the maximum release was about 0–18 days. There were significant correlations among the same forms of nitrogen in different water layers, among the different forms of the same water layer, and among the different forms of nitrogen in different water layers. The various forms of nitrogen in different water layers had significant effects on the TN/Chla of the overlying water in the upstream and midstream, but had no significant correlation with the TN/Chla of the overlying water in the downstream. Among them, the contribution rate of NH_4^+-N and NO_3^--N to the change of TN of overlying water on the upstream section was 76.85%; the contribution rate of NO_3^--N to the change of TN of overlying water on the midstream section was 65.02%. NO_3^--N in sediments was the main contributor of TN and Chla changes in the overlying water and its content can reflect the nitrogen pollution trend of the water body to a certain extent. TLI in the water body was increased when water stays for 4–6 days. After effective control of exogenous pollution, the release of endogenous nutrients in Liaohe River should be paid more attention.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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References

Antunes M, Antunes MT, Fernandes AN et al. (2013) Nutrient contents in bottom sediment samples from a southern razilian microbasin. Environ Earth Sci 69:959–968. https://doi.org/10.1007/s12665-012-1980-9

Beutel MW (2006) Inhibition of ammonia release from anoxic profundal sediments in lakes using hypolimnetic oxygenation. Ecol Eng 28:271–279. https://doi.org/10.1016/j.ecoleng.2006.05.009

Bhatnagar A, Sillanpää M (2011) A review of emerging adsorbents for nitrate removal from water. Chem Eng J 168:493–504. https://doi.org/10.1016/j.cej.2011.01.103

Bowden WB (1986) Nitrification, Nitrate reduction, and nitrogen immobilization in a Tidal Freshwater Marsh Sediment. Ecology 67:88–99. https://doi.org/10.2307/1938506

Braga ES, Bonetti CV, Burone L et al. (2000) Eutrophication and bacterial pollution caused by industrial and domestic wastes at the Baixada Santista Estuarine System-Brazil. Mar Pollut Bull 40:165–173. https://doi.org/10.1016/s0025-326x(99)00199-x

Camargo JA, Alonso Á (2006) Ecological and toxicological effects of inorganic nitrogen pollution in aquatic ecosystems: a global assessment. Environ Int 32:831–849. https://doi.org/10.1016/j.envint.2006.05.002

Carrey R, Otero N, Vidal-Gavilan G et al. (2014b) Induced nitrate attenuation by glucose in groundwater: Flow-through experiment. Chem Geol 370:19–28. https://doi.org/10.1016/j.chemgeo.2014.01.016

Carrey R, Rodriguez-Escales P, Otero N et al. (2014a) Nitrate attenuation potential of hypersaline lake sediments in central Spain: flow-through and batch experiments. J Contam Hydrol 164:323–337. https://doi.org/10.1016/j.jconhyd.2014.06.017

Chen QY, Lu ZS, Zhang XY et al. (2019) Study on the accumulation characteristics and conduction trend of water environment risk from taizihe river basin, china. Ecotoxicology 28(6):619–630. https://doi.org/10.1007/s10646-019-02058-6

China State Environmental Protection Administration (CSEPA) (2012) Monitoring and analysis methods for water and wastewater (Fourth Edition). China Environmental Science Press (In Chinese)

Chong LS, Prokopenko MG, Berelson WM et al. (2012) Nitrogen cycling within suboxic and anoxic sediments from the continental margin of Western North America. Mar Chem 128:13–25. https://doi.org/10.1016/j.marchem.2011.10.007

Daniel S, Didier A, Hélène H et al. (1990) Variation of nutrient stocks in the superficial sediments of Lake Geneva from 1978 to 1988. Hydrobiologia 207(1):161–166. https://doi.org/10.1007/BF00041453

Dimitrios AM, Georgios KS, Vassilios AT et al. (2007) Water quality of Vistonis Lagoon, Northern Greece: seasonal variation and impact of bottom sediments. Desalination 210:83–97. https://doi.org/10.1016/j.desal.2006.05.035

Domagalski J, Lin C, Luo Y et al. (2007) Eutrophication study at the Panjiakou-Daheiting Reservoir system, northern Hebei Province, People's Republic of China: chlorophyll-a model and sources of phosphorus and nitrogen. Agr Water Manage 94:43–53. https://doi.org/10.1016/j.agwat.2007.08.002

Fan CX, Morihiro A (1997) Effects of aerobic and anaerobic conditions on exchange of nitrogen and phosphorus across sediment-water interface in lake kasumigaura. J Lake Sci 9(4):337–342. In Chinese

Fan CX, Yang LY, Zhang L (2002) The vertical distributions of nitrogen and phosphorus in the sediment and interstitial water in Taihu Lake and their interrelations. J Lake Sci 12(4):359–366. In Chinese

Galloway JN, Townsend AR, Erisman JW et al. (2008) Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320:889–892. https://doi.org/10.1126/science.1136674

Gibson R, Atkinson R, Gordon J et al. (2012) Anthropogenic nutrient enrichment and blooms of harmful phytoplankton. Oceanogr Mar Biol Annu Rev 50:65–126. https://doi.org/10.1201/b12157-3

Hasegawa H, Rahman MA, Kitahara K et al. (2010) Seasonal changes of arsenic speciation in lake waters in relation to eutrophication. Sci Total Environ 408:1684–1690. https://doi.org/10.1016/j.scitotenv.2009.11.062

Havens KE, Fukushima T, Xie P et al. (2001) Nutrient dynamics and the eutrophication of shallow lakes Kasumigaura (Japan), Donghu (PR China), and Okeechobee (USA). Environ Pollut 111:263–272. https://doi.org/10.1016/s0269-7491(00)00074-9

Hu Q, Feng S, Guo H et al. (2007) Interactions of the Yangtze River flow and hydrologic processes of the Poyang Lake, China. J Hydrol 347:90–100. https://doi.org/10.1016/j.jhydrol.2007.09.005

Hu WF, Lo W, Chua H et al. (2001) Nutrient Release and Sediment Oxygen Demand in a Eutrophic Land-locked Embayment in Hong Kong. Environment International 26(5-6):369–375. https://doi.org/10.1016/S0160-4120(01)00014-9

Jin XC, Liu HL, Tu QY et al. (1995) Eutrophication of lakes in China [M]. Beijing: China Environment Press, 133-134

Li ZY, Zhang HJ (1993) Trophic state index and its correlation with lake parameters (in Chinese). Acta Scien Circum 13:391–397

Lu M, Zeng DC, Liao Y et al. (2012) Distribution and characterization of organochlorine pesticides and polycyclic aromatic hydrocarbons in surface sediment from Poyang Lake, China. Sci Total Environ 433:491–497. https://doi.org/10.1016/j.scitotenv.2012.06.108

Ma YQ, Zhang L, Zhao YM et al. (2015) Input Characteristics and Pollution Assessment of Nutrients Pollution in the Primary Pollution Source of the Daliao River (in Chinese). Environtal Sci 36:4013–4020

Nyenje PM, Foppen JW, Uhlenbrook S et al. (2010) Eutrophication and nutrient release in urban areas of sub-Saharan Africa-A review. Sci Total Environ 408:447–455. https://doi.org/10.1016/j.scitotenv.2009.10.020

Pedro T, Kimberley S, Fernando P (2013) Dynamics of phosphorus in sediments of a naturally acidic lake. Int J Sediment Res 28:90–102. https://doi.org/10.1016/S1001-6279(13)60021-9

Perkins RG, Underwood GJC (2001) The potential for phosphorus release across the sediment-water interface in an eutrophic reservoir dosed with ferric sulphate. Water Res 35(6):1399–1406. https://doi.org/10.1016/S0043-1354(00)00413-9

Rex JF, Petticrew EL (2010) Salmon-derived nitrogen delivery and storage within a gravel bed: sediment and water interactions. Ecol Eng 36:1167–1173. https://doi.org/10.1016/j.ecoleng.2010.02.001

Rozan TF, Taillefert M, Trouwborst RE et al. (2002) Iron-sulfur-phosphorus Cycling in the Sediments of a Shallow Coastal Bay: Implications for Sediment Nutrient Release and Benthic Macro-algal Blooms. Limnology Oceanography 47(5):1346–1354. https://doi.org/10.2307/3068954

Spears BM, Carvalho L, Perkins R et al. (2008) Effects of light on sediment nutrient flux and water column nutrient stoichiometry in a shallow lake. Water Res 42:977–986. https://doi.org/10.1016/j.watres.2007.09.012

Trimmer M, Nedwell DB (1998) Nitroge fluxes through the lower estuary of the River Great Ouse, England: the role of the bottom sediments. Marine Ecology-Progress Series. 163:109–124

Wang H, Wang CX, Wu WZ et al. (2003) Persistent organic pollutants in water and surface sediments of Taihu Lake, China and risk assessment. Chemosphere 50:557–562. https://doi.org/10.1016/s0045-6535(02)00484-8

Wang LQ, Liang T, Zhong BQ et al. (2014) Study on nitrogen dynamics at the sediment-water interface of Dongting Lake, China. Aquat Geochem 20:501–517. https://doi.org/10.1007/s10498-014-9232-0

Wang Q, Chen QY, Yan D et al. (2018) Distribution, ecological risk and source analysis of heavy metals in sediments of Taizihe River, China. Environ Earth Sci 77(569):1–14. https://doi.org/10.1007/s12665-018-7750-6

Wang YC, Wan GJ, Yin CQ et al. (2002) Distribution of total, exchangeable and fixed nitrogen in the sediments of two lakes in Guizhou province. J Lake Sci 2002 14(4):301–309. In Chinese

Wu F, Qing H, Wan G (2001) Regeneration of N, P and Si near the sediment/water interface of lakes from Southwestern China Plateau. Water Res 35:1334–1337. https://doi.org/10.1016/s0043-1354(00)00380-8

Xie YX, Xiong ZQ, Xing GX et al. (2007) Assessment of nitrogen pollutant sources in surface waters of taihu lake region. Pedosphere 17:200–208. https://doi.org/10.1016/s1002-0160(07)60026-5

Xu X, Gao BY, Zhao YQ et al. (2012) Nitrate removal from aqueous solution by Arundo donax L. reed based anion exchange resin. J Hazard Mater 203:86–92. https://doi.org/10.1016/j.jhazmat.2011.11.094

Yang ZP, Wang LQ, Liang T et al. (2015) Nitrogen distribution and ammonia release from the overlying water and sediments of Poyang Lake. China. Environ Earth Sci 74(1):771–778. https://doi.org/10.1007/s12665-015-4081-8

Ye XF, Bai JH, Lu QQ et al. (2014) Spatial and seasonal distributions of soil phosphorus in a typical seasonal flooding wetland of the Yellow River Delta. China. Environ Earth Sci 71:4811–4820. https://doi.org/10.1007/s12665-013-2872-3

Zhang LL, Yin JX, Jiang YZ et al. (2012) Relationship between the hydrological conditions and the distribution of vegetation communities within the Poyang Lake National Nature Reserve, China. Ecol Inform 11:65–75. https://doi.org/10.1016/j.ecoinf.2012.05.006

Zhou GY (2013) The balance of nitrogen and phosphorus during the trandportion in Daliao River (in Chinese) [D]. Donghua University

Zhu YX, Chen YQ (2011) SPSS multivariate statistical analysis method and application. Tsinghua University Press, Beijing, In Chinese

Zhu YY, Tang WZ, Jin X (2019) Using biochar capping to reduce nitrogen release from sediments ineutrophic lakes. Sci Total Environ 646:93–104. https://doi.org/10.1016/j.scitotenv.2018.07.277