

Article

Impacts of Humic Acid and Potassium Fulvate on Cadmium and Lead Accumulation and Translocation in Maize (*Zea mays* L.) Grown in Co-Contaminated Soil

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Abstract

To explore strategies for the safe utilization of farmland co-contaminated with cadmium (Cd) and lead (Pb), this field study systematically evaluated the impacts of humic acid (HA) and potassium fulvate (PF) at different application rates (0, 1500, 3000, and 4500 kg·ha⁻¹) on the growth, yield, and translocation of Cd and Pb within the soil–plant system of maize (*Zea mays* L.). The results showed that while HA and PF did not significantly alter total soil Cd and Pb concentrations, they markedly reduced their bioavailable fractions. This mitigation of heavy metal phytotoxicity significantly promoted maize growth and yield, with the high-dose HA treatment increasing yield by a maximum of 32.9%. Both amendments dose-dependently decreased Cd and Pb concentrations, bioconcentration factors (BCF), and translocation factors (TF) in all maize tissues, particularly in the grains. At equivalent application rates, PF was slightly more effective than HA in reducing heavy metal concentrations in the grains. Notably, a significant positive correlation was observed between Cd and Pb concentrations across all plant parts, confirming a synergistic accumulation and translocation mechanism. This synergy provides a physiological explanation for the broad-spectrum immobilization efficacy of these humic substances. In conclusion, applying HA and PF presents a dual-benefit strategy for increasing yield and reducing risks in Cd- and Pb-contaminated farmlands. This study proposes a differentiated application approach: PF is the preferred option when ensuring food-grade safety is the primary goal, whereas high-dose HA is more advantageous for maximizing yield in soils with low-to-moderate contamination risk.

Keywords: heavy metals; humic acid; potassium fulvate; maize; in situ immobilization; food security

1. Introduction

Soil forms the basis for nearly 95% of human food production and is therefore the cornerstone of global food security [1]. However, accelerated global industrialization and



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agricultural intensification have made soil heavy metal contamination a severe environmental problem, directly threatening ecosystem stability, food security, and human health [2]. An estimated 242 million hectares of arable land worldwide (approximately 16% of the global total arable land) are affected by excessive heavy metal levels, with 900 million to 1.4 billion people residing in high-risk areas [3]. Due to their non-degradable nature, heavy metals accumulate in soil, posing a persistent threat to ecosystems [4]. Extensive epidemiological research has linked heavy metal exposure to cardiovascular diseases, cancer, cognitive impairment, and damage to multiple organs, including the kidneys and nervous system [5,6]. Among various heavy metal pollutants, cadmium (Cd) and lead (Pb) have been designated as priority pollutants by many countries due to their high toxicity, mobility, and widespread distribution [7]. Consequently, exploring economical, efficient, and environmentally friendly technologies for remediating heavy metal-contaminated soils to ensure safe agricultural production is a critical challenge in environmental science and agriculture [8].

Among various soil remediation technologies, in situ immobilization and stabilization is a mainstream strategy due to its cost-effectiveness, operational simplicity, rapid efficacy, and suitability for large-scale farmland application without disrupting soil structure [9,10]. The core principle involves applying passivating agents to soil to alter the speciation of heavy metals through physicochemical processes such as adsorption, precipitation, ion exchange, and complexation [11,12]. This converts them from highly bioavailable forms to stable, less active forms, thereby blocking their migration in the soil–plant system and reducing crop uptake [13,14].

Humic substances (HS), the core component of soil organic matter, are widely available, environmentally friendly natural polymers recognized as highly promising immobilization materials [15]. HS are rich in oxygen-containing functional groups, such as carboxyl and phenolic hydroxyl groups, which facilitate strong complexation and chelation with heavy metal ions [16,17]. Based on their acid-base solubility, HS are classified into humic acid (HA), fulvic acid (FA), and humin [18]. High-molecular-weight HA tends to form stable macromolecular complexes with heavy metals, effectively immobilizing them and reducing their bioavailability [16]. In contrast, low-molecular-weight FA, despite its strong complexing ability, forms water-soluble complexes that can sometimes enhance heavy metal mobility [19]. Potassium Fulvate (PF), a short-chain, small-molecule organic compound derived from natural fulvic acid and potassium salts, not only inherits the high functional group density of fulvic acid but is also valued for its high physiological activity and function as a potassium fertilizer [20]. It stimulates root growth, enhances nutrient uptake, and improves plant stress resistance [21]. Although the application of HA and PF in soil remediation has been reported, most studies are limited to single materials or are conducted under controlled conditions such as hydroponics and pot experiments [22–24]. Field-scale comparative studies of HA and PF application on farmland co-contaminated with Cd and Pb, particularly those that systematically evaluate their effects on major crop yields and the complete heavy metal translocation pathway from soil to grain via the root, stem, leaf, and cob, remain scarce. Elucidating how the immobilization effects of HA and the biostimulatory properties of PF perform in a field setting, and how they regulate heavy metal distribution and translocation within the plant, is crucial for their precise and safe utilization on contaminated farmland.

Maize (*Zea mays* L.) is one of the world's three major cereal crops, and its production safety directly impacts the entire food chain [25]. This study conducted a field experiment in a typical Cd- and Pb-co-contaminated agricultural area in eastern Yunnan, China, using locally dominant maize cultivars. The objectives were: (1) to compare the effects of different HA and PF application rates on maize biomass and yield; (2) to investigate the differential

impacts of the two amendments on the uptake, accumulation, and translocation of Cd and Pb in various maize tissues (roots, stems, leaves, cobs, and grains); and (3) to analyze the interactions between Cd and Pb within the maize plant. Based on the existing literature, we hypothesized that: (1) Both HA and PF would reduce the bioavailability of Cd and Pb in the soil, thereby increasing maize yield while decreasing heavy metal concentrations in plant tissues. (2) Due to their distinct molecular structures and functional properties, the larger-molecule HA would be more effective at enhancing biomass and yield, particularly at high application rates, whereas the smaller-molecule, more physiologically active PF would be more efficient at reducing heavy metal concentrations in the grains. (3) Cd and Pb would exhibit synergistic accumulation and translocation patterns within the maize plant due to their similar ionic properties. The findings aim to provide a scientific basis and precise technical guidance for the safe and efficient management of heavy metal co-contaminated farmland.

2. Materials and Methods

2.1. Study Area

The experimental site was located in Zhehai Town, Huize County, Qujing City, Yunnan Province, China (26°33′8.43″ N, 103°37′31.15″ E). The area is situated in the mountainous plateau of Southwest China and is characterized by a Karst topography with Red soil (Ferralsol in the WRB classification). Zhehai Town features the deepest lead–zinc mine in Asia and serves as the largest basin in the county, covering an area of 55.6 km². The region was historically a major non-ferrous metal mining and smelting hub in Yunnan, and prolonged industrial activities have led to severe heavy metal contamination of the surrounding soils. The baseline physicochemical properties and heavy metal concentrations of the soil are presented in Table 1. According to China’s “Soil Environmental Quality—Risk Control Standard for Soil Contamination of Agricultural Land (Trial)” (GB 15618-2018) [26], the soil Cd concentration exceeded the risk intervention value (2.0 mg·kg^{−1} for 5.5 < soil pH ≤ 6.5) by 2.8-fold, and the Pb concentration exceeded the risk screening value (90 mg·kg^{−1} for 5.5 < soil pH ≤ 6.5) by 3.0-fold. The site was classified as severely co-contaminated, requiring safe utilization or strict control measures.

Table 1. Baseline physicochemical properties and heavy metal concentrations of the soil.

pH	Organic Matter (g·kg ^{−1})	Available N (mg·kg ^{−1})	Available P (mg·kg ^{−1})	Available K (mg·kg ^{−1})	Total Cd (mg·kg ^{−1})	Available Cd (mg·kg ^{−1})	Total Pb (mg·kg ^{−1})	Available Pb (mg·kg ^{−1})
6.14 ± 0.17	24.7 ± 3.3	200.4 ± 33.5	18.9 ± 1.7	402.7 ± 13.0	5.62 ± 0.23	1.64 ± 0.15	271.9 ± 12.2	18.3 ± 3.2

2.2. Materials

The two hybrid maize cultivars used were “Ludan 12” (LD12), from Yunnan Shifeng Seed Co., Ltd. (Kunming, China), and “Shengyu 607” (SY607), from Fuyuan County Shengyu Seed Co., Ltd. (Qujing, China), both widely cultivated in Yunnan. The soil amendments were mineral-source Humic Acid (HA) and Potassium Fulvate (PF), both in solid powdered form, derived from weathered coal (leonardite). The HA was sourced from Shanxi Yicheng Hongye Humic Acid Technology Co., Ltd. (Xinzhou, China), and the PF was from Xinjiang Shuanglong Humic Acid Co., Ltd. (Urumqi, China).

2.3. Experimental Design

The experiment was conducted on a flat area of approximately 4700 m². A randomized complete block design was used with 14 treatments (Table 2) and three replications, for a total of 42 plots. Each plot was approximately 110 m², with maize planted in double rows

(60 cm row spacing, 40 cm plant spacing). Each plot contained 24 rows with 25 plants per row; the four outermost rows served as a border. Three seeds were sown per hole at a depth of 2–3 cm. Seedlings were thinned to one plant per hole at the two-leaf stage, resulting in 600 plants per plot. Before sowing, the HA and PF amendments were weighed according to the experimental design, broadcast evenly onto the surface of each corresponding plot. A compound fertilizer ($N + P_2O_5 + K_2O \geq 45\%$, $N: P_2O_5: K_2O = 15:15:15$; Yunnan Yuntianhua Co., Ltd., Kunming, China) was then applied at $900 \text{ kg} \cdot \text{ha}^{-1}$. Both the amendments and the fertilizer were subsequently incorporated into the 0–20 cm soil layer by rotary tillage. The soil was then covered with mulch film for sowing. Standard field management for irrigation, weeding, and pest control was uniformly applied. At the large-bell-mouth stage, urea (total N $\geq 46\%$; Yunnan Yuntianhua Co., Ltd.) was applied at $600 \text{ kg} \cdot \text{ha}^{-1}$. Sowing occurred on 6 April 2022, and sampling was conducted on 6 October 2022.

Table 2. Experimental treatments and amendment application rates.

Treatment		Amendment	Application Rate ($\text{kg} \cdot \text{ha}^{-1}$)	Maize Cultivar
CK1	CK	/	/	LD12
T1	HA1	HA	1500	
T2	HA2		3000	
T3	HA3		4500	
T4	PF1	PF	1500	
T5	PF2		3000	
T6	PF3		4500	
CK2	CK	/	/	SY607
T7	HA1	HA	1500	
T8	HA2		3000	
T9	HA3		4500	
T10	PF1	PF	1500	
T11	PF2		3000	
T12	PF3		4500	

Note: CK represents the control group; HA1, HA2, and HA3 represent low, medium, and high ($1500, 3000$, and $4500 \text{ kg} \cdot \text{ha}^{-1}$) application rates of humic acid, respectively; PF1, PF2, and PF3 are analogous for potassium fulvate. The same abbreviations are used hereafter.

2.4. Sample Collection and Analysis

At maturity, soil (0–20 cm) and whole maize plant samples were collected from each plot using a five-point ‘S’-shaped sampling pattern. Soil samples were air-dried at room temperature ($25 \pm 5 \text{ }^\circ\text{C}$) in the dark, cleared of debris (stones, plant residues), ground with a mortar, passed through a 0.15 mm nylon sieve, and stored in sealed plastic bags. Harvested maize plants were washed with deionized water and dissected into five parts: roots, stems, leaves, cobs, and grains. Each part was first heat-deactivated at $105 \text{ }^\circ\text{C}$ for 30 min and then oven-dried at $65 \text{ }^\circ\text{C}$ to a constant weight, with the dry mass recorded. Dried samples were pulverized, passed through a 0.15 mm nylon sieve, and stored in sealed bags for analysis.

Soil properties were analyzed as follows. (1) Soil pH was determined potentiometrically using a PHS-3E pH meter (Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China) in a 1:2.5 soil-to-water suspension, following the national standard HJ 962-2018 [27]. (2) Soil organic matter was determined by the potassium dichromate oxidation-external heating method (NY/T 1121.6-2006) [28]. (3) Available nitrogen (N) was measured using the alkaline hydrolysis diffusion method (LY/T 1228-2015) [29]. (4) Available phosphorus (P) was extracted with 0.5 mol L^{-1} sodium bicarbonate and quantified colorimetrically using the molybdenum-antimony method, following HJ 704-2014 [30]. (5) Available potas-

sium (K) was extracted with 1 mol L⁻¹ ammonium acetate (NH₄OAc) and measured by flame photometry (NY/T 889-2004) [31]. (6) For total heavy metal analysis, soil samples were prepared using microwave-assisted acid digestion. The concentrations of total Cd and Pb in the digestates were then determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo Fisher Scientific Inc., Waltham, MA, USA), according to methods DZ/T 0279.5-2016 [32] and DZ/T 0279.3-2016 [33], respectively. (7) Available Cd and Pb were extracted using the diethylenetriaminepentaacetic acid (DTPA) method and subsequently measured by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Thermo Fisher Scientific Inc.), in accordance with HJ 804-2016 [34].

For heavy metal analysis in maize tissues, the samples were first prepared by microwave digestion. The concentrations of Cd and Pb in the digested solutions were then measured by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS; Shimadzu Corporation, Kyoto, Japan) following the Chinese National Food Safety Standards GB 5009.15-2023 (for Cd) [35] and GB 5009.12-2023 (for Pb) [36], respectively.

All chemicals were of analytical grade, and all experiments used deionized water. Glassware was cleaned, soaked overnight in 10% (*v/v*) nitric acid, rinsed with deionized water, and air-dried. Quality assurance and control (QA/QC) were maintained using certified reference materials for soil (GBW07405) and maize (GBW10012), produced by Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences (Langfang, China). To ensure accuracy and precision, 20% of samples were re-analyzed as duplicates, and spike recovery rates were maintained between 90% and 110%. The relative standard deviation for all tests was <10%.

2.5. Data and Statistical Analysis

Data were processed using Microsoft Excel 2019. Analysis of variance (ANOVA) was conducted with IBM SPSS 23.0. Correlation analysis and graphing were performed using OriginPro 2021. Redundancy analysis (RDA) was completed via the Genescloud platform (<https://www.genescloud.cn>, accessed on 1 July 2025). Means were compared using the Least Significant Difference (LSD) test. Data are presented as the mean ± standard deviation (SD), with significance set at $p < 0.05$.

2.5.1. Bioconcentration Factor (BCF)

The bioconcentration factor (BCF) quantifies a crop's ability to accumulate heavy metals from the soil. A higher BCF indicates stronger accumulation capacity. It was calculated as:

$$BCF_i = \frac{C_{plant\ part}}{C_{soil}} \quad (1)$$

where BCF_i is the BCF of heavy metal i ; $C_{plant\ part}$ is the concentration of metal i in a specific plant part (e.g., root, stem, leaf, cob, or grain) (mg·kg⁻¹); and C_{soil} is the total concentration of metal i in the soil (mg·kg⁻¹).

2.5.2. Translocation Factor (TF)

The translocation factor (TF) represents the efficiency of heavy metal transport between plant parts. It was calculated as:

$$TF_i = \frac{C_{pb}}{C_{pa}} \quad (2)$$

where TF_i is the TF of heavy metal i from an originating plant part (a) to a destination plant part (b). Specifically, this study calculated two types of TF: (1) from root to stem, where C_{pa} is the concentration in the root and C_{pb} is the concentration in the stem, and (2) from

stem to grain, where C_{pa} is the concentration in the stem and C_{pb} is the concentration in the grain. C_{pa} and C_{pb} are the concentrations of metal i in the respective plant parts ($\text{mg}\cdot\text{kg}^{-1}$).

3. Results

3.1. Effects of HA and PF on Soil Cd and Pb Concentrations

Application of HA and PF significantly reduced the bioavailability of soil Cd and Pb during the maize growing season but had a minor impact on their total concentrations (Figure 1). At harvest, total Cd and Pb concentrations in all treatments (including controls) showed no significant difference compared to the initial level. This aligns with the principle of in situ immobilization, where amendments stabilize metals rather than remove them.

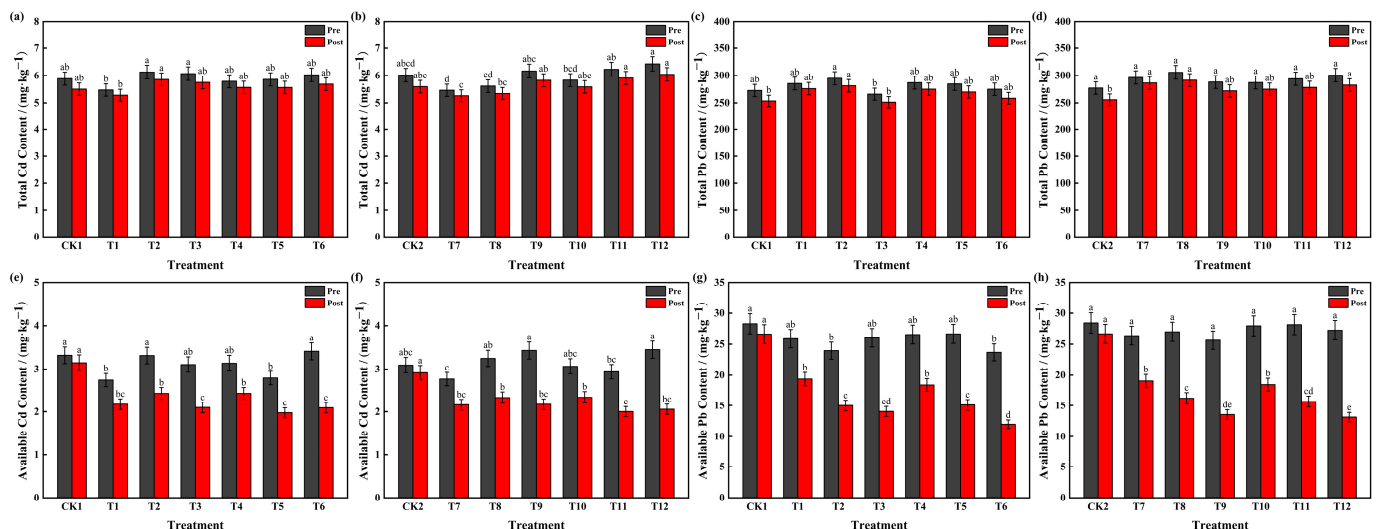


Figure 1. Changes in soil Cd and Pb concentrations before planting and at harvest under different treatments. (a,b) Total soil Cd, (c,d) Total soil Pb, (e,f) Available soil Cd, (g,h) Available soil Pb. Different lowercase letters indicate significant differences ($p < 0.05$) among treatments between the pre-planting and harvest stages.

In contrast, both amendments caused a significant reduction in bioavailable soil Cd and Pb. From pre-planting to harvest, available Cd and Pb in all HA and PF treatments decreased by 20–50%, far exceeding the modest 5–6% decrease in the control groups. This immobilization effect exhibited a clear dose dependency: higher amendment rates led to greater reductions in available Cd and Pb. For instance, at the highest rate ($4500 \text{ kg}\cdot\text{ha}^{-1}$), the PF3 treatments (T6, T12) achieved the greatest reduction in available soil Cd and Pb, by 38.7% and 49.5% (LD12) and 40.4% and 51.8% (SY607), respectively. Similarly, the HA3 treatments (T3, T9) reduced them to the greatest extent by 32.4% and 46.1% (LD12) and 36.7% and 47.2% (SY607), respectively. At equivalent application rates, the immobilization efficacy of PF was slightly superior to that of HA. These results indicate that the functional groups in HA and PF effectively complexed and chelated bioavailable Cd^{2+} and Pb^{2+} ions into more stable forms, such as organically bound species, thereby reducing their availability for plant uptake.

3.2. Effects of HA and PF on Maize Growth, Yield, and Correlation with Soil Heavy Metals

Both HA and PF significantly promoted the growth of both maize cultivars in the co-contaminated soil. Compared to controls (CK1, CK2), all amended treatments showed improved dry weight of all plant parts (roots, stems, leaves, cobs, and grains) and enhanced agronomic traits, including plant height, stem diameter, and root length, which translated into greater biomass and yield (Table 3). The yield-enhancing effects of both amendments

were highly significant and generally dose-dependent. For the LD12 cultivar, HA and PF increased yield by 2.2–26.3% and 15.9–23.0%, respectively. For SY607, the increases were 13.4–32.9% for HA and 14.0–26.1% for PF. However, their performance varied with application rate. At the high application rate (4500 kg·ha⁻¹), HA showed slightly greater yield enhancement potential, with treatment T9 (HA3) achieving the study's highest yield for SY607 (10,650 kg·ha⁻¹, a 32.9% increase). Conversely, at low and medium application rates (1500 and 3000 kg·ha⁻¹), PF's performance was comparable or superior to HA. For example, the yield increase for LD12 with T4 (PF1) was 15.9%, significantly higher than the 2.2% from T1 (HA1). The trends in agronomic traits paralleled yield changes, confirming that both amendments increased yield by optimizing overall plant growth.

To elucidate the relationship between soil heavy metals and maize growth, a redundancy analysis (RDA) was performed. The results (Figure 2) showed that the first two RDA axes explained 77.0% of the total variance in biometric traits (RDA1: 76.3%, RDA2: 0.7%). A permutation test ($p = 0.001$) confirmed the model's high significance, indicating that soil Cd and Pb concentrations were key environmental stressors driving growth differences. The RDA plot illustrates a negative correlation between the heavy metal vectors and all biometric indicators, demonstrating a comprehensive inhibitory effect of heavy metal stress on maize growth. Available Pb, with the longest arrow positioned directly opposite most growth arrows, was identified as the strongest single inhibitory factor. The marginal effects test showed that stem dry weight ($R^2 = 0.51$), stem diameter ($R^2 = 0.50$), and root length ($R^2 = 0.48$) were the most sensitive indicators of stress, while grain yield was less directly affected ($R^2 = 0.19$).

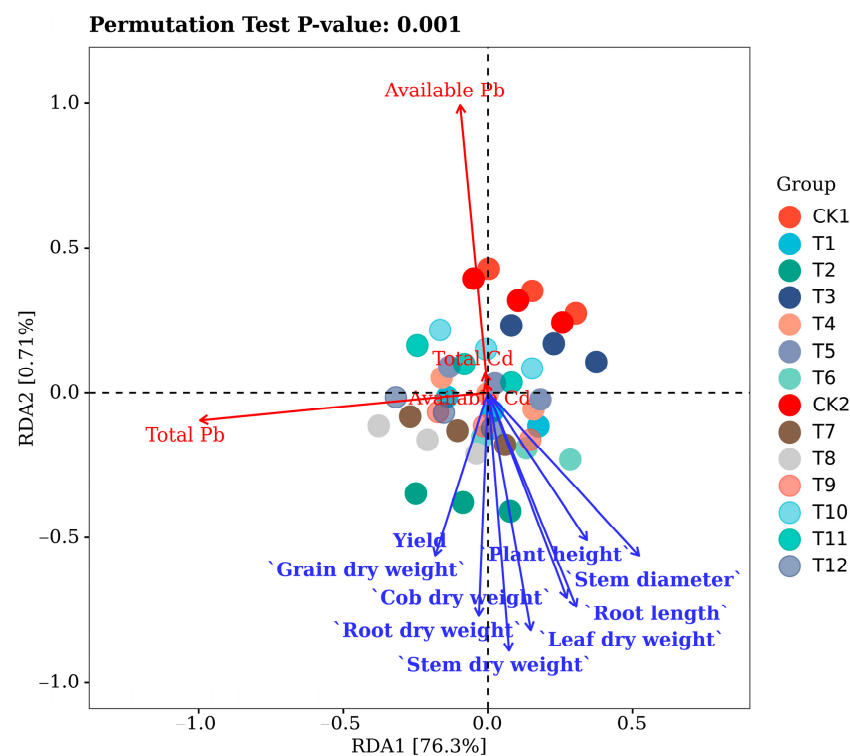


Figure 2. Redundancy analysis (RDA) of maize biometric traits and soil Cd and Pb concentrations. Red arrows represent soil environmental variables (heavy metal concentrations), and blue arrows represent maize biometric traits. The angle between arrows indicates the correlation (acute for positive, obtuse for negative), and arrow length represents the factor's explanatory power. Different colored points represent different treatment groups. The p -value was obtained from a non-parametric permutation test.

Table 3. Biometric traits of maize under different treatments.

Treatment	Root Dry Weight (g·plant ^{−1})	Stem Dry Weight (g·plant ^{−1})	Leaf Dry Weight (g·plant ^{−1})	Cob Dry Weight (g·plant ^{−1})	Grain Dry Weight (g·plant ^{−1})	Yield (kg·ha ^{−1})	Plant Height (cm)	Stem Diameter (mm)	Root Length (cm)
CK1	17.6 ± 1.7 b	53.8 ± 5.3 e	63.5 ± 6.2 c	52.3 ± 5.1 b	169.3 ± 8.3 b	6840 ± 333 b	250.0 ± 5.7 b	19.1 ± 2.5 b	22.3 ± 1.2 b
T1	21.6 ± 2.1 ab	77.3 ± 7.6 d	115.7 ± 11.3 ab	61.8 ± 6.1 ab	173.0 ± 10.0 b	6990 ± 404 b	254.0 ± 9.0 b	22.5 ± 4.2 ab	23.0 ± 2.3 b
T2	22.5 ± 2.2 ab	88.2 ± 8.6 cd	123.3 ± 12.1 ab	66.1 ± 6.5 ab	197.0 ± 8.0 a	7960 ± 324 a	271.3 ± 13.1 ab	23.8 ± 2.0 ab	28.7 ± 0.9 a
T3	23.9 ± 2.3 a	107.3 ± 10.5 bc	132.1 ± 12.9 ab	72.2 ± 7.1 a	213.8 ± 10.9 a	8638 ± 441 a	275.3 ± 10.2 ab	24.6 ± 1.6 ab	29.3 ± 3.4 a
T4	24.6 ± 2.4 a	84.5 ± 8.9 d	113.1 ± 11.1 b	62.3 ± 6.1 ab	196.2 ± 10.3 a	7927 ± 418 a	261.0 ± 6.7 b	23.8 ± 2.0 ab	28.3 ± 1.2 a
T5	25.3 ± 2.5 a	112.3 ± 11.0 ab	118.0 ± 11.6 ab	65.3 ± 6.4 ab	205.7 ± 8.7 a	8310 ± 352 a	275.0 ± 18.8 ab	24.3 ± 3.3 ab	28.7 ± 0.9 a
T6	25.9 ± 2.5 a	128.6 ± 12.6 a	141.4 ± 13.9 a	66.2 ± 6.5 ab	208.3 ± 11.9 a	8415 ± 480 a	294.3 ± 18.5 a	26.8 ± 1.8 a	29.7 ± 1.2 a
Average	23.1	93.1	115.3	63.8	194.8	7869	268.7	23.5	27.1
Coefficient of Variation	11.3%	24.8%	20.0%	8.8%	8.2%	8.2%	5.2%	9.3%	10.6%
CK2	18.4 ± 1.8 c	55.2 ± 5.4 d	77.8 ± 7.6 d	62.3 ± 6.1 b	198.3 ± 11.1 c	8011 ± 450 c	251.0 ± 10.7 b	22.2 ± 4.4 a	24.0 ± 2.4 c
T7	19.0 ± 1.9 c	65.0 ± 6.4 cd	87.1 ± 8.5 cd	63.5 ± 6.2 ab	224.9 ± 9.7 b	9086 ± 393 b	253.0 ± 48.1 b	22.8 ± 2.1 a	25.3 ± 2.9 c
T8	27.8 ± 2.7 b	83.9 ± 8.2 bc	109.0 ± 10.7 bc	72.6 ± 7.1 ab	228.9 ± 1.7 b	9249 ± 70 b	276.3 ± 22.7 ab	24.3 ± 3.3 a	26.0 ± 0.8 c
T9	28.0 ± 2.7 b	93.9 ± 9.2 b	159.8 ± 15.7 a	76.9 ± 7.5 ab	263.6 ± 8.0 a	10,650 ± 322 a	305.0 ± 15.6 ab	25.5 ± 0.3 a	30.3 ± 0.9 ab
T10	28.9 ± 2.8 b	118.9 ± 11.7 a	119.9 ± 11.7 b	70.5 ± 6.9 ab	226.0 ± 7.6 b	9130 ± 307 b	261.0 ± 6.7 b	23.8 ± 1.9 a	25.7 ± 2.5 c
T11	34.0 ± 3.3 ab	132.2 ± 13.0 a	122.6 ± 12.0 b	75.1 ± 7.4 ab	244.7 ± 11.0 ab	9887 ± 446 ab	276.3 ± 22.7 ab	24.5 ± 4.3 a	27.5 ± 0.4 bc
T12	39.0 ± 3.8 a	138.4 ± 13.6 a	124.8 ± 12.2 b	80.0 ± 7.8 a	250.1 ± 9.0 a	10,104 ± 363 a	323.0 ± 9.2 a	27.1 ± 4.2 a	31.7 ± 1.2 a
Average	27.9	98.2	114.4	71.6	233.8	9445	278.0	24.3	27.2
Coefficient of Variation	24.7%	30.7%	21.9%	8.6%	8.4%	8.4%	9.0%	6.3%	9.6%

Note: For each cultivar, different lowercase letters within the same column indicate significant differences ($p < 0.05$) in the corresponding biometric trait among treatments.

The spatial distribution of samples in the RDA plot illustrates the remedial efficacy of HA and PF. Control samples (CK1, CK2) clustered in the first and second quadrants, closer to the vectors for stress factors like available Pb and total Cd, reflecting significant growth inhibition. In contrast, samples from HA and PF treatments, especially at high doses, migrated to the third and fourth quadrants. These samples clustered with positive growth indicators (e.g., yield, plant height) and were positioned far from the heavy metal stress vectors. This distinct spatial separation demonstrates that the amendments mitigated phytotoxicity, shifting the maize growth trajectory away from a state of stress, which aligns with the observed increases in biomass and yield (Table 2).

3.3. Effects of HA and PF on Cd and Pb Concentrations in Maize Tissues

Cd and Pb accumulation revealed distinct tissue-specific accumulation patterns, with a consistent concentration pattern across all treatments and cultivars: root > leaf > stem > cob > grain (Figure 3). As the primary barrier, roots accumulated the highest concentrations of Cd ($3.13\text{--}6.36\text{ mg}\cdot\text{kg}^{-1}$) and Pb ($3.96\text{--}12.60\text{ mg}\cdot\text{kg}^{-1}$). Conversely, the grains, the economic product, had the lowest concentrations (Cd: $0.02\text{--}0.11\text{ mg}\cdot\text{kg}^{-1}$; Pb: $0.17\text{--}0.42\text{ mg}\cdot\text{kg}^{-1}$), indicating a physiological mechanism that sequesters heavy metals in the roots and vegetative organs.

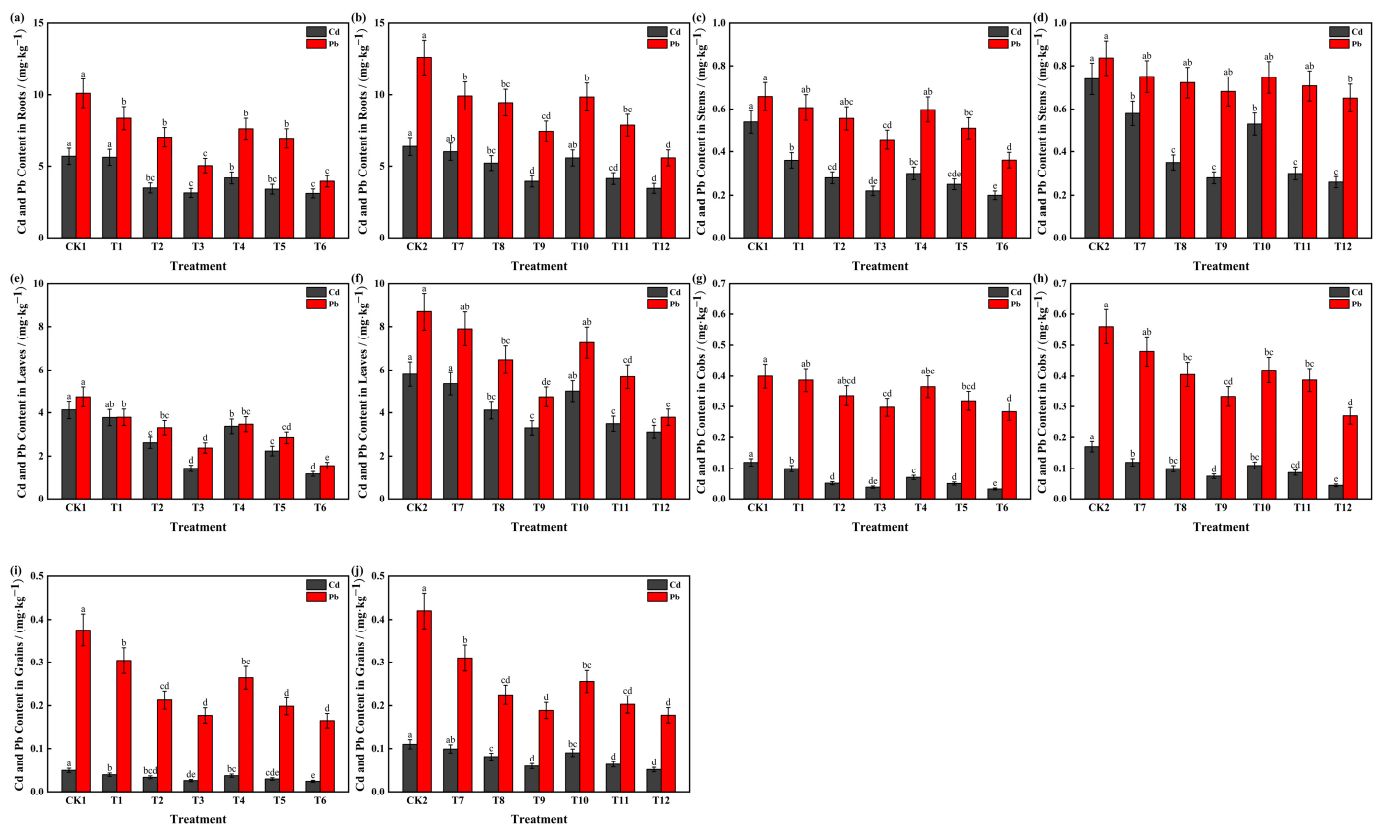


Figure 3. Cd and Pb concentrations in different maize plant tissues under various treatments. (a,b) Concentrations in Roots; (c,d) Concentrations in Stems; (e,f) Concentrations in Leaves; (g,h) Concentrations in Cobs; (i,j) Concentrations in Grains. Different lowercase letters indicate significant differences ($p < 0.05$) in grain Cd and Pb concentrations among treatments.

Application of HA and PF significantly reduced Cd and Pb concentrations in all maize tissues in a dose-dependent manner. For grain safety, as amendment rates increased from 1500 to $4500\text{ kg}\cdot\text{ha}^{-1}$, the reduction in grain Cd concentration for LD12 rose from 20.4% (HA1) to 47.8% (HA3), and the Pb reduction rose from 19.0% (HA1) to 52.7% (HA3). PF treatments showed a similar trend. At equivalent application rates, PF was generally more

effective than HA at reducing grain metal concentrations. For example, in SY607 at the highest application rate, the reductions in grain Cd and Pb for T12 (PF3) were 53.6% and 57.6%, respectively, both higher than for T9 (HA3) (46.4% and 55.0%).

From a food safety perspective, grains from all treatments met the national feed safety standard (GB 13078-2017: $\text{Cd} \leq 1.0 \text{ mg} \cdot \text{kg}^{-1}$, $\text{Pb} \leq 10.0 \text{ mg} \cdot \text{kg}^{-1}$) [37]. However, the grain Cd in the CK2 treatment ($0.11 \text{ mg} \cdot \text{kg}^{-1}$) and the grain Pb in all but the high-dose treatments (T3, T9, T6, T12) exceeded the national food safety standard (GB 2762-2022: $\text{Cd} \leq 0.1 \text{ mg} \cdot \text{kg}^{-1}$, $\text{Pb} \leq 0.2 \text{ mg} \cdot \text{kg}^{-1}$) [38]. This indicates that high-dose HA and PF treatments effectively controlled heavy metal risks to within food-grade thresholds, demonstrating the necessity of immobilization for ensuring food security. It also implies that on severely contaminated soil, the intended use of crops (food vs. feed) must be determined by rigorous testing.

3.4. Effects of HA and PF on Cd and Pb Bioconcentration in Maize

The bioconcentration factor (BCF) for Cd (BCF_{Cd} : 0.004–1.137) was substantially higher than for Pb (BCF_{Pb} : 0.001–0.049) across all tissues, indicating that Cd had far greater bioavailability and mobility than Pb in this soil (Figure 4). The distribution of BCF values among tissues mirrored the concentration pattern (root > leaf > stem > cob > grain), confirming the root system as the primary site of accumulation.

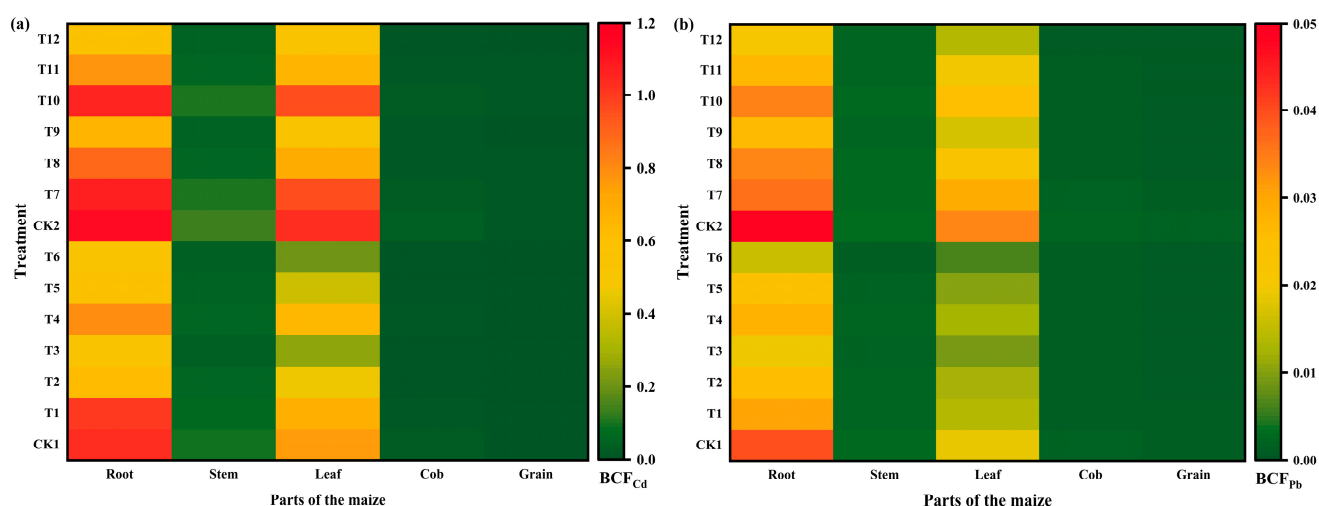


Figure 4. Bioconcentration factors (BCF) of Cd and Pb in different maize plant tissues under various treatments. (a) BCF_{Cd} , (b) BCF_{Pb} .

Both HA and PF significantly reduced BCF values in all maize tissues, particularly the grains, with the effect positively correlating with the application rate. For the SY607 cultivar, for example, increasing the application rate from 1500 to $4500 \text{ kg} \cdot \text{ha}^{-1}$ increased the reduction in grain BCF_{Cd} from 9.9% (HA1) to 50.4% (HA3) and in grain BCF_{Pb} from 31.4% (HA1) to 59.3% (HA3), compared to the control. This demonstrates at a systemic level that both amendments obstructed initial root uptake, likely by reducing soil bioavailability, thereby lowering overall plant accumulation.

At equivalent application rates, potassium fulvate (PF) was slightly more effective than humic acid (HA) in reducing the grain BCF. For instance, compared to the controls, the highest PF application rate (PF3) achieved greater reductions in grain BCF for both Cd (53.4–55.5%) and Pb (55.5–60.1%) than the highest HA application rate (HA3) (Cd: 49.5–50.4%; Pb: 53.6–59.3%). This suggests that PF is more efficient at inhibiting heavy metal uptake by maize roots.

3.5. Effects of HA and PF on Cd and Pb Translocation in Maize

The translocation factor (TF) revealed a consistent pattern of elemental migration within the plant: Stem-to-Leaf > Cob-to-Grain > Stem-to-Cob > Root-to-Stem > Root-to-Grain (Figure 5). The stem-to-leaf TF was the highest (TF_{Cd} : 6.02–12.23; TF_{Pb} : 4.42–10.73), indicating that leaves are a primary sink for metals transported from the stem, likely driven by transpiration. In contrast, the root-to-stem TF was generally low, confirming that the maize root system acts as a strong barrier, restricting long-distance transport to aerial parts.

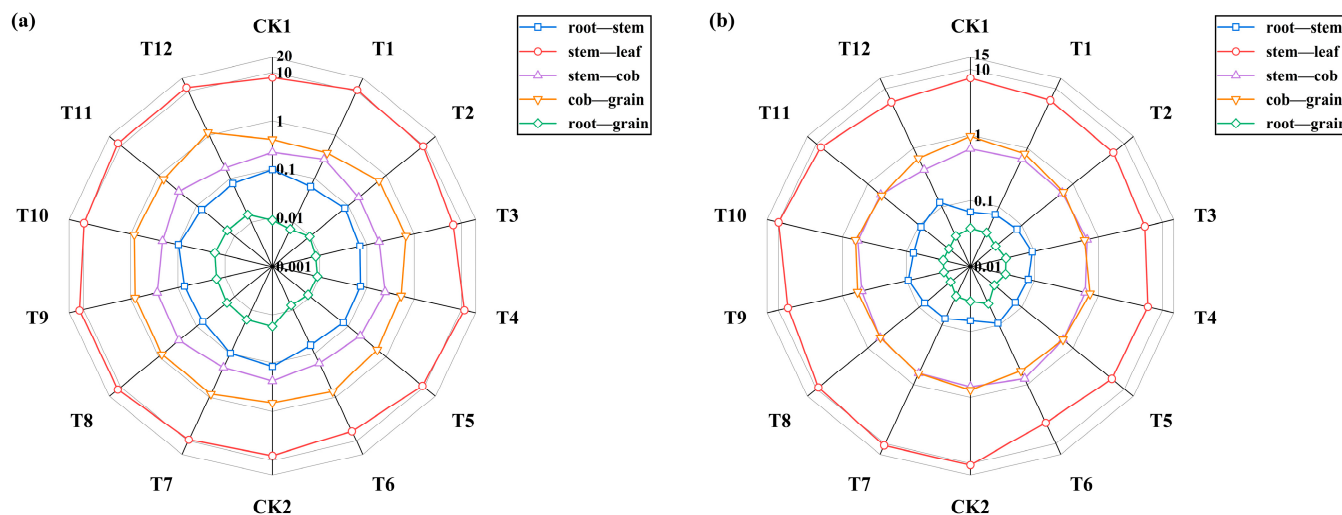


Figure 5. Translocation factors (TF) of Cd and Pb between different maize plant tissues under various treatments. (a) TF_{Cd} , (b) TF_{Pb} .

Application of HA and PF decreased TF values for all translocation pathways. This suggests a dual-action mechanism: the amendments not only inhibit root uptake (lower BCF) but also hinder internal redistribution and upward migration (lower TF). This comprehensive inhibition, from uptake to translocation, is key to ensuring the safety of edible parts. By reducing the critical root-to-stem TF, the amendments effectively reinforce the root's “firewall,” decreasing the total amount of heavy metals entering the shoots and ultimately lowering grain concentrations. The overall trend indicates that the amendments enhanced heavy metal compartmentalization in the roots, safeguarding the final agricultural product.

3.6. Synergistic Accumulation and Translocation of Cd and Pb in Maize

To elucidate the co-migration patterns of Cd and Pb, Pearson correlation analysis was performed. The results revealed a significant to highly significant positive correlation between Cd and Pb concentrations in all maize tissues, from roots to grains (Figure 6). This consistent co-distribution pattern across the entire plant indicates a prominent synergistic effect in the uptake, translocation, and compartmentalization of these two metals under co-contamination stress. This finding strongly suggests that the chemically similar Cd^{2+} and Pb^{2+} ions may share common transmembrane transport pathways, such as non-selective cation channels or transporters for essential elements like Ca^{2+} and Zn^{2+} , leading to their concurrent movement within the plant.

This synergistic effect highlights the complex biological consequences of co-contamination and underscores the broad-spectrum efficacy of the humic amendments. Because Cd and Pb exhibit synergy in uptake and translocation, HA and PF can simultaneously block their common entry pathways by reducing bioavailability at the soil-root interface or by influencing the activity of non-specific uptake channels on the root membrane. This provides a compelling physiological explanation for why a single type of amendment

can produce a universal remedial effect on Cd and Pb co-contamination and offers a basis for developing efficient immobilization solutions for multi-metal contaminated farmland.

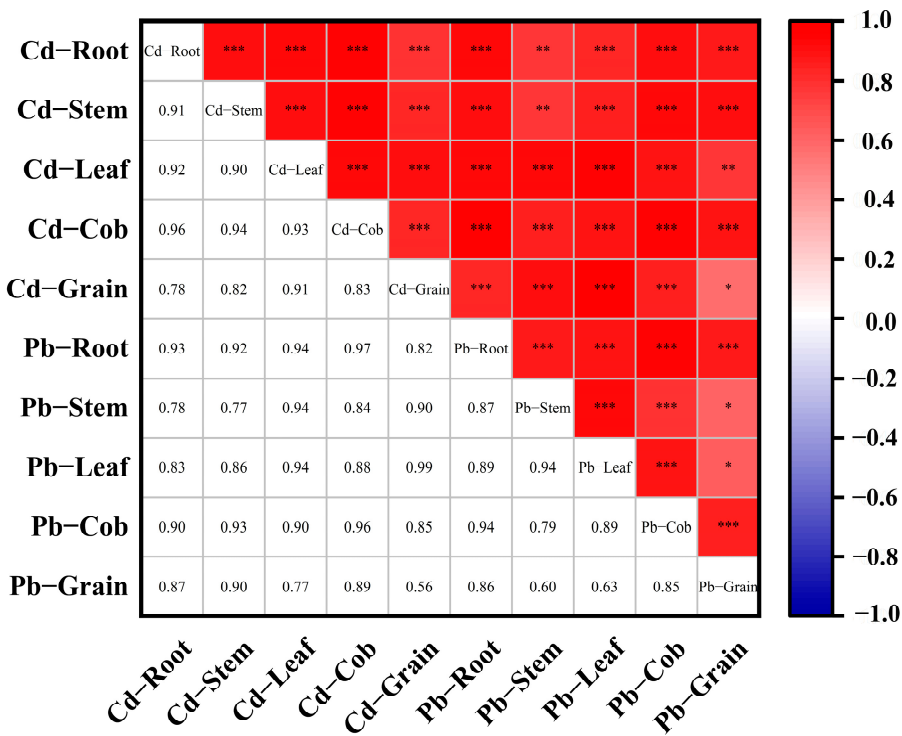


Figure 6. Pearson correlation heatmap of Cd and Pb concentrations in different maize plant tissues. The color and intensity of the squares represent the correlation coefficient. *, **, and *** indicate significance at $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively.

4. Discussion

This field-scale study systematically demonstrates that applying HA and PF is an effective strategy for achieving safe maize production in a Cd- and Pb-co-contaminated Red soil. Both amendments reduced heavy metal contents in maize grains while increasing crop yield, offering the dual benefits of risk reduction and yield enhancement. This provides important practical guidance for managing heavy metal contamination in agricultural lands globally.

4.1. Immobilization Mechanisms and Efficacy Differences in HA and PF

The immobilization effect of HA and PF on soil Cd and Pb is primarily due to their abundant oxygen-containing functional groups (e.g., carboxyl, phenolic hydroxyl) [39]. The core mechanisms include: (1) Surface complexation and chelation, where functional groups form stable, low-solubility organo-metallic complexes with metal ions, thereby reducing free metal ion concentrations in the soil solution [11]; (2) Ion exchange, where H^+ on functional groups is exchanged for Cd^{2+} and Pb^{2+} , binding them to the humic molecules [16]; and (3) Indirect precipitation, as HA and PF can increase soil pH and cation exchange capacity (CEC), creating favorable conditions for metal precipitation as hydroxides or carbonates [12].

This study found that at equivalent application rates, PF was slightly more effective in reducing grain metal concentrations, whereas high-dose HA ($4500\text{ kg}\cdot\text{ha}^{-1}$) performed better for yield enhancement. This functional differentiation likely stems from differences in their molecular structure and physiological activity [40,41]. HA, with its large molecular weight and complex structure, excels at forming stable macromolecular complexes, achieving “physical encapsulation” and long-term chemical fixation of heavy metals [42].

In contrast, PF has a smaller molecular weight and a higher density of functional groups, providing more active sites per unit mass and thus a stronger metal-binding capacity, which aligns with previous findings [43,44]. Furthermore, as a potent biostimulant, PF can more directly promote root growth, improve nutrient uptake, and enhance plant stress resistance, explaining its superior detoxification effects [45]. Conversely, HA is an excellent soil conditioner. At high application rates, its ability to improve soil aggregation and water and nutrient retention is more pronounced, likely explaining why its yield surpassed that of PF at the highest application rate [46,47]. This is supported by our RDA (Figure 2), where high-dose HA treatments showed the greatest deviation along the yield vector. Beyond these efficacy differences, a critical consideration for practical application is the economic feasibility of the amendment rates. The higher application rates tested (3000 and $4500 \text{ kg} \cdot \text{ha}^{-1}$) represent a substantial financial investment that could be a barrier to widespread adoption. Nonetheless, these rates should be interpreted within the context of the study's objectives and the site's severe contamination, which necessitated evaluating a wide dose range to establish a comprehensive dose–response relationship. Importantly, our results demonstrate that even the lowest application rate ($1500 \text{ kg} \cdot \text{ha}^{-1}$) yielded significant positive effects, substantially reducing heavy metal accumulation while increasing yield. In many instances, this low-dose treatment was sufficient to bring grain contamination levels close to the stringent food safety limits, offering a viable and more cost-effective option for moderately contaminated soils. The high-dose treatments, therefore, should not be viewed as a standard recommendation but rather as an effective solution for high-risk scenarios where ensuring food safety is the paramount objective, or in situations where agricultural subsidies support intensive remediation efforts. Ultimately, this study provides a practical framework, allowing for a differentiated application strategy where the choice of amendment and its rate can be tailored to the specific contamination level, production goals, and economic constraints of a given agricultural system.

4.2. Accumulation and Translocation Mechanisms of Heavy Metals in Maize

Our results clearly show that the maize root system is a key barrier restricting Cd and Pb translocation to aerial parts, consistent with the common “root sequestration” mechanism in plants [4]. After root uptake, a large fraction of heavy metals is compartmentalized in cell walls and vacuoles, limiting their long-distance transport via the xylem [48,49]. The application of HA and PF strengthened this barrier, not only by reducing total root uptake through source-level immobilization but also potentially by inhibiting the loading of metals into the xylem [50,51].

The synergistic accumulation of Cd and Pb in maize organs, a critical finding of this study, provides strong evidence that the two metal ions may share uptake or transport pathways, such as non-specific cation channels or transporters for essential elements (Ca^{2+} , Zn^{2+}) [52–54]. The comprehensive soil improvements from HA and PF (e.g., changes in pH, organic matter, nutrient status) could have simultaneously affected the activity of these shared channels or substrate competition, leading to synchronous inhibition of uptake and translocation for both metals [55,56]. The discovery of this synergistic mechanism provides a compelling physiological explanation for why a single humic-based amendment can produce a broad-spectrum remedial effect on Cd and Pb co-contamination.

4.3. Future Perspectives

Although this study demonstrates positive results, in situ immobilization does not remove heavy metals from the soil but converts them into less active forms [57,58]. The long-term stability of these immobilization metals, particularly under future environmental stresses like climate change or soil acidification, remains a key question requiring continu-

ous monitoring. Future research should focus on: (1) conducting long-term field trials to evaluate the durability of immobilization and its impacts on soil microbial communities; (2) developing novel composite materials (e.g., combining humic acids with biochar, clay minerals, or beneficial microbes) to enhance immobilization efficiency and stability through synergistic effects; and (3) integrating multi-omics technologies (e.g., transcriptomics, metabolomics) to investigate the molecular mechanisms by which HA and PF regulate heavy metal translocation, providing a theoretical basis for breeding low-accumulation crop varieties.

5. Conclusions

This study confirmed that applying humic acid (HA) and potassium fulvate (PF) is an effective strategy for achieving both safe utilization and yield enhancement in Cd- and Pb-co-contaminated farmland. Mechanistically, both amendments acted by reducing the bioavailability of Cd and Pb at the source. Within the plant, they exerted a dual effect by lowering the root BCF and inhibiting the TF to aerial parts, achieving comprehensive control over heavy metal uptake and transport. This study also revealed a high degree of synergistic accumulation and translocation between Cd and Pb in maize, providing a key physiological explanation for the ability of HA and PF to simultaneously immobilize both metals. In terms of efficacy, the “yield-increasing and pollution-reducing” effects of both amendments were dose-dependent. Comparatively, PF was more effective at reducing grain heavy metal concentrations, while high-dose HA showed greater potential for boosting yield. In conclusion, this research thus delineates a differentiated application strategy for the precise remediation of co-contaminated farmland: potassium fulvate (PF) should be prioritized when ensuring food safety is the primary objective in high-risk areas. Conversely, in soils with low-to-moderate risk where maximizing crop yield is the main goal, high-dose humic acid (HA) is the optimal choice.

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