

Article

Characteristics and Release Risk of Phosphorus from Sediments in a Karst Canyon Reservoir, China

Liu-Ying Yang^{1,2}, Shu-Lin Jiao^{1,2,*} , Lei Wang¹, Yin-Jiu Li¹, Mei Yang¹, Ye-Lin Feng¹, Juan Li¹ and Zong-Xiao Wei¹

¹ School of Geography and Environmental Science/Karst Research Institute, Guizhou Normal University, Guiyang 550025, China; 20030090030@gznu.edu.cn (L.-Y.Y.); 460181587@gznu.edu.cn (L.W.); 19010090214@gznu.edu.cn (Y.-J.L.); 201508062@gznu.edu.cn (M.Y.); 20010090276@gznu.edu.cn (Y.-L.F.); 21010090309@gznu.edu.cn (J.L.); 21010090319@gznu.edu.cn (Z.-X.W.)

² The State Key Laboratory Incubation Base for Karst Mountain Ecological Environment of Guizhou Province, Guiyang 550025, China

* Correspondence: jiaoshulin@gznu.edu.cn

Abstract: With the continuous improvement of surface water environmental quality in China, sediment has gradually become the focus of research on internal pollution in reservoirs. To investigate the forms, distribution, and migration patterns of phosphorus in karst canyon reservoir sediments, we employed an improved sequential graded extraction method to determine phosphorus content in the sediments of the Wanfeng Reservoir. We studied the spatial distribution characteristics and release risk of phosphorus form in the sediments. The results showed that the total phosphorus (TP) content ranged from 79.37 to 438.04 mg·kg⁻¹, while inorganic phosphorus (IP) content ranged from 77.32 to 424.64 mg·kg⁻¹. Iron–aluminum-bound inorganic phosphorus (Fe/Al-Pi) accounted for 36.41% and was found to be the dominant form of IP. Organic phosphorus (OP) content ranged from 1.84 to 13.59 mg·kg⁻¹, with weakly adsorbed organic phosphorus (H₂O-Po) being the dominant form of OP. Potentially active inorganic phosphorus (NaHCO₃-Pi) showed a highly significant positive correlation ($p < 0.01$) with Fe/Al-Pi, residual phosphorus (Res-P), and TP. This indicates that potentially active phosphorus (NaHCO₃-P) is a significant potential source of phosphorus (P) in the reservoir. Biologically active phosphorus (BAP) content ranged from 66.97 to 201.46 mg·kg⁻¹, with BAP/TP ratios ranging from 55.6% to 59.6%. The risk of phosphorus release from Wanfeng Reservoir sediments is high. The release of various forms of phosphorus from sediments is one of the important factors leading to the deterioration of water quality in the reservoir area in the future. To effectively manage water ecology in karst canyon reservoirs, it is essential to reduce the risk of endogenous phosphorus release.

Keywords: sediments; phosphorus forms; bioavailable phosphorus; Wanfeng Reservoir



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1. Introduction

Phosphorus plays a critical role as a limiting factor for primary productivity, and is a significant driver of eutrophication in aquatic ecosystems [1–3]. In reservoirs, phosphorus can be categorized as exogenous and endogenous phosphorus [4]. Exogenous phosphorus enters the reservoir through rivers and is either suspended or dissolved in the overlying water. As it settles in the lake basin, it becomes adsorbed and immobilized by the bottom sediment, primarily in mineral form. The dynamics of the water environment, including factors such as dissolved oxygen (DO), pH, hydrodynamics, water temperature, and bioturbation, can lead to the release of a fraction of the inorganic phosphorus adsorbed by the sediment into the overlying water. This released phosphorus then becomes a potential source of water pollution [5–7]. The bonding and association of phosphorus in sediments influence its biogeochemical behavior, including release, migration, and transformation

in the water column. The variations in content and distribution characteristics of different forms of inorganic phosphorus have varying degrees of influence on the release of phosphorus from sediments [3,8–11]. Therefore, it is crucial to investigate the spatial distribution and biogeochemical bonding characteristics of different phosphorus forms in reservoir sediments. This research is essential for a scientific assessment of the risk of phosphorus release from sediments and effective prevention and control of eutrophication in reservoirs [12].

Karst canyon reservoirs are characterized by a deep “V”-shaped valley, a narrow reservoir, large water depth, high levels of dissolved solids, high calcium concentration, and high alkalinity [13]. The environmental conditions of production and consumption in the aquatic ecosystem of karst canyon reservoirs differ from those of shallow reservoirs in the plains, resulting in a unique pattern of nutrient transport and transformation. The water column in a karst canyon reservoir exhibits stratification, and the low temperature of the bottom water hinders the release of endogenous phosphorus. However, improper reservoir operation can easily lead to the release of endogenous phosphorus, leading to the enrichment of nutrients such as nitrogen and phosphorus in the water and the occurrence of cyanobacterial blooms. Enhancing the anaerobic conditions at the bottom of the reservoir, such as increasing the frequency and intensity, can promote the release of bioavailable phosphorus, which may result in the deterioration of water quality. In recent years, scholars have paid extensive attention to the research on the water ecosystem of canyon-type reservoirs in karst areas.

With the continuous deepening of research on the water environment of karst canyon reservoirs, domestic and foreign scholars have accumulated rich research results. Research mainly focuses on topics such as aquatic ecology [14–18], the carbon cycle [19–25], microbial community structure [26–33], and contamination with metals [34–38]. However, there is a lack of research on the forms of phosphorus and the associated release risks from sediments in karst canyon reservoirs. Consequently, our understanding of phosphorus pollution in karst reservoirs resulting from sediment phosphorus release is currently limited, hindering effective mitigation efforts. To address this research gap, our study investigates the forms and distribution of sediment phosphorus at the Wanfeng Reservoir, a typical karst canyon reservoir in China. By providing insights into sediment phosphorus dynamics, this study serves as a foundation for integrated phosphorus management in karst canyon reservoirs, with the overarching goal of preserving water quality and ecosystem health.

2. Materials and Methods

2.1. Study Area

Wanfeng Reservoir is located in the middle part of the Nanpan River at the junction of Guizhou and Guangxi in southwest China (Figure 1). Construction of the Wanfeng Reservoir was completed in 1997, resulting in a total reservoir capacity of $10.26 \times 10^8 \text{ m}^3$, a regulating reservoir capacity of $5.76 \times 10^8 \text{ m}^3$, a water surface area of approximately 176 km^2 , a multi-year average flow of $612 \text{ m}^3 \cdot \text{s}^{-1}$, and an average annual runoff of $19.3 \times 10^8 \text{ m}^3$ [39].

The study area has a subtropical monsoon climate characterized by hot and rainy summers, mild and relatively dry winters, and annual average temperatures of $15\text{--}18 \text{ }^\circ\text{C}$. Precipitation is relatively abundant, with annual sums ranging from $1300\text{--}1600 \text{ mm}$. The water in the reservoir has high nitrogen and phosphorus content [22].

Wanfeng Reservoir is surrounded by karst landforms, with limestone and dolomite being the dominant geological features in the vicinity. The presence of karst hydrology and geomorphology in the watershed makes the Wanfeng Reservoir a representative example of a high-altitude karst canyon reservoir. Therefore, studying the Wanfeng Reservoir can provide valuable insights and references for the management and conservation of this reservoir type, with relevance to the characteristics and challenges associated with karst canyon reservoirs.

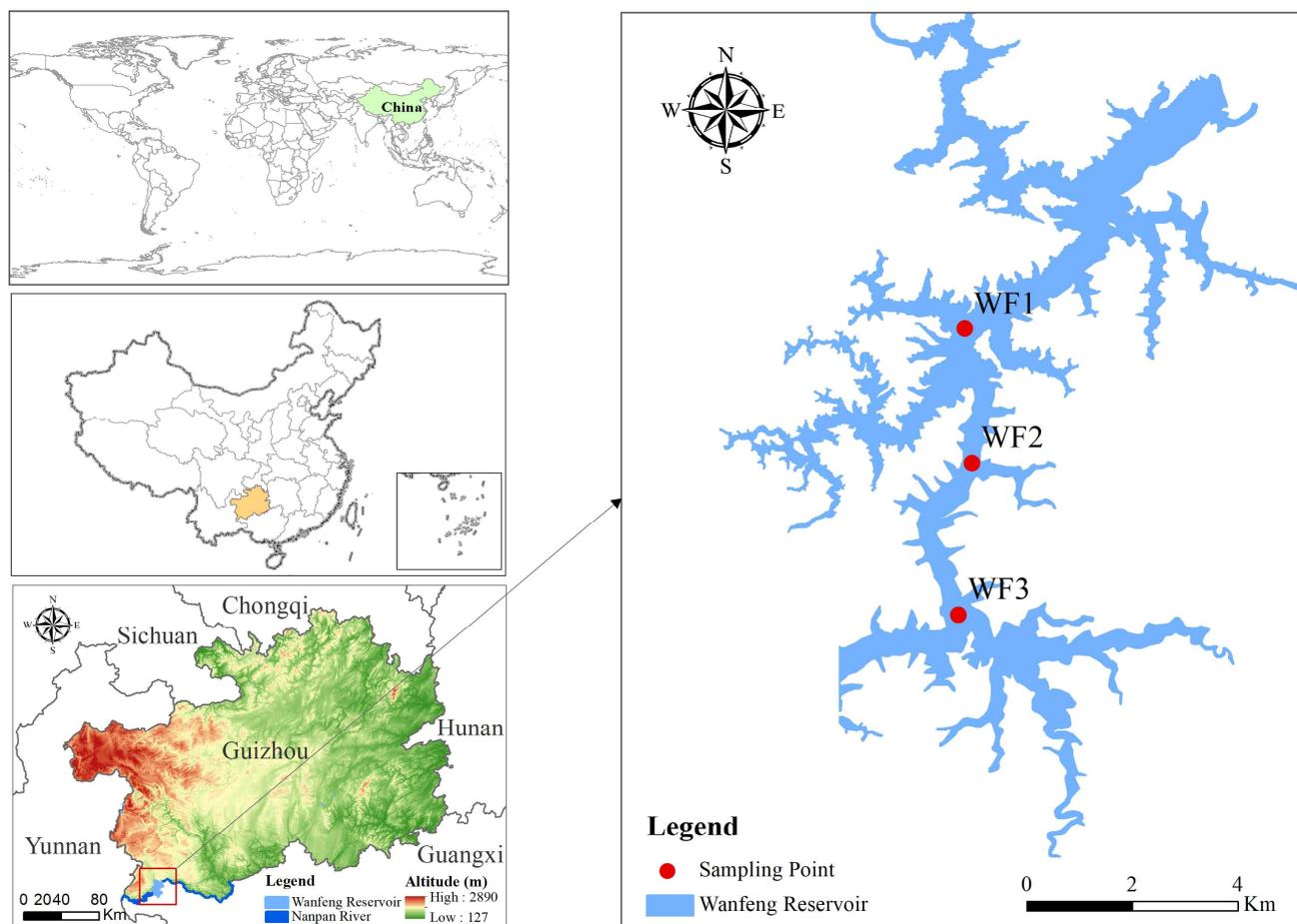


Figure 1. The location and sampling sites of the study area.

2.2. Sample Collection and Processing

In December 2021, sediment cores were collected from the reservoir using a gravity sampler. Due to the reservoir's deep-water nature and its location in a karst area, sampling sediments presented challenges. To address this, we selected three sampling points (WF1, WF2, WF3) based on the reservoir's characteristics and pollution status (Figure 1). The sediment cores obtained from these points had lengths of 19 cm (WF1), 13 cm (WF2), and 14 cm (WF3). Each sediment core was sliced into 1 cm intervals, resulting in a total of 46 samples.

To ensure sample integrity, the stratified sediment samples were immediately placed in acid-rinsed polythene plastic bags, with air removed to minimize oxidation, and then sealed for cryogenic storage. Subsequently, the samples were transported to the laboratory and subjected to a 48 h drying process using a freeze dryer (LGJ-12). Once dried, the samples were ground to a particle size below 100 mesh to facilitate subsequent chemical analysis.

2.3. Experimental Methods and Data Analysis

The inorganic phosphorus forms in the sediment samples were extracted using a modified sequential extraction method [12,40–43]. The concentrations of orthophosphate in the stepwise supernatant and decoction obtained from each extraction step were determined as shown in Table 1. The extracted forms included weakly adsorbed phosphorus (H_2O -P), potentially active phosphorus ($NaHCO_3$ -P), iron–aluminum-bound phosphorus (Fe/Al-P), calcium-bound phosphorus (Ca-P) and residual phosphorus (Res-P). The molybdenum blue method was used to measure the phosphorus content in the extraction solution. The total phosphorus (TP) and inorganic phosphorus (IP) concentrations in the extraction solutions

were determined using an ultraviolet spectrophotometer (UV-1801). The content of organic phosphorus (OP) was calculated as the difference between TP and IP.

Table 1. Graded extraction method for sediment phosphorus forms.

Phosphorus Forms	Methods
H ₂ O-P	0.5 g of dry sediment was taken and mixed with 25 mL of deionized water. The mixture was then oscillated for 2 h. Afterward, centrifugation was carried out at a speed of 4500 r/min for 5 min to obtain the supernatant. The phosphorus content in the extract solution was then determined.
NaHCO ₃ -P	To extract phosphorus from the residue of the previous stage, 25 mL of NaHCO ₃ (0.5 mol/L) was added. The mixture was then oscillated for 16 h. Afterward, centrifugation was conducted at a speed of 4500 r/min for 5 min to obtain the supernatant. The phosphorus content in the extract solution was then measured.
Fe/Al-P	To extract phosphorus from the residue obtained in the previous stage, 25 mL of NaOH (0.1 mol/L) was added. The mixture was then oscillated for 16 h. Afterward, centrifugation was conducted at a speed of 4500 r/min for 5 min to obtain the supernatant. The phosphorus content in the extract solution was then measured.
Ca-P	To extract phosphorus from the residue obtained in the previous stage, 25 mL of HCl (1 mol/L) was added. The mixture was then oscillated for 16 h. Afterward, centrifugation was conducted at a speed of 4500 r/min for 5 min to obtain the supernatant. The phosphorus content in the extract solution was then measured.
Res-P	To determine the residual phosphorus (Res-P), 25 mL of NaOH (1 mol/L) was added to the residue from the previous stage. The mixture was then boiled for 2 h. After boiling, centrifugation was performed at a speed of 4500 r/min for 5 min to obtain the supernatant. The phosphorus content in the extract solution was measured to determine the Res-P.

3. Results

3.1. Content and Characteristics of the P in Sediments

The sediment TP content in the Wanfeng Reservoir ranged from 79.37 to 438.04 mg·kg⁻¹, with an average of 224.55 mg·kg⁻¹. There was a significant spatial heterogeneity in TP distribution, as depicted in Figure 2. The variation in extreme TP values was as much as 5.5 times, indicating substantial differences across sampling locations. Among the sampling points, WF3 exhibited the highest TP content in the surface sediments, with an average of 259.78 mg·kg⁻¹. On the other hand, WF2 had the lowest TP content, averaging at 151.90 mg·kg⁻¹.

The TP content in WF1 and WF2 displayed similar patterns, with a relatively gradual change in TP content within the 1–13 cm depth range. However, at the WF1 sampling site, there was an increasing trend in TP content between the 13–19 cm depth range. In contrast, WF3 showed a top-down decreasing trend in TP distribution. Across all sampling sites, there was an abrupt trend in the distribution of sediment TP content.

IP content in the sediments of the Wanfeng Reservoir ranged from 60.91 to 337.88 mg·kg⁻¹, with an average of 174.82 mg·kg⁻¹. IP accounted for 73.26% to 78.84% of the TP content. There was a strong positive correlation between IP and TP (correlation coefficient $r = 0.994$, $p < 0.01$, $n = 47$), and a consistent distribution trend between IP and TP.

OP content in the sediments of the Wanfeng Reservoir ranged from 1.84 to 13.59 mg·kg⁻¹, with an average of 6.55 mg·kg⁻¹. OP accounted for 2.92% of the TP content. In terms of the surface sediment, WF2 and WF3 exhibited significantly higher OP content compared to the bottom sediment, resulting in a negative correlation between OP and sediment depth. WF3, being closer to the urban area and more influenced by human activities, is at the

confluence of the Mengli and Hongran rivers, which provides favorable conditions for organic matter accumulation. At the WF1 sampling site, sediment OP showed an increasing trend with depth, with the highest value recorded at $13.59 \text{ mg}\cdot\text{kg}^{-1}$.

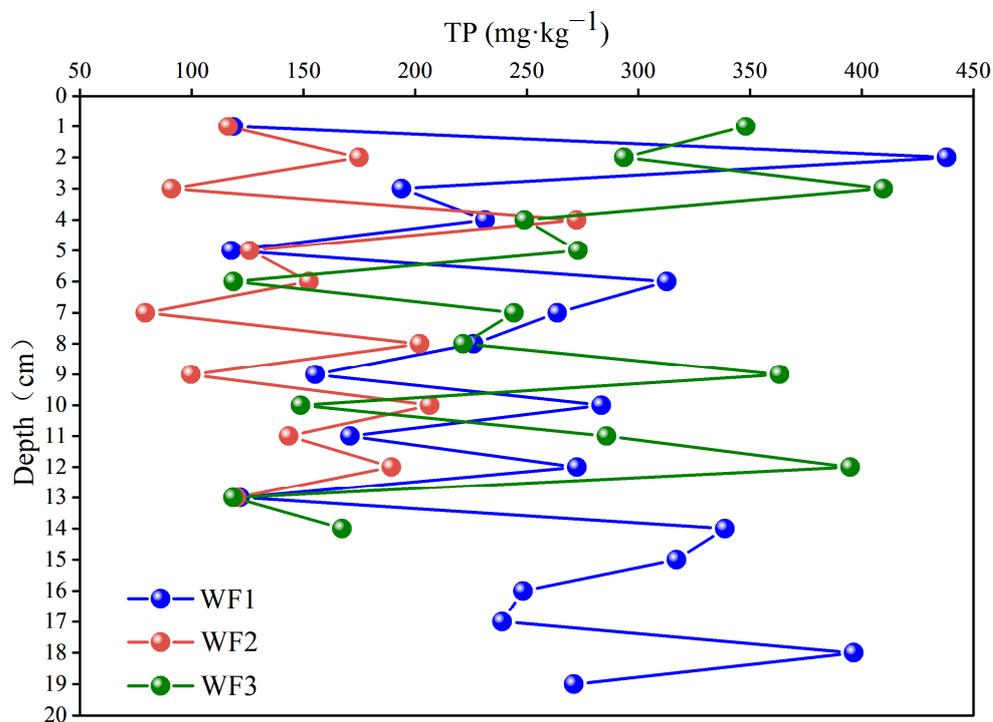


Figure 2. Vertical distribution of total phosphorus (TP) in the three sediment cores (WF1–3).

3.2. Distribution Characteristics of Phosphorus Forms in Sediments

The phosphorus content in the sediments of the Wanfeng Reservoir followed the order of $\text{Fe}/\text{Al-P} > \text{Res-P} > \text{Ca-P} > \text{H}_2\text{O-P} > \text{NaHCO}_3$ and those trends in phosphorus forms within the sediment columns at each site were consistent with the trends observed for TP content (Figure 3).

The distribution of phosphorus forms revealed that the proportion of $\text{NaHCO}_3\text{-P}$ in Wanfeng Reservoir sediments was the lowest, accounting for 19.52% to 19.49% of TP (mean 18.69%). The proportion of $\text{Fe}/\text{Al-P}$ was the highest, ranging from 17.34 to 94.39 $\text{mg}\cdot\text{kg}^{-1}$ (mean 49.86 $\text{mg}\cdot\text{kg}^{-1}$), accounting for 20.4% to 31.38% of the TP (mean 22.41%). In terms of lateral distribution, the $\text{Fe}/\text{Al-P}$ content increased in the sequence of $\text{WF3} > \text{WF1} > \text{WF2}$. The presence of higher $\text{Fe}/\text{Al-P}$ content in the sediments indicates a heavier contamination of phosphorus, reflecting the pollution level of the reservoir [44].

The average content of Res-P in the sediments was $44.92 \text{ mg}\cdot\text{kg}^{-1}$, accounting for 20.05% of TP. The average content of Ca-P was $44.15 \text{ mg}\cdot\text{kg}^{-1}$, accounting for 19.6% of TP. Res-P and Ca-P are considered relatively stable and inert forms of phosphorus, exhibiting limited exchange with the overlying water and being less affected by general changes in environmental conditions. The combined content of $\text{H}_2\text{O-P}$, $\text{NaHCO}_3\text{-P}$ and $\text{Fe}/\text{Al-P}$ accounted for 60.35% of TP, indicating their significant contribution within the sediment phosphorus pool.

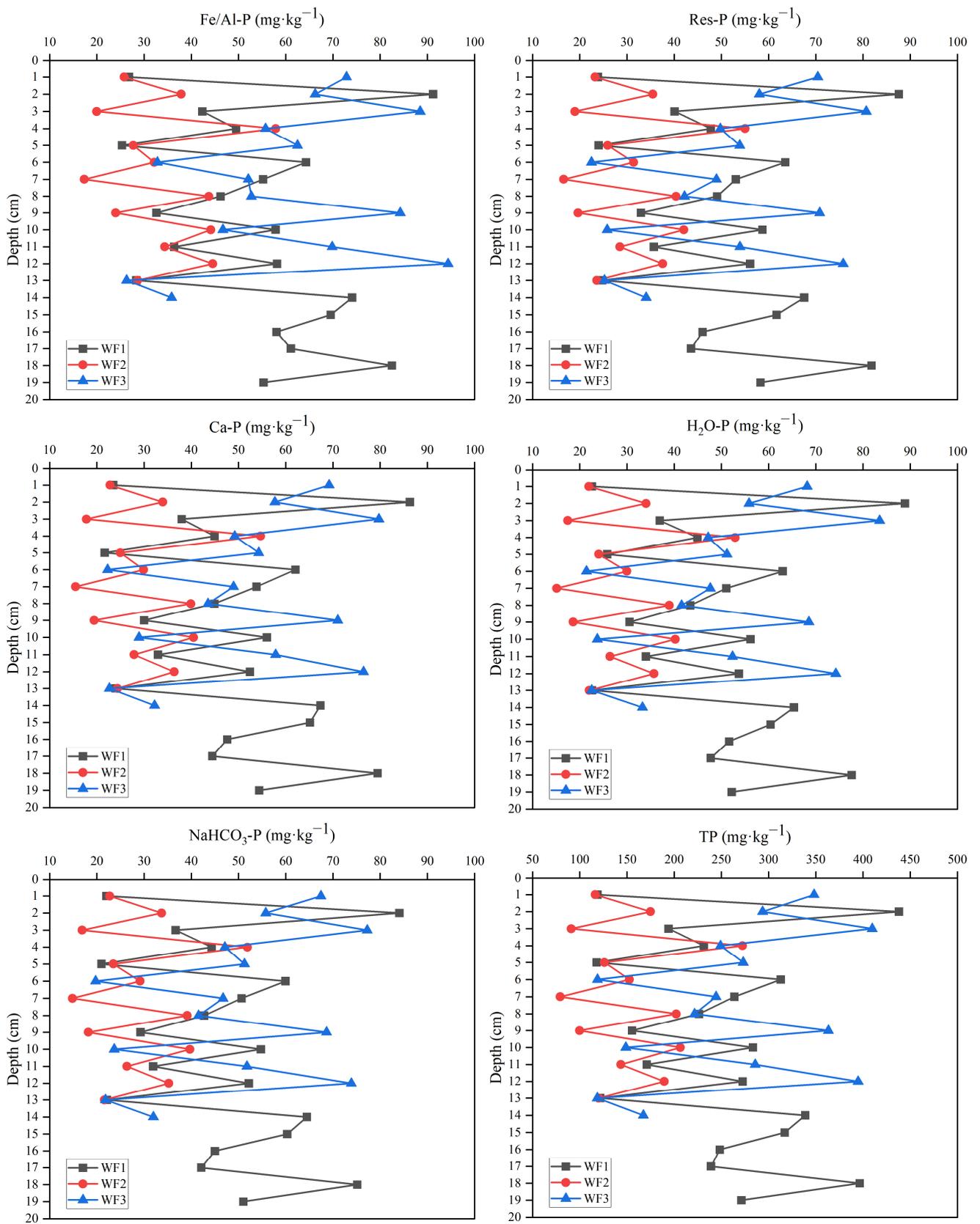


Figure 3. Contents of sediment phosphorus fractions across the sampling sites (WF1–3).

3.3. Spatial Distribution and Contents of Sediment IP

The IP content in each form showed $\text{Fe/Al-Pi} > \text{Ca-Pi} > \text{NaHCO}_3\text{-Pi} > \text{H}_2\text{O-Pi}$ (Figure 4). The $\text{H}_2\text{O-Pi}$ represents an easily mobilizable form of phosphorus mainly derived from interstitial water [45]. It had the smallest proportion within IP, with a content ranging from 14.43 to 82.13 $\text{mg}\cdot\text{kg}^{-1}$ (mean 41.21 $\text{mg}\cdot\text{kg}^{-1}$). The Ca-Pi content ranged from 14.98 to 82.65 $\text{mg}\cdot\text{kg}^{-1}$ (mean 42.48 $\text{mg}\cdot\text{kg}^{-1}$), while $\text{NaHCO}_3\text{-Pi}$ ranged from 14.64 to 83.3 $\text{mg}\cdot\text{kg}^{-1}$ (mean 41.23 $\text{mg}\cdot\text{kg}^{-1}$). Fe/Al-Pi had the highest proportion within IP, with a content ranging from 16.86 to 91.82 $\text{mg}\cdot\text{kg}^{-1}$ (mean 48.15 $\text{mg}\cdot\text{kg}^{-1}$), accounting for 36.41% of IP in the sediment.

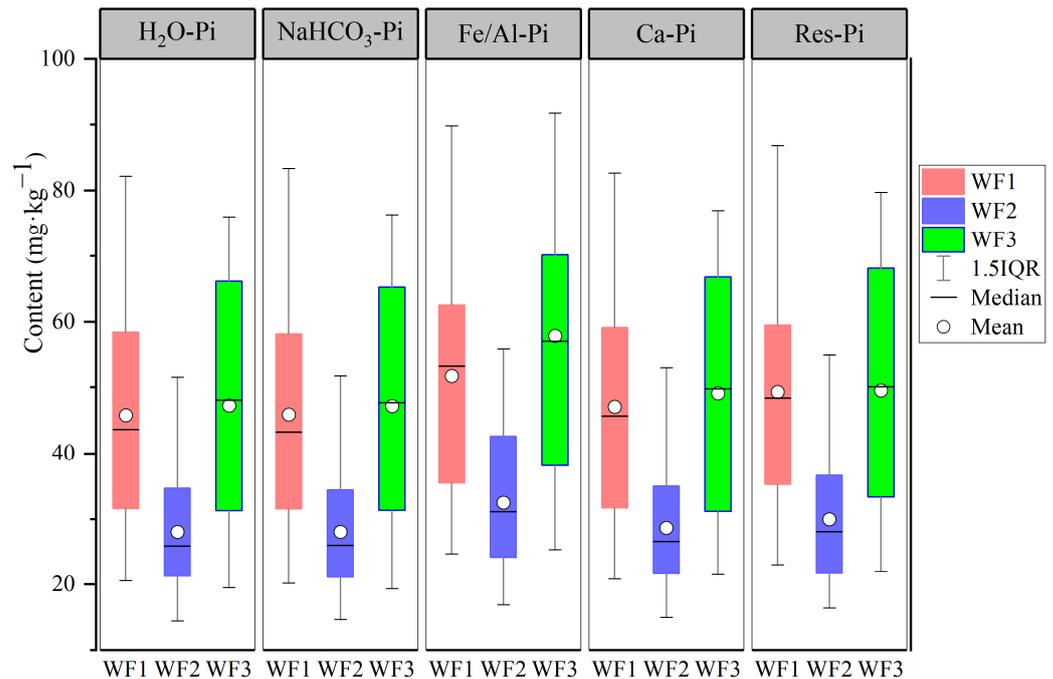


Figure 4. Distribution of sediment inorganic phosphorus (IP) fractions across the sampling sites (WF1–3).

In terms of the surface sediments, WF3 exhibited the highest IP content, followed by WF2 and WF1. The IP content of WF3 was significantly higher than that of WF1 and WF2. Within the sediment column, the IP content of each form in WF1 and WF2 tended to increase with depth. However, in WF3, the IP content of each form decreased with depth. Furthermore, the IP content of each form in the surface sediment was significantly higher compared to the bottom sediment, showing a negative correlation with sediment depth.

3.4. Spatial Distribution and Contents of Sediment OP

The sediment OP contents of individual fractions followed the order of $\text{H}_2\text{O-Po} > \text{Fe/Al-Po} > \text{Ca-Po} > \text{NaHCO}_3\text{-Po}$ (Figure 5). $\text{H}_2\text{O-Po}$ content was similar to $\text{H}_2\text{O-Pi}$ and represented the most easily transported form of phosphorus. $\text{H}_2\text{O-Po}$ contents range from 0.27 to 8.03 $\text{mg}\cdot\text{kg}^{-1}$ (mean 2.21 $\text{mg}\cdot\text{kg}^{-1}$), accounting for 33.76% of OP in the sediments. The contents of Fe/Al-Po ranged from 0.47 to 8.57 $\text{mg}\cdot\text{kg}^{-1}$ (mean 1.71 $\text{mg}\cdot\text{kg}^{-1}$). Ca-Po content in the Wanfeng Reservoir ranged from 0.5 to 3.63 $\text{mg}\cdot\text{kg}^{-1}$ (1.66 $\text{mg}\cdot\text{kg}^{-1}$). $\text{HCO}_3\text{-Po}$ content was in the range of 0.14 to 2.48 $\text{mg}\cdot\text{kg}^{-1}$ (mean 0.97 $\text{mg}\cdot\text{kg}^{-1}$), accounting for only 14.78% of OP.

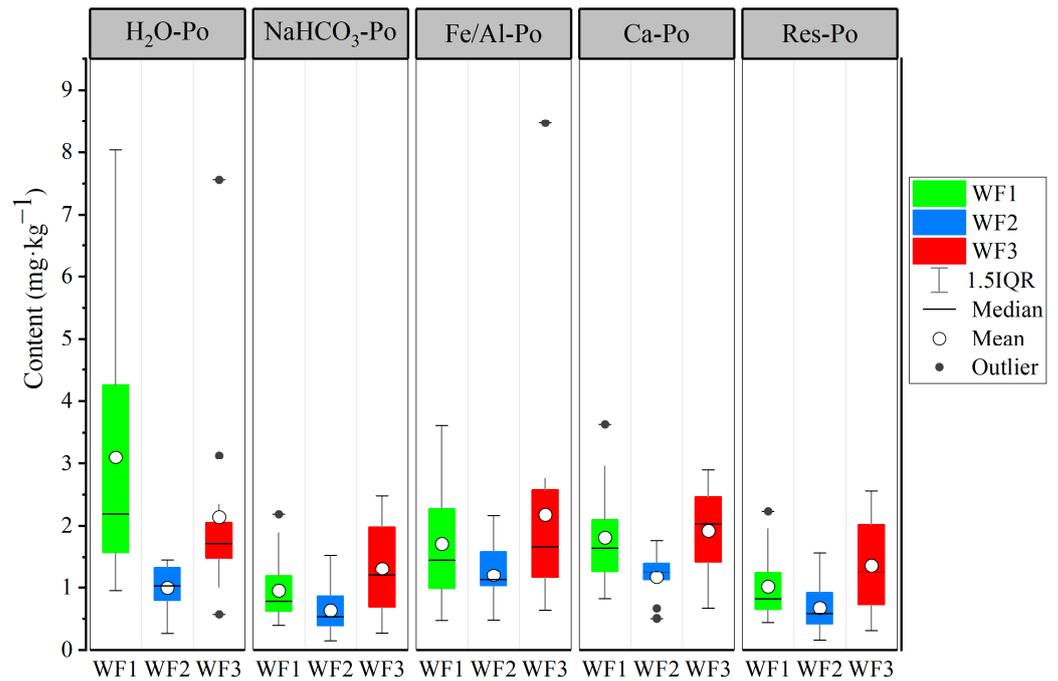


Figure 5. Distribution of sediment organic phosphorus (OP) fractions across the sampling sites (WF1–3).

4. Discussion

4.1. Potential Relationships between Sediment Phosphorus Forms

The correlation analysis (Figure 6) revealed highly significant correlations ($p < 0.01$) between sediment Ca-Pi in the Wanfeng Reservoir and Ca-Po, H₂O-Pi, H₂O-Po, NaHCO₃-Pi, NaHCO₃-Po, Fe/Al-Pi, Res-P, and TP. It was also significantly correlated ($p < 0.05$) with Fe/Al-Po. These results highlight the importance of Ca-P as a crucial component of phosphorus in reservoir sediments.

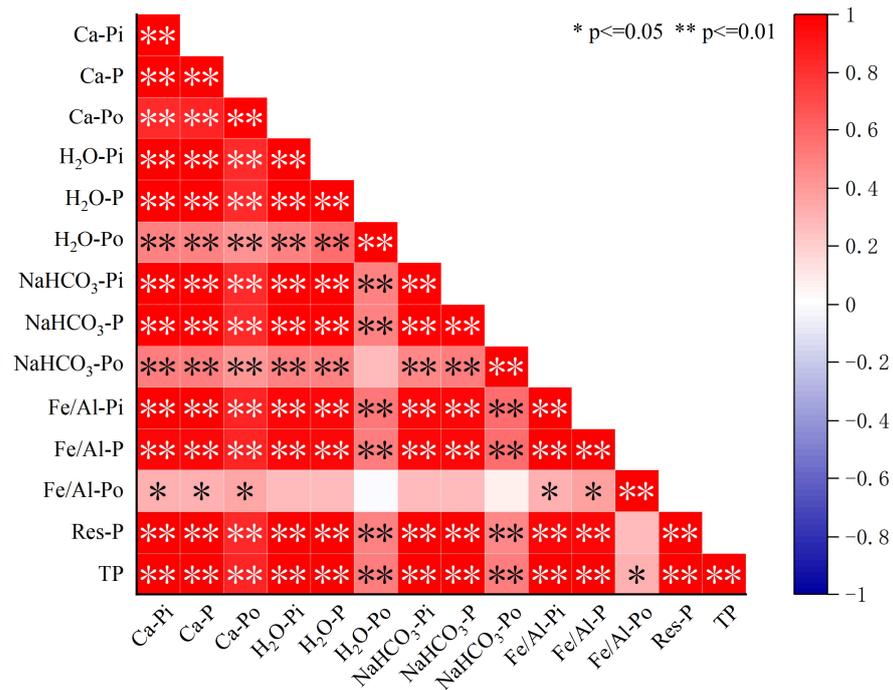


Figure 6. Heatmap for correlation analysis of cumulative phosphorus fugacity patterns.

The correlation coefficients of sediment H₂O-Pi with Ca-Pi, NaHCO₃-Pi, Fe/Al-Pi, Res-P, and TP were 0.965, 0.985, 0.859, 0.956, and 0.954, respectively. However, the correlation coefficients with each form of OP were 0.692, 0.509, 0.399, and 0.503, respectively. These results indicate that other forms of phosphorus also influence the sediment–water interface H₂O-Pi. It also suggests that controlling eutrophication in the water may not be sufficient in the presence of attenuated exogenous contamination, as endogenous release can become a new source of contamination.

Fe/Al-Pi exhibited highly significant positive correlations ($p < 0.01$) with Res-P and TP, with correlation coefficients of 0.838 and 0.901, respectively. Fe/Al-P is considered a relatively active form of phosphorus in water and is primarily influenced by factors such as pH and redox potential. Sources of Fe/Al-P typically include domestic sewage and industrial wastewater, an essential indicator of the eutrophication status of the water [46]. It is an essential indicator of the eutrophication status of the water. Under alkaline conditions, the sorption capacity of oxidizable metals such as Fe/Mn for phosphate is reduced, leading to enhanced phosphate release [47].

Sediment Ca-Pi in the Wanfeng Reservoir was highly significantly correlated ($p < 0.01$) with H₂O-P, NaHCO₃-P, Fe/Al-P, Res-P, and TP. These findings emphasize the importance of Ca-P as a crucial component of phosphorus in reservoir sediments. Ca-Pi mainly consists of detritus phosphorus and apatite, which are generally not rapidly released by sediments. Only when the water's pH drops will a portion of Ca-Pi be released into the water [48]. Due to the unique geographical characteristics of karst canyon reservoirs, which have weakly alkaline water, the release of Ca-P is highly unlikely, resulting in its minimal contribution to water eutrophication.

The correlation coefficients between reservoir sediment H₂O-Pi and Ca-Pi, NaHCO₃-Pi, Fe/Al-Pi, Res-P, and TP were 0.965, 0.985, 0.859, 0.956, and 0.954, respectively. However, the correlation coefficients with each form of OP were 0.692, 0.509, 0.399, and 0.503, respectively. These results indicate that other forms of phosphorus also influence the sediment–water interface H₂O-Pi. It suggests that controlling eutrophication in water may not be sufficient, and endogenous phosphorus release can become a new source of contamination.

NaHCO₃-Pi exhibited highly significant positive correlations ($p < 0.01$) with Fe/Al-Pi, Res-P and TP, with correlation coefficients of 0.855, 0.963 and 0.950, respectively. This highlights the significant potential of NaHCO₃-P as a phosphorus in the reservoir.

Furthermore, Fe/Al-Pi had highly significant positive correlations ($p < 0.01$) with Res-P and TP, with correlation coefficients of 0.838 and 0.901, respectively. Res-P, as the most stable form of phosphate in the sediment, is not easily involved in the phosphorus cycle in water.

These findings highlight the significance of NaHCO₃-P as a potential phosphorus source in karst canyon reservoirs and the role of Fe/Al-Pi in phosphorus dynamics. NaHCO₃-P and Fe/Al-Pi play a crucial role in the overall phosphorus load and cycling within the karst canyon reservoirs ecosystem.

4.2. Sediment Bioavailability and Risk of Phosphorus Release

Sediment TP contents below 600 mg·kg⁻¹ are considered environmentally safe, while TP content between 600 mg·kg⁻¹ and 2000 mg·kg⁻¹ reflects moderate pollution, and TP content higher than 2000 mg·kg⁻¹ indicates severe pollution [49]. In this study, the maximum sediment TP content observed was 438.04 mg·kg⁻¹, and the mean values of WF1–3 were lower than 600 mg·kg⁻¹, indicating that the overall sediment TP content in the Wanfeng Reservoir is at a safe level. However, solely measuring phosphorus contamination by comparing sediment TP levels and standard values may not accurately assess the risk of sediment phosphorus release. To better evaluate the status of sediment phosphorus release risk in the Wanfeng Reservoir, this study used the ratio of biologically active phosphorus (BAP) to TP as an indicator [11].

BAP represents the amount of bioavailable phosphorus released as dissolved phosphate that can be utilized by aquatic organisms, thus serving as an indicator to evaluate

the potential for sediment phosphorus release [50]. The $\text{H}_2\text{O-Pi}$ and $\text{NaHCO}_3\text{-Pi}$ forms of phosphorus are easily released into the water, while Fe/Al-Pi is susceptible to migration and transformation under changes in pH and redox potential. Therefore, this study considers the sum of $\text{H}_2\text{O-P}$, Fe/Al-P and $\text{NaHCO}_3\text{-P}$ as the potential BAP. The BAP content and the proportion of BAP in TP were calculated from the measured results as the phosphorus contamination index of the sediment.

The BAP content in the sediments of the Wanfeng Reservoir ranged from 66.97 to 201.46 $\text{mg}\cdot\text{kg}^{-1}$, with an average content of 130.59 $\text{mg}\cdot\text{kg}^{-1}$. The phosphorus pollution index ranged from 55.6% to 59.6%. The spatial distribution of sediment BAP content in the reservoir area exhibits significant heterogeneity, with the highest pollution index observed at WF3 (Figure 7). The phosphorus contamination index of surface sediments ranged from 57.5% to 57.9%, indicating relatively similar contamination levels among the sites. The spatial distribution pattern is characterized as $\text{WF3} > \text{WF1} > \text{WF2}$, consistent with the spatial differentiation of TP. The pollution index of WF3 is higher than that of WF1 and WF2 due to its proximity to areas of human activities, which has a more pronounced impact on the sedimentary environment. Additionally, WF3 is located at the confluence of Mengli River and Hongran River, where the water level is relatively low and the water environment is unstable. These conditions can lead to alternating redox reactions in the sediments, causing the diffusion of inorganic phosphorus and resulting in significantly higher levels of surface active phosphorus compared to WF1 and WF2.

The research results show that the risk of phosphorus release from sediment in the Wanfeng Reservoir is high. Sediment phosphorus has a significant impact on the trophic state of the water, and the release of various phosphorus forms may become a potential risk for water quality deterioration in the reservoir in the future. On one hand, the areas surrounding the reservoir are heavily influenced by human activities, resulting in a higher exogenous contamination load, with phosphorus in the sediment primarily present in easily degradable forms. Additionally, Wanfeng Reservoir is a typical karst canyon reservoir with alkaline water conditions. Under alkaline conditions, the sorption capacity of oxidizable metals such as Fe/Mn for phosphate is reduced, leading to enhanced phosphate release [49]. Therefore, future water ecology management in karst canyon reservoirs should focus on regulating human production activities and reducing the risk of endogenous phosphorus release.

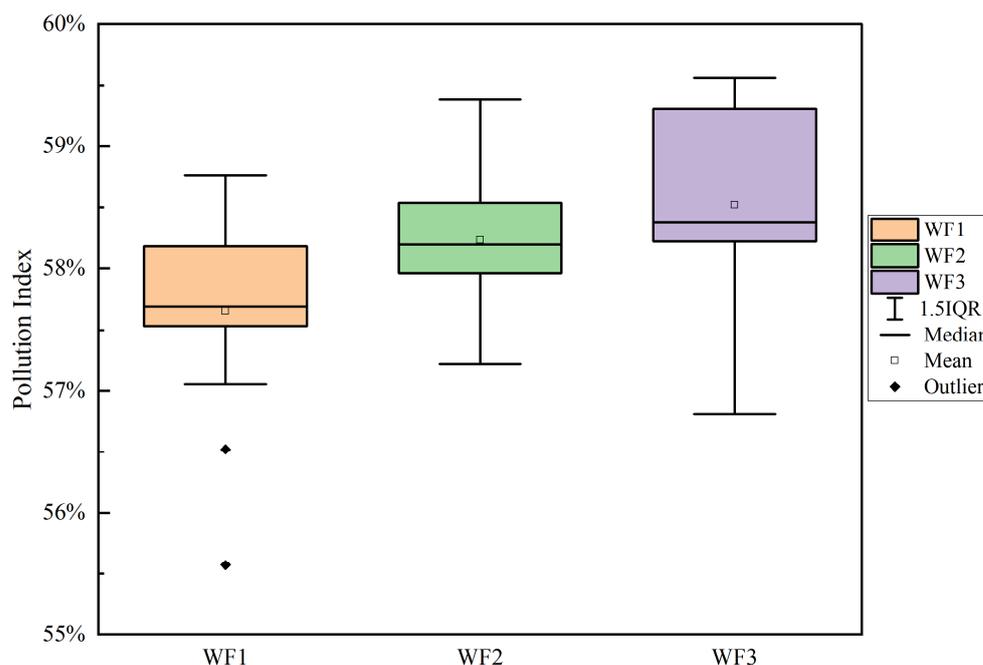


Figure 7. Cont.

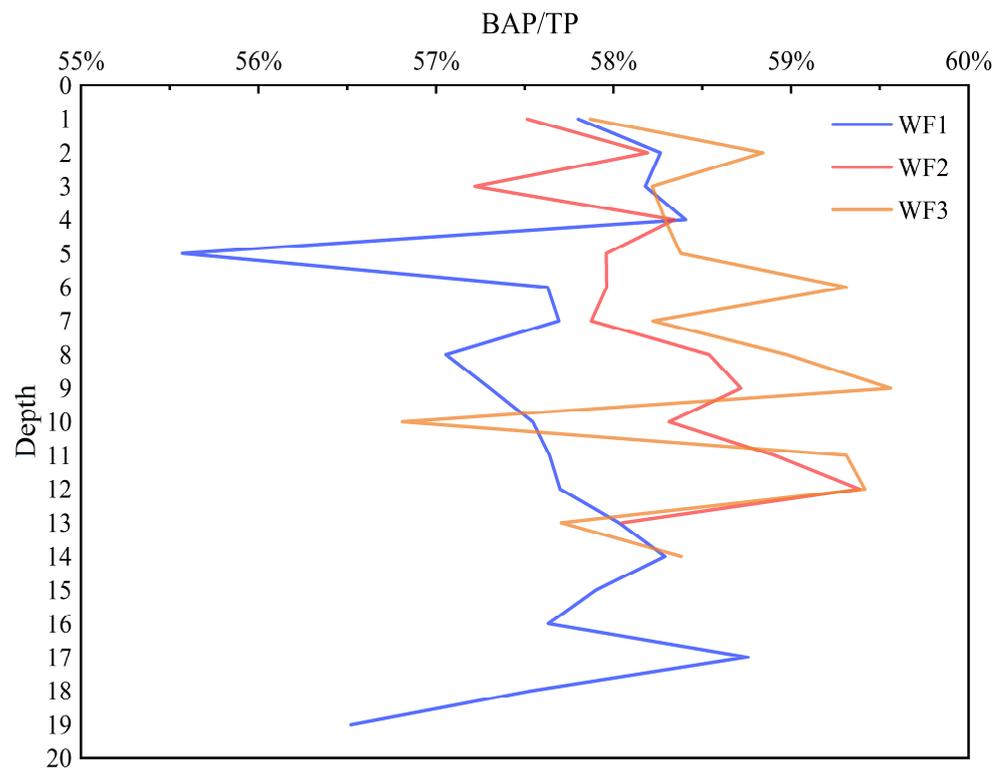


Figure 7. Characteristics of the distribution of phosphorus pollution index in reservoir sediments.

5. Conclusions

The overall TP content in the sediments of Wanfeng Reservoir falls within a safe range. Among the different forms of sediment phosphorus, IP is the predominant form. Within the IP fraction, Fe/Al-Pi is the primary occurrence form, while OP is primarily present as H₂O-Po. Additionally, NaHCO₃-P serves as a significant potential phosphorus source in reservoirs. Human activities related to production have a substantial on sediment nutrient levels. Although there is only a slight spatial variation in BAP across the sediment, the risk of phosphorus release from sediments is high, significantly affecting the nutritional status of the water bodies. This phosphorus release poses a potential risk to the water quality of the karst canyon reservoir. To effectively manage water ecology in karst canyon reservoirs, it is essential to reduce the risk of endogenous phosphorus release. These measures will help mitigate the potential impacts of phosphorus on water quality in such reservoirs.

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

References

1. Sanclements, M.D.; Fernandez, I.J.; Norton, S.A. Soil and sediment phosphorus fractions in a forested watershed at Acadia National Park, ME, USA. *For. Ecol. Manag.* **2009**, *258*, 2318–2325. [[CrossRef](#)]
2. Memet, V. Spatio-temporal changes in surface water quality and sediment phosphorus content of a large reservoir in Turkey. *Environ. Pollut.* **2020**, *259*, 113860.
3. Li, Q.X.; Jin, H.H.; Zhao, H.P.; Sun, J. Distribution characteristics of sediments phosphorus species of Xiangjiaba Reservoir and release risk. *Acta Sci. Circumstantiae* **2022**, *42*, 182–190.
4. Wang, X.Q.; Ruan, W.Y.; Yi, K.K. Internal phosphate starvation signaling and external phosphate availability have no obvious effect on the accumulation of cadmium in rice. *J. Integr. Agric.* **2019**, *18*, 2153–2161. [[CrossRef](#)]
5. Cui, H.; Ou, Y.; Wang, L.X.; Wu, H.; Yan, B.; Li, Y. Distribution and release of phosphorus fractions associated with soil aggregate structure in restored wetlands. *Chemosphere* **2019**, *223*, 319–329. [[CrossRef](#)] [[PubMed](#)]
6. Zhu, Y.; Li, Y.P.; Tang, C.Y.; Li, R.H.; Wei, Y.; Chen, G.; Gou, J.C.; Luo, F.; Cheng, Y.X.; Pan, H.Z. Effects of the disappearance of seasonal thermal stratification on the mobilization of iron and phosphorus in reservoirs, southern China—A case of Tianbao Reservoir, Nanning City. *J. Lake Sci.* **2021**, *33*, 1153–1162.
7. Li, L.; Wang, Y.; Guo, Z.L.; Cao, X.Y. Effect of algae growth on phosphorus migration and transformation on sediments. *Period. Ocean Univ. China* **2020**, *50*, 88–94.
8. Sundby, B.; Gobeil, C.; Silverberg, N.; Mucci, A. The Phosphorus Cycle in Coastal Marine Sediments. *Hydrobiologia* **1993**, *253*, 320. [[CrossRef](#)]
9. Andrieux, F.; Aminot, A. A two-year survey of phosphorus speciation in the sediments of the Bay of Seine (France). *Cont. Shelf Res.* **1997**, *17*, 1229–1245. [[CrossRef](#)]
10. Wang, C.; Zou, L.M.; Wang, P.F.; Lin, Z.P. Relation Between Distribution of Phosphorus Form in the Sediment of Typical Urban Shallow Lakes and Eutrophication. *Environ. Sci.* **2008**, *29*, 1303–1307.
11. Gao, C.M.; Zhang, Z.F.; Zhang, S. Speciation and bioavailability of phosphorus in sediments (autumn) of Haizhou Bay. *China Environ. Sci.* **2018**, *38*, 1499–1509.
12. Chen, T.; Liang, Q.B.; Wang, Y.X.; Hou, L. Effects of Environmental Factors on the Spatial Distribution of Phosphorus Fractions in the Estuarine Wetland Sediments of Erhai Lake. *J. Hydroecology* **2022**, *43*, 1–10.
13. Yan, N.; Chen, C. The Distribution of Phytoplankton and Water Quality Evaluation in Wujiangdu Reservoir, a Canyon-style Reservoir, Guizhou. *Guizhou Sci.* **2011**, *29*, 69–75.
14. Chen, J.A.; Wang, J.F.; Yu, J.; Zeng, Y.; Yang, H.Q.; Zhang, R.Y.; Guo, J.Y. Eco-environmental Characteristics of Reservoirs in Southwest China and Their Research Prospects. *Earth Environ.* **2017**, *45*, 115–125.
15. Yuan, Z.Y.; Cao, Y.P.; Jiao, S.L. Analysis of Temporal and Spatial Variation Characteristics on Water Environment in Malinghe River Backwater Area of Karst Plateau Reservoir. *J. Shandong Agric. Univ. Nat. Sci. Ed.* **2019**, *50*, 582–586.
16. Yuan, Z.H.; Li, Q.H.; He, Y.; Ma, X.Y.; Han, M.S.; Sun, R.G.; Zhang, H.J. Variation and evaluation of nutrients in Baihua Reservoir in Guizhou Plateau based on Bayesian method, 2014–2018. *J. Lake Sci.* **2019**, *31*, 1623–1636.
17. Dan, Y.S.; Zhou, Z.F.; Wu, Y.; Li, S.H.; Chen, Q. Water quality assessment of Pingzhai Reservoir based on fractal interpolation model. *Environ. Chem.* **2020**, *39*, 987–998.
18. Gou, Y.J.; Li, H.B.; Wang, S.M.; Bai, Y.J.; Ren, L.S.; Ding, A.Z. Contribution Analysis of External Source Pollution Load and Environmental Capacity Estimation of Reservoirs in Central Yunnan Plateau. *Environ. Sci.* **2023**, *44*, 1508–1518.
19. Jiao, S.L.; Tao, Z.; Gao, Q.Z.; Liu, K.; She, J.W.; Ding, J.; Liu, Z.F. Stable isotopic composition of riverine dissolved inorganic carbon of the Xijiang River Inner Estuary. *J. Geogr. Sci.* **2008**, *18*, 363–372. [[CrossRef](#)]
20. Jiao, S.L.; Gao, Q.Z.; Liu, K. Riverine DIC and its $\delta^{13}\text{C}_{\text{DIC}}$ of the Xijiang and the Beijiang tributaries in the Pearl River Basin, South China. *Acta Sci. Nat. Univ. Sunyatseni* **2009**, *48*, 99–105.
21. Zhao, Z.Q.; Zhang, J.; Jiao, S.L.; Mo, Y.S.; Cao, Y.P. Sources and Variation Characteristics of Dissolved Inorganic Carbon in Longtan Reservoir, China. *Mt. Res.* **2020**, *38*, 19–30.
22. Zhao, Z.Q.; Sou, H.Y.; Jiao, S.L. Source and spatio-temporal variation characteristics of dissolved inorganic carbon in Wanfenghu Reservoir, China. *Chin. J. Appl. Ecol.* **2020**, *31*, 1783–1790.
23. Wei, Y.; Yang, C.P.; Yan, H.; Liu, Z.H. Coupled Cycling of Carbon and Silica in Karst Reservoirs: Insights from Hongfeng Lake, Puding Reservoir and Pingzhai Reservoir. *Earth Environ.* **2020**, *48*, 1–9.
24. Ma, S.; Wei, Y.; Han, C.H.; Yan, H.; Liu, Z.H.; Sun, H.L.; Bao, Q. Hydrochemical characteristics in karst reservoirs and its implication for inorganic carbon deposition fluxes. *J. Lake Sci.* **2021**, *33*, 1701–1713.
25. Yi, Y.B.; Wang, W.F.; Wang, B.L.; Wang, F.S.; Li, S.L. Research progress on the dissolved and particulate carbon of reservoirs in karst areas of Southwest China. *Bull. Geol. Sci. Technol.* **2022**, *41*, 341–346.
26. Li, L.; Li, Q.; Chen, J.; Wang, J.; Jiao, S.; Chen, F. Temporal and spatial distribution of phytoplankton functional groups and role of environment factors in a deep subtropical reservoir. *J. Oceanol. Limnol.* **2018**, *36*, 761–771. [[CrossRef](#)]
27. Li, Q.H.; Han, L.B.; Ma, Y.M.; Liu, Y.L. The relationship between and Cyanobacteria composition characteristics environmental factors in Hongfeng Reservoir of Guizhou plateau. *J. Guizhou Norm. Univ. Nat. Sci.* **2021**, *39*, 1–7.
28. Han, L.B.; Wang, X.; Li, Q.H.; Huang, G.J.; Ma, Y.M.; Pan, S.P.; Li, Y.J. Dynamic changes and driving factors of phytoplankton functional groups in Baihua Reservoir, Guizhou Plateau. *J. Lake Sci.* **2022**, *34*, 1102–1114.

29. Ge, Q.S.; Zhang, P.; Ni, M.F.; Guo, Y.; Wang, Z.K.; Zhou, H.; Zhang, Z.W.; Zhou, Y. Relationships between phytoplankton and environmental factors in a typical karst plateau reservoir. *Ecol. Environ. Sci.* **2021**, *30*, 156–164.
30. Han, L.B.; Li, Q.H.; Chen, W.S.; Wang, X.; Zhou, S.H.; Han, M.S.; Anton, B. The key environmental factors driving the succession of phytoplankton functional groups in Hongfeng Reservoir, southwest China. *J. Oceanol. Limnol.* **2022**, *40*, 1472–1484. [[CrossRef](#)]
31. Ma, Y.M.; Li, Q.H.; Pan, S.P.; Kuang, P.; Jin, S. Dynamic analysis of niche and interspecific association of dominant phytoplankton species in Huaxi Reservoir of Guizhou Plateau. *J. Lake Sci.* **2021**, *33*, 785–796.
32. Hu, Y.; Li, Q.H.; He, Y.; Meng, C.L.; Han, M.S. Spatial and temporal distribution characteristics and influencing factors of metazooplankton in Aha Reservoir, Guizhou Province. *China Environ. Sci.* **2020**, *40*, 227–236.
33. Pan, S.P.; Li, Q.H.; Meng, C.M.; Han, M.S.; Ma, Y.M.; Anton, B. Using a structural equation model to assess the spatiotemporal dynamics and driving factors of phytoplankton in the plateau Hongfeng Reservoir in southwest China. *Aquat. Ecol.* **2022**, *56*, 1297–1313. [[CrossRef](#)]
34. Guan, T.H.; Li, X.D.; Wang, Y.Y.; Yang, M.D.; Gui, G.Y.; Ding, S.Y.; Zhang, X.C. Distribution characteristics, influencing factors and sources of heavy metals in karst deep-water reservoirs: A case study of Longtan Reservoir. *J. Shanghai Univ. Nat. Sci. Ed.* **2021**, *27*, 236–249.
35. Kuang, P.; Li, Q.H.; Jin, S.; Ma, Y.M.; Pan, S.P. Spatial and Temporal Distribution of Heavy Metals in Water Environment of Puding Reservoir in Guizhou Province and Risk Assessment. *Res. Environ. Sci.* **2021**, *34*, 576–588.
36. Jia, S.Q.; Li, Q.H.; Liao, H.Q.; Chen, Q.; Jin, S.; Kuang, P. Enrichment characteristics of metal contents in phytoplankton in Hongfeng Reservoir, Guizhou Plateau. *China Environ. Sci.* **2020**, *40*, 3972–3980.
37. Lyu, H.; Yang, M.D.; Cui, G.Y.; Wang, Y.Y.; Ding, S.Y.; Li, X.D. Study on Coupling Relationship between Heavy Metals and Nutrients in Plateau Deep-water Reservoirs: A Case Study of the Goupitan Reservoir in Wujiang River Catchment. *Earth Environ.* **2019**, *47*, 777–785.
38. Zhang, W.; Zhang, L.L. Distribution characteristics and pollution assessment of heavy metals in water and sediments of Aha Reservoir of Guizhou in different seasons. *Chin. J. Ecol.* **2021**, *40*, 1753–1765.
39. Li, Q.H.; Shang, L.H.; Gao, T.J.; Zheng, L.; Ou, T.; Huang, G.J.; Chen, C. Eutrophication characteristics of a karst plateau deepwater Wanfeng Reservoir. *Ecol. Sci.* **2013**, *32*, 194–199.
40. Hedley, M.J.; Stewart, J.W.B.; Chauhan, B.S. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* **1982**, *46*, 970–976. [[CrossRef](#)]
41. Sui, Y.; Thompson, M.L.; Shang, C. Fractionation of Phosphorus in a Mollisol Amended with Biosolids. *Soil Sci. Soc. Am. J.* **1999**, *63*, 1174. [[CrossRef](#)]
42. Wang, X.F.; Liu, T.T.; Gong, X.J.; Yuan, X.Z.; Liu, H.; Kong, W.W. Phosphorus forms in rhizosphere soils of four typical plants in the Littoral Zone of the Three Gorges Reservoir. *Acta Ecol. Sin.* **2020**, *40*, 1342–1356.
43. Huang, J.J.; Wang, C.; Fang, B.; Feng, L.; Fang, F.; Li, Z.; Guo, J.S. Characterization of Phosphorus Fractions in the Soil of Water-Level-Fluctuation Zone and Unflooded Bankside in Pengxi River, Three Gorges Reservoir. *Environ. Sci.* **2017**, *38*, 3673–3681.
44. Zhao, H.C.; Wang, S.R.; Jiao, L.X.; Yang, S.W.; Liu, W.B. Characteristics of temporal and spatial distribution of different forms of phosphorus in the sediments of Erhai Lake. *Res. Environ. Sci.* **2013**, *26*, 227–234.
45. Sun, S.J.; Huang, S.L.; Sun, X.M.; Wen, W. Phosphorus fractions and its release in the sediments of Haihe River, China. *J. Environ. Sci.* **2009**, *21*, 291–295. [[CrossRef](#)] [[PubMed](#)]
46. Peng, Y.H.; Tian, C.C.; Chi, M.X.; Yang, H.W. Distribution of phosphorus species and their release risks in the surface sediments from different reaches along Yellow River. *Environ. Sci. Pollut. Res. Int.* **2019**, *26*, 28202–28209. [[CrossRef](#)]
47. Ren, W.P.; Li, X.X.; Zhang, W.S. Research progress in phosphorus forms in sediments and environmental factors that influence phosphorus releasing. *Environ. Pollut. Control* **2012**, *34*, 53–60.
48. Geng, X.; Wen, S.L.; Sun, P.R.; Xu, C.T.; Li, D.P.; Huang, Y. Environmental Significance of Phosphorus Fractions of Phytoplankton and Macrophyte-Dominated Zones in Taihu Lake. *Environ. Sci.* **2019**, *40*, 5358–5366.
49. Persaud, D.; Jaagumagi, R.; Hayton, A. *Guidelines for the Protection and Management of Aquatic Sediment Quality in Ontario*; Ministry of Environment and Energy: Toronto, ON, Canada, 1993.
50. Reynolds, C.S.; Davies, P.S. Sources and bioavailability of phosphorus fractions in freshwaters: A British perspective. *Biol. Rev.* **2001**, *76*, 27–64. [[CrossRef](#)]

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