Sedimentary nitrogen fractions and source assignment from different inflows to a receiving lake
Xiaojun Li, Yanping Zhao, Guoxiang Wang, Ruiming Han, Xinyi Dang, Zhuoran Li, Jiafeng Ren and Chenxi Gao

ABSTRACT

The spatial distribution of the sediment nitrogen in ten typical estuaries of Lake Taihu was determined. A simple quantitative estimation model and principal component analysis (PCA) method were applied to find the source and major factors of estuarine sediment nitrogen loading. The average concentrations of total nitrogen (TN), organic nitrogen (Org-N), ammonium nitrogen (NH\textsubscript{4}^{+}-N) and nitrate-nitrogen (NO\textsubscript{3}^{-}-N) in the sediments of the ten estuaries were 1315.5, 1220.1, 82.53 and 6.45 mg/kg, with the organic fraction dominating. Results showed a significant difference for the TN concentration in sediments of different estuaries, which was mainly caused by geographical location, land use type and vegetation restoration measures. An important result was that sediment nitrogen in 80% of the estuaries was mainly originated from autochthonous algae and presettled organic matter, although there has been continuous pollution input from inflow rivers. The source estimation results found that the autochthonous aquaculture excretion, algae and hydrophyte debris and buried biodebris accounted for 58.9% of the total nitrogen loading, which dominated the nitrogen sources compared with the pollution input. In addition, the PCA method was used to find that phosphorus loading and redox conditions were the major limiting factors affecting the distribution of inorganic NH\textsubscript{4}^{+}-N and NO\textsubscript{3}^{-}-N, respectively.

Key words: estuary, Lake Taihu, PCA, sediment nitrogen, source assignment

HIGHLIGHTS

- Nitrogen loading in Lake Taihu estuarine sediments shows obvious spatial differences.
- The average sediment nitrogen loading was 1315.5 mg/kg, dominated by organic nitrogen.
- Hongxiang estuary was hazardously polluted (2096.1 mg/kg) mainly by the aquaculture industry.
- The nitrogen pollution of 80% of the estuaries was mainly autochthonous sourced.
- Sediment organic matter, phosphorus loading and the microenvironment were the three main factors determining the nitrogen distribution in the ten estuaries.
GRAPHICAL ABSTRACT

INTRODUCTION

Eutrophication in lacustrine ecosystems is complex enough to trigger serious problems for the health and sustainability of lakes (Bricker 1988). The over-loading of nitrogen or phosphorus itself is not a risk. The ecological consequence of over-stimulated primary production poses a serious risk for the entire lacustrine ecosystem (Camargo & Alonso 2006). Nitrogen, one of the essential elements for biological metabolism in aquatic ecosystems, is one of the controlling elements for lake eutrophication (Wang 2015).

The inflow river is an important material source of the receiving lake water. Estuaries, the boundary of rivers and lakes, often suffer from multiple allochthonous nutrients and serious environmental changes (Goñi et al. 2003). Estuarine sediment is actually an important repository for a large sum of nutrients and contaminants (Wu et al. 2017). In estuaries, there are two possibilities for reducing the transfer of pollutants to the lake water: by deposition or by gaseous emission (Castro et al. 2005). Sediment deposition constitutes an important removal pathway for suspended matter, particulate organic carbon, and dissolved components following fixation, sorption or precipitation (Bricker 1988; Robertson & Thamdrup 2017). The particulate and dissolved nitrogen can also be removed from estuaries by gas exchange following biogeochemical transformations such as the mineralization of particulate organic matter and denitrification from nitrate to nitrite and nitrous oxide (Oenema 1988; Łukawska-Matuszewska et al. 2014). Finally, after the biochemical sedimentation, mineralization (ammonification), nitrification and denitrification (Wang et al. 2015; Tye et al. 2018), riverine nitrogen is redistributed and retained in sediments, pore water and overlying water.

Lake Taihu is one of the typical eutrophic shallow lakes along the middle and lower reaches of the Yangtze River. There are more than 200 rivers around Lake Taihu, among which 15 inflow rivers lie in Jiangsu Province. The 15 major inflow rivers attached to Jiangsu Province contribute more than 80% of the total pollutant input of Lake Taihu (Sun et al. 2009). As the major path of nitrogen and phosphorus input, the inflow rivers carry pollutants from industrial wastewater, sanitary sewage, and agricultural effluent (Goñi et al. 2003; Qin et al. 2007). In addition, the major inflow rivers of Lake Taihu are mainly distributed west and northwest of the lake. Under the prevailing E and ESE wind flows, the eastward lake current from western and northwestern rivers encounters an opposing wave flow at the estuaries (Qin 1999). In the estuaries, the backwater effect creates a nutrient ‘sink’. Meanwhile, some of the pollutants are deposited and contribute to the endogenous pollutant pool (Jin et al. 1990, 1992, 2007). Therefore, even when the exogenous pollutants are effectively controlled, nutrients might be released from the pollutant sink under certain conditions that create secondary water pollution.

There have been many studies on the distribution characteristics of the sediment nitrogen related to the inflow estuaries of Lake Taihu (Zhang et al. 2006; Lu et al. 2012; Liu et al. 2015). Reports find that sediment nitrogen
loading has close relationships with the location and anthropogenic influences (Chen et al. 2011; Yang et al. 2013). Land-based aquaculture, hydrophytes (aquatic plants) coverage and industrial discharges have increased the nitrogen loading of river and lake sediments (Lu et al. 2012; Ma et al. 2014). However, after a series of mineralization and incomplete decomposition processes, the remaining nitrogen might be deposited and buried in the surface sediment in different forms. In this sense, the exogenous nitrogen is converted to endogenous (Fan & Zhang 2009). In addition, as far as we know, the local government has taken measures to control sediment pollution in Lake Taihu, such as sediment dredging (Wang et al. 2014). Several problems may need to be further evaluated, including the variation of the existing forms of nutrients in sediment and the stability of sediment, which is related to the release potential of sediment nutrients after dredging. Accordingly, new and detailed data about the nutrients’ distribution and the corresponding source estimation is needed to support the assessment of the effectiveness of treatment measures.

Given the nitrogen carrying characteristics of inflow rivers and the significant position of estuaries, ten major inflow river estuaries of western Lake Taihu were selected, and the distribution trends of TN, Org-N, NO₃⁻-N and NH₂⁻-N were analyzed. Pearson correlations were applied to determine the connection between nitrogen and other active and explanatory variables. In addition, principal component analysis (PCA) and quantitative estimation were used to speculate about the possible causes and limiting factors of nitrogen loading in the different estuaries, with the aim of preparing basic data for the comprehensive management of eutrophication in Lake Taihu.

METHODS

Study sites and sampling

Lake Taihu (31°10’ N, 120°24’ E), one of the largest shallow freshwater lakes in China, is situated south of the Yangtze River Delta. It has a mean water depth of 1.9 m and an area of approximately 2,338 km². Located at the center of the Taihu Basin, Lake Taihu is responsible for the flood storage, water irrigation, shipping, water supply, aquaculture, and tourism of the whole basin (Chen et al. 2011). There are more than 200 rivers connected to Lake Taihu, a large number of which are situated in the western and northwestern regions of Lake Taihu (Sun et al. 2009). These densely covered waterways play an important role in the economic and ecological development of the Taihu Basin (Qin et al. 2007).

Sediment samples were collected from ten estuaries of the inflow rivers west of Lake Taihu in August 2015 (Figure 1 and Table 1) using a Pederson grab. Basic physicochemical parameters, including dissolved oxygen (DO), pH, and reduction/oxidation potential (Eh) of the overlying water at the sampling sites were detected in situ using a Hach multi-parameter water quality analyzer (HQ30d, HACH, USA). The sediment samples were kept at 4 °C and delivered immediately to the laboratory. All of the sediment samples were freeze-dried at -45 °C after the water content and loss on ignition determination, finely ground with a common mortar, homogenized well and dry sieved with a nylon mesh (<150 μm) for analysis.

Chemical analytical methods

The water content and loss on ignition of the sediment samples were measured before being freeze-dried. The sediment water content was based on the weight losses after drying the samples at 105 °C for 24 h to a constant weight (Shi et al. 1990). The loss on ignition, which refers to the organic matter content, was based on the weight losses after combustion at 550 °C (Qian et al. 2011).

The total nitrogen concentration was extracted by persulfate digestion, which was followed by a spectrophotometric analysis for nitrate with a UV-vis spectrophotometer (UV-6100, Mapada, China) (Qian & Fu 1987). The ammonium nitrogen (NH₄⁺-N) and nitrate-nitrogen (NO₃⁻-N) were extracted by a potassium chloride solution (Xu et al. 2012) and then determined by an AA3 autoanalyzer (Seal, Norderstedt, Germany). The organic nitrogen concentration was determined by subtracting the inorganic NO₃⁻-N and NH₂⁻-N from the total nitrogen value. 50 mg of the freeze-dried sediment samples were treated with 10% HCl overnight, dried at 60 °C for 12 h and used for the measurement of total organic carbon in a TOC analyzer (Micro N/C model HT 1300, Analytic Jena, Germany).
Each sample was analyzed in triplicates and the average value and standard deviation (SD) were used for further calculations.

Estimation methodology

The organic matter from different sources differs significantly in terms of molar ratio of the total organic carbon and the total nitrogen (C/N ratio) (Hettiyadura et al. 2018). To determine the quantitative contribution of terrestrial and autochthonous carbon and nitrogen, a binary model was applied to clarify the major source of sediment carbon and nitrogen deposition (Qian et al. 1997):

\[
\begin{align*}
    C(i) &= C_w(i) + C_l(i), \quad N = N_w(i) + N_l(i) \\
    C_w(i)/N_w(i) &= R_w(i), \quad C_l(i)/N_l(i) = R_l(i)
\end{align*}
\]
where the concentrations of total organic carbon (TOC) and total nitrogen (TN) at the sampling site \( (i) \) were \( C \ (i) \) and \( N \ (i) \), respectively. The terrestrial and autochthonous sources of \( C \ (i) \) and \( N \ (i) \) were \( C_t \ (i) \), \( C_w \ (i) \), \( N_t \ (i) \) and \( N_w \ (i) \), respectively. The \( R_t \) and \( R_w \) parameters represent the TOC: TN ratios of the terrestrial and autochthonous sources. It could be deduced from Equation (1) that:

\[
N_t(i) = \frac{[TOC(i) - R_w*TN(i)]/[R_t - R_w]}{R_t}
\]

\[
N_w(i) = \frac{[TOC(i) - R_t*TN(i)]/[R_w - R_t]}{R_w}
\]

\[
C_t(i) = \frac{R_t[TOC(i) - R_w*TN(i)]/[R_t - R_w]}{R_t}
\]

\[
C_w(i) = \frac{R_w[TOC(i) - R_t*TN(i)]/[R_w - R_t]}{R_w}
\]

(2)

The values of Equation (2) were largely determined by the values of \( R_t \) and \( R_w \). According to previous studies, the values of \( R_t \) and \( R_w \) should meet the following requirement:

\( R_w \leq TOC/TN \) and \( R_t \geq TOC/TN \). Therefore, the zeroth order approximation could be the following:

\[
R_t = \max[TOC/TN] + \delta_t
\]

\[
R_w = \min[TOC/TN] - \delta_w
\]

(3)

where \( \delta_t \) and \( \delta_w \) were the adjusting parameters, which depended on Equation (2) and other related results.

Statistical analyses

Multivariate PCA and Pearson correlation analysis were performed on the data to characterize the elements controlling the nitrogen distribution using SPSS 18.0 software. Sigma-plot was used to draw the graphs for this study.

RESULTS AND DISCUSSION

**General physicochemical properties of water and sediments**

In general, the physicochemical properties varied greatly across the ten sampling sites (Table 1). Overall, the pH values varied from 6.61 to 7.51 with small deviation. The changes of water pH had a significant influence on the microbial activity and the nitrogen sorption and desorption equilibria. When the pH value ranged from 6 to 8, the ammonifiers were active enough to accelerate nitrogen release from sediments (Reddy 1983). Therefore, the nitrogen release of the ten estuaries was relatively strong in this study. The reduction/oxidation potential value of different lake waters varied from 103.2 to 179.5 mV, suggesting a weak reduction condition (Tokarz et al. 2015). The sediment water content indicates the compaction conditions, which...
determine the resuspension of sediment nutrients (Pan 2014). Lacustrine sediments mainly originated from terrestrial carrying and soil erosion at the lakeside (Fan & Zhang 2009), which is characterized by coarse particles and insufficient water holding capacity. Estuaries are always open to the great lake area with strong wind disturbance, where fine particles and detritus are relatively hard to deposit (Nitsche et al. 2007). Therefore, the sediment water contents of the ten estuaries in this study were relatively small, ranging from 34.32% to 54.76% (Table 1). Aquatic plants to some extent had positive effects on the increase of sediment water content. In Dagang estuary in this study, the large sum of bio Potamogeton crispus detritus increased the water content of the surface sediment (Table 1). The particle refinement by the silt-promotion effect of aquatic plants could also increase the water-holding capacity (Li & Yang 2007). However, during the growth period of aquatic plants, the silt-promotion has a close relationship with the plant biomass (Hughen 2004). In Wuxi, Miaodu, Dapu, Shedu and Taige estuaries in this study, the loose plants’ coverage has a weak effect on hydrodynamic alleviation and silt-promotion, the water contents were relatively low (Table 1).

Loss on ignition is widely used to estimate the loading of organic matter in sediments (Santisteban et al. 2004). The limnic organic matter is mainly from the synthesis of autotrophic organisms and the exogenous input of microorganisms, their organic debris and the intermediate product of their decomposition (Li et al. 1998). Like the water content variation, the upstream water scouring together with the opposing E and ESE wind flow reduces the deposition possibility of organic particles. In the ten estuaries in this study, the loss on ignition values varied from 1.88% to 7.13%, with a mean value of 4.26% (Table 1). The high organic matter loading in Guandu and Dagang estuaries was in line with the deposition of hydrophytic debris, whose incomplete decomposition laid a heavy burden on the organic matter loading. In addition, the contribution of aquaculture in terms of metabolism excretions of fish and crabs and their residuals is of great significance (Shi et al. 1999). In Hongxiang estuary in this study, a 700-acre aquaculture base along the lakeshore was one of the causes of organic matter enrichment. While in Dapu and Miaodu estuaries, where sediment organic matter loading was supposed to be heavy due to the hydrophytes distribution, the loss on ignition values were only 1.88% and 2.01% (Table 1). Reports found that ecological dredging in these regions has been carried out since 2007; a sharp decrease in the organic matter concentration (Wang et al. 2014) illustrated the effective control of ecological dredging on the organic matter loadings in the sediments of these estuaries.

Spatial distribution of the sedimentary nitrogen fractions

Nitrogen is one of the indispensable elements for the life and reproduction of lake ecosystems (Robertson & Thamdrup 2017), existing in both organic and inorganic forms. Concentrations of total nitrogen and different nitrogen forms (organic nitrogen, NO3-N and NH4+-N) in surface sediment in the ten estuaries are presented in Figure 2. The total nitrogen concentration ranged from 562.7 to 2096.1 mg/kg, with a mean of 1315.5 mg/kg (Figure 2). According to USEPA (2002), the estuary sediment was moderately polluted (1,000 mg/kg ≤ total nitrogen concentration ≤ 2,000 mg/kg), with only Hongxiang estuary at the hazardously polluted level (total nitrogen concentration ≥ 2000 mg/kg). Comparing the total nitrogen loading in the ten estuaries, the concentration variation is determined by the geographical location, the land-use type and the application of vegetation restoration measures. The higher nitrogen concentrations usually occur in areas of urban and agriculture activities (Carpenter et al. 1998). Nitrogen is essential for life, but the majority has weak activity and is unavailable to organisms. Unactive nitrogen could be activated by human activities and natural processes (Castro et al. 2005). Much higher nitrogen concentration was found in Hongxiang estuary, where a large amount of nitrogen came into the estuary through the inflow river, which carried heavy aquaculture excretions and organic residues, indicating the anthropogenic influence of nitrogen loading there. In addition to the particle tapping of the aquatic plants, the mineralization and decomposition of biological residues are regarded as other motivators of nitrogen enrichment (Li & Yang 2007). The significant positive correlation of the total nitrogen and total organic carbon (R2 = 0.900, p < 0.01) in this study reflected the significance of aquatic...
plants, especially in Dagang and Guandu estuaries, which was in good agreement with the variation of loss on ignition (Table 1). However, it’s worth noting that in the Miaodu estuary, with algae debris in surface sediments and reeds distributed around, the TOC:TN ratio was 18.53, which indicated more influence from higher plants (Meyers 1994). However, the total nitrogen concentration was only 562.7 mg/kg, which could be largely due to the sludge dredging along the western coastline.

Indeed, nearly all the estuaries in this study had experienced large-scale source control measures, ecological restoration and sludge dredging projects, which had been carried out within a short period of time. However, after a longer period of time, the nitrogen release potential equals 97.8% of the undredged sediments at high temperatures (Hu et al. 2016). In this sense, the endogenous nitrogen release is decisive. In this study, it had been six years since the latest sludge dredging and the nitrogen loading had been greatly recovered.

Organic nitrogen was the dominant nitrogen fraction in the riverine sediment (Kemp & Mudrochova 1972), and only a small amount of nitrogen was mineralized during the diagenesis process. With the presence of enzymolysis and active microorganisms, organic nitrogen could be transformed into bioavailable forms such as NH$_4^+$-N and NO$_3^-$-N (Wu et al. 1996). The organic nitrogen concentration ranged from 526.9 to 1875.5 mg/kg, with a mean of 1220.1 mg/kg (Figure 2). The spatial variation was similar to that of the total nitrogen. According to Figure 2 and Table 2, the organic nitrogen concentration was positively correlated with the total nitrogen ($R^2 = 0.994$, $p < 0.01$) and the organic nitrogen accounted for 92.7% of the total nitrogen. The organic fraction of nitrogen is mainly in terms of humus and organic matter (Li et al. 2016), which could be transformed into other nitrogen forms with the help of microorganisms. The highest absolute and relative values of organic nitrogen were in Hongxiang and Chendong estuaries. In both estuaries, organic residues from anthropogenic and aquaculture releases increased the organic nitrogen loadings (Shi et al. 1999; Liu et al. 2015).

In general, the exchange of nitrogen between the water and sediment interface is in the form of different nitrogen compounds (Fan & Morihiro 1997). NH$_4^+$-N and NO$_3^-$-N are the main reactive inorganic nitrogen forms that

![Figure 2](http://iwaponline.com/ws/article-pdf/20/5/1950/728972/ws020051950.pdf)
participate in the migration and transformation process at the sediment-water interface (Camargo & Alonso 2006), with NO$_2^-$-N left out of the total nitrogen value due to its small quantity. In this study, the NH$_4^+$-N concentration ranged from 8.98 mg/kg to 218.33 mg/kg, with a mean value of 82.53 mg/kg (Figure 2). In total, the average NH$_4^+$-N concentration accounted for 85.6% of the inorganic nitrogen, but only 6.16% of the total nitrogen concentration. The anaerobic conditions of surface sediments inhibit the nitrification process and favor the increase of NH$_4^+$-N content (Kemp & Mudrochova 1972). Moreover, under neutral to alkaline conditions (6 < pH < 8), the ammonifiers are the most active, which greatly favors the ammonification and the transformation from other nitrogen forms to NH$_4^+$-N (Reddy 1983). In this sense, the sediment inorganic nitrogen always shows the tendency to higher NH$_4^+$-N and lower NO$_3^-$-N preservation (Kamei et al. 2018). The NO$_3^-$-N concentration was only 6.45 mg/kg, one-twelfth of the NH$_4^+$-N concentration (Figure 2), contributing 14.4% to the inorganic nitrogen. The deposition of inorganic nitrogen is not only controlled by redox condition, microorganisms, but also by the hydrophyte disturbances at the water-sediment interface (Ma et al. 2014). Hydrophytes could create an alteration of aerobic and anaerobic conditions through rhizosphere oxygen secretion and respiration (Lijklema 1994), which favors the denitrification phase. With the NH$_4^+$-N consumption by hydrophytes absorption and NO$_3^-$-N consumption by denitrification, NH$_4^+$-N and NO$_3^-$-N concentrations were both low in estuaries with high densities of hydrophytes, such as Dapu, Shedu and Taige estuaries in this study. The runoff volume of the adjacent inflow rivers could to some extent change the diffusive balance of nutrients in relevant estuaries (Ma et al. 2014). In Chendong estuary in particular, large runoff volumes kept the lake in good self-purification condition with frequent transformation between the different nitrogen fractions.

**Contribution assignment of terrestrial- and autochthonous-sourced nitrogen**

The molar ratio of total organic carbon and total nitrogen (C/N ratio) is a sensitive indicator to reflect the balance of carbon and nitrogen in sediments (Martínez-Soto & Martínez 2012). It can, to some extent, refer to the source of organic matter and the contribution of autochthonous and allochthonous sources in lacustrine sediment (Hettiyadura et al. 2018). If all the organic matter in sediments is from the algae, the C/N ratio will range from 3 to 8. And if they are from a terrestrial source, the ratio is generally more than 20 (Meyers 1994). With regard to the mixture of autochthonous and allochthonous sourced organic matter, the following applies: the higher the percentage of terrestrial-sourced organic matter, the greater the C/N ratio (Li & Yang 2007).

### Table 2

Pearson correlations of dissolved oxygen (DO) in the near-bottom water, the water content (WC), the loss on ignition (LOI), total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and organic nitrogen (Org-N) in the surface sediment layer, and the molar ratios of TOC, TN and TP.

<table>
<thead>
<tr>
<th>WC</th>
<th>LOI</th>
<th>TOC</th>
<th>TN</th>
<th>TP</th>
<th>Org-N</th>
<th>TOC:TN</th>
<th>TOC:TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>DO</td>
<td>0.784**</td>
<td>0.756*</td>
<td>-0.20</td>
<td>-0.137</td>
<td>0.846**</td>
<td>0.878**</td>
<td>-0.523</td>
</tr>
<tr>
<td>WC</td>
<td>0.890**</td>
<td>0.784**</td>
<td>0.902**</td>
<td>0.474</td>
<td>0.887**</td>
<td>-0.749**</td>
<td>-0.071</td>
</tr>
<tr>
<td>LOI</td>
<td>0.575**</td>
<td>0.483**</td>
<td>0.538**</td>
<td>0.846**</td>
<td>0.878**</td>
<td>-0.523</td>
<td>-0.572</td>
</tr>
<tr>
<td>TOC</td>
<td>0.900**</td>
<td>0.483**</td>
<td>0.538**</td>
<td>0.846**</td>
<td>0.878**</td>
<td>-0.523</td>
<td>-0.572</td>
</tr>
<tr>
<td>TN</td>
<td>0.204</td>
<td>0.994**</td>
<td>-0.816**</td>
<td>-0.816**</td>
<td>0.994**</td>
<td>-0.816**</td>
<td>-0.816**</td>
</tr>
<tr>
<td>TP</td>
<td>0.606</td>
<td>-0.209</td>
<td>-0.787**</td>
<td>-0.787**</td>
<td>0.606</td>
<td>-0.209</td>
<td>-0.787**</td>
</tr>
<tr>
<td>Org-N</td>
<td>-0.827**</td>
<td>-0.388</td>
<td>-0.577</td>
<td>-0.577</td>
<td>0.816**</td>
<td>0.816**</td>
<td>0.816**</td>
</tr>
</tbody>
</table>

*Correlation is significant at 0.05 level (two-tailed).
**Correlation is significant at 0.01 level (two-tailed).
The sediment nitrogen concentration is the sum of organic and inorganic nitrogen. While inorganic nitrogen is mainly from nitrate, nitrite in overlying water and the adsorption on fine particles from water (Datta et al. 1999). Therefore, a source analysis utilizing the C/N ratio should take no account of inorganic nitrogen and could be adjusted to the molar ratio of total organic carbon and organic nitrogen (abbreviated as C/N ratio in the following) (Liu et al. 2015).

A quantitative estimation method was applied to the contribution of terrestrial and autochthonous organic matter to total nitrogen loadings using the C/N ratio (Qian et al. 1991) (mentioned in 2.3). Leaving out the influence from other environmental factors, it was supposed that the C/N ratios of terrestrial (Cl/Nl) and autochthonous (Cw/Nw) organic matter were 24 and 5 (based on Equation (3) mentioned in the Estimation methodology section), respectively (as a zeroth order approximation). The estimated results of the contribution of terrestrial and autogenetic organic matter in this study are shown in Table 3.

The average adjusted C/N ratio of the ten estuaries was 12.80 (Table 3), indicating that the organic matter was mixed-sourced. The average contributions of Nl and Nw were 41.1% and 58.9%, respectively (Figure 3). As shown in

<table>
<thead>
<tr>
<th>Station</th>
<th>C/N</th>
<th>Cl (g·kg⁻¹)</th>
<th>Cw</th>
<th>Nl</th>
<th>Nw</th>
</tr>
</thead>
<tbody>
<tr>
<td>DG</td>
<td>11.32</td>
<td>11.86</td>
<td>4.96</td>
<td>0.49</td>
<td>0.99</td>
</tr>
<tr>
<td>WX</td>
<td>11.41</td>
<td>7.82</td>
<td>3.20</td>
<td>0.33</td>
<td>0.64</td>
</tr>
<tr>
<td>MD</td>
<td>18.53</td>
<td>9.01</td>
<td>0.76</td>
<td>0.38</td>
<td>0.15</td>
</tr>
<tr>
<td>DP</td>
<td>11.67</td>
<td>8.69</td>
<td>3.55</td>
<td>0.36</td>
<td>0.67</td>
</tr>
<tr>
<td>CD</td>
<td>9.97</td>
<td>10.19</td>
<td>6.00</td>
<td>0.42</td>
<td>1.20</td>
</tr>
<tr>
<td>HX</td>
<td>11.87</td>
<td>16.27</td>
<td>5.99</td>
<td>0.68</td>
<td>1.20</td>
</tr>
<tr>
<td>GD</td>
<td>9.01</td>
<td>8.72</td>
<td>6.78</td>
<td>0.36</td>
<td>1.36</td>
</tr>
<tr>
<td>SD</td>
<td>12.24</td>
<td>10.58</td>
<td>5.58</td>
<td>0.44</td>
<td>0.72</td>
</tr>
<tr>
<td>ST</td>
<td>11.75</td>
<td>10.15</td>
<td>3.84</td>
<td>0.42</td>
<td>0.77</td>
</tr>
<tr>
<td>TG</td>
<td>20.28</td>
<td>12.00</td>
<td>0.61</td>
<td>0.50</td>
<td>0.12</td>
</tr>
<tr>
<td>Mean</td>
<td>12.80</td>
<td>10.53</td>
<td>3.91</td>
<td>0.44</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Figure 3 | Proportions of Nl and Nw input to the total nitrogen loadings at ten estuaries of the western coast of Lake Taihu.
Figure 3, the relative autochthonous-sourced nitrogen ranged from 19.58% to 78.88%, with 80% of the estuary nitrogen being mainly originated from autochthonous-sourced organic matter. The influence of the allochthonous inputs of human beings has been progressively increasing since the 1970s (Ni et al. 2014). However, only a small portion of the allochthonous organic matter is decomposed, leaving the majority of incompletely decomposed organic nitrogen buried and deposited in the deep layer of the sediments, which shift into the potential nutrient pool (Fan & Zhang 2009). Therefore, the dominance of autochthonous-sourced organic was rational.

However, in the Miaodu and Taige estuaries, terrestrial-sourced nitrogen accounted for more than 70% percent of the total nitrogen source, indicating a dominance of terrestrial input (Figure 3). In general, the high C/N ratio was in agreement with the intensive terrestrial input areas, including point and non-point organic sources as well as the land-based hydrophytes (Figure 4). The opposing fluvial scouring and prevailing westward current favor the deposition of coarse organic particles, increasing the proportions of total organic carbon there. The significant negative correlation between total nitrogen and C/N ratio ($R^2 = -0.816$, $p < 0.01$) was a good proof of the deposition characteristics of estuaries (Table 2). In Miaodu estuary, the nitrogen loading was light because of the sludge dredging. But the variation of the C/N ratio from lakeshore to 1,000 m away could, to some extent, reflect the decrease of terrestrial organic intake of the sediments (Figure 4(c)). While in Taige estuary, the river channel was more heavily polluted than the adjacent lake due to industrial and domestic emissions (Fan & Zhang 2009). At 1,200 m away from the estuary mouth with an aquaculture base, the animal excrements and excessive baiting there was the main cause of the exceptional increase of C/N ratio (Figure 4(e) and Table 1).

Figure 4 Spatial variations of the total nitrogen and the C/N ratio from river to the receiving lake in five typical estuaries (a) is for Dagang estuary; (b) is for Wuxi estuary; (c) is for Miaodu estuary; (d) is for Dapu estuary; and (e) is for Taige estuary) with the negative distance representing the sites inside the inflow river channel.
Factors affecting the nitrogen loadings in different estuaries

PCA was used in this study to distinguish the controlling and supplementary variables affecting the nitrogen loadings in the different estuaries (Figure 5). Under the condition that only factors with eigenvalues greater than 1 (Kaiser criterion) have explanatory power, three principal components were extracted, accounting for 85.6% of the variation in the data.

The first component (PC1) explained 49.5% of the physicochemical variables of the estuaries, with the total nitrogen, organic nitrogen, total organic carbon, sediment water content, loss on ignition, C/N ratio and NH$_4^+$-N having substantial loadings on the PC1 axis. It indicated that the water content, organic matter, total carbon and source of organic matter were the controlling factors of nitrogen loading. The average C/N ratio was 12.80, indicating the mixed source of terrestrial inputs and autochthonous releases. With phytodetritus deposited and buried, the particle size was enlarged, which accordingly decreased the water content (Bianchi et al. 2002). In addition, in sediments mixed with phytodetritus, the absorbing ability of inorganic nitrogen, NH$_4^+$-N in particular, is enhanced (Henry & Aherne 2014). The significant correlations of the loss on ignition with the total nitrogen, organic nitrogen and total organic carbon (Table 2) combined with the absorbing capacity to inorganic NH$_4^+$-N suggested that loss on ignition

![PCA plot of active and explanatory variables](http://iwaponline.com/ws/article-pdf/20/5/1950/728972/ws020051950.pdf)

Figure 5 | Outcome of principal component analysis of active variables (total carbon, total nitrogen, organic nitrogen, NH$_4^+$-N, NO$_3^-$-N, total phosphorus and organic phosphorus) and molar ratios of total carbon, total nitrogen and total phosphorus (C/N, C/P and N/P ratios) in sediments and explanatory variables (near-bottom concentration of dissolved oxygen, sediment water content and loss on ignition on the plane (number of active cases – 10) the concentrations of total and organic fraction of sediment phosphorus were derived from the study on the phosphorus distribution of the western Taihu (Sun et al. 2017).
could be considered a basis for the characterization of estuarine sediments. Therefore, PC1s reflected the mixed source of terrestrial inputs and autochthonous releases, with organic matter (reflected by loss on ignition) as a controlling factor in the sediment nitrogen distribution.

PC2 explained 24.8% of all the related variables, and was associated with total phosphorus, organic phosphorus, dissolved oxgen, molar ratios of total carbon and total phosphorus (C/P ratio), total nitrogen and total phosphorus (N/P ratio). The negative DO loading on PC2 indicated the strong transformation ability of sediment nitrogen and phosphorus. Under anaerobic conditions, organic phosphorus could be degraded to bioavailable inorganic and exchangeable phosphorus to satisfy the growth needs of algae and hydrophytes (Sun et al. 2017). Therefore, the organic phosphorus fraction could be a potential phosphorus pool for algae blooms and black water aggregation. Elser et al. (2009) reported that when N/P ratio is <14, N could be the limiting nutrient of algae growth. The average N/P ratio in the ten estuaries was 1.87, suggesting the limiting role of nitrogen. In addition, the significant correlations of total nitrogen, organic nitrogen with total phosphorus and total carbon (Table 2) suggested the terrestrial input from upstream rivers and hydrophytes may be one of the major sources of organic nitrogen. The input, rich in organic matter, had enlarged the adsorption capacity for carbon and nitrogen and raised the nutrient loadings, which in turn increased the lake productivity (nutrient consumption from water) and phosphorus release potential (nutrient migration from sediments). In short, PC2 reflected the influence of the deposition environment and phosphorus loading on the sedimentary nitrogen distribution.

PC3 explained 11.3% of the total variables, with NO$_3$-N having a strong negative loading. The deposition of NO$_3$-N in lake sediments is mainly affected by the redox environment, the disturbance of benthic fauna and microorganisms at the water-sediment interface (Liu et al. 2015). In this study, the high organic matter load of the surficial sediment created an oxygen-free environment that favored ammonification and denitrification (Ding 2010). Therefore, the high negative loading of NO$_3$-N on PC3 represented the decomposition capacity of organic matter.

**CONCLUSIONS**

The sediment nitrogen in estuaries was mainly determined by the geographical location, the land-use type and the application of vegetation restoration measures. Estuaries, the first places that receive the terrestrial fraction of industrial, domestic and agricultural pollution through the dense river net, should have been greatly affected by terrestrial pollution. However, the source contribution estimation found that the autochthonous source of aquaculture excretion, algae and hydrophyte debris and buried biodepositus accounted for 58.9% of the total nitrogen loading, which dominated the nitrogen sources. Areas with high NH$_4$+-N concentrations were consistent with the high organic matter loading estuaries. The strong reducing conditions in the surface sediment favors the ammonification and denitrification processes; the inorganic nitrogen was therefore characterized by high NH$_4$+-N and low NO$_3$-N loadings.

By factor analysis of PCA, the sediment organic matter, phosphorus loading and the microenvironment were the three main factors that determined the nitrogen distribution in the ten estuaries. Loss on ignition value was a good predictor of total and organic nitrogen, and organic phosphorus in sediments, and could be used as an effective screening tool for the investigation and pollution assessment of Lake Taihu. Moreover, the microenvironment was the factor that limited the mineralization ability of the sediment organic matter. Further research should be conducted on the contribution of each controlling factor.

**ACKNOWLEDGEMENTS**

This work was supported by the Major Science and Technology Program for Water Pollution Control and Treatment (No. 2017ZX07203-003), the National Natural Science Foundation of China (No. 41573061, 21407076, 41773081, 41703105) and the Natural Science Foundation of the Higher Education Institutions of Jiangsu Province, China (No. 18KJB610011).
CONFLICTS OF INTEREST

All of the authors claim that they do not have any actual or potential conflict of interest, including any financial, personal or other relationships with other people or organizations.

REFERENCES


Comparison of different extract methods on extractable 
nitrogen in sediments from an urban polluted river. *Journal 
Yang, Z., Wang, L., Liang, T. & Huang, M. 2015 Nitrogen 
distribution and ammonia release from the overlying water 
and sediments of Poyang Lake, China. *Environmental Earth 
evaluation on surface layer sediment of typical estuarine 
aquatic-terrestrial ecotone in west Taihu Lake. 
*Environmental Science & Technology* 29 (5), 4–6.

First received 16 January 2020; accepted in revised form 12 May 2020. Available online 25 May 2020