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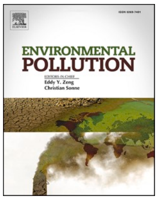

Fertilizer application alters cadmium and selenium bioavailability in soil-rice system with high geological background levels[☆]

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ABSTRACT

The co-occurrence of cadmium (Cd) pollution and selenium (Se) deficiency commonly exists in global soils, especially in China. As a result, there is great interest in developing practical agronomic strategies to simultaneously achieve Cd remediation and Se mobilization in paddy soils, thereby enhancing food quality/safety. To this end, we conducted a field-plot trial on soils having high geological background levels of Cd (0.67 mg kg^{-1}) and Se (0.50 mg kg^{-1}). We explored 12 contrasting fertilizers (urea, potassium sulfate (K_2SO_4), calcium-magnesium-phosphate (CMP)), amendments (manure and biochar) and their combinations on Cd/Se bioavailability. Soil pH, total organic carbon (TOC), soil available Cd/Se, Cd/Se fractions and Cd/Se accumulation in different rice components were determined. No significant differences existed in mean grain yield among treatments. Results showed that application of urea and K_2SO_4 decreased soil pH, whereas the CMP fertilizer and biochar treatments increased soil pH. There were no significant changes in TOC concentrations. Three treatments (CMP, manure, biochar) significantly decreased soil available Cd, whereas no treatment affected soil available Se at the maturity stage. Four treatments (CMP, manure, biochar and manure + urea + CMP + K_2SO_4) achieved our dual goal of Cd reduction and Se enrichment in rice grain. Structural equation modeling (SEM) demonstrated that soil available Cd and root Cd were negatively affected by pH and organic matter (OM), whereas soil available Se was positively affected by pH. Moreover, redundancy analysis (RDA) showed strong positive correlations between soil available Cd, exchangeable Cd and reducible Cd with grain Cd concentration, as well as between pH and soil available Se with grain Se concentration. Further, there was a strong negative correlation between residual Cd/Se (non-available fraction) and grain Cd/Se concentrations. Overall, this study identified the primary factors affecting Cd/Se bioavailability, thereby providing new guidance for achieving safe production of Se-enriched rice through fertilizer/amendment management of Cd-enriched soils.

1. Introduction

Cadmium is one of the most prevalent and toxic heavy metals in soils displaying a high mobility in soils. It is readily absorbed by crop roots and transferred to the above-ground parts, thereby leading to food safety issues (Li et al., 2021). Cd pollution not only inhibits crop growth (El Rasafi et al., 2022; Haider et al., 2021), but long-term consumption of food with excessive Cd content can lead to a series of human health problems, such as impaired immune function, metabolic disorders and Itai-itai disease (Rai et al., 2019). Cd pollution in agricultural soils of China is a serious issue with 7.0% of soils exceeding Chinese paddy Cd pollution standards and a progressive accumulation occurring over the past decade (Zou et al., 2021; Huang et al., 2019).

Selenium is an essential trace element for human health, with antioxidant, immune regulatory and antiviral functions. Moderate intake of Se ($\geq$55 μg day^{-1}) effectively reduces the risk of several diseases and is therefore important in the human diet (Kuria et al., 2020). There is an antagonism between Se and Cd levels in agronomic management (Yang et al., 2021). Exogenous addition of Se can improve crop tolerance to Cd stress (Hasanuzzaman et al., 2020; Shahid et al., 2019) by reducing plant Cd uptake and translocation (Natasha et al., 2018; Cui et al., 2018). Similarly, moderate intake of Se by humans can reduce Cd toxicity

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through improving antioxidant and immune system capacity, but excessive intake of Se will induce the risk of selenosis (Etteieb et al., 2020; He et al., 2018). Se in soils is mainly derived from the weathering of primary minerals (Tabelin et al., 2018) and exists primarily in the form of selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) (Ali et al., 2020). Approximately 51% of Chinese soils are considered deficient in Se, and 39–61% of Chinese residents have Se intake below WHO/FAO recommended values (Dinh et al., 2018).

Rice (*Oryza sativa* L.) is a globally-important, staple food crop contributing ~20% of all the calories consumed by the world's population (Yu et al., 2023). Given the co-occurrence of Cd pollution and Se deficiency in soils worldwide (Vareda et al., 2019; Tan et al., 2016), research addressing agronomic management strategies to reduce Cd and enrich Se in rice grain is of great global importance. Application of fertilizers (e.g., urea, CMP) (Rao et al., 2018) and soil amendments (e.g., lime, manure) (Hamid et al., 2019a) are economical and environmentally-friendly chemical approaches to alter the bioavailability of elements in soil (Hou et al., 2020) by changing soil properties, such as pH, Eh (soil redox potential) and organic matter quantity/quality (Hussain et al., 2021). These changes in elemental bioavailability strongly influence the uptake and accumulation of these elements in crops, thereby affecting food quality/safety. For example, biochar has been shown to modify the bioavailability of Cd and Se by affecting adsorption-desorption processes and complexation reactions. Application of biochar in paddy fields can fix Cd into non-bioavailable forms in soil (Hamid et al., 2019b); it can also regulate the fixation and release of Cd and Se in soil through altering OM dynamics (Dinh et al., 2017). Moreover, alkaline calcium-magnesium-phosphate (CMP) fertilizer, a commonly used fertilizer in agriculture, can also influence Cd and Se bioavailability by altering soil pH (Deng et al., 2020) and the soil microbial community (Wu et al., 2017).

Although numerous studies have examined soil Cd pollution remediation and Se biofortification (Schiavon et al., 2020; Trippe and Pilon-Smits, 2021), several issues still require practical solutions: (1) there is little research on strategies to simultaneously reduce Cd bioavailability and improve Se bioavailability in soil to achieve the dual goals of Cd reduction and Se enrichment in crops; and (2) there is little emphasis on the mechanisms by which fertilizers affect Cd and Se bioavailability in the soil-rice system. Hence, the primary aims of this research were to evaluate the effects of different fertilizer and fertilizer-amendment combinations on Cd and Se bioavailability and their effects on Cd and Se accumulation in different parts of the rice plant. A replicated field experiment was conducted to assess several fertilizer-amendment combinations with respect to Cd reduction and Se enrichment in rice using soils containing high geological background concentrations of Cd and Se. We hypothesized that treatments with CMP, manure and biochar will play an important role in Cd reduction and Se enrichment through their affects on altering soil pH, sorption/desorption, complexation, precipitation/dissolution and redox dynamics. Based on changes in soil properties, Cd/Se solid-phase fractionation and Cd/Se accumulation in various plant components, we explored how fertilizer and fertilizer-amendment combinations affected Cd and Se bioavailability in the soil-rice system.

2. Materials and methods

2.1. Field description and experimental design

Field trials were carried out in Yanglin town, Zhejiang province, China (E 29°3′11'', N 118°7′18''). The site has an average annual temperature of 16.3 °C and precipitation of 1799 mm. Due to long-term mining activities and the common occurrence of Cd and Se in minerals, the study area has high average soil concentrations of total Cd (0.67 mg kg^{-1}) and Se (0.50 mg kg^{-1}). Based on Chinese Paddy Standards, the paddy soils are characterized as having high geological background levels of Cd (>0.6 mg kg^{-1}) and Se (>0.4 mg kg^{-1}). Basic properties of the paddy soil were: pH: 7.06; total N: 0.73 g kg^{-1}; and TOC content: 16.3 g kg^{-1}.

A completely randomized plot experiment (30 m^2 plots: 5 m × 6 m) with each plot separated by a cement berm contained 12 fertilizer/amendment treatments (Table 1). Each treatment was replicated three times (3 replicates × 12 treatments = 36 plots). N fertilizer was applied as a split application with a ratio of 4:3:3 for the base, tillering and panicle growth stages. All others treatment amendments were applied at the base stage. Selected properties of the fertilizers and amendments are given in Table S1. The local rice cultivar, Zhongzheyou8, was transplanted in early July, a week after base amendment application and stabilization. Plants were harvested in late October. Continuous flood irrigation was provided followed by a final drainage at the filling stage.

2.2. Sample collection

Soil samples were randomly collected at the tillering (early August) and maturity (late October) stages. Rice roots, stems and grains were collected at the maturity stage. Five random soil and rice samples were collected from each plot and homogenized to form a single composite sample. Subsamples were air dried and ground to pass either a 2-mm or 0.15-mm mesh sieve, and then stored for subsequent analyses. The <2-mm soil was used for pH determination, while the <0.15-mm soil was used for TOC, total N and Cd/Se analyses. Rice biomass samples were washed with tap water and dried to a constant weight at 60 °C. The dried rice samples were ground using a stainless-steel mill and passed through a 0.15-mm mesh sieve for analysis of total Cd and Se concentrations.

2.3. Analytical methods

Soil pH was measured with a pH electrode (1:2.5 H_2O). TOC (a proxy for soil organic matter) and total N was determined by dry combustion using a carbon analyzer (Analytic Jena multi N/C 3100, Jena, Germany). Soil available Cd was determined by extraction with DTPA (0.005 M DTPA-0.1 M TEA (triethanolamine, $C_6H_{15}NO_3$)-0.01 M $CaCl_2$) for 2 h at 180 rpm shaking rate. Soil available Se was extracted with 0.1 M KH_2PO_4 for 2 h at 180 rpm shaking rate.

A modified four-step BCR method (Rauret et al., 1999) was employed to differentiate soil Cd fractions: exchangeable (F1), reducible (F2), oxidizable (F3) and residual (F4). A 0.500 g sample of air-dried soil was sequentially extracted with 0.1 M HOAc, 0.1 M $NH_2OH{\cdot}HCl$, and 30% H_2O_2 to determine the exchangeable, reducible, and oxidizable fractions, respectively. The residue was treated by microwave digestion, as reported below, to obtain the residual fraction.

A five-step sequential extraction method (Wang et al., 2012) was employed to differentiate soil Se fractions: soluble (F1), exchangeable and carbonate-bound (F2), iron (Fe)/manganese (Mn) oxide-bound (F3), organic matter-bound and elemental (F4) and residual fraction

Table 1
Fertilizer treatments and their abbreviations used in this study.

Treatments	Application rate (kg ha^{-1})	Abbreviations
Control	0	CK
Urea	90	N
CMP fertilizer	45	P
K_2SO_4	75	K
Urea + CMP fertilizer	90 + 45	NP
Urea + K_2SO_4	90 + 75	NK
CMP fertilizer + K_2SO_4	45 + 75	PK
Urea + CMP fertilizer + K_2SO_4	90 + 45+75	NPK
Manure	4500	LOM
Biochar	4500	LBR
Manure + Urea + CMP fertilizer + K_2SO_4	4500 + 90+45 + 75	LM
Biochar + Urea + CMP fertilizer + K_2SO_4	4500 + 90+45 + 75	LR

(F5). A 1.00 g sample of air-dried soil was extracted with 0.25 M KCl, 0.7 M KH_2PO_4 (pH 5.0), 2.5 M HCl, and 5% $K_2S_2O_8$ with concentrated HNO_3 to determine the soluble, exchangeable/carbonate-bound, Fe/Mn oxide-bound, and organic matter-bound/elemental fractions, respectively. The residue was treated by microwave digestion to obtain the residual fraction.

Total Cd and Se concentrations of soil/plant materials were determined following microwave digestion. A 0.10 g sample of air-dried soil/plant material was placed in a sealed polytetrafluoroethylene (PTFE) tube and digested with a mixed solution of HNO_3–HF–H_2O_2 (2:2:1 ratio) at 180 °C for 2–3 h.

The Fe and Mn contents of iron-manganese plaque (IP) on the rice root surface were determined using a modified dithionite-citrate-bicarbonate (DCB) extraction. Rice roots were immersed in a DCB solution (0.03 M $Na_3C_6H_5O_7 \cdot 2H_2O$, 0.125 M $NaHCO_3$ and $Na_2S_2O_4$ as a catalyzer) for 1 h at room temperature (25 °C).

The Cd and Se concentrations in all digestion/extraction solutions and the Fe and Mn contents of IPs were determined by inductively-coupled plasma mass spectrometry (ICP-MS, PerkinElmer Nexlon300X). A standard reference soil (GBW07980, GSS-38) was used for quality control/quality assurance. Total Cd and Se recoveries from the standard reference soil were 98.4–101.6% and 90.9–108.4%, respectively.

2.4. Data analysis

Statistical analyses were performed using Microsoft Excel 2016 and SPSS 26.0. Mean and standard deviation (SD) values were calculated for all analytes (e.g., pH, organic matter, available Cd/Se, Cd/Se fractions, soil/rice total Cd/Se), with results expressed as mean ± SD ($n = 3$). Treatment differences were assessed by analysis of variance (ANOVA), followed by a Tukey's test. A $P < 0.05$ was used to designate statistical significance. Structural equation modeling (SEM) was performed using Amos 28.0 software and redundancy analysis (RDA) was performed using Canoco 5.0. Figures were constructed using Origin 2021.

3. Results

3.1. Soil pH and TOC

Changes of soil pH and TOC with different fertilizer/amendment treatments at tillering and maturity stages are given in Table 2. There were few differences ($P < 0.05$) in pH and TOC between tillering and maturity stages as all amendments, except for urea, were applied at the onset of the field trial. Soil pH decreased at the tillering stage from 7.13 (CK) to 6.76 (N) and 6.83 (K) with the addition of N and K fertilizers owing to physiological acidity generated to maintain the root cation-anion uptake balance. Similarly, the NK (6.59/6.50 tillering/maturity) treatment displayed a decrease in soil pH relative to CK. This highlights the potential for soil acidification with long-term applications of urea and K_2SO_4. In contrast, the P fertilizer, and biochar treatments (P, LBR, LR) increased the soil pH (7.54–7.82) at both tillering and maturity due to their alkalinity. Overall, there was no significant difference in TOC content between any treatment and the control (CK; $P < 0.05$) throughout the experimental period. While treatments with manure and biochar showed elevated TOC contents (19.4–21.3 g kg^{-1} versus 16.5–16.8 g kg^{-1} for CK), these differences were not significant. Similarly, the NPK treatment experienced an apparent reduction in TOC from 16.8 to 12.2 g kg^{-1} at maturity, but the difference was not significant.

Table 2
Soil pH and OM content of different fertilizer/amendment treatments at two growth stages. Values are presented as means ± standard deviations (SD). Different letters indicate a significant difference among treatments at the same growth stage ($P < 0.05$).

Treatment	Soil properties			
	pH (H_2O)		TOC (g kg^{-1})	
	Tillering stage	Maturity stage	Tillering stage	Maturity stage
CK	7.13 ± 0.15cd	7.08 ± 0.11cde	16.5 ± 1.5a	16.8 ± 1.1abc
N	6.76 ± 0.09ef	6.73 ± 0.07ef	16.7 ± 1.7a	15.6 ± 1.4bc
P	7.54 ± 0.09 ab	7.57 ± 0.19 ab	15.2 ± 0.6a	16.2 ± 2.3abc
K	6.83 ± 0.12ef	6.75 ± 0.16ef	17.2 ± 1.2a	18.2 ± 2.7 ab
NP	7.27 ± 0.09bc	7.19 ± 0.07cd	15.4 ± 1.6a	16.2 ± 0.5abc
NK	6.59 ± 0.06f	6.50 ± 0.16f	16.5 ± 2.5a	17.0 ± 2.7abc
PK	7.28 ± 0.08bc	7.26 ± 0.17bcd	16.1 ± 2.0a	16.7 ± 1.4abc
NPK	6.94 ± 0.09de	6.92 ± 0.08de	12.3 ± 1.5a	12.2 ± 1.2c
LOM	7.37 ± 0.08bc	7.38 ± 0.11bc	21.6 ± 2.3a	21.2 ± 3.1a
LBR	7.76 ± 0.12a	7.82 ± 0.14a	21.7 ± 0.7a	21.3 ± 0.2a
LM	7.30 ± 0.05bc	7.38 ± 0.11bc	19.4 ± 2.7a	20.9 ± 1.4 ab
LR	7.56 ± 0.14 ab	7.62 ± 0.08 ab	19.8 ± 2.2a	20.4 ± 2.0 ab

3.2. Available soil Cd and Se

Effects of fertilizer/amendment treatments on available Cd and Se concentrations are presented in Fig. 1. DTPA-extractable Cd in CK was 0.178 mg kg^{-1} at tillering stage and 0.172 mg kg^{-1} at maturity stage. At the tillering stage, the only significant effect was a 38.8% decrease in available Cd in the biochar treatment compared to CK. At the maturity stage, the effects of fertilizer treatments were more pronounced. The application of N and NK fertilizer significantly increased available Cd by 41.3% and 26.2%, respectively, whereas P fertilizer, manure (LOM) and biochar (LBR) significantly decreased available Cd by 27.3%, 27.3% and 31.4%, respectively.

The KH_2PO_4-extractable Se in CK was 0.038 mg kg^{-1} at tillering stage and 0.036 mg kg^{-1} at maturity stage. The effect of different fertilizer/amendment treatments on available Se was not significant at the tillering stage versus CK, despite mean values being 20.5% higher in the manure treatment and 23.1% lower in the N treatment. At maturity stage, the only significant difference was an increase in available Se (+44.4%) for the biochar treatment (LBR).

3.3. Soil Cd and Se fractions

With respect to the various Cd and Se fractions, the earlier the form is released in the sequential extraction, the more available/accessibly it is considered for plant uptake. Cd was mainly bound in the residual fraction (F4), followed by the exchangeable (F1), reducible (F2) and oxidizable (F3) fractions (Fig. 2 and Table S2). At tillering stage, the only significant difference among Cd fractions was a reduction in the reducible (F2) Cd by P fertilization. In contrast, treatment effects on Cd fractions were more pronounced at maturity stage. The exchangeable (F1) fraction of the P, LOM and LBR treatments showed significant decreases of 32.8%, 39.6% and 38.6% relative to CK. In contrast, the residual (F4) fraction of the N, NP and NK treatments showed significant increases of 21.2%, 14.9% and 19.1%.

Soil Se was mainly found in the Fe/Mn oxide-bound (F3), organic matter-bound/elemental (F4) and residual (F5) fractions (Fig. 3 and Table S3). The sum of soluble (F1) and exchangeable/carbonate-bound (F2) fractions is generally considered the available Se (Peng et al., 2016). Compared to the other fractions, available Se content (F1+F2) was relatively small (<14%). In comparison to CK, differences in Se fractions at tillering were a lower soluble (F1) fraction for LM, a higher exchangeable/carbonate (F2) fraction for K, a lower F2 fraction for NP, NPK, LOM, LBR and LM, and a higher Fe/Mn oxide-bound (F3) fraction for the NPK treatment. At maturity stage, the NPK (+63.1%) and LR (+58.7%) treatments showed an increase in the combined F1+F2 fractions (i.e., available Se) relative to CK. The Fe/Mn oxide-bound (F3) Se decreased for LBR (−22.9%) and LR (−19.6%), while the organic matter-bound/elemental (F4) Se increased in the LBR (+22.4%) and LR (+21.5%) treatments. The LR treatment showed a decrease (−28.3%) in the residual (F5) fraction.

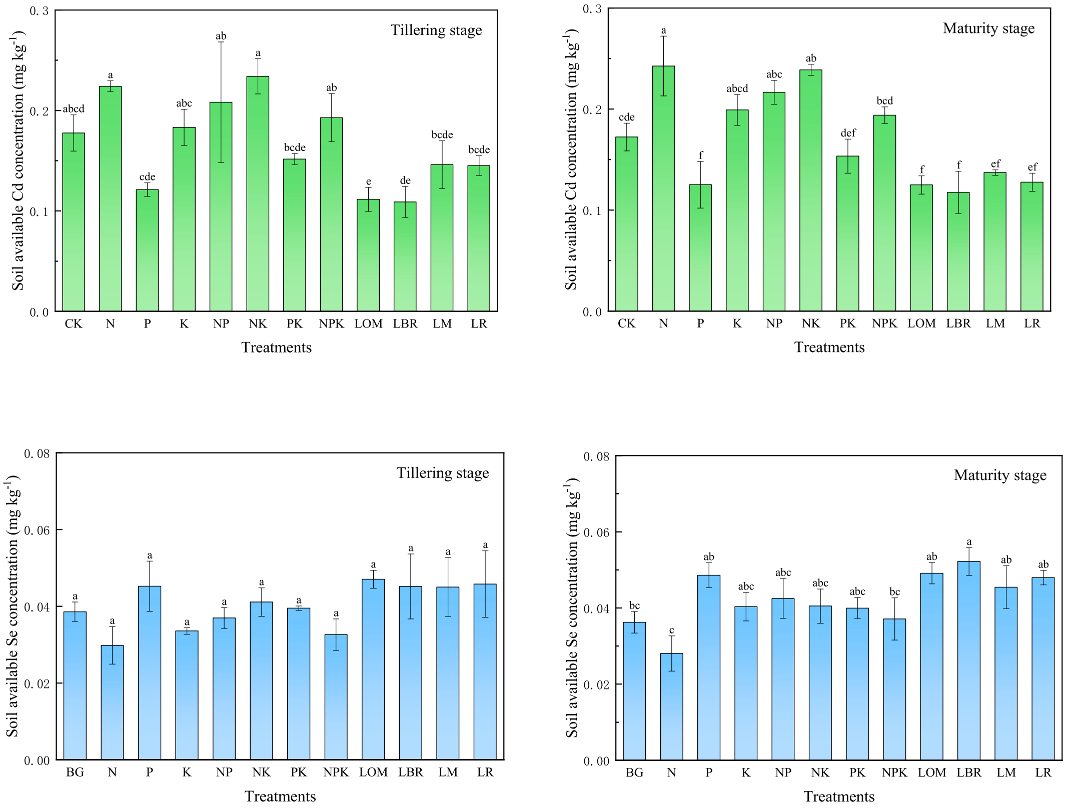

Fig. 1. Effect of different fertilizer/amendments on soil available Cd and Se concentrations (mean ± standard deviation) at tillering and maturity growth stages. Different letters indicate a significant difference among treatments at the same stage ($P < 0.05$).

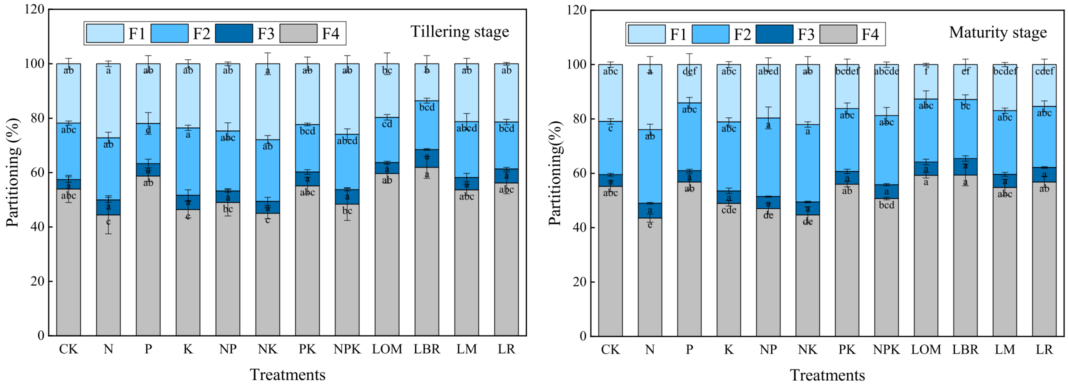

Fig. 2. Effects of different fertilizer/amendments on Cd fractions in the soil at the tillering and maturity growth stages (mean ± standard deviation). F1, F2, F3 and F4: exchangeable fraction, reducible fraction, oxidation fraction and residual fraction. Total Cd concentration of all treatments are the same (0.67 mg kg^{-1}). Different letters indicate a significant difference among Cd fractions of different treatments ($P < 0.05$).

3.4. *Cd and Se accumulation in different rice plant components*

Across all fertilizer/amendment treatments, the mean grain yield ranged from 7.61 to 8.50 t ha^{-1} with no significant differences among treatments (Table S4). As for IP-Fe and IP-Mn contents on the root surface (Table S5), there was no significant difference in IP-Mn. On the other hand, the LOM and LBR treatments showed significant increases of 18.9% and 18.4% in IP-Fe compared to CK. Effects of fertilizer/amendment treatments on Cd and Se concentrations in roots, stems and grain at the maturity stage are presented in Fig. 4. There were no significant differences in Cd or Se concentrations in roots among the various treatments compared to CK. Cd concentrations in stems of the P, LOM, LBR and LM treatments showed a significant decrease of 38.6%, 45.1%, 43.4% and 41.3%, respectively, whereas the N treatment showed an increase of 75.7%. As for Se in stems, the P and LM treatments showed a significant increase of 70.4% and 81.3%, respectively.

As a food safety issue, the Cd concentration of grain in CK (0.21 ± 0.01 mg kg^{-1}) exceeded the Chinese Food Hygiene Standards (0.2 mg kg^{-1}). Grain Cd concentrations of seven treatments were below 0.2 mg kg^{-1} with four treatments (P: 31.3%, LOM; −34.5%, LBR: 41.2% and LM: 28.5%) showing a significant decrease relative to CK. As for Se in grain, all treatments were within the range of the Chinese Rich Selenium Paddy Standards (0.04–0.30 mg kg^{-1}) due to the high geological background levels of Se. Five treatments (P: +89.3%, LOM: +62.5%, LBR: +60.9%, LM: +97.2% and LR: +86.2%) showed a significant increase in Se concentration relative to CK. Overall, four treatments (P, LOM, LBR and LM) achieved the overall objective of simultaneously decreasing grain Cd concentration and increasing grain Se

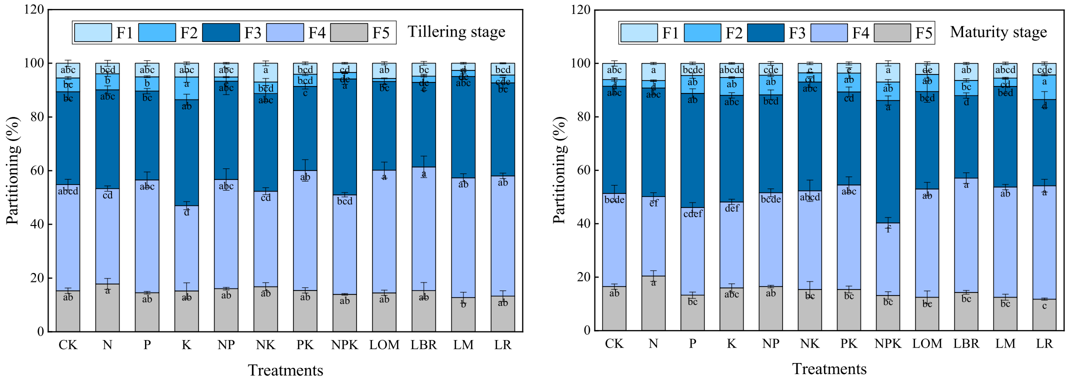

Fig. 3. Effects of different fertilizer/amendments on Se fractions in the soil at the tillering and maturity growth stages (mean ± standard deviation). F1, F2, F3, F4 and F5: soluble fraction, exchangeable and carbonate-bound fraction, iron (Fe)/manganese (Mn) oxide-bound fraction, organic matter-bound and elemental fraction, and residual fraction. Total Se concentration of all treatments are the same (0.50 mg kg^{-1}). Different letters indicate a significant difference among Se fractions of different treatments ($P < 0.05$).

concentration.

3.5. SEM and RDA analysis

We found four fertilizer/amendment treatments (P, LOM, LBR and LM) were successful at meeting our dual objective of Cd reduction and Se enrichment in rice grain. To examine relationships between different factors and Cd/Se bioavailability, SEM (Fig. 5) and RDA (Fig. 6) were conducted. The SEM was made to explain the relationships between soil properties, soil available Cd/Se, and root, stem and grain Cd/Se concentrations. According to the path coefficient, soil available Cd was negatively affected by soil pH ($P < 0.001$) and OM ($P < 0.05$). Similar to soil available Cd, root Cd concentration was negatively affected by soil pH ($P < 0.01$), OM ($P < 0.05$) and IP-Fe ($P < 0.05$). In contrast, soil available Se was positively affected by soil pH ($P < 0.001$), but OM had little effect on plant Se accumulation. With respect to Cd and Se concentrations in different plant parts, as the two elements were transported from roots to grain, the accumulation of Cd and Se in roots strongly affected the concentration in the grain ($P < 0.001$).

An RDA was performed to identify the factors influencing grain Cd and Se concentrations, with soil properties and Cd/Se fractions combined. RDA showed that the interpretation of the two sorting axes reached 90.5%. Among them, the first (horizontal axis) and second (vertical axis) axes explained 85.2% and 5.3% of the information, respectively. As for soil properties, the longer arrow for soil pH than OM and IP-Fe indicates that pH had a relatively stronger explanatory effect for the Cd and Se concentrations of grain. In addition, the degree of the angle between grain Cd and other factors demonstrated that the positive correlations between A-Cd, F1–Cd and F2–Cd with grain Cd, and the negative correlation between F4–Cd and grain Cd were strong. Similarly, the positive correlations between pH and available Se with grain Se, and the negative correlation between F5–Se and grain Se were strong. The results from SEM and RDA help explain how the changes in soil properties induced by different fertilizer/amendment treatments affect Cd/Se bioavailability.

4. Discussion

4.1. Factors affecting Cd and Se bioavailability under different fertilizer/amendments

The SEM and RDA suggested that pH, OM and IP-Fe play important roles in the bioavailability of Cd and Se. Soil available Cd was negatively related to pH and OM, whereas soil available Se was positively related to pH. Hence, the application of alkaline fertilizers/amendments, such as CMP and biochar, increased soil pH resulting in a reduction of bioavailable Cd and an enrichment of bioavailable Se. In contrast, the application of N and K fertilizers resulted in a decrease in soil pH and a corresponding increase in bioavailable Cd and decrease in bioavailable Se. While the application of fertilizers/amendments with high OM content (LOM, LBR, LM and LR) should reduce Cd bioavailability, there were no significant changes in soil OM content compared to the control for any treatments tested in this study. This infers that much of the added OM was either mineralized directly or created a priming effect for endogenous SOM mineralization during the study period.

Soil Cd bioavailability has been shown to depend on several soil chemical and physical properties, especially pH and OM. As soil pH increases, the sorption affinity of soil colloids for Cd increases, which results in the reduction of soil Cd mobilization and lower Cd uptake and accumulation in rice (Egene et al., 2018; Gong et al., 2021). On the contrary, soil acidification results in Cd desorption and transforms Cd from more strongly bound forms (e.g., reducible and oxidizable fractions) to more weakly bound forms (e.g., exchangeable fraction), thereby increasing Cd bioavailability and rice Cd accumulation (Wen et al., 2021; Hu et al., 2016). The increase of soil pH also promotes the formation of iron plaque on the surface of rice roots (Kong et al., 2023). The iron plaque forms a barrier to Cd movement to the plant root as Cd is sorbed or coprecipitated in the iron plaque. This immobilization of Cd within the iron plaque limits the uptake and accumulation of Cd in the above-ground rice components (Li et al., 2017). The SEM analysis (Fig. 5) showed a strong relationship between pH and IP-Fe ($P < 0.001$) indicating the role of higher pH values in generating greater iron plaque formation.

SOM is another key soil factor affecting Cd bioavailability (Yuan et al., 2019; Grüter et al., 2019). SOM contains several functional groups (e.g., –COOH and –OH) that can form complexes with Cd^{2+}. This complexation reduces the mobility and bioavailability of Cd (Zeng et al., 2011). Organic acids produced by plants and microbes can further react with Cd^{2+} resulting in Cd immobilization (Li et al., 2019) and further by decreasing soil pH. The addition of OM to paddy soils also provides a microbial substrate that facilitates reduction of Fe in the bulk soil and formation of iron plaque in the oxidized rice-root rhizosphere. There was a significant increase of IP-Fe in the LBR and LOM treatments, which contained the highest OM contents (Table S5).

Selenium can exist in soils in four different oxidation states: Se (-II), Se (0), Se (IV) and Se (VI). Among inorganic forms, Se (VI) (selenate = SeO_4^{2-}) is more bioavailable than Se (IV) (selenite = SeO_3^{2-}) (Peng et al., 2017). As with Cd, soil pH plays an important but opposing role in the sorption dynamics of selenate and selenite (Xiao et al., 2020). As soil pH increases, the adsorption of negatively charged selenate/selenite on the surface of soil colloids decreases (Li et al., 2016). This trend is particularly evident for selenate, as it is mainly retained by soil colloids through

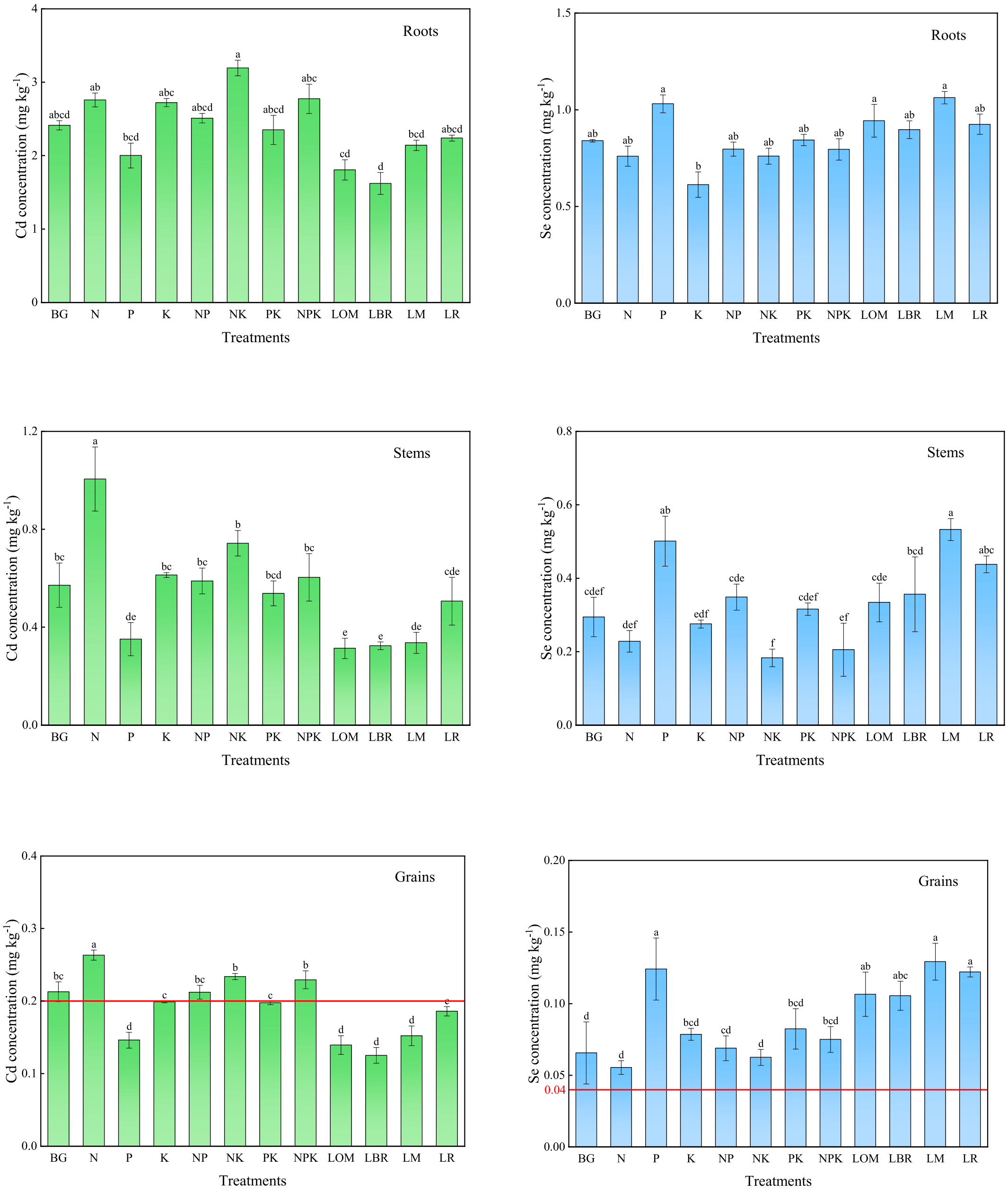

Fig. 4. Effects of different fertilizer/amendment treatments on Cd and Se concentrations in roots, stems and grains at maturity stage (mean ± standard deviation). The red line in the figure of Grain Cd concentrations represents Chinese Food Hygiene Cd Standards (0.2 mg kg^{-1}), while the red line in the figure Grain Se concentrations represents Chinese Rich Selenium Paddy Standards (0.04 mg kg^{-1}). Different letters indicate a significant difference among treatments ($P < 0.05$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

electrostatic interactions. Higher soil pH increases the negative charge on variable-charged colloids that repels SeO_4^{2-} and SeO_3^{2-}. As a result, the selenate/selenite accumulates in the aqueous phase, which is readily available for plant uptake. In contrast, when soil acidification occurs, variable-charge Fe/Al (hydr)oxides can obtain a zero or positive charge state that facilitates sorption (ligand exchange) and/or electrostatic attraction of selenate/selenite, thereby decreasing Se bioavailability (Li et al., 2015).

Although the SEM and RDA in this study indicated that SOM had no significant effect on Se bioavailability, it has been shown that SOM can play a role in the mobility and bioavailability of Se. The effect of SOM on Se bioavailability can be bidirectional (Li et al., 2017). For instance, due to its large specific surface area and strong chelating ability, OM is able to retain Se by sorption to organo-metal complexes, hence immobilizing Se (Wang et al., 2020). In contrast, SOM can increase Se bioavailability by serving as a substrate for microbial generation of low-molecular-weight organic acids (LMWOAs), which can dissolve and release Se retained by soil colloids (Sharma et al., 2015). In this study, the two opposing effects of SOM on Se bioavailability may offset each other resulting in the lack of a significant relationship in the SEM and RDA.

4.2. *Other mechanisms affecting Cd and Se bioavailability*

Although fertilizer/amendment treatments with CMP, manure and biochar achieved our dual goals of Cd reduction and Se enrichment in rice grain, other chemical fertilizer treatments appeared to exacerbate the Cd pollution risk. In addition to changing soil pH and OM, fertilizer/amendments can affect Cd and Se bioavailability through Cd/Se sorption-desorption reactions, precipitation-dissolution reactions,

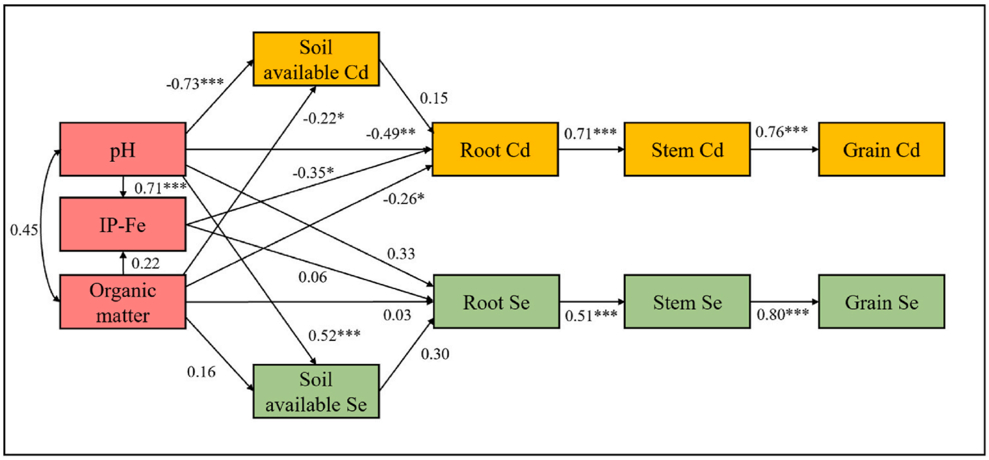

Fig. 5. SEM framework describing the relationships among soil properties, soil available Cd/Se and grain Cd/Se. *, ** and *** indicate significant differences at $P < 0.05$, $P < 0.01$ and $P < 0.001$.

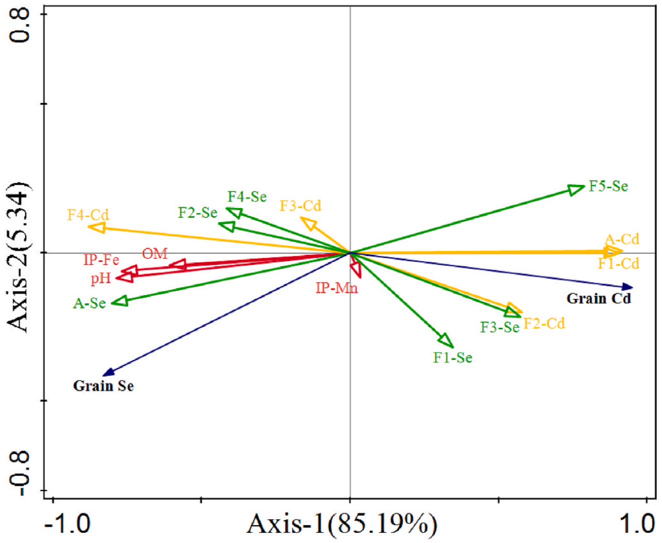

Fig. 6. Contribution of soil properties, soil available Cd/Se and Cd/Se fractions to grain Cd/Se concentrations. Red arrows with red words represent soil properties, yellow arrows with yellow words represent soil available Cd and Cd fractions, and green arrows with green words represent soil available Se and Se fractions in RDA (A-Cd: soil available Cd; A-Se: soil available Se). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

alterations of the microbial community and so on. In this study, the urea treatment increased soil Cd pollution risk. In addition to affecting Cd bioavailability by changing soil pH, nitrogen fertilizer can also increase the accumulation of Cd in plants (Cheng et al., 2016; Yang et al., 2020) by regulating NO-induced divalent cation transporter and cell wall components that allow greater Cd uptake (Cheng et al., 2018). However, the addition of biochar can reduce Cd mobilization after N fertilizer application by promoting nitrification and ammonia-oxidizing bacteria (AOB) (Zhao et al., 2020). Fertilizer can play an indirect role in increasing Se accumulation in rice (Reis et al., 2018) by stimulating root uptake pathways as selenite is transported by phosphate transport mechanisms (Li et al., 2008) and selenate is transported through sulfate transporters and channels (Feist and Parker, 2001; Zhang et al., 2003).

The K_2SO_4 treatment showed little effect on Cd and Se bioavailability. Compared to other fertilizers, there is little research on the relationship between potassium fertilizers and Cd/Se bioavailability. Electrostatic competition between K^+ and Cd^{2+} for cation exchange sites is not strong in soils. Rather, potassium-based fertilizers mainly effect Cd and Se bioavailability via its anions (SO_4^{2-} or Cl^-). For K_2SO_4, SO_4^{2-} can be reduced to S^{2-} in paddy soils, which can produce a CdS precipitate to decrease Cd bioavailability (Li et al., 2022; Huang et al., 2021b). Additionally, SO_4^{2-} can act as a competitive ion with SeO_4^{2-} and SeO_3^{2-}, thereby inducing Se exchange/desorption to increase Se bioavailability (Violante, 2013).

The CMP fertilizer treatment was effective in decreasing Cd and increasing Se concentrations in rice grain. Phosphate fertilizer, especially CMP, is often used to reduce Cd bioavailability (Seshadri et al., 2017). In addition to its alkalinity, CMP can promote the formation of iron plaque in the rice rhizosphere (Zhao et al., 2020), thereby reducing the uptake of Cd to plant tissues. Phosphate can further immobilize Cd in soil through formation of $Cd_3(PO_4)_2$ precipitates (Seshadri et al., 2016). For Se accumulation, the PO_4^{3-} in CMP is a competitive ion with SeO_4^{2-} and SeO_3^{2-} and will release Se into the soil solution through competitive adsorption/desorption reactions (Dinh et al., 2019).

Treatments incorporating manure and biochar were effective in decreasing Cd and increasing Se concentrations in rice grain. In addition to their impact on soil pH and SOM, these organic sources play an important role in altering soil structure (especially biochar) (Dai et al., 2021) and determining soil microbial abundance and community structure (Lehmann et al., 2011). Changes in microbial communities can alter their mediation of element biogeochemical cycles (e.g., N, P, Fe cycling), and changes of elements can alter Cd and Se bioavailability by affecting complexation, precipitation-dissolution and oxidation-reduction reactions. (Muehe et al., 2013a, b; Wang et al., 2021). Since Se is a redox sensitive element, organic compounds that stimulate reduction processes might decrease Se bioavailability as selenate is reduced to selenite (more strongly sorbed) and selenides (forming insoluble precipitates).

4.3. *Management of fertilizer/amendment applications*

Other fertilizers/amendments have shown the ability to alter Cd and Se bioavailability. For instance, the application of silicon fertilizer decreased Cd bioavailability (Wang et al., 2020), through Si–Cd complexes formed between Cd and Si–O groups (Guo et al., 2022; Zhao et al., 2022). Applying Se fertilizer is a direct way to achieve Se bioaugmentation, and the Se will also antagonize soil Cd bioavailability and uptake in crops (Affholder et al., 2019; Guo et al., 2021) by promoting iron plaque formation and enhancing free radical oxygen loss (Huang et al., 2020). It has shown that application of Se and Si will affect Cd toxicity amelioration via a synergistic effect (Huang et al., 2021a) by regulating gene expression to sequester Cd in the root cell walls and organelles, and reduce Cd transfer to the shoots.

This study demonstrated that application of CMP fertilizer, manure and biochar effectively reduced Cd uptake and increased Se uptake. However, previous studies have shown that long-term fertilization can increase the risk of heavy metal pollution (e.g., Cd, As, Zn, etc.) in paddy soils (Xu et al., 2018; Gao et al., 2021; Wang et al., 2020). First, long-term fertilization with urea- and ammonium-based fertilizers will lead to soil acidification, with induces a corresponding increase in Cd bioavailability and decrease in Se bioavailability. Second, Cd is often found as a contaminant in fertilizers (especially phosphate fertilizers) and can accumulate in the soils experiencing long-term fertilization (Wiggenhauser et al., 2019). Therefore, strategies that reduce soil environmental risks while maintaining the soil nutrient balance are required. The combination of fertilizers and other amendments (lime, biochar, manure) may provide some opportunities, but these amendments may increase the input cost of rice cultivation. One study found that sourcing 40% or greater of total N from manure can prevent soil acidification while simultaneously meeting the phosphorus needs of plants (Cai et al., 2021), which may be a reasonable solution to balance soil fertility and pollution risks. Similarly, we found that the combined manure + urea + CMP + K_2SO_4 treatment met the nutrient needs of the rice plants while suppressing Cd uptake and enhancing Se uptake. It is notably that all treatments in our study, even those not receiving a completely balanced fertilizer application, achieved the same mean yield during this one-year cultivation period.

5. Conclusions

This study reports on the effects of fertilizers/amendments on Cd and Se bioavailability in a soil-rice system growing on soil with high geological background concentrations of Cd and Se. Treatments with urea or K_2SO_4 decreased soil pH, whereas treatments with CMP and biochar increased soil pH. There was no significant change in SOM concentrations, even in treatments receiving manure and biochar. The CMP, LOM and LBR treatments significantly decreased DTPA-extractable Cd by 27.3%, 27.3% and 31.4% at the rice maturity stage, whereas the fertilizer/amendment treatments did not affect KH_2PO_4-extractable Se. The CMP, LOM, LBR and LM treatments achieved our dual goals of Cd reduction and Se enrichment in rice grain. Considering the nutrient requirements of rice, the LM treatment perhaps presents the best choice. There was no significant difference in grain yield between treatments. SEM showed that DTPA-extractable Cd and root Cd were negatively related to pH and SOM, whereas KH_2PO_4-extractable Se was positively related to pH. Root Cd was also negatively related to IP-Fe. Further, RDA showed a strong positive correlation between available Cd, exchangeable Cd and reducible Cd with grain Cd content, as well as a strong positive correlation between pH and available Se with grain Se content. There was also a strong negative correlation between the residual Cd/Se fractions (non-available fraction) and grain Cd/Se contents. These results are generally consistent with our hypothesis. Treatments with CMP, manure and biochar play an important role in Cd reduction and Se enrichment by altering soil properties such as pH, SOM and IP-Fe. This research demonstrates that common fertilizer/amendment applications can be effectively utilized to decrease Cd and increase Se in rice grain, thereby meeting food quality/safety standards, even in soils with high background concentrations of Cd.

CRediT authorship contribution statement

Cheng Zhou: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Lianghui Zhu:** Validation. **Tingting Zhao:** Validation. **Randy A. Dahlgren:** Writing – review & editing. **Jianming Xu:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124033.

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