agriculture

Article

Risk Assessment of Heavy Metal Accumulation in Cucumber Fruits and Soil in a Greenhouse System with Long-Term Application of Organic Fertilizer and Chemical Fertilizer

Yuwei Zhang [1,2,†], Shan Tang [1,3,†], Yali Li [1], Ruonan Li [4], Shaowen Huang [1,5,*] and Hong Wang [1,*]

1 State Key Laboratory of Efficient Utilization of Arid and Semi-arid Arable Land in Northern China, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China; 82101211151@caas.cn (Y.Z.); tsago@163.com (S.T.); lanou163163@163.com (Y.L.)
2 China Land Reclamation (Group) General Corporation, Beijing 100035, China
3 Key Laboratory of Nutrient Cycling and Arable Land Conservation of Anhui Province, Soil and Fertilizer Institute, Anhui Academy of Agricultural Sciences, Hefei 230031, China
4 Institute of Agricultural Resources and Environment, Hebei Academy of Agriculture and Forestry Sciences, Shijiazhuang 050051, China; liruonan2004@163.com
5 Key Laboratory of Plant Nutrition and Fertilizer, Ministry of Agriculture, Institute of Agricultural Resources and Regional Planning, Chinese Academy of Agricultural Sciences, Beijing 100081, China
* Correspondence: huangshaowen@caas.cn (S.H.); wanghong01@caas.cn (H.W.); Fax: +86-010-82108650 (H.W.)
† These authors contributed equally to this work.

Abstract: Combining organic and chemical fertilizers is a sustainable strategy for vegetable production. However, there is limited research concerning the risks associated with heavy metals (HMs) in greenhouse systems with long-term location application. A three-year investigation, conducted from 2021 to 2023, explored a fifteen-year field experiment with combinations of chemical fertilizer (CH), corn straw (SW) and pig manure (PM). Five treatments were evaluated: excessive fertilization (high CH and PM), conventional fertilization (normal CH), organic–inorganic fertilization (3/4CN + 1/4PN, 2/4CN + 2/4PN and 2/4CN + 1/4PN + 1/4SN). This study evaluated the risks associated with heavy metals (HMs) by analyzing and quantifying their concentrations in soil and cucumber fruits, as well as by calculating the bioconcentration factors (BCFs), the geo-accumulation index (Igeo), and both the non-carcinogenic and carcinogenic risks. The results indicated that excessive fertilization (CF) increased the concentrations of Cu and Zn in fruits, as well as the Igeo values of Cu, Zn, and Cd, and the non-carcinogenic Cu risk, while decreasing the BCFs of Cu and Zn. Organic–inorganic fertilization also elevated the Igeo values of Cu and Zn. Redundancy analyses confirmed a positive correlation between the soil concentrations of Cu and Zn and higher levels of available phosphorus contents (48.4%), alongside a lower pH (4.9%). The concentrations of Cu, Zn, and Cd in both soil and cucumber fruits increased linearly with the duration of application and amount of input. Although the combined application of CH with PM or SW did not significantly elevate the non-carcinogenic or carcinogenic risks associated with most heavy metals, the carcinogenic risks of Cd and As emerged as potential risk factors after 15 years of organic–inorganic fertilization. Utilizing a combination of CH with PM and SW as a fertilizer management strategy can effectively address both the control of heavy metal inputs in the facility and the safety and quality of cucumbers.

Keywords: heavy metals; health risk assessment; greenhouse cucumber production; fertilizer management; pig manure; corn straw

Citation: Zhang, Y.; Tang, S.; Li, Y.; Li, R.; Huang, S.; Wang, H. Risk Assessment of Heavy Metal Accumulation in Cucumber Fruits and Soil in a Greenhouse System with Long-Term Application of Organic Fertilizer and Chemical Fertilizer. *Agriculture* **2024**, *14*, 1870. https://doi.org/10.3390/agriculture14111870

Academic Editor: Jose Joaquin Ramos-Miras

Received: 2 August 2024
Revised: 18 October 2024
Accepted: 21 October 2024
Published: 23 October 2024

1. Introduction

China is the country with the largest vegetable production and planting area in the world [1], accounting for 13% of the global vegetable production and consuming 25% of the world's agricultural chemical fertilizers each year [2]. Between 2001 and 2015, the average fertilizer application rates for vegetable reached 364 kg N/ha, 79 kg P/ha and

142 kg K/ha, which are twice the fertilizer application rates for cereal crops [2]. Because more economic benefits can be generated, China's greenhouse vegetable production (GVP) area increased rapidly in the past 30 years [3]. Compared to vegetables grown in the open field, greenhouse vegetable production requires a higher amount of fertilizer [4]. However, the overuse of chemical fertilizers in vegetable systems not only leads to a reduction in the yield and quality of vegetables but also leads to environmental issues, contributing to greenhouse gas emission [2], nutrient leaching [5] and soil degradation [6].

Organic fertilizers, such as crop straw (SW) and animal manure (AM), contain plant essential nutrients and organic matter. It is estimated that China has more than 1 billion tons of SW [7] and 4 billion tons of livestock and poultry waste [8] annually. Since 2017, China has implemented the Organic-Substitute-Chemical-Fertilizer action for fruit, vegetables, and tea (MOA, 2017) to promote the use of organic nutrients derived from livestock and poultry manure in vegetable production. The return of SW to fields has become a mandatory agricultural policy in China, serving as both a method for agricultural waste treatment and an important management technology [9].

According to relevant estimates, approximately 76.2%, 46.2%, 4.09%, 17.3%, and 12.8% of the total inputs of Cu, Zn, Pb, Cd, and Ni to agricultural soils in China were derived from AM application [10]. While these amendments provide essential nutrients for vegetable production, research has shown that excessive application of heavy metal (HM)-enriched organic fertilizer can lead to HM accumulation in soils, which would affect crop growth and even threaten human health through food chain. A study conducted in the oasis of Hexi Corridor in North China revealed that four years of livestock manure application increased the Cu, Zn, Pb, Cd, and Ni content in the topsoil, and the risk assessment indicated that the concentrations of Cd, Cu, and Zn could exceed the soil thresholds with application rates of 15–60 t/ha manure over a period of 8–65 years [11]. Based on data from a 15-year vegetable experiment data in protected areas, it was found that the total concentrations of Cd, Zn, Cr, and Cu in the soil increased with the continuous high amount of application of AM, but the cumulative risk of Zn, Cu, and Cr would not exceed the soil threshold in 100 years if the recommended amount of AM was applied [12].

The uptake of HMs by vegetables is influenced by soil properties such as the water, temperature, texture, pH, organic matter content, and nutrient availability, and vegetable species [13]. The results of a study using three organic wastes as fertilizers showed that the application of poultry manure increased the concentrations of Co, Cu, Fe, and Zn in coriander (*Coriandrum sativum* L.), but the concentration of HMs in the soil remained lower than the declared USEPA permissible limits, where most HMs' health risk index value was less than 1, except for Cd showing a potential carcinogenic risk [14]. Compared with open field, the concentration of heavy metals in greenhouse vegetable soils was higher, which might be mainly associated with high inputs of HMs from fertilizers. The carcinogenic risk of HMs caused by the consumption of leafy vegetables produced in greenhouses should be given sufficient attention, especially Cd [15].

Overall, most of the existing studies on the impact of manure application on soil and vegetable HMs are limited to short-term observations or even focus on the comparison of a single time point [16]. The long-term effects of continuous organic fertilizer continuous application on soil HM pollution, HM accumulation in vegetable plants and subsequent potential risks to human health have not been extensively studied.

The strategy of utilizing SW in combination with animal manure has the potential to minimize the input of HMs at the source. At the same time, the multi-parameter approach can better understand and evaluate the health risks of combined SW with PM application in GVP. This study tracked the long-term cumulative trends of HMs in a greenhouse cucumber system over a period of 13 to 15 years, during which CH, PM and SW were applied. The specific objectives of this study were (1) to assess the effects of long-term PM/SW application on the concentrations of Zn, Cu, Cd, Pb, As, and Cr in cucumber fruits and soil, (2) to evaluate the potential health risks associated with the long-term consumption of cucumber fruits containing HMs that pose significant risks to public health, and (3) to investigate the factors influencing changes in HM accumulation and changes in cucumber fruits and soil through the co-application of SW and PM. This study will supplement crucial information on GVP in relation to human health risks.

2. Materials and Methods

2.1. Site Description and Experiment Design

The field experiment was conducted from 2009 to 2023 at the DaHe Experiment Station (38°08′ N, 114°23 E) in Hebei Province, China. The experimental site features a warm, sub-humid continental monsoon climate, with an average annual temperature of 11.5 °C and annual precipitation of 540 mm. The solar greenhouse size is set at 8 m × 48 m. A crop rotation of winter–spring cucumber (*BoMei 11*) and autumn–winter tomato (*Jinpeng 11*) was used. The field was left fallow without growing the two crops. The soil is a typical Calcaric Cambisol soil based on the World Reference Base classification (Harmonized World Soil Database V2.0). The initial soil (0–20 cm depth) had the following characteristics: soil bulk density of 1.35 g cm^{-3}; electrical conductivity of 185.4 mS·cm^{-1}; pH of 8.0, soil organic matter of 9.1 g·kg^{-1}; nitrate nitrogen of 18.3 mg·kg^{-1}, available phosphorus of 6.2 mg·kg^{-1} and available K of 98.2 mg·kg^{-1}.

A randomized block design was arranged with 5 different treatments: (1) CF (customary fertilization, with excessive chemical fertilizer and pig manure), (2) CN (chemical nitrogen, with a reasonable amount of chemical fertilizer), (3) 3/4CN + 1/4PN (equivalent nutrients to the CN treatment, 25% of the nitrogen comes from pig manure), (4) 2/4CN + 2/4P N (equivalent nutrients to the CN treatment, 50% of the nitrogen comes from pig manure), and (5) 2/4CN + 1/4PN + 1/4SN (equivalent nutrients to the CN treatment, 25% of the nitrogen comes from pig manure, 25% of the nitrogen comes from straw). Each treatment was set with 3 replications. The five treatments except for CF had equal amounts of nitrogen, phosphorus and potassium inputs, with 600 kg N ha^{-1}, 300 kg P_2O_5 ha^{-1}, and 525 kg K_2O ha^{-1}, respectively. CF was used as urea, calcium superphosphate, and potassium chloride. The organic fertilizers included PM (pig manure) and SW (straw). Table 1 presents the amounts of N, P_2O_5, and K_2O from the CH (chemical fertilizer), PM (pig manure), and SW (straw) for each treatment. Each plot covered an area of 14.4 m^2 (2.4 m wide × 6 m long), with 4 rows of plants. To prevent lateral and transverse migration of nutrients and water between plots, polyvinyl chloride plates were embedded into the soil at a depth of 100 cm and above the ground by 5 cm. The soil moisture content was controlled through furrow irrigation to maintain 75% of the field capacity. The heavy metal content in the corn straw and pig manure is shown in Table S1.

Table 1. Amounts of N, P_2O_5, and K_2O used in each treatment during the winter–spring cucumber season.

Nutrient	Treatments	CH Input (kg·ha^{-1})	PM Input (kg·ha^{-1})	SW Input (kg·ha^{-1})	Total Input (kg·ha^{-1})
N	CF	900.0	900.0	0	1800.0
	CN	600.0	0	0	600.0
	3/4CN + 1/4PN	450.0	150.0	0	600.0
	2/4CN + 2/4PN	300.0	300.0	0	600.0
	2/4CN + 1/4PN + 1/4SN	300.0	150.0	300.0	600.0
P_2O_5	CF	900.0	700.0	0	1600.0
	CN	300.0	0	0	300.0
	3/4CN + 1/4PN	183.3	116.7	0.	300.0
	2/4CN + 2/4 PN	66.7	233.3	0	300.0
	2/4CN + 1/4PN + 1/4SN	143.0	116.7	40.3	300.0
K_2O	CF	900.0	564.0	0	1463.0
	CN	525.0	0	0	525.0
	3/4CN + 1/4PN	431.0	94.0	0	525.0
	2/4CN + 2/4 PN	337.0	188.0	0	525.0
	2/4CN + 1/4PN + 1/4SN	190.1	94.0	240.9	525.0

2.2. Sampling and Analyses

2.2.1. Cucumber Sampling and Analyses

The winter–spring cucumbers, planted in early March and harvested in May of the following year, were sampled in 2021, 2022, and 2023. Cucumber fruits were harvested by randomly collecting from plants with uniform height. The harvested fruit samples were first washed with deionized water, then dried at 105 °C for two hours and dried at 60–65 °C until a constant weight was achieved. The dried cucumber samples were ground using a grinder (Retsch, ZM 200, Foulds, Shanghai, China) for the elemental analysis.

The plant sample powder was digested using nitric acid (GR, guaranteed reagent, 65.0~68.0%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and H_2O_2 (GR, guaranteed reagent, ≥30.0%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China). The concentrations of Zn, Cu, Cd, Pb, As, and Cr in the digest solution were determined using inductively coupled plasma mass spectrometry (7700X, Agilent Technologies Inc., Palo Alto, CA, USA). Quality assurance of the elemental analysis was performed using blanks and national certified plant reference materials (GBW10014a, Chinese Academy of Geological Sciences, Beijing, China). Based on the instrument performance, the limit of detection (LOD) of Pb and As in the plant sample was 0.02 $mg \cdot kg^{-1}$, the LOD of Zn, Cu, Cd, and Cr was 0.002 $mg \cdot kg^{-1}$, and the limit of quantification (LOQ) was 10^5 times the LOD.

2.2.2. Soil Sampling and Analyses

At the same time as the cucumber sampling, four soil samples were collected from each plot at a 0–20 cm depth. The soil samples from each plot were pooled, air dried, ground, and then sieved for further analysis. The soil sample, after being passed through a 100-mesh sieve, was digested with HNO_3 and HF in a microwave (MARS-5, CEM Microwave Technology Ltd., Matthews, NC, USA) (USEPA Method 3052). The concentrations of Zn, Cu, Cd, Pb, As, and Cr in the digest solution were determined using inductively coupled plasma spectroscopy (7700X, Agilent Technologies Inc., Palo Alto, CA, USA). Quality assurance of the elemental analysis was performed using blanks and national certified soil reference materials (GBW 070045, Chinese Academy of Geological Sciences, Beijing, China).

The soil pH through a 10-mesh sieve was measured using a pH electrode (PB-10, Sartorius, Göttingen, Germany) at a 1:2.5 (*w/v*) ratio of soil to deionized water. The soil organic matter was determined using the potassium dichromate–volumetric method [17]. Based on the instrument performance, the limit of detection (LOD) of Pb and As in the soil sample was 0.025 $mg \cdot kg^{-1}$, while the LOD of Zn, Cu, Cd, and Cr was 0.0025 $mg \cdot kg^{-1}$. The limit of quantification (LOQ) was 10^5 times the LOD.

2.3. Calculations

2.3.1. Bioconcentration Factor

The BCF was used utilized to evaluate the translation ability of HMs from soil to cucumber fruit (Adamo et al., 2014) [18]. The formula was expressed as follows:

$$BCF = \frac{C_{fruit}}{C_{soil}} \quad (1)$$

where C_{fruit} and C_{soil} were the HM concentrations in cucumber fruit and soil, respectively.

2.3.2. Soil Contamination Level Analysis

The value for risk screening the soil HM contamination was the threshold value with a soil pH > 7.5, which is regulated by the standard "Environmental quality evaluation standard for farmland of greenhouse vegetables production (HJ 333–2006)" [19], issued by the Ministry of Ecology and Environment, China. Additionally, the geo-accumulation index (Igeo) was employed to assess the extent of the HM contamination in the soils.

$$I_{geo} = \log_2(Csoil/1.5\,B_n) \quad (2)$$

where Csoil is the measured concentration of HMs in soil and Bn is the concentration of HMs in the initial soil. The constant 1.5 served as the background matrix correction coefficient, which was used to minimize the natural fluctuations (Wei and Yang, 2010) [20]. The geological background values of Hebei Province used to calculate the I_{geo} values in this paper are as follows: As 13.6 mg·kg^{-1}, Cd 0.094 mg·kg^{-1}, Cr 68.3 mg·kg^{-1}, Cu 21.8 mg·kg^{-1}, Hg 0.036 mg·kg^{-1}, Ni 30.8 mg·kg^{-1}, Pb 21.5 mg·kg^{-1}, Zn 78.4 mg·kg^{-1}. Seven subclasses (0–6) of pollution levels were classified based on the Igeo values (Table S3).

2.3.3. Human Health Risk Assessment

The human health risks associated with the consumption of vegetables were assessed using the equation provided by the United States Environmental Protection Agency (USEPA, 2016). The formula was expressed as follows:

$$CDI = \frac{C \times DI \times EF \times ED_{total}}{BW \times AT} \tag{3}$$

$$HQ = \frac{CDI}{RfD} \tag{4}$$

where C = HMs concentration in cucumber fruits; DI = daily intake of cucumber fruits; EF = exposure frequency; EDtotal = exposure duration; RfD = reference dose; BW = average body weight; AT = average time of exposure to non-carcinogenic (non-CR) or carcinogenic risk (CCR) HMs (EDtotal × 365 days/year). The specific definitions and parameters are shown in Table S4.

Non-carcinogenic effects (Non-CR): The hazard quotient (HQ) for each HM was aggregated to assess the Non-CR expressed as the hazard index (HI). The total hazard index (HIt) represents the overall non-cancer risk (non-CR) associated with all the HMs and exposure pathways, which are computed from:

$$HI = \sum_{n=1}^{i} HQi \tag{5}$$

$$HIt = \sum_{n=1}^{i} HIi \tag{6}$$

where HQi represents the hazard quotient from the HMs i or the exposure pathway i. HIi was the hazard index from the exposure pathway i. Calculated HQ, HI and HIt values were $\leq$1, indicating no significant risk of Non-CR effect. Conversely, indicating a greater likelihood of toxic effects.

Carcinogenic effects (CCR): Typically, the threshold CR and cumulative CR parameters are utilized to determine the incremental probability of an individual developing cancer over their entire lifetime (USEPA, 2005; U.S. EPA. 2005. Guidelines for Carcinogen Risk Assessment. 70 FR 17765-17817). The formula is expressed as follows:

$$CR = CDI \times SF \tag{7}$$

$$CCR = \sum_{n=1}^{i} CDIi \times SFi \tag{8}$$

where the cancer slope factor (SF) is a parameter used to quantify the potential risk of developing cancer. CDIi represents the chronic daily intake of HMs i or exposure pathway i, while SFi denotes the cancer slope factor for HMs i or exposure pathway i. Table S5 provides the reference values for toxic parameters such as the RfD and SF for various exposure pathways. Based on the calculated CR value, there were generally three levels of risk to human health: negligible risk (<1 $\times 10^{-6}$), acceptable risk (ranging from 1×10^{-6} to 1×10^{-4}), and high risk (>1 $\times 10^{-4}$) [21].

2.4. Statistical Analysis

The statistical analyses were conducted using analysis of variance (ANOVA). All the data were presented as the mean ± standard deviation. When the effect was significant, the differences among treatments were compared using the least significant difference (LSD) test at $p < 0.05$. A linear regression model was developed to estimate the contribution of fertilizer HM inputs to soil HM accumulation, using the SW and PM exogenous HM additions (g/ha) as dimensional input data X, and the soil HM concentrations as dimensional input data Y.

3. Results

3.1. Concentrations of HMs in Soils and Cucumber Fruits

The mean concentrations of Cr, Cu, Zn, As, Cd, and Pb in soil and cucumber fruits were found to be below the limited levels (Table S2). In 2021, treatment CF exhibited a higher soil Cr concentration than CN, 3/4CN + 1/4PN, and 2/4CN + 2/4PN ($p < 0.05$) (Figure 1). From 2022 to 2023, all five treatments demonstrated consistent Cr concentrations in the soil. In treatment CF, the soil concentration of Cu, Zn, Cd, and Pb was higher than in the other four treatments. Additionally, in 2022 and 2023, the soil Cu concentration in the 2/4CN + 2/4PN treatment increased significantly by 21.6 mg/kg and 24.4 mg/kg, respectively, compared to CN. Concurrently, the concentration of Zn in the soil in the 2/4CN + 2/4PN treatment rose by 64.7 mg/kg and 84.3 mg/kg, respectively. In 2021, the soil Cd concentration in the 3/4CN + 1/4PN treatment was 0.10 mg/kg higher than in CN, while in 2023, 2/4CN + 2/4PN exhibited a 0.06 mg/kg increase. Throughout the three-year period, the As concentration did not differ significantly among the five treatments (Figure 1).

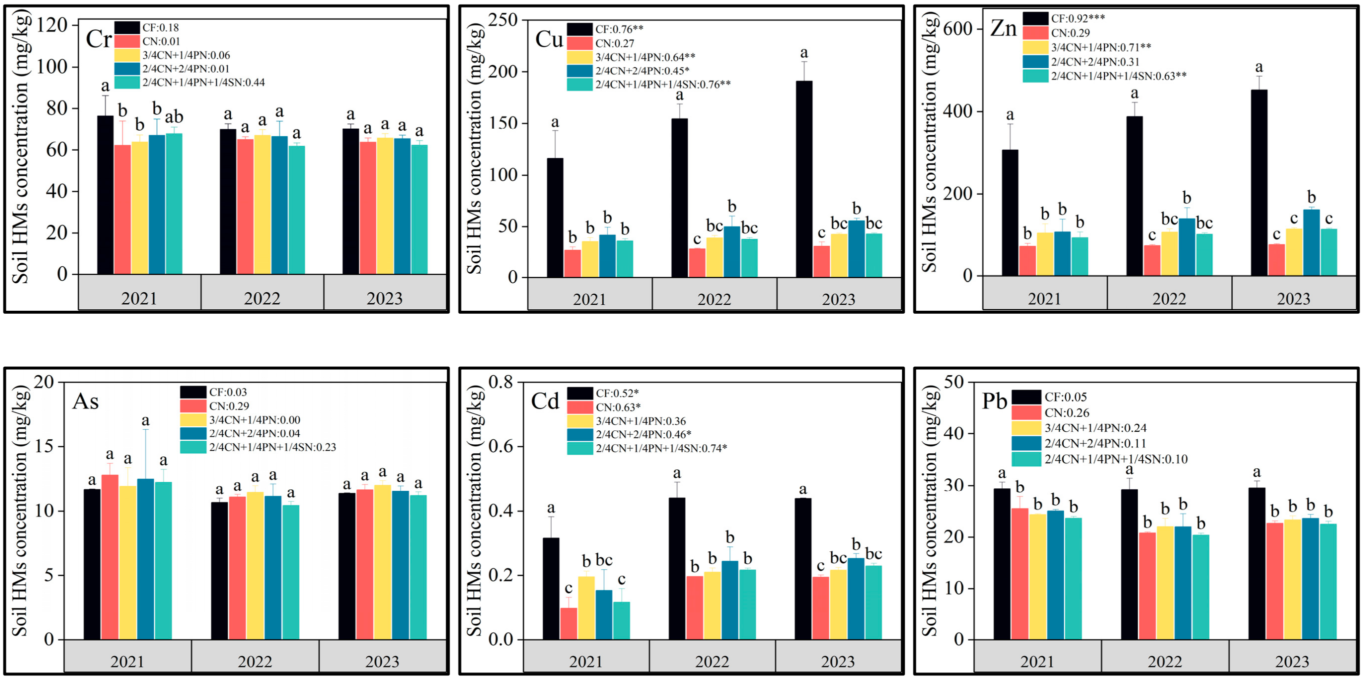

Figure 1. Soil HM concentrations under different fertilization treatments. Legend numbers represent R^2 calculated by linear regression. "*", "**", and "***" indicate the linear regression between the soil HM concentration and the planting age or the differences among the fertilization treatments reached significant ($p < 0.05$), ($p < 0.01$) or extremely significant ($p < 0.001$) levels, respectively. Different lower-case letters indicate significant differences in Soil HM concentration among different treatments ($p < 0.05$, LSD).

The Cu concentrations in cucumber fruit from the CF treatment were demonstrably higher than those observed in the other four treatments (Figure 2). Compared to the CN treatment, the Cu concentration in cucumber fruits from the 2/4CN + 1/4PN + 1/4SN treatment significantly increased by 5.47 mg/kg in 2021. In the same year, the cucumber fruit concentrations of Cr and Cd in the CF treatment were significantly higher than those in CN, 3/4CN + 1/4PN, and 2/4CN + 2/4PN. Furthermore, the Cd concentrations in the

CN treatment fruits increased by 0.13 mg/kg compared to 3/4CN + 1/4PN. By 2023, the Zn concentrations in the CN and 2/4CN + 1/4PN + 1/4SN treatment had significantly decreased compared to CF, by 32.35 mg/kg and 18.12 mg/kg, respectively. There were no significant differences in the concentration of Cr and As in the fruits among the five treatments (Figure 2).

The concentrations of Cu, Zn, and Cd in cucumber fruits and soil demonstrated a positive correlation with the duration of application. A notable trend emerged from the linear regression models regarding the Zn concentration in cucumber fruits across the CF, 3/4CN + 1/4PN, and 2/4CN + 1/4PN + 1/4SN treatments, which revealed a significant increase over the application period (p < 0.05). The concentrations of Cu in cucumber fruit from the CF treatment displayed a significant upward trend over the application duration. Additionally, the soil concentration of Cu and Zn in the CF, 3/4CN + 1/4PN, 2/4CN + 2/4PN and 2/4CN + 1/4PN + 1/4SN treatments, as well as the concentration of Cd in CF, CN, 2/4CN + 2/4PN and 2/4CN + 1/4PN + 1/4SN, showed a significant increase over the application period. However, no discernible upward trend was observed for the concentrations of Cr, As and Pb in both cucumber fruits and soil throughout the application period.

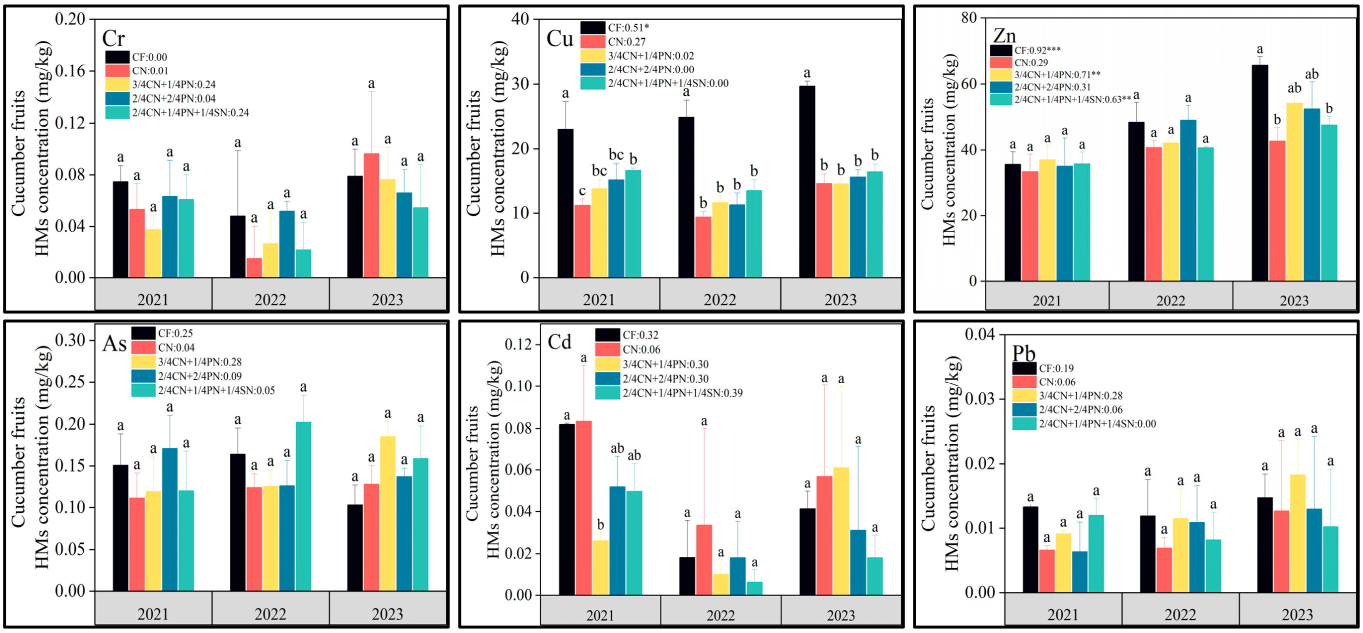

Figure 2. HM concentrations in cucumber fruits under different fertilization treatments. Legend numbers represent R^2 values calculated by linear regression. "*", "**", and "***" indicate the linear regression between the soil HM concentration and the planting age or the differences among the fertilization treatments reached significant (p < 0.05), (p < 0.01) or extremely significant (p < 0.001) levels, respectively. Different lower-case letters indicate significant differences in Cucumber fruits' HM concentration among different treatments (p < 0.05, LSD).

BCF calculations were conducted to investigate the transfer of HMs from the soil to cucumber fruits (Figure 3). The highest value for the Cd BCF was observed among all the HMs, with the CN treatment exhibiting the greatest increase in the BCF values of Cd compared to the control, in 2021. From 2021 to 2023, the BCF value of Cu rose significantly in the CN, 3/4CN + 1/4PN, and 2/4CN + 1/4PN + 1/4SN treatments, compared to CF. In contrast to the CN treatment, the BCF values of Cu were notably lower than 3/4CN + 1/4PN in 2023. It is noteworthy that a 17.4% reduction of the Cu BCF values was observed in 2/4CN + 2/4PN (in 2022) in comparison to 2/4CN + 1/4PN + 1/4SN. The BCF values of Zn in CF consistently remained at significantly lower concentrations than the other four treatments from 2021 to 2023. Compared to the CN treatment, the BCF values of Zn in 3/4CN + 1/4PN, 2/4CN + 2/4PN and 2/4CN + 1/4PN + 1/4SN were significantly decreased by 28.0%, 34.9% and 27.1%, respectively. In 2023, the BCF values of Zn in the 2/4CN + 2/4PN and 2/4CN + 1/4PN + 1/4SN treatments dropped by 41.6% and 25.0%, respectively, compared to CN. However, the BCF values of Cr, Pb, and As remained unchanged among all five treatments.

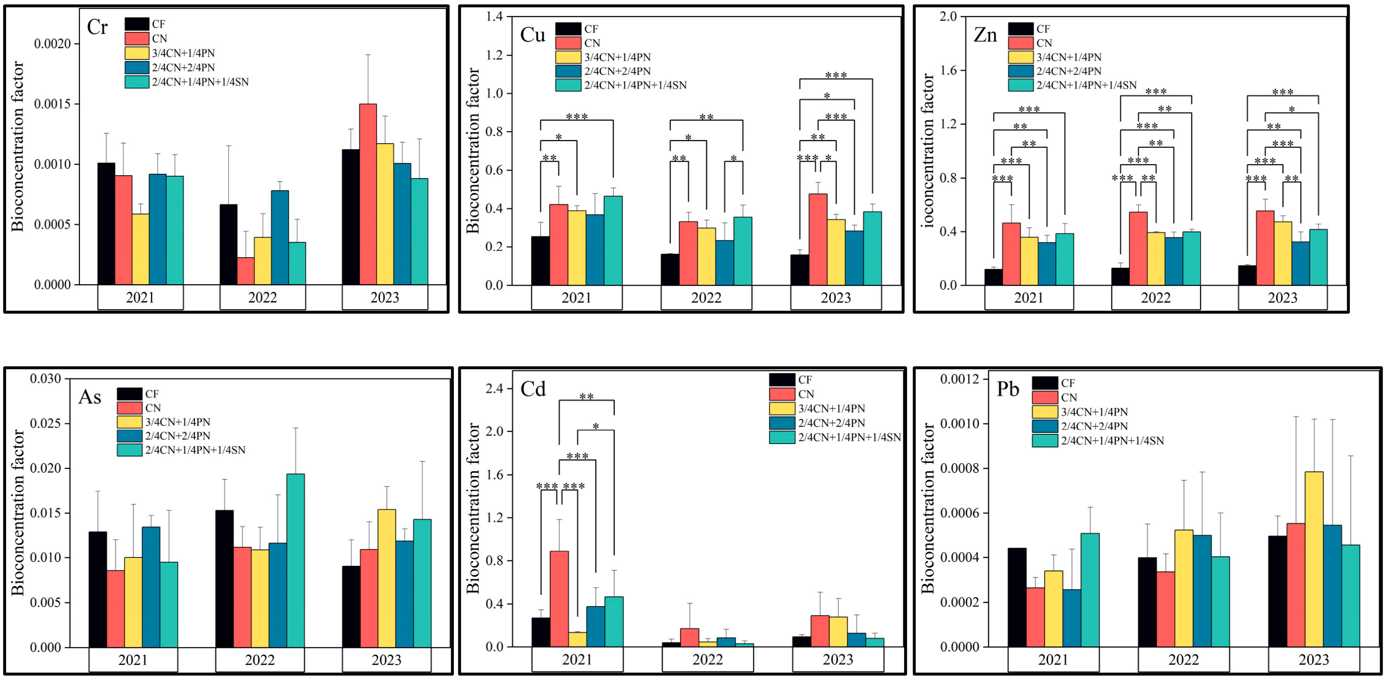

Figure 3. Bioconcentration factor of Zn, Cu, Cd, Pb, As and Cr affected by different fertilizer application. Bars represent the SD of the replicates, "*", "**", and "***" indicate significant differences at the 0.05, 0.01, and 0.001 level among the five treatments.

3.2. Soil Contamination Level

The Igeo values were employed to assess the soil quality across the five treatments (Figure 4), and a geo-accumulation index analysis was conducted (Table S3). The mean Igeo values of Pb (−0.39), Cr (−0.64), and As (−0.82) were all below 0, indicating unpolluted conditions. In contrast, Cd, Cu, and Zn showed a range from unpolluted to moderate pollution, with mean Igeo values of 0.54 for Cd, 0.48 for Cu, and 0.07 for Zn. The class distribution of the Igeo values (Figure 4) revealed that Cu exhibited the most variation, ranging from class 0 (unpolluted) to class 3 (moderately to heavily polluted), with approximately 80.1% of soils classified as polluted and 11.9% as moderately polluted. For Cd, 59.5% of the soil samples exhibited Igeo values that indicated pollution levels ranging from unpolluted to moderately polluted (0 < Igeo < 1). In contrast, for Pb, this value was 11.9%. Furthermore, Cr and As were characterized as unpolluted (Igeo < 0). When considering Cu and Zn, the soil pollution levels were complex, encompassing four distinct classes. Notably, 66.7% and 21.4% of Cu and Zn in all the soils were classified as unpolluted to moderately polluted (0 < Igeo < 1), while 2.4% and 11.9% of Cu and Zn soils fell into the unpolluted levels (1 < Igeo < 2). Additionally, 11.9% and 2.4% of the Cu and Zn soils exhibited moderate to heavy contamination.

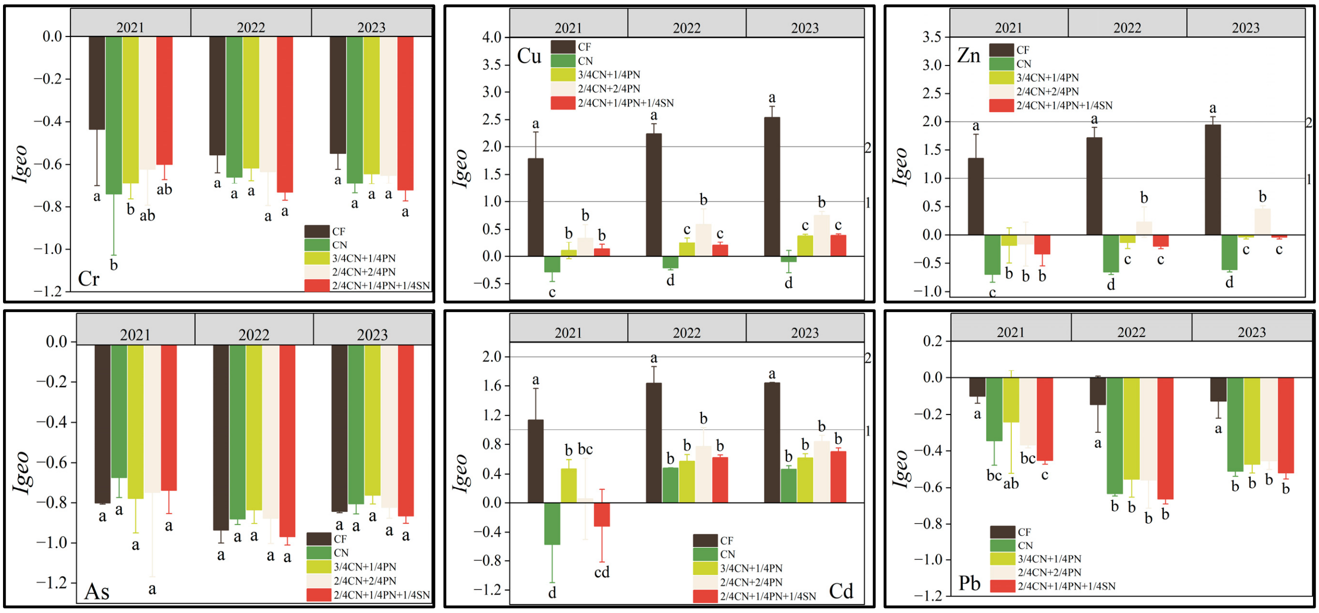

Figure 4. Histogram of the geological accumulation index (Igeo) of each HM for the different treatments. Different letters represent significance at $p < 0.05$. Different lower-case letters indicate significant differences in Igeo index among different treatments ($p < 0.05$, LSD).

3.3. Human Health Risk

The potential non-CR and CCR associated with HMs in soil and cucumber fruits were estimated and calculated for both children and adults (Table S6). The mean HQ and CR values showed a descending order: diet > soil ingestion > dermal contact > soil inhalation. The HI values of Zn and Cu exceeded 1 for children, while for adults, only Cu surpassed the threshold. The CR values of As and Cd resulting from vegetable consumption for children and adults significantly exceeded the threshold of 1×10^{-4}, indicating a higher CR compared to soil ingestion. The mean CCR values from vegetable consumption were 3.02×10^{-4} for children and 9.83×10^{-4} for adults, which were 21 times and 81 times higher than the CCR through soil ingestion, respectively.

3.3.1. Non-CR of Cr, Zn, Cu, Cd, As and Pb

The mean HI values for Cu in all the treatments exceeded 1 for both children (2.22–7.03) and adults (1.35–4.26). Cu and Zn had the highest contributions to the HIT values, accounting for 57.8% and 23.0% for children, and 59.0% and 23.5% for adults, respectively (Figure S1). A significant decrease in the Cu HI values was observed from 2021 to 2023 compared to the CF treatment. In 2021, the HI value of Cu in the 2/4CN + 1/4PN + 1/4SN treatment significantly increased by 48.7% for both children and adults when compared to the CN treatment. However, no differences were detected 2022 and 2023. Regarding Zn, the mean HI values for children (1.06–1.35) indicated elevated non-CR from 2021 to 2023 across the five treatments (Figure 5). Specifically, in 2023, the HI values of Zn in the CN and 2/4CN + 1/4PN + 1/4SN treatments were significantly decreased by 27.6% and 35.1% for both children and adults, respectively, in comparison to CF. Furthermore, the HI values of Cr, As, Cd, and Pb were all below 1 for both adults and children. In 2021, compared to the CF treatment, a significant decrease in the HI values for Cr, As, Cd, and Pb was observed compared to CF in CN, 3/4CN + 1/4PN, and 2/4CN + 2/4PN for both adults and children. Moreover, in 2021, compared to the CN treatment, the HI value of Cd in 3/4CN + 1/4PN decreased by 68.5% for children and 70.1% for adults. Based on the Monte Carlo simulation, the non-CCR and CCR of HMs in soil and cucumber fruits were assessed for both adults and children (Figures S4 and S5). The mean HIt values were above 1 for both children (2.35) and adults (4.67), indicating a probability approaching 100% of non-CR.

The sensitivity analysis examining uncertainty (Figure S4) revealed that the concentration of Cu in cucumber fruits had the greatest impact on the non-CR for children, contributing 53.7% and 23.7%, respectively. Body weight negatively impacted non-CR, contributing 53.7%, followed by the exposure factor (EF) value at 23.7%.

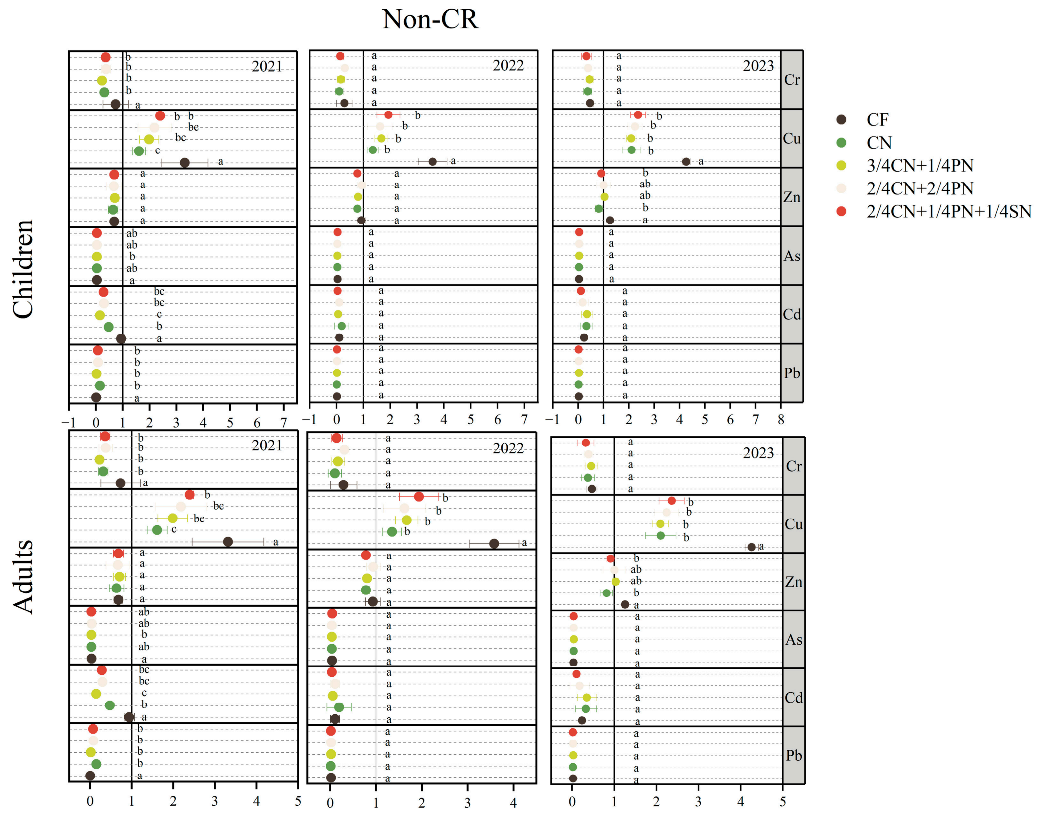

Figure 5. The HI values of the HMs in terms of exposure for children and the adults, as affected by the different treatments. Different lower-case letters indicate significance at $p < 0.05$.

3.3.2. CCR of Cr, Cd, As, and Pb

The CCR values of the HMs were generally greater for adults than for children (Figure 6). The CCR values of Cr and Pb remained consistently below 1×10^{-4} for both children and adults. In contrast, As and Cd surpassed this threshold. As and Cd dominated the CCR, contributing 42.5% each to the overall treatments for both children and adults (Figure S2). Across the five treatments, the mean CCR values of As ranged from 0.7×10^{-4} to 2.9×10^{-4} for children and from 2.1×10^{-4} to 7.5×10^{-4} for adults. In 2021, no significant variation was observed in the CCR values of As among the five treatments. However, in 2022, the CCR values of As were significantly lower in the CN, 3/4CN + 1/4PN and 2/4CN + 2/4PN treatments, compared to 2/4CN + 1/4PN + 1/4SN. In 2023, the CCR of As in 3/4CN + 1/4PN was significantly lower than in the CF treatment for children. Conversely, the adults CCR values of As remained consistent across the five treatments from 2021 to 2023. In 2023, the CCR value of Cd in the 2/4CN + 1/4PN + 1/4SN treatment was lower than in 3/4CN + 1/4PN for children. Across the five treatments, the Cd CCR values exceeded 1×10^{-4} for adults. In 2021, the CCR values of Cd for adults in CF were significantly higher than those in the other four treatments. Notably, in 2022 and 2023, there was no significant difference in the CCR value of Cd for adults among the five treatments. In the sensitivity analysis examining uncertainty (Figure S5), body weight had a negative impact on CCR, resulting in a decrease of 6.8%. For adults, the concentrations of As (32.9%) and Cu (20.4%), along with the IRveg (26.4%) and EF (11.1%) values, positively influenced the CCR, whereas body weight had a negative effect of 4.7%. The sensitivity analysis results also indicated that the concentration of As had an average contribution of 71.36%, while EF had a contribution of 19.0% in cucumber fruits.

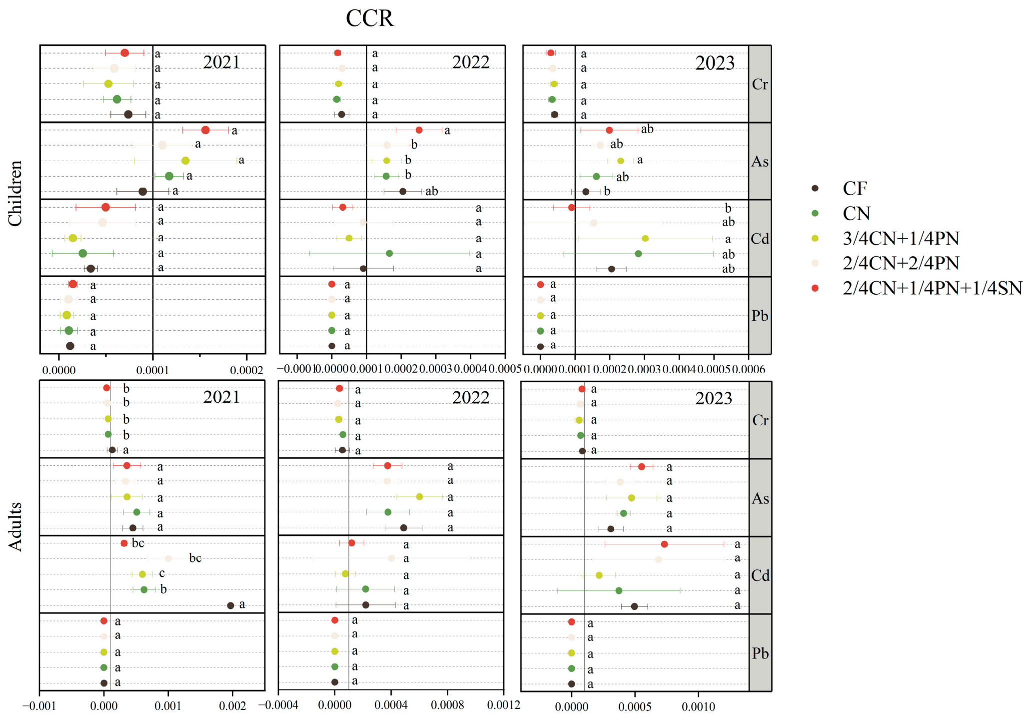

Figure 6. The CCR values of the HMs in terms of exposure for children and the adults, as affected by the different treatments. Different lower-case letters indicate significance at $p < 0.05$.

3.4. Relationship between Soil Nutrients and Soil HM Concentrations

Redundancy analyses (RDAs) were conducted to examine the relationship between the soil nutrient contents (Table 2) and the soil HM concentrations, further exploring the effects of applying SW and PM on soil HM accumulation. The first component (RDA1) explained 53.1% of the soil HM concentration variation in the soil HM concentrations, while the second component (RDA2) contributed an additional 11.1% (Figure 7A). The soil available phosphorus (AP) content exhibited a strong positive correlation with the soil Cr, Cu, Zn, Pb, and Cd concentrations, while the soil pH value showed a negative correlation with them. The soil C/N ratio demonstrated a positive correlation with the concentrations of Zn, Cu, and Cd while negatively affecting the concentrations of Cr and Pb. The soil AP content was identified as the most influential factor, explaining 48.4% of the variation in the soil HM concentrations and contributing 64.8%. The soil pH value (Table 2) accounted for 4.9% of the soil HM concentrations, with a contribution of 6.6% (Figure 7A). The concentrations of Cr, Cu, Zn, Cd, and Pb in the soil displayed significant positive correlations with one another (Figure 7B). A linear regression analysis revealed that all the HMs except As showed a significant decrease with an increasing pH value, while the AP content exhibited the opposite trend (Figure 7F,G). The CF treatment exhibited the lowest soil pH and highest soil AP among the five treatments ($p < 0.05$), while no significant differences were observed in the soil C/N ratio among the five treatments (Figure 7C).

Table 2. The pH and soil nutrients during the cucumber harvest period.

Treatments	pH	Total N (g·kg^{-1})	SOM (g·kg^{-1})	AP (mg·kg^{-1})	AK (mg·kg^{-1})	C/N ratio	NH^{4+}-N (mg·kg^{-1})	NO^{3}-N (mg·kg^{-1})
CF	5.08 ± 0.08	4.61 ± 0.82	118.1 ± 17.1	285.1 ± 47.8	1058.1 ± 116.8	9.81 ± 1.75	854.5 ± 91.7	104.3 ± 11.3
CN	7.67 ± 0.16	0.86 ± 0.05	22.2 ± 0.9	38.4 ± 1.5	257.0 ± 89.6	10.09 ± 1.66	230.5 ± 14.6	55.1 ± 20.9
3/4CN + 1/4PN	7.54 ± 0.16	1.14 ± 0.11	41.8 ± 12.7	62.4 ± 7.0	239.2 ± 93.3	10.22 ± 2.27	357.7 ± 71.8	57.8 ± 20.1
2/4CN + 2/4PN	7.53 ± 0.20	1.44 ± 0.19	36.3 ± 4.3	76.2 ± 14.0	261.0 ± 80.6	10.08 ± 1.89	414.5 ± 26.3	46.1 ± 12.1
2/4CN + 1/4PN + 1/4SN	7.45 ± 0.11	1.62 ± 0.18	42.6 ± 3.1	68.3 ± 6.7	320.7 ± 70.9	10.34 ± 1.48	615.0 ± 33.9	42.6 ± 11.9

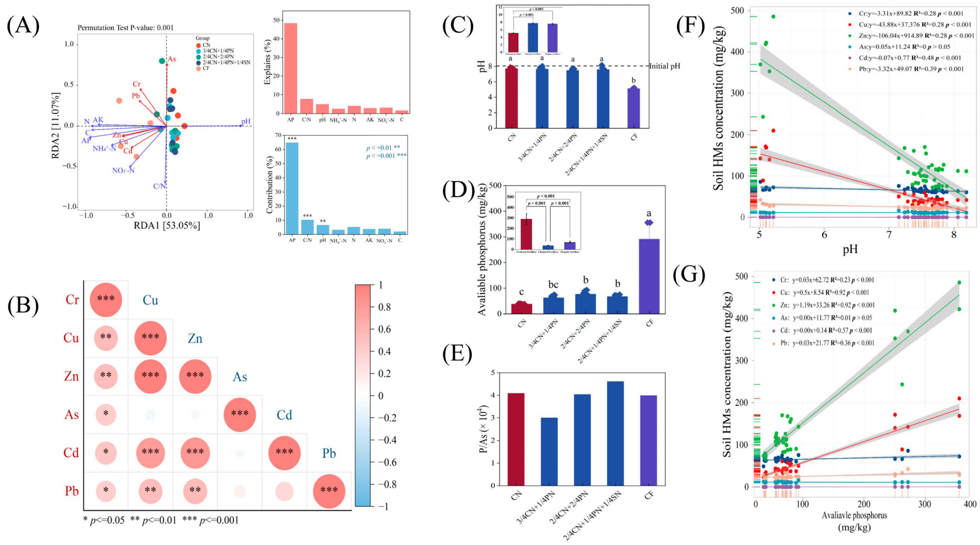

Figure 7. Relationship between the soil nutrients and the soil HM accumulation. (**A**) RDA analysis of the soil HM concentrations and soil nutrients. (**B**) Correlation of the HM concentrations in soil. (**C**) Soil pH of different treatments. (**D**) AP concentration of different treatments. (**E**) Linear regression modeling of six HM concentrations with the soil pH. (**F**) Linear regression modeling of six HM concentrations with the soil AP concentration. (**G**) Ratio of P to six HMs in cucumber fruits. "*", "**", and "***" indicate the correlation among different HM concentrations in soil reached significant ($p < 0.05$), ($p < 0.01$) or extremely significant ($p < 0.001$) levels, respectively. Different lower-case letters indicate significant differences among treatments ($p < 0.05$, LSD).

4. Discussion

4.1. Concentrations of HMs in Cucumber Fruits as Affected by SW and PM Application

Relevant studies have shown that Cu is primarily derived from pesticides and fertilizers, and it is readily transferred from soil to plants, posing human health risks through bioaccumulation in plant tissues [22,23]. Research on the application of organic fertilizers for 10 years also confirmed this conclusion [24]. The PM used in this study contained a particularly high amount of Cu (Table S1). The application of high levels of PM and CH led to Cu accumulation in cucumber fruits, which was persistently higher than that observed in cucumbers treated with low levels of PM/SW and CH between 2021 and 2023. At lower levels of fertilizer application, the combination of CH with SN/PW application also increased the Cu and Zn concentrations in cucumber fruits compared to CH application alone (Figure 2). This increase was primarily attributed to the input of Cu from the SW and PM application. The results of the linear regression analysis demonstrated a significant positive linear positive correlation between the concentrations of Cu ($R^2 = 0.65$) and Zn ($R^2 = 0.09$) in cucumber fruits and the input levels of these elements (Figure S3).

Another important factor in the accumulation of HMs in vegetables is the transfer from soil to plant [25]. In the present study, the BCF values of Cu and Zn in the CF treatment were significantly lower than those in the other four treatments ($p < 0.001$). This finding aligns with previous research suggesting high nitrogen inputs hinder the plant uptake of Cu and Zn [26]. In 2023, it was observed that the BCF value of Cu and Zn in the 2/4CN + 2/4PM treatment were significantly lower than those in 3/4CN + 1/4PM (Figure 3). This further confirms that increasing the amount of PM applied does not enhance the BCF of Cu and Zn from soil to cucumber fruit.

Moreover, at the 2/4 ratio, the BCF values of Cu increased in the combination of SW and PM with CH compared with the combination of PM with CH, especially in 2022 (Figure 3). This phenomenon can be attributed to the fact that the application of SW enhances Cu bioavailability [27]. SW contains reactive organic carbon, which serves as a ligand for Cu, thereby increasing its mobility and effectiveness in the soil [28]. For instance, the combination of sheep and horse manure with pine bark compost resulted in higher concentrations of soluble Cu in the soil [29]. This suggests that modifying the soil's reactive organic carbon content through the application of SW could enhance the Cu bioavailability and its uptake by cucumber fruits.

4.2. Concentrations of HMs in Soil as Affected by SW and PM Application

Our research revealed that there were no instances of HMs exceeding the permissible limits in the soils subjected to various fertilization practices (Table S2). However, the soil from the treatment with high levels of CH and PM inputs exhibited significantly elevated concentrations of Cr, Cu, Zn, Cd, and Pb compared to the low-input treatments (Figure 1). The results of the analysis (Figure 4) indicate that the soil was primarily contaminated with Cd, Cu, and Zn, with the latter two elements predominantly resulting from increased PM application. PM was identified as the primary source of Cu and Zn in the soil (Table S1). These findings are consistent with a study that documented the accumulation of Cu and Zn in the surface soil due to the application of pig manure over 8 consecutive years [30].

In our study, we observed a linear increase in the soil concentrations of Cu, Zn, and Cd with the rise in exogenous HM inputs (Figure S3) and the duration of fertilization (Figure 1). Compared to the application of CH alone, the soils were classified as unpolluted to moderately polluted by Cu and Zn after the combined application of CH with PM/SN. The regression coefficients (k) calculated from the linear regression models (Table S7) indicated that Cu and Zn were 3.59 and 4.92 (3/4CN + 1/4PN), 6.72 and 3.43 (2/4CN + 1/4PN + 1/4SN), and 26.73 and 10.39 (2/4CN + 2/4PN). The combination of CH with SW and PM was more effective than the combination of CH with PM in controlling the accumulation of Cu and Zn in the soil (Figure 1).

However, the soil ranged from unpolluted to moderately polluted with Cd when PM and SW were combined with CH application compared with pure CH inputs. The Igeo values of Cd showed little variation among the four treatments with low-level inputs, indicating that the PM and SW inputs were not the primary contributors to soil Cd pollution. This may be attributed to the presence of Cd in the applied phosphate fertilizer [31].

Excessive fertilization, particularly with CH, has been associated with soil acidification and the migration of HMs [32]. The soil pH is closely related to the formation and mobility of HMs [33]. In this study, the initial soil pH was measured at 8.08. The soil pH under CF was found to be 5.11, while a pH range of 7.49–7.72 was observed with lower application of CH and PM/SW (Figure 7C). PM and SW generally exhibit high pH levels and alkalinity, which neutralizes the protons released during nitrification, thereby helping to maintain the soil pH [34,35].

Additionally, a decrease in the soil pH enhances the AP and HM concentrations, thereby increasing the risk of HM migration in the soil–crop system [36]. This finding is further supported by the higher concentration of AP in soils treated with the CF treatment compared to the other four treatments. Notably, the soil AP concentrations in the 2/4CN + 2/4PN and 2/4CN + 1/4PN + 1/4SN treatments were significantly higher than those in the CN treatment, with increases of 100.4% and 75.8%, respectively (Figure 7D). As previously noted in numerous studies, the immobilization of Cu, Pb, and Ni in soil increases as the soil P content increases [37]. Our study also identified a significant negative correlation between the soil AP concentration and soil Cr, Cu, Zn, Cd, and Pb (Figure 7G). Consequently, the increased AP concentrations and decreased soil pH enhance the solubility and effectiveness of Cu, Zn, and Cd in the soil.

4.3. Relative Contribution of HMs to Health Risk and Priority Control HMs

Quantifying the risk contributions, ranking hazardous substances, and identifying key exposure parameters can enhance the management of cultivation and the risk control by decision-makers [10]. The consumption of vegetables containing HMs poses a significant risk, particularly for children, who are more susceptible due to their low body weight, dietary intake, and finger-sucking habits [15]. The HIts results indicated that the HI values of Cu and Zn exceeded 1, with Cu contributing more than 50% of the overall risk (Figure S1).

Additionally, the CR values of Cd and As surpassed the established standards, designating Cd and As as the priority HMs for crop and soil target management [38]. The primary sources of Cd and As were the application of phosphate and organic fertilizer [31]. It was observed that the most effective reduction in the Cd levels was achieved through the combination of PM and SW for both the non-CR and CCR values (Figures 5 and 6). This effectiveness can be explained by the role of SW application in reducing the concentration of H^+, which creates a more negative soil surface charge and promotes the adsorption of Cd [39]. SW possesses a large specific surface area and a highly porous structure [40], enhancing the interaction between HM ions and its surface, thereby facilitating the adsorption and immobilization of Cd. Conversely, substituting PM for CH resulted in an increased mean CR of As for both children and adults, which was further amplified with the addition of SW (Figure 6). As is the most abundant element in clayey soils [41], and its high risk value is primarily attributed to its low RFD value [42]. The absorption patterns of P and As in plants are similar [43], and the combination of PM and SW with CH enhanced the ratio of P/As in cucumber fruits (Figure 7E), thus providing further evidence of the increased CCR values of As under PM and SW application.

4.4. Fertilization Management Strategy of GVP

The production of high-quality products that minimize health risks while providing adequate nutrients is a fundamental aspect of sustainable agriculture. The combined application of CH with PM and SW represents an environmentally friendly and cost-effective approach to fertilizer management for producers and farmers [44]. In subsequent field management, it is crucial to control the amount of CH and manure inputs to mitigate soil acidification. Research has reported that, as a source of more than 40% of the total N, it effectively prevents or even reverses red soil acidification [45].

In this study, a semi-substitution management approach utilizing organic fertilizer was adopted. The statistical results demonstrated the positive impact of using PM and SW in reducing the HM concentrations in both soil and cucumber fruits. Additionally, as essential trace elements, the potential health risks of Cu and Zn in greenhouse cucumber cultivation cannot be overlooked. Therefore, it is crucial to consider the safety and nutritional quality of the human diet.

Compared to the combination of CH and PM, the integrated application of CH and PM with SW management significantly reduces the resource waste, environmental pollution, and exposure risk over the long term while maintaining same nutrient input levels. The long-term implementation of this application strategy enhances the longevity of both soil and vegetables, increases the Cu and Zn accumulation in cucumber fruits, and mitigates soil Cu and Zn pollution. Nevertheless, presenting only one combination scheme is insufficient for optimizing the cucumber yield, improving the soil quality, and reducing the HM risks. Therefore, future research on partial substitution of CH with PM and SW should consider the ratio of PM to SW, HM bioavailability, and the evaluation adjustment plans for extended fertilization periods.

5. Conclusions

Three consecutive years of sampling and monitoring of a 15-year long-term greenhouse vegetable system revealed heavy metal contamination and associated health risks in soil and cucumber cultivation. The concentrations of Cr, Cu, Zn, As, Cd, and Pb in both soil and fruit were below the regulatory limits under combined CH and PM or SW at two nutrient levels (900 kg/ha N + 900 kg/ha P_2O_5 + 900 K_2O and 600 kg/ha N + 300 kg/ha P_2O_5 + 525 kg/ha K_2O, respectively). It is crucial to consider the potential risks of exposure to Cu and Zn, particularly for children, while Cd and As necessitate control measures for GVP management. Compared to low nutrient inputs, long-term application of high levels CH and PM application resulted in soil acidification, increased the soil AP content, and impeded the transfer of Cu and Zn from the soil to the aboveground parts of plants. This led to the elevated Non-CR of Cu in cucumber fruits and contributed to the geological pollution of Cu, Zn, and Cd in the soil. Under equal N-P_2O_5-K_2O levels, the combination of CH with PM and SW increased the soil Cu and Zn geological pollution levels compared with CH application alone. This increase is attributed to the long-term inputs of PM and SW and higher soil AP contents. The 2/4 ratio of CH combined with PM and SW improved the transfer of Cu and Zn and reduced the soil contamination compared to 2/4 ratio of PM and CH. Although this study did not significantly reduce the Non-CR and CCR of HMs, it suggests that managing the Cu and Zn levels can be achieved by reducing the CH inputs, combining the PM and SW applications, and monitoring the soil pH and AP levels.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agriculture14111870/s1, Table S1: The total concentration of six heavy metals in pig manure and straw; Table S2: Total concentrations of heavy metals (mg/kg) in soil and cucumber, as affected by different treatments; Table S3: Seven subclasses of the geo-accumulation index; Table S4: Specific definitions and parameters for the human health risk assessment and exposure risk; Table S5: Reference values of the toxic parameters (RfD and SF) in various exposure pathways; Table S6: Assessment of non-cancer (hazard quotient, HQ; hazard index, HI), carcinogenic risk (CR) and cumulative cancer risk (CCR) from HMs in all the samples; Table S7: Linear regression to estimate the soil HM accumulation rate; Figure S1: Percentage contribution of the hazard index (HI) for non-carcinogenic risks in soil and cucumber fruits of children and adults under organic fertilizer substitution for chemical fertilizer; Figure S2: Percentage contribution of the cumulative carcinogenic risk (CCR) for carcinogenic risks in soil and cucumber fruits of children and adults under organic fertilizer substitution for chemical fertilizer; Figure S3: Linear model estimating the contribution of straw and pig manure HM input to soil and cucumber with Cr, Cu, Zn, As, Cd and Pb accumulation; Figure S4: The sensitivity analysis of the total hazard index (HIt) and HIts from multiple heavy metals; Figure S5: The sensitivity analysis of the total CCR value and CCR values from multiple heavy metals [46–54].

Author Contributions: Conceptualization, H.W. and Y.Z.; methodology, H.W., Y.L. and S.T.; resources, R.L. and S.T.; formal analysis, Y.L.; investigation, Y.Z.; writing—original draft, Y.Z.; writing—review and editing, Y.Z., S.T., H.W. and S.H.; supervision, H.W. and S.H.; funding acquisition, S.T., H.W. and S.H. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key Research and Development Program of China (grant numbers 2021YFD1901200), the National Key Research and Development Program of China (grant numbers 2022YFD1700603), China Agriculture Research System (grant numbers CARS-23-B04), HAAFS Science and Technology Innovation Special Project (grant numbers 2022KJCXZX-ZHS-2), Anhui Province Agricultural Eco-Environmental Protection and Quality Safety Industry Technology System (grant numbers MAITS-Anhui-15), and Ministry of Agriculture and Rural Affairs Soil Testing and Formulated Fertilization Project (grant numbers 2019–2022).

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article/Supplementary Materials; further inquiries can be directed to the corresponding authors.

Conflicts of Interest: Author Yuwei Zhang was employed by the China Land Reclamation (Group) General Corporation. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Wang, R.; Min, J.; Kronzucker, H.J.; Li, Y.; Shi, W. N and P runoff losses in China's vegetable production systems: Loss characteristics, impact, and management practices. *Sci. Total Environ.* **2019**, *663*, 971–979. [CrossRef] [PubMed]
2. Wang, X.; Dou, Z.; Shi, X.; Zou, C.; Liu, D.; Wang, Z.; Guan, X.; Sun, Y.; Wu, G.; Zhang, B. Innovative management programme reduces environmental impacts in Chinese vegetable production. *Nat. Food* **2021**, *2*, 47–53. [CrossRef] [PubMed]
3. Li, J.; Wan, X.; Liu, X.; Chen, Y.; Slaughter, L.C.; Weindorf, D.C.; Dong, Y. Changes in soil physical and chemical characteristics in intensively cultivated greenhouse vegetable fields in North China. *Soil Tillage Res.* **2019**, *195*, 104366. [CrossRef]
4. Zhang, B.; Li, Q.; Cao, J.; Zhang, C.; Song, Z.; Zhang, F.; Chen, X. Reducing nitrogen leaching in a subtropical vegetable system. *Agric. Ecosyst. Environ.* **2017**, *241*, 133–141. [CrossRef]
5. Xu, Y.; Ma, Y.; Cayuela, M.L.; Sánchez-Monedero, M.A.; Wang, Q. Compost biochemical quality mediates nitrogen leaching loss in a greenhouse soil under vegetable cultivation. *Geoderma* **2020**, *358*, 113984. [CrossRef]

6. Bai, X.; Gao, J.; Wang, S.; Cai, H.; Chen, Z.; Zhou, J. Excessive nutrient balance surpluses in newly built solar greenhouses over five years leads to high nutrient accumulations in soil. *Agric. Ecosyst. Environ.* **2020**, *288*, 106717. [CrossRef]
7. Li, H.; Dai, M.; Dai, S.; Dong, X. Current status and environment impact of direct straw return in China's cropland—A review. *Ecotoxicol. Environ. Saf.* **2018**, *159*, 293–300. [CrossRef]
8. Li, F.; Cheng, S.; Yu, H.; Yang, D. Waste from livestock and poultry breeding and its potential assessment of biogas energy in rural China. *J. Clean. Prod.* **2016**, *126*, 451–460. [CrossRef]
9. Liang, F.; Li, B.; Vogt, R.D.; Mulder, J.; Song, H.; Chen, J.; Guo, J. Straw return exacerbates soil acidification in major Chinese croplands. *Resour. Conserv. Recycl.* **2023**, *198*, 107176. [CrossRef]
10. Peng, H.; Chen, Y.; Weng, L.; Ma, J.; Ma, Y.; Li, Y.; Islam, M.S. Comparisons of heavy metal input inventory in agricultural soils in North and South China: A review. *Sci. Total Environ.* **2019**, *660*, 776–786. [CrossRef]
11. Guan, T.-X.; Lu, Z.-P.; Yue, M.; Li, B.-G.; Fu, A.-G.; Zhang, X.-D.; Li, Z.-H. Accumulation of livestock manure–derived heavy metals in the Hexi Corridor oasis agricultural alkaline soil and bioavailability to Chinese cabbage (*Brassica pekinensis L.*) after 4-year continuous application. *Environ. Pollut.* **2024**, *341*, 122969. [CrossRef] [PubMed]
12. Zhen, H.; Jia, L.; Huang, C.; Qiao, Y.; Li, J.; Li, H.; Chen, Q.; Wan, Y. Long-term effects of intensive application of manure on heavy metal pollution risk in protected-field vegetable production. *Environ. Pollut.* **2020**, *263*, 114552. [CrossRef]
13. Xiang, Y.; Li, Y.; Luo, X.; Liu, Y.; Yue, X.; Yao, B.; Xue, J.; Zhang, L.; Fan, J.; Xu, X. Manure properties, soil conditions and managerial factors regulate greenhouse vegetable yield with organic fertilizer application across China. *Front. Plant Sci.* **2022**, *13*, 1009631. [CrossRef] [PubMed]
14. Hussain, M.I.; Khan, Z.I.; Akhter, P.; Al-Hemaid, F.M.; Al-Hashimi, A.; Elshikh, M.S.; Ahmad, K.; Yang, H.-H. Potential of organic amendments for heavy metal contamination in soil–coriander system: Environmental fate and associated ecological risk. *Sustainability* **2022**, *14*, 11374. [CrossRef]
15. Liu, J.; Wang, Y.; Liu, X.; Xu, J. Occurrence and health risks of heavy metals in greenhouse soils and vegetables across China. *Agric. Ecosyst. Environ.* **2021**, *321*, 107632. [CrossRef]
16. Wu, P.; Guo, Z.; Hua, K.; Wang, D. Long-term application of organic amendments changes heavy metals accumulation in wheat grains by affecting soil chemical properties and wheat yields. *J. Soils Sediments* **2023**, *23*, 2136–2147. [CrossRef]
17. Bao, S. *Soil and Agricultural Chemistry Analysis*; China Agriculture Press: Beijing, China, 2000.
18. Adamo, P.; Iavazzo, P.; Albanese, S.; Agrelli, D.; De Vivo, B.; Lima, A. Bioavailability and soil-to-plant transfer factors as indicators of potentially toxic element contamination in agricultural soils. *Sci. Total Environ.* **2014**, *500*, 11–22. [CrossRef]
19. State Environmental Protection Administration of China. *Environmental Quality Evaluation Standards for Farmland of Greenhouse Vegetables Production (HJ/T 333)*; China Environmental Science Press: Beijing, China, 2006.
20. Wei, B.; Yang, L. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem. J.* **2010**, *94*, 99–107. [CrossRef]
21. Wu, W.; Wu, P.; Yang, F.; Sun, D.-l.; Zhang, D.-X.; Zhou, Y.-K. Assessment of heavy metal pollution and human health risks in urban soils around an electronics manufacturing facility. *Sci. Total Environ.* **2018**, *630*, 53–61. [CrossRef]
22. Hu, W.; Huang, B.; Shi, X.; Chen, W.; Zhao, Y.; Jiao, W. Accumulation and health risk of heavy metals in a plot-scale vegetable production system in a peri-urban vegetable farm near Nanjing, China. *Ecotoxicol. Environ. Saf.* **2013**, *98*, 303–309. [CrossRef]
23. Liu, B.; Ai, S.; Zhang, W.; Huang, D.; Zhang, Y. Assessment of the bioavailability, bioaccessibility and transfer of heavy metals in the soil-grain-human systems near a mining and smelting area in NW China. *Sci. Total Environ.* **2017**, *609*, 822–829. [CrossRef] [PubMed]
24. Da Rosa Couto, R.; Faversani, J.; Ceretta, C.A.; Ferreira, P.A.A.; Marchezan, C.; Facco, D.B.; Garlet, L.P.; Silva, J.S.; Comin, J.J.; Bizzi, C.A. Health risk assessment and soil and plant heavy metal and bromine contents in field plots after ten years of organic and mineral fertilization. *Ecotoxicol. Environ. Saf.* **2018**, *153*, 142–150. [CrossRef] [PubMed]
25. Yang, L.; Liu, G.; Di, L.; Wu, X.; You, W.; Huang, B. Occurrence, speciation, and risks of trace metals in soils of greenhouse vegetable production from the vicinity of industrial areas in the Yangtze River Delta, China. *Environ. Sci. Pollut. Res.* **2019**, *26*, 8696–8708. [CrossRef]
26. Yu, H.; Xiao, H.; Cui, Y.; Liu, Y.; Tan, W. High nitrogen addition after the application of sewage sludge compost decreased the bioavailability of heavy metals in soil. *Environ. Res.* **2022**, *215*, 114351. [CrossRef]
27. Su, Y.; Kwong, R.W.; Tang, W.; Yang, Y.; Zhong, H. Straw return enhances the risks of metals in soil? *Ecotoxicol. Environ. Saf.* **2021**, *207*, 111201. [CrossRef]
28. Kalbitz, K.; Wennrich, R. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Sci. Total Environ.* **1998**, *209*, 27–39. [CrossRef] [PubMed]
29. Pérez-Esteban, J.; Escolástico, C.; Masaguer, A.; Vargas, C.; Moliner, A. Soluble organic carbon and pH of organic amendments affect metal mobility and chemical speciation in mine soils. *Chemosphere* **2014**, *103*, 164–171. [CrossRef]
30. De Conti, L.; Ceretta, C.A.; Ferreira, P.A.; Lourenzi, C.R.; Girotto, E.; Lorensini, F.; Tiecher, T.L.; Marchezan, C.; Anchieta, M.G.; Brunetto, G. Soil solution concentrations and chemical species of copper and zinc in a soil with a history of pig slurry application and plant cultivation. *Agric. Ecosyst. Environ.* **2016**, *216*, 374–386. [CrossRef]
31. Zu, Y.; Bock, L.; Schvartz, C.; Colinet, G.; Li, Y. Factors affecting trace element content in periurban market garden subsoil in Yunnan Province, China. *J. Environ. Sci.* **2011**, *23*, 488–496. [CrossRef]

32. Kalkhajeh, Y.K.; Huang, B.; Hu, W.; Ma, C.; Gao, H.; Thompson, M.L.; Hansen, H.C.B. Environmental soil quality and vegetable safety under current greenhouse vegetable production management in China. *Agric. Ecosyst. Environ.* **2021**, *307*, 107230. [CrossRef]
33. Król, A.; Mizerna, K.; Bożym, M. An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. *J. Hazard. Mater.* **2020**, *384*, 121502. [CrossRef] [PubMed]
34. Cai, Z.; Xu, M.; Wang, B.; Zhang, L.; Wen, S.; Gao, S. Effectiveness of crop straws, and swine manure in ameliorating acidic red soils: A laboratory study. *J. Soils Sediments* **2018**, *18*, 2893–2903. [CrossRef]
35. Qian, X.; Wang, Z.; Shen, G.; Chen, X.; Tang, Z.; Guo, C.; Gu, H.; Fu, K. Heavy metals accumulation in soil after 4 years of continuous land application of swine manure: A field-scale monitoring and modeling estimation. *Chemosphere* **2018**, *210*, 1029–1034. [CrossRef]
36. Heimann, L.; Roelcke, M.; Hou, Y.; Ostermann, A.; Ma, W.; Nieder, R. Nutrients and pollutants in agricultural soils in the peri-urban region of Beijing: Status and recommendations. *Agric. Ecosyst. Environ.* **2015**, *209*, 74–88. [CrossRef]
37. Song, Y.C.; Sivakumar, S.; Nguyen, T.T.; Kim, S.; Kim, B.G. The immobilization of heavy metals in biosolids using phosphate amendments—Comparison of EPA (6010 and 3051) and selective sequential extraction methods. *J. Hazard. Mater.* **2009**, *167*, 1033–1037. [CrossRef] [PubMed]
38. Chen, H.; Teng, Y.; Lu, S.; Wang, Y.; Wang, J. Contamination features and health risk of soil heavy metals in China. *Sci. Total Environ.* **2015**, *512*, 143–153. [CrossRef]
39. Hale, B.; Evans, L.; Lambert, R. Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged soils. *J. Hazard. Mater.* **2012**, *199*, 119–127. [CrossRef]
40. Wang, S.; Kwak, J.-H.; Islam, M.S.; Naeth, M.A.; El-Din, M.G.; Chang, S.X. Biochar surface complexation and Ni (II), Cu (II), and Cd (II) adsorption in aqueous solutions depend on feedstock type. *Sci. Total Environ.* **2020**, *712*, 136538. [CrossRef]
41. Yang, S.; Zhao, J.; Chang, S.X.; Collins, C.; Xu, J.; Liu, X. Status assessment and probabilistic health risk modeling of metals accumulation in agriculture soils across China: A synthesis. *Environ. Int.* **2019**, *128*, 165–174. [CrossRef]
42. Li, J.; Li, C.; Sun, H.-J.; Juhasz, A.L.; Luo, J.; Li, H.-B.; Ma, L.Q. Arsenic relative bioavailability in contaminated soils: Comparison of animal models, dosing schemes, and biological end points. *Environ. Sci. Technol.* **2016**, *50*, 453–461. [CrossRef]
43. Watanabe, T.; Urayama, M.; Shinano, T.; Okada, R.; Osaki, M. Application of ionomics to plant and soil in fields under long-term fertilizer trials. *Springerplus* **2015**, *4*, 781. [CrossRef] [PubMed]
44. Wang, Y.; Zhu, Y.; Zhang, S.; Wang, Y. What could promote farmers to replace chemical fertilizers with organic fertilizers? *J. Clean. Prod.* **2018**, *199*, 882–890. [CrossRef]
45. Cai, Y.; Zheng, Z.; Schaefer, F.; Stinner, W.; Yuan, X.; Wang, H.; Cui, Z.; Wang, X. A review about pretreatment of lignocellulosic biomass in anaerobic digestion: Achievement and challenge in Germany and China. *J. Clean. Prod.* **2021**, *299*, 126885. [CrossRef]
46. The Risk Assessment Information System. Toxicity Profiles, Condensed Toxicity Summary for Mercury. 2018. Available online: https://rais.ornl.gov/cgi-bin/tools/TOX_search (accessed on 22 June 2024).
47. Ministry of Environmental Protection of the People's Republic of China (MEP). *Exposure Factors Handbook of Chinese Population*; China Environmental Science Press: Beijing, China, 2013.
48. United States Environmental Protection Agency (USEPA). *Hazardous Waste Management System*; Identification and Listing of Hazardous Waste; Toxicity Characteristics Revisions; Final Rule; USEPA: Washington, DC, USA, 1990.
49. Integrated Risk Information System (IRIS). *Assessments*; U.S. Environmental Protection Agency: Washington, DC, USA, 2006. Available online: https://cfpub.epa.gov/ncea/iris_drafts/AtoZ.cfm (accessed on 5 May 2024).
50. US Environmental Protection Agency (USEPA). *Exposure Factors Handbook*; Office of Research and Development, USEPA: Washington, DC, USA, 2011.
51. *Pre-Feasibility Study of Coal Mine Methane Recovery and Utilization at the Sawang Colliery, East Bokaro Coal Field, India*; Advanced Resources International, Inc. under Contract to the U.S. Environmental Protection Agency: Washington DC, USA, 2015.
52. Wang, X.; Dan, Z.; Cui, X.; Zhang, R.; Zhou, S.; Wenga, T.; Yan, B.; Chen, G.; Zhang, Q.; Zhong, L. Contamination, ecological and health risks of trace elements in soil of landfill and geothermal sites in Tibet. *Sci. Total Environ.* **2020**, *715*, 136639. [CrossRef]
53. WHO. *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*; World Health Organization: Lyon, France, 1990; Volume 49. Available online: https://publications.iarc.fr/67 (accessed on 10 June 2024).
54. Yuan, Y.; Xiang, M.; Liu, C.; Theng, B.K.G. Chronic impact of an accidental wastewater spill from a smelter, China: A study of health risk of heavy metal(loid)s via vegetable intake. *Ecotoxicol. Environ. Saf.* **2019**, *182*, 109401. [CrossRef]