Original Paper

Root Iron Plaque: A natural Barrier and Potential Risk for Rice against Heavy Metal Pollution

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Abstract

Root iron plaque is a colloidal film of iron-manganese oxides formed on the root surface of rice. Its formation process involves oxygen released by rice roots oxidizing Fe^{2+} to Fe^{3+}, which then combines with elements such as manganese to form precipitates that ultimately cover the surfaces of root tips and root hairs. With a large specific surface area and abundant functional groups, iron plaque can regulate the migration and accumulation of heavy metals through processes like adsorption and coprecipitation, serving as a "natural barrier" against heavy metal pollution. This paper systematically elaborates on the external resistance and internal tolerance mechanisms of plants to heavy metals mediated by iron plaque, and analyzes the effects of factors such as water management, fertilization methods, root aeration capacity, and soil microorganisms on the formation of iron plaque as well as the migration and accumulation of heavy metals. In addition, this paper also summarizes the potential risks of iron plaque in practical applications and prospects future research directions.

Keywords

root iron plaque, heavy metal pollution, mechanism of action, influencing factors, potential risks

1. Introduction

Iron plaques is formed through the following process: rice roots release oxygen into the rhizosphere via aerenchyma, which in turn increases the redox potential (Eh) of the rhizospheric microenvironment. In the surrounding soil, ferrous iron ions (Fe^{2+}) with high reducibility are oxidized to ferric iron ions (Fe^{3+})

in the oxygen-rich rhizospheric environment. Fe^{3+} further undergoes hydrolysis and polymerization reactions, and combines with elements such as manganese (Mn) to form iron-manganese (hydr)oxide precipitates (YU, LI, LIU et al., 2016). These precipitates adhere to the root surface, accumulate gradually, and cover the surfaces of root tips and root hairs (Xia Xintong, Dai Shuting, Zhang Mengen, et al., 2024; LIU & ZHU, 2005). Owing to its large specific surface area, abundant surface functional groups, and unique physicochemical properties, this special structure exerts a significant regulatory effect on the migration and accumulation of heavy metals in rice through processes such as adsorption, coprecipitation, and redox reactions (HANSEL, FENDORF, SUTTON et al., 2001). Numerous studies have confirmed that iron plaque can "sequester" heavy metal ions and reduce their translocation to root cells, thus being regarded as a "natural barrier" for rice against heavy metal pollution (SUI, KANG, WU et al., 2021). Studies have shown that the application of ferrous sulfate can induce the formation of iron plaque, thereby significantly reducing the cadmium (Cd) content in rice stems, leaves, and brown rice (Li, Xie et al., 2024). A field experiment revealed that at the maturity stage, there was a significant positive correlation between the iron concentration and Cd concentration in the iron plaque (Li, Xu, Chen et al., 2024). This indicates that the Iron plaques can enhance the adsorption of heavy metals in the soil (Dong, Fan, Liao et al., 2016). However, the role of Iron plaque is not an absolute "protective shield"; its regulatory effect on heavy metals is complex and dual-sided (YANG, LIU etal., 2016). On the one hand, the formation of iron plaque is comprehensively influenced by various factors, including soil physicochemical properties (e.g., pH, Eh), agronomic practices (e.g., water management, fertilizer type), and biological factors (e.g., microbial community) (LIU, ZHANG, CHEN et al., 2013). Excessive or structurally unstable iron plaque may act as a "temporary storage reservoir" for heavy metals. When environmental conditions change (such as soil acidification or long-term waterlogging), heavy metals may be released, thereby increasing the risk of heavy metal uptake by rice (Dong, Fan, Liao et al., 2016; Fu, Yu, Cai et al., 2010). On the other hand, there is a competitive relationship between iron plaque and rice in the absorption of other nutrients. This may affect the uptake of essential elements such as phosphorus and zinc by rice, thereby indirectly restricting rice growth and development (Xu, Song, Chen et al., 2023; FU, YANG, & SHEN, 2014).

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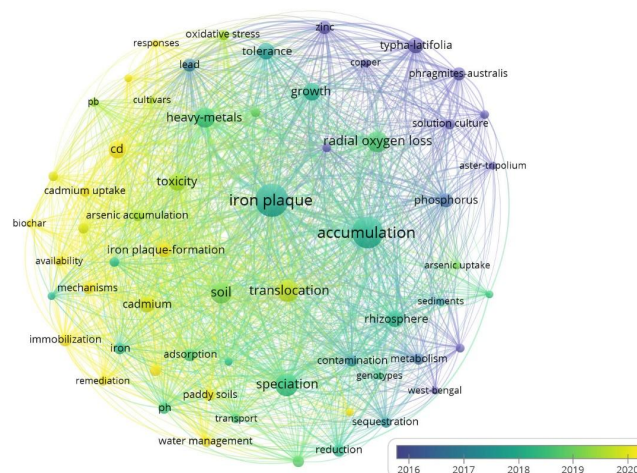
Figure 1. Bibliometric Diagram of the Surface Iron Plaque

Bibliometric Analysis and Mechanisms of Iron Plaque in Heavy Metal Regulation Bibliometric analysis shows that current research hotspots on iron plaque mainly focus on three aspects: first, the adsorption, complexation, and immobilization processes of heavy metals by iron plaque, as well as its regulatory role in the migration, speciation transformation, and bioavailability of heavy metals in the soil-plant system; second, the formation and evolution of Iron plaque in soil environments; third, the effects of Iron plaque on plant physiological characteristics such as growth and development, photosynthesis, and antioxidant systems. Early studies mainly concentrated on heavy metal pollution (e.g., As, Cd), the accumulation mechanism of heavy metals by iron plaque, the correlations between iron plaque and factors such as soil pollution and groundwater, as well as plant health risks. In recent years, research has become increasingly in-depth and diversified: while continuing to focus on heavy metals, studies have expanded to the material cycle of Iron plaque and its relationships with the regulation of heavy metal transport in plants and stress-resistant physiology; additionally, investigations have been conducted on the effects of Iron plaque on plant growth and development, photosynthesis, nutrient metabolism, and the regulation of related gene expression. Although existing studies have revealed some functional mechanisms of iron plaque (XING, CAI, LIU et al., 2006), there are still many controversies and gaps in aspects such as potential risks in practical applications. In-depth analysis of the mechanism of Iron plaque in heavy metal pollution is of great significance for clarifying the stress resistance mechanism of rice and optimizing the remediation strategies for contaminated paddy fields. Therefore, based on research achievements in recent years, this paper systematically sorts out the mechanism of Iron plaque as a "natural barrier", discusses the key factors affecting the formation and function of iron plaque, and analyzes the potential risks of iron plaque, aiming to provide theoretical support for the safe utilization of heavy metal-contaminated paddy fields and the quality control of rice.

2. Modes of Iron Plaque Affecting Heavy Metal Migration and Accumulation in Soil-Root Systems

2.1 Mediating External Resistance of Plants

The external resistance mechanism refers to the process where Iron plaque retains heavy metals on the root surface through adsorption or coprecipitation with them, while simultaneously binding to heavy metal elements in the soil, thereby reducing the bioavailability and toxicity of these heavy metals (Xia, Dai, Zhang et al., 2024). Iron plaque affects the migration and accumulation of heavy metals mainly through physicochemical processes (Fu, Yu, Cai et al., 2010). On one hand, iron plaque has a large specific surface area and abundant active sites, which can immobilize heavy metal ions on the root surface through adsorption, thereby reducing the migration of heavy metal ions to the root system (Liu, Hu, Zhang et al., 2007; LIU & ZHU, 2005; XING, CAI, LIU et al., 2006). A researcher conducted a hydroponic experiment to induce the formation of Iron plaque by adding ferrous sulfate. The results showed that the contents of Cu and Zn in the iron plaque on rice roots with iron plaque were increased, while the contents of Cu and Zn in roots, stems, and leaves were significantly decreased. This indicates that Iron plaque has a strong adsorption capacity for Cu and Zn, which can effectively reduce the absorption and accumulation of these heavy metals by rice (Wu, Tao, Li et al., 2018). On the other hand, Iron plaque combines heavy metal ions with components in the iron plaque through coprecipitation to form insoluble compounds, thereby reducing the bioavailability of heavy metals (ISHIMARU, SUZUKI, TSUKAMOTO et al., 2006). A study found that iron and manganese oxides in Iron plaque can form coprecipitates with heavy metals such as Cd and Pb, thereby reducing the translocation of heavy metals to the aboveground parts of rice (DONG, FENG, WANG et al., 2016; ISHIMARU, SUZUKI, TSUKAMOTO et al., 2006).

2.2 Mediating Internal Tolerance of Plants

The internal tolerance mechanism refers to the ability of Iron plaque to absorb a large amount of iron from the medium, enabling it to compete with other heavy metals for metabolically sensitive sites, and deposit the heavy metals that enter the roots in insensitive sites such as plant cell walls and vacuoles, thereby enhancing plant tolerance (Xia, Dai, Zhang et al., 2024; YU, LI, LIU et al., 2016; HANSEL, FENDORF, SUTTON et al., 2001; FENG, SU, ZHU et al., 2022). The presence of Iron plaque can affect the physiological and biochemical processes of rice and enhance its internal tolerance to heavy metals (YU, LI, LIU et al., 2016; HANSEL, FENDORF, SUTTON et al., 2001; FENG, SU, ZHU et al., 2022). A study showed that the addition of Fe^{2+} could significantly reduce reactive oxygen species (ROS) in the leaves of rice seedlings and alleviate the toxicity of ROS to rice seedlings, indicating that Iron plaque can enhance rice tolerance to heavy metal stress by regulating the redox state in rice (FU, YANG, & SHEN, 2014). In addition, Iron plaque may affect the absorption and transport of other nutrient elements by rice roots, indirectly improving rice tolerance to heavy metals (YANG, LIU, WANXM et al., 2016). A study found that Iron plaque can promote the absorption of silicon by rice, and the increase in silicon content helps to improve the stress resistance of rice to heavy metal stress

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(Li, Xu, Chen et al., 2024; LIU, JI, CHEN et al., 2023).
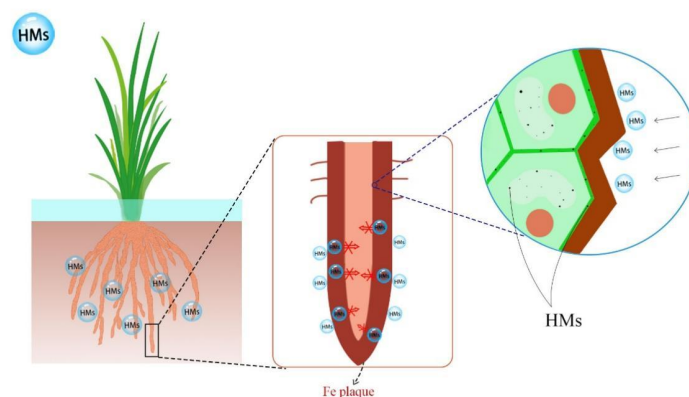
Figure 2. Shows the Mechanism of Action of the Surface Iron Film on Heavy Metals

3. Factors Influencing Iron Plaque Formation and Heavy Metal Accumulation & Migration

3.1 Water Management

Water management exerts a significant impact on the formation of iron plaque in rice and the accumulation and migration of heavy metals (Fu, Shen, & Yang, 2017). Some scholars have confirmed that alternate wetting and drying irrigation is more conducive to the formation of root surface iron plaque than single flooding irrigation or single moist irrigation, and the contents of DCB-As and DCB-Cd increase with the increase in iron plaque content (Chen & Zhao, 2021). This is because under flooded conditions, the soil is in a reduced state, and iron oxides are reduced to ferrous ions. When rice roots secrete oxygen, ferrous ions are oxidized, forming iron plaque on the root surface (KHAN, SESHADRI, BOLAN et al., 2016). However, other studies have pointed out that flooding treatment is more favorable for the formation of rice iron plaque (Fu, Shen, & Yang, 2017). Research has found that the content of rice iron plaque under flooding treatment is higher than that under moist irrigation and intermittent irrigation. Moreover, the contents of Fe and Mn in iron plaque under flooding conditions are significantly higher than those under drainage conditions, indicating that flooding treatment can promote the formation of rice iron plaque and the immobilization of heavy metals (Zhong, Yin, Chen et al., 2016). Different water management modes change the redox potential of the soil, thereby affecting the formation of iron plaque, as well as the speciation and bioavailability of heavy metals, and further influencing the absorption and accumulation of heavy metals by rice (CAO, QIN, LIN et al., 2018).

3.2 Fertilization Methods

3.2.1 Soil Fertilization Organic Fertilizers

Organic fertilizers play an important role in regulating the formation of rice iron plaque and reducing the migration and accumulation of heavy metals in rice (Lin, Sun, Wang et al., 2016). The application of organic fertilizers increases the content of soil organic matter, changes the speciation of heavy

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metals in the soil to reduce their bioavailability, and at the same time promotes the formation of iron plaque and enhances the adsorption capacity of iron plaque for heavy metals, thereby reducing the absorption and translocation of heavy metals by rice (WANG & ZHANGGY, 2020; GAO, CAO, GAOJ et al., 2017). Li Kaiye et al. conducted a pot experiment to study the effects of five organic materials on rice iron plaque and the absorption and translocation of As and Cd. The results showed that the application of organic materials was beneficial to the formation of rice iron plaque, increasing the Cd and As contents in it by 17.73%–151.03% and 28.49%–94.86%, respectively, while reducing the Cd and As contents in brown rice by 15.87%–79.45% and 27.04%–82.51%, respectively (Li, Zhao, Chen et al., 2021).

3.2.2 Chemical Fertilizers

The application of chemical fertilizers can affect the formation of iron plaque and the accumulation of heavy metals in rice by regulating the physical and chemical properties of the soil. Xu Junhui et al. used calcium magnesium phosphate and lime to prepare phosphorus-calcium base fertilizer and studied its effects on rice iron plaque and Cd content in rice grains. The results showed that base fertilizer application at a concentration of 0.2‰-0.5‰ could promote the formation of rice iron plaque; however, application of phosphorus-calcium base fertilizer exceeding 0.8‰ would reduce the bioavailability of Fe and Mn and inhibit the formation of iron plaque. The application of base fertilizer increased the soil pH, reduced the effective concentration of Cd in the soil, and thus decreased the Cd content in various plant organs and rice grains (Xu, Song, Chen et al., 2023). Zhang Xinhu et al. carried out a pot experiment to explore the effects of different application rates of ferrous disodium ethylenediaminetetraacetate (EDTA·Na$_2$Fe, a chelated iron fertilizer) on the bioavailability of Cd and As in soil, the formation of iron plaque, and its role in the immobilization of Cd and As and their translocation in rice plants. The results showed that the application of EDTA·Na$_2$Fe could reduce the bioavailability of Cd and As in the soil, promote more Cd and As to be immobilized on the iron plaque, and significantly reduce the Cd and As contents in grains by 27.8–39.2% and 17.7–28.4%, respectively (Zhang, Hong, Chao, Wang, Zheng, Zhu, Huang, Zhang, & Zhu, 2024).

3.2.3 Foliar Fertilization

Foliar fertilizers play a key regulatory role in the formation of rice iron plaque and the migration and accumulation of heavy metals. Qiu Yonghong et al. found that spraying manganese-containing foliar fertilizer on rice leaves during the critical growth period of rice resulted in thicker iron plaque, with an average increase in thickness of 38.6%, and an increase in the deposition of iron-manganese oxides per unit area, with a density increase of approximately 21.5% per unit area. Additionally, after spraying foliar manganese fertilizer, the Cd content in rice grains decreased significantly by 83.6%-86.9%, and the Cd enrichment coefficient dropped to 0.05 (Qiu, Tang, Li, Chen, Wei, Guo, & Wu, 2024). This may be because after the foliar manganese fertilizer is absorbed by the leaves, it affects the microenvironment around the roots through the translocation mechanism in plants, changes the redox conditions of iron in the soil, thereby stimulating the formation of iron plaque, significantly improving

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the affinity of iron-manganese plaque for Cd, and enhancing its adsorption and immobilization capacity for Cd (Xia, Dai, Zhang et al., 2025). At the same time, manganese can activate the antioxidant system of rice and enhance its tolerance to Cd stress (LIU, JI, CHEN et al., 2023).

3.2.4 Root Aeration Capacity

Rice has a well-developed aerenchyma, and its root aeration capacity is crucial for the formation of iron plaque. Some researchers have pointed out that root aeration capacity is one of the key factors affecting the formation of iron plaque (CHAN, DYKES, HOOVER et al., 2023). Roots with good aeration can release more oxygen into the rhizospheric environment, promoting the oxidation of ferrous ions in the rhizospheric soil to form iron plaque. Rice varieties with stronger aeration capacity tend to form a higher amount of iron plaque and have a stronger ability to adsorb and immobilize heavy metals, thereby reducing the translocation of heavy metals to the aboveground parts (Zheng, Huang, Li, Ma, Xu, Zhu, Zhu, & Zhang, 2022). For example, some flood-tolerant rice varieties, due to their more developed root aerenchyma, can form more iron plaque under flooded conditions and have relatively higher tolerance to heavy metals (LEE, HSIEH, LIN et al., 2013).

3.3 Soil Microorganisms

Soil microorganisms play an important regulatory role in the formation of iron plaque and the bioavailability of heavy metals. A researcher selected three arsenic-resistant iron-oxidizing bacteria (Bacillus sp. T2, Pseudomonas sp. Yangling I4, and Bacillus sp. TF1-3), applied them to rice growing in different As-contaminated environments, studied the effects of iron-oxidizing bacteria on As accumulation in rice, and clarified the possible mechanism. The results showed that inoculation with iron-oxidizing bacteria significantly reduced the concentration of inorganic As in brown rice in both pot experiments and paddy fields. Iron-oxidizing bacteria reduced the inorganic As concentration in brown rice by affecting the formation of iron plaque, the absorption kinetics of As(III), and the properties of rhizospheric soil (Xiao, Li, & Ye, 2020). Soil microorganisms can affect the formation of root surface iron plaque and the bioavailability of heavy metals in multiple ways. On one hand, microorganisms can participate in the redox reactions of substances in the soil, thereby affecting the speciation of iron and the formation of iron plaque. For example, some iron-oxidizing bacteria can oxidize ferrous ions to ferric ions, promoting the formation of iron plaque (Emerson, Weiss, & Johanna, 1999). On the other hand, microorganisms can interact with heavy metals, changing the speciation and bioavailability of heavy metals, and thus influencing the absorption of heavy metals by rice and the adsorption of heavy metals by root surface iron plaque. For instance, an Enterobacter sp. M5 strain with sulfate-reducing ability can reduce sulfate in the soil to sulfide through metabolic activities under flooded paddy field conditions. Sulfide can combine with highly active soluble Cd^{2+} in the soil to form insoluble cadmium sulfide (CdS) precipitates, directly reducing the bioavailability of Cd in the soil and decreasing its migration flux to rice roots (Weiss, Emerson, Backer, & Megonigal, 2003; Neubauer, Toledo-Duran, Emerson, & Megonigal, 2007).
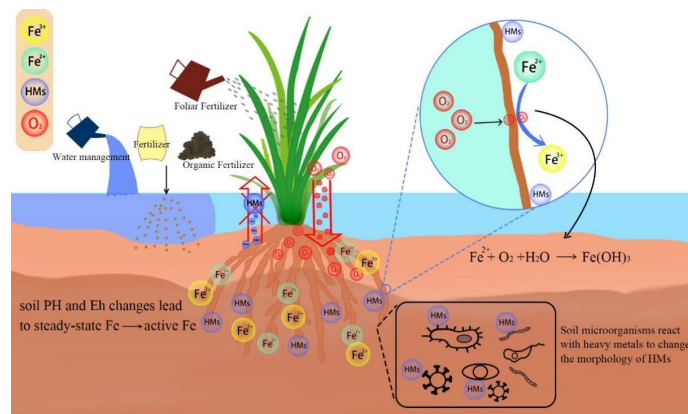
Figure 3. Iron Plaque Formation and Its Influencing Factors

4. Potential Risks of Iron Plaque in the Plant-Soil System

4.1 Effects of Iron Plaque on the Absorption of Other Nutrient Elements

Although iron plaque reduces the absorption of heavy metals by rice roots to a certain extent, it also affects the absorption of other nutrient elements by rice. Studies have found that the absorption of phosphorus by rice influences the formation of iron plaque. Fe^{3+} in iron plaque may undergo adsorption or coprecipitation reactions with phosphate ions, reducing the content of available phosphorus in the soil and thereby affecting the absorption and utilization of phosphorus by rice (FU, YANG, & SHEN, 2014). A study revealed that iron plaque decreases the capacity of roots to absorb nutrients and adsorbs/immobilizes nutrient ions, thus inhibiting plant nutrient absorption. Another study also found that when the thickness of iron plaque ranges from 0.2 to 24.5 g/kg, the phosphorus absorption increases with the increase in iron plaque quantity; however, when the plaque thickness increases to 28.3 g/kg, the phosphorus content in plants does not increase but decreases instead (Zhang, Zhang, & Mao, 1999). In addition, iron plaque may exhibit competitive or synergistic effects on the absorption of other trace elements such as Zn and Mn. This is because the iron oxide colloidal film contains numerous negatively charged groups, making iron plaque an enrichment reservoir for Zn and thereby increasing Zn absorption by rice (Wu, Tao, Li et al., 2018). Nevertheless, when iron plaque is excessive, the absorption of Zn by rice is hindered. This is because Zn adsorbed in iron plaque must undergo complex processes such as desorption and crossing the iron plaque to reach the root surface, which is unfavorable for Zn absorption (SUI, KANG, WU et al., 2021; YANG, LIU, et al., 2016; FU, YANG, & SHEN, 2014). Therefore, whether plants can absorb nutrient elements depends on factors such as the thickness of iron plaque and the concentration of nutrient elements.

4.2 Risk of Secondary Release of Heavy Metals from Iron Plaque

The immobilization of heavy metals by iron plaque is not irreversible. When the environmental conditions of paddy fields change drastically (e.g., long-term flooding, soil acidification), iron plaque may dissolve, leading to the secondary release of adsorbed heavy metals and thereby increasing the risk of absorption by rice (CHAN, DYKES, HOOVER et al., 2023). If the soil environment changes, heavy

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metals in iron plaque may desorb from the plaque, re-enter the soil solution, and be absorbed by rice roots, which increases the risk of heavy metal accumulation in rice. On one hand, a decrease in redox potential (Eh) triggers the disintegration of iron plaque and the release of heavy metals (LIU, ZHANG, CHEN et al., 2013). If the rhizosphere hypoxia intensifies due to factors such as long-term waterlogging in paddy fields or excessive input of organic matter, the Eh of the rhizospheric microenvironment will decrease significantly. At this point, the originally stable Fe^{3+} in iron plaque will be reduced to soluble Fe^{2+}, and the structure of iron plaque will disintegrate accordingly. Heavy metals such as Cd and As previously adsorbed and immobilized by iron plaque will be released into the soil synchronously with the disintegration of iron plaque, and re-converted into bioavailable forms that can be directly absorbed by rice (Lin, Sun, Wang et al., 2016). On the other hand, soil acidification promotes the desorption of heavy metals through ion competition. When the soil pH drops to the acidic range, the concentration of H^+ in the soil solution increases significantly. These H^+ ions compete with heavy metal ions adsorbed on the surface of iron plaque for adsorption sites, displacing heavy metal ions from the functional groups of iron plaque (LIU & ZHU, 2005). Meanwhile, the acidic environment also accelerates the dissolution of iron oxides in iron plaque, further impairing the immobilization capacity of iron plaque for heavy metals. As a result, the desorbed heavy metals re-enter the soil solution and are absorbed by rice roots (Li, Xie et al., 2024). Therefore, both the disintegration of iron plaque caused by a decrease in redox potential and the desorption of heavy metals induced by soil acidification will disrupt the equilibrium of heavy metal immobilization by iron plaque, triggering the secondary release of heavy metals (Emerson, Weiss, & Johanna, 1999). This risk persists in long-term agricultural production; once triggered by environmental conditions, it may lead to an increase in heavy metal accumulation in rice, ultimately endangering the quality and safety of rice grains.

4.3 Potential Impacts of Iron Plaque on Rhizospheric Microorganisms

The physical structure and chemical properties of iron plaque directly alter the attachment patterns and spatial distribution of microorganisms. On one hand, the porous structure on the surface of iron plaque provides "habitats" for microorganisms, allowing them to attach to the surface or interior of iron plaque via substances such as extracellular polysaccharides (DONG, FENG, WANG et al., 2016); on the other hand, the charge differences on the surface of iron plaque screen microorganisms with specific adsorption capacities, thereby altering the community structure (Xiao, Li, & Ye, 2020). This screening is essentially a process of "natural selection": microorganisms with iron oxidation/reduction functions (e.g., iron-oxidizing bacteria *Sideroxydans* and *Gallionella*, iron-reducing bacteria *Geobacter* and *Shewanella*) can utilize iron in iron plaque as an energy source (iron-oxidizing bacteria obtain energy by oxidizing Fe^{2+}, while iron-reducing bacteria release electrons by reducing Fe^{3+}) (Emerson, Weiss, & Johanna, 1999; Weiss, Emerson, Backer, & Megonigal, 2003). Thus, they can reproduce rapidly in the iron plaque microenvironment and gradually become dominant flora. In contrast, microbial groups that cannot adapt to the physicochemical conditions of iron plaque will gradually decrease or even disappear due to disadvantages in the competition for survival resources, ultimately

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leading to a decline in rhizospheric microbial diversity. The loss of microbial diversity usually reduces the resilience and resistance of microbial communities, weakening their ability to cope with environmental fluctuations such as drought and pest/disease infestations. Furthermore, changes in microbial communities indirectly affect the behavior of heavy metals. The enriched iron-reducing bacteria may reduce immobilized Fe^{3+}, causing the dissolution of iron plaque and the release of adsorbed heavy metals, which in turn exacerbates the pollution risk (CHAN, DYKES, HOOVER et al., 2023).
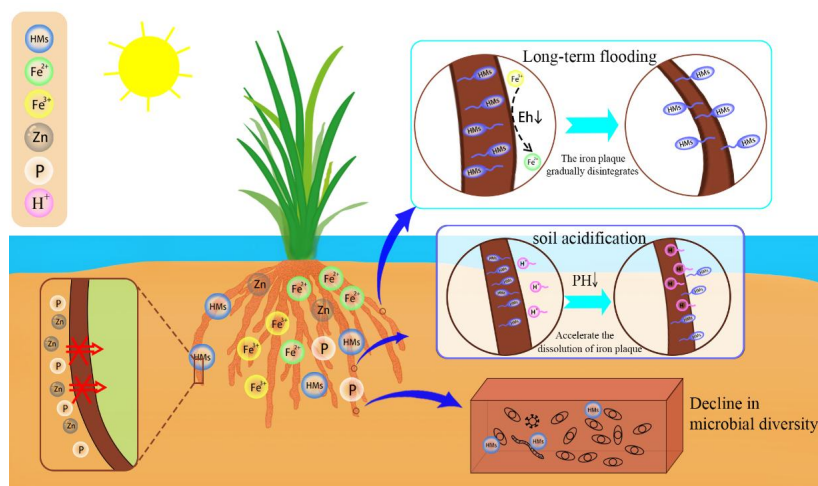

Figure 4. Potential Risks of Iron Plaque

5. Future Prospects

As a crucial pathway for nutrients and pollutants to enter plants, exploring the functions and regulatory mechanisms of root surface iron plaque holds significant ecological and environmental significance. Future research can be carried out in the following aspects:

(1) Utilize more advanced technologies to further investigate the adsorption, immobilization, and desorption mechanisms of root surface iron plaque on different heavy metals, and clarify the law governing its influence on the behavior of heavy metals under complex environmental conditions.

(2) Strengthen research on the environmental factors affecting the formation and function of iron plaque, particularly focusing on the comprehensive impacts of factors such as temperature, precipitation, acid rain, and soil acidification on iron plaque against the backdrop of global climate change and worsening environmental pollution.

(3) Explore the use of biotechnological approaches or agricultural management measures to regulate the formation and properties of iron plaque, so as to enhance its adsorption and immobilization capacity for heavy metals while reducing the negative impacts on the absorption of other nutrient elements.

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