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Potential Drivers of the Level and Distribution of Nitrogen in the Hyporheic Zone of Lake Taihu, China

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Abstract: The hyporheic zone is the connection between surface water and groundwater that often plays an important function in nutrient transport and transformation, and acts as an active source of or sink for nutrients to the surface water, depending on its potential water flow patterns. Bottom surface water and sediments in the shallow hyporheic zone (approximately 100 cm depth) were sampled at 12 sites near the shoreline and two sites at the center of Lake Taihu (China) during spring and winter of 2016. Concentrations of total nitrogen, ammonium, nitrate, and nitrite in the bottom surface water and porewater (obtained from sediments using a frozen centrifugation method) were analyzed in a laboratory to establish the nitrogen distribution and potential drivers. The results show that, in general, the quality of bottom water and porewater near the shoreline was poor compared to that at the center, and it gradually improved from the northwestern to the southeastern zones of Lake Taihu. No significant relationship in nitrogen concentration was found between the bottom water and porewater in surface sediments. Nitrogen concentrations in porewater differed between sampling sites and sediment depths in Lake Taihu. Vertical profiles of nitrogen in porewater and differences in nitrogen between the winter and spring seasons indicated that potential upwelling water flow occurred in the hyporheic zone in the south, west, north, and center zones of Lake Taihu, but potentially weak water flow in variable directions likely occurred in the east zone. A strong reducing environment dominated the deep parts of the hyporheic zone (i.e., below 40 cm depth), while a weak oxidizing environment dominated the shallow parts. Furthermore, the decreasing total nitrogen and ammonium nitrogen from the deep to shallow depths in the hyporheic zones in the south, west, north, and center zones indicated that potential anammox and/or denitrification processes occurred. In the east zone, potential weak nitrification processes occurred in the hyporheic zone, and plant fixation and sedimentation of nitrogen also contributed to the surface sediments. In conclusion, the hyporheic zone near the shoreline in the south, west, and north sites of Lake Taihu acts as an active source of nitrogen for the lake water due to potential upwelling water flows, whereas the east site acts as an active source or sink due to seasonally variable directions in water flow. Water flow and biogeochemistry in the hyporheic zone jointly influence nutrient distribution in the hyporheic zone and even switch or alternate the source/sink function of sediment in surface water.

Keywords: nitrogen; sediment; bottom water; porewater; biogeochemistry; Lake Taihu

1. Introduction

Lake Taihu, the third-largest freshwater lake in China, is a typical shallow and subtropical lake. Its water quality and aquatic ecosystem have severely degraded in recent decades due to continuously increasing inputs of pollutants and nutrients [1,2], and water eutrophication has consequently become a serious environmental problem [3,4]. Moreover, severe algal bloom over most of Lake Taihu in May

2007 led to a drinking water crisis in Wuxi City (north of Lake Taihu) that interrupted the drinking water supply for the approximately two million inhabitants for at least a week [4,5]. Since then, governments at all levels have taken more comprehensive countermeasures to control and reduce pollutant and nutrient inputs, including point and nonpoint pollution sources in the watershed [5,6]. Nevertheless, water quality in Lake Taihu has shown little improvement, and algal blooms still occur locally during summer. Particularly, the northern zone of the lake is often covered by algal bloom during summer, autumn, and even spring. During 2011, the cyanobacterial bloom covered 505 km^2, and distributed in the northern and western zones of Lake Taihu [4].

Increased inputs of exogenous-source pollutants from surrounding rivers, particularly from the north and west regions, are considered principally responsible for the environmental problems of Lake Taihu [7–9]. Since the 1980s, rapid industrialization and urbanization have resulted in an enormous amount of wastewater and sewage discharged into the lake. From 2000 to 2005, the annual total nitrogen (TN) load into Lake Taihu from rivers ranged from 2.08×10^7 to 2.69×10^7 kg $year^{-1}$ [8], whereas during 2014, it ranged from 4.06×10^7 to 5.45×10^7 kg $year^{-1}$ [10], indicating that the pollution loads flowing into the lake increased largely because of rapid economic development in this region. Additionally, intensifying agricultural production has been implemented with increasingly high fertilizer application in the Lake Taihu basin during recent decades to guarantee enough food for the increasing population [11,12]. For example, during 2010, the TN load from agricultural lands accounted for about 25.5% of the total input into Lake Taihu [4]. Controlling nutrient input is considered the most effective way to reduce the risk of blooms [13], and although significant efforts have been made to reduce the external nutrient loads in Lake Taihu [5], blooms have as yet shown no sign of decline.

Sediments in shallow lakes are considered another important source of nutrients [14,15]. Sediment–water interactions driven by hydrodynamics, disturbance, or diffusion have been shown to play important roles in nutrient cycling dynamics [16–19]. Xu et al. [10] estimated that the annual internal TN loading from sediment in Lake Taihu was about 5.52×10^6 to 8.93×10^6 kg $year^{-1}$ during 2009–2012, equivalent to 13–20% of its external TN loading, suggesting that the release of nutrients from sediments also contributes significantly to nutrients in the surface water [17,20]. Generally, nutrient releases from sediment are subject to many environmental factors, including wind current flow and the exchange flow patterns between the hyporheic zone and surface water systems [17,21,22]. Biogeochemical reactions are thought to occur at elevated rates within the hyporheic zone because this is where microbes and solutes are able to interact within a porous substrate [17,18,23]. Different flow patterns and heat transfer mechanisms in the two systems lead to complex interactions of diverse solute transport and transformations in the hyporheic zone. An upwelling or downwelling flow pattern in the hyporheic zone makes surface sediment a source or a sink to its overlying water [18,21,24]. Static flow patterns in the hyporheic zone generally have no significant function on sediment release, which is mainly dependent on solute diffusion or subject to disturbances by wind currents and benthic animals [19,23,25].

How flow patterns and biogeochemical processes influence nutrient distribution in the hyporheic zone and nutrient releases from surface sediments has attracted the attention regarding the management of large, shallow freshwater lakes. In this study, we selected several sampling sites (including both surface water and the hyporheic zone at about 100 cm depth) near the shoreline in Lake Taihu to (1) characterize the spatial biogeochemistry patterns of both porewater in the hyporheic zone and the corresponding bottom water; (2) analyze the relationships between porewater in surface sediments and bottom water; (3) determine the relationships in nitrogen concentration and distribution in porewater by comparing them between sampling sites and sediment depths; and (4) discuss the effects of potential flow patterns and biogeochemical processes on nitrogen distribution in the porewater of the hyporheic zone. Additionally, whether the surface sediments at the different sites tend to be sources or sinks for the lake water was compared and discussed based on the potential flow patterns in the hyporheic zone.

2. Materials and Methods

2.1. Study Area

Lake Taihu (30°55′40′′–31°32′58′′ N, 119°52′32′′–120°36′10′′ E) is a large, shallow, subtropical lake in the Yangtze Delta of China. The Lake Taihu basin is subject to East Asian monsoonal systems. Average annual temperature in this region is 16.0 °C, and average annual precipitation is approximately 1181 mm, with most precipitation occurring from May through September. The lake covers 2338 km^2, with maximum and mean water depths of approximately 3.0 and 1.9 m, respectively [4]. The Lake Taihu basin contains 117 main rivers and tributaries draining into the lake. Annual freshwater input to Lake Taihu is approximately 8.8×10^9 m^3, and the water retention time is approximately 310 days [1,4]. Generally, freshwater enters the lake through northwestern rivers, and leaves through southeastern rivers (e.g., Taipu River) [4,10]. The hydrodynamics of Lake Taihu are predominately controlled by wind solar heating [1,26,27]. Frequent wind-induced currents have notable effects on water and nutrient mixing and nutrient release from surface sediments in Lake Taihu [27,28].

2.2. Sample Collecting and Analysis

Bottom water (0.5 m above the surface sediments) and core sediment samples in Lake Taihu were collected once in March and once in December 2016, from 14 sites, including 12 near the shoreline and two at the center (Figure 1). The three sites near the shoreline on each side (E_1, E_2, and E_3 in the east; S_1, S_2, and S_3 in the south; W_1, W_2, and W_3 in the west; and N_1, N_2, and N_3 on the north side) and the two center sites (C_1 and C_2) were selected using a handheld GPS (Qcool, Hi-Target, Hong Kong, China). The first site (i.e., E_1, S_1, W_1, and N_1) on each side was 500 m away from the nearest shoreline, the second site (i.e., E_2, S_2, W_2, and N_2) was 2000 m away, and third (i.e., E_3, S_3, W_3, and N_3) was 6000 m away. At each site, the water depth was first recorded, and then water samples were collected at a depth of 0.5 m above the sediment surface using a self-made sample collector and replicated three times within a 10 m range. The sample collector was equipped with a water depth gauge and a polyvinyl chloride (PVC) tube (2 mm diameter) connected to a DC power peristaltic pump for drawing water at a specific depth. All water samples were stored on ice and transported within 2 h to the laboratory for further analysis. The filtered water (0.45 µm filter membrane) was analyzed for concentrations of ammonium nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), nitrite nitrogen (NO_2^--N), and TN.

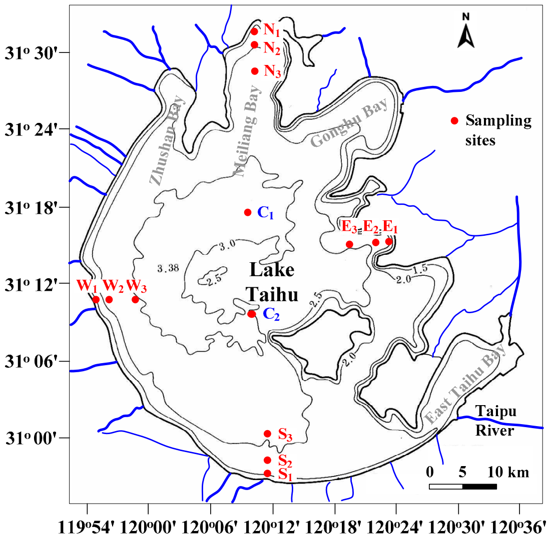


Figure 1. Main rivers (blue lines) surrounding Lake Taihu and sampling sites (red dots) of surface water and the hyporheic zone.

Three core sediment samples were collected at each site (the same as the water sample sites) using Plexiglas tubes (6.5 cm diameter) vertically inserted into the sediment to about 100–140 cm depth (depending on the sediment hardness) and gently extracted. Depending on the depth of sediment penetration, the upper and lower lids automatically opened when the Plexiglas tube was inserted into sediments to freely drain overlying water. When the tube was extracted, the upper and lower lids automatically closed to avoid disturbance of the core sediments. The core sediments were then sliced into several 20 cm depth sub-core sediments within 5 min, starting from the bottom of the tubes. All sediment samples were enclosed in black plastic bags, stored on ice, and transported to the laboratory within 2 h for further analysis. All sediment samples were refrigerated at 4 °C and centrifuged (Centrifuge, 07SUMEC/DZ6005-49A, Beckman Coulter, Fullerton, CA, USA) at 4000 rpm for 30 min. Then the supernatant liquid (porewater) was separated from the sediments and filtered using a 0.45 μm filter membrane.

Concentrations of NH_4^+-N, NO_3^--N, NO_2^--N, and TN in surface water and porewater samples were determined using Standard Methods 4500NH3-H, 4500NO3-I, 4500NO2-B, and 4500N-C, respectively, on a continuous flow injection autoanalyzer (FIA-6000, Skalar, The Netherlands). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NH_4^+-N, NO_3^--N, and NO_2^--N.

2.3. Data Processing

Nitrogen concentrations in the surface water or porewater are shown as mean ± standard deviation (mean ± *SD*). Independent sample *t*-tests were used to compare mean values, and differences were reported at two levels of significance: $p < 0.05$ and $p < 0.01$. A bivariate correlation procedure was used to calculate the Pearson's correlation coefficient (R) and significance level. Spatial differences were examined using one-way analysis of variance (ANOVA). The relationships among the measured independent variables were examined by a simple linear regression. All statistical analyses were performed in SPSS (version 19.0, IBM Corporation, Chicago, IL, USA).

3. Results

3.1. Nitrogen Concentrations in Bottom Water

NH_4^+-N concentrations in bottom water ranged from 0.09 to 1.98 mg L^{-1} (mean ± SD: 0.60 ± 0.56 mg L^{-1}) and peaked at site C_2 (winter) (Table 1), whereas the minimum value was found at site W_3 (spring). A significant difference in NH_4^+-N concentrations was found among sampling sites ($p < 0.05$). During both winter and spring seasons, NH_4^+-N concentrations in bottom water declined from the northwest to southeast zones, and a higher average concentration was found at the center zone (mean 1.75 mg L^{-1}) during winter and at the south zone (mean 0.25 mg L^{-1}) during spring. Average NH_4^+-N concentration during winter (mean 0.97 mg L^{-1}) was markedly higher than that during spring (mean 0.19 mg L^{-1}). Overall, the center, north and west zones were severely polluted by NH_4^+-N.

The NO_3^--N concentrations in the bottom water ranged between 0.06 and 2.82 mg L^{-1} (1.15 ± 0.78 mg L^{-1}), and peaked at site N_3 (winter) (Table 1). The minimum NO_3^--N concentration was found at site S_2 (spring). Significantly different NO_3^--N concentrations were also found among sampling sites ($p < 0.05$). Similar to NH_4^+-N distribution, a higher average NO_3^--N concentration was found at the center zone (mean 2.38 mg L^{-1} in winter and 1.35 mg L^{-1} in spring), and the overall NO_3^--N concentration in the lake declined from the northwest to the southeast zone. Almost all NO_3^--N concentrations during winter were markedly higher than those during spring, except at the west zone. NO_2^--N concentrations in bottom water ranged from 0.00 to 0.07 mg L^{-1}, which was relatively low compared to NO_3^--N concentrations. Higher average NO_2^--N concentrations were found at the east and center zones of the lake.

TN concentrations in the bottom water ranged from 1.27 to 9.86 mg L^{-1} (3.72 ± 2.08 mg L^{-1}). A significant difference was found among sampling sites ($p < 0.05$). The maximum concentration of TN in the bottom water peaked at site N_3 (winter) and the minimum at site E_1 (spring) (Table 1). The center and north zones had relatively high TN concentrations during both winter and spring. For the entire lake, the TN concentrations declined from northwest to southeast. Comparably, nitrogen concentrations including NH_4^+-N, NO_3^--N, NO_2^--N, and TN during winter were notably higher than those found during spring.

Table 1. Water depth (m) and nitrogen concentrations (mg L^{-1}) in bottom water at 14 sites of Lake Taihu during spring and winter 2016.

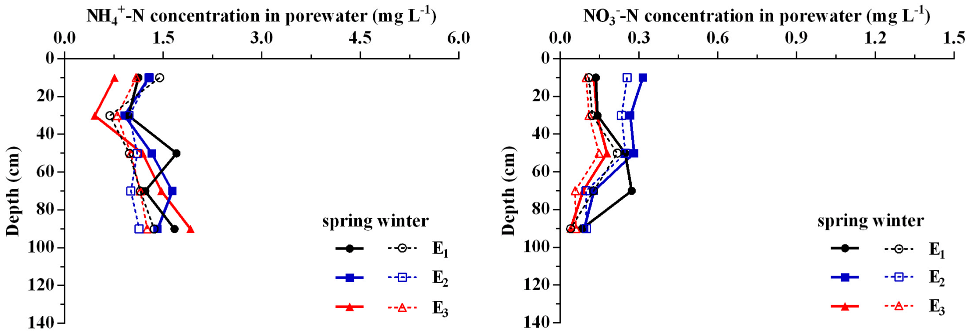
Sites	E_1	E_2	E_3	S_1	S_2	S_3	W_1	W_2	W_3	N_1	N_2	N_3	C_1	C_2
spring														
Depth	2.1	2.7	2.8	2.5	3.0	3.0	2.7	3.0	2.8	2.2	2.9	3.4	3.2	3.3
NH_4^+	0.15	0.28	0.22	0.25	0.27	0.22	0.27	0.16	0.08	0.17	0.11	0.12	0.16	0.19
NO_3^-	0.34	0.58	0.32	0.67	1.06	0.88	1.68	1.46	0.41	0.59	0.48	0.55	1.52	1.18
NO_2^-	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.02	0.00	0.01	0.01	0.01	0.01	0.01
TN	1.27	1.46	1.33	1.90	2.63	1.53	4.39	3.81	1.70	1.99	1.85	2.27	3.11	3.32
winter														
Depth	1.5	1.9	2.1	1.9	2.1	2.2	2.0	2.2	2.1	1.5	2.2	2.8	2.7	2.7
NH_4^+	0.22	0.73	0.80	1.22	0.47	0.93	1.06	0.25	0.26	1.03	1.32	1.80	1.98	1.52
NO_3^-	1.55	1.58	1.59	2.02	1.08	1.03	1.43	1.37	1.12	1.47	1.81	2.82	2.39	2.37
NO_2^-	0.05	0.02	0.07	0.04	0.00	0.01	0.00	0.01	0.02	0.00	0.00	0.03	0.03	0.03
TN	4.00	5.23	5.03	6.52	2.97	3.92	2.76	4.75	2.20	5.99	5.91	9.86	6.14	6.36

3.2. Nitrogen Distributions in the Porewater of the Hyporheic Zone

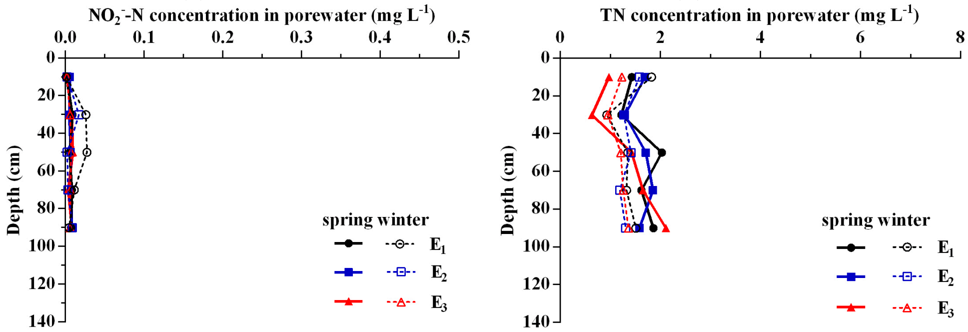
In the shallow hyporheic zone (about 100 cm) of Lake Taihu, NH_4^+-N concentrations in porewater at the east zone (sites E_1, E_2, and E_3) ranged from 0.69 to 1.44 mg L^{-1} (1.10 ± 0.2 mg L^{-1}) during winter and from 0.46 to 1.92 mg L^{-1} (1.27 ± 0.39 mg L^{-1}) during spring (Figure 2a). The NH_4^+-N concentrations had similar vertical distributions during both seasons. Lower concentrations were found at 20–40 cm depth and higher values at 80–100 cm depth. The mean NH_4^+-N concentrations during spring at the east zone were slightly higher than those during winter. NO_3^--N concentrations in porewater at the east zone (Figure 2b) ranged between 0.04 and 0.25 mg L^{-1} (0.13 ± 0.07 mg L^{-1}) during winter and between 0.04 and 0.31 mg L^{-1} (0.16 ± 0.09 mg L^{-1}) during spring. Higher NO_3^--N concentrations were found at 40–60 cm depth (at E_1 and E_3) or in surface sediments (at E_2) during both seasons, whereas lower values were all observed at 80–100 cm depth. NO_2^--N concentrations in porewater at the east zone (Figure 2c) were low compared to NO_3^--N and NH_4^+-N concentrations. TN concentrations in porewater at the east zone ranged from 0.93 to 1.82 mg L^{-1} (1.31 ± 0.22 mg L^{-1}) during winter and from 0.63 to 2.11 mg L^{-1} (1.54 ± 0.39 mg L^{-1}) during spring (Figure 2d). Relatively low TN concentrations were measured at 20–40 cm depth at the three sites. The overall distributions of TN in porewater of the hyporheic zone at east zone were similar to those of NH_4^+-N (Figure 2a).

At the south sites (S_1, S_2, and S_3), NH_4^+-N concentrations in porewater ranged from 1.24 to 4.31 mg L^{-1} (2.53 ± 0.80 mg L^{-1}) during winter and from 1.40 to 4.11 mg L^{-1} (2.64 ± 0.73 mg L^{-1}) during spring (Figure 3a). These values were markedly higher and ranged wider than those at the east sites. The NH_4^+-N concentrations increased sharply from shallow to deep depths. The mean NH_4^+-N concentrations at sites S_1 and S_2 during winter were slightly higher than those during spring and were slightly lower at S_3. NO_3^--N concentrations in porewater (Figure 3b) ranged between 0.05 and 0.44 mg L^{-1} (0.21 ± 0.13 mg L^{-1}) during winter and between 0.08 and 0.50 mg L^{-1} (0.25 ± 0.12 mg L^{-1}) during spring. Mean NO_3^--N concentrations at the three sites during spring were slightly higher than those during winter. NO_2^--N concentration distributions in porewater (Figure 3c) differed markedly between sampling sites. Relatively high NO_2^--N concentrations at site S_1 and relatively low values at site S_2 were measured at 20–60 cm depth. NO_2^--N concentrations at the south sites were higher than those at the east sites. TN concentrations in porewater ranged from 1.69 to 5.08 mg L^{-1} (3.00 ± 0.88 mg L^{-1}) during winter and from 1.92 to 4.91 mg L^{-1} (3.08 ± 0.82 mg L^{-1}) during spring

(Figure 3d). At sites S_2 and S_3, the TN concentrations increased sharply from shallow to deep depths during both seasons. At sites S_1 and S_2, the mean TN concentrations during winter were slightly higher than those during spring, but were slightly lower at site S_3.

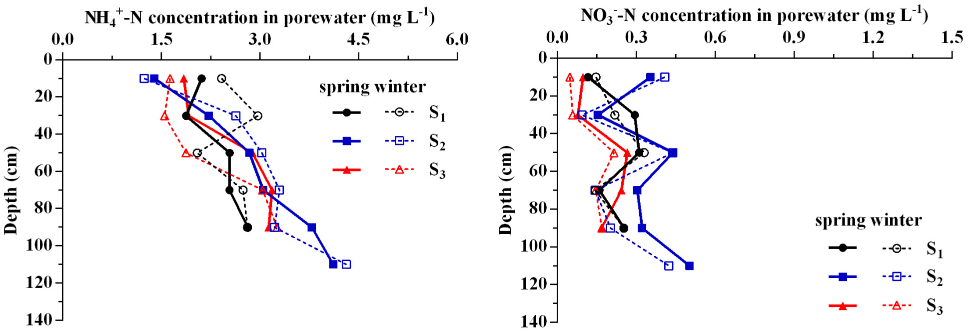


(**a**) NH_4^+-N (**b**) NO_3^--N

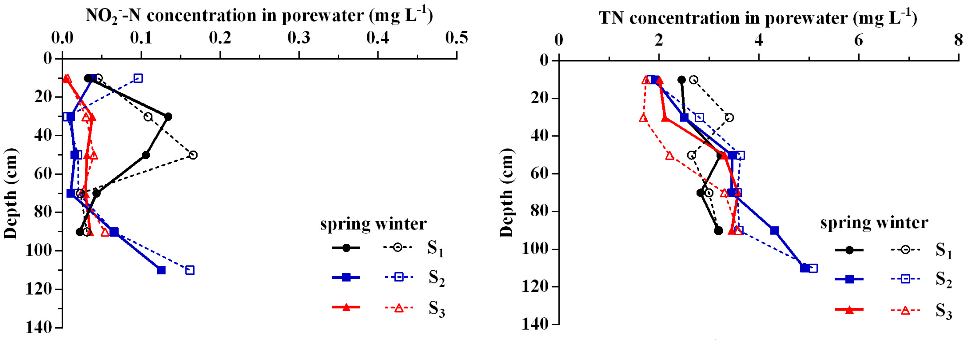


(**c**) NO_2^--N (**d**) TN

Figure 2. Vertical profiles of nitrogen in the porewater of the hyporheic zone at the east sites in Lake Taihu during spring and winter 2016.



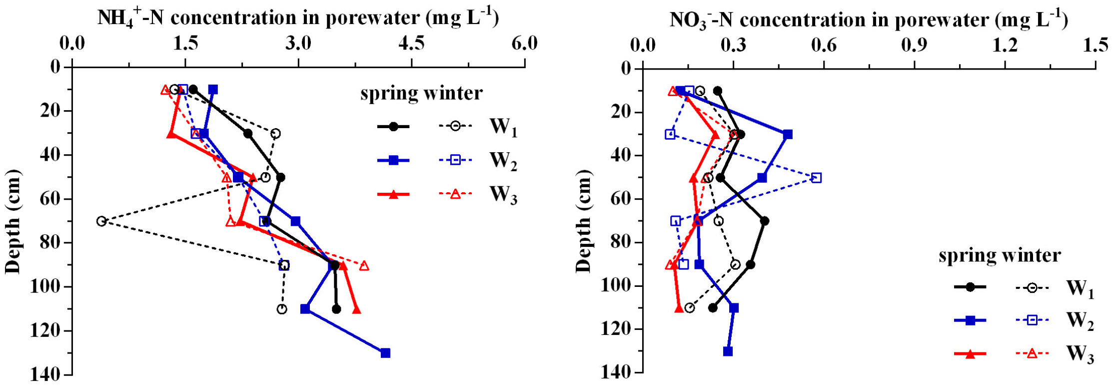
(**a**) NH_4^+-N (**b**) NO_3-N



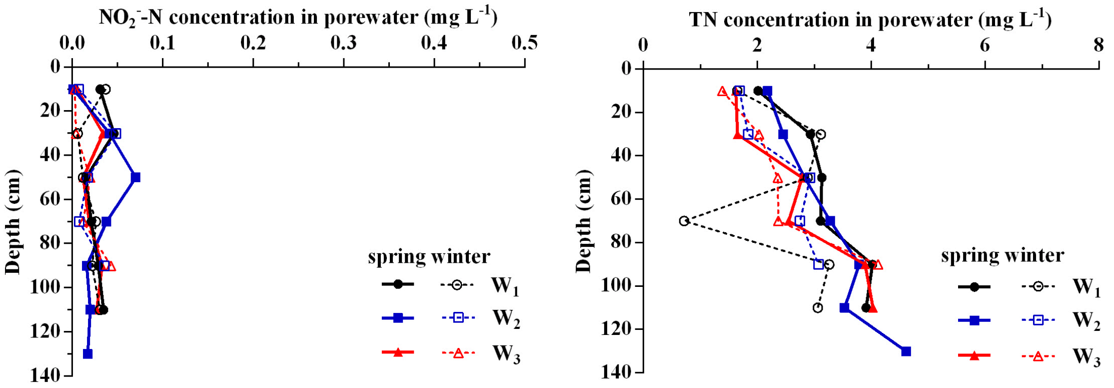
(**c**) NO_2^--N (**d**) TN

Figure 3. Vertical profiles of nitrogen in the porewater of the hyporheic zone at the south sites in Lake Taihu during spring and winter 2016.

At the west zone (sites W_1, W_2, and W_3), NH_4^+-N concentrations in porewater ranged from 0.39 to 3.87 mg L^{-1} (2.14 ± 0.83 mg L^{-1}) during winter and from 1.31 to 4.15 mg L^{-1} (2.66 ± 0.85 mg L^{-1}) during spring (Figure 4a). Similar to findings at the south sites, NH_4^+-N concentrations continuously increased from shallow to deep depths. The mean NH_4^+-N concentrations during spring were higher than those during winter at the three sites. NO_3-N concentrations in porewater (Figure 4b) ranged between 0.09 and 0.58 mg L^{-1} (0.21 ± 0.12 mg L^{-1}) during winter and between 0.10 and 0.48 mg L^{-1} (0.25 ± 0.11 mg L^{-1}) during spring. Relatively low $NO_3^{—}$N concentrations at the three sites were measured in the surface sediments, and relatively high values mainly were found at 20–40 cm depth. Compared to winter, mean NO_3^--N concentration increased slightly during spring at sites W_1 and W_2, but decreased slightly at site W_3. Distribution of NO_2^--N concentration (Figure 4c) was similar to that at the east sites, with relatively high values. TN concentration in the porewater ranged from 0.71 to 4.12 mg L^{-1} (2.45 ± 0.86 mg L^{-1}) during winter and from 1.62 to 4.61 mg L^{-1} (3.07 ± 0.86 mg L^{-1}) during spring (Figure 4d). Almost all TN concentration at the three sites during both seasons increased with sediment depth, except at site S_1 during winter. At sites W_1 and W_2, the mean TN concentration during spring was higher than during winter, whereas at site W_3 the mean TN concentration was similar during both seasons.



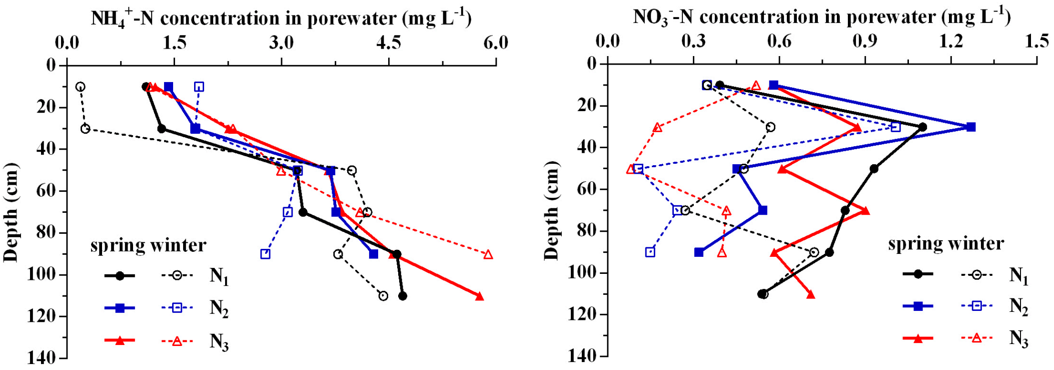
(**a**) NH_4^+-N (**b**) NO_3^--N



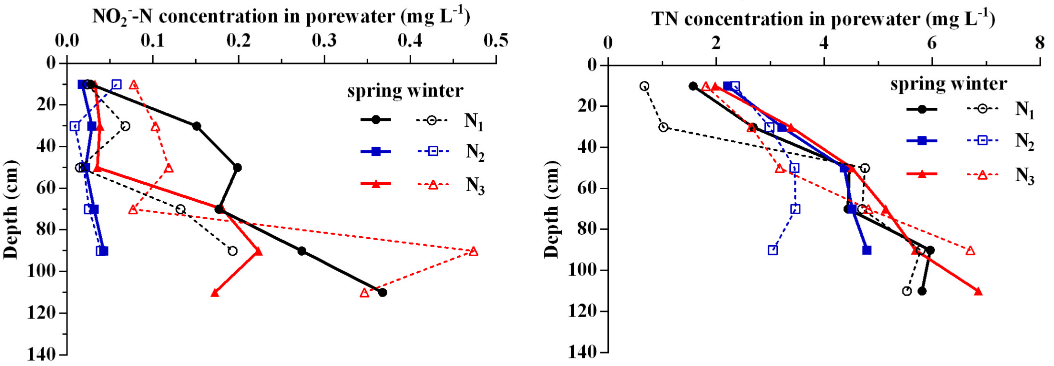
(**c**) NO_2^--N (**d**) TN

Figure 4. Vertical profiles of nitrogen in the porewater of the hyporheic zone at the west sites in Lake Taihu during spring and winter 2016.

In the north zone (sites N_1, N_2, and N_3), NH_4^+-N concentration in the porewater ranged from 0.19 to 5.89 mg L^{-1} (2.88 ± 1.56 mg L^{-1}) during winter and from 1.11 to 5.77 mg L^{-1} (3.21 ± 1.43 mg L^{-1}) during spring (Figure 5a). Compared to other zones, NH_4^+-N concentration at the north zone increased much more from shallow to deep depths. Mean concentration of NH_4^+-N at each of the three sites during spring was markedly higher than the respective values during winter. NO_3^--N concentration in porewater (Figure 5b) ranged between 0.08 and 1.01 mg L^{-1} (0.40 ± 0.24 mg L^{-1}) during winter and between 0.32 and 1.27 mg L^{-1} (0.70 ± 0.25 mg L^{-1}) during spring. A marked difference in NO_3^--N concentration was found among the three sites and between both seasons. At N_1 and N_2, NO_3^--N concentration increased notably from the surface, peaking at 20–40 cm depth and then decreased quickly to deep depth during spring, whereas at N_3 the NO_3^--N concentration oscillated on the vertical between 0.55 and 0.90 mg L^{-1}. Furthermore, the NO_3^--N concentration below surface during winter decreased notably compared with that during spring. Similar to the findings at the south sites, the NO_2^--N concentration distribution in porewater (Figure 5c) differed markedly between sampling sites. At sites N_1 and N_3, NO_2^--N concentration increased from the surface sediment downward, and increased rapidly below 40 cm depth, whereas at site N_2, NO_2^--N concentration varied little vertically and values remained relatively low. TN concentration in porewater ranged from 0.67 to 6.70 mg L^{-1} (3.56 ± 1.71 mg L^{-1}) during winter and from 1.57 to 6.85 mg L^{-1} (4.21 ± 1.51 mg L^{-1}) during spring (Figure 5d). Similar to the NH_4^+-N profiles, relatively low concentrations of TN were measured in surface sediments, and these increased sharply with sediment depth. Comparably, TN concentration at site N_1 showed relatively large differences between winter and spring. Vertically, TN concentration below 40 cm depth varied widely between the three sites.



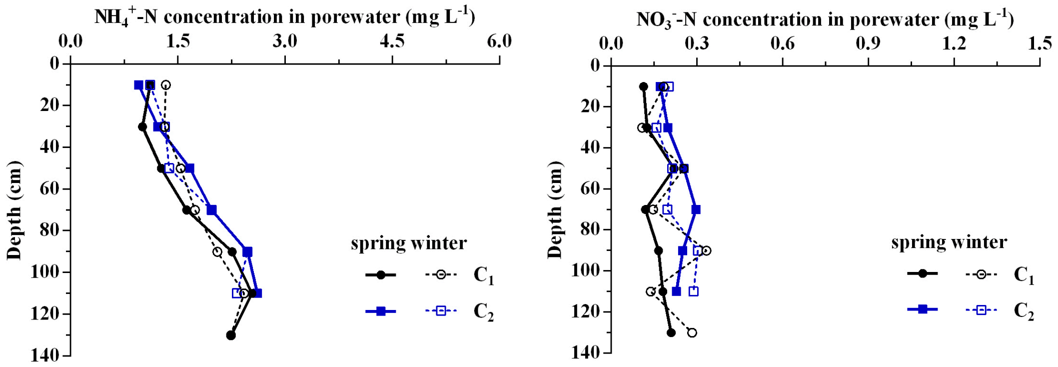
(**a**) NH_4^+-N (**b**) NO_3^--N



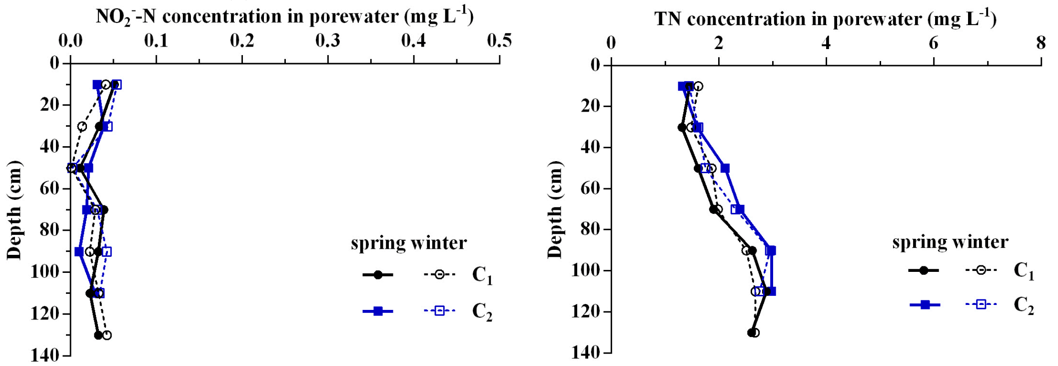
(**c**) NO_2^--N (**d**) TN

Figure 5. Vertical profiles of nitrogen in the porewater of the hyporheic zone at the north sites in Lake Taihu during spring and winter 2016.

At the center sites (C_1 and C_2), the NH_4^+-N concentration in the porewater ranged from 1.11 to 2.48 mg L^{-1} (1.79 ± 0.48 mg L^{-1}) during winter and from 0.95 to 2.61 mg L^{-1} (1.77 ± 0.62 mg L^{-1}) during spring (Figure 6a). The NH_4^+-N concentration at the two sites showed similar distribution and levels during both seasons. The NO_3^--N concentration in the porewater (Figure 6b) ranged between 0.11 and 0.33 mg L^{-1} (0.22 ± 0.07 mg L^{-1}) during winter and between 0.11 and 0.30 mg L^{-1} (0.19 ± 0.06 mg L^{-1}) during spring. Compared to findings at other zones, the NO_3^--N concentration at the center sites showed a uniform vertical distribution. The NO_2^--N concentration (Figure 6c) varied slightly on the vertical and maintained low values. The TN concentration in porewater ranged from 1.44 to 2.95 mg L^{-1} (2.13 ± 0.54 mg L^{-1}) during winter and from 1.31 to 2.98 mg L^{-1} (2.14 ± 0.64 mg L^{-1}) during spring (Figure 6d). Overall, the TN concentration increased from shallow to deep depths and maintained low values. Additionally, similar to findings at the east sites, differences in nitrogen concentration were small between sites C_1 and C_2 and between winter and spring.



(**a**) NH_4^+-N (**b**) NO_3^--N



(**c**) NO_2^--N (**d**) TN

Figure 6. Vertical profiles of nitrogen in the porewater of the hyporheic zone at the center sites in Lake Taihu during spring and winter 2016.

3.3. Nitrogen Percentages and Correlation Between Bottom Water and Porewater

In all bottom water samples (Table 1), the DIN comprised 28.8–90.2% (mean 51.0%) of the TN with highest value at W_1 (winter) (Appendix A Table A1). Furthermore, NH_4^+-N comprised 5.0–19.4% (mean 14.3%) of the TN. These percentages were significantly higher at the center zone (mean 16.8%) and at the north south zone (16.0%). Site W_1 had the highest average percentage of TN consisting of NH_4^+-N (22.3%) during both seasons, followed by site C_1 (18.7%). Overall, at the west and north zones, the average percentages of TN consisting of NH_4^+-N during both seasons decreased from the near-shore sites (W_1, N_1) to the far-shore sites (W_3, N_3). However, at the south zone, the average percentages increased from the near-shore site (S_1) to the far-shore site (S_3), whereas at the east zone, E_2 had a higher percentage of TN consisting of NH_4^+-N compared to those at E_1 and E_3.

In all porewater samples, DIN comprised 85.4–97.8% (mean 95.6%) of TN during winter and 87.6–97.5% (mean 94.6%) during spring (Appendix A Table A1), indicating that inorganic nitrogen predominated in porewater. Furthermore, NH_4^+-N in porewater comprised an average 84.6% of TN during winter and 82.2% during spring. NH_4^+-N was the dominant species of nitrogen in the porewater of the hyporheic zone, markedly different from the lake bottom water, where NH_4^+-N comprised about 14.3% of the TN. The percentages of TN consisting of DIN clearly decreased from the northwestern to southeastern zones over the entire lake. In addition, significant differences among sampling sites ($p < 0.05$) were found in the ratios of NH_4^+-N to NO_3-N, ranging from 0.45 to 48.73, with an average of 11.57. TN concentration in the porewater had a significantly positive relationship with NH_4^+-N ($R = 0.977$, $p < 0.01$), NO_3^--N ($R = 0.469$, $p < 0.01$), and NO_2^--N ($R = 0.640$, $p < 0.01$). NH_4^+-N concentration in the porewater had a positive relationship with NO_3^--N ($R = 0.285$, $p < 0.05$), and NO_2^--N ($R = 0.521$, $p < 0.01$), and NO_3^--N also had a positive relationship with NO_2^--N ($R = 0.549$,

$p < 0.01$). No significant relationship in nitrogen concentration was found between porewater in surface sediments and bottom water.

4. Discussion

4.1. Relationships between Porewater in Surface Sediment and Bottom Water

The overall nitrogen distribution in bottom water was closely related to input of nitrogen from polluted rivers around Lake Taihu and the overall flow direction from northwest to southeast [8,27,29]. The north and west zones of the lake receive large nutrient loads from some main rivers (Figure 1), including a large amount of agricultural runoff and drainage during the irrigation period (summer and winter), and the south zone also receives effluents and agricultural runoff from Zhejiang Province through rivers [4,29,30]. High percentages of TN consisting of DIN in the bottom water also responded well to the nitrogen source distribution surrounding Lake Taihu. Other studies [1,8,16,25] have also reported that serious pollution often occurs in the northwest zone of Lake Taihu, compared to the southeast zone, and cyanobacterial blooms usually occur and aggregate in the northwest zone.

The percentage of TN consisting of DIN and nitrogen concentration in the porewater closely corresponded with the current and long-term water pollution distribution in Lake Taihu [4]. Comparably, the NH_4^+ concentration in the porewater at most sites was higher than respective values in the bottom water during both seasons, except at C_1, C_2, S_3, N_1, and N_3 during winter (Table 1 and Figures 2–6). However, the TN and NO_3^- concentrations in the porewater at most sites were notably lower than respective values the in the bottom water during both seasons. In general, nutrients in surface sediments exchange with overlying water by diffusion or disturbance, and the nutrient concentration in the porewater of surface sediments significantly correlated with those in the overlying water because of ease of release from surface sediments [21,31,32]. Many studies [14,19,32,33], including laboratory incubation, in-situ monitoring, and mathematical simulation, have reported that nutrient release across the water–sediment interface strongly influenced the nutrient concentration in overlying water. However, in this study, no significant relationships in nitrogen concentrations were found between the porewater of surface sediments and the bottom water during either season, suggesting that the nitrogen levels in the bottom water were not dominated by the release of surface sediments. One possibility was that the bottom water in this study was sampled at a location 0.5 m from the sediment surface, a larger distance than samples in other studies (e.g., ~5 cm in [32]). Another possiblility was that frequent wind currents on Lake Taihu mixed the water vertically [25,27] and consequently weakened the relationship between the porewater in surface sediments and bottom water.

4.2. Effect of Potential Flow Patterns in the Hyporheic Zone

The hyporheic zone is a region where surface water and groundwater exchange occurs and where chemical reactions and microbial activities are enhanced [17,18], which serve important functions for hydraulic relationships and nutrient transport and transformation between the two systems [17,21,34]. In Lake Taihu, the surrounding groundwater table is subject to uneven yearly precipitation and seasonal agricultural irrigation, whereas the lake level is mostly artificially controlled. As a result, the hydraulic gradients between the lake and surrounding groundwater vary seasonally and yearly. Water flow in the hyporheic zone near the shoreline is easily driven by the hydraulic gradient, resulting in upwelling or downwelling water flow [34]; however, water flow quantities and direction at the center of the lake are difficult to decipher because there is very little difference in hydraulic heads [22,27]. Consequently, the major exchange between the lake water and the groundwater occurs in a narrow band zone near the shoreline. The exchange direction commonly depends on the hydraulic gradients between the lake water and the surrounding groundwater, and even changes seasonally [22]. Upwelling flow generally carries nutrients from the shallow groundwater into the hyporheic zone and then releases them into the overlying water, whereas downwelling flow carries nutrients from the overlying water into the hyporheic zone and then into the groundwater [35].

In this study, based on the observed vertical chloride concentration distribution in the porewater of the hyporheic zone (not shown here), the surface sediments at the south, west, and north sites during winter were mainly subject to lake water with similar chloride concentrations of 26.3–35.1 mg L^{-1}, whereas during spring they were likely influenced by relatively high chloride concentrations from shallow groundwater (60–180 mg L^{-1}). Additionally, at the south, west, and north sites, the chloride concentrations gradually decreased from deep to shallow depths during both the spring and winter seasons. Particularly, the chloride concentrations in the porewater increased markedly in shallow sediments and were slightly higher than those in the bottom water. Accordingly, upwelling or upward sloping water flow largely occurs in the hyporheic zone at these sites. Comparably, the water flow in the hyporheic zone was weaker at the center sites and varied alternately in flow direction at the east sites.

The nutrients in the deep sediments were mainly derived from deposition over the past years or were transported along with water flow and transformed based on the sediment environment. Relatively high concentrations of TN, and NH_4^+-N existed at lower parts of the hyporheic zone at the south, west, north, and center sites and decreased toward shallow sediments (Figures 3–6), suggesting that the nitrogen was probably derived from shallow groundwater through upwelling or upward sloping flow. In this way, the nitrogen derived from surrounding agricultural lands during irrigated periods (summer and winter) contributed substantially to the shallow groundwater and consequently resulted in differences in nitrogen concentration in the hyporheic zone between the winter and spring seasons (Figures 3–6). However, at the east zone, the overall vertical profiles of the nitrogen concentration were relatively uniform with limited variability (Figure 2), further suggesting that no obvious water flow occurred at the east zone, or only weak water flow existed, with seasonally alternating direction. Furthermore, the slightly low concentration of nitrogen exhibited at 20–40 cm depth at the east zone (Figure 2a,d), which apparently differed from other zones (Figures 3–6), indicated that the interacting location of the lake water and the groundwater was possibly at the subsurface. In general, pronounced upwelling or upward sloping water flow often occurs across the sediment–water interface and acts as an active source of nutrients to surface water, but downwelling or downward sloping seepage is usually weakened by clogged surface sediments caused by sedimentation and the infusion of fine particles from surface water [22,34]. Accordingly, even if the downwelling water flow potentially existed at the east zone, the infiltration depth of lake water remained limited (e.g., 20–40 cm, Figure 2a,b).

4.3. Effect of Potential Biogeochemical Processes in the Hyporheic Zone

In addition to the effects of potential water flow, the nitrogen in the porewater of the hyporheic zone was likely subject to complex biogeochemistry processes based on the vertical distribution of different nitrogen species. First, high proportions of DIN (average 95.6% and 94.6% during winter and spring, respectively) suggested that mineralization was predominant in the porewater of the hyporheic zone. At most sites, the DIN concentrations were highest at deeper depths of the hyporheic zone, and NH_4^+-N comprised a majority of the TN. In oxygen-depleted zones with high organic matter, mineralization of organic matter, which is the major source of NH_4^+-N, generally results in NH_4^+-N accumulation at deeper depths [35–37]. Additionally, in deep sediment, the dissimilatory nitrate reduction to ammonium (DNRA) process should not be neglected within reducing environments, which decreases the NO_3^--N and correspondingly increases the NH_4^+-N in porewater [38,39].

Second, NH_4^+-N concentrations at all sites decreased rapidly from the bottom to the surface of the hyporheic zone, in particular at the south, west, and north sites (Figures 3–5), indicating that the NH_4^+-N was possibly removed or transformed by biogeochemical processes in the hyporheic zone, such as nitrification and anaerobic ammonium oxidation (anammox) [34,40]. Oxygen is considered a main factor influencing nitrogen transformations in the hyporheic zone; however, the oxygen penetration depth below the sediment–water interface is limited by higher levels of consumption and lower diffusion efficiency [18,31,32]. The redox conditions in the porewater of the hyporheic zone were mostly reductive [33,41], a finding also supported by the dominant reduced form of Fe, Fe^{2+} (percentages of Fe^{2+} to Fe ranged from 0.12 to 0.99 with an average of 0.73) in the hyporheic zone, especially below about 40 cm. Anammox possibly occurred in the porewater of the deep hyporheic zone (i.e., below 40 cm depth), a process frequently reported by other studies from lake, river, or ocean sediments [32,33,38]. Relatively high ratios of NH_4^+-N to NO_3^--N in porewater might be subject to a sluggish nitrification process caused by low oxygen concentration [19,32,42]; however, positive relationships among NH_4^+-N, NO_2^--N, and NO_3^--N indicated that the NO_3^--N and NO_2^--N in porewater were mainly derived from the nitrification of NH_4^+-N during both seasons. Nitrification could mostly occur in shallow sediments (i.e., above 40 cm depth), where low oxygen could exist due to diffusion and disturbance but is limited to deep sediments. In general, the nitrification process transforms NH_4^+-N into NO_2^--N and then NO_3^--N in the porewater while anammox would remove NH_4^+-N by the production of gaseous-N and decrease N-oxide concentrations [32,37,39].

Third, the vertical profiles of NO_3^--N and NO_2^--N were relatively uniformly distributed except those at the north and south sites (Figures 3 and 5), indicating that NO_3^--N and NO_2^--N concentrations changed little along upwelling water flow, or that increased NO_2^--N was removed again through biogeochemical processes (e.g., anammox) at these sites. The NO_3^--N concentration in shallow groundwater was usually high (4–15 mg L^{-1}). If potential upwelling water flow existed at the south, west, and north sites, some removal processes of NO_3^--N such as denitrification, anammox, and DNRA likely occurred in the hyporheic zone [43,44]. However, DNRA is not the dominant process based on declining vertical distributions of NH_4^+-N, although it has been documented as an important fate of NO_3^- in anoxic sediments [43,45–47]. The prevailing conceptual model of DNRA also suggests that it is restricted to highly reducing conditions [44,45,48]. At the north sites, NO_3^--N significantly increased from deep areas to a depth of 20–40 cm, and then decreased to surface sediments, but the NO_2^--N decreased continuously (Figure 5). This finding indicates that, excepting the denitrification or anammox processes, nitrification processes occurred below a depth of 40 cm at these sites, likely due to low oxygen from some vertical macropore flow or groundwater (Figure 7).

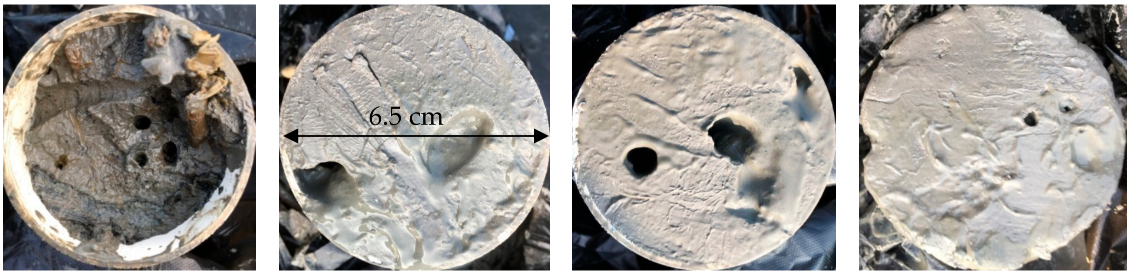


Figure 7. Vertical macropores in the hyporheic zone at a north sampling site of Lake Taihu (left to right represent deep sediment to shallow sediment).

Furthermore, the vertical TN distribution in the porewater was similar to the NH_4^+-N distribution, inferring that the nitrogen losses were mainly derived from the direct loss of NH_4^+-N or the indirect loss of N-oxides. We can at least infer that the removal processes (denitrification or anammox, or both) indeed occurred in the porewater of the hyporheic zone, based on marked declining patterns of TN from deep to shallow depths in the porewater at the south, west, north, and center sites (Figures 3–6) and high percentages of DIN to TN. For example, during winter, TN decreased on average about 87.9%, 23.0%, and 73.0% from deep to shallow porewater at sites N_1, N_2, and N_3, respectively, and 73.0%, 53.8%, and 71.1% during spring, respectively. The reduced nitrogen was probably lost as gaseous N_2/N_2O through denitrification and anammox processes, considered the most important processes for removing reactive nitrogen from natural aquatic sediments and wetland soils [32,41,49]. Furthermore, these two processes occurred mostly in deep sediment. Due to the concurrent rapid decline of TN, NO_2^--N, and NH_4^+-N at sites N_1 and N_3, we deduced that the anammox process dominated in the lower part of the hyporheic zone. Additionally, at these two sites the NO_3^--N concentrations increased rapidly from deeper areas to 20–40 cm depth, and we therefore deduce that nitrification also occurred below a depth of 20 cm, possibly owing to the existence of some macropores in the hyporheic zone at these sites (Figure 7). At the east sites, both nitrification and denitrification occurred slightly, leading to small decreases in TN from deep to shallow porewater (Figure 2). Similar to the vertical profiles of NH_4^+-N and NO_3^--N at the east zone in this study, Sheibley et al. [42] deduced that nitrification and denitrification occurred in a hyporheic zone of the Shingobee River (USA). Additionally, slightly high concentrations of NH_4^+-N, NO_3^--N, and TN in surface sediments at the east zone (Figure 2a,b,d) indicated that sedimentation or plant fixation of nitrogen occurred at the surface sediments [50] together with seasonally downwelling water flow. However, the south zone had different nitrogen profiles than the east zone, although the south zone also has large quantities of hydrophytes. This phenomenon possibly occurred because the sedimentation and infusion of nitrogen at the south zone were restricted by potential upwelling water flow. Overall, at most sites of Lake Taihu, possible denitrification and anammox processes dominated in the lower part of the hyporheic zone, but both nitrification and denitrification dominated in the upper part, while at the north zone nitrification likely also dominated below a depth of 40 cm because of existing macropores.

In conclusion, differences in nitrogen distribution among sampling sites and among sediment depths in Lake Taihu were subject to both biogeochemistry and water flow in the hyporheic zone. Potential water flow in the hyporheic zone plays a key function in nutrient exchange between surface water and groundwater as an active source or sink, while biogeochemistry processes also determine the exchange concentrations and quantities of nutrients. Further study is needed to elucidate these processes and detail the nitrogen losses in such a large, shallow, eutrophic lake.

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Author Contributions: Yong Li conceived and designed the experiments; Shuang Wang, Weiwei Zhang, Jiahui Yuan and Chun Xu performed the experiments; Shuang Wang, Weiwei Zhang, Jiahui Yuan and Chun Xu analyzed the data; Yong Li contributed reagents/materials/analysis tools; Yong Li wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Average percentages of total nitrogen (TN) consisting NH_4^+-N and dissolved inorganic nitrogen (DIN) and ratios of NH_4^+-N to NO_3^--N in bottom surface water and porewater in the hyporheic zone at 14 sampling sites in Lake Taihu during 2016.

Sites	E_1	E_2	E_3	S_1	S_2	S_3	W_1	W_2	W_3	N_1	N_2	N_3	C_1	C_2
Bottom water														
NH_4^+/NO_3^- *	0.29	0.47	0.60	0.49	0.34	0.58	0.45	0.15	0.21	0.49	0.48	0.43	0.47	0.40
NH_4^+/TN **	0.09	0.17	0.16	0.16	0.13	0.19	0.22	0.05	0.08	0.13	0.14	0.12	0.19	0.15
DIN/TN **	0.42	0.52	0.45	0.50	0.51	0.61	0.68	0.39	0.46	0.40	0.43	0.39	0.63	0.52
Porewater														
NH_4^+/NO_3^- *	11.39	7.57	14.79	12.62	11.81	19.65	9.37	13.59	17.39	5.37	10.10	10.31	10.33	7.74
NH_4^+/TN **	0.81	0.81	0.85	0.85	0.85	0.90	0.83	0.86	0.88	0.66	0.79	0.79	0.84	0.81
DIN/TN **	0.92	0.95	0.95	0.95	0.96	0.97	0.96	0.96	0.96	0.95	0.96	0.96	0.94	0.93

Notes: * Ratios of NH_4^+-N to NO_3^--N. ** Percentages of TN consisting NH_4^+-N or DIN (NH_4^+-N + NO_3^--N + NO_2^--N).

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