Phosphorus Speciation and Release Risk from Riparian Zone Sediments of the Lanzhou Section of the Yellow River (Postprint)

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Abstract

Phosphorus pollution, as an important component of water systems, can cause water eutrophication when excessively accumulated. Riverbank zones, serving as transitional areas connecting terrestrial and aquatic systems, are crucial for controlling phosphorus loss. This study employed the SMT method and Psenner sequential extraction method to investigate the phosphorus forms and distribution characteristics in sediments of the riverbank zone in the Lanzhou section of the Yellow River, and assessed phosphorus release risk using the equilibrium concentration evaluation method, single-factor pollution index, and bioavailable phosphorus pollution index. The results indicated that the average total phosphorus content in sediments of the study area was at a relatively high level (1240.07 mg kg-1), with phosphorus forms dominated by inorganic phosphorus, which was mainly present as calcium-bound phosphorus. The phosphorus equilibrium concentration in sediments of the study area exceeded the soluble reactive phosphorus concentration in the overlying water, demonstrating that the sediments function as a "phosphorus source" for the overlying water. According to the evaluation results of the single-factor pollution index and bioavailable phosphorus pollution index, although total phosphorus pollution in the area was primarily classified as severe, the bioavailable phosphorus pollution evaluation results revealed that the phosphorus ecological pollution status in the Lanzhou section of the Yellow River was relatively good.

Full Text

Phosphorus Distribution Patterns and Release Risks in the Riparian Zone Sediments of the Lanzhou Section of the Yellow River

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Abstract

Phosphorus pollution is a significant concern in aquatic systems, as excessive accumulation can lead to eutrophication. The riparian zone, a vital transitional area between land and water, is crucial for mitigating phosphorus loss. This study investigated the forms and distribution characteristics of phosphorus in riparian zone sediments along the Yellow River in Lanzhou using the SMT method and the Psenner classification extraction method. Additionally, we assessed the risk of phosphorus release using the equilibrium concentration assessment method, single-factor analysis, and the bioavailable phosphorus pollution index. The results indicate that the average total phosphorus content in the sediments of the study area is relatively high, measuring 1240.07 mg·kg^-1, with inorganic phosphorus as the dominant form, primarily calcium phosphorus. The phosphorus equilibrium concentration in the sediments exceeds that of dissolved reactive phosphorus in the overlying water, indicating that the sediments act as a "phosphorus source" for the overlying water. Furthermore, evaluations of the single-factor pollution index and the bioavailable phosphorus pollution index reveal that while total phosphorus pollution in the area is primarily classified as heavy, the ecological pollution status of phosphorus in the Lanzhou section of the Yellow River is relatively good.

Keywords: Northwest China; the Yellow River Basin; riparian zone; phosphorus forms; phosphorus release risk

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1.1 Study Area Overview

The Lanzhou section of the Yellow River (36°54 N, 103°40 E) is located in the upper reaches of the Yellow River Basin within an arid and semi-arid region, spanning 152 km from Xigu District in the west to the northern part of Yuzhong County in the east [Figure 1: see original paper]. This area receives an average annual precipitation of 200–300 mm, experiences high evaporation rates, and frequently suffers from consecutive spring and summer droughts. The riparian zone along the Lanzhou section undergoes periodic inundation during winter and spring, creating alternating wet-dry cycles that facilitate the release, migration, and transformation of nitrogen and phosphorus nutrients from sediments. In recent years, the Lanzhou urban area has experienced increasing surface water pollution loads due to extensive non-point source pollution and industrial and domestic wastewater discharge along the river, causing a continuous decline in riparian zone ecological service functions. The concentrations of ammonia nitrogen (NH_3-N) and chemical oxygen demand (COD_{Mn}) have shown increasing trends, posing threats to water quality in the upper Yellow River.

1.2 Sampling Site Selection and Sample Pretreatment

Field investigations were conducted during the dry season (December) and wet season (July) of 2023. Based on drainage systems, population activities, sampling conditions, and the distribution of wastewater treatment plant outlets and industrial/agricultural activities, 12 sampling sites were established along both banks of the Yellow River, extending from the water intake to the outlet of Lanzhou' s main urban area [Figure 1: see original paper]. Sites 11# and 12# were designated as special sampling points to investigate the impact of wastewater treatment plant effluent on sediment phosphorus release risk. Sediment samples were collected using the plum-blossom method to ensure representativeness and uniformity. Surface sediments (0–10 cm) were mixed at each site, placed in polyethylene bags, and transported to the laboratory. Overlying water samples were simultaneously collected for environmental analysis, and water temperature was measured on-site. In the laboratory, sediment samples were air-dried, ground, and sieved through a 100-mesh screen. Water samples were pretreated and analyzed for physicochemical properties including pH (measured with a PHSJ-4F pH meter), dissolved oxygen (measured with a JPSJ-605F dissolved oxygen meter), NH3-N (determined by nessler' s reagent spectrophotometry), CODMn (determined by the acidic method), and total phosphorus (determined by potassium persulfate oxidation-molybdenum-antimony spectrophotometry). All analyses followed strict quality control procedures, including parallel tests for each sample and blank experiments to eliminate systematic errors.

1.3 Phosphorus Form Determination Methods

Total phosphorus (TP) and inorganic phosphorus (IP) in sediments were measured using the SMT method [Figure 2: see original paper], with organic phosphorus (OP) calculated as the difference between TP and IP. The Psenner sequential extraction method was then applied to fractionate inorganic phosphorus into: weakly adsorbed phosphorus (NH4Cl-P), reducible phosphorus (Fe-P), metal oxide-bound phosphorus (Al-P), calcium-bound phosphorus (Ca-P), and residual phosphorus (Res-P) [Figure 3: see original paper]. Extractions were performed using NH4Cl, Na2S2O4/NaHCO3, NaOH, and HCl solutions, with the final residue digested using potassium persulfate. A thermostatic oscillator and high-speed centrifuge were used for extraction, and phosphorus concentrations in all extracts were determined by ammonium molybdate spectrophotometry using a UV spectrophotometer.

1.4.1 Equilibrium Concentration Assessment Method

The phosphorus equilibrium concentration (EPC0) was determined through thermodynamic adsorption experiments using a modified Freundlich isotherm model [19]. By comparing EPC0 with the phosphorus concentration in overlying water, we can determine whether sediments act as a phosphorus source (releasing phosphorus when EPC0 > overlying water concentration) or sink (adsorbing phosphorus when EPC0 < overlying water concentration) [20]. Higher

EPC0 values indicate greater phosphorus release potential.

1.4.2 Single-Factor Pollution Index Assessment Method

The single-factor pollution index (P_{TP}) was calculated using the formula $P_{TP} = C_{TP} / C_S$, where C_{TP} is the measured total phosphorus concentration and C_S is the evaluation standard value (600 $mg \cdot kg^{-1}$) established by the Ontario Ministry of Environment and Energy, Canada [21-22]. Risk levels are classified as: clean ($P_{TP} < 0.5$), slight pollution ($0.5 \leq P_{TP} < 1$), moderate pollution ($1 \leq P_{TP} < 1.5$), and heavy pollution ($P_{TP} \geq 1.5$) .

1.4.3 Bioavailable Phosphorus Pollution Index Assessment Method

The bioavailable phosphorus pollution index (P_{KTP}) was calculated using the formula $P_{KTP} = C_{BAP} / C_S$, where C_{BAP} represents the concentration of bioavailable phosphorus (BAP = OP + NH_4Cl-P + Fe-P + Al-P) and C_S is the same standard value used in the single-factor assessment [10]. This approach provides a more comprehensive evaluation of ecological risk by considering only the phosphorus fractions that can be released to water and utilized by organisms.

2.1 Characteristics of Overlying Water in the Riparian Zone

Physicochemical properties of overlying water at each sampling site are presented in . The water temperature ranged from 9.9-14.6°C in the dry season and 1.0–5.5°C in the wet season. pH values ranged from 7.48–8.44 (dry season) and 7.32–8.12 (wet season), indicating weak alkalinity. Dissolved oxygen concentrations were 8.52–9.67 $mg \cdot L^{-1}$ (dry season) and 9.14–11.26 $mg \cdot L^{-1}$ (wet season), showing weak oxygen enrichment. NH_3-N concentrations were 0.12–0.36 $mg \cdot L^{-1}$ (dry season) and 0.12–0.27 $mg \cdot L^{-1}$ (wet season), while COD_{Mn} values were 1.21–2.23 $mg \cdot L^{-1}$ (dry season) and 1.32–1.85 $mg \cdot L^{-1}$ (wet season). Total phosphorus concentrations were 0.04–0.05 $mg \cdot L^{-1}$ (dry season) and 0.02–0.04 $mg \cdot L^{-1}$ (wet season). All parameters met the Class III national surface water environmental quality standards.

2.2 Phosphorus Content and Form Distribution in Sediment Samples

Total phosphorus content in sediments ranged from 1173.42–1393.77 $mg \cdot kg^{-1}$, with an average of 1240.07 $mg \cdot kg^{-1}$—significantly higher than the 660 $mg \cdot kg^{-1}$ average measured in alpine shrub soils of the Qilian Mountains [11] but slightly lower than the 1520.67 $mg \cdot kg^{-1}$ average in the Yellow River' s lower reaches at Huayuankou, Zhengzhou [12]. Average TP was 1206.28 $mg \cdot kg^{-1}$ in the dry season and 1273.86 $mg \cdot kg^{-1}$ in the wet season, with the higher wet season values likely resulting from surface runoff carrying phosphorus-rich particles into the river during concentrated rainfall events (July–September accounts for 50-70% of annual precipitation).

Inorganic phosphorus dominated, accounting for 92.07% of TP on average, while organic phosphorus comprised 7.93%. Inorganic phosphorus averaged 1138.48 mg · kg^-1 in the dry season and 1241.42 mg · kg^-1 in the wet season. Among inorganic phosphorus fractions, calcium-bound phosphorus (Ca-P) was the predominant form, ranging from 815.28–971.56 mg · kg^-1 and representing 71.64% of inorganic phosphorus. Other fractions followed the order: Res-P (112.14–149.99 mg · kg^-1, 10.78%), Fe-P (25.15–49.49 mg · kg^-1, 3.01%), Al-P (16.85–47.35 mg · kg^-1, 2.56%), and NH4Cl-P (6.22–13.60 mg · kg^-1, 0.79%) [FIGURE:4, FIGURE:5].

Bioavailable phosphorus (BAP = OP + NH4Cl-P + Fe-P + Al-P) ranged from 80.15–260.49 mg · kg^-1, accounting for 6.46–20.99% of TP with an average of 16.7%. Although NH4Cl-P represented only 1.42–2.30% of inorganic phosphorus, it is the most unstable and biologically active fraction that can be rapidly released through diffusion and desorption when sediments are disturbed. Fe-P and Al-P are potentially mobile and bioavailable, converting to soluble phosphorus under anaerobic conditions. Res-P, while the largest fraction, is inert and has minimal impact on phosphorus cycling at the sediment-water interface.

2.3 Correlations Between Different Phosphorus Forms

Correlation analysis revealed strong relationships between various phosphorus fractions and overlying water characteristics [Figure 6: see original paper]. TP showed extremely high correlation with Ca-P ($P \leq 0.01$), confirming that sediment phosphorus is primarily derived from Ca-P. In the wet season, Fe-P and Al-P showed significant correlation ($P \leq 0.01$), while NH4Cl-P was significantly correlated with Al-P ($P \leq 0.05$), indicating that different phosphorus forms can transform under specific physicochemical conditions. These relationships demonstrate that assessing phosphorus release risk based solely on TP content is insufficient, necessitating analysis of individual phosphorus fractions.

2.4.1 Adsorption Equilibrium Index (EPC0)

EPC0 values for all sampling sites ranged from 18.588–30.729 mg · L^-1, substantially higher than overlying water phosphorus concentrations (0.02–0.05 mg · L^-1) . This indicates that sediments in the Lanzhou section of the Yellow River have high phosphorus release potential, with desorption exceeding adsorption at the sediment-water interface. Sites 11# and 12#, located downstream of wastewater treatment plant outlets, showed particularly elevated EPC0 values (29.460–30.729 mg · L^-1), demonstrating that continuous phosphorus accumulation from sewage discharge significantly increases release risk [27].

2.4.2 Single-Factor Pollution Index Assessment

All sediment samples exhibited P_{TP} values > 1.5, classifying them as heavily polluted according to Canadian environmental quality standards . Sites 3#–6#, located in densely populated urban areas, showed the highest P_{TP} values due to abundant phosphorus-rich particles from various sewage sources. The average TP concentration (1240.07 mg · kg^-1) was below the 2000 mg · kg^-1 threshold for ecological toxicity effects, suggesting that while heavily polluted, the system may not exhibit acute toxic effects.

2.4.3 Bioavailable Index Assessment

Bioavailable phosphorus pollution indices (P_{KTP}) ranged from 0.30–0.47, classifying all sites as clean . This represents a significant reduction in risk level compared to the single-factor assessment. The highest P_{KTP} value (0.47) occurred at site 12# during the wet season, likely due to continuous wastewater discharge and increased surface runoff.

Wet season P_{KTP} values were generally higher than dry season values, attributed to elevated temperatures and increased hydrological disturbance enhancing bioavailable phosphorus release. Organic phosphorus accounted for 60.89% of BAP, and its mineralization under microbial activity can convert it to bioavailable forms. However, the alkaline conditions (pH 7.32–8.44) of these calcareous soils limit organic phosphorus mineralization, reducing eutrophication risk.

3 Conclusions and Discussion

This study investigated phosphorus forms and distribution in sediments of the Lanzhou section of the Yellow River using Psenner sequential extraction and assessed release risks through multiple evaluation methods. The main conclusions are:

1) Riparian zone sediments contained high TP concentrations (average 1240.07 mg · kg^-1), with all sampling sites classified as heavily polluted. Inorganic phosphorus dominated (92.07% of TP), primarily as Ca-P, with other fractions following the order: Res-P > Fe-P > Al-P > NH4Cl-P.

2) Strong correlations existed between TP and Ca-P ($P \leq 0.01$), while Fe-P and Al-P showed significant correlation in the wet season ($P \leq 0.01$). NH4Cl-P correlated significantly with Al-P ($P \leq 0.05$), confirming that different phosphorus forms can transform under specific conditions.

3) Sediment EPC0 values exceeded overlying water phosphorus concentrations, indicating that sediments function as a phosphorus source. While total phosphorus pollution is severe, bioavailable phosphorus pollution indices suggest relatively good ecological conditions. However, continued anthropogenic impacts warrant ongoing attention to phosphorus release risks.

This study focused on natural release risks under ambient conditions. Future research should further investigate influencing factors, establish more precise pollution assessment systems, and develop targeted control measures to support ecological quality monitoring and management in the Yellow River Basin.

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Note: Figure translations are in progress. See original paper for figures.