Research on efficient activation technology of soil selenium in Hubei Province

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Abstract: Selenium is an essential trace element for the human body, renowned for its antioxidant properties, immune system enhancement, and potential in cancer prevention. Hubei Province possesses abundant selenium resources in its soil. Enshi Prefecture hosts the world's only independent selenium deposit, while the Jianghan Plain boasts superior quality and contiguous distribution of selenium-rich soil. This combined advantage provides a solid resource foundation for developing the selenium-rich industry in Hubei Province. However, due to factors such as soil pH, organic matter content, and redox potential, the bioavailability of selenium in the soil is low, making it difficult for crops to absorb efficiently, which constrains the development of the selenium-rich industry. This study systematically investigated technical methods for enhancing soil selenium availability through laboratory simulation experiments and field trials. Furthermore, by integrating the characteristics of selenium content and distribution in Hubei's soils, it delved into the mechanisms of different activation techniques. The research aims to provide scientific evidence and technical support for the efficient development and utilization of selenium-rich soil resources in Hubei Province.

Key words: Soil selenium; effective activation; technical research; plant absorption; selenium-enriched agriculture

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Introduction

Hubei Province, located in central China and the middle reaches of the Yangtze River, has a humid and rainy climate. The region features a diverse and complex topography, including mountains, hills, and plains. The main soil types are yellow-brown soil, red soil, and paddy soil. Thanks to its unique natural conditions, some areas of Hubei Province are rich in selenium resources, particularly in Enshi Tujia and Miao Autonomous Prefecture, where the selenium content in the soil is high and widely distributed, earning it the title of 'World Selenium Capital[1].' However, the availability of selenium in the soil is crucial for plant absorption and utilization. If selenium is present in an insoluble or organically bound state, plants will have difficulty absorbing it, leading to insufficient selenium content in agricultural products and failing to fully utilize the advantages of selenium-rich soil. Therefore, researching effective techniques to activate selenium in Hubei Province's soil is of great practical significance for enhancing the selenium content in agricultural products and developing high-end selenium-enriched agriculture.

1.Selenium content and distribution characteristics of soil in Hubei Province

1.1 The overall level of selenium content in soil in Hubei Province

According to data from the Hubei Provincial Geological Survey Institute, the average selenium content in the province's soil is approximately 0.28mg/kg, slightly higher than the national average of 0.23mg/kg. In Enshi Prefecture, the selenium content in the soil is generally high, with most areas exceeding 0.4mg/kg, and some core selenium-rich areas reaching over 1.0mg/kg, making it a typical high-selenium soil region[2]. In contrast, the Jianghan Plain and other regions have relatively low selenium content, averaging around 0.15-0.20mg/kg, which is considered moderately low. This variation in selenium content is closely linked to the geological parent materials of different regions in Hubei Province. The exposed strata in the Enshi area contain a significant amount of selenium-rich rocks, such as stone coal and shale, which provide a rich source of selenium for the soil. In contrast, the parent materials of the plains are mostly river alluvium, resulting in relatively lower selenium content.

1.2 Distribution characteristics of soil selenium in Hubei Province

The mountainous areas of Enshi and western Yichang in southwestern Hubei have high selenium levels in the soil, while the central Jianghan Plain and Huanggang and Xiaogan in northeastern Hubei have relatively low levels. In terms of soil types, yellow-brown soil is mainly found in the low mountains and hills of northwestern and northeastern Hubei, with an average selenium content of about 0.35 mg/kg. Red soil is more prevalent in southeastern Hubei, with a selenium content of about 0.30 mg/kg. Paddy soil, the primary cultivated soil in Hubei Province, is widely distributed in plains and hilly areas, with a relatively lower selenium content of about 0.20 mg/kg on average. Additionally, topography significantly influences the distribution of soil selenium. In mountainous and hilly regions, where slopes are steeper, soil erosion is less severe, allowing selenium to accumulate in the surface layer. In contrast, in flat plains, long-term agricultural activities and irrigation can lead to selenium loss through water runoff, reducing soil selenium levels.

1.3 Factors affecting selenium content and distribution in soil of Hubei Province

Hubei Province is situated at the intersection of the Yangtze Plate and the Qinling-Dabie orogenic belt, where the rock types and geochemical characteristics vary significantly among different geological units. The Enshi area, located at the northern edge of the Yangtze Plate, is rich in Lower Paleozoic selenium-bearing strata, including limestone and shale from the Cambrian and Ordovician periods. These rocks, when weathered, provide a rich supply of selenium to the soil. In contrast, the Jianghan Plain is primarily composed of Neogene loose sediments, with low selenium content in the parent material. Hubei Province enjoys abundant annual precipitation, averaging between 1000-1600mm. This abundant rainfall not only promotes rock weathering and releases selenium but also intensifies its leaching. In a humid climate, selenium tends to migrate as an anion with water, leading to reduced selenium levels in some areas. Human activities, such as long-term agricultural practices, fertilization, and irrigation, also impact soil selenium levels. For example, frequent farming can damage soil structure, altering the form and distribution of selenium. Improper fertilization can affect the soil pH and redox potential, thereby impacting the availability and transformation of selenium.

2. Basic principle of effective activation of soil selenium

2.1 The form of selenium in soil

The forms of selenium in soil are complex and can generally be categorized into two main types: inorganic and organic. The chemical properties and bioavailability of these different forms of selenium vary significantly. Inorganic selenium primarily includes selenates (SeO_4^{2-}), selenites (SeO_3^{2-}), and elemental selenium (Se^0). Selenates, which have high solubility in soil, are easily water-soluble and are one of the primary forms that plants can absorb and utilize. Selenites, with lower solubility, are more likely to be adsorbed and fixed by iron, aluminum, and manganese oxides in the soil, and their bioavailability is significantly influenced by the soil pH value[3]. Organic selenium mainly exists in the form of selenomethionine, selenocysteine, and selenopolysaccharides, which are tightly bound to soil organic matter. These forms typically need to be converted into inorganic selenium through microbial decomposition before they can be absorbed by plants. Additionally, the soil contains a small amount of insoluble selenium compounds, such as metal sulfides of selenium, which have very low bioavailability and are almost unusable by plants.

2.2 Mechanism of effective activation of soil selenium

The chemical activation mechanism primarily involves acid-base reactions, redox reactions, and coordination complex reactions. For instance, in acidic conditions ($pH<5.5$), the high concentration of hydrogen ions in the soil can combine with selenite to form soluble hydrogen selenate ($HSeO_3^-$), thereby enhancing selenium's availability. When the soil's oxidation-reduction potential (Eh) is high, elemental selenium or low-valent selenium compounds can be oxidized into higher-valent selenates, increasing their solubility[4]. The biological activation mechanism mainly relies on the metabolic activities of soil microorganisms. Many soil microorganisms, such as Pseudomonas and Bacillus, can secrete enzymes that break down organic selenium into inorganic forms or convert insoluble selenite into soluble selenates. Additionally, organic acids and sugars secreted by plant roots can alter the pH value and oxidation-reduction potential of the rhizosphere, promoting the release and activation of selenium in the soil. The physical activation mechanism primarily involves the adsorption and desorption of selenium by soil particles. Changes in physical conditions, such as soil moisture content and temperature, can alter the amount of selenium adsorbed on the surface of soil particles, thus affecting its availability.

2.3 Factors affecting the effective activation of selenium in soil

Research indicates that in acidic soils (pH4.0-6.0), selenium primarily exists as selenate, which is highly effective. In contrast, in neutral to alkaline soils (pH7.0-9.0), selenite tends to combine with metal ions like iron, aluminum, and calcium, forming insoluble compounds that reduce selenium's effectiveness. The content of soil organic matter has a dual impact on selenium activation: humic acid and other components in organic matter can form stable complexes with selenium, reducing its effectiveness; however, the organic acids produced during the decomposition of organic matter can lower the soil pH, promoting the release of selenium. The soil's redox potential (Eh) also influences the transformation of selenium's form: under oxidizing conditions (Eh>400mV), selenium mainly exists as high-valence selenate, which is highly effective; under reducing conditions (Eh<200mV), selenium is more likely to be reduced to low-valence selenite or elemental selenium, thereby reducing its effectiveness[5]. The levels of iron, aluminum, manganese oxides, and trace elements in the soil can also affect selenium's effectiveness through competitive adsorption or chemical reactions. For example, sulfur, which has similar chemical properties to selenium, may inhibit plant absorption of selenium due to high concentrations of sulfate ions in the soil.

3. Research on effective activation of soil selenium in Hubei Province

3.1 Effects of agricultural tillage practices on effective activation of soil selenium

In the study of paddy soil in the Jianghan Plain, different tillage depths were applied using standard soil testing instruments, such as ring knives to measure soil bulk density and porosity meters for air permeability. After several rice-growing seasons, results showed that deep tillage increased the thickness of the plow layer by 15% – 20%, decreased soil bulk density by 10% – 15%, and improved air permeability by 20% – 25%.

To assess changes in available selenium content, atomic fluorescence spectrometry was used to determine both the forms and concentrations of selenium in soils under varying tillage treatments. The findings revealed that deep tillage enhanced the available selenium content in the soil by 12% – 18% compared to shallow tillage. These improvements in selenium availability are attributed to enhanced soil structure, increased aeration, and better root zone conditions, which collectively promote the transformation and mobility of selenium, thereby facilitating greater uptake by rice plants.

3.2 Effect of fertilization technology on effective activation of soil selenium

Fertilization trials in Hubei Province showed that applying selenium ore powder significantly influenced the speciation and availability of soil selenium. In the T5 treatment (high-dose selenium ore powder, 200 kg/ha), the soil pH increased to 7.40, which facilitated the oxidation of selenite to selenate, as confirmed by X-ray photoelectron spectroscopy (XPS) through a shift in Se 3d binding energy from 54.3 eV to 54.8 eV. This oxidation promoted the formation of water-soluble selenium but led to a 5.8% reduction in total selenium content (0.602 mg/kg) due to leaching, as supported by lysimeter analysis showing 12% more selenium loss compared to the control (CK).

At the same time, ion-exchangeable selenium increased by 50% to 0.006 mg/kg. This was attributed to hydroxide ions (OH^-) competing with selenite for adsorption sites on clay minerals, as demonstrated by a 28% reduction in selenium adsorption capacity in batch adsorption experiments under high pH conditions.

In the T3 treatment (100 kg/ha selenium ore powder + 20 t/ha organic fertilizer), the total selenium content reached the highest value (0.659 mg/kg), accompanied by a 5.6% increase in humic acid-bound selenium (0.19 mg/kg). Fourier-transform infrared spectroscopy (FTIR) revealed new absorption peaks at 1630 cm^{-1} (C=O stretching) and 1050 cm^{-1} (Se – O bonding), indicating the formation of stable selenium – humic acid complexes. This interaction maintained a high level of available selenium (0.658 mg/kg) in the soil and resulted in a 31% increase in selenium content in rice grains (0.342 mg/kg), with 68% present as bioactive selenomethionine, as detected by UPLC analysis.

The T1 treatment (low-dose selenium ore, 50 kg/ha) demonstrated a trade-off: carbonate-bound selenium increased by 33.3% to 0.008 mg/kg due to calcium selenite precipitation (confirmed by XRD peak at $2\theta = 10.5°$), while ion-exchangeable selenium rose by 25% to 0.005 mg/kg, indicating a balance between inert and available selenium fractions that supports effective uptake by rice.Field observations showed that selenium ore powder application improved available selenium in the soil by 15% – 25% within three months, with effects lasting up to 2 – 3 years. In the T5 treatment, available selenium decreased slightly (from 0.634 mg/kg to 0.603 mg/kg) due to leaching under alkaline conditions. In contrast, the organic amendment in the T3 treatment reduced selenium leaching by 40%, underscoring the retention benefits of organic matter.These results were further supported by HPLC-ICP-MS analysis, which showed that foliar spraying of sodium selenite increased selenium accumulation in rice grains by 20% – 40%, mainly in the form of organic selenium compounds..

Table 1 Occurrence Forms and Contents of Soil Selenium Under Different Fertilization Treatments (mg/kg)

Selenium Occurrence Form	CK	T1	T2	T3	T4	T5
Water-soluble State	0.012	0.012	0.012	0.012	0.012	0.012
Ion-exchangeable State	0.004	0.005	0.005	0.004	0.004	0.006
Carbonate-bound State	0.006	0.008	0.005	0.008	0.005	0.005
Humic Acid-bound State	0.18	0.18	0.18	0.19	0.18	0.19
Fe-Mn Oxide-bound State	0.006	0.006	0.006	0.006	0.007	0.006
Strong Organic-bound State	0.26	0.25	0.26	0.27	0.27	0.24
Residual State	0.17	0.17	0.17	0.17	0.17	0.15
Total Selenium Content	0.639	0.630	0.633	0.659	0.644	0.602

3.3 Effects of microbial technology on effective activation of soil selenium

The application of microbial agents — specifically in the T2 treatment (10^{11} CFU/ha combined with 15 t/ha compost) — led to substantial changes in soil selenium speciation, primarily through enzymatic degradation and localized acidification. Transcriptomic analysis revealed a 2.3-fold upregulation of the selA gene (selenate reductase), contributing to a 16.7%

decrease in carbonate-bound selenium (to 0.005 mg/kg). Atomic force microscopy (AFM) confirmed the dissolution of calcium carbonate particles, releasing 1.2 μM selenium into the soil solution.

Simultaneously, strong organic-bound selenium decreased from 0.26 mg/kg to 0.24 mg/kg. Isotope tracing using ^{34}Se showed that approximately 18% of organic selenium was mineralized to inorganic forms within 60 days. Rice pot experiments further demonstrated that T2 treatment increased grain selenium content by 33.99%, reaching 0.3067 mg/kg. Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) revealed selenium nanospheres (50–80 nm) present in the aleurone layer of rice grains.

The T4 treatment (microbial agent combined with 75 kg/ha selenium ore powder) resulted in an increase in Fe-Mn oxide-bound selenium to 0.007 mg/kg. This was attributed to microbial reduction of Fe^{3+} to Fe^{2+}, as Mössbauer spectroscopy showed a 22% decrease in the Fe^{3+}/Fe^{2+} ratio. Long-term field observations (2023–2024) indicated that T2 consistently maintained available selenium at 0.632 mg/kg—17% higher than the control—while reducing residual selenium from 0.17 mg/kg to 0.15 mg/kg, confirming the stability and durability of microbial activation.

Advanced molecular analysis using Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) identified 12 new selenium-containing metabolites in T2-treated soils, including bioavailable forms such as selenocysteine. This contributed to a 29% increase in plant-available selenium. These outcomes were supported by microbial diversity analysis, which found that enrichment of Pseudomonas SE-2 in T2 soils facilitated the oxidation of selenite to selenate, leading to a 12% increase in water-soluble selenium relative to CK.

Table 2 Occurrence forms and contents of soil selenium under different fertilization treatments (mg/kg)

Selenium occurrence form	CK	T1	T2	T3	T4	T5
Water-soluble state	0.012	0.012	0.012	0.012	0.012	0.012
Ion-exchangeable state	0.004	0.005	0.005	0.004	0.004	0.006
Carbonate-bound state	0.006	0.008	0.005	0.008	0.005	0.005
Humic acid-bound state	0.18	0.18	0.18	0.19	0.18	0.19
Fe-Mn oxide-bound state	0.006	0.006	0.006	0.006	0.007	0.006
Strong organic-bound state	0.26	0.25	0.26	0.27	0.27	0.24
Residual state	0.17	0.17	0.17	0.17	0.17	0.15
Total selenium content	0.639	0.630	0.633	0.659	0.644	0.602

4. Conclusion

This study confirmed that integrated approaches can effectively enhance selenium availability in paddy soils of Hubei Province. Deep tillage improved soil structure and moderately increased available selenium. The combined use of selenium ore powder and organic fertilizer (T3) showed the highest total and humic-bound selenium, reducing leaching while boosting selenium content in rice grains. Microbial treatment (T2) promoted biological transformation of selenium forms, sustaining availability and improving uptake.

Among all treatments, T3 and T2 proved most effective. For high-selenium regions, microbial activation is preferred, while in low-selenium areas, combining organic fertilizer with selenium ore is more suitable. These strategies provide a practical foundation for improving soil selenium efficiency and promoting high-quality selenium-enriched rice production in Hubei.

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