

Article

Effects of Fertilizers and Conditioners on Chromium Uptake of Maize in Chromium-Polluted Farmland

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Abstract: Using agronomic measures to remediate heavy metal chromium (Cr) on farmland is the main measure to achieve the safe utilization of crops. This study was conducted under field trial conditions using locally formulated fertilizers (urea–ammonium phosphate–potassium chloride) as the control. Different fertilizer-type treatments such as ammonium sulfite, calcium magnesium phosphate, and diammonium phosphate were set up. Biochar and soil conditioner PX5B were chosen to compare the impacts of each to study the effects of different fertilizer types on maize yield, Cr content in each part, the bioconcentration factor, the translocation factor, and the available content of Cr in the soil. The results show that, compared with the formulated fertilizer, all treatments improved pH and soil organic matter and reduced the effective state of Cr content in the soil by 15.05% to 42.66%. The Cr content of maize grains under biochar and soil conditioner PX5B treatments were $0.80 \text{ mg}\cdot\text{kg}^{-1}$ and $0.88 \text{ mg}\cdot\text{kg}^{-1}$ with a 39.95% and 33.83% reduction, respectively, whereas the Cr content of maize grains under various fertilizer treatments was in the range of $0.82\text{--}1.32 \text{ mg}\cdot\text{kg}^{-1}$ with a 0.75%~38.19% reduction, respectively. Among the different fertilizer treatments, urea–calcium magnesium phosphate–potassium chloride, urea–diammonium phosphate–potassium chloride, ammonium sulfite–calcium magnesium phosphate–potassium chloride, and ammonium sulfite and urea–calcium magnesium phosphate–potassium chloride treatments reduced the Cr content of maize grains to within the range of the national food safety standard of China ($1.0 \text{ mg}\cdot\text{kg}^{-1}$). The best reductions in the effective state Cr content of the soil and the Cr content of maize grains were achieved by ammonium sulfite–calcium magnesium phosphate–potassium chloride treatment, which was able to achieve similar reductions to the two conditioners. It also had a reduction effect on the Cr content of maize roots and straws, the aboveground bioconcentration factor (BCF), and the primary translocation factor (PTF). Therefore, the combination of ammonium sulfite and calcium magnesium phosphate is the best fertilizer combination to block the absorption of Cr by maize and has some implications for the fertilization of farmland under acidic soil conditions of Cr contamination.



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1. Introduction

Chromium (Cr) is considered one of the most toxic heavy metals found naturally [1]. It is influenced by both natural and human causes and is directly tied to the parent material that forms the soil, the kind of soil, the geological topography, the pH, the climate, and the type of land use [2]. The Cr pollution in the environment is mainly due to the emission of waste from industrial production—for example, metallurgical, minerals, steel, metal plating, textile dyeing, and other industrial fields [3]. There are several different valence forms of Cr in soil, but Cr (III) and Cr (VI) are the most prevalent and stable states in the environment [4]. Cr (III) exists in nature mainly in the form of Cr_2O_3 and tends to produce $\text{Cr}(\text{OH})_3$ precipitation under alkaline to slightly acidic conditions in soil [5,6]. Cr (III) is a trace element that is necessary for humans and plays a vital part in glucose, protein, and

fat metabolism [1,7]. Cr (VI) usually presents in the form of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, which are easily transported and highly soluble in water [8]. Cr (VI) is significantly more toxic than Cr (III) because of its high water solubility and membrane permeability [9,10], and its toxicity is attributed to highly unstable Cr (V/IV) producing reactive oxygen species within cells [8,11]. Cr is not an essential element for plants, and its presence affects plant growth and development [12], such as inhibition of seed germination, inhibition of cell development, pigment degradation, and alteration of antioxidant enzyme activity [13,14], and the effect of Cr (VI) on plants is greater than that of Cr (III) [15]. When plants are grown in Cr-contaminated areas, Cr is taken up by the plant and accumulates in the edible parts, thus entering the food chain [16,17]. Cr (VI) is a potential carcinogen for humans [18]. It can also cause a variety of diseases such as asthma, neurological and cardiovascular diseases, and organ failure when it enters the body through the food chain [19].

Fertilizer application as an agricultural activity is an essential part of agricultural production, but it has a certain impact on heavy metals in the soil [20]. It has become an agronomic measure with the potential for heavy metal remediation in recent years due to its simple operation, low cost, and easy promotion in large fields [21,22]. Fertilizers not only increase the nutrients in the soil to improve crop yield and quality but also change the form of heavy metals in the soil and thus affect the uptake of heavy metals by plants. Fertilizers not only increase the nutrient elements in the soil to improve crop yield and quality but also change the morphology of heavy metals in the soil, which in turn affects the uptake of heavy metals by plants [23]. For example, urea can significantly reduce the water soluble plus exchangeable fraction of Cu, Cr, and Ni and increase those in Fe–Mn oxide-bound fractions. KH_2PO_4 can reduce the soluble plus exchangeable fraction and carbonate-bound fractions of Cu, Cr, and Ni and increase Cu and Ni in the residual fraction and Cr in the Fe–Mn oxide-bound fraction [24]. Ammonium iron (II) sulphate $((\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2)$ reduces Cr (VI) to Cr (III) and forms a precipitate, decreasing the availability of Cr in the soil [25]. However, different types of fertilizers have different remediation effects on heavy metals as a result of the different elements they contain [26]. Nitrogen fertilizer affects the activity of heavy metals such as Cd, Pb, and Zn mainly through inter-root acidification and alkalization of nitrate and ammonium nitrogen [27,28], and its transport affects the physical and chemical environment of soil, the iron film on the root surface, and the subcellular structure of various organs of the crop. Therefore, the application of nitrogen fertilizers mitigates the toxic effects of heavy metals such as Cr, Cd, Cu, and Ni on plants [29,30]. Fertilizers containing phosphorus have a solidifying effect on Cd, Pb, and Cu in the soil by altering the soil environment, such as pH, cation exchange capacity, and organic matter [31,32], as well as influencing the uptake and transport of heavy metals (Cd, Pb, and As) by plants through the regulation of plant physiological metabolism [33]. Some organic fertilizers and restoration fertilizers can also be very effective in reducing the effectiveness of heavy metals in the soil and reducing the accumulation of heavy metals by plants. Yi et al. found that seaweed organic fertilizer reduced Cr bioavailability, and in combination with apatite, biochar (1:0.5:1.5) resulted in a 65.7% decrease in Cr content in maize grain [34]. However, it has also been shown that the long-term application of nitrogen and phosphorus fertilizers can, on the contrary, increase the biological effectiveness of heavy metals [35]. The effects of different nitrogen and phosphorus fertilizers on heavy metals have been studied in different ways, which may be related to different fertilizer application rates, crop types, or soil environmental conditions.

Soil conditioners have been widely used in recent years due to their effectiveness in the remediation of heavy metals in agricultural fields [36]. For example, sewage sludge biochar tubule can significantly decrease the total Cr and Pb content in contaminated soil by adsorption, ion exchange, complexation, and precipitation, which was concluded from a characteristic analysis [37]. Nanoscale zero-valent iron (nZVI) and modified nZVIs can reduce Cr (VI) to Cr (III) in contaminated soils, which in turn generates $\text{Cr}(\text{OH})_3$ precipitate, thereby reducing its bioavailability and plant bioaccumulation [38,39]. It has also been found that the use of some soil conditioners may cause some damage to the nutrients,

structure, and microbial community of the soil [40]; add additional costs; and affect whether they can be used all year. Therefore, it is necessary to study the effect of fertilization on heavy metals [41].

In this research, maize was used as the planting crop, urea and ammonium sulfite were selected as nitrogen fertilizers, and ammonium phosphate, calcium–magnesium phosphate, and diammonium phosphate were selected as phosphorus fertilizers. Different fertilizer combinations were set up and two soil conditioners (biochar and soil conditioner PX5B) were selected that were more effective in repairing heavy metals in previous trials in this laboratory to carry out an effect comparison to investigate the effects of different fertilizer combinations on maize yield, characteristics of Cr accumulation in various parts of maize, soil effective state Cr content, and physicochemical properties under mild to moderate Cr-contaminated soils and to screen for suitable fertilization measures for local Cr-contaminated soils.

2. Materials and Methods

2.1. Study Area Overview

The test site was located in a village of Jianxi Town, Mingguang City, Anhui Province, China, which has a warm–temperate continental monsoon climate with four distinct seasons, rain and heat, enough light, and an average annual temperature of 15.2 °C. Rice, maize, and wheat are the main crops grown locally. The crop in the experiment was maize, which was previously planted as rice. The soil type is volcanic ash soil (also known as Guan Shan chicken dung soil), which has a medium soil fertility level. Before the test plot was divided, a background soil sample of one mixed soil sample from 0 to 20 cm was obtained using the five-point sampling method to determine the background values of each index in the test site. The physicochemical properties and total Cr content of the soil in the test site are shown in Table 1.

Table 1. Physicochemical properties and total Cr content of soil.

Detection Indicators	Concentration	Unit
pH	5.23	/
Soil organic matter	18.81	g·kg ⁻¹
Total nitrogen (N)	1.31	g·kg ⁻¹
Hydrolytic nitrogen (N)	154.82	mg·kg ⁻¹
Available phosphorus (P)	10.57	mg·kg ⁻¹
Available potassium (K)	164.00	mg·kg ⁻¹
Total Cr	255.73	mg·kg ⁻¹

2.2. Experimental Materials and Design

The field trial was conducted in Ming Guang City in 2021. The test maize variety was Denghai 605, which was purchased at the local agricultural market. The test conditioner included biochar and soil conditioner PX5B. The biochar was purchased from Woda Environmental Protection Material, and the soil conditioner PX5B was purchased from Gefeng Environmental Protection Technology (GFTEM) and was mainly composed of nanomaterials, clay minerals, and ferrous sulphate. Fertilizers for testing included locally formulated fertilizers (18-12-15), urea (N > 46%), ammonium sulfite (N > 24%), calcium magnesium phosphate (P₂O₅ > 12%), diammonium phosphate (N > 18%, P₂O₅ > 46%), and potassium chloride (K₂O > 60%). Locally formulated fertilizers (18-12-15) were purchased and provided by local farmers, and the rest of the fertilizers were purchased from GFTEM.

Trial sites were divided into a zone of additional conditioner application (Zone D), a zone of different fertilizer types (Zone Y), and a control group (CK), for a total of 8 treatments. Fertilizers used in Zone D were the same as for CK, and only nitrogen and phosphorus fertilizers were changed in Zone Y. All treatments were potassium chloride. Treatment-specific fertilizer and conditioner applications and dosages are shown in Table 2. The

fertilizer dosage is the discounted pure amount of each element, and the conditioning agent dosage is the actual amount of each conditioner.

Table 2. Specific application rates of fertilizers and conditioners for each treatment.

Treatment	Application Materials		Material Usage (kg·hm ⁻²)			
	Fertilizer	Conditioner	N	P	K	Conditioner
CK	Formulated fertilizer (urea–ammonium phosphate–potassium chloride)	/				/
D1	Formulated fertilizer (urea–ammonium phosphate–potassium chloride)	Biochar				4500.00
D2	Formulated fertilizer (urea–ammonium phosphate–potassium chloride)	Conditioner PX5B				4500.00
Y1	Urea–calcium magnesium phosphate–potassium chloride	/	81.00	54.00	67.50	/
Y2	Urea–diammonium phosphate–potassium chloride	/				/
Y3	Urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride	/				/
Y4	Ammonium sulfite–calcium magnesium phosphate–potassium chloride	/				/
Y5	Ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride	/				/

Note: In the table, “calcium magnesium phosphate, diammonium phosphate” indicates that calcium magnesium phosphate and diammonium phosphate are applied in a ratio of 1:1; “ammonium sulfite, urea” indicates that ammonium sulfite and urea are applied in a ratio of 1:1.

Each treatment plot was set up with three replications, and the plot experimental design was randomized in groups, with a total of 24 treatment plots with an area of 24 m² (4 m × 6 m), surrounded by a small trench of about 20 cm. Conditioner was applied one week before planting, turned into the soil after application, and mixed well. Fertilizer was applied as a base fertilizer one day after the balance of the conditioner application. Maize was sown by hole sowing with 130 holes per plot. Urea 225 kg·hm⁻² was applied to each plot as a top-dressing when the maize reached the trumpet stage. Irrigation was carried out with clean water sources to cut off the source of pollution, and the maize was sampled for harvest when it was ripe.

2.3. Sample Collection and Determination

When samples were harvested, whole maize samples (including roots, straws, and grains) and soil samples were collected in batches from each plot. The plant samples were separated according to the roots, straws, and grains, and the roots, straws, and grains were first washed with tap water, then with deionized water, followed by killing in an oven at 105 °C for 30 min and drying at 40 °C to constant weight. The dried plant samples were crushed, sieved, and put in dry self-sealing bags for the determination of Cr content. The Cr extraction method from plants was as follows: 0.3~0.5 g of plant sample was weighed in a polytetrafluoroethylene ablation tube; 4 mL of HNO₃, 2 mL of H₂O₂, and 2 mL of deionized water were added; and the sample was left for 2 h. It was then placed in the microwave ablation apparatus for ablation. The digestion procedure involved gradually increasing the temperature to 180 °C for the first 20 min, then holding the temperature at 180 °C for 20 min, and then reducing the temperature to room temperature during the last 25 min. After completion of the ablation, it was placed on a thermostatic hot plate at 160 °C to drive the acid until nearly dry, then transferred to a 25 mL volumetric flask to fix the volume, and finally, inductively coupled plasma emission spectroscopy was used for the determination. The soil was dried naturally to remove debris, ground, and individually passed through 2 mm (10 mesh) and 0.149 mm (100 mesh) nylon mesh sieves for analytical determination. The physical and chemical properties of the soil were determined by referring to the Soil and Agrochemical Chemistry Analysis [42]. The method for the determination of Cr in soil was as follows: 5.00 g (passed through a 2 mm sieve) of soil sample were weighed and placed in a conical flask, and 50 mL of DTPA (0.005 mol·L⁻¹ DTPA–0.1 mol·L⁻¹ TEA–0.01 mol·L⁻¹ CaCl₂) leaching agent were added. Then, the lid

was covered and it was put into a reciprocating oscillator to oscillate 180 times per minute for 2 h before being removed for filtration. Finally, inductively coupled plasma emission spectroscopy was used for the determination.

2.4. Statistical Data Analysis

The experimental data were calculated using Microsoft Excel 2016, with Origin 2018 applied for the graphs. Statistical analysis and ANOVA between different treatments were calculated using IBM SPSS Statistics 22.0 software, and the differences mentioned in the text were significant, all referring to $p < 0.05$. The aboveground bioconcentration factor (BCF), primary translocation factor (PTF), and secondary translocation factor (STF) in the upper part of the maize ground were used to characterize the uptake and translocation capacity of maize for Cr.

Relevant indicators were calculated according to the following formulae:

$$\text{BFC} = \text{Cr content in maize aboveground parts (mg}\cdot\text{kg}^{-1}) / \text{soil total Cr (mg}\cdot\text{kg}^{-1}) \quad (1)$$

$$\text{PTF} = \text{Cr content in maize straws (mg}\cdot\text{kg}^{-1}) / \text{Cr content in maize roots (mg}\cdot\text{kg}^{-1}) \quad (2)$$

$$\text{STF} = \text{Cr content in maize grains (mg}\cdot\text{kg}^{-1}) / \text{Cr content in maize straws (mg}\cdot\text{kg}^{-1}) \quad (3)$$

3. Results

3.1. Effect of Fertilizers and Conditioners on Maize Yield

Figure 1 illustrates how several treatments affected the yield of maize, which ranged from 5945.40 to 6800.40 $\text{kg}\cdot\text{hm}^{-2}$. Compared to CK (6511.50 $\text{kg}\cdot\text{hm}^{-2}$), maize yield was enhanced to 6733.35 $\text{kg}\cdot\text{hm}^{-2}$ under the D2 treatment, with an increase of 2.5%, whereas the D1 treatment led to a decrease in maize yield but with no significant difference.

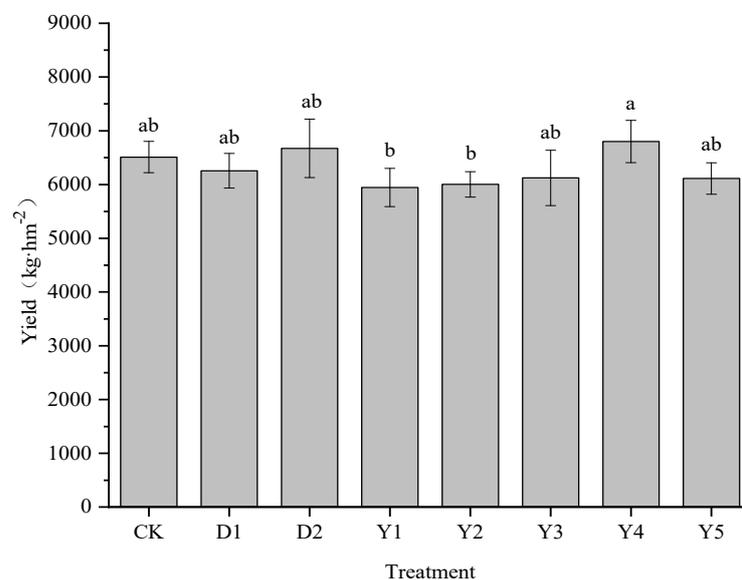


Figure 1. Effect of fertilizers and conditioners on maize yield. Note: Different letters indicate significant differences ($p < 0.05$), the same as below. D1 is formulated fertilizer + biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride.

Under several other fertilization conditions (Y1–Y5), the highest maize yield of 6800.40 $\text{kg}\cdot\text{hm}^{-2}$ was achieved under the Y4 treatment, which was the treatment with the best effect on maize yield improvement compared to both the CK and D2 treatments,

which increased it by 4.44% and 1.90%, respectively. Although the maize yields under the Y1, Y2, Y3, and Y5 treatments varied from 5945.33 to 6124.44 kg·hm⁻², all of them were lower than the CK, D1, and D2 treatments, but none of them differed significantly from each other.

3.2. Differences in Cr Content of Various Parts of Maize by Fertilizers and Conditioners

3.2.1. Cr Content in Maize Grains

The main concern for the safe use of agricultural products mainly lies in the edible parts. The Cr content of maize grains under different treatments is shown in Figure 2. The Cr content of maize grains in the CK treatment was 1.33 mg·kg⁻¹, which exceeds the national food safety standards of China. Therefore consumption of maize grown in this area could lead to a threat to human health. With the addition of the two conditioners, the Cr content in maize grains was 0.80 mg·kg⁻¹ and 0.88 mg·kg⁻¹, with a reduction rate of 39.95% and 33.42%, respectively, and the Cr content in maize grains was reduced to within the national food safety standards of China.

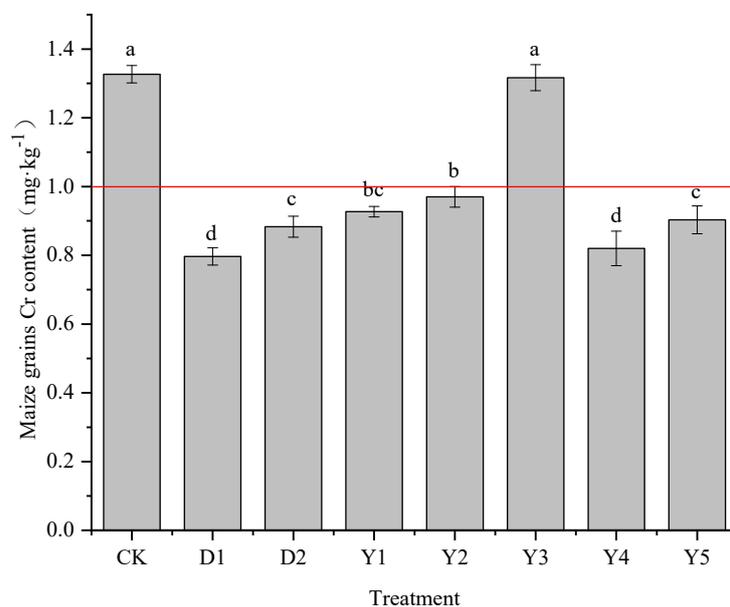


Figure 2. Effect of fertilizers and conditioners on Cr content in maize grains. Note: The solid red line represents the national food standard limit of Cr in China (1.0 mg kg⁻¹). D1 is formulated fertilizer + biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride. Different letters indicate significant differences ($p < 0.05$).

Under several other fertilization conditions (Y1–Y5), the Cr content of maize grains ranged from 0.82 to 1.32 mg·kg⁻¹, which was reduced compared to CK, with the rate of reduction ranging from 0.75% to 38.19%. The Cr content of the Y1, Y2, Y4, and Y5 treatments ranged from 0.82 to 0.97 mg·kg⁻¹, all of which reduced the Cr content in maize grains to less than 1.0 mg·kg⁻¹. The maize grains had the lowest Cr concentration of all in Y4, the best treatment, with a decrease rate of 38.19% in comparison to CK. When compared to the D1 and D2 treatments, the reducing effect of the Y4 treatment was superior to D2, and there was no significant difference from D1. The Y1 and Y5 treatments were also effective in reducing the Cr content of maize grains, with reduction rates of 30.15% and 31.91%, respectively, and the reduction effects were similar to those of the D2 treatment. The reduction rate of the Y2 treatment was only 26.89%. However, the Y3 treatment had little effect on reducing the Cr content of maize grains, and the grain Cr content was

1.32 mg·kg⁻¹, which was only 0.01 mg·kg⁻¹ less compared to CK. The reduction effect was not significant and exceeded the limit value standard of China.

3.2.2. Cr Content in Maize Roots and Straws

After the uptake of heavy metal Cr by maize, the distribution of Cr in various plant tissues eventually affects the content in the maize grains. Figure 3 shows the Cr content in maize roots and straws under different treatments, combined with Figure 2, which shows that the different treatments had some effect on the Cr content in various parts of the maize. The Cr content of maize roots, straws, and grains under the CK treatment was 94.99, 16.93, and 1.33 mg·kg⁻¹, respectively, which showed a rapidly decreasing pattern of root > straw > grain Cr content in each tissue. The Cr content in roots reached more than 5 times the Cr content in straws and 10 times the Cr content in grains. The Cr level of roots under the D1 and D2 treatments was 76.89 mg kg⁻¹ and 83.85 mg kg⁻¹, respectively, whereas the Cr content of straws was 10.51 mg kg⁻¹ and 13.73 mg kg⁻¹, respectively. The Cr content of roots and straws was significantly lower under the D1 and D2 treatments compared to the CK treatments, just like with the grains. The decrease in Cr concentration in all components of maize was improved by both conditioners, and the D1 treatment had a better reduction impact than the D2 treatment.

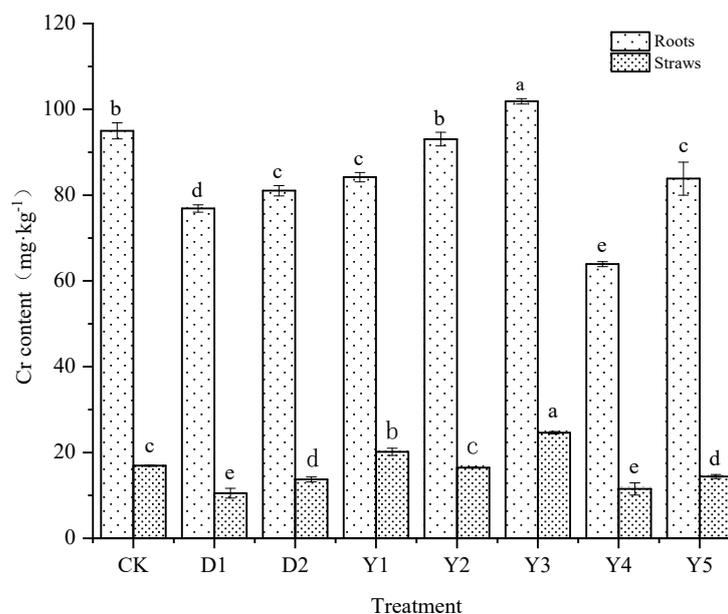


Figure 3. Effect of fertilizers and conditioners on Cr content in maize roots, straws. Note: D1 is formulated fertilizer + biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride. Different letters indicate significant differences ($p < 0.05$).

Under several other fertilization conditions (Y1–Y5), the Cr content in maize roots and straws under the Y2, Y4, and Y5 treatments ranged from 63.92 to 93.06 mg·kg⁻¹ and from 11.52 to 16.47 mg·kg⁻¹, respectively, which all reduced the Cr content in maize roots and straws compared to CK. Among them, the Y4 treatment had the best effect on reducing Cr content in maize roots and straws, with a reduction rate of 32.71% and 31.96%, respectively. The reduction effect for roots was better than with the D1 and D2 treatments, and the reduction effect for straws was slightly worse than with the D1 treatment but better than with the D2 treatment. Second, the Y5 treatment produced the same reduction impact as the D2 treatment, with reductions of 14.69% and 15.03% on roots and straws, respectively.

Although the Y2 treatment reduced the Cr content in maize roots and straws, the effect was not significant, whereas Y3 did not reduce the Cr content of maize roots and straws compared to CK and the D1 and D2 treatments.

3.3. Effect of Fertilizers and Conditioners on Bioconcentration and Translocation Factor of Maize

Crops' own enrichment and heavy metal transport capacity are important factors influencing the content of heavy metals in various parts of the plant. The bioconcentration factor reflects the magnitude of the plant's ability to absorb heavy metals from the soil, and the translocation factor reflects the magnitude of the crop's ability to transport heavy metals between sites after uptake. Figure 2 shows the bioconcentration and translocation factor of Cr in maize under different treatments. The enrichment capacity of Cr in the upper portion of the maize ground was lower, as shown in Figures 2 and 3, and it was primarily concentrated in the roots after being absorbed by the maize. After Cr entered the maize roots, it started to transport to above ground, and the PTF of maize to Cr was significantly stronger than the STF (Figure 4). Both the D1 and D2 treatments reduced BCF, PTF, and STF, and the D1 treatment was more effective in reducing BCF and PTF than the D2 treatment, with a reduced rate of 38.31% and 23.55%, respectively, but D2 was more effective in reducing STF than the D1 treatment, with a reduced rate of 17.80%.

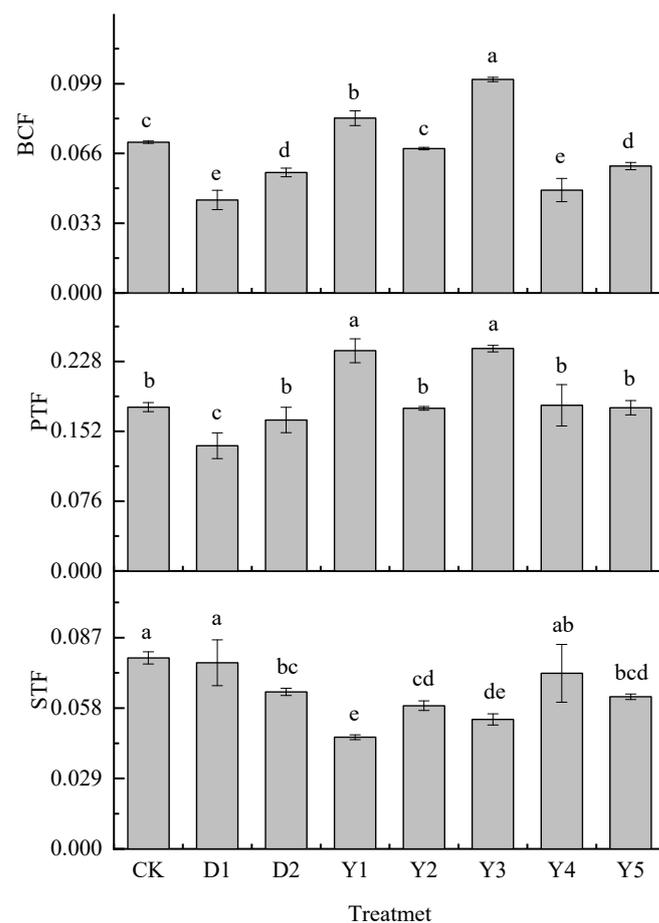


Figure 4. Enrichment and translocation factor of Cr in maize. Note: D1 is formulated fertilizer+ biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride. Different letters indicate significant differences ($p < 0.05$).

The Y2, Y4, and Y5 treatments were equally effective at reducing BCF and STF in maize compared to CK. The reduction of BCF under these three treatments reached 4.21%, 31.77%, and 15.88%, respectively, with the Y4 treatment showing the best reduction effect, even better than the D1 and D2 treatments. The reduction of STF reached 25.00%, 8.06%, and 20.34%, respectively, and the reduction effect of Y2 and Y5 was better than that of the D1 and D2 treatments. The Y4 treatment was better than the D1 treatment but not as good as the D2 treatment. The Y1 and Y3 treatments also reduced STF of maize, with the reduction rate reaching 41.53% and 32.21%, respectively, and the reduction effect was also better than the D1 and D2 treatments, with the two treatments having the best effect in reducing STF of maize despite leading to an increase in BCF and PTF.

Overall, it appears that the Y2 treatment reduced both BCF, PTF, and STF of maize, similar to the D1 and D2 treatments, but it was less effective at reducing BCF and STF than the D1 and D2 treatments, whereas the other fertilization treatments only partially reduced BCF, PTF, and STF of maize.

3.4. Effect of Fertilizers and Conditioners on Available Content of Cr

The available content of heavy metal is an important indicator of the bioavailability of heavy metals, and its level can be used to determine whether different treatments can achieve certain remediation effects. The effects of different treatments on soil available content of Cr are shown in Figure 5, and the available content of Cr in the soil under the CK treatment reached more than 0.7, showing that this location has a high level of bioaccessibility of Cr in the soil. The available content of Cr in D1- and D2-treated soils was $0.50 \text{ mg}\cdot\text{kg}^{-1}$ and $0.55 \text{ mg}\cdot\text{kg}^{-1}$, respectively, which significantly reduced the effective state of Cr compared with CK, with a reduction of 31.24% and 24.62%, respectively, which had a better effect on reducing the available content of Cr.

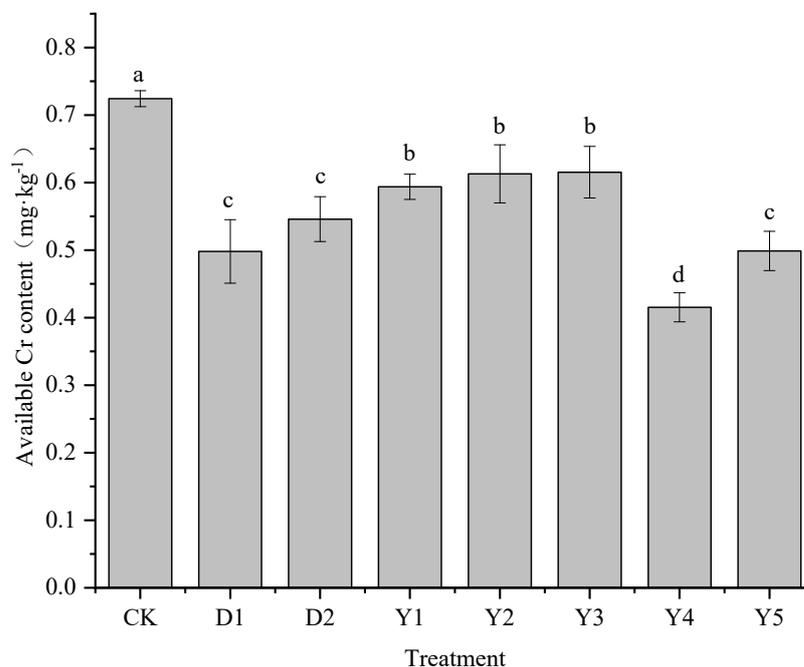


Figure 5. Effects of fertilizers and conditioners on available Cr in soil. Note: D1 is formulated fertilizer + biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride. Different letters indicate significant differences ($p < 0.05$).

Under several other fertilization conditions (Y1–Y5), the Y1 to Y5 treatments significantly reduced the effectiveness of soil Cr compared to CK, with the content ranging from 0.42 to 0.59 mg·kg⁻¹ and the reduction rate ranging from 15.05% to 42.66%. The reduction effect of the Y1–Y5 treatments was Y4 > Y5 > Y1 > Y2 > Y3. Both the Y4 and Y5 treatments achieved a better effect of reducing the available content of Cr, with the reduction rate reaching more than 30% in all cases. Compared to the conditioners, the Y4 treatment reduced the available content of Cr better than the D1 and D2 treatments, with 11.42% and 18.05% higher reduction rates than D1 and D2, respectively. The available content of Cr in the soil under the Y5 treatment was 0.50 mg·kg⁻¹, which was not as effective as Y4 but had a similar remediation effect as the D1 treatment. The Y1, Y2, and Y3 treatments were not as effective as the D1 and D2 treatments in reducing Cr in the available soil, with the Y3 treatment being the least effective at reducing the available content of Cr.

3.5. Effect of Fertilizers and Conditioners on pH and Soil Organic Matter

The pH and soil organic matter (SOM) have a significant impact on how well plants absorb Cr. The most important factor influencing the effectiveness and morphological distribution of heavy metals is pH; the higher the pH, the less effective the heavy metals are and the less likely they are to be utilized by plants. SOM is also useful in reducing the effectiveness of heavy metals by increasing the content of SOM because it exhibits a large number of groups and also has certain adsorption properties. After maize maturity, soil pH (Figure 6a) and SOM (Figure 6b) under the CK treatment were 5.28 and 20.91 g·kg⁻¹, respectively. The D1 and D2 treatments led to an increase in both pH and SOM. pH was increased by 0.29 and 0.36 units, with an increase of 5.49% and 6.82%, respectively, whereas SOM was increased by 24.44 g·kg⁻¹ and 22.22 g·kg⁻¹, with an increase of 16.88% and 6.27%, respectively.

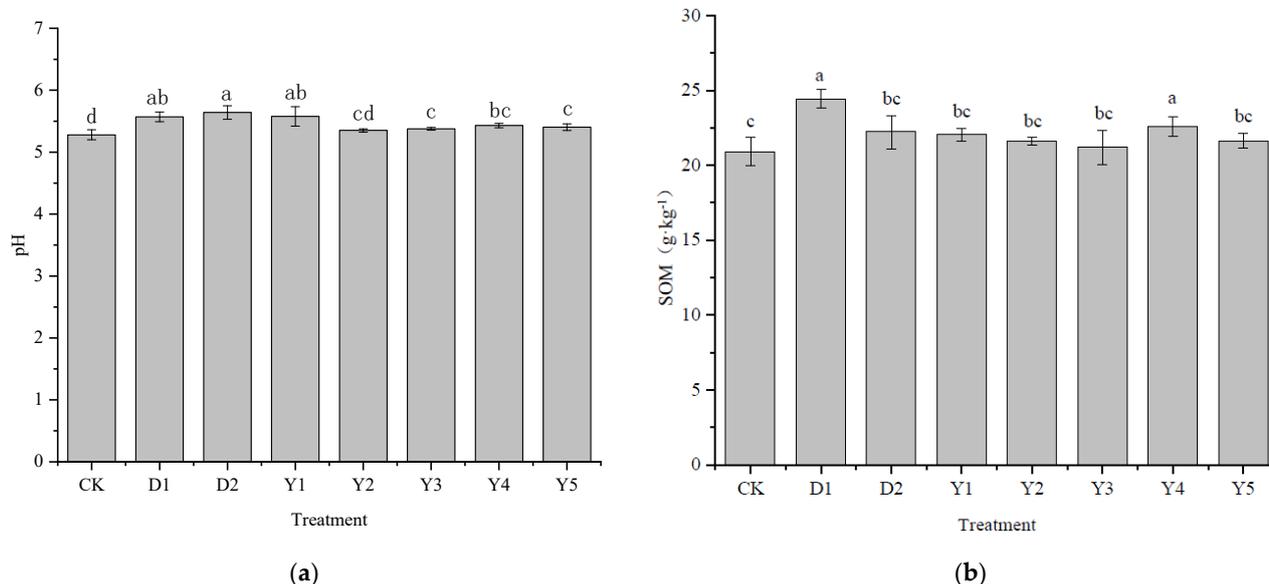


Figure 6. (a) Effects of fertilizers and conditioners on pH; (b) effects of fertilizers and conditioners on SOM. Note: D1 is formulated fertilizer + biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride. Different letters indicate significant differences ($p < 0.05$).

Under the amended fertilizer treatments (Y1–Y5), both soil pH and SOM content also increased, with increases ranging from 1.33% to 5.62% and 1.32% to 8.00%, respectively. The best increase in soil pH was achieved by the Y1 treatment (5.58), with an increase of 0.3 units compared to CK. However, the effect of changing the fertilizer type on SOM was only significant for the Y4 treatment, where SOM reached $22.58 \text{ g}\cdot\text{kg}^{-1}$, an increase of $1.67 \text{ g}\cdot\text{kg}^{-1}$ compared to CK. In contrast, compared to the D1 and D2 treatments, all fertilizer treatments were less effective at increasing pH than the D2 treatment, whereas all treatments were less effective at increasing SOM than the D1 treatment. The Y1 and D1 treatments were similar in their ability to increase pH to around 5.57. The effect of the Y4 treatment on SOM enhancement was not as good as that of D1, but it was non-significant and better than D2 compared to D1.

3.6. Effect of Fertilizers and Conditioners on Soil Nutrient Content

The impact of different fertilizers on soil nutrients is crucial, as is limiting the uptake of Cr by maize, and changes in fertilizer can also result in changes in soil nutrients (Table 3). Total N in the soil was $1.53 \text{ g}\cdot\text{kg}^{-1}$ during the CK treatment, whereas hydrolytic N, available P, and available K were each 162.86 , 12.02 , and $253.33 \text{ mg}\cdot\text{kg}^{-1}$, respectively. The soil total N and available P content of this plot in the maturity stage of maize were moderate, and available K was high, with good soil nutrients, according to the grading standard for the primary traits of arable land quality in Anhui Province. After the conditioners were added, the total N and available K levels under the D1 treatment were $1.43 \text{ mg}\cdot\text{kg}^{-1}$ and $219.67 \text{ mg}\cdot\text{kg}^{-1}$, respectively, which were lower than those under the CK treatment. However, the available P and hydrolytic N levels increased relative to the CK treatment by $2.21 \text{ mg}\cdot\text{kg}^{-1}$ and $23.02 \text{ mg}\cdot\text{kg}^{-1}$, respectively. Except for available P, which was considerably lower, by 8.57%, compared to the CK treatment, none of the other nitrogen content measurements—total N, hydrolytic N, and available K—were significantly different under the D2 treatment than those under CK.

Table 3. Effects of fertilizers and conditioners on soil nutrients.

Treatment	Total N ($\text{g}\cdot\text{kg}^{-1}$)	Hydrolytic N ($\text{mg}\cdot\text{kg}^{-1}$)	Available P ($\text{mg}\cdot\text{kg}^{-1}$)	Available K ($\text{mg}\cdot\text{kg}^{-1}$)
CK	1.50 ± 0.05 a	162.86 ± 5.17 b	12.02 ± 0.59 bc	253.33 ± 22.50 a
D1	1.43 ± 0.04 ab	185.88 ± 7.08 a	14.23 ± 0.31 a	219.67 ± 3.21 c
D2	1.46 ± 0.12 a	163.07 ± 2.74 b	10.99 ± 0.55 cd	245.33 ± 9.24 ab
Y1	1.32 ± 0.02 bc	143.96 ± 5.97 c	12.24 ± 0.33 b	160.33 ± 7.23 e
Y2	1.32 ± 0.11 bc	137.59 ± 8.70 c	8.79 ± 0.94 e	228.33 ± 3.51 bc
Y3	1.30 ± 0.1 bc	133.62 ± 6.46 c	10.02 ± 0.62 d	217.33 ± 1.15 c
Y4	1.23 ± 0.0 6c	134.58 ± 5.22 c	12.28 ± 0.56 b	230.33 ± 4.16 bc
Y5	1.23 ± 0.04 c	137.59 ± 4.75 c	12.67 ± 0.84 b	186.00 ± 8.54 d

Note: The data are the mean \pm standard deviation ($n = 3$). D1 is formulated fertilizer + biochar; D2 is formulated fertilizer + conditioner PX5B; Y1 is urea–calcium magnesium phosphate–potassium chloride; Y2 is urea–diammonium phosphate–potassium chloride; Y3 is urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride; Y4 is ammonium sulfite–calcium magnesium phosphate–potassium chloride; Y5 is ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride. Different letters indicate significant differences ($p < 0.05$).

Under several other fertilization conditions (Y1–Y5), the Y1, Y4, and Y5 treatments increased the soil available P content with an increase ranging from 1.80% to 5.41%, but none of them were significant, whereas the Y2 and Y3 treatments led to a decrease in soil available P content. All fertilizer treatments resulted in a reduction in soil total N, hydrolytic N, and available K contents. The reduction in total N ranged from 12.00% to 18.00%, hydrolytic N from 11.60% to 17.96%, and available P from 9.08% to 36.71%. Total N was decreased by 12.0% to 18.0%, hydrolytic N by 11.60% to 17.96%, and available P by 9.08% to 36.71%.

4. Discussion

4.1. Effect of Different Fertilizers on Cr Content, Bioconcentration, and Translocation Factor of Various Parts of Maize

Different fertilizers can influence the growth of crops and the uptake of heavy metals by affecting the physiological activity of plants due to the presence of different elements [33,43]. After changing the type of fertilizer, only the ammonium sulfite–calcium magnesium phosphate–potassium chloride treatment showed an increase in maize yield compared to the locally formulated fertilizers, which may be because of the fact that the reduction of effective state Cr in the soil was best under this treatment, having reduced the toxic effects of Cr on maize [44,45]. However, the efficiency of releasing nutrients in the soil varies depending on the type of fertilizer [46], which could be the reason why the other treatments led to a reduction in maize yield compared to the locally formulated fertilizers.

It was found that phosphorus fertilizer reduced Cr uptake and accumulation by rice roots and migration to above ground and also reduced Cr uptake by crops such as tomato [47,48]. Mahmut Tepecik et al. found lower Cr content in herbs with different fertilizer applications with added mono-ammonium phosphate treatment compared to NPK compound fertilizer (15:15:15) treatment [49]. The effectiveness of different types of phosphate fertilizers on the remediation of different heavy metals also varies. Zhang et al. found that calcium magnesium phosphate can reduce the uptake of heavy metals Cd and Pb by vegetables [50], and Dong et al. found that calcium magnesium phosphate can reduce the uptake of Cd and As by maize [51]. Shen et al. found that diammonium phosphate had a significant blunting effect on soil heavy metal Cd and reduced the content of As, Pb, Cd, and Zn in rape roots, stems, husks, and rape grains [52], but the effects of different types of phosphorus fertilizers on Cr uptake have rarely been reported. In this study, no significant effect of each treatment on maize yield was found. Cr content in maize grains was significantly reduced by replacing phosphate fertilizer with calcium magnesium phosphate or diammonium phosphate, and the reduction effect of calcium magnesium phosphate was better. Cr is mainly concentrated in maize roots after being absorbed by maize, which is consistent with previous studies [53,54]. The uptake and translocation of heavy metals can be characterized differently in different crops [55], and the same crops can be characterized differently in the uptake and translocation of different heavy metals [56]. Generally, most plants use roots as the main organ for heavy metal accumulation [57], whereas some hyperaccumulator plants accumulate more heavy metals in stems and leaves than in roots [58]. Zayed et al. suggested that the concentration of Cr in the roots may be influenced by reductase activity in the root system [59]. Wang et al. concluded that plants immobilize or confine heavy metal ions within the root cortex to mitigate heavy metal toxicity [60]. Cr begins to transit through the xylem to above ground after being taken up by maize [61]. Although both calcium magnesium phosphate and diammonium phosphate reduced the straw-to-grain translocation of Cr in maize, calcium magnesium phosphate increased the aboveground bioconcentration and root-to-straw translocation of Cr in maize, resulting in increased Cr content in straws. This is different from previous studies that showed that phosphates such as calcium magnesium phosphate can promote the synthesis of phytochelatin in rice root, thereby inhibiting the uptake of Cd by the root and its transport to above ground [62], which may be due to the different types of crops and the different elements of heavy metals. In contrast, diammonium phosphate had no significant effect on Cr transport in maize or the aboveground bioconcentration factor or on Cr content in roots and straws. The 1:1 combination of both calcium magnesium phosphate and diammonium phosphate not only failed to significantly reduce the Cr content of maize grains but also increased the Cr content of maize roots and straws, indicating that these two phosphate fertilizers may not be suitable for simultaneous application.

The Cr content in maize grains, straws, and roots was further reduced by replacing all or part of the urea with ammonium sulfite. The PCS-AS@PVA-Fe₃O₄ composite made by a method with the participation of ammonium sulfite (AS) reduced Cr (VI) to Cr (III) by SO₃²⁻, which effectively controlled the migration of Cr (VI) in soil and plant uptake and

also released ammonium salts to promote plant growth [63]. Meanwhile, the addition of ammonium sulfite was able to significantly reduce the Cr bioconcentration factor in the upper part of the maize ground but did not have a significant effect on the Cr translocation factor of maize, indicating that the main effect of ammonium sulfite may be to reduce the Cr (VI) in the soil, reduce the uptake of Cr by maize, and then reduce the Cr content in maize grains, whereas it had less effect on the Cr transport in maize, and the reduction effect increased with the increase in ammonium sulfite application.

4.2. Changes in Effective State Cr Content and pH and Organic Matter of Soils

Soil pH and organic matter are two important factors affecting the effectiveness of heavy metals, whereas nitrogen, phosphorus, and potassium are not only essential macro elements for crop growth, but the level of their contents can also affect the effectiveness of heavy metals in various ways [29,64]. The amount of calcium magnesium phosphate and diammonium phosphate that was applied to the soil reduced the effective state of heavy metals Cd and Pb, but after reaching a certain amount, the effective state of heavy metals did not decrease with the increase of the applied amount, and the effect was better with calcium magnesium phosphate in small applied amounts [65], which is similar to the findings of this paper. In addition, the reduction of effective state Cr was better with calcium magnesium phosphate, and the available phosphorus in the soil was higher after the application of calcium and magnesium phosphate fertilizers compared to the locally formulated fertilizers and other fertilization treatments. Zhou et al. found that diammonium phosphate significantly reduced soil pH and TCLP-extracted state content of Cd by passivating Cd-contaminated soil with the different phosphate fertilizers, and the TCLP-extracted state content was significantly negatively correlated with soil available phosphorus content [66]. The same relationship may exist between the available phosphorus content of the soil and the effective state Cr content. On the other hand, this may be caused by the different effects of calcium magnesium phosphate and diammonium phosphate on soil pH. According to several studies, adding calcium magnesium phosphate raises soil pH while lowering Eh [62,67], but Zhao et al. found that the soil pH was significantly increased in the early stage of diammonium phosphate application and began to decrease after 15 days [68]. Calcium magnesium phosphate, diammonium phosphate, or calcium magnesium phosphate applied 1:1 with diammonium phosphate all increased soil pH and organic matter, but the effect on organic matter enhancement was not significant. Therefore, calcium magnesium phosphate and diammonium phosphate mainly affect the effective state Cr by influencing soil pH, and calcium magnesium phosphate can raise soil pH better than diammonium phosphate, which is more effective at reducing the effective state of Cr.

Ammonium sulfite is often used in industry to treat certain wastes due to its strong oxidizing effect [69]. The reduction of soil effective state Cr after replacing all or part of urea with ammonium sulfite was superior to the treatment that changed only phosphorus fertilizer, which is a result of the reduction of Cr (VI) to Cr (III) under acidic conditions by utilizing the decreasing property of SO_3^{2-} , which converts Cr (VI) to a precipitate of hydroxide, thus making the leaching of Cr (VI) less toxic [70]. Simultaneous application of calcium magnesium phosphate together can increase soil pH, which not only reduces the effectiveness of Cr [71], but the oxidation rate of ammonium sulfite also increases with increasing pH at $\text{pH} < 7$ [69]. These may be the reasons that led to a better effect on the reduction of effective state Cr after changing both nitrogen and phosphate fertilizers compared to changing only phosphate fertilizers.

Changing both nitrogen and phosphorus fertilizers reduced the content of Cr in maize grains and the effectiveness of Cr in soil, but there were some differences in the effects and mechanisms of action, and the effects of different combinations or dosages of fertilizers on the uptake of Cr in maize under chromium-contaminated conditions could be further explored subsequently. At the same time, the effect of fertilizers on the nutrients in the soil is also very important, and it directly affects the growth and development of crops and

yields. Therefore, the actual application process also requires comprehensive consideration based on the actual conditions of the soil and planting to choose the most appropriate fertilization method.

5. Conclusions

The effects of different fertilizer combinations on the uptake of heavy metals by plants and the activity of heavy metals in the soil vary. The results obtained in this study revealed that all treatments increased soil pH and organic matter content and decreased the effectiveness of Cr in the soil compared to formulated fertilizers. However, changing the fertilizer mix also resulted in lower levels of total nitrogen, hydrolytic nitrogen, and available potassium. Cr is absorbed by the maize and is mainly concentrated in the roots. During transport to above ground, both ammonium sulfite–calcium magnesium phosphate–potassium chloride and ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride treatments did a good job of reducing Cr enrichment in above ground. On the other hand, urea–calcium magnesium phosphate–potassium chloride, urea–diammonium phosphate–potassium chloride, and urea–calcium magnesium phosphate, diammonium phosphate–potassium chloride treatments were effective in reducing Cr transport from straws to grains. Eventually, urea–calcium magnesium phosphate–potassium chloride, urea–diammonium phosphate–potassium chloride, ammonium sulfite–calcium magnesium phosphate–potassium chloride, and ammonium sulfite, urea–calcium magnesium phosphate–potassium chloride treatments were all able to significantly reduce the Cr content in maize grains ($p < 0.05$), bringing the Cr content of maize grains up to the national food safety standards of China. Among them, ammonium sulfite–calcium magnesium phosphate–potassium chloride was the most effective and achieved the same effect as the two conditioners while also increasing maize yields. Therefore, in Cr-contaminated areas, the effective state of soil Cr content and crop uptake of heavy metal Cr can be reduced by choosing reasonable fertilizer combinations to improve crop yields and ensure the safe production of agricultural products.

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