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Effects of Iron on the Occurrence Form and Release of Phosphorus in The Yellow River Sediments

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Abstract: There is a close relationship between Fe and P in the sediments of the Yellow River, and iron has a great influence on the occurrence form of phosphorus, except that the content of exchangeable iron increases, and the content of P_{ex} and PAl decreases, showing a negative correlation; Water soluble iron and residual iron have a significant positive relationship with ΣP, water soluble iron and P_{org}, residual iron and P_{aut}, P_{De}, and the correlation coefficient is high, indicating that the contents of P_{ex}, P_{Al}, P_{org}, P_{aut}, P_{De}, and ΣP in the Yellow River sediments are controlled by iron forms.

Keywords: The sediments of Yellow River, Iron forms, Phosphorus forms, correlation, Phosphorus releasing.

1. Introduction

In the process of oxidation and reduction in nature, iron has a profound geochemical cycle. This cycle is not only its own cycle, but also interdependent and coupled with O, C, S, P, etc., so iron has a special importance in environmental biogeochemical cycle. Iron is an essential micronutrient element and limiting factor in the photosynthesis and nitrogen fixation processes of aquatic plants and planktic algae [1]. As one of the most abundant elements in the crust, iron participates in a series of biogeochemical processes and is of great significance to the biogeochemistry of the global ocean. Studies have shown that iron plays an important role in regulating aquatic environmental quality and biological productivity. The total amount of iron can be used as an important factor to evaluate the degree of water pollution, but it cannot really reflect its ecological characteristics, because it exists in different forms in sediments, and different forms can produce different environmental effects, directly affecting its ecological characteristics such as bioavailability, toxicity and migration in the environment.

Lake eutrophication is a global environmental problem, and phosphorus is the main limiting factor of algae growth in lakes. There are two sources of phosphorus in the lake: exogenous input and endogenous release. Even if exogenous is controlled, endogenous phosphorus load will also affect the eutrophication degree of the lake. The physical and chemical characteristics of sediments control the phosphorus exchange process, and the form of phosphorus occurrence, adsorption and release are closely related to the form of iron in the sediments. Iron and phosphorus exist independently in different forms in natural water sediments, and can also be combined with each other through a series of physical and chemical processes, such as soluble or insoluble combined iron and phosphorus [2]. The cycle of iron and phosphorus not only plays an important role in phosphate exchange between sediments and overlying water. It also plays an important role in regulating aquatic environment quality and biological productivity. Therefore, phosphorus and iron in sediments are interdependent and mutually restrictive [3,4]. Studies by domestic experts mainly focus on the morphological distribution and correlation of phosphorus and iron in sediments of lakes and gulf waters [5-9]. Zhang Shijun et al. studied Erhai Lake [4], and Wang Zhenhua et al. studied the occurrence forms and phosphorus in the sediments of four eutrophic lakes[11] in the eastern plain

Yang Wenbin et al.[10] studied the distribution characteristics of iron morphology and correlation analysis of phosphorus and iron in sediments of Taihu Lake. The Yellow River is a world famous river with less water and more sand. Its sediment sources are complex, including its own sediments, desert particles and dust particles entering the river (the upper reaches of the Yellow River, the Ulanbuhe Desert and Kubuqi Desert on both sides, Yanhai in the west, Yanhai in the east, Badain Jaran Desert, Tengger Desert, Mu Us Sandy Land, surface particles in Hexi Corridor, etc.), and soil and water loss in the middle reaches through the Loess Plateau all increase the capacity of suspended solids in the Yellow River. The phosphorus load in sediments is higher, and the total phosphorus content (1.36 $g{\bullet}kg^{-1}$)[12] is higher than that of Lake Taihu (0.88 $g{\bullet}kg^{-1}$)[13] and Chaohu Lake (0.55 g•kg-1)[14] and other lakes with serious eutrophication problems.

In recent years, artificial damming has led to a decrease in the concentration of total particulate matter in the Yellow River. These factors have a certain impact on the migration and transformation of nutrients iron and phosphorus in the water body of the Yellow River. However, there are few reports on the relationship between the forms of organic matter, iron and phosphorus in such a complex river. In recent years, with the rapid economic development, the discharge of industrial and domestic sewage tends to exceed the carrying capacity of the Yellow River water body, especially in the middle and lower reaches of the Yellow River, the eutrophication phenomenon in the delta area and the southern area of the Yellow River estuary is increasingly serious[15-17], which has a great impact on fisheries and aquaculture and human consumption water. At present, a large number of researches have been carried out around the ecological environment of the Yellow River. However, from the content of the researches, most of them focus on the separate studies on the form of iron or phosphorus in the Yellow River sediments, and there are few researches on the correlation between iron and phosphorus, and the effect of iron on the occurrence form of phosphorus and the release of phosphorus.

2. Effects of Different Forms of Iron On the Occurrence of Phosphorus in Sediments of the Yellow River

(1) Correlation analysis between different forms of iron and different forms of phosphorus

There is a close relationship between Fe and P in the Yellow River sediments, and the occurrence form of phosphorus is greatly influenced by iron. Except that the contents of exchangeable Fe increased and the contents of Pex and PAl decreased, which showed a negative correlation, the other Fe forms were positively correlated with the phosphorus forms, and the correlation coefficient was high.

Porg content is controlled by water soluble iron. Water soluble iron is the most easily absorbed and utilized by organisms, and its chemical properties are very active. It is easy to interact with phosphate in water, thus affecting the occurrence form of phosphorus. In the mineralization process, Porg releases a large number of phosphate ions, which can be absorbed into mineral particles (including Fe_2O_3, Al_2O_3, etc.) through exclusive adsorption to bind with iron and other metal cations [18].

There is a significant negative correlation between exchangeable iron and Pex and PAl in the Yellow River sediments, indicating that the contents of Pex and PAl in the sediments are affected by exchangeable iron. Pex and PAl are very active forms. When environmental conditions change, PO_4^{3-} will be released into water [3,10,19], and PO_4^{3-} and Fe^{2+} will produce $Fe_3(PO_4)_2$ precipitate (Ksp=$1.3x10^{-22}$) and buried in sediments. $FePO_4$ (Ksp=$9.91x10^{-16}$) precipitated or adsorbed on the surface of FeO(OH), which increased the content of Pex. The Yellow River is a weakly alkaline water body with a pH value of 8.0-8.5. OH^- and PO_4^{3-} compete for surface adsorption sites, leading to partial release of P_{ex} and P_{Al}. Therefore, there is a significant negative correlation between exchangeable iron and Pex and P_{Al} states.

There is a significant positive correlation between residual Fe and P_{aut} and P_{De} in the Yellow River sediments, indicating that the content of calcium-bound phosphorus-P_{Ca} (P_{Ca}=P_{aut}+P_{De}) is affected by residual Fe to a certain extent. Because PDe mainly refers to the residual phosphorus with strong binding force in the crystal lattice of primary minerals, and the residual iron mainly comes from the primary iron minerals in the sediments, and part of it comes from the recrystallization products of iron silicate minerals after weathering. The single iron mineral is the main form of iron in the sediments of the middle and lower reaches of the Yellow River. These results indicate that the significant positive correlation between residual iron and P_{aut} and P_{De} is determined by the geology and geomorphology of the Yellow River Basin. Residual iron and P_{De} have strong stability and are difficult to be utilized by organisms. P_{aut} is mainly composed of calcium carbonate combined with phosphorus, dicalcium phosphate, octadecalcium phosphate (Ca8-P), hydroxyapatite and fluorapatite [20], in which Ca2-P has certain activity and is the most direct phosphorus source of soil available phosphorus[26]. In addition, microbial metabolism can also cause the transformation of the solubility and morphology of P_{aut} and P_De [27]. Therefore, when the external environment changes, P_{aut} and P_{De} may undergo reactions such as increasing solubility or morphological transformation to release active groups or ions, and then interact with iron ions.

(2) Correlation analysis of different forms of iron and total phosphorus

There is a significant positive correlation between the water-soluble Fe and ∑P in the sediments of the Yellow River. The residual iron was positively correlated with ∑P. As water-soluble iron is the most easily absorbed and utilized iron, it is easy to interact with phosphate in water. In the sediments of the Yellow River, phosphorus is strongly adsorbed on the surface of iron oxide and deposited on the bottom of the river. For example, amorphous iron oxide has a strong adsorption capacity for phosphorus due to its huge surface area [24], thus increasing the content of ∑P.

3. Effects of Iron On Phosphorus Release from Sediments of the Yellow River and Risk Assessment of Phosphorus Release

The Yellow River is a buffer system of high pH and high carbonate. Iron mainly exists in the form of ferric hydroxide, and the presence of $Fe(OH)_3$ greatly increases the phosphorus adsorption capacity of the sediments. There is a significant positive correlation between ∑Fe and ∑P in the sediments of the Yellow River, indicating a close relationship between Fe and P in the Yellow River sediments, which may be because in an alkaline environment, the phosphorus adsorption capacity of sediments is mainly related to iron oxides, iron hydroxides and calcium carbonate [22].

The research results of many experts show that[11,20] : w(∑Fe)/w(∑P) is the indicator to judge the phosphorus release potential in the sediments. If the sediment w(∑Fe)/w(∑P) is greater than 15 or 20, iron controls the phosphorus release. And the higher the ratio of w(∑Fe)/w(∑P), the higher the iron content, the stronger the adsorption capacity, the greater the iron control effect. With the aggravation of water pollution, the adsorption amount of iron to phosphorus increases, resulting in the increase of w(∑P) and the decrease of w(∑Fe)/w(∑P) ratio in sediments. Therefore, the ratio of w(∑Fe)/w(∑P) in the sediments of heavily eutrophicated lakes and rivers is lower than that in the sediments of moderately mildly eutrophicated lakes and rivers. From the point of view of phosphorus adsorption by sediments, the higher the iron content in sediments, the stronger the adsorption capacity, the higher the w(∑Fe)/w(∑P) in lake and river sediments indicates that the water body has a strong phosphorus adsorption capacity.

The w(∑Fe)/w(∑P) are all less than 15, indicating that the phosphorus release in these reaches is greatly influenced by human factors. For example, Xigu Section of Lanzhou is an important petrochemical base in western China, and Zhongwei section has a large scale of agricultural production, which is greatly influenced by the input of exogenous phosphorus such as pesticides and fertilizers. There are two DAMS built from Wuhai Section to Sansheng section, namely Haibo Bay and Sansheng water conservancy project hub, and there is a dam built upstream of Tongguan section. The artificial dam has intercepted the sediment, resulting in the decrease of the total particle concentration.

4. Conclusion

There is a close relationship between Fe and P in the Yellow River sediments, and iron has a great effect on the occurrence of phosphorus, except that the content of exchangeable iron increases and the content of P_{ex} and P_{Al}

decreases, showing a negative correlation. The correlations between water-soluble iron and residual iron and ∑P, water-soluble iron and Porg, and residual iron and P_{aut} and P_{De} are significantly positive, and the correlation coefficient is high, indicating that the contents of P_{ex}, P_{Al}, P_{org}, P_{aut}, P_{De} and ∑P in the Yellow River sediments are controlled by iron morphology.

According to the ratio of w(∑Fe)/w(∑P), the phosphorus release in sediments of most reaches of the Yellow River is controlled by iron, while the phosphorus release in sediments in other sections of the Yellow River is greatly affected by human factors, such as industrial and agricultural production level and artificial damming.

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