

Article

Persistence of Hg-Contaminated Soil Stabilization in Typical Areas of Dehua County, Fujian Province, China

Rui Wang¹, Nan Chen^{2,*}, Guannan Liu¹ , Jianhua Ding¹, Ming Chen¹ and Jiawen Zhang¹

¹ Ministry of Natural Resources Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China

² Environmental Development Centre of Ministry of Ecology and Environment, Beijing 100029, China

* Correspondence: chennan@edcmep.org.cn

Abstract: The in-situ stabilization remediation of Hg-contaminated soil in Qianyang, Dehua County, Fujian Province, was studied through the pre-experiments (stabilization orthogonal experiment and pot experiment) and field plot experiments for two consecutive years. The pre-experiments results showed that the main factors of the stabilization were the initial concentration of Hg in the soil and the amount of amendment added, followed by the amendment type, while the aging time had less effect. When the initial concentration of Hg in the soil was less than $10 \text{ mg}\cdot\text{kg}^{-1}$ and the amendment (modified biochar with modified attapulgite) added ratio was 0.2–0.4%, indicating optimized stabilization effect. After one-time application of 6750 and 11,250 $\text{kg}\cdot\text{hm}^{-2}$ amendment in low ($1.38 \text{ mg}\cdot\text{kg}^{-1}$), medium ($2.46 \text{ mg}\cdot\text{kg}^{-1}$), and high ($8.52 \text{ mg}\cdot\text{kg}^{-1}$) Hg-contaminated soils, it could accelerate the transformation of Hg from exchangeable to residual and oxidizable Hg, enhance the activities of catalase, urease, and invertase in the soil. After one year of remediation, the case of adding 6750 $\text{kg}\cdot\text{hm}^{-2}$ amendment showed a significant stabilization effect. Compared to the control group, the available Hg content in the soil and Hg content in the water spinach reduced to 52.1–62.0% and 58.2–66.6%, respectively. When the application amount was increased to 11,250 $\text{kg}\cdot\text{hm}^{-2}$, the reduction rates were 43.2–46.0% and 58.2–62.0%, respectively. After two years of remediation, the stabilization effect was weakened, but the available Hg content in the soil and the water spinach was still significantly lower than that of the control, indicating that the persistence of the stabilization was good. For the soil contaminated slightly by Hg, the Hg content in the water spinach within two years was lower than the limit value of the Chinese standard ($0.01 \text{ mg}\cdot\text{kg}^{-1}$). Although the Hg content in the water spinach for the soil contaminated highly by Hg was higher than the limit value, it could reduce to 67.3%, indicating an acceptable stabilization effect on heavily contaminated soil.

Keywords: soil; mercury; amendment; stabilization; persistence



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1. Introduction

As one of the most toxic pollutants in nature, Hg exhibits high neurotoxicity and teratogenicity, a significant accumulation effect, and bio-genetic toxicity. In fact, Hg has been listed as one of the pollutants under strict control by the United States Environmental Protection Agency [1–5]. When it is transferred into the human body via the food chain, Hg and its compounds can have a biomagnification effect, inhibiting the activity of enzymes, interfering with cellular metabolism, and endangering human health [6,7].

The emission sources of Hg can be divided into natural and anthropogenic sources [8,9]. However, natural emissions of Hg are only a small fraction compared with those related to human activities [3]. Anthropogenic sources of Hg include mining, fossil fuel combustion, and various industrial processes. Among them, gold mining activities still represent a widely recognized source of soil Hg. The gold extraction process based on amalgam metallurgy requires a large amount of Hg [10,11]. There are “three small” gold extraction methods commonly used to carry out secondary gold extraction from tailing slag in China,

namely the small-mix Hg mill, small cyanide tank, and small ball mill methods. Since only 50–60% of the Hg can be recovered, the rest of the Hg residue in the slag is directly dumped beside the river channel and in the plains or valleys, aggravating the soil Hg contamination [12,13].

In-situ chemical stabilization is one of the most common remediation techniques for Hg-contaminated soil [14–18]. In this process, amendments (e.g., clay minerals, phosphates, metal oxides, biochar, and nanomaterials) are added to soil to induce the adsorption, complexation, precipitation, and ion exchange of Hg. This method can reduce the mobility and bioavailability of Hg to achieve the purpose of soil remediation [19–25]. However, the surface activity and adsorption performance of natural materials have some limitations. Recently, they are often modified or formulated with multiple materials for better stabilization [26–29]. Additionally, most of the current studies on the stabilization remediation of Hg-contaminated soils are indoor cultivation or pot experiments. However, the results of pot experiments need to be verified by field tests due to the complexity of the soil properties and the dependence of crops on the growing environment [30]. To date, there have been relatively few studies on the field effects of in-situ stabilization remediation on Hg-contaminated soil, especially in terms of the long-term effects. It has been demonstrated that after in-situ stabilization remediation the soil is exposed to the reactivation of heavy metals during long-term crop planting. As a result, heavy metals can migrate into the crops and cause potential harm [31,32].

Based on the principle of stabilization remediation, this study took biochar and attapulgite as the basic amendments and conducted an orthogonal experiment and pot experiment to determine the suitable conditions for stabilization remediation of typical Hg-contaminated soil in Dehua County, Fujian Province. Then, the field plot experiment was conducted to verify the in-situ stabilization persistence of typical Hg-contaminated soil after the one-time application of amendment for two consecutive years. This study is expected to provide a scientific basis for ensuring the quality and safety of the local farmland.

2. Materials and Methods

2.1. The Study Area

Dehua is in the central part of Fujian, northwest of Quanzhou, and it has a high terrain and complex topography. The annual average temperature is 18.0 °C, and the annual average rainfall is 1600–2100 mm. The strata are relatively well-developed, and the gold deposits are distributed on a large scale. Previous studies show that the Hg contamination of the soil due to gold mining is serious in Dehua and is typical of the Qianyang area. A greenhouse was built as the fieldwork site here. The geographical location and sampling sites are shown in Figure 1.

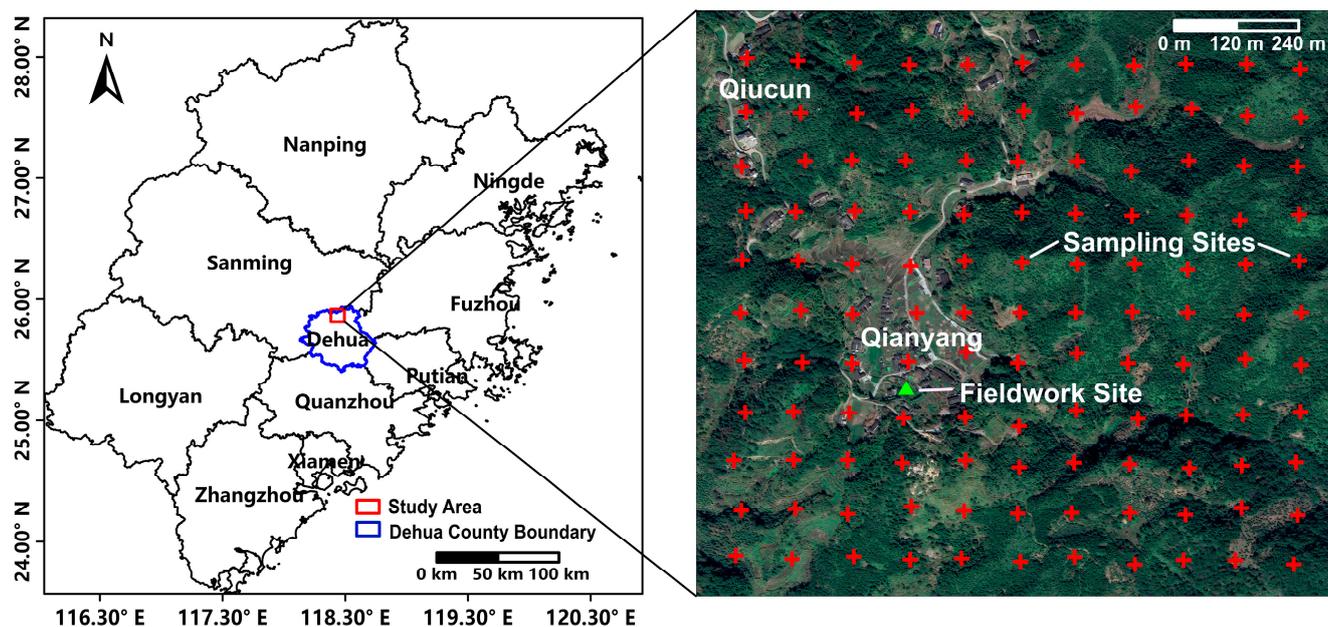


Figure 1. Geographical location and the fieldwork site in the study area.

2.2. Chemicals

Biochar was purchased from Yangzhong Huafeng Agricultural Biological Engineering Co., Ltd. (Yangzhong, China). Attapulgitite was purchased from Xuyi Sinoma Attapulgitite Clay Co., Ltd. (Huaian, China). Experimental acids (HCl, HNO₃, HF, and HClO₄), H₂O₂, KMnO₄, NaClO, and the organic solvent (C₆H₅ONa, C₇H₄N₂O₇) used in the determination of soil enzyme activity were purchased from Chemical Works (Beijing, China). The purity of all the experimental acids was guaranteed reagent (GR), while the purity of other chemicals mentioned above was analytical reagent (AR). HAc, NH₂OH·HCl, and NH₄OAc were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. (Beijing, China), and their purity was GR.

2.3. Experimental Design and Processing

2.3.1. Pre-Test

Soil

A total of 121 dryland surface soil samples were collected in Qianyang with a sampling density of 100 × 100 m (Figure 1). The amount of soil that was collected ranged from 0 to 20 cm for each sample point and weighed about 2 kg. According to the measured content of Hg at the sampling points, we divided the 121 values into seven different Hg concentration intervals, ranging from 0 to 1.5 mg·kg⁻¹, 1.5 to 3.0 mg·kg⁻¹, 3.0 to 4.5 mg·kg⁻¹, 4.5 to 6.0 mg·kg⁻¹, 6.0 to 7.5 mg·kg⁻¹, 7.5 to 9.0 mg·kg⁻¹ and > 9.0 mg·kg⁻¹, respectively. Then, the soil samples at different initial Hg concentrations for the orthogonal experiment and pot experiment were prepared by mixing the soils from the above intervals. All soil samples were air-dried and sieved through a 2-mm polyethylene sieve for use.

Amendments

Four different amendments (A1 = modified biochar, A2 = modified attapulgitite, A3 = biochar with attapulgitite, and A4 = modified biochar with modified attapulgitite; the ratio of biochar to attapulgitite in A3 and A4 was 3:5) were used in this study. The modified attapulgitite was prepared by acid modification combined with thermal modification. The natural attapulgitite was dried, passed through a 200-mesh sieve, and mixed with 4 mol·L⁻¹ HNO₃ solution at a ratio of 1:3 of solid to liquid. Then, it was soaked and stirred for 2 h at 70–80 °C, and it was heat-treated at 300–450 °C for 2–4 h. In addition, the biochar was modified by KMnO₄. The biochar, 65% HNO₃ solution, and 0.5 mol·L⁻¹ KMnO₄

solution were mixed at a ratio of 1:2:5, then it was left to cool, and oxidation was conducted at 90 °C for 2 h. Subsequently, it was washed, centrifuged, and dried for further use.

Stabilization Orthogonal Experiment

We weighed 200 g of the sieved soil into plastic flowerpots and added the four different amendments according to the additional amounts of 0.5%, 1%, 2%, and 3% (mass fractions, which is the ratio of application amounts of the amendment to the total mass of the soil), and they were mixed well with the Hg-contaminated soil (initial concentrations: 3.85, 8.97, 18.4, and 28.7 mg·kg⁻¹, respectively). We regularly added DI water to the soil to keep the soil moist, and the flowerpots were placed in a ventilated area of the test greenhouse to mature and stabilize for 30, 60, 90, and 120 d for each treatment. There were three replicates for each of the above treatments, and a control group was set up at the same time to compare the effects of the amendment type, amount of amendment added, initial concentration of Hg, and aging time on the reduction rate of the available Hg content in the soil (Table 1). This study adopted a four-factor and four-level orthogonal experiment design scheme, which did not consider interactions, and an empty column was set as the experimental error to measure the reliability of the experiment. The selected orthogonal table $L_{16}(4^5)$ is shown in Table 2.

Table 1. Factor levels.

Level	Factors			
	A (Amendment Type)	B (Amendment Added Ratio/%)	C (Initial Concentration of the Hg in the Soil/mg·kg ⁻¹)	D (Aging Time/d)
1	Modified biochar	0.5	3.85	30
2	Modified Attapulgite	1	8.97	60
3	Biochar + Attapulgite	2	18.4	90
4	Modified biochar + Modified attapulgite	3	28.7	120

Table 2. Orthogonal experiment design.

Test Number	Factors					Test Group
	A (Amendment Type)	B (Amendment Added Ratio/%)	C (Initial Concentration of the Hg in the Soil/mg·kg ⁻¹)	D (Aging Time/d)	E (Null Columns)	
T1	1	1	1	1	1	A ₁ B ₁ C ₁ D ₁
T2	1	2	2	2	2	A ₁ B ₂ C ₂ D ₂
T3	1	3	3	3	3	A ₁ B ₃ C ₃ D ₃
T4	1	4	4	4	4	A ₁ B ₄ C ₄ D ₄
T5	2	1	2	3	4	A ₂ B ₁ C ₂ D ₃
T6	2	2	1	4	3	A ₂ B ₂ C ₁ D ₄
T7	2	3	4	1	2	A ₂ B ₃ C ₄ D ₁
T8	2	4	3	2	1	A ₂ B ₄ C ₃ D ₂
T9	3	1	3	4	2	A ₃ B ₁ C ₃ D ₄
T10	3	2	4	3	1	A ₃ B ₂ C ₄ D ₃
T11	3	3	1	2	4	A ₃ B ₃ C ₁ D ₂
T12	3	4	2	1	3	A ₃ B ₄ C ₂ D ₁
T13	4	1	4	2	3	A ₄ B ₁ C ₄ D ₂
T14	4	2	3	1	4	A ₄ B ₂ C ₃ D ₁
T15	4	3	2	4	1	A ₄ B ₃ C ₂ D ₄
T16	4	4	1	3	2	A ₄ B ₄ C ₁ D ₃

2.3.2. Pot Experiment

Based on the stabilization orthogonal experiment results, we weighed 200 g of sieved soil into plastic flowerpots, and the initial Hg concentrations were about 4.32, 9.81, 13.5, 18.7, and 29.3 mg·kg⁻¹. Amendment A4 was selected, and the addition ratios were 0, 0.2%, 0.4%, 0.6%, and 0.8% (mass fractions). After aging for 90 d, 10 water spinach seeds with full grains and uniform size were sown at a depth of 2 cm, and the soil was kept moist every day. The seedlings were thinned about 7 d after emergence, with six evenly spaced plants per pot. There were three replicates for each group, and compound fertilizer (N:P₂O₅:K₂O = 10:4:3) was added to the soil during growth. The plants and soil samples were collected at the maturity of the water spinach, and indicators such as the available Hg content in the soil, Hg content in the water spinach, and dry weight of the water spinach were measured.

2.3.3. Field Plot Experiment

Based on the pre-experiment results, the low, medium, and high levels of the Hg-contaminated soil were set at the initial concentrations of about 1.38, 2.46, and 8.52 mg·kg⁻¹, respectively. There were three treatments for the amendment A4 application ratio for each level, which were 0, 0.3%, and 0.5% (mass fractions). Based on the soil thickness of the 20 cm tillage layer, the actual application amounts of the amendment in each plot were about 0, 6750, and 11,250 kg·hm⁻², respectively. Each group had three replicates, with a total of 27 plots, and each plot area was 6 m² (3 × 2 m), with a random arrangement. To prevent each community from influencing the other, ridges were used to separate the plots, and they were covered with a film to protect the peripheral plots. After the land was leveled in July 2015, amendment A4 was applied (one-time application) and mixed with the soil. After aging for 90 d, water spinach was planted in the first year (September 2015) and the second year (August 2016), with 15 rows per plot, 20 plants per row, 20 cm row spacing, and 10 cm plant spacing. The selected water spinach seeds and compound fertilizers were the same as those used in the pot experiment. During the experiment, the water content was maintained at 60% to 70% of the maximum water-holding capacity in the field and was checked every day. The crop planting, fertilization, and control of pests and weeds were all carried out in accordance with the local planting habits. After the water spinach matured, the actual yield of each plot was measured by the multi-point sampling method. Then, 30 water spinach samples with the same growth rate were simultaneously collected with corresponding root soil samples, and the pH value of the soil, total Hg content, available Hg content, morphological Hg content, enzyme activity, Hg content in the water spinach, and the water spinach yield, were determined.

2.3.4. Sample Pretreatment and Analysis Methods

The soil samples were naturally air-dried to remove the plant residues, gravel, and other debris, and they were placed in a dry and ventilated place to dry out in the shade. Then, the soil samples were quartered and passed through a 200-mesh sieve. The water spinach samples were first rinsed with water to remove the adhered soil and pollution due to fertilization, and then they were rinsed 1–2 times with DI water, drained, and air-dried at room temperature. Next, they were dried at 65 °C to a constant mass, weighed, and passed through a 100-mesh sieve.

The total Hg in the soil was extracted using an HCl-HNO₃-H₂O₂ (3:1:1 volume ratio). The available Hg was extracted with a 0.1 mol·L⁻¹ NH₄OAc. The morphological analysis of the Hg was continuously extracted by the BCR method, which included the exchangeable (F1), reducible (F2), oxidizable (F3), and residual (F4) Hg [33,34]. The Hg in the water spinach was extracted with an HNO₃. Furthermore, the Hg in the extracts was measured by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x, Agilent, CA, USA). The limit of detection (LOD) and the limit of quantitation (LOQ) was 0.007 mg·kg⁻¹ and 0.024 mg·kg⁻¹, respectively. Duplicate samples, blank samples, and reference materials (GBW series) were inserted into each batch of samples during the testing process to control

the analytical quality. The Hg recoveries of the total Hg content, available Hg content, morphological Hg content, and Hg content in the water spinach during the analysis were 93.7–98.3%, 90.0–93.3%, 95.6–107.8%, and 93.5–106.3%, respectively. The relative double-differences of the repeatable samples were 1.85–6.12%, 1.37–7.16%, 1.56–4.34%, and 5.08–6.21%, respectively.

The pH value of the soil was determined by the glass electrode method. The soil catalase activity (CAT) was determined by the KMnO_4 titration method [35]. The urease activity (URE) was determined by the sodium phenate-sodium hypochlorite colorimetric method [36,37]. In addition, the invertase activity (INV) was determined by the 3,5-dinitrosalicylic acid colorimetric method [37].

2.3.5. Assessment of the Stabilization Effect

The stabilization effect (SE) was evaluated by the reduction rate of the available Hg content in the soil (SE_1), the reduction rate of the Hg content in the water spinach (SE_2), or the growth rate of the dry weight of the water spinach when collected at maturity (SE_3):

$$\text{SE}_1 = \frac{c_0 - c_s}{c_s} \times 100\% \quad (1)$$

$$\text{SE}_2 = \frac{c_p - c_r}{c_p} \times 100\% \quad (2)$$

$$\text{SE}_3 = \frac{m_a - m_b}{m_a} \times 100\% \quad (3)$$

where c_0 is the available Hg content in the soil of the control group; c_s is the available Hg content in the soil after the addition of the amendment; c_p is the Hg content in the water spinach in the control group; c_r is the Hg content in the water spinach after adding the amendment; m_a is the dry weight of the water spinach when collected after the addition of the amendment; m_b is the dry weight of the water spinach in the control group.

2.3.6. Data Processing

Excel 2010 and SPSS 25.0 were used for data processing and statistical analysis, a one-way analysis of variance method (ANOVA) was used to determine the significant differences, the Pearson correlation coefficient was used to analyze the correlation, and the graphs were drawn using Sigmaplot 14.0 (Systat Software Inc., San Jose, CA, USA), Surfer 13.0 (Golden Software Inc., Golden, CO, USA) and R 4.2.1 (Ihaka, R. and Gentleman, R., Auckland, New Zealand).

3. Results

3.1. Results of the Stabilization Orthogonal Experiment

Through the four-level and four-factor stabilization orthogonal experiment, the effects of the amendment type, amount of amendment added, initial concentration of Hg, and aging time on the available Hg content in the soil were investigated, as shown in Table 3.

When compared to the control group without the amendment addition, the 16 groups could reduce the available Hg content in the soil, and the average SE_1 was 20.5–42.5%. The R -value showed that the influence of the four factors on the SE_1 was in the order of $C > B > A > D$. According to the average k value of the different treatments, the optimal combination of each factor was A4-B1-C2-D3, that is, the addition of amendment A4 with a mass fraction of 0.5%, with an initial Hg concentration of $8.97 \text{ mg} \cdot \text{kg}^{-1}$, and after aging for 90 d, it had the best stabilization effect on the soil Hg.

The results of the ANOVA (Table 4) showed that there were significant differences in the effects of the four factors on the stabilization. Specifically, the p -values of factors C and B were 0.024 and 0.032, respectively, suggesting that the initial concentration of Hg and the amount of amendment that was added had a more significant effect on the results. Moreover, the p -value of factor A was 0.069, suggesting that the amendment type had a

significant effect on the results. Then, the p -value of factor D was greater than 0.1. Thus, the effect of the aging time was not significant. Hence, it can be concluded that the initial concentration of Hg and the amount of amendment added were the primary factors, and the amendment type was a secondary factor, while the aging time had less impact on the stabilization.

Table 3. Stabilization orthogonal experiment results.

Test Number	Factor					SE ₁ /%
	A (Amendment Type)	B (Amendment Added Ratio/%)	C (Initial Concentration of the Hg in the Soil/mg·kg ⁻¹)	D (Aging Time/d)	E (Null Columns)	
T1	1	1	1	1	1	30.7 ± 1.61
T2	1	2	2	2	2	34.8 ± 1.93
T3	1	3	3	3	3	27.6 ± 2.62
T4	1	4	4	4	4	20.5 ± 2.52
T5	2	1	2	3	4	42.5 ± 3.25
T6	2	2	1	4	3	33.2 ± 2.40
T7	2	3	4	1	2	24.3 ± 2.26
T8	2	4	3	2	1	24.2 ± 0.95
T9	3	1	3	4	2	35.7 ± 1.61
T10	3	2	4	3	1	29.1 ± 2.07
T11	3	3	1	2	4	26.3 ± 1.45
T12	3	4	2	1	3	29.7 ± 2.70
T13	4	1	4	2	3	32.5 ± 1.92
T14	4	2	3	1	4	33.4 ± 1.57
T15	4	3	2	4	1	37.6 ± 2.46
T16	4	4	1	3	2	35.5 ± 3.06
k_1	28.4	35.4	31.4	29.5	30.4	
k_2	31.1	32.6	36.2	29.4	32.6	
k_3	30.2	29.0	30.2	33.7	30.8	
k_4	34.8	27.5	26.6	31.2	30.7	
R	6.35	7.88	9.55	4.23	2.18	
Order of factors			C > B > A > D			
Superior level	A4	B1	C2	D3		

$k_1, k_2, k_3,$ and k_4 are the average SE₁ of each factor at the same level, respectively, $n = 4$; R is the maximum k minus the minimum k for each factor.

Table 4. Variance analysis of stabilization orthogonal experiment.

Factor	Deviation Sum of Squares	Degree of Freedom	Mean Square	F Value	p Value	Significance
A	85.700	3	28.567	7.217	0.069	*
B	152.605	3	50.868	12.851	0.032	**
C	186.495	3	62.165	15.705	0.024	**
D	49.025	3	16.342	4.128	0.137	
Error	11.875	3	3.958			

** indicates a more significant impact on the test results at the level of $p < 0.05$; * indicates a significant impact on the test results at the level of $p < 0.1$.

3.2. Results of the Pot Test

Based on the analysis results of the stabilization orthogonal experiment, to obtain better experimental conditions, we further determined the optimal level of the two factors that had a significant impact on the stabilization, namely the initial concentration of the soil Hg and the amount of amendment added, through the pot experiment. The changes in the available Hg content in the soil, Hg content in the water spinach, and dry weight of the water spinach that was collected at maturity are illustrated in Figure 2.

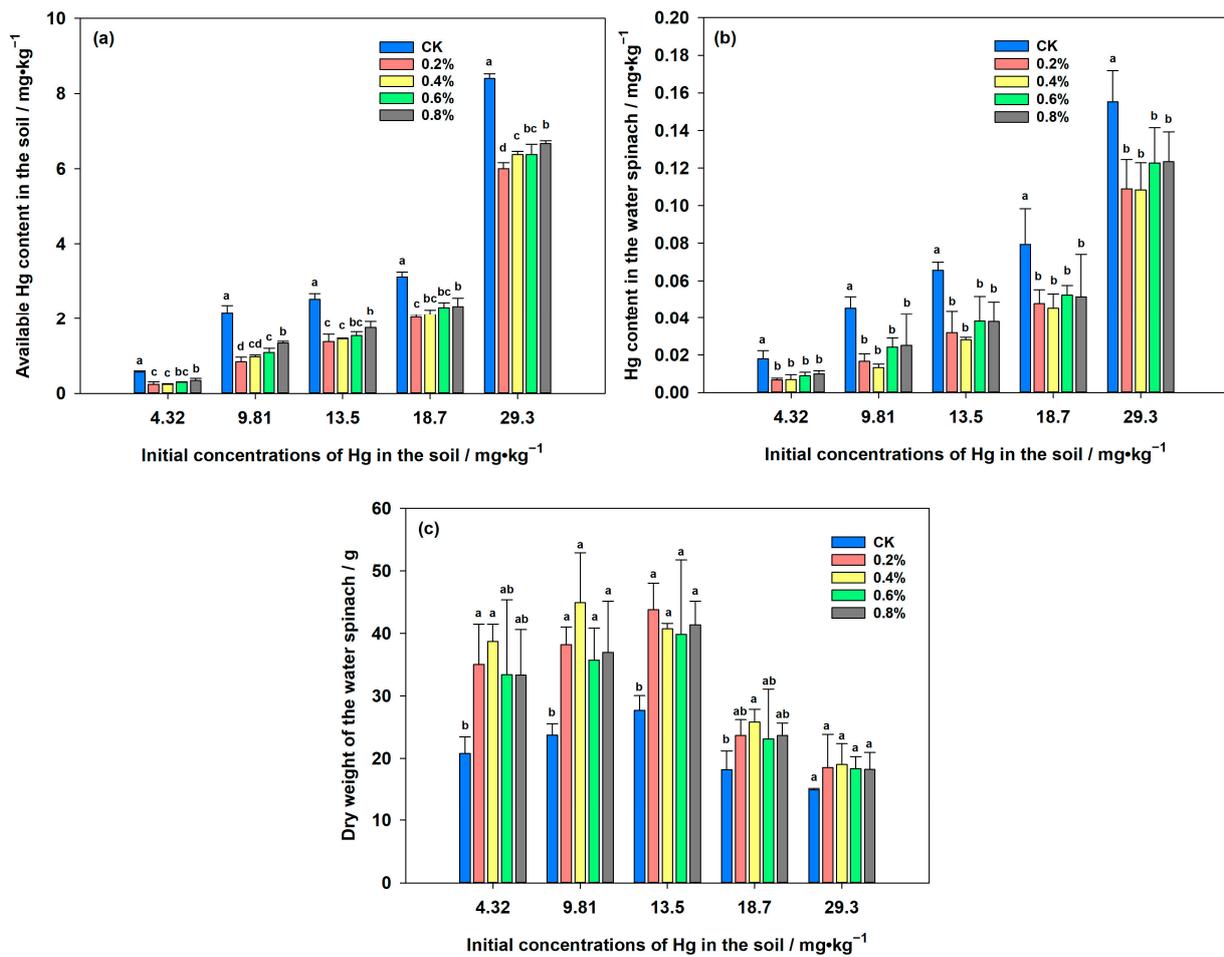


Figure 2. Indicators (a) available Hg content in the soil; (b) Hg content in the water spinach; (c) dry weight of the water spinach under different treatments in the pot tests. The different lowercase letters indicate that there were significant differences among the treatments with different amendment application amounts ($p < 0.05$) for the same initial Hg concentration. The same lowercase letters indicate no significant difference at the level of $p > 0.05$.

As shown in Figure 2a, compared to the control group, the average reduction in the available Hg content in the soil decreased from 45.5% to 30.8% as the amendment added ratio increased from 0.2% to 0.8%. When the amendment added ratio was 0.4%, the average reduction in the Hg content in the water spinach with different initial concentrations of Hg was the largest, at about 52.6%. When the addition ratio was increased to 0.8%, the average Hg content in the water spinach was reduced to 37.5% (Figure 2b). Additionally, the available Hg content in the soil, the Hg content in the water spinach, and the dry weight of the water spinach decreased from 50.7% to 24.3%, 55.1% to 25.4%, and 40.6% to 19.2%, respectively, as the initial concentration of Hg increased from 4.32 to 29.3 mg·kg⁻¹.

In order to investigate the optimal applicable conditions of Hg-contaminated soil stabilization, the amount of amendment added was taken as the horizontal coordinate and the initial concentration of Hg in the soil was taken as the vertical coordinate, and then the changes in SE₁, SE₂, and SE₃ under the dual influence of the two factors were plotted, as shown in Figure 3.

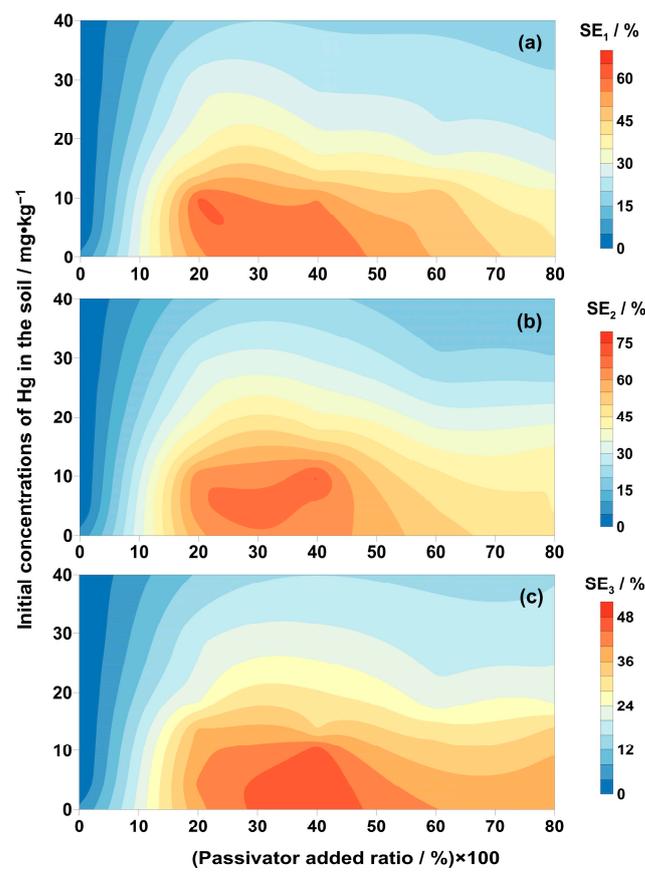


Figure 3. Stabilization effect (a) the reduction rate of the available Hg content in the soil (SE_1); (b) the reduction rate of Hg content in the water spinach (SE_2); (c) the growth rate of the dry weight of the water spinach (SE_3). The different color areas indicate the changes in the SE_1 , SE_2 , and SE_3 under the dual influence of the initial concentration of Hg in the soil and the amount of amendment added. The sequential transitions of the color from dark blue to light blue, white, light yellow, yellow, orange, and dark orange indicate a gradual increase in SE_1 , SE_2 , and SE_3 .

For the soil with an initial concentration of Hg that was less than $10 \text{ mg}\cdot\text{kg}^{-1}$, when the amendment added ratio was 0.2% and 0.4%, the SE_1 , SE_2 , and SE_3 were about 55.0–61.2%, 66.2–70.9%, and 37.8–47.1%, respectively. When the amendment added ratio increased to 0.6% and 0.8%, the SE_1 , SE_2 , and SE_3 were 37.9–49.6%, 46.7–50.1%, and 33.6–37.8%, respectively. For the soil with an initial Hg concentration between 10 and $20 \text{ mg}\cdot\text{kg}^{-1}$, after applying 0.2–0.8% amendment, the SE_1 , SE_2 , and SE_3 were 25.5–45.4%, 34.0–57.2%, and 21.2–36.8%, respectively. In addition, for the soil with an initial concentration of Hg that was as high as $29.3 \text{ mg}\cdot\text{kg}^{-1}$, the stabilization efficiency value did not exceed 30%. An overall evaluation of the SE_1 , SE_2 , and SE_3 revealed that the initial Hg concentration in the soil was below $10 \text{ mg}\cdot\text{kg}^{-1}$ when the amendment added ratio was 0.2–0.4%, indicating an optimized stabilization effect.

3.3. Results of the Field Plot Experiment

3.3.1. Variation in the Available Hg Contents in the Soil

Figure 4 shows the available Hg contents in the soil for two consecutive years in the field plot experiment.

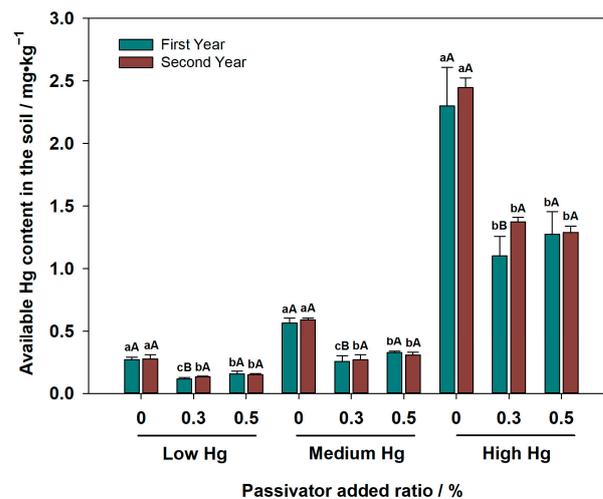


Figure 4. The available Hg content in the soil in two consecutive years. The different lowercase letters indicate that there were significant differences among the treatments with different amendment application amounts ($p < 0.05$) for the same initial Hg concentration in the same year. The different capital letters indicate that there were significant differences among the treatments in different years ($p < 0.05$) for the same initial Hg concentration and the same amendment application amount.

After one year of remediation, the SE_1 of each treatment's available Hg content decreased with the increase in the initial concentration of Hg in the soil. When the amendment added ratio was 0.3% and 0.5%, the SE_1 values were 52.1–62.0% and 43.2–46.0%, respectively. After two years of remediation, with the amendment application ratio of 0.3% and 0.5%, the SE_1 values were 43.8–52.4% and 47.3–50.8%, respectively. In summary, with the prolongation of the stabilization time, the available Hg content of each treatment increased year-on-year but was still significantly lower than that of the control group ($p < 0.05$), and the persistence of the stabilization was good.

3.3.2. Soil Hg Form Changes

Figure 5 shows the changes in the proportion of Hg in each form in the soil for two consecutive years.

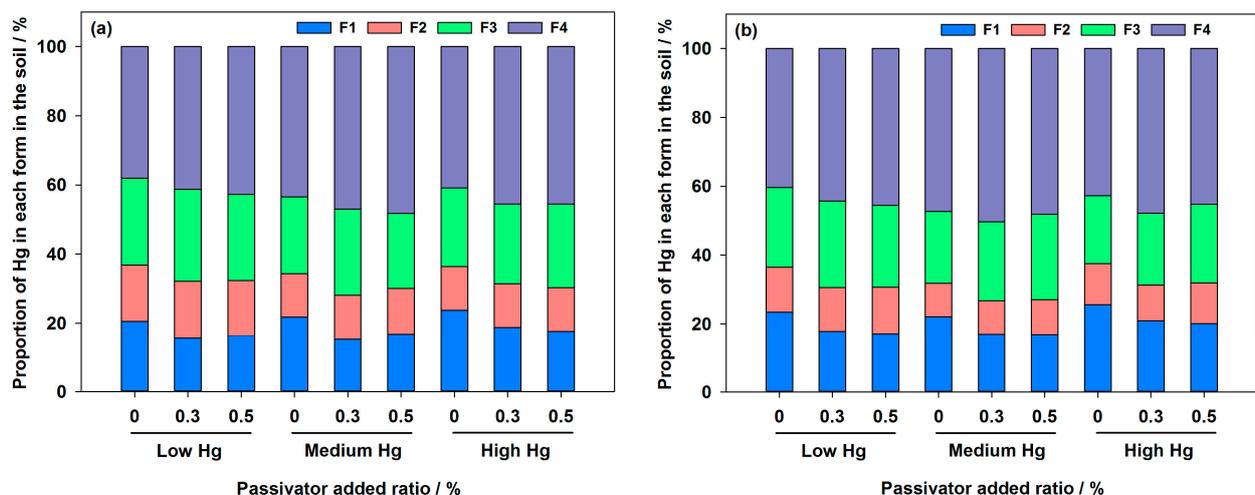


Figure 5. Proportion of Hg in each form in the soil in two consecutive years (a) the first year; and (b) the second year.

Before applying the amendment, the morphology of the soil Hg was dominated by residual Hg, accounting for about 38.1–47.3%. The proportions of F3, F2, and F1 were

about 19.7–25.1%, 9.76–16.3%, and 20.5–25.6%, respectively. Compared to the control group, the addition of the amendment could effectively reduce the proportion of F1 and increase the proportion of F2, F3, and F4. That is, it could accelerate the transformation of Hg from an active form to a stable form. In the first year, the F1 content in the high, medium, and low Hg-contaminated soils reduced to 23.4%, 26.7%, and 22.6%, respectively, while the F4 content increased to 10.3%, 8.59%, and 9.30%, respectively, and the proportion of F3 and F2 did not change significantly. With the prolongation of the stabilization time, although the proportion of F1 in each treatment increased, it was always lower than that of the control group. In addition, the average F1 content in the high, medium, and low Hg-contaminated soils reduced to 19.7%, 23.1%, and 25.6%, respectively. The average increments of F3 were 9.84%, 12.2%, and 4.93%, and the averages of F4 were 7.93%, 3.92%, and 10.2%. The proportion of F2 did not change significantly.

3.3.3. Hg content in the Water Spinach and the Water Spinach Yield

Figures 6 and 7 show the changes in Hg content in the water spinach at maturity and the yield of the water spinach in two consecutive years.

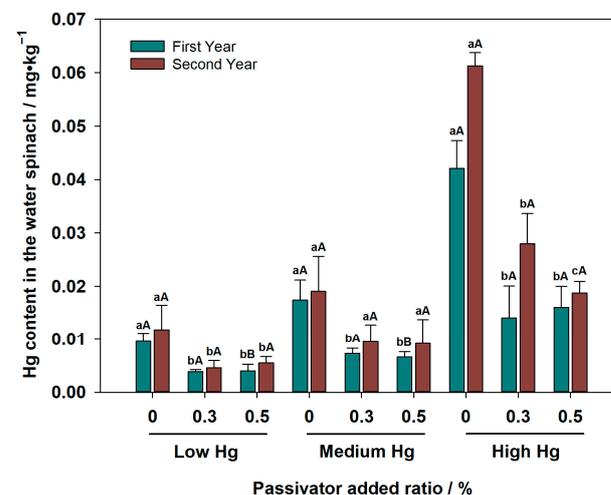


Figure 6. Hg content in the water spinach in two consecutive years. The different lowercase letters indicate that there were significant differences among the treatments with different amendment application amounts ($p < 0.05$) for the same initial Hg concentration in the same year. The different capital letters indicate that there were significant differences among the treatments in different years ($p < 0.05$) for the same initial Hg concentration and the same amendment application amount.

According to Figure 6, after one year of remediation, when the amendment added ratio was 0.3% and 0.5%, the SE_2 values were 58.2–66.6% and 58.2–62.0%, respectively. The difference between the two different amounts of each amendment was not significant ($p > 0.05$). After two years of remediation, the SE_2 values were 50.1–61.4% and 51.9–69.4%, respectively. Additionally, for the medium and low Hg-contaminated soils, the average Hg content in the water spinach in the control group were about 0.009 and 0.018 $\text{mg}\cdot\text{kg}^{-1}$, respectively, which is at or close to the limit value of Chinese standard for Hg in vegetables (0.01 $\text{mg}\cdot\text{kg}^{-1}$) [38]. After the amendment application, the Hg content in the water spinach could be reduced to less than 0.01 $\text{mg}\cdot\text{kg}^{-1}$, which is in line with the national food safety standards. For the soil contaminated highly by Hg, the Hg content in the water spinach in the control group was 0.052 $\text{mg}\cdot\text{kg}^{-1}$, which is about five times higher than the limit value. After applying 0.3% or 0.5% amendment, the average Hg content in the water spinach in two consecutive years decreased to 0.021 and 0.017 $\text{mg}\cdot\text{kg}^{-1}$, respectively, and the average SE_2 values were about 59.6% and 67.3%, respectively.

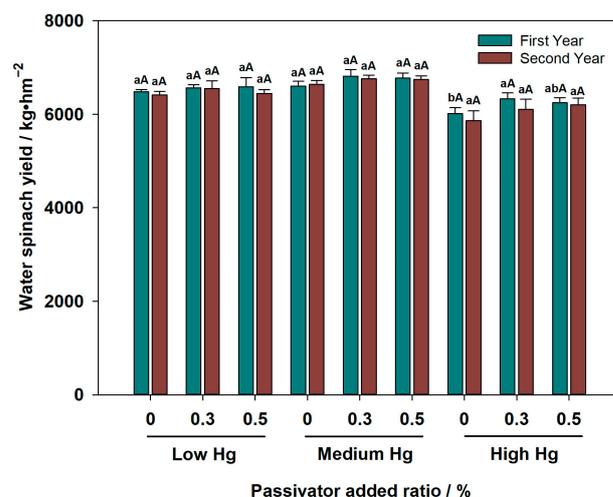


Figure 7. The yield of the water spinach in two consecutive years. The same lowercase letters indicate that there were no significant differences among the treatments with different amendment application amounts ($p > 0.05$) for the same initial Hg concentration in the same year. The same capital letters indicate that there were no significant differences among the treatments in different years ($p > 0.05$) for the same initial Hg concentration and the same amendment application amount.

In Figure 7, the water spinach yield decreased as the initial concentration of Hg in the soil increased. After the one-time amendment application, the water spinach yield increased to a certain extent within two years, but it did not reach a significant level ($p > 0.05$). For the high, medium, and low Hg-contaminated soils, after applying 0.3% amendment, the average water spinach yield increased by about 4.39%, 2.84%, and 1.46% when compared with that of the control group in two years. Whereas in the 0.5% treatment group, the average increment of the water spinach yields were 4.81%, 1.61%, and 1.29%, respectively.

3.3.4. Changes in the Enzyme Activity in the Soil

The enzyme activity in the soil is one of the most sensitive indicators for evaluating soil fertility and measuring changes in soil quality. It plays an important role in the material cycle and energy flow of the soil ecosystem [39]. Moreover, it can characterize the metabolic functions of the microorganisms well and control the release of biological nutrients in the soil. Recently, soil catalase, urease, and invertase have been widely used to monitor the biological properties of contaminated soil [40]. Catalase is a kind of soil oxidoreductase, and it is used to decompose hydrogen peroxide in the soil and plays a vital role in crop growth. When its content is too high or too low, it is not conducive to crop growth. Then, urease can directly reflect the level and ability of the nitrogen supply in the soil, and it is closely related to the nitrogen cycle system in the soil. In addition, invertase can convert sucrose into glucose and fructose through hydrolytic conversion, which can be utilized by plants and microorganisms. The enzyme activities in the Hg-contaminated soil are shown in Table 5.

It has been demonstrated that the enzyme activity in the soil is susceptible to heavy metals in the soil. In this study, the catalase, urease, and invertase activities were reduced to about 26.3%, 53.0%, and 43.9%, respectively, indicating that urease and invertase have a higher sensitivity to Hg-contaminated soil. Firstly, heavy metals may form stable complexes by coordinating with the active sites, such as the sulfhydryl groups in enzyme molecules, thereby inhibiting enzyme activity. Secondly, heavy metals may affect the growth and reproduction of microorganisms and reduce the synthesis and secretion of enzymes in the organism, resulting in a decrease in enzyme activity [41].

Table 5. Soil enzyme activities in two consecutive years.

Initial Concentration of Hg in Soil/mg·kg ⁻¹	Amendment Added Ratio/%	CAT/mL·g ⁻¹		URE/mg·g ⁻¹		INV/mg·g ⁻¹	
		First Year	Second Year	First Year	Second Year	First Year	Second Year
L	CK	1.24 ± 0.10 bA	1.20 ± 0.07 bA	1.34 ± 0.05 bA	1.21 ± 0.21 bA	7.87 ± 1.56 bA	7.54 ± 1.23 bA
	0.3	1.74 ± 0.23 aA	1.54 ± 0.14 aA	1.91 ± 0.08 aA	1.61 ± 0.14 aA	11.4 ± 0.96 aA	9.92 ± 1.22 aA
	0.5	1.63 ± 0.15 aA	1.37 ± 0.14 abA	1.87 ± 0.09 aA	1.47 ± 0.10 abA	10.7 ± 0.56 aA	9.43 ± 0.81 abA
M	CK	1.08 ± 0.13 bA	1.02 ± 0.30 aA	1.14 ± 0.09 bB	1.26 ± 0.13 bA	6.27 ± 0.54 bA	6.34 ± 1.03 aA
	0.3	1.54 ± 0.21 aA	1.33 ± 0.12 aA	1.76 ± 0.11 aA	1.73 ± 0.11 aA	9.32 ± 0.78 aA	8.37 ± 1.32 aA
	0.5	1.48 ± 0.20 aA	1.25 ± 0.14 aA	1.69 ± 0.28 aA	1.54 ± 0.15 aB	9.04 ± 0.26 aA	7.83 ± 0.83 aA
H	CK	0.95 ± 0.11 bA	0.87 ± 0.15 aA	0.66 ± 0.09 aA	0.54 ± 0.12 aB	4.61 ± 1.34 aA	4.43 ± 0.68 aA
	0.3	1.22 ± 0.15 aA	1.06 ± 0.11 aA	0.85 ± 0.07 aA	0.68 ± 0.08 aA	5.80 ± 0.88 aA	5.11 ± 0.69 aA
	0.5	1.20 ± 0.14a bA	0.97 ± 0.12 aA	0.88 ± 0.27 aA	0.63 ± 0.15 aA	6.00 ± 0.90 aA	5.40 ± 0.49 aA

The different lowercase letters indicate that there were significant differences among the treatments with different amendment application amounts ($p < 0.05$) for the same initial Hg concentration in the same year. The different capital letters indicate that there were significant differences among the treatments in different years ($p < 0.05$) for the same initial Hg concentration and the same amendment application amount.

After applying 0.3% or 0.5% amendment to the soil, the average catalase, urease, and invertase activities increased by 25.5–29.3%, 30.6–32.8%, and 28.5–31.9%, respectively, suggesting that amendments can accelerate biochemical reactions in the soil. This is beneficial for the material circulation and energy flow in the soil system, which enhances the environmental quality of the soil. The reason for this response may be that the amendment enhances the structure and the water-holding capacity of the soil and is beneficial for the enhancement of microbial activity. Thus, the toxic effect of the heavy metal on the enzyme activity in the soil was slowed down [42,43]. In this study, as the amendment added ratio increased from 0.3% to 0.5%, the enzyme activity in the soil gradually decreased. This may be because the amendment adsorbs the enzyme molecules in the soil to create a protective effect on the binding site of the enzymatic reaction, thereby inhibiting the enzyme activity in the soil [42,43].

3.3.5. Correlation Analysis

The correlation analysis of various environmental factors is shown in Figure 8.



Figure 8. Correlation analysis of various environmental factors. The color of the squares on the right represents the strength of positive and negative correlations among various environmental factors. The size of the squares represents the magnitude of the Spearman correlation coefficient. Ava, available Hg content in the soil; F1, exchangeable Hg content; F2, reducible Hg content; F3, oxidizable Hg content; F4, residual Hg content; CAT, catalase activity; URE, urease activity; INV, invertase activity; Abs, Hg content in the water spinach; Yield, water spinach yield.

There were extremely significant correlations ($p < 0.01$) or significant correlations ($p < 0.05$) among the available Hg content in the soil, the content of exchangeable, reducible, oxidized, and residual Hg in the soil, enzyme activities, Hg content in the water spinach and the yield of water spinach. As shown in Figure 8, the Hg in the water spinach was significantly correlated with the content of available Hg, exchangeable Hg, oxidized Hg, and residual Hg in the soil, the urease and invertase activities, and the water spinach yield. The correlation coefficients were between 0.5 and 0.8, indicating a moderate correlation. The available Hg content in the soil was positively correlated with exchangeable Hg and negatively correlated with urease and invertase activities, and the correlation coefficients were above 0.8, indicating a strong correlation. Therefore, they can be used as an evaluation index to guide the stabilization effect of Hg-contaminated soil.

4. Discussion

In this study, a composite amendment of modified biochar and modified attapulgite was used for Hg-contaminated soil, and a good stabilization effect was obtained. Previous studies showed that after adding the composite amendments to the soil, the activity of Hg^{2+} can be reduced by physical and chemical reactions with Hg^{2+} , and the mechanism of stabilization mainly involves ion exchange, complexation reactions, and precipitation reactions [44–46]. Among them, the biochar surface contains sufficient oxygen-containing functional groups, which can reduce the effectiveness of Hg through adsorption and complexation. Attapulgite is a hydrous silicate mineral that mainly contains aluminum and magnesium. It has a unique layered chain structure, good ion exchange performance, and good adsorbing performance; it can also transform Hg in the soil from a highly active exchangeable form to a more stable obligate binding form through the complexation reaction, reducing the activity of the heavy metal in the soil [47]. Additionally, biochar and attapulgite can promote the adsorption of heavy metals by soil colloids and clay particles by increasing the pH value of the soil and increasing the variable negative charge on the soil surface [28,48]. After the pH value increases, it promotes the hydrolysis of Hg^{2+} to $\text{Hg}(\text{OH})^+$, and the affinity of $\text{Hg}(\text{OH})^+$ on the adsorption site in the soil is significantly higher than that of Hg^{2+} . Moreover, OH^- reacts with CO_2 and generates CO_3^{2-} , and carbonate can form insoluble carbonic acid Hg with Hg^{2+} , which can increase the stabilization effect of Hg [47,49]. In this study, it could be seen that the pH value of the soil increased gradually with the increase in the amount of amendment added, and the average increase was 0.26–1.41 units with different initial concentrations of Hg in the soil.

The in-situ stabilization technology mainly reduces the mobility of the Hg in the soil by changing the existing form of the Hg. However, Hg still exists in the soil and maintains a dynamic balance. As environmental conditions change, the immobilized Hg may be re-released, so the persistence of the stabilization of the amendment on Hg is important. After the one-time amendment application, the application of $6750 \text{ kg}\cdot\text{hm}^{-2}$ amendments showed a significant effect in the first year. When the application amount was increased to $11,250 \text{ kg}\cdot\text{hm}^{-2}$, the stabilization effect was decreased. The correlation analysis results showed that the Hg in the water spinach had an extremely significant positive correlation with the available Hg content in the soil, while the available Hg content in the soil had an extremely significant negative correlation with the activities of urease and invertase, and the correlation coefficient was high. Therefore, it was inferred that excessive amendment inhibited the soil enzyme activities and thus affected the adsorption performance of Hg. For the medium and low Hg-contaminated soil, there was no significant difference between treatments with different amounts of the amendment. After applying 6750 and $11,250 \text{ kg}\cdot\text{hm}^{-2}$ amendment, Hg contents in the water spinach within two consecutive years were lower than the limit value of Chinese standard ($0.01 \text{ mg}\cdot\text{kg}^{-1}$). Therefore, from an economic point of view, the application of the $6750 \text{ kg}\cdot\text{hm}^{-2}$ amendment can be used to achieve the target effect. For the high Hg-contaminated soil, applying different amounts of the amendment, although the Hg content in the water spinach was still higher than the limit value, it decreased greatly, indicating that the persistence of the stabilization was

good. It has been demonstrated that water-soluble organic substances and species, such as K, Ca, P, N, and S, dissolve and diffuse into the surrounding soil either in the carbon lattice or in the micron-scale mineral phase and will change the pH value and oxidation-reduction potential of the soil, thereby changing the surface structure and chemical properties of the amendment and leading to its aging. It can form new heavy metal adsorption sites and ensure that the amendment surface remains active and continuously adsorbs heavy metals [50]. To sum up, these findings could be used to improve the efficiency of stabilization remediation for Hg-contaminated soil over a longer time scale. In the practical application, the appropriate amount of amendment added should be considered in combination with the degree of soil Hg pollution and economic benefits.

5. Conclusions

The main factors of the stabilization of Hg-contaminated soil in Qianyang, Gekeng, and Dehua County were the initial concentration of Hg in the soil and the additional amount of amendment, followed by the amendment type, while the aging time had less effect. When the initial concentration of Hg in the soil was less than $10 \text{ mg}\cdot\text{kg}^{-1}$ and the amendment (modified biochar with modified attapulgite) added ratio was 0.2–0.4%, indicating optimized stabilization effect. The field plot experiment confirmed that the persistence of the stabilization was good for two consecutive years. After one year of remediation, the case of adding $6750 \text{ kg}\cdot\text{hm}^{-2}$ amendment showed a significant stabilization effect. Compared to the control group, the available Hg content in the soil and Hg in the water spinach reduced to 52.1–62.0% and 58.2–66.6%, respectively. When the application amount was increased to $11,250 \text{ kg}\cdot\text{hm}^{-2}$, the reduction rates were 43.2–46.0% and 58.2–62.0%, respectively. After two years of remediation, the stabilization effect was weakened, but they were still significantly lower than the control. For the soil contaminated slightly by Hg, Hg contents in the water spinach within two years were lower than the limit value of Chinese standard ($0.01 \text{ mg}\cdot\text{kg}^{-1}$). Although the Hg content in the water spinach for the soil contaminated highly by Hg was higher than the limit value, Hg contents could reduce to 67.3%, indicating an acceptable stabilization effect on heavily contaminated soil.

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