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Effects of Returning Green Manure-Chinese Milk Vetch on the Availability and Transformation of Zinc in Purple Tidal Mud Soil under Rice Cultivation

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Abstract: This study aimed to investigate the impact of different levels of Chinese milk vetch (*Astragalus sinicus* L.) incorporation on the availability and transformation of zinc in purple tidal mud soil under rice cultivation. A two-year pot experiment was conducted, comprising seven treatments: a control group without fertilizer, a control group with Chinese milk vetch application, a control group with chemical fertilizer application, and four treatment groups with varying levels of Chinese milk vetch application following chemical fertilizer application. Results showed that Chinese milk vetch application increased the content of available zinc (DTPA-Zn) in purple tidal mud soil. Sole application of Chinese milk vetch ultimately enhanced the transfer factor of zinc in purple tidal mud soil and reduced the distribution index. However, applying Chinese milk vetch after chemical fertilizer application ultimately decreased the transfer factor of zinc and increased the distribution index. Furthermore, sole application of Chinese milk vetch facilitated the conversion of zinc in purple tidal mud soil into available forms, while applying it after chemical fertilizer application promoted the transformation of zinc into ineffective forms, with a greater conversion observed at higher levels of Chinese milk vetch application.

Keywords: Chinese milk vetch; purple tidal mud; zinc availability; zinc form transformation; rice cultivation

Citation: Yang, Z.; Rao, Z.; Li, H.; Zeng, X.; Xie, J. Effects of Returning Green Manure-Chinese Milk Vetch on the Availability and Transformation of Zinc in Purple Tidal Mud Soil under Rice Cultivation. *Agronomy* **2024**, *14*, 1126. https://doi.org/10.3390/agronomy14061126

Academic Editor: Domenico Ronga

Received: 16 April 2024
Revised: 22 May 2024
Accepted: 22 May 2024
Published: 24 May 2024

1. Introduction

Zinc is an essential trace nutrient for life [1]. Zinc deficiency affects approximately 17% of the global population [2,3], with Asia having a prevalence rate of 19% [4]. Rice (*Oryza sativa* L.), which is cultivated on approximately 155 million hectares of land worldwide, serves as a staple food for over 50% of the global population. China is the largest rice producer, accounting for 30% of the world's total production [5]. Micronutrient deficiencies frequently occur in rice [6–8], and there is a significant disparity between the actual average zinc concentration in rice and the target range for human health (40–50 mg/kg) [9–12]. Increasing the zinc content in rice grains would contribute to improving consumers' zinc intake [13]. Agronomic biofortification, aimed at enhancing the zinc content in rice grains, is considered a direct and effective approach to addressing human zinc deficiency [14].

The bioavailability of soil zinc is not solely determined by its total content but also by the forms in which it exists within the soil. The transformation of zinc forms is influenced by various factors, including the quantity and types of exogenous zinc inputs, soil physico-chemical properties, and soil composition, which includes mineral components (such as calcium carbonate and iron oxides), texture, pH value, moisture, and organic matter [15–17]. The bioavailability of zinc in calcareous soils is somewhat limited, and calcareous soils account for approximately 30% of the world's arable land [18]. In China, as much as 51% of cultivated land is deficient in available zinc [17]. Purple tidal mud soil, which is mainly found in the northwest region of Dongting Lake in the Changde, Yueyang, and Yiyang areas, develops on calcareous lacustrine sediments. In Hunan Province, there are a total of 163.94 thousand hectares of such soil, accounting for 5.9% of the rice soil types. It is a typical calcareous paddy soil with insufficient available zinc [19].

In agricultural production, the application of green manure is regarded as a beneficial management practice that can enhance the sustainability of cropping systems. It achieves this by reducing soil erosion, improving soil physical properties, and increasing soil organic matter and fertility levels [20]. However, there is limited research on the effects of green manure application on soil zinc availability and subsequent crop uptake.

Green manure, as one of the cleanest and most efficient organic fertilizer sources, can improve soil structure and increases soil nutrient content when incorporated into the soil through plowing. Furthermore, it enhances the activation capacity of soil zinc, thereby promoting a higher zinc content in crops [21]. Studies have shown that incorporating different green manure crops, such as red clover, sunflower, safflower, and sorghum, into low-zinc calcareous soils can increase the availability of soil zinc. This process also enhances organic carbon and amino acid concentrations in the rhizosphere, facilitating the accumulation of zinc during subsequent wheat cultivation [22,23].

Regular incorporation of legume cover crops, such as Sesbania aculeata, Crotalaria juncea, or Vigna unguiculata, before transplanting rice not only improves soil physico-chemical properties but also enhances the availability of certain micronutrient cations. This is particularly beneficial for overcoming limitations in the productivity improvement of Basmati rice. The incorporation of green manure residues into the soil can exhibit different efficiencies through interactions with soil components, thereby affecting stability. The rate of dissociation in such soil and this efficiency ultimately influence the effective pool of zinc in soil solution [24].

Incorporating green manure provides a significant amount of readily decomposable organic matter, which improves the status of soil organic matter and zinc [25]. This leads to the recycling of zinc back into the soil, thereby increasing its availability. Singh et al. [26] have indicated that growing green manure crops can increase the soil and rice zinc content, and there is a significant positive correlation between the two. Grüter et al. [27] found that legume green manure increased the soil's available zinc content through biological nitrogen fixation. Yang et al. [28], through field experiments, have demonstrated that intercropping with green manure not only increases the content of available zinc in the soil but also enhances soil alkaline nitrogen, available phosphorus, and quick-acting potassium content.

Incorporating green manure into the soil enhances the effectiveness of DTPA-extractable zinc, primarily due to the uptake and utilization of zinc by green manure crops from the subsoil [29]. The ability of green manure itself to take up zinc is crucial for activating soil zinc and increasing zinc content in subsequent crops [30]. Soil zinc serves as the fundamental source of zinc uptake and utilization by plants, and its effectiveness is influenced by various factors.

Studies have found that the decomposition and release of endogenous zinc from organic materials, following their incorporation into the soil, can facilitate zinc activation through complexation reactions with their own components or degradation products. This, in turn, affects the effectiveness of soil zinc [31]. He et al. [32] observed that growing green manure increased soil organic matter content, decreased soil pH, and increased the availability of zinc, thereby enhancing its effectiveness. Habiby et al. [22] demonstrated that incorporating green manure into the soil increased the availability of zinc. The soluble organic carbon produced from the decomposition of green manure residues promoted the uptake of zinc by wheat roots, particularly its transfer to grains.

Research results [33] also indicated that incorporating spring oilseed rape significantly increased the availability of zinc in the soil. Crop rotation involving legume green manure can activate soil zinc and increase zinc content in subsequent crops [21]. Intercropping Chinese milk vetch with rice has been shown to increase the availability of zinc in the soil [34].

However, studies on the incorporation of Chinese milk vetch have primarily focused on its effects on crop yield, soil fertility, soil microorganisms, and enzyme activity [35,36]. Further research is needed to examine the impact of incorporating different amounts of Chinese milk vetch under rice cultivation on the forms of zinc in alkaline paddy soils with purple tidal mud soil. It is also important to investigate whether this incorporation increases the availability of zinc in the purple tidal mud soil.

Therefore, conducting research on the transformation process of different forms of zinc in alkaline paddy soils with purple tidal mud soil and exploring methods to enhance the activity and effectiveness of zinc is of great significance. This research aims to maintain nutrient balance and maximize the role of zinc in agricultural systems.

This study focuses on the alkaline paddy soils in the northwest region of Dongting Lake, specifically on the purple tidal mud soil found in Nan County, Hunan Province. The study aims to investigate the effects of incorporating different amounts of Chinese milk vetch under rice cultivation on the transformation and effectiveness of zinc in the purple tidal mud soil. A two-year consecutive pot experiment was conducted to achieve this objective.

This research aims to uncover the driving factors and mechanisms behind zinc transformation in the purple tidal mud soil when Chinese milk vetch is incorporated and subsequently used as green manure. The findings of this study will provide valuable insights into improving rice yield and grain zinc content in purple tidal mud soil through agricultural practices. Ultimately, the goal is to meet the food demands of the population and enhance zinc nutrition.

2. Materials and Methods

2.1. Experimental Soil

The pot experiment of this study was conducted in the net house at the Hunan Soil and Fertilizer Institute. The soil used in the experiment was representative of calcareous paddy soil, commonly known as "purple tidal mud soil", which is a water-retentive paddy soil found in Hunan Province. The experimental soil was collected from a rice field located in Lotus Village, Nanzhou Town, Nan County, Yiyang City, Hunan Province (112°20′17″ E, 29°20′11″ N).

Table 1 presents the main physicochemical properties and nutrient status of the experimental soil.

Table 1. Basic conditions and properties of experimental soils.

Soil Depth	pH	Available Nitrogen mg/kg	Available Phosphorus mg/kg	Available Potassium mg/kg	Total Nitrogen g/kg	Total Phosphorus g/kg	Total Potassium g/kg	Oganic Matter g/kg
0–20 cm	7.97	106.37	14.30	95.86	0.85	0.67	19.40	10.53
Soil depth	**DTPA-Zn mg/kg**	**Exchangeable zinc mg/kg**	**Loosely bound organic zinc mg/kg**	**Carbonate-bound zinc mg/kg**	**Manganese-oxide-bound zinc mg/kg**	**Tightly bound organic zinc mg/kg**	**Residual zinc in minerals mg/kg**	**T-Zn mg/kg**
0–20 cm	0.68	0.03	0.30	0.27	0.21	0.10	94.07	94.98

2.2. Experimental Crops

The basic information regarding the experimental crops is presented in Table 2.

Table 2. Experimental crops.

Year	Crops	Variety	Zinc Content (Dry Basis, mg/kg)	Moisture Content (%)
2020	Green manure	Xiangzi-1	75.4	91.03
	Early rice	Zhuliangyou 39	40.9	91.47
	Late rice	Y-liangyou 911	39.5	88.19
2021	Green manure	Xiangzi-1	38.1	89.71
	Early rice	Lingliangyou 268	75.0	88.44
	Late rice	Shenyou 9586	70.9	85.66

2.3. Experimental Design

The project utilized a pot experiment with seven treatments, with each treatment being replicated three times. The basic information for each treatment is provided in Table 3. The timing of each farming operation is outlined in Table 4.

Table 3. Treatments.

Treatment	Rice Season	Fertilizer					Chinese Milk Vetch	
		N (kg/hm^2)		P_2O_5 (kg/hm^2)	K_2O (kg/hm^2)			
		Basal Fertilizer	Topdressing	Basal Fertilizer	Basal Fertilizer	Topdressing	(t/hm^2)	g/pot
CK	Early rice	0	0	0	0	0	0.00	0
	Late rice	0	0	0	0	0	0.00	0
1.5Z	Early rice	0	0	0	0	0	2.25	93.75
	Late rice	0	0	0	0	0	0.00	0
H	Early rice	150 × 70%	150 × 30%	75	75 × 50%	75 × 50%	0.00	0
	Late rice	180 × 70%	180 × 30%	45	90 × 50%	90 × 50%	0.00	0
H+Z	Early rice	150 × 70%	150 × 30%	75	75 × 50%	75 × 50%	1.50	62.50
	Late rice	180 × 70%	180 × 30%	45	90 × 50%	90 × 50%	0.00	0
H+1.5Z	Early rice	150 × 70%	150 × 30%	75	75 × 50%	75 × 50%	2.25	93.75
	Late rice	180 × 70%	180 × 30%	45	90 × 50%	90 × 50%	0.00	0
H+2Z	Early rice	150 × 70%	150 × 30%	75	75 × 50%	75 × 50%	3.00	125.00
	Late rice	180 × 70%	180 × 30%	45	90 × 50%	90 × 50%	0.00	0
H+2.5Z	Early rice	150 × 70%	150 × 30%	75	75 × 50%	75 × 50%	3.75	156.25
	Late rice	180 × 70%	180 × 30%	45	90 × 50%	90 × 50%	0.00	0

Table 4. Farming operations schedule.

Farming Operations	Time	
	First Year	Second Year
Potting the container with soil	9-Oct-19	-
Sowing Chinese milk vetch	21-Oct-19	18-Nov-20
Incorporating Chinese milk vetch	31-Mar-20	8-Apr-21
Applying basal fertilizer for early rice	15-Apr-20	23-Apr-21
Transplanting early rice seedlings	15-Apr-20	23-Apr-21
Applying topdressing fertilizer for early rice	22-Apr-20	30-Apr-21
Harvesting early rice	17-Jul-20	27-Jul-21
Applying basal fertilizer for late rice	17-Jul-20	27-Jul-21
Transplanting late rice seedlings	20-Jul-20	27-Jul-21
Applying topdressing fertilizer for late rice	24-Jul-20	3-Aug-21
Harvesting late rice	12-Nov-20	27-Oct-21

Oct: October, Nov: November, Mar: March, Apr: April, Jul: July, Aug: August.

Each pot was filled with 10.0 kg of air-dried soil that had passed through a 2 mm sieve. No fertilizer was applied after sowing the Chinese milk vetch. The seeding rates for the 1.5Z, H+Z, H+1.5Z, H+2Z, and H+2.5Z treatments were all set at 30 kg/hm^2, calculated based on the pot area of 0.07 m^2 (with an inner diameter of 30 cm). This corresponds to a seed amount of approximately 0.21 g, which was approximately 60 seeds.

Fresh grass was incorporated into the pots 15 days prior to transplanting the early rice. It was moistened with shallow water to facilitate decomposition. Before incorporating the Chinese milk vetch, all the Chinese milk vetch in the pots was harvested. This was necessary because the quantity of Chinese milk vetch in the original pots was insufficient for the intended amount required by the experimental design for incorporation. To overcome this, additional Chinese milk vetch of the same variety was harvested from a different location. The harvested Chinese milk vetch was then cut into approximately two-centimeter-long segments, thoroughly mixed, and added to the pots according to the designated quantities specified in the experimental design. The Chinese milk vetch segments were then mixed with the soil in the pots to ensure a uniform distribution.

The specific fertilizers used for nitrogen, phosphorus, and potassium were urea (46% N), calcium superphosphate (12% P_2O_5), and potassium chloride (60% K_2O), respectively.

2.4. Sample Collection and Analysis

Soil samples were collected at different time points: 1 April, 7 April, 30 April, 29 June, and 12 November 2020 (corresponding to 1, 7, 30, 90, and 225 days after the incorporation of Chinese milk vetch), as well as on 15 April, 8 May, 7 July, and 27 October 2021 (corresponding to 7, 30, 90, and 202 days after the incorporation of Chinese milk vetch). The collected samples were air-dried for analysis.

Several parameters were assessed in the soil samples, including soil pH, exchangeable zinc, carbonate-bound zinc, loosely bound organic zinc, tightly bound organic zinc, manganese-oxide-bound zinc, and residual zinc in minerals. Additionally, the DTPA-Zn content was also analyzed as part of the assessment.

2.5. Analytical Methods

Here are the methods used to analyze the different forms of zinc in the soil:

Soil pH: The soil pH was determined by immersing the soil in water and measuring it using a potentiometric method.

DTPA-Zn: A 15 g portion of soil passing through a 20-mesh sieve was weighed and mixed with 30 mL of DTPA solution. The mixture was then immersed at 25 °C for 2 h. After that, it was filtered and analyzed using the atomic absorption spectrophotometer.

Total zinc (T-Zn): A 0.15 g portion of soil passing through a 100-mesh sieve was weighed and treated with a mixture of acids (HCl-HNO_3-$HClO_4$-HF) for digestion on a hot plate. The resulting solution was then measured using atomic absorption spectrophotometry.

The reference methods used for these measurements were given by Bao et al. [37].

The classification of zinc forms in soil followed the modified Tisser continuous extraction method as revised by Wei et al. [38] and Liu et al. [39]. The experimental operating temperature was 25 °C, and the liquid-to-soil ratio was 10:1. The specific extraction methods for each form are as follows:

Exchangeable form (Ex-Zn): Weigh 2 g of soil passing through a 20-mesh sieve and extract with 1 mol/L Mg $(NO_3)_2$ (pH 7.0) by shaking for 2 h.

Loosely bound organic form (Wbo-Zn) [39]: Extract the soil with 0.1 mol/L $Na_4P_2O_7$ (pH 9.5) by shaking for 2 h. Centrifuge the mixture at 4000 rpm for 10 min and collect the supernatant.

Carbonate-bound form (Carb-Zn): Extract the soil with 0.1 mol/L NaOAc-HOAc (pH 5.0) by shaking for 5 h. Centrifuge the mixture at 4000 rpm for 10 min and collect the supernatant.

Manganese-oxide-bound form (OxMn-Zn): Extract the soil with 0.1 mol/L $NH_2OH{\cdot}HCl$ hydroxylamine hydrochloride (pH 7.0) by shaking for 0.5 h. Centrifuge the mixture at 4000 rpm for 10 min and collect the supernatant.

Tightly bound organic form (Sbo-Zn) [39]: Solution A: 30% H_2O_2 at pH 2.0. Solution B: 1 mol/L Mg $(NO_3)_2$ (magnesium nitrate, pH 7.0). Dry the soil in Solution A at 85 °C until nearly dry, repeat once, and then soak it in Solution B at 25 °C for 2 h. Centrifuge the mixture at 4000 rpm for 10 min and collect the supernatant.

Mineral residual form (Min-Zn): Calculate the mineral residual form as the difference between total zinc and the sum of exchangeable, loosely bound organic, carbonate-bound, manganese-oxide-bound, and tightly bound organic forms.

2.6. Calculation Methods

2.6.1. The Transfer Factor (T_F) of Zinc

The transfer factor (T_F) of zinc in soil was utilized to assess the interconversion between different forms of zinc in the purple tidal mud soil [40]. The T_F indicates the conversion of zinc from ineffective forms to effective forms in the purple tidal mud soil, with an increase in T_F suggesting this transformation, while a decrease in T_F suggests the conversion to ineffective forms. The calculation formula for T_F is as follows:

$$T_F\ (\%) = (F_1 + F_2)/(\text{T-Zn}) \times 100$$

In the formula, F_1 and F_2 represent the contents of Ex-Zn and Wbo-Zn (mg/kg) in the purple tidal mud soil, respectively [40].

2.6.2. The Distribution Index (D_I) of Zinc

The distribution index (D_I) of zinc in soil was also utilized to assess the interconversion between different forms of zinc in the purple tidal mud soil [40,41]. When the D_I exceeds 90%, it signifies that the majority of zinc in the purple tidal mud soil is distributed in the Min-Zn fraction. An increase in D_I indicates the transformation of zinc from effective forms to ineffective forms, while a decrease in D_I suggests the conversion to effective forms. The calculation formula for D_I is as follows:

$$D_I\ (\%) = (1^2F_1 + 2^2F_2 + 3^2F_3 + 4^2F_4 + 5^2F_5 + 6^2F_6)/(6^2\text{T-Zn}) \times 100$$

In the formula, F_1, F_2, F_3, F_4, F_5, and F_6 represent the contents of Ex-Zn, Wbo-Zn, Carb-Zn, OxMn-Zn, Sbo-Zn, and Min-Zn (mg/kg) in the purple tidal mud soil, respectively [41].

2.7. Data Processing

The collected data were analyzed using SPSS 20.0 software. Variance analysis and correlation analysis were performed. Single-factor analysis of variance was utilized to examine the differences between groups, and multiple comparisons of means were conducted using Duncan's new multiple range test. The significance level was set at $p = 5\%$. For correlation analysis, the Pearson correlation coefficient was used to calculate the correlation coefficients between variables.

3. Results

3.1. Proportions of Different Forms of Zinc in Purple Tidal Mud Soil to the Total Zinc Content

In purple tidal mud soil, zinc is primarily present in the form of Min-Zn, accounting for 95.49% to 97.95% of the total zinc content, with a mean value of 96.54%. The proportions of the other five zinc forms to the total zinc content are relatively small. The relative magnitudes of the zinc forms, from highest to lowest, are as follows: Min-Zn (95.49% to 97.95%, with a mean of 96.54%) > Sbo-Zn (0.67% to 1.33%, with a mean of 1.02%) > Ex-Zn (0.62% to 1.16%, with a mean of 0.95%) > Carb-Zn (0.00% to 1.82%, with a mean of 0.82%) > Wbo-Zn (0.03% to 0.77%, with a mean of 0.41%) > OxMn-Zn (0.00% to 0.62%, with a mean of 0.27%) (Table 5).

Table 5. Proportions of different forms of zinc in purple tidal mud soil to the total zinc content (%).

Zinc Forms	Treatment	Time								
		1/2020	7/2020	30/2020	90/2020	225/2020	7/2021	30/2021	90/2021	202/2021
Ex-Zn	CK	1.12	1.13	1.11	0.88	0.92	1.10	1.08	0.92	0.88
	1.5Z	1.05	1.08	0.95	0.90	0.87	1.09	0.95	0.96	0.87
	H	1.10	1.16	0.90	0.90	0.87	1.11	0.95	0.88	0.85
	H+Z	1.07	1.07	0.92	0.91	0.88	1.09	0.97	0.89	0.85
	H+1.5Z	0.99	1.04	0.87	0.91	0.89	0.97	0.93	0.85	0.73
	H+2Z	0.96	1.11	0.86	0.89	0.92	0.97	0.92	0.88	0.76
	H+2.5Z	1.06	1.06	0.88	0.89	0.86	0.96	0.91	0.82	0.62
Wbo-Zn	CK	0.68	0.77	0.62	0.27	0.41	0.21	0.17	0.16	0.41
	1.5Z	0.58	0.53	0.36	0.42	0.48	0.18	0.14	0.23	0.52
	H	0.60	0.49	0.45	0.41	0.47	0.19	0.05	0.32	0.54
	H+Z	0.55	0.51	0.48	0.43	0.50	0.23	0.12	0.40	0.47
	H+1.5Z	0.54	0.48	0.41	0.46	0.50	0.29	0.24	0.57	0.44
	H+2Z	0.64	0.52	0.44	0.47	0.49	0.20	0.03	0.52	0.47
	H+2.5Z	0.71	0.53	0.41	0.53	0.51	0.12	0.10	0.48	0.45
Carb-Zn	CK	1.17	1.09	1.14	0.08	1.20	0.00	1.61	0.00	0.98
	1.5Z	1.08	0.96	0.00	0.25	1.13	0.00	0.41	0.44	1.03
	H	0.40	0.98	0.73	1.28	1.21	0.00	0.00	1.82	1.03
	H+Z	1.01	0.90	1.01	1.53	1.09	0.00	0.02	1.32	0.98
	H+1.5Z	0.93	1.03	0.82	0.84	1.26	1.20	1.47	0.95	0.58
	H+2Z	0.94	0.97	1.01	0.96	1.28	1.35	0.00	0.97	0.63
	H+2.5Z	1.03	1.02	0.98	0.97	1.12	0.00	0.00	0.71	0.49
OxMn-Zn	CK	0.45	0.33	0.31	0.00	0.33	0.11	0.31	0.07	0.33
	1.5Z	0.33	0.27	0.00	0.00	0.37	0.11	0.15	0.11	0.43
	H	0.00	0.00	0.25	0.00	0.39	0.12	0.08	0.26	0.43
	H+Z	0.62	0.20	0.00	0.19	0.39	0.12	0.07	0.31	0.43
	H+1.5Z	0.30	0.34	0.29	0.48	0.39	0.32	0.33	0.34	0.41
	H+2Z	0.28	0.39	0.26	0.38	0.40	0.25	0.06	0.38	0.40
	H+2.5Z	0.39	0.31	0.28	0.41	0.54	0.10	0.07	0.43	0.31
Sbo-Zn	CK	1.10	0.81	0.84	0.82	1.33	1.23	1.32	1.11	1.22
	1.5Z	0.92	0.80	0.81	0.84	1.20	1.20	1.15	1.18	1.17
	H	0.97	0.89	0.77	0.78	1.21	1.19	1.17	1.08	1.20
	H+Z	0.95	0.87	0.88	0.81	1.26	1.26	1.15	1.31	1.21
	H+1.5Z	0.85	0.76	0.77	0.72	1.21	1.23	1.20	0.99	1.02
	H+2Z	0.72	0.67	0.79	0.74	1.22	1.22	1.09	1.11	1.16
	H+2.5Z	0.75	0.72	0.84	0.82	1.21	1.25	1.09	1.04	1.00
Min-Zn	CK	95.49	95.87	95.98	97.95	95.80	97.34	95.52	97.75	96.18
	1.5Z	96.05	96.37	97.88	97.59	95.94	97.41	97.20	97.09	95.99
	H	96.93	96.48	96.90	96.63	95.85	97.39	97.75	95.64	95.95
	H+Z	95.81	96.45	96.72	96.14	95.89	97.30	97.67	95.76	96.05
	H+1.5Z	96.40	96.35	96.85	96.59	95.75	96.00	95.83	96.30	96.83
	H+2Z	96.47	96.34	96.64	96.56	95.69	96.01	97.90	96.15	96.57
	H+2.5Z	96.06	96.36	96.60	96.39	95.75	97.56	97.84	96.52	97.13

3.2. Effects of Returning Chinese Milk Vetch on DTPA-Zn Content in Purple Tidal Mud Soil

The effect of returning Chinese milk vetch during four crops of rice cultivation over two years on the DTPA-Zn content in the soil varied between 0.26 and 0.73 mg/kg. Among the treatments, the 1.5Z treatment showed the highest fluctuation, while the CK treatment exhibited the lowest fluctuation.

During the nine samplings conducted, only during the late rice maturity stage in 2021 did the 1.5Z (0.69 mg/kg) and H+2.5Z (0.73 mg/kg) treatments have a higher DTPA-Zn content than the initial value (0.68 mg/kg). During the rice maturity stages of the four crops, except for the early rice maturity stage in 2021, where the H+Z treatment had the highest content, the H+2.5Z treatment had the highest content in the other three crops.

During the early rice maturity stage in 2020, the H treatment had the lowest DTPA-Zn content, and, in the other three crops, the CK treatment followed by the H treatment had the lowest content.

In each year, except for the CK treatment, the soil DTPA-Zn content of all fertilization treatments was the highest during the late rice harvest stage. Throughout the four crops of rice planting, the soil DTPA-Zn content showed both increases and decreases.

During the late rice maturity stage in 2021, the CK treatment had a lower content than the first day after incorporating Chinese milk vetch, while the other treatments had a higher content. Except for the CK treatment in 2020, the DTPA-Zn content of each treatment was highest during the late rice maturity stage in both years.

By the end of the experiment, the order of treatments from highest to lowest DTPA-Zn content was H+2.5Z > 1.5Z > H+1.5Z > H+Z > H+2Z > H > CK. Compared to the H treatment, the H+Z, H+1.5Z, H+2Z, and H+2.5Z treatments increased the DTPA-Zn content by 11.94%, 20.75%, 1.89%, and 37.74%, respectively. Compared to the CK treatment, the 1.5Z treatment increased by 94.37%. In other words, incorporating Chinese milk vetch alone or incorporating it after chemical fertilization both increased the soil DTPA-Zn content (Figure 1).

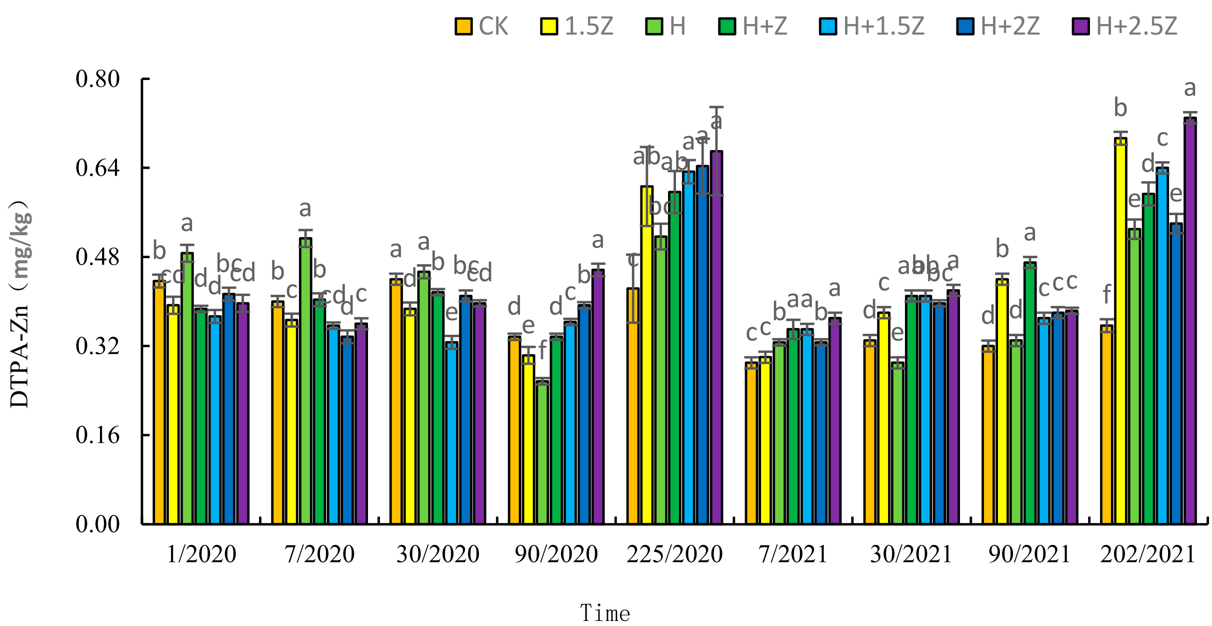


Figure 1. Effects of returning Chinese milk vetch on DTPA-Zn content in purple tidal mud soil. Different lowercase letters in the figure indicate significant differences among different treatments at the 0.05 level.

3.3. *Effects of Returning Chinese Milk Vetch on Soil pH in Purple Tidal Mud Soil*

The effects of returning Chinese milk vetch during four crops of rice cultivation over two years resulted in fluctuations in soil pH ranging from 7.77 to 8.38. However, except for the H+2.5Z treatment during the late rice maturity stage in 2020, which had a significantly lower pH compared to the other treatments at that time, there were no significant differences among the treatments during the other sampling periods.

In the final sampling, the treatments that involved incorporating Chinese milk vetch after chemical fertilization showed a decrease in pH compared to the H treatment. Additionally, the 1.5Z treatment showed a decrease in pH compared to the CK treatment. These findings indicate that incorporating Chinese milk vetch can slightly lower the pH of purple tidal mud soil (Figure 2).

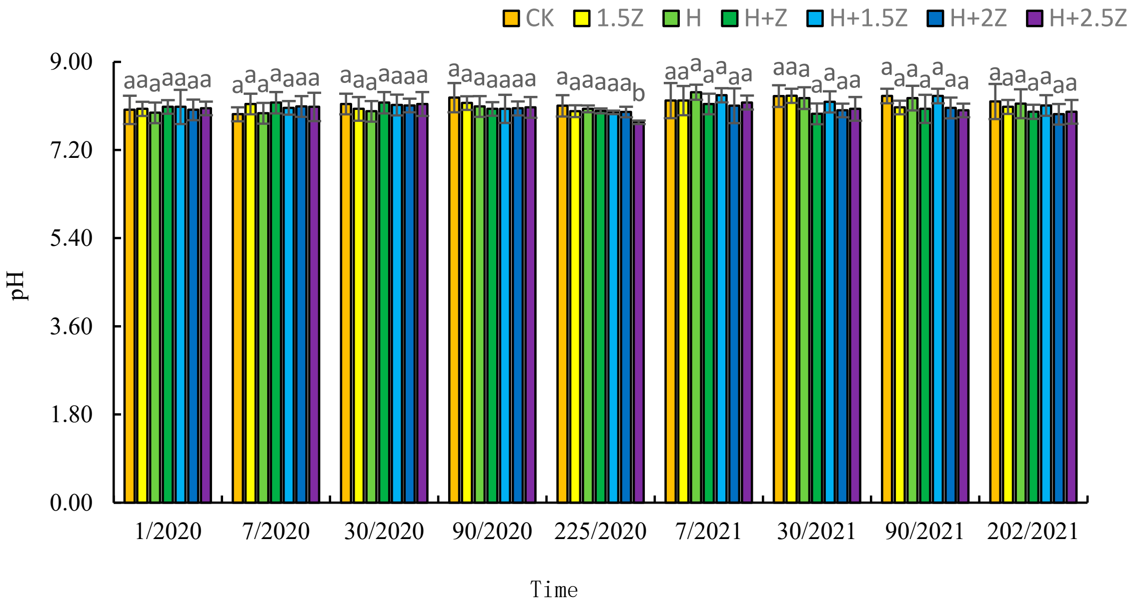


Figure 2. Effects of returning Chinese milk vetch on soil pH in purple tidal mud soil. Different lowercase letters in the figure indicate significant differences among different treatments at the 0.05 level.

3.4. Effects of Returning Chinese Milk Vetch on the Content of Different Forms of Zinc in Purple Tidal Mud Soil

According to Table 6, all treatments resulted in an increase in the content of Ex-Zn and Sbo-Zn in purple tidal mud soil at different sampling periods after watering. By the end of the experiment, they also increased the content of Wbo-Zn, Carb-Zn, and OxMn-Zn. The content of Min-Zn in purple tidal mud soil during the early rice growth stage in 2020 generally increased, except for the CK treatment in the first sampling. However, the Min-Zn content fluctuated during other sampling periods. By the end of the experiment, the CK, H+Z, and H+2Z treatments led to a decrease in the Min-Zn content in purple tidal mud soil. Among the different forms of zinc, the largest increase was observed in Ex-Zn content. The lowest value of 0.71 mg/kg was observed in the H+2.5Z treatment during the late rice maturity stage in 2021, which was 23.31 times the initial value. These results indicate that the treatments had varying effects on the distribution of different zinc forms in purple tidal mud soil, with an overall increase in Ex-Zn and Sbo-Zn content and a decrease in Min-Zn content by the end of the experiment.

During the experiment, the incorporation of different amounts of Chinese milk vetch had varying degrees of impact on the content of different forms of zinc in the soil. The extent of the impact also varied at different sampling periods. By the end of the experiment, compared to the H treatment, the H+Z, H+1.5Z, H+2Z, and H+2.5Z treatments resulted in a decrease in Ex-Zn content in purple tidal mud soil by 0.79%, 4.80%, 12.00%, and 15.19% respectively; Wbo-Zn decreased by 14.36%, 9.38%, 15.00%, and 4.37%; Carb-Zn decreased by 6.86%, 38.56%, 40.85%, and 45.42%; Sbo-Zn content decreased by 0.85%, 6.47%, 5.63%, and 4.50%; OxMn-Zn content in purple tidal mud soil decreased by 7.93% and 15.07% in H+2Z and H+2.5Z treatments, respectively, but increased by 7.14% in the H+1.5Z treatment; Min-Zn content in purple tidal mud soil decreased by 1.30% and 1.69% in H+Z and H+2Z treatments, respectively, while it increased by 11.67% and 16.76% in H+1.5Z and H+2.5Z treatments, respectively. By the end of the experiment, compared to the CK treatment, the 1.5Z treatment increased the content of Ex-Zn, Wbo-Zn, Carb-Zn, OxMn-Zn, and Min-Zn in purple tidal mud soil, while decreasing the content of Sbo-Zn. These results indicate that incorporating different amounts of Chinese milk vetch had varying effects on the content of different forms of zinc in purple tidal mud soil, with some treatments leading to increases or decreases depending on the specific form of zinc and treatment comparison.

Table 6. Changes in zinc content in different forms in purple tidal mud soil (mg/kg).

Zinc Forms	Treatment	Time								
		1/2020	7/2020	30/2020	90/2020	225/2020	7/2021	30/2021	90/2021	202/2021
Ex-Zn	CK	1.10 a	1.13 a	1.11 a	0.94 b	0.87 ab	1.04 ab	0.98 a	0.91 ab	0.85 a
	1.5Z	1.08 a	1.11 a	0.99 b	0.95 b	0.86 ab	1.03 b	0.96 ab	0.93 a	0.86 a
	H	1.11 a	1.15 a	0.97 bc	0.96 ab	0.85 b	1.08 a	0.93 abc	0.88 bc	0.83 ab
	H+Z	1.09 a	1.12 a	0.94 cd	0.93 b	0.84 b	1.02 b	0.94 abc	0.87 bc	0.83 ab
	H+1.5Z	1.08 a	1.15 a	0.95 bcd	1.00 a	0.87 ab	0.95 c	0.93 bc	0.86 c	0.79 b
	H+2Z	1.09 a	1.18 a	0.92 d	0.97 ab	0.90 a	0.96 c	0.90 c	0.86 c	0.73 c
	H+2.5Z	1.08 a	1.12 a	0.95 bcd	0.95 b	0.84 b	0.93 c	0.91 bc	0.85 c	0.71 c
Wbo-Zn	CK	0.67 b	0.77 a	0.62 a	0.28 d	0.39 d	0.20 c	0.15 b	0.16 f	0.39 d
	1.5Z	0.59 cd	0.54 bc	0.38 d	0.45 c	0.47 bc	0.17 d	0.14 c	0.22 e	0.51 a
	H	0.60 c	0.49 d	0.49 b	0.44 c	0.46 c	0.18 d	0.05 f	0.32 d	0.53 a
	H+Z	0.56 d	0.53 c	0.49 b	0.44 c	0.48 abc	0.22 b	0.12 d	0.39 c	0.46 c
	H+1.5Z	0.58 cd	0.53 bc	0.45 c	0.51 b	0.48 ab	0.29 a	0.24 a	0.58 a	0.48 b
	H+2Z	0.72 a	0.55 bc	0.48 b	0.51 b	0.48 ab	0.20 c	0.03 g	0.51 b	0.45 c
	H+2.5Z	0.72 a	0.56 b	0.45 c	0.57 a	0.50 a	0.11 e	0.10 e	0.50 b	0.51 a
Carb-Zn	CK	1.14 a	1.09 b	1.15 a	0.08 f	1.14 cd	0.00 c	1.47 a	0.00 f	0.94 b
	1.5Z	1.10 ab	0.99 d	0.00 f	0.26 e	1.11 de	0.00 c	0.42 b	0.42 e	1.03 a
	H	0.41 d	0.96 de	0.79 e	1.37 b	1.18 bc	0.00 c	0.00 c	1.81 a	1.02 a
	H+Z	1.03 c	0.94 e	1.04 c	1.57 a	1.05 e	0.00 c	0.02 c	1.28 b	0.95 b
	H+1.5Z	1.02 c	1.14 a	0.90 d	0.92 d	1.24 ab	1.19 b	1.47 a	0.97 c	0.63 c
	H+2Z	1.06 bc	1.04 c	1.09 b	1.04 c	1.25 a	1.33 a	0.00 c	0.95 c	0.60 c
	H+2.5Z	1.05 bc	1.09 b	1.06 bc	1.03 c	1.10 de	0.00 c	0.00 c	0.73 d	0.56 d
OxMn-Zn	CK	0.44 b	0.33 c	0.31 ab	0.00 e	0.32 d	0.11 c	0.28 b	0.07 g	0.32 e
	1.5Z	0.34 d	0.27 d	0.00 d	0.00 e	0.36 c	0.11 c	0.15 c	0.10 f	0.42 b
	H	0.00 f	0.00 f	0.27 c	0.00 e	0.38 bc	0.11 c	0.08 d	0.26 e	0.42 b
	H+Z	0.63 a	0.21 e	0.00 d	0.20 d	0.37 c	0.11 c	0.07 e	0.30 d	0.42 b
	H+1.5Z	0.32 de	0.37 b	0.32 a	0.52 a	0.38 bc	0.31 a	0.33 a	0.35 c	0.45 a
	H+2Z	0.32 e	0.42 a	0.28 c	0.42 c	0.39 b	0.25 b	0.06 f	0.37 b	0.39 c
	H+2.5Z	0.40 c	0.33 c	0.30 b	0.43 b	0.53 a	0.10 d	0.07 e	0.45 a	0.36 d
Sbo-Zn	CK	1.07 a	0.81 b	0.84 b	0.87 ab	1.27 a	1.16 ab	1.20 a	1.10 bc	1.17 abc
	1.5Z	0.95 bc	0.82 b	0.85 b	0.89 a	1.18 b	1.14 b	1.16 ab	1.15 b	1.16 abc
	H	0.98 b	0.88 a	0.83 b	0.84 bc	1.18 b	1.16 ab	1.15 abc	1.07 c	1.18 a
	H+Z	0.97 b	0.91 a	0.90 a	0.83 bcd	1.21 b	1.17 ab	1.12 bc	1.28 a	1.17 ab
	H+1.5Z	0.93 c	0.83 b	0.85 b	0.79 d	1.18 b	1.21 a	1.20 a	1.00 d	1.11 c
	H+2Z	0.82 d	0.71 d	0.85 b	0.81 cd	1.19 b	1.20 a	1.06 d	1.08 c	1.12 bc
	H+2.5Z	0.76 e	0.77 c	0.90 a	0.87 ab	1.18 b	1.21 a	1.09 cd	1.07 c	1.13 abc
Min-Zn	CK	93.30 b	95.72 c	96.43 c	104.03 ab	90.82 a	91.94 a	87.24 b	96.69 abc	92.09 b
	1.5Z	98.66 b	99.49 b	102.02 ab	103.64 ab	94.23 a	92.30 a	98.08 a	94.20 bc	95.34 b
	H	97.51 b	95.43 c	104.50 a	103.09 ab	93.28 a	94.74 a	95.77 a	95.01 bc	94.43 b
	H+Z	97.91 b	100.80 b	99.32 bc	98.95 b	92.05 a	91.05 a	94.85 a	93.10 c	93.20 b
	H+1.5Z	105.01 a	106.22 a	106.24 a	106.02 a	93.57 a	94.70 a	95.83 a	97.89 ab	105.45 a
	H+2Z	109.42 a	102.44 ab	104.38 a	104.90 ab	93.69 a	94.99 a	95.51 a	94.09 bc	92.83 b
	H+2.5Z	97.62 b	102.43 ab	103.67 ab	103.15 ab	93.51 a	94.60 a	98.11 a	99.55 a	110.25 a

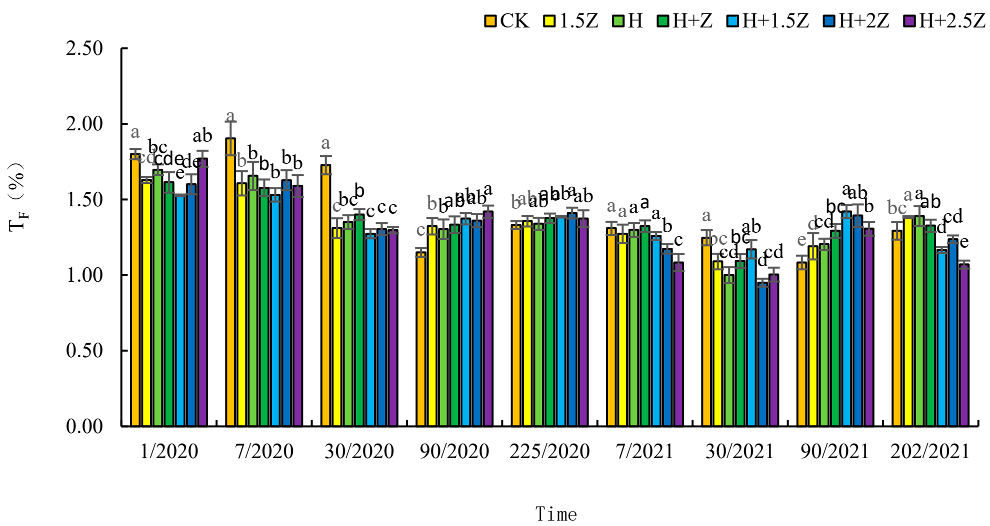
Different lowercase letters indicate significant differences among different treatments at the 0.05 level.

Incorporating Chinese milk vetch alone can increase the content of Ex-Zn, Wbo-Zn, Carb-Zn, OxMn-Zn, and Min-Zn in purple tidal mud soil, while decreasing the content of Sbo-Zn. However, when Chinese milk vetch is incorporated after chemical fertilization, it leads to a decrease in the content of Ex-Zn, Wbo-Zn, Carb-Zn, and Sbo-Zn in purple tidal mud soil. The extent of the decrease in Ex-Zn and Carb-Zn content in purple tidal mud soil is greater with an increase in the amount of plowed Chinese milk vetch. Incorporating 3.00 t/hm^2 and 3.75 t/hm^2 of Chinese milk vetch after chemical fertilization decreases the content of OxMn-Zn in purple tidal mud soil. On the other hand, incorporating 2.25 t/hm^2 and 3.75 t/hm^2 of Chinese milk vetch after chemical fertilization increases the content of Min-Zn in purple tidal mud soil. However, incorporating 1.50 t/hm^2 and 3.00 t/hm^2 of Chinese milk vetch after chemical fertilization decreases the content of Min-Zn in purple tidal mud soil. These findings suggest that the effects of incorporating Chinese milk vetch on the different forms of zinc in purple tidal mud soil depend on whether it is applied alone or after chemical fertilization, as well as the specific amount of Chinese milk vetch incorporated.

3.5. Effects of Returning Chinese Milk Vetch on Zn Transfer Factor (T_F) and Distribution Index (D_I) in Purple Tidal Mud Soil

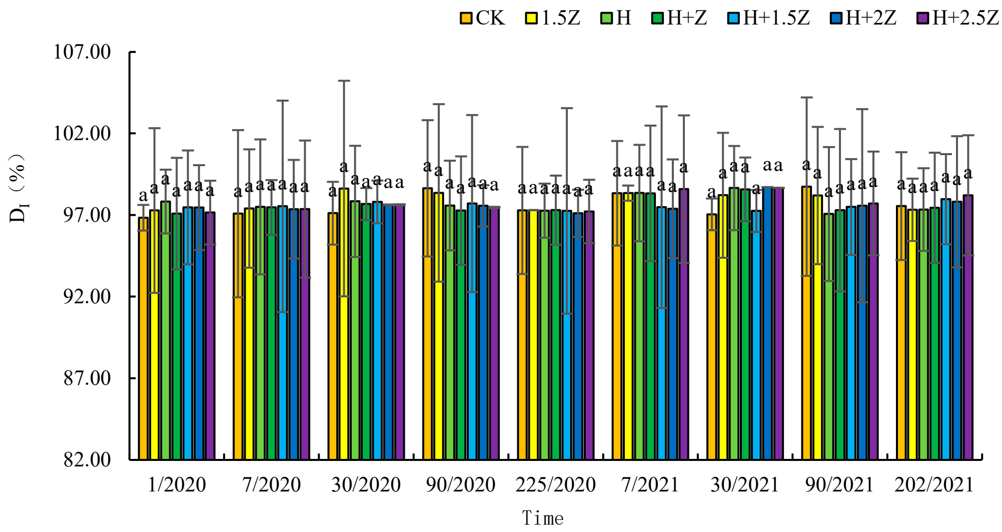
As shown in Figure 3a, the transfer factor (T_F) of Zn in purple tidal mud soil ranged from 0.95% to 1.90%. Significant differences in T_F were observed among the treatments in the nine sampling periods. The H+1.5Z treatment showed the smallest fluctuation over time, while the CK treatment exhibited the largest fluctuation. Generally, there was a decreasing trend in T_F values over time. In the last sampling compared to the first sampling, the following percentage decreases in T_F were observed: CK: 28.2%, 1.5Z: 15.1%, H: 18.1%, H+Z: 17.8%, H+1.5Z: 23.6%, H+2Z: 22.7%, H+2.5Z: 39.5%. These results indicate a tendency toward the conversion of Zn in purple tidal mud soil to less available forms over time. In the last sampling, the 1.5Z treatment had a higher T_F compared to the CK treatment, while the H+Z, H+1.5Z, H+2Z, and H+2.5Z treatments had a lower T_F compared to the H treatment. This suggests that incorporating Chinese milk vetch alone increased the T_F of Zn in purple tidal mud soil, while incorporating Chinese milk vetch after chemical fertilization decreased the T_F of Zn. The average T_F of Zn in purple tidal mud soil over the entire study period was highest in the CK treatment and lowest in the H+2.5Z treatment. Among the four treatments where Chinese milk vetch was plowed after chemical fertilization, the T_F decreased with an increase in the amount of Chinese milk vetch added.

As shown in Figure 3b, the distribution index (D_I) of Zn in purple tidal mud soil ranged from 96.84% to 98.74%. This indicates that Zn was mainly distributed in the Min-Zn fraction of the soil. There were no significant differences in D_I among the treatments in the nine sampling periods. The H+1.5Z treatment exhibited the least fluctuation over time, while the CK treatment showed the highest fluctuation. In the last sampling compared to the first sampling, all treatments, except for the H treatment, showed an increase in D_I. This suggests that, with prolonged time, there is an enhanced trend of converting Zn in purple tidal mud soil to less available forms. In the last sampling, the 1.5Z treatment had a lower D_I compared to the CK treatment, while the H+Z, H+1.5Z, H+2Z, and H+2.5Z treatments had a higher D_I compared to the H treatment. This implies that incorporating Chinese milk vetch alone decreased the D_I of Zn in purple tidal mud soil while incorporating Chinese milk vetch after chemical fertilization increased the D_I of Zn. The average D_I of Zn in purple tidal mud soil over the entire study period was highest in the 1.5Z treatment and lowest in the H+1.5Z treatment.



(**a**)

Figure 3. *Cont.*



(**b**)

Figure 3. (**a**) Effects of returning Chinese milk vetch on the Zn transfer factor (T_F) in purple tidal mud soil. (**b**) Effects of returning Chinese milk vetch on the distribution index (D_I) in purple tidal mud soil. Different lowercase letters in the figure indicate significant differences among different treatments at the 0.05 level.

3.6. Relationship between the Effectiveness and Transformation of Zn in Purple Tidal Mud Soil and pH as Well as Different Zn Forms

The relationships between the effectiveness and transformation of Zn in purple tidal mud soil and pH, as well as different Zn forms, vary among the different treatments. However, based on the results of all treatments, the following correlations were observed:

DTPA-Zn shows a highly significant positive correlation with OxMn-Zn and Sbo-Zn content, a significant positive correlation with Wbo-Zn and 5Zn content, and a highly significant negative correlation with pH and Ex-Zn content. It also exhibits a significant negative correlation with the distribution index (D_I).

The Zn transfer factor (T_F) shows a highly significant positive correlation with Ex-Zn, Wbo-Zn, Carb-Zn, OxMn-Zn, 2Zn, 3Zn, 4Zn, and 5Zn content, a highly significant negative correlation with Sbo-Zn content, and a significant negative correlation with pH.

The distribution index (D_I) shows a significant positive correlation with pH and a highly significant negative correlation with Wbo-Zn, Carb-Zn, OxMn-Zn, 2Zn, 3Zn, 4Zn, and 5Zn content.

Additionally, the soil Zn transfer factor (T_F) and distribution index (D_I) show a highly significant negative correlation (Table 7).

Table 7. Correlation between the effectiveness and transformation of Zn in purple tidal mud soil with pH and various forms of Zn components.

Treatment	Indicator	pH	Ex-Zn	Wbo-Zn	Carb-Zn	OxMn-Zn	Sbo-Zn	Min-Zn	2Zn	3Zn	4Zn	5Zn	D_I	T_F
CK	DTPA-Zn	−0.725 *	0.361	0.831 **	0.667 *	0.754 *	−0.295	−0.001	0.743 *	0.801 **	0.803 **	0.758 *	−0.739 *	0.743 *
	T_F	−0.897 **	0.817 **	0.944 **	0.545	0.718 *	−0.528	−0.034	0.985 **	0.807 **	0.802 **	0.713 *	−0.729 *	
	D_I	0.638 *	−0.423	−0.658 *	−0.959 **	−0.951 **	0.008	0.540	−0.636 *	−0.976 **	−0.984 **	−0.995 **		
1.5Z	DTPA-Zn	−0.515	−0.713 *	0.342	0.628	0.737 *	0.518	−0.409	−0.029	0.476	0.545	0.644 *	−0.612	0.053
	T_F	−0.467	0.539	0.877 **	0.629 *	0.521	−0.560	0.218	0.974 **	0.811 **	0.770 **	0.648 *	−0.683 *	
	D_I	0.418	0.014	−0.711 *	−0.980 **	−0.958 **	−0.129	0.265	−0.590	−0.954 **	−0.980 **	−0.996 **		
H	DTPA-Zn	−0.644 *	0.041	0.715 *	0.090	0.418	0.055	−0.271	0.597	0.278	0.353	0.377	−0.431	0.681 *
	T_F	−0.718 *	0.612	0.807 **	0.058	−0.258	−0.411	0.026	0.970 **	0.372	0.285	0.207	−0.336	
	D_I	0.376	0.363	−0.649 *	−0.919 **	−0.452	0.114	0.115	−0.331	−0.944 **	−0.976 **	−0.987 **		
H+Z	DTPA-Zn	−0.493	−0.701 *	0.229	0.170	0.370	0.590	−0.478	−0.204	0.079	0.165	0.307	−0.284	−0.109
	T_F	0.635	0.616	0.838 **	0.420	0.511	−0.462	0.522	0.976 **	0.636 *	0.680 *	0.615	−0.657 *	
	D_I	−0.095	0.069	−0.904 **	−0.908 **	−0.681 *	0.215	−0.310	−0.655 *	−0.942 **	−0.987 **	−0.995 **		
H+1.5Z	DTPA-Zn	−0.421	−0.632 *	0.054	−0.194	0.347	0.512	−0.232	−0.352	−0.413	−0.343	−0.000	0.050	−0.310
	T_F	−0.306	0.694 *	0.734 *	0.036	−0.047	−0.566	0.257	0.922 **	0.653 *	0.684 *	0.289	−0.242	
	D_I	−0.049	−0.176	0.292	−0.913 **	0.463	−0.457	0.749 *	0.089	−0.765 *	−0.686 *	−0.938 **		

Table 7. *Cont.*

Treatment	Indicator	pH	Ex-Zn	Wbo-Zn	Carb-Zn	OxMn-Zn	Sbo-Zn	Min-Zn	2Zn	3Zn	4Zn	5Zn	D_I	T_F
H+2Z	DTPA-Zn	−0.778 **	−0.508	0.163	0.004	0.266	0.433	−0.370	−0.117	−0.051	0.000	0.124	−0.185	−0.000
	T_F	0.157	0.622	0.914 **	0.612	0.753 *	−0.581	0.549	0.966 **	0.849 **	0.870 **	0.767 *	−0.744 *	
	D_I	−0.215	−0.327	−0.671 *	−0.949 **	−0.776 **	0.082	−0.180	−0.648 *	−0.930 **	−0.945 **	−0.990 **		
H+2.5Z	DTPA-Zn	−0.735 *	−0.747 *	0.173	0.094	0.403	0.469	0.291	−0.214	−0.020	0.059	0.183	−0.020	−0.274
	T_F	−0.059	0.707 *	0.819 **	0.795 **	0.581	−0.804 **	−0.117	0.971 **	0.893 **	0.865 **	0.798 **	−0.891 **	
	D_I	0.351	−0.412	−0.886 **	−0.962 **	−0.841 **	0.627	0.041	−0.886 **	−0.970 **	−0.979 **	−0.973 **		
DTPA-Zn		−0.583**	−0.485 **	0.316 *	0.184	0.424 **	0.334 **	−0.085	0.014	0.148	0.220	0.308 *	−0.265 *	0.044
T_F		−0.299*	0.659 **	0.833 **	0.434 **	0.343 **	−0.522 **	0.083	0.954 **	0.694 **	0.669 **	0.579 **	−0.650 **	
D_I		0.262*	−0.138	−0.677 **	−0.930 **	−0.684 **	0.105	0.134	−0.587 **	−0.944 **	−0.958 **	−0.979 **		

* $p < 0.05$, ** $p < 0.01$; 2Zn = Ex-Zn + Wbo-Zn, 3Zn = Ex-Zn + Wbo-Zn + Carb-Zn, 4Zn = Ex-Zn + Wbo-Zn + Carb-Zn + OxMn-Zn, 5Zn = Ex-Zn + Wbo-Zn + Carb-Zn + OxMn-Zn + Sbo-Zn.

4. Discussion

4.1. Effects of Chinese Milk Vetch on Available Zinc in Purple Tidal Mud Soil

The determination of available zinc in soil is commonly performed by extracting zinc using diethylenetriaminepentaacetic acid (DTPA) and 0.1 mol/L HCl solution, which extract zinc from alkaline and acidic soils, respectively. The extracted amount represents the content of available zinc in the soil, which can reflect the soil's zinc-supplying capacity [42]. Furthermore, studies have found a close relationship between the content of available zinc in soil and different forms of zinc components. Alvarez and Gonzalez [43] pointed out that the content of exchangeable zinc and carbonate-bound zinc is most closely related to the bioavailability of zinc. Research conducted by Ding [44] found an important relationship between the distribution of zinc forms and the actual zinc-supplying capacity of the soil after zinc fertilizer application. Different forms of zinc also exhibit differences in bioavailability, with the bioavailability of exchangeable zinc, loosely bound organic zinc, carbonate-bound zinc, manganese-oxide-bound zinc, and tightly bound organic zinc decreasing in that order. When the DTPA-Zn content in the soil is the same, the differences in the content of different forms of zinc can result in different actual zinc-supplying capacities of the soil. Exchangeable zinc contributes the most to the DTPA-Zn content, and the higher the bioavailability of zinc forms in the soil, the greater their contribution to the DTPA-Zn content. When the soil zinc content is low, zinc forms with lower bioavailability contribute more to the DTPA-Zn content. Organic amendments, such as the addition of straw and other organic materials, can promote the transformation of zinc forms in the soil, increase the contribution of forms with higher bioavailability to DTPA-Zn, and reduce the contribution of forms with lower bioavailability, although it may not significantly increase the content of DTPA-Zn in the soil [44].

There is a mutual transformation and equilibrium relationship among different forms of zinc in soil, which is crucial for the bioavailability of zinc in soil and is influenced by its chemical forms. Numerous studies [42–48] have shown that loosely bound organic zinc has a persistent zinc-supplying capacity and contributes significantly to DTPA-Zn. There is a highly significant positive correlation between loosely bound organic zinc and DTPA-Zn in soil. Research by Yang et al. [49] also found that organically bound zinc in soil has a higher bioavailability, with loosely bound organic zinc contributing much more to active zinc than tightly bound organic zinc. Therefore, increasing the content of available zinc in the soil and enhancing the proportion of loosely bound organic zinc are of great significance for improving the zinc-supplying capacity. Wang et al. [50] found that there is no necessary correlation between the content of available zinc and total zinc in soil, and that the organic matter content in soil plays an important role in the content of available zinc. In alkaline soils, carbonate-bound zinc serves as an important source of available zinc. Research by Chen et al. [31] found that organic materials returning to the soil can release endogenous zinc through their own decomposition, and the complexation reaction between organic components or degradation products and zinc can activate zinc, thereby affecting the bioavailability of zinc in soil.

According to the results of this study, the incorporation of Chinese milk vetch significantly affects the content of available zinc (DTPA-Zn) in purple tidal mud soil. Compared to the unfertilized control (CK), the treatment with only Chinese milk vetch incorporation

(1.5Z) increased the DTPA-Zn content by 94.37%. Compared to the treatment with fertilizer application only (H), the addition of fertilizer along with different ratios of Chinese milk vetch incorporation (H+Z, H+1.5Z, H+2Z, and H+2.5Z) significantly increased the DTPA-Zn content. Among them, the H+2.5Z treatment showed the highest increase, reaching 37.74%. Over the course of two years, all treatments exhibited the highest DTPA-Zn content during the mature stage of late rice (except for the CK treatment in 2020). This indicates that the incorporation of Chinese milk vetch can significantly enhance the content of available zinc in purple tidal mud soil.

Based on the above results, it would be beneficial to further investigate and compare the effects of different organic amendment measures on the content of available zinc in purple tidal mud soil. This will help to optimize and improve methods to enhance the zinc-supplying capacity of purple tidal mud soil. These studies will contribute to a better understanding of the relationship between the bioavailability and chemical forms of zinc in purple tidal mud soil, providing a scientific basis for zinc management in purple tidal mud soil.

4.2. Effects of Chinese Milk Vetch on the Content of Different Forms of Zinc in Purple Tidal Mud Soil

A study by Yang et al. [51] found that zinc exists in various forms in soil, and its transformation is influenced by reactions such as dissolution–precipitation, adsorption–desorption, and complexation–activation. These transformation processes determine the migration behavior and bioavailability of zinc in soil. Through sequential extraction method, soil zinc can be divided into exchangeable forms, carbonate-bound forms, oxide-bound forms, organically bound forms, and residual forms. Among them, exchangeable zinc and organically bound zinc exhibit higher reactivity and are readily absorbed by plants. Carbonate-bound zinc represents potential available zinc, which can be transformed into plant-accessible forms under certain conditions. On the other hand, oxide-bound zinc and residual forms are difficult for plants to absorb and utilize [52]. The application of exogenous zinc can influence the content and transformation processes of different forms of zinc in soil.

Research [53] revealed that the addition of fresh organic materials can alter the physicochemical properties and metal complexation capacity of soil, thereby influencing the transformation of zinc forms in the soil. After the application of organic materials, soluble organic compounds rich in zinc-complexing functional groups are generated, forming soluble organic zinc complexes that contribute to the improvement of zinc availability and mobility in the soil. The study also found that only incorporating Chinese milk vetch increased the content of exchangeable zinc, loosely bound organic zinc, carbonate-bound zinc, manganese-oxide-bound zinc, and mineral residual zinc in purple tidal mud soil while reducing the content of tightly bound organic zinc. Incorporating Chinese milk vetch alone also increased the transfer factor of zinc in purple tidal mud soil and decreased the distribution index of zinc, indicating that incorporating Chinese milk vetch alone helps to promote the transformation of zinc into bioavailable forms in purple tidal mud soil. However, when Chinese milk vetch was incorporated after fertilizer application, it resulted in a decrease in the content of exchangeable zinc, loosely bound organic zinc, carbonate-bound zinc, and tightly bound organic zinc in purple tidal mud soil. The content of exchangeable zinc and carbonate-bound zinc decreased more significantly with an increase in the amount of Chinese milk vetch incorporated. Incorporating Chinese milk vetch at rates of 3.00 t/hm^2 and 3.75 t/hm^2 after fertilizer application reduced the content of manganese-oxide-bound zinc in purple tidal mud soil. Under the treatment of fertilizer application with Chinese milk vetch incorporation at rates of 2.25 t/hm^2 and 3.75 t/hm^2, the content of mineral residual zinc in purple tidal mud soil increased, while it decreased under the treatment of Chinese milk vetch incorporation at rates of 1.50 t/hm^2 and 3.00 t/hm^2. Incorporating Chinese milk vetch after fertilizer application resulted in a decrease in the transfer factor of zinc and an increase in the distribution index of zinc in purple tidal mud soil in the final stage, indicating that the addition of organic materials can alter the properties of soil and the transformation of zinc, thereby affecting its availability and mobility. Soluble organic compounds in organic materials can form complexes with zinc, increasing its solubility and mobility. Incorporating Chinese milk vetch can increase the content of exchangeable zinc, loosely bound organic zinc, carbonate-bound zinc, manganese-oxide-bound zinc, and mineral residual zinc in the soil while reducing the content of tightly bound organic zinc. This treatment helps to facilitate the transformation of zinc into more available forms. However, incorporating Chinese milk vetch after fertilizer application decreases the content of exchangeable zinc, loosely bound organic zinc, carbonate-bound zinc, and tightly bound organic zinc, particularly significantly reducing exchangeable zinc and carbonate-bound zinc. In some treatments, incorporating Chinese milk vetch also increases the content of mineral residual zinc. Furthermore, incorporating Chinese milk vetch after fertilizer application reduces the transfer factor of zinc and increases the distribution index of zinc. This study also found that the average transfer factor of zinc in purple tidal mud soil for the four treatments with Chinese milk vetch incorporation after fertilizer application decreased with an increase in the amounts of Chinese milk vetch. This indicates that incorporating Chinese milk vetch after fertilizer application enhances the conversion of soil zinc into less effective forms as the amount of Chinese milk vetch incorporated increases. Looking at the changes in the transfer factor of zinc over time for each treatment, there was an overall decreasing trend, suggesting an increasing trend of the conversion of soil zinc into less effective forms with prolonged time. The distribution index of zinc for each treatment, compared to the first sampling, increased for all treatments except for the treatment with fertilizer application only, indicating an increasing trend of the conversion of soil zinc into less effective forms with prolonged time. Xiang et al. [54] also demonstrated that, over time, the forms of zinc in soil can undergo transformation, with the most bioavailable forms converting into more stable or less effective forms. The transformation of forms in alkaline soils tends to be faster than in acidic or neutral soils, which is consistent with the findings of this study.

In general, the addition of organic materials and incorporation of Chinese milk vetch can impact the transformation and migration behavior of zinc in purple tidal mud soil. These findings are significant for understanding the behavior of zinc in purple tidal mud soil and the uptake of zinc by plants. However, further research is needed to determine the specific effects based on specific treatment methods.

4.3. Effects of Rice Cultivation on the Content of Different Forms of Zinc in Purple Tidal Mud Soil

The research conducted by Wei et al. [55] revealed that rice cultivation has a certain impact on the content of different forms of zinc in soil. They found that, during the rice growth process, the content of available zinc in the soil followed the order of EXC-Zn (exchangeable zinc) > OM-Zn (organically bound zinc) > R_2O_3-Zn (oxide-bound zinc). Zinc absorbed by rice accounted for approximately 97% of the zinc supplied by the soil. Most of the applied zinc was transformed into various forms of zinc in the soil, with the distribution order being RES-Zn (residual zinc) > CA-Zn (carbonate-bound zinc) > R_2O_3-Zn > OM-Zn > EXC-Zn. Additionally, the transformation of zinc was influenced by the soil's acidity, alkalinity, and basic properties. The study results also showed that rice cultivation promoted the conversion of zinc in the soil into the residual form, thereby reducing the effectiveness of soil zinc and applied water-soluble zinc. This transformation process is primarily influenced by the microbial decomposition of soil organic matter and the respiration and secretion of rice roots, and it is closely related to soil properties. The results of this study indicate that zinc in purple tidal mud soil primarily exists in the form of mineral residues, with a relatively lower content of other forms of zinc, which is consistent with the findings of the previous study by Wei et al. [55].

Based on these findings, further exploration can be conducted to better understand the influence of rice cultivation on the content of different forms of zinc in purple tidal mud soil. For example, the impact of rice root exudates on the transformation of zinc forms in purple tidal mud soil can be investigated, as well as the regulatory role of soil microbial activity in zinc form conversion. Additionally, comparative studies can be conducted to examine the differences in zinc form transformation under different soil types and environmental conditions during rice cultivation, revealing their inter-relationships and mechanisms. These studies will contribute to a deeper understanding of the complexity of rice–soil zinc interactions and provide a scientific basis for optimizing rice cultivation management.

5. Conclusions

Based on the results, it is important to note that this study was conducted under pot-based experimental conditions, which may introduce certain limitations. However, despite this limitation, the study successfully researched the effects of incorporating different amounts of Chinese milk vetch on zinc transformation and effectiveness in purple tidal mud soil under rice cultivation. The research was conducted in the alkaline paddy soils of Nan County, Hunan Province, specifically focusing on the purple tidal mud soil in the northwest region of Dongting Lake. A two-year consecutive pot experiment was conducted to examine the driving factors and mechanisms behind zinc transformation when Chinese milk vetch is used as green manure. The findings of this study will provide insights into improving rice yield and grain zinc content in purple tidal mud soil, with the ultimate goal of meeting food demand and enhancing zinc nutrition.

The findings revealed that incorporating Chinese milk vetch alone promoted the conversion of zinc into more available forms in purple tidal mud soil. However, when Chinese milk vetch was incorporated after chemical fertilization, it facilitated the transformation of zinc into less available forms, with a more pronounced effect observed at higher amounts of Chinese milk vetch. The predominant form of zinc in purple tidal mud soil was identified as mineral residue zinc, while the other five forms accounted for relatively minor proportions of the total zinc content. These findings provide important insights into the mechanisms underlying zinc transformation and suggest potential strategies for optimizing zinc availability in purple tidal mud soil during rice cultivation. It is important to consider these results within the context of pot-based experiments, and further validation is needed under field conditions to affirm the applicability of these findings in practical agricultural production.

In conclusion, while this study was conducted under pot-based experimental conditions, it contributes significant findings regarding the effects of Chinese milk vetch incorporation on zinc transformation in purple tidal mud soil. Further research is warranted to validate these results in field trials and explore their implications for improving rice yield and grain zinc content in practical agricultural settings.

Author Contributions: Conceptualization, Z.Y. and J.X.; methodology, Z.R.; validation, Z.R. and H.L.; formal analysis, Z.Y.; investigation, Z.R. and X.Z.; data curation, X.Z.; writing—original draft preparation, Z.Y.; writing—review and editing, Z.Y. and J.X.; visualization, Z.Y.; supervision, Z.Y.; funding acquisition, Z.Y. and Z.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Joint Funds of the National Natural Science Foundation of China, grant number U21A20294, and Hunan Provincial Natural Science Foundation General Project of China, grant number 2019JJ40168.

Data Availability Statement: The data supporting this study's findings are available from the corresponding author upon reasonable request.

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

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