Seasonal and Spatial Distribution and Pollution Assessment of Nitrogen and Phosphorus in Sediments from One of the World’s Largest Tidal Reservoirs

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Abstract: Endogenous nutrients released from sediments are a potential hazardous source in aquatic ecosystems, especially reservoirs. Here, we investigated seasonal and spatial variations of different species of nitrogen and phosphorus and evaluated the pollution levels of nutrients in sediments from one of the world’s largest tidal reservoirs. The results indicate that most of the total nitrogen and phosphorus were accumulated in sediments from the reservoir downstream, which were enhanced by runoff and precipitation during seasonal alteration. Total nitrogen was increased to 2471.17 mg/kg during the saltwater intrusion period. Nitrate and ammonium were the major nitrogen fractions in flood and dry seasons, respectively, while the highest level of phosphorus, especially inorganic phosphorus, was found in summer. The sediment was slightly to moderately contaminated by nitrogen but not phosphorus, especially downstream in winter, according to the applied indices. Multivariate statistical analyses reveal that nutrient input in flood seasons was more complex than that in dry seasons, which possibly originated from upstream agricultural and domestic sewage.

Keywords: nitrogen; phosphorus; spatial distribution; seasonal variation; surface sediment; pollution index

1. Introduction

Sediment, an irreplaceable component of water bodies, derives naturally from the weathering and erosion of bedrock minerals, organic matter, soil, and other river sources [1], and acts as both sink and secondary release source [2–4]. Most pollutants are retained in sediments because of their stability in the sedimentary column [5]. Excessive anthropogenically produced nutrients from industry and agriculture are dumped into water bodies, destroying the balance of the aquatic environment, and causing eutrophication, further resulting in harmful algal blooms and water deterioration [6,7]. Simultaneously, nutrients can be transferred from water to sediment by ion exchange, adsorption, and precipitation. Total nitrogen (TN) and total phosphorus (TP) in sediments from the Yangtze River Basin were 0.98 and 0.75 g/kg on average, respectively, which both exceeded Chinese soil background values [6]. It has been reported that over 90% of phosphorus enrichment occurred within the top 10 cm of surface sediment [8].

Nutrients in sediment can also be released to the overlying water through frequent hydrodynamic disturbance and other biochemical and physical reactions [4,9], which are
closely related to the eutrophication of the water body [3,10]. Notably, up to 50 mg/m$^2$/day of phosphorus were released from sediments in lakes and reservoirs under eutrophication [11]. The sorption and release of nutrients in sediments are affected by comprehensive environmental factors. Previous studies indicated that higher levels of nutrients were associated with warmer temperature and precipitation during seasonal changes, especially in flood seasons [12], in addition to the influence of dissolved oxygen, water chemical composition, and organic matter [13]. Nutrients are frequently variable in accumulation and distribution under changing climatic conditions [14]. Sondergaard et al. [15] reported that the TP concentration in the overlying water of shallow lakes in Denmark in summer was 2–4 times that in winter. Additionally, anthropogenic activities (e.g., hydrological alteration and agricultural management) significantly changed the transport of nutrients [16].

Coastal areas are usually at the end of catchment confluences with relatively larger runoff and more water-holding landforms (e.g., gulf). Under the dual actions of runoff and tide, the hydrodynamic characteristics and sediment transport characteristics of tidal reservoirs are more complicated [17]. Pollutants tend to be more variable under intense hydraulic conditions. Sediments in tidal reservoirs receive pollutants from both continental riverine systems and marine environment through erosion, tides, and runoff [11,18]. Coastal sediments are complex in composition and are mainly composed of sands, bedrock, silt, and submarine coastal slope [19,20]. Qingcaosha (QCS) Reservoir is a young tidal reservoir supplied by the Yangtze River for only 10 years, the water supply of which covers more than 13 million people, about 57% of the total supply capacity in Shanghai, China [21]. Due to the geographical location and potential of saltwater intrusion, the hydrodynamic factors and water quality variety are complex in QCS Reservoir. Once the level of chloride exceeds 250 mg/L in dry seasons, water gate outlets must be closed in case of backward-flowing salt tides [22], thus resulting in variable distributions of nutrients. Climate changes, including temperature and precipitation, coupled with obvious seasonal variation in Shanghai, are key factors affecting water quantity and quality (e.g., water availability and the hydrological cycle) [12]. Therefore, we hypothesized that the distribution and species of nutrients in the sediment of QCS Reservoir varied during rainy and dry seasons. Previous studies mainly focused on the effects of a single contaminant or stimulations on changes of water quality in the QCS Reservoir [23–25], while the information on seasonal variations of different species of nutrients in sediments from the tidal reservoirs was still limited.

The primary objectives of this study were to (1) identify the seasonal variation and spatial distribution characteristics of nutrients in sediments of the QCS Reservoir, (2) explore the relationship between spatial distribution and species of N and P in sediments, and (3) evaluate the environmental and ecological risks of nutrients in sediments. In achievement of these goals, we collected sediments from different sites in the QCS Reservoir, investigated the concentrations of different species of N and P in sediments seasonally, assessed the risk of nutrients by pollution index ($P_i$) and Nemerow pollution index ($P_N$), and used multivariate statistical analyses to identify the pollution sources. This study will be of significance to evaluate the pollution of a tidal reservoir and secure the safety of water supply in a coastal mega-city such as Shanghai.

2. Materials and Methods
2.1. Study Area and Sediment Sampling

QCS Reservoir is one of world’s largest tidal reservoirs and the largest drinking water reservoir in Shanghai, located in the middle of Yangtze River Estuary (31°48′ N, 121°57′ E), which was designed to limit salty tides and improve the channel flow conditions [25]. The reservoir is long and narrow in shape with a surface area of approximately 70 km$^2$, an average depth of 2.7 m, and a water retention time of 25 days [24]. A small island is located in the upper-middle reaches. Sampling points S1–S6 were allocated from upstream to downstream, which almost covered the whole reservoir (Figure 1). Thereinto, sites S1 and S2 were set in the upriver, S3 and S4 were located in the middle portion, and S5 and S6 were placed in the downriver. Specifically, site S1 was located near the pumping
station, while site S6 was close to the water delivery site. Flood seasons (from May to October) and dry seasons (from November to next April) were taken into consideration during the sampling period. All the surface sediment samples (10 cm from top) were collected from sampling points using a Peterson sampler in May, August, November 2018, and February 2019, corresponding to spring, summer, autumn, and winter, respectively. Sediment samples were collected in duplicate at each point during the four seasons. In order to guarantee the statistical accuracy, each measurement was repeated thrice to obtain the average. After the sampling, impurities such as screes, twigs, and other debris were discarded, and sediment samples were air-tightly stored in polyethylene bags at 0–4 °C in the dark. Then, the samples were transported to the laboratory immediately and were frozen at −20 °C until analysis.

![Figure 1](image-url) Location of the study area and sediment sampling sites in Qingcaosha (QCS) Reservoir, Shanghai, China.

2.2. Determination of Different Species of N and P in Sediments

The extraction and detection methods of ammonium nitrogen (NH$_4^+$-N), nitrate nitrogen (NO$_3^-$-N), and nitrite nitrogen (NO$_2^-$-N) were described in a previous study [26]. Briefly, 5 g fresh sediment was extracted using 50 mL KCl solution (2 mol/L) in a shaker for 1 h [27]. The concentrations of NH$_4^+$, NO$_3^-$, and NO$_2^-$ in the extracted solution were measured by using the phenol–hypochlorite method [28], ultraviolet spectroscopy method [29], and sulfanilamide–naphthalenediamine reaction [30], respectively. Total nitrogen (TN) was detected by applying the Kjeldahl method, in which lyophilized sediments reacted with a catalyst mixture (CuSO$_4$·5H$_2$O, K$_2$SO$_4$, and Se) and concentrated H$_2$SO$_4$ in Kjeldahl flasks at 400 °C for 5 h and were directly titrated with an automatic Kjeldahl analyzer [6]. Quantitative analysis of P fractions in sediments was conducted based on a Standards, Measurements, and Testing (SMT) sequential extraction method [31]. Specifically, the P fractions were divided into total P (TP), inorganic P (IP), organic P (OP), HCl-P (HCl extractable P), and NaOH-P (NaOH extractable P). In brief, TP was extracted using concentrated HCl after the samples were calcined at 450 °C for 3 h. IP was extracted using HCl solution, while OP was extracted using HCl solution from the calcined residue. Sediment samples were extracted using NaOH solution, and then NaOH-P was extracted using concentrated HCl from the extracting solution, while HCl-P was extracted using HCl solution from the residue. The molybdenum–antimony anti-spectrophotometric method was applied to determine the concentrations of P in the extracting solution [32].
2.3. Assessment of Nutrient Pollution in Sediments

2.3.1. Pollution Index

The pollution index \((P_i)\) is an established contaminant assessment method based on the single pollution index by the Ministry of Environment and Energy, Ontario, Canada, which has been widely applied in ecological risk assessment of nutrient elements [10,33]. It is concise and simple to implement which is defined as follows:

\[
P_i = \frac{C_i}{C_{0i}}
\]  

where \(C_i\) (mg/kg) is the measured concentration of nutrient \(i\) in the sediments, \(C_{0i}\) (mg/kg) is the environmental background value of nutrient \(i\) in the sediments, which is 620 and 500 mg/kg for TN and TP of coastal sediments in China, respectively [34]. The classification of \(P_i\) is as follows: for TN, unpolluted \((P_i \leq 0.8)\), slightly polluted \((0.8 < P_i \leq 2.5)\), moderately polluted \((2.5 < P_i \leq 4.25)\), heavily polluted \((P_i \geq 4.25)\); for TP, unpolluted \((P_i \leq 0.5)\), slightly polluted \((0.5 < P_i \leq 1.0)\), moderately polluted \((1.0 < P_i \leq 1.5)\), heavily polluted \((P_i \geq 1.5)\).

2.3.2. Nemerow Pollution Index

The Nemerow pollution index is an effective evaluation method that takes extreme values, which has been extensively applied in environmental water quality assessment [35,36]. The index can be calculated as follows:

\[
P_N = \sqrt{\left(\frac{1}{n} \sum_{i=1}^{n} P_i\right)^2 + \left[(P_{i_{\text{max}}})\right]^2}
\]

where \(n\) is the total number of sediment quality parameters, \((P_{i_{\text{max}}})\) is the maximum value of \(P_i\). The classified standard of \(P_N\) is accordance with that for TN in Section 2.3.1.

2.4. Data Analysis

ArcGIS (Version 10.2) was applied in mapping and distribution analysis. Pearson correlation and principal components analysis (PCA) for nutrients were performed to identify the pollution sources of sediments using SPSS (Version 24.0) package.

3. Results and Discussion

3.1. Seasonal Variation and Spatial Distribution of Total Nitrogen in Surface Sediments

Seasonal and spatial distributions of total nitrogen in surface sediments are shown in Figure S1. The concentrations of total nitrogen in surface sediments varied from 110.87 to 2471.15 mg/kg during a whole year in the reservoir. TN was highly accumulated in sites S5 and S6, corresponding to the downstream of the reservoir, ranging from 1269.43 to 2471.12 mg/kg in four seasons. However, the average TN concentration in the Yangtze River Basin was 984 mg/kg [6], suggesting that excessive nitrogen flux was enriched downstream. Large amounts of pollutants are discharged into water systems including reservoirs primarily through runoff [37]. Dams not only reduce the river’s flow but also restrain sediments and pollutants from flowing naturally downstream [38]. Moreover, in order to avoid the backflow of salty tides into the QCS Reservoir, sluice gates are shut termly in winter. Thus, more nutrients were deposited in the downstream of QCS Reservoir due to the lower flow rate. The TN concentration of the sediment in winter was almost twice as high as that in autumn, suggesting that more spatial variations of TN could be found in dry seasons rather than in flood seasons (Figure S1b,c). The maximum TN concentration was obtained in winter, since saltwater intrusion usually occurs in dry seasons, especially in winter [39]. Meanwhile, a relatively higher TN was stored in Site S2 in autumn, which was affected by the prevailing east–northeast wind direction. Although the level of TN was almost unchanged in flood seasons (Figure S1a,b), the distribution characteristics of
TN were still complex because of the frequent rainfall. The least nitrogen flux was found in Sites S3 and S4 located on the middle reaches, while a moderate concentration of TN occurred in the upstream area, especially in Site S1 in summer. These variations could be attributed to the precipitation changes in different seasons, influencing the seasonal distribution of runoff and nutrient load [12]. The highest TN concentration (1686.36 mg/kg) was almost 16 times as high as the lowest one (110.87 mg/kg) in summer. The uneven distribution of TN in the reservoir and the larger TN content in Site S1 may be related to the higher microbial activity in the sediment in summer, especially in the surface layer [3]. However, the distribution of TN in spring was consistent with the runoff.

3.2. Seasonal and Spatial Variations of Different Inorganic Nitrogen in Sediments

Diverse species of inorganic nitrogen showed significant variations over different seasons (Figure 2). Most inorganic N presented as NO$_3^-$-N in sediments from all sites, exhibiting 76.28% and 73.70% among inorganic N fractions in spring and summer, respectively (Figure 2a,b). Thereinto, NO$_3^-$-N was widely dispersed in Sites S5 and S6 in the flood seasons, which is in accordance with Zheng et al.’s [40] study. Notably, the highest level of NO$_3^-$-N (130.06 mg/kg) was found in the sediment from Site 1 in spring, while in summer, the sediment in Site S6 accumulated highest concentration of NO$_3^-$-N, which was up to 141.38 mg/kg. Torrential precipitation occurred shortly before the sampling scheduled in May, which might cause a fierce hydraulic disturbance in the overlying water, thus leading to abundant particle resuspension in the Yangtze River. Resuspended particles and nutrients caused by heavy precipitation were more easily deposited in Site S1 near the pumping station. Moreover, plenty of oxygen enters the water body under fluctuating currents, which may accelerate the nitrification by nitrobacteria [41]. The average concentration of NO$_3^-$-N in summer was higher than that in spring, which may result from higher temperature and frequent hydraulic disturbance by flood events in summer that weaken the denitrification rate [12,42]. The proportion of NH$_4^+$-N was drastically increased, but NO$_3^-$-N was decreased between the seasonal alteration of summer and autumn. Furthermore, NH$_4^+$-N was mainly distributed in lower reaches with average concentrations of 60.85 and 33.41 mg/kg in autumn and winter, respectively (Figure 2c,d), indicating that NH$_4^+$-N was the principal fraction in dry seasons, especially in winter. In Shanghai, seasonal typhoons regularly occur between land and sea in late July and early August. Keys et al. [43] found doubled NH$_4^+$-N flux under storm events regardless of overall downward trends of nutrients in the water. The dramatically enhanced NH$_4^+$-N may be released from the sediment, which causes the lower concentration of NH$_4^+$-N in summer with respect to dry seasons. In autumn, the proportions of NO$_3^-$-N and NH$_4^+$-N in inorganic nitrogen were similar and mainly distributed in Sites S5 and S6. In winter, despite downward concentrations of N fractions, NH$_4^+$-N was stated to be the dominant form, covering nearly 80% of downstream inorganic nitrogen. It may be enhanced by denitrification and dissimilatory NO$_3^-$-N reduction to NH$_4^+$-N [42]. In addition, low levels of NO$_2^-$-N were monitored in the sediments from Sites S1 to S6 in spring, summer, and autumn. However, the sediments accumulated abundant NO$_2^-$-N in all sites in winter compared with other seasons, in which the maximum concentration of NO$_2^-$-N was 2.26 mg/kg in Site S5. Nitrobacteria are less active in converting NO$_2^-$-N to NO$_3^-$-N under cold temperatures, resulting in more enriched NO$_2^-$-N in the middle and lower reaches.
3.3. Seasonal and Spatial Variations of Total Phosphorus in Surface Sediments

The spatial distributions of TP in surface sediments have significant seasonal characteristics and vary between flood seasons and dry seasons (Figure S2). Except in spring, TP shared an analogous distribution in which TP enrichment gradually elevated along with the water flow direction. Average concentrations of TP were in the decreasing rank of 196.37, 159.86, 147.52, and 94.81 mg/kg in summer, winter, autumn, and spring, respectively, which were far below the average TP of 750 mg/kg in the Yangtze River Basin [6]. Notably, in the downstream, the highest level of TP in summer (279.40 mg/kg) was three times higher than the lowest TP in spring (63.62 mg/kg) (Figure S2a,b). The augmentation in TP concentrations seems to be a climate change response [44]. Additionally, the frequent rain washing in summer can cause the loss of phytoplankton and submerged plants in reservoirs [12], thus leading to higher enriched TP in sediment in summer. Further, high concentrations of TP were accumulated in Sites S5 and S6, the reservoir’s estuary to the Yellow Sea. Slow water flow reduces vertical water exchange and leads to nutrient deposition in Sites S5 and S6 [45] and such transition zones; thus, the reservoir downstream can be the latent risk region for water quality degradation [46]. In dry seasons, TP distribution was generally homogeneous, except for medium-to-high concentration of TP in Sites S3 and S4 only in autumn (Figure S2c,d). Nevertheless, the distribution of TP in spring was almost inversed to that in other seasons (Figure S2a). The highest TP of 126.01 mg/kg was observed in Site S3, while lower TP flux was measured in Sites S5 and S6 with a minimum value of 63.62 mg/kg. Coastal areas are the most vulnerable to increasing human activities [20], and Site S3 was located closer to Changxing Island than the other sites. Hence, livestock and poultry breeding activities nearby may accumulate more TP in sediments. Abundant TP was relatively enriched in sediments at the upper and middle reaches in spring, while its overall concentration was the lowest—approximately half of that in summer. This could be a synergistic effect due to current change around Changxing Island and anthropogenic behavior. Moreover, higher nutrient concentration frequently appears in urban and agricultural areas [47].
3.4. Spatial Distribution and Seasonal Variation of Different Forms of Phosphorus in Sediments

Different forms of phosphorus were also distributed variably across seasonal changes (Figure 3). HCl-P means P associated with Ca (Ca-P), while NaOH-P represents P bond to Fe, Mn, and Al oxides and hydroxides (Fe-P). IP and Ca-P were major fractions in the flood and dry seasons, respectively. Moreover, P fractions were inclined to be stored in sediment from the reservoir downstream. The highest and lowest concentrations of IP in sediment were 182.28 mg/kg in Site S6 in summer and 44.78 mg/kg in Site S5 in spring, respectively. IP may be released from pore water, demineralization, and the decomposition of phytodetrital organic matter [48]. In addition to the aquatic organisms thriving with the climbing temperature in summer, recurrent floods may be the primary factor that takes mineral compositions along from upstream to the estuary. Ca-P mainly exists in the form of calcium phosphate in sediments, which is poor in solubility and bioavailability [49], verifying its widespread distribution in the reservoir. In detail, OP was the minor component throughout the reservoir with the highest value of 67.03 mg/kg in Site S2 in autumn because sediment in the estuary was dominated by inorganic phosphorus [50]. Despite Fe-P accumulation in upper reaches in spring, most Fe-P was distributed in Sites S5 and S6 in the other three seasons. However, the spatial percentage distributions of IP and Ca-P in dry seasons were discovered to be opposite, compared with those in flood seasons. Degradation of Fe-P and OP can stimulate the formation of Ca-P [9]. The increase of temperature weakens the adsorption capacity of minerals to phosphorus, which facilitates more P migration from sediment to the overlying water [49]. Notably, the smallest average of P flux was detected in spring, and most P fractions especially IP were found in Site S3. Without extreme climate and environmental alteration in spring, it may be attributed to the unique hydraulics in QCS reservoir where the flow rate was faster in the south than in north [51], encouraging the concentration of more P fractions in Site S3.

Figure 3. Spatial distribution of different forms of phosphorus (mg/kg) in spring (a), summer (b), autumn (c), and winter (d) in surface sediments of the QCS Reservoir, Shanghai.
3.5. Assessment of N and P Pollution in Sediments

Phosphorus and nitrogen concentrations are the limiting variables in the eutrophication process [52]. According to the Nemerow pollution index, comprehensive pollution assessment of nutrients in sediments ranged from unpolluted to slightly polluted, except for the moderate contamination that occurred downstream in winter (Table 1). Due to the long residence time, the self-purification level of the reservoir is sufficient [23]. Further, nitrogen was the principal parameter, affecting the sediment quality in the QCS Reservoir. The pollution index for TN in summer ranged from 0.23 to 2.72, indicating an unbalanced contamination. The downstream location was the most polluted area, corresponding to the medium level. Specifically, Site S5 was moderately polluted in flood seasons. However, TP was signified as unpolluted in rainy seasons with slight contamination only in Site S5. Seasons may have an influence on nutrient limitation in temperate regions [53]. In addition, the pollution level increased generally from upstream to downstream, and slight contamination was observed in the middle and lower reaches in spring. Notably, pollution rank of nitrogen in Site S5 was considered as middle level, indicating a mass of nitrogen flux stored in the reservoir downstream. In flood seasons, light nitrogen pollution occurred throughout the reservoir, and Site S5 was moderately contaminated by nitrogen.

| Season | Site | \(P_{i}-\text{TN} \) | Pollution Level of Nitrogen | \(P_{i}-\text{TP} \) | Pollution Level of Phosphorus | \(P_{N} \) | Pollution Level |
|--------|------|----------------------|-----------------------------|---------------------|-------------------------------|---------|----------------|
| Spring | S1   | 0.55                 | Unpolluted                  | 0.20                | Unpolluted                    | 0.47    | Unpolluted     |
|        | S2   | 0.79                 | Unpolluted                  | 0.14                | Unpolluted                    | 0.65    | Unpolluted     |
|        | S3   | 1.36                 | Slightly polluted           | 0.25                | Unpolluted                    | 1.12    | Slightly polluted |
|        | S4   | 0.29                 | Unpolluted                  | 0.13                | Unpolluted                    | 0.25    | Unpolluted     |
|        | S5   | 2.86                 | Moderately polluted         | 0.16                | Unpolluted                    | 2.29    | Slightly polluted |
|        | S6   | 2.45                 | Slightly polluted           | 0.13                | Unpolluted                    | 1.96    | Slightly polluted |
| Summer | S1   | 1.59                 | Slightly polluted           | 0.30                | Unpolluted                    | 1.31    | Slightly polluted |
|        | S2   | 0.23                 | Unpolluted                  | 0.24                | Unpolluted                    | 0.24    | Unpolluted     |
|        | S3   | 1.48                 | Slightly polluted           | 0.39                | Unpolluted                    | 1.24    | Slightly polluted |
|        | S4   | 0.18                 | Unpolluted                  | 0.23                | Unpolluted                    | 0.22    | Unpolluted     |
|        | S5   | 2.72                 | Moderately polluted         | 0.56                | Slightly polluted             | 2.24    | Slightly polluted |
|        | S6   | 2.22                 | Slightly polluted           | 0.43                | Unpolluted                    | 1.83    | Slightly polluted |
| Autumn | S1   | 0.69                 | Unpolluted                  | 0.25                | Unpolluted                    | 0.59    | Unpolluted     |
|        | S2   | 1.44                 | Slightly polluted           | 0.28                | Unpolluted                    | 1.19    | Slightly polluted |
|        | S3   | 1.07                 | Slightly polluted           | 0.27                | Unpolluted                    | 0.89    | Slightly polluted |
|        | S4   | 0.35                 | Unpolluted                  | 0.30                | Unpolluted                    | 0.34    | Unpolluted     |
|        | S5   | 1.25                 | Slightly polluted           | 0.29                | Unpolluted                    | 1.04    | Slightly polluted |
|        | S6   | 2.05                 | Slightly polluted           | 0.34                | Unpolluted                    | 1.68    | Slightly polluted |
| Winter | S1   | 1.28                 | Slightly polluted           | 0.28                | Unpolluted                    | 1.06    | Slightly polluted |
|        | S2   | 0.76                 | Unpolluted                  | 0.32                | Unpolluted                    | 0.66    | Unpolluted     |
|        | S3   | 2.59                 | Moderately polluted         | 0.02                | Unpolluted                    | 2.05    | Slightly polluted |
|        | S4   | 1.20                 | Slightly polluted           | 0.25                | Unpolluted                    | 0.99    | Slightly polluted |
|        | S5   | 3.98                 | Moderately polluted         | 0.38                | Unpolluted                    | 3.21    | Moderately polluted |
|        | S6   | 3.64                 | Moderately polluted         | 0.36                | Unpolluted                    | 2.94    | Moderately polluted |

Based on the evaluation criteria, sediment contamination in winter tended to be worse than in the other seasons. Moderate nitrogen contamination was investigated in Sites S3, S5, and S6 with high \(P_{i} \) values of 2.59, 3.21, and 2.94 (Table 1), respectively, which occupied 50% of the total sampling sites. Although mild nitrogen pollution was widespread in autumn, sediment in autumn was the least polluted with average \(P_{i} \) values of 1.14 for TN. In dry seasons, sediments in all sites were unpolluted by P because the highest value of 0.38 was under the limiting threshold. Hence, N was suggested to be the main contributor to the nutrient pollution, especially in the middle and lower reaches.
3.6. Identification of Pollution Sources Based on Statistical Analysis

According to Tables S1 and S2, the significance test results for the data of nutrients is normally distributed. Hence, Pearson correlation analysis and PCA could be applied to identify potential pollution sources. Correlation coefficients and principal components analysis indicated that different species of N and P had diverse sources and migrations during flood seasons and dry seasons. In rainy seasons, there were significantly positive correlations among TN, NO$_3^-$-N, TP, and NaOH-P (Table 2), suggesting that they derived from homologous sources, such as agricultural and domestic sewage from upstream urbanization [54]. TN was highly positively correlated with NO$_3^-$-N ($r = 0.802$) indicating an oxidizing environment in the sediments [40]. Notably, NO$_2^-$-N was only significantly positively correlated to OP ($r = 0.729$, $p < 0.01$). The result of PCA in flood seasons illustrates three components accounting for 84.78% of total variance (Figure 4a and Table S3).

Table 2. Pearson correlation matrix between nutrients in sediments of the QCS Reservoir in flood and dry seasons ($n = 48$).

|           | TN    | NH$_4^+$-N | NO$_3^-$-N | NO$_2^-$-N | TP    | OP    | IP    | NaOH-P | HCl-P |
|-----------|-------|------------|------------|------------|-------|-------|-------|--------|-------|
| Flood     |       |            |            |            |       |       |       |        |       |
| TN        | 1.000 | 0.331      | 0.802 **   | 0.245      | 0.779 ** | 0.537 | 0.318 | 0.709 ** | 0.092 |
| NH$_4^+$-N|       | 1.000      |            | 0.462      | -0.163 | 0.451 | 0.430 | -0.250 | -0.130 |
| NO$_3^-$-N| 0.802 **| 0.293      | 1.000      |            | 0.293 | 0.195 | 0.361 | 0.747 **| -0.055 |
| NO$_2^-$-N| 0.802 **| 0.195      | 1.000      |            | -0.163 | 0.458 | 0.361 | 0.729 **| -0.369 |
| TP        | 0.779 **| 0.683 *    | 0.293      | 0.361      | 1.000 |      |      | 0.239 |      |
| OP        | 0.537 | 0.451      | 0.195      | 0.361      | 0.239 | 0.419 | 0.546 |        |      |
| IP        | 0.318 | 0.430      | 0.195      | 0.361      | 0.747 **| 0.147 | 0.535 | 1.000 |      |
| NaOH-P    | 0.709 **| 0.747 **   | 0.729 **   | 0.361      | 0.747 **| 0.147 | 0.535 | 0.819 **|        |
| HCl-P     | 0.092 | -0.055     | -0.369     | -0.369     | -0.255 | 0.200 | -0.124 |        |      |

Dry Seasons

|           | TN    | NH$_4^+$-N | NO$_3^-$-N | NO$_2^-$-N | TP    | OP    | IP    | NaOH-P | HCl-P |
|-----------|-------|------------|------------|------------|-------|-------|-------|--------|-------|
| TN        | 1.000 | 0.787 **   | -0.026     | -0.297     | 0.508 | 0.731 **| -0.021 | 0.715 **| 0.713 |
| NH$_4^+$-N|       | 1.000      | -0.441     | -0.212     | 0.533 | 0.791 **| -0.005 | 0.898 **| 1.000 |
| NO$_3^-$-N| -0.026| -0.441     | 0.949      | 0.615 *    | -0.506 | 0.754 **| 0.707 * | -0.333 | -0.055 |
| NO$_2^-$-N| -0.297| -0.212     | 0.615 *    | 1.000      | 0.771 **| 0.856 **| 0.712 * | -0.507 | -0.369 |
| TP        | 0.508 | 0.533      | -0.506     | 0.754 **   | 0.771 **| 0.856 **| 0.712 * | -0.507 | -0.369 |
| OP        | 0.731 **| 0.791 **  | 0.856 **   | 0.712 *    | 0.819 **| 0.906 **| 0.712 * | -0.507 | -0.369 |
| IP        | -0.021| -0.005     | -0.055     | -0.369     | 0.707 * | 0.712 * | 0.712 * | -0.507 | -0.369 |
| NaOH-P    | 0.715 **| 0.898 **  | 0.819 **   | 0.906 **   | 0.712 * | 0.819 **| 0.906 **| -0.507 | -0.369 |
| HCl-P     | 0.713 | -0.055     | -0.369     | -0.369     | -0.255 | 0.200 | -0.124 | 1.000 |

* Correlation is significant at $p < 0.05$ (one-tailed). ** Correlation is significant at $p < 0.01$ (two-tailed).

Figure 4. Principal score plots for nitrogen and phosphorus in sediments from the QCS Reservoir in flood seasons (a) and dry seasons (b).

Component 1 including TN, NO$_3^-$-N, TP, OP and HCl-P, accounted for 42.65% of total variance, which might reflect the impact of agricultural sources due to the extensive...
application of nitrogen fertilizer and livestock manure in agricultural cultivation in the Yangtze estuary basin [35]. After the initial fertilizer application in spring, rainfall in flood seasons can cause nitrate leaching into the groundwater. Component 2 including NH$_4^+$-N, IP, and NO$_2^-$-N, accounted for 30.09% of total variance, which might represent the pollution from domestic sewage. A large amount of organic matter in the domestic sewage can be decomposed to ammonia. Meanwhile, factor 3 was only dominated by NaOH-P, which might be related to the industrial pollution. Nutrients in the intertidal sediment varied along with seasonal changes. However, in dry seasons, significantly positive correlations could be found among TN, NH$_4^+$-N, NO$_2^-$-N, OP, and NaOH-P (Table 2). Moreover, NO$_3^-$-N was significantly positively correlated with IP ($r = 0.615$, $p < 0.05$) but negatively correlated with HCl-P ($r = -0.652$, $p < 0.05$). In addition, TP showed high positive correlations with NO$_2^-$-N, OP, NaOH-P, and HCl-P but a high negative correlation with IP, indicating that OP, NaOH-P, and HCl-P mainly contributed to TP. External P loading is the main contributor of NaOH-P in sediment [9]. The element pairs of IP–OP and IP–HCl-P had significantly negative correlations.

In dry seasons, principal component 1 including TN, NH$_4^+$-N, NO$_2^-$-N, and HCl-P, accounted for 61.30% (Figure 4b and Table S3), which might reflect the sediment pollution induced by domestic sewage discharge [37]. Principal component 2 was dominated by NaOH-P, suggesting that it might derive from other anthropogenic sources rather than biological sources [3]. However, TP and IP were both associated with components 1 and 2. River discharge from inland areas contributed most of the nutrient input, especially for TP discharge to the coastal estuary [56]. Nutrient load in flood seasons was more complex due to strengthened runoff, rainfall, and warmer temperatures. Specifically, pollutant sources in dry seasons were more identical. The QCS Reservoir is located at the Yangtze River estuary, where all tributaries’ runoffs converge, resulting in positive correlation among several fractions of N and P. Additionally, aquaculture can contribute to the input of nutrients [6]. Furthermore, maintenance of the wetland park nearby, as an external nutrient input source, cannot be neglected.

4. Conclusions

The seasonal spatial distributions, variations, and risk assessment of nitrogen and phosphorus in sediments were studied to secure the water supply of the QCS Reservoir. The spatial distributions of TN and TP were closely associated with seasonal alteration and exhibited characteristics of distribution along the runoff, in which most nutrients were distributed in the downstream sediment rather than upstream, except for the distribution of TP in spring. The highest concentration of TN was enriched in winter, while most TP accumulated in summer. Furthermore, NO$_3^-$-N and NH$_4^+$-N were the major components among all nitrogen fractions in flood and dry seasons, respectively. NO$_2^-$-N was the smallest N fraction but was observed at reservoir downstream only in winter. Likewise, high-proportioned IP and Ca-P dominated the sediment in flood and dry seasons, respectively. Most P fractions tended to enrich at the reservoir downstream, and Ca-P presented a wide distribution regardless of seasonal changes. N was the principal contributor to the contamination of sediment in the QCS Reservoir, leading to moderate contamination in the reservoir downstream in both flood and dry seasons. Furthermore, TN and TP were significantly correlated, suggesting that they originated from similar agricultural and domestic sources. This work has studied the horizontal spatial distribution of pollutants in the sediments of a tidal reservoir. However, the reservoir may encounter strong hydraulic disturbance and cause the release of pollutants in deep sediments during actual operation. Thus, the vertical distribution characteristics of pollutants in the deep sediments of a tidal reservoir should be investigated in the following study.
Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4441/13/4/395/s1, Table S1: Tests of normality. Table S2: One-sample K-S tests of normality. Table S3: Rotation component matrix for nutrients in the sediments from the Qingcaosha Reservoir. Figure S1: Spatial distribution of total nitrogen (mg/kg) in spring (a), summer (b), autumn (c), and winter (d) in surface sediments of the QCS Reservoir, Shanghai. Figure S2: Spatial distribution of total phosphorus (mg/kg) in spring (a), summer (b), autumn (c), and winter (d) in surface sediments of the QCS Reservoir, Shanghai.

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References
1. Chon, H.S.; Ohandja, D.G.; Voulvoulis, N. The role of sediments as a source of metals in river catchments. Chemosphere 2012, 88, 1250–1256. [CrossRef]
2. He, J.; Deng, W.; Chen, C.; Xu, X.; Wang, S.; Liu, W.; Wu, X. Ammonia nitrogen adsorption and release characteristics of surface sediments in Dianchi Lake, China. Environ. Earth Sci. 2015, 74, 3917–3927.
3. Duan, L.; Song, J.; Xu, Y.; Li, X.; Zhang, Y. The distribution, enrichment and source of potential harmful elements in surface sediments of Bohai Bay, North China. J. Hazard. Mater. 2010, 183, 155–164. [CrossRef]
4. Yang, Y.; Gao, B.; Hao, H.; Zhou, H.; Lu, J. Nitrogen and phosphorus in sediments in China: A national-scale assessment and review. Sci. Total Environ. 2017, 576, 840–849. [CrossRef] [PubMed]
5. Zhang, W.; Jin, X.; Liu, D.; Lang, C.; Shan, B. Temporal and spatial variation of nitrogen and phosphorus and eutrophication assessment for a typical arid river-Fuyang River in northern China. J. Environ. Sci. 2017, 55, 41–48. [CrossRef]
6. Rozpondek, K.; Rozpondek, R.; Pachura, P. Characteristics of Spatial Distribution of Phosphorus and Nitrogen in the Bottom Sediments of the Water Reservoir Poraj. J. Ecol. Eng. 2017, 18, 178–184. [CrossRef]
7. Sun, S.; Huang, S.; Sun, X.; Wen, W. Phosphorus fractions and its release in the sediments of Haihe River, China. J. Environ. Sci. 2009, 21, 291–295. [CrossRef]
8. Zhu, M.; Zhu, G.; Li, W.; Zhang, Y.; Zhao, L.; Gu, Z. Estimation of the algal-available phosphorus pool in sediments of a large, shallow eutrophic lake (Taihu, China) using profiled SMT fractional analysis. Environ. Pollut. 2013, 173, 216–223. [CrossRef]
9. Mlynarczyk, N.; Bartoszek, M.; Polak, J.; Śulkowski, W.W. Forms of phosphorus in sediments from the Goczalkowice Reservoir. Appl. Geochem. 2013, 37, 87–93. [CrossRef]
10. Zhang, Z.; Lv, Y.; Zhang, W.; Zhang, Y.; Sun, C.; Marhaba, T. Phosphorus, organic matter and nitrogen distribution characteristics of the surface sediments in Nansi Lake, China. Environ. Earth Sci. 2014, 73, 5669–5675. [CrossRef]
11. Nikolai, S.J.; Dzialowski, A.R. Effects of internal phosphorus loading on nutrient limitation in a eutrophic reservoir. Limnologica 2014, 49, 33–41. [CrossRef]
12. Zhang, C.; Lai, S.; Gao, X.; Xu, L. Potential impacts of climate change on water quality in a shallow reservoir in China. Environ. Sci. Pollut. Res. Int. 2015, 22, 14971–14982. [CrossRef] [PubMed]
13. Chen, C.; Deng, W.; Xu, X.; He, J.; Wang, S.; Jiao, L.; Zhang, Y. Phosphorus adsorption and release characteristics of surface sediments in Dianchi Lake, China. Environ. Earth Sci. 2015, 74, 3689–3700. [CrossRef]
14. Kundzewicz, Z.W.; Mata, L.J.; Arnell, N.W.; Döll, P.; Jimenez, B.; Miller, K.; Oki, T.; Šen, Z.; Shiklomanov, I. The implications of projected climate change for freshwater resources and their management. Hydrol. Sci. J. 2009, 53, 3–10. [CrossRef]
15. Sondergaard, M.; Bjerring, R.; Jeppesen, E. Persistent internal phosphorus loading during summer in shallow eutrophic lakes. Hydrobiologia 2013, 710, 95–107. [CrossRef]
16. Zhao, Y.; Zheng, B.; Jia, H.; Chen, Z. Determination sources of nitrates into the Three Gorges Reservoir using nitrogen and oxygen isotopes. Sc. Total Environ. 2019, 687, 128–136. [CrossRef] [PubMed]
17. Chen, J.; Tang, H.-W.; Xiao, Y.; Ji, M. Hydrodynamic characteristics and sediment transport of a tidal river under influence of wading engineering groups. China Ocean. Eng. 2014, 27, 829–842. [CrossRef]
18. Cao, L.; Liu, J.; Shi, X.; He, W.; Chen, Z. Source-to-sink processes of fluvial sediments in the northern South China Sea: Constraints from river sediments in the coastal region of South China. J. Asian Earth Sci. 2019, 185. [CrossRef]
19. Zhang, L.; Chen, S.; Yi, L. The Sediment Source and Transport Trends around the Abandoned Yellow River Delta, China. Mar. Georos. Geotecl. 2015, 34, 440–449. [CrossRef]
20. Liu, N.; Zhang, D.; Cen, K.; Cui, L.; Li, J.; Liu, Q.; Lu, J.; Lin, X. Influence of anthropogenic activities on the temporal and spatial variation of polycyclic aromatic hydrocarbons in the sediments of Jiangsu coastal zone, China. Cont. Shelf Res. 2018, 170, 11–20. [CrossRef]
21. Li, M.; Chen, J.; Finlayson, B.; Chen, Z.; Webber, M.; Barnett, J.; Wang, M. Freshwater Supply to Metropolitan Shanghai: Issues of Quality from Source to Consumers. Water 2019, 11, 2176. [CrossRef]
22. Guan, X.; Wu, C.; Dai, B.; Liu, X. Study on water availability in Qingcaosha Reservoir under extremely low water conditions. Water Resour. Protec. 2013, 29, 75–78. (In Chinese)
23. Jin, X.; He, Y.; Kirumba, G.; Hassan, Y.; Li, J. Phosphorus fractions and phosphate sorption-release characteristics of the sediment in the Yangtze River estuary reservoir. Ecol. Eng. 2013, 55, 62–66. [CrossRef]
24. Liu, H.; Pan, D.; Chen, P. A two-year field study and evaluation of water quality and trophic state of a large shallow drinking water reservoir in Shanghai, China. Desalination Water Treat. 2015, 57, 13829–13838. [CrossRef]
25. Xu, C.; Zhang, J.; Bi, X.; Xu, Z.; He, Y.; Gin, K.Y. Developing an integrated 3D-hydrodynamic and emerging contaminant model for assessing water quality in a Yangtze Estuary Reservoir. Chemosphere 2017, 188, 218–230. [CrossRef]
26. Yuan, P.; Wu, X.; Xia, Y.; Peng, C.; Tong, H.; Liu, J.; Jiang, L.; Wang, X. Spatial and seasonal variations and risk assessment for heavy metals in surface sediments of the largest river-embedded reservoir in China. Environ. Sci. Pollut. Res. Int. 2020. [CrossRef]
27. Wang, H.; Gilbert, J.A.; Zhu, Y.; Yang, X. Salinity is a key factor driving the nitrogen cycling in the mangrove sediment. Sci. Total Environ. 2018, 631–632, 1342–1349. [CrossRef]
28. Weatherburn, M.W. Phenol-hypochlorite reaction for determination of ammonia. Anal. Chem. 1967, 39, 971–974. [CrossRef]
29. Kelso, B.H.L.; Smith, R.V.; Laughlin, R.J.; Lennox, S.D. Dissimilatory nitrate reduction in anaerobic sediments leading to river nitrite accumulation. Appl. Environ. Microbiol. 1997, 63, 4679–4685. [CrossRef]
30. Rice, E.W.; Baird, R.B.; Eaton, A.D.; Clesceri, L.S. (Eds.) Standard Methods for the Examination of Water and Wastewater; American Public Health Association: Washington, DC, USA, 2012.
31. Dong, L.; Yang, Z.; Liu, X. Phosphorus fractions, sorption characteristics, and its release in the sediments of Baiyangdian Lake, China. Environ. Monit. Assess. 2011, 179, 335–345. [CrossRef]
32. Ruban, V.; López-Sánchez, J.F.; Pardo, P.; Rauret, G.; Muntau, H.; Quevauviller, P. Harmonized protocol and certified reference material for the determination of extractable contents of phosphorus in freshwater sediments—A synthesis of recent works. Fresenius J. Anal. Chem. 2001, 370, 224–228. [CrossRef] [PubMed]
33. Mudroch, A.; Azcue, J.M. Manual of Aquatic Sediment Sampling; CRC Press: Boca Raton, FL, USA, 1995.
34. Chi, Q.; Yan, M. Handbook of Elemental Abundance for Applied Geochemistry; Geological Publishing House: Beijing, China, 2007. (In Chinese)
35. Ji, X.; Dahlgren, R.A.; Zhang, M. Comparison of seven water quality assessment methods for the characterization and management of highly impervious river systems. Environ. Monit. Assess. 2016, 188, 15. [CrossRef] [PubMed]
36. Liu, X.; Heilig, G.K.; Chen, J.; Heino, M. Interactions between economic growth and environmental quality in Shenzhen, China’s first special economic zone. Ecol. Econ. 2007, 62, 559–570. [CrossRef]
37. Da Silva, G.S.; de Sousa, E.R.; Konrad, C.; Carla, C.B.; Pauli, J.; Pereira, A. Phosphorus and Nitrogen in Waters of the Oco River Sub-basin, Itaipu Reservoir Tributary. J. Braz. Chem. Soc. 2009, 20, 1580–1588. [CrossRef]
38. Li, N.X.; Xu, J.F.; Yin, W.; Chen, Q.Z.; Wang, J.; Shi, Z.H. Effect of local watershed landscapes on the nitrogen and phosphorus concentrations in the waterbodies of reservoir bays. Sci. Total Environ. 2020, 716, 137132. [CrossRef]
39. Le, Q.; Guan, X.; Liu, X.; Wang, Z.; Liu, C. Study on the water intake site selection and water intake mode of Qingcaosha Reservoir. Water Wastewater Eng. 2009, 35, 46–51. (In Chinese)
40. Zheng, M.; Sheng, Y.; Sun, R.; Tian, C.; Zhang, H.; Ning, J.; Sun, Q.; Li, Z.; Bottrell, S.H.; Mortimer, R.J. Identification and Quantification of Nitrogen in a Reservoir, Jiaodong Peninsula, China. Water Environ. Res. 2019, 87, 369–377. [CrossRef]
41. Guo, J.; Peng, Y.; Wang, S.; Zheng, Y.; Huang, H.; Wang, Z. Long-term effect of dissolved oxygen on partial nitrification performance and microbial community structure. Bioresour. Technol. 2009, 100, 2796–2802. [CrossRef]
42. Wall, L.G.; Tank, J.L.; Royer, T.V.; Bernot, M.J. Spatial and Temporal Variability in Sediment Denitrification within an Agriculturally Influenced Reservoir. Biogeochemistry 2005, 76, 85–111. [CrossRef]
43. Keys, T.A.; Caudill, M.F.; Scott, D.T. Storm effects on nitrogen flux and longitudinal variability in a river–reservoir system. River Res. Appl. 2019. [CrossRef]
44. Carvalho, L.; Miller, C.; Spears, B.M.; Gunn, I.D.M.; Bennion, H.; Kirika, A.; May, L. Water quality of Loch Leven: Responses to enrichment, restoration and climate change. Hydrobiologia 2011, 681, 25–47. [CrossRef]
45. Yang, Z.; Liu, D.; Ji, D.; Xiao, S. Influence of the impounding process of the Three Gorges Reservoir up to water level 172.5 m on water eutrophication in the Xiangxi Bay. *Sci. China Technol. Sci.* 2010, 53, 1114–1125. [CrossRef]

46. Scott, J.T.; Stanley, J.K.; Doyle, R.D.; Forbes, M.G.; Brooks, B.W. River–reservoir transition zones are nitrogen fixation hot spots regardless of ecosystem trophic state. *Hydrobiologia* 2009, 625, 61–68. [CrossRef]

47. Tang, X.Q.; Wu, M.; Dai, X.C.; Chaia, P.H. Phosphorus storage dynamics and adsorption characteristics for sediment from a drinking water source reservoir and its relation with sediment compositions. *Ecol. Eng.* 2014, 64, 276–284. [CrossRef]

48. Kumar, B.; Anshumali. Phosphorus fractionation in surface water and sediments of industrially polluted freshwater reservoir, India. *Chem. Ecol.* 2018, 35, 219–234. [CrossRef]

49. Wang, Y.; Li, K.; Liang, R.; Han, S.; Li, Y. Distribution and Release Characteristics of Phosphorus in a Reservoir in Southwest China. *Int. J. Environ. Res. Public Health* 2019, 16, 303. [CrossRef]

50. Quan, W.; Shi, L.; Han, J.; Ping, X.; Shen, A.; Chen, Y. Spatial and temporal distributions of nitrogen, phosphorus and heavy metals in the intertidal sediment of the Changjiang River Estuary in China. *Acta Oceanol. Sin.* 2010, 29, 108–115. [CrossRef]

51. Wu, X.; Ni, B. Analysis and evaluation of heavy metal in sediment of Qingcaoasha reservoir. *Water Purif. Technol.* 2018, 37, 5–8. (In Chinese)

52. Mhamdi, B.A.; Azzouzi, A.; Mhamdi, M.A.; Sime-Ngando, T. Dynamics of the relative nitrogen and phosphorus concentrations in a reservoir situated in a semi-arid zone (Sahela, Morocco). *Water Resour. Manag.* 2006, 21, 983–995. [CrossRef]

53. Gin, K.Y.-H.; Ramaswamy, U.; Gopalakrishnan, A.P. Comparison of Nutrient Limitation in Freshwater and Estuarine Reservoirs in Tropical Urban Singapore. *J. Environ. Eng.* 2011, 137, 913–919. [CrossRef]

54. Xu, X.; Zhou, G.; Ding, J.; Cao, L.; Zhang, S. Pollution status of surface sediments and assessment of its potential ecological risk in the intertidal flats of Changxing Island. *Mar. Sci. Bull.* 2012, 31, 223–227. (In Chinese)

55. Huang, Q.; Shen, H.; Wang, Z.; Liu, X.; Fu, R. Influences of natural and anthropogenic processes on the nitrogen and phosphorus fluxes of the Yangtze Estuary, China. *Reg. Environ. Chang.* 2006, 6, 125–131. [CrossRef]

56. Tong, Y.; Bu, X.; Chen, J.; Zhou, F.; Chen, L.; Liu, M.; Tan, X.; Yu, T.; Zhang, W.; Mi, Z.; et al. Estimation of nutrient discharge from the Yangtze River to the East China Sea and the identification of nutrient sources. *J. Hazard. Mater.* 2017, 321, 728–736. [CrossRef] [PubMed]