



# Poorly crystalline Fe(II) mineral phases induced by nano zero-valent iron are responsible for Cd stabilization with different soil moisture conditions and soil types

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## ABSTRACT

Nano zero-valent iron (nZVI) is a promising remediation material for Cd-contaminated soil, but questions remain regarding the effects of nZVI-induced Fe oxides on Cd availability with different soil types and moisture conditions. To identify the changes in Cd availability and Fe mineral phases resulting from the application of nZVI, three types of Cd-spiked soils with 0.1% nZVI amendment were incubated under different moisture conditions with water-holding capacities (WHCs) of 30%, 60%, and 180%. The availability of Cd was significantly decreased in yellow and black soils amended with nZVI, with fewer changes being observed in cinnamon soil. The limited effect of nZVI on Cd stabilization was due to the extremely low content of poorly crystalline Fe phases in cinnamon soil. The Cd stabilization efficiency of nZVI was higher in the flooding soils (180% WHC) than in the non-flooding yellow and black soils (30% and 60% WHC, respectively). Moreover, the addition of nZVI promoted the formation of less-available forms of Cd (Fe-oxide-bound Cd in yellow soil and Fe-oxide-bound and organic-material-bound Cd in black soil) under the flooding condition. The decrease in extractable Cd was strongly related to the increase in poorly crystalline Fe(II) mineral phases among the three soils and various soil moisture contents. Although 0.1% nZVI amendment induced the dissolution of Mn oxides, it did not hinder the Cd stabilization in the three soils. Overall, this study indicates that increased amounts of poorly crystalline Fe(II) compounds due to nZVI amendment play a critical role in the stabilization of Cd in soils.

## 1. Introduction

Soil health is the basis for food security and sustainable human development. However, human activities, such as sewage irrigation and improper fertilization, deposit large amounts of heavy metal into soils (Muehe et al., 2013a). Cd is one such heavy metal and is known to be extremely hazardous (Rehman et al., 2018). Due to its toxicity, persistence, and biomagnification, long-term consumption of foods contaminated by Cd can result in serious human health issues, such as low bone density and Itai-itai disease (Zou et al., 2016; Chen et al., 2018). A meta-analysis of Cd pollution in China from 2000 to 2019, revealed that the average Cd content of farmland soil was two-fold higher than the background value (Yuan et al., 2021). To limit the transfer of Cd from soil to grains, some environmental remediation methods have been

attempted to reduce the mobility and bioavailability of Cd in soils (Chen et al., 2018).

Nano zero-valent iron (nZVI), as a nanoscale material, has been successfully used to reduce the mobility of Cd in contaminated soils (Liu et al., 2015; Cao et al., 2018). Due to its core-shell structure (i.e., an Fe<sup>0</sup> core wrapped by a thin Fe-oxide shell), large surface area, and numerous active sites, nZVI can effectively interact with Cd via ion adsorption, complexation, and redox reaction processes (Martin et al., 2008; Calderon and Fullana, 2015; Danila et al., 2020). However, nZVI can rapidly oxidize into Fe oxide in soils (Komarek et al., 2013). In addition, with the reductive nature of nZVI, increased dissolution of Mn in pore water was found in nZVI treatment (Mitzia et al., 2020). Numerous studies have emphasized that Fe and Mn oxides are responsible for the variation of Cd bioavailability in soils (Muehe et al., 2013a; Li et al.,

*Abbreviations:* nZVI, nano zero-valent Fe; WHC, water-holding capacity; XPS, X-ray photoelectron spectroscopy; DOC, dissolved organic carbon; RDA, redundancy analysis; SOC, soil organic carbon.

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2021; Suda and Makino, 2016). The mobility of Cd is altered during the chemical or microbiological redox cycling of Fe/Mn during dissolution, formation and transformation of Fe/Mn-containing minerals (Suda and Makino, 2016). Cd is mobilized due to Mn mineral dissolution from the nZVI treated samples. However, Fe(II) released upon nZVI corrosion can catalyze the formation of secondary Fe oxides (e.g., hematite or magnetite) via a re-precipitation mechanism for Cd transformation (Liu et al., 2005; Yu et al., 2016). Further, the process of Fe/Mn redox cycling depends on the geochemical conditions, such as pH, inorganic N, or dissolved organic matter (Mejia et al., 2016). It has not yet been investigated in detail whether soil conditions affect the Cd remediation performance of nZVI or how the Fe/Mn redox cycling driven by nZVI influence the mobility of Cd.

Soil moisture content is a key factor in controlling the mobility and bioavailability of Cd through its effects on the soil Eh, pH, changes in Fe oxide species, and transformation of soil organic matter (Huang et al., 2019; Li and Xu, 2017). Previous research showed that draining water from soils markedly increased Cd mobility (Wang et al., 2019). Solid phases of Cd originating from Fe/Mn-oxide-bound phase may be released during soil flooding by the dissolution of Mn(III/IV)- and Fe(III)-oxyhydroxides (Hindersmann and Mansfeldt, 2014). On the other hand, the new formation of secondary Fe minerals during reduction can re-arrest dissolved Cd through adsorption and/or inner-sphere complexes (Boparai et al., 2013; Yu et al., 2016). In general, long-term flooding conditions resulted in net-stabilization of Cd. Huang et al. (2019) studied the effects of three moisture regimes on the stabilization of Cd in a paddy soil and observed that the efficiency in decreasing the Cd availability followed the order: continuous flooding > 70% water-holding capacity (WHC) > wetting-drying cycle. However, information on the processes of Fe/Mn oxide transformation and the fate of Cd availability in soils under different redox statuses combined with nZVI amendment is still lacking.

In this study, three types of Cd-spiked soils amended with 0.1% nZVI under 30%, 60%, or 180% WHC were conducted. The solid phases of Fe, Cd availability and soil physicochemical properties were analyzed. The objectives of the present work were to explore the Fe solid phases transformation with nZVI addition under various soil conditions, and to elucidate the relationship among nZVI-induced Fe solid phases and Cd stabilization with respect to different soil types and various soil moisture contents.

## 2. Materials and methods

### 2.1. Soil samples and nZVI preparation

Three agricultural soil samples (0–20 cm depth) were collected from three locations due to the inherent complexity of the soil environment; specifically, Shanxi (36° 13' N, 113° 08' E), Jilin (43° 57' N, 125° 12' E), and Zhejiang (29° 01' N, 119° 28' E), China. According to the Genetic Soil Classification of China, they are denoted as cinnamon soil, black soil, and yellow soil, respectively. The soil samples were transported to the laboratory in plastic bags. Plant roots and coarse gravel were removed, and all samples were air-dried, crushed, and sieved to < 2 mm. The three types of soils were individually spiked with the desired amount of Cd(NO<sub>3</sub>)<sub>2</sub>, homogeneously mixed, and stabilized at 60% WHC for one month. Spiked soils were then air-dried and sieved for further analysis. The soils were digested with HNO<sub>3</sub>-HF-HClO<sub>4</sub>, and final Cd concentrations were 13.69, 13.08, and 12.47 mg kg<sup>-1</sup> in yellow, black, and cinnamon soils, respectively. Table S1 in the supplementary materials shows the detailed characteristics of the soils. The nZVI particles were purchased from Xuzhou Jiechuang New Material Technology Co., Ltd. (China). The nanoparticles were analyzed by scanning electron microscopy and energy-dispersive spectrometry (Bruker Nano, Berlin, Germany). Fig. S1 provides more detailed information.

### 2.2. Incubation experiments

The spiked soils were used to investigate the effects of the physicochemical properties of soil on the Fe solid phase transformation with 0.1% nZVI (w/w) amendment. The amendment amount was very low compared to that typically employed for environmental remediation (Mele et al., 2015; Lefevre et al., 2016) and has been previously shown to have a low or negligible impact on soil biota (Fajardo et al., 2012). The dry nZVI particles were thoroughly mixed with the prepared soils, and distilled water was added to bring the soil moisture contents to 30%, 60%, or 180% WHC, which represented low, middle, and high (i.e., flooding conditions with a 2-cm-deep water layer above the soil surface) moisture levels, respectively. Soils without nZVI with 30%, 60%, and 180% WHC were used as control groups. These were subsequently placed in plastic pots. All the pots were covered with ventilated film to avoid excessive evaporation. Treatments were prepared in triplicate and incubated under controlled conditions (25 °C and 60–70% relative humidity in the dark) for 31 days. During this period, the soil moisture was maintained through gravimetric determination every three days. Soil samples were collected at the end of the 31-day incubation period.

Another experiment was performed to determine the extent of the nanoscale-specific effect on solid Fe transformation upon ZVI treatment. Typically, 0.1% (w/w) nZVI, 0.1% (w/w) microscale ZVI (mZVI), and FeSO<sub>4</sub>·7H<sub>2</sub>O were added to the Cd-spiked yellow soil mentioned above at doses (as FeSO<sub>4</sub>, [w/w]) of 0.05% (I Fe<sup>2+</sup>), 0.1% (II Fe<sup>2+</sup>), and 0.27% (III Fe<sup>2+</sup>). No Fe was added to the control sample. For all the samples, the soil was maintained at 60% WHC with ultrapure water. The soil samples were incubated as described above and sampled at 0, 2, 4, and 7 days.

### 2.3. Sample analysis

The soil pH was measured after suspension in distilled water (1:2.5, w/v) using a pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China). The dissolved organic carbon (DOC) was extracted from the soil with distilled water (1:5, w/v) and measured using a TOC/TN analyzer (Multi N/C 2100, Analytik Jena, Germany). NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N were extracted from the fresh soil with 2 M KCl at a soil-to-solution ratio of 1:10 after passing the fresh soil through a 3 mm sieve (Li et al., 2012) and measured with a UV spectrophotometer (TU-1810, Beijing Purkay General Instrument Co. Ltd., China). Soil organic carbon (SOC) concentrations were determined using the potassium dichromate external heating method (Tang et al., 2021).

The available Cd and Mn were extracted using 0.01 M CaCl<sub>2</sub> extractants at a ratio of 1:10 (w/v) (Pueyo et al., 2004) and centrifuged at 11,000 × g for 5 min. Sequential Fe extractions were performed to investigate the solid phase Fe redox transformation with and without amendment (Lueder et al., 2020). In brief, a centrifuge tube with 2 mL of 1 M anoxic Na-acetate (pH 5) was charged with 1 g of homogenized freeze-dried soil, and the obtained mixture was incubated in the dark for 24 h. After centrifugation at 11,000 × g for 6 min, the supernatant was stabilized with anoxic 1 M HCl (1:9, v/v); the residue was added to 2 mL of 1 M anoxic HCl, mixed, and incubated in the dark for 2 h. After centrifugation, the supernatant was retained for analysis and the residue was utilized for extraction in the next step. The residual Fe phases were extracted using 2 mL of 6 M anoxic HCl. The solid phase of Fe was divided into three different Fe phases with increasing crystallinity: 1) Fe adsorbed on Fe(III) oxyhydroxides and poorly crystalline carbonates as well as Fe from FeS, 2) poorly crystalline Fe minerals, and 3) highly crystalline Fe minerals. The Fe(II) and Fe(III) contents of the supernatant were quantified via the colorimetric phenanthroline method (Li et al., 2020b). Tessier' sequential extraction procedure was applied to determine the influence of nZVI on changes in the various species of Cd, Mn, and Fe (Tessier et al., 1979). Accordingly, Cd was divided into five species, including exchangeable-bound, carbonate-bound, Fe/Mn-oxide-bound, organic-material-bound, and residual. The relative

availability of these various forms (mainly for plant uptake) decreases following this extraction order, and the last three species are relatively stable (Lyu et al., 2018). Table S3 describes the detailed extraction procedure. The Cd/Mn content was quantified by inductively coupled plasma mass spectrometry (PerkinElmer NexION 300X). Specifically, all the extractions mentioned above were centrifuged and filtered with 0.22  $\mu\text{m}$  pore size filters.

An X-ray photoelectron spectroscopy (XPS) instrument (Thermo Scientific ESCALAB 250Xi) equipped with an Al X-ray source was used to investigate the changes in the oxidation state of Fe in the three soils with and without nZVI amendment (Fan et al., 2014; Lyu et al., 2018). The C 1s binding energy corresponding to graphitic C at 284.8 eV was used as a reference for charge correction. The binding energy forms of the narrow scan spectra for Fe 2p<sub>3/2</sub> were fitted using a theoretical model of non-linear least-squares curve-fitting with the XPSPEAK41 software.

#### 2.4. Statistical analysis

The data are shown as mean  $\pm$  SD. Following the Shapiro–Wilk test to assess variable normality, the differences in the physicochemical characteristics of the soil among different treatments were evaluated by performing a one-way analysis of variance with Tukey's test at a 0.05 significance level. The differences between samples with and without nZVI treatments were determined through a *t*-test. Moreover, the Pearson correlation was applied to selected physicochemical characteristics and available metals extracted with CaCl<sub>2</sub>. The soil characteristic data were analyzed by principal component analysis (IBM SPSS Statistics, USA). Detrended correspondence analysis was conducted to assess the gradient lengths of the variables before applying redundancy analysis (RDA) to assess the relationships among variables with the CANOCO 5.0 software.

### 3. Results and discussion

#### 3.1. Basic characterization of spiked soils

Three different soils were spiked with Cd solution, and the stabilization of Cd by nZVI was investigated. Table S1 describes the characteristics of the yellow, black, and cinnamon-spiked soils. Among these, the yellow soil had the lowest pH (4.85) and Mn content (269.6 mg kg<sup>-1</sup>) but the highest total Fe content (23.1 g kg<sup>-1</sup>), the black soil had the highest available-N and total-Mn contents, and the cinnamon soil had the highest pH (7.21). In addition, the SOC content of the cinnamon soil was 2.1 times and 1.7 times higher than that in the yellow and black soils, respectively. Although the same amount of Cd was spiked in the three soil types, a crucial difference was observed in their CaCl<sub>2</sub>-extractable Cd concentrations, which followed the concentration trend of yellow soil > black soil > cinnamon soil.

#### 3.2. Changes in soil pH and solid-phase crystallinity of Fe with nZVI amendment

Soil Eh can cause phase transformation of Fe/Mn oxides (Li et al., 2020a), whereas nZVI amendment was found to have a negligible effect on the soil Eh in the three soils (data not shown). Application of nZVI significantly increased the soil pH ( $p < 0.05$ ) compared to that of the non-amended soil, owing to the rapid corrosion of Fe<sup>0</sup> and release of OH<sup>-</sup> (Calderon and Fullana, 2015). With 30%, 60%, and 180% WHC, nZVI amendment increased the soil pH by 0.11, 0.10, and 0.51 units in the yellow soil, by 0.14, 0.10, and 0.36 units in the black soil, and by 0.26, 0.14, and 0.06 units in the cinnamon soil, respectively, relative to that of the control soil (Fig. S2). The variation in pH changes of the three soils indicates the different abilities of nZVI to interact with the potential oxidants (e.g., O<sub>2</sub>, H<sub>2</sub>O and Mn oxides) (Zhang et al., 2017; Mitzia et al., 2020).

Fe redox cycling has a critical effect on Cd stabilization in the soil

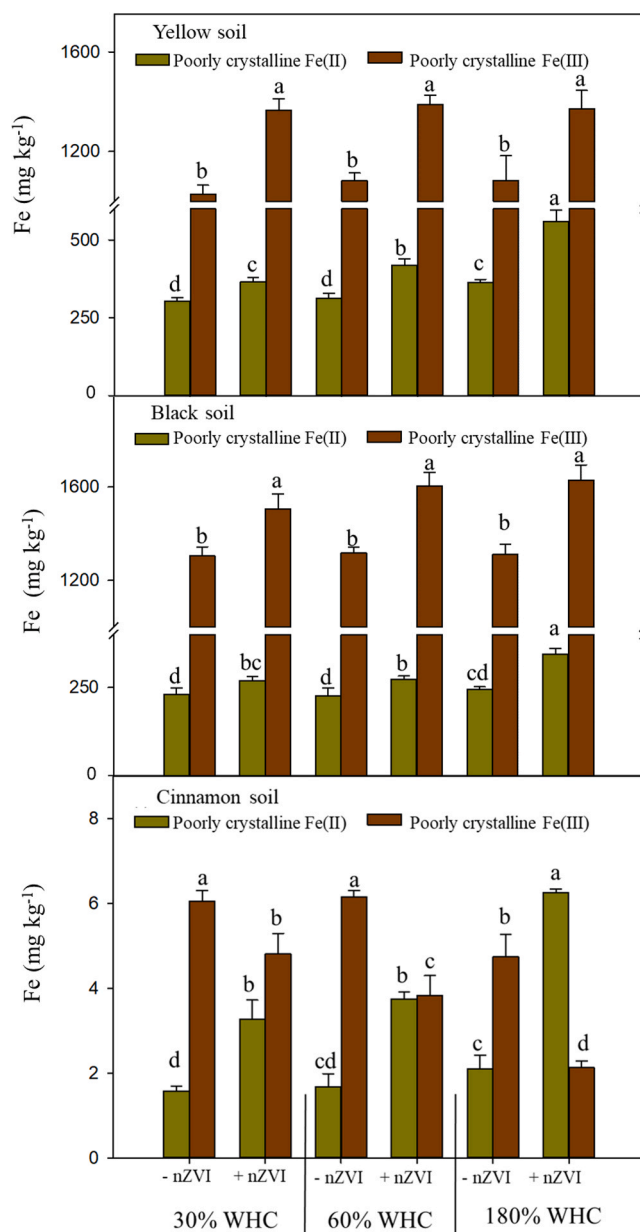


Fig. 1. Poorly crystalline Fe(II) and Fe(III) mineral phases in soil with different treatments. Bars with the same letters indicate non-significant differences ( $p > 0.05$ ) for poorly crystalline Fe(II) or poorly crystalline Fe(III) among different treatments. +nZVI and -nZVI represent soils treated with and without nZVI, respectively.

system (Wang et al., 2019). To track the effects of nZVI on Fe oxide transformation, sequential extractants were used to investigate the changes in the Fe solid-phase crystallinity (Muehe et al., 2013a; Lueder et al., 2020). Soil Fe mineral phases were greatly ( $p < 0.05$ ) altered with nZVI amendment. Regardless of whether or not nZVI was applied, the Fe adsorbed on Fe(III) oxyhydroxides and/or poorly crystalline carbonates (using 1 M Na-acetate) was Fe(II) (Fig. S3). Moreover, the amorphous/adsorbed Fe(II) contents of the nZVI-amended yellow and black soils increased to values that were 1.1–4.1 times and 1.4–2.8 times greater, respectively, than those in the non-amended soils (Fig. S2). These increases were due to the release of Fe(II) by nZVI, which interacted with H<sub>2</sub>O and O<sub>2</sub> under both aerobic and anaerobic soil conditions (Lefevre et al., 2016).

As shown in Fig. 1, the addition of nZVI increased the content of poorly crystalline Fe(II) in all three soils as follows: 0.21–0.54-fold

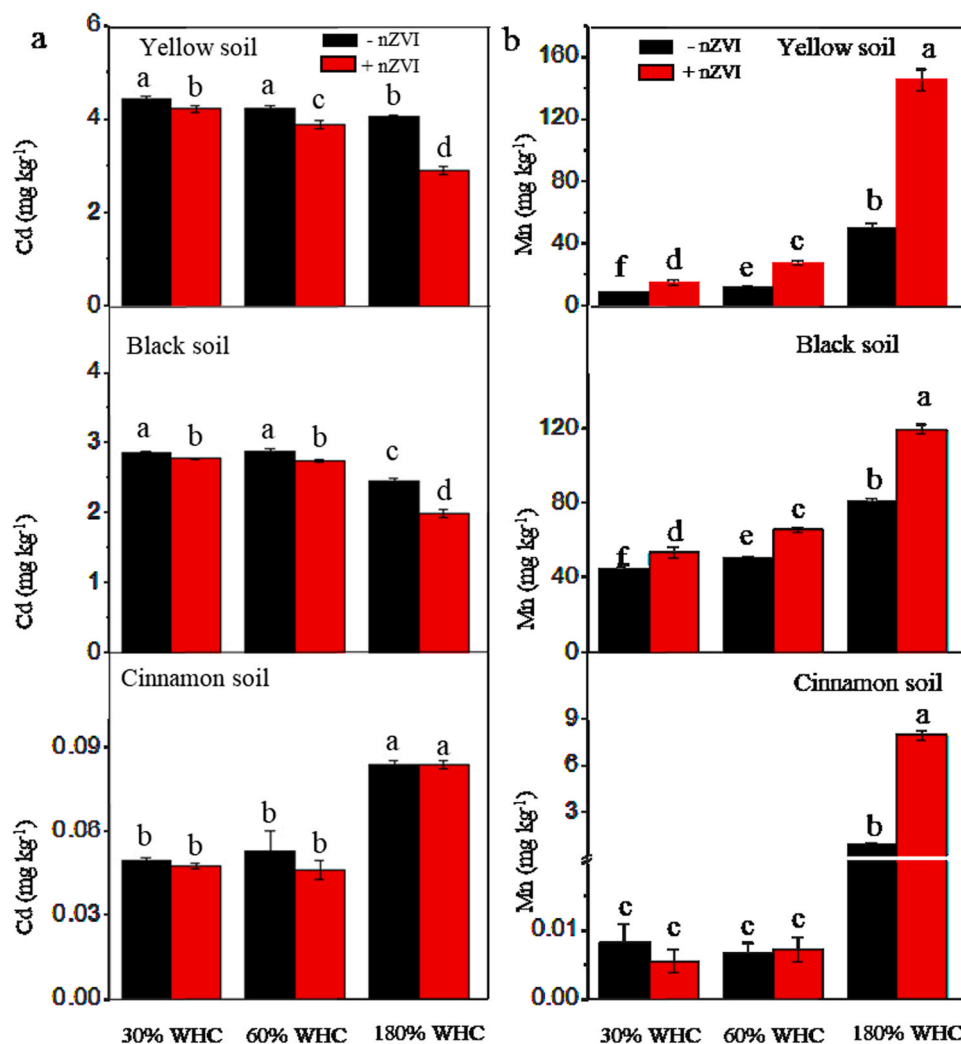


Fig. 2. Extractable Cd (a) and Mn (b) in the soil subjected to different treatments. Bars with the same letters indicate non-significant differences ( $p > 0.05$ ). +nZVI and -nZVI represent soils treated with and without nZVI, respectively.

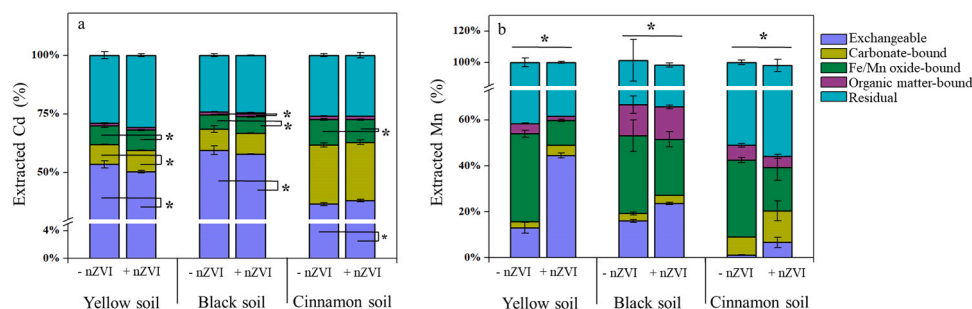
increases in the yellow soil, 0.17–0.24-fold increases in the black soil, and 1.23–2.00-fold increases in the cinnamon soil. The content of poorly crystalline Fe(II) mineral phases in the three nZVI-modified soils was affected by the soil water content, with the changes observed under flooding conditions being larger than those under the non-flooding conditions. Under anaerobic conditions, the higher content of poorly crystalline Fe(II) could be attributed to the reduction of Fe(III)-oxyhydroxides (Muehe et al., 2013a). Meanwhile, the content of poorly crystalline Fe(III) increased by 26.5–32.6% and 15.5–24.3% in the yellow and black soils with nZVI addition, respectively. However, an opposite trend in response to the changes in poorly crystalline Fe(III) in the cinnamon soil was observed. The large difference in the initial soil pH may explain why the concentration of poorly crystalline Fe(III) in the cinnamon soil with nZVI amendment shows an opposite trend compared to that in the yellow and black soils. Meanwhile, nZVI application had a limited effect on the highly crystalline Fe content of the soil (data not shown).

XPS is a surface analysis technique that can be used to identify the Fe minerals detected in soils with and without nZVI amendment. Narrow scan spectra of the Fe  $2p_{3/2}$  peaks were selected for the analysis of Fe oxides because their peaks are stronger and narrower peaks than those of Fe  $2p_{1/2}$  (Fan et al., 2014). For each of the three soils, the Fe  $2p_{3/2}$  spectrum was decomposed into five or six peaks. The binding energy peaks at 708.3, 709.7, 710.8, 711.9, and 713.6 eV were assigned to FeO, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>,  $\alpha$ -FeOOH,  $\gamma$ -FeOOH and its satellite peak, respectively

(McIntyre and Zetaruk, 1977; Yamashita and Hayes, 2008; Xu et al., 2018). Fig. S4 shows the fitting of the spectra from the three soils with different treatments, and Table S3 provides the detailed fitting results. The relative intensities of the peaks of the nZVI-amended soils are larger than those of the peaks of the control soils. A possible origin of the surface structure is the reduction of active compounds by nZVI at the soil surface (Fan et al., 2014). In addition, the percentages of the specific Fe crystalline states changed upon nZVI amendment, and the variations were different among the various soils and soil moisture conditions. The poorly crystalline Fe(II)-containing mineral mentioned above is most likely Fe<sub>3</sub>O<sub>4</sub> under the various soil moisture conditions. Fe<sub>3</sub>O<sub>4</sub> could be extracted by both 0.1 M and 6 M HCl (Muehe et al., 2013a), indicating that Fe<sub>3</sub>O<sub>4</sub> is a potential candidate for nZVI corrosion product and Cd stabilization. Moreover, Fe<sub>3</sub>O<sub>4</sub> was shown to be the main oxidized product of nZVI in soil (Wu et al., 2019) and to incorporate Cd<sup>2+</sup> into its mineral structure (Shen et al., 2009; Su et al., 2017).

### 3.3. Changes in the mobility of Cd and Mn with nZVI amendment

To investigate the effects of nZVI on Cd stabilization in different soils with various moisture contents, the available-Cd and -Mn concentrations in the soils were determined. The dissolution or precipitation of Mn phases have a critical effect on Cd<sup>2+</sup> mobility in soils (Wang et al., 2019). As shown in Fig. 2b, nZVI application increased the solubility of Mn in all three soil types. The available Mn concentrations observed in the



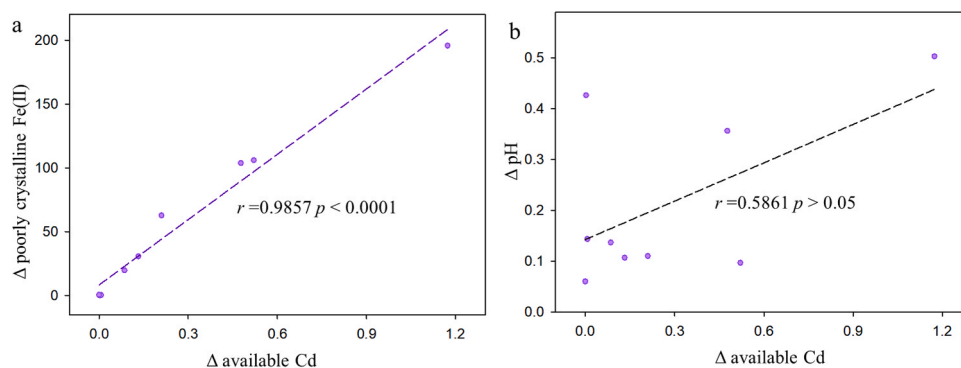
**Fig. 3.** Distributions of Cd (a) and Mn (b) species in soils with (+nZVI) and without (-nZVI) nZVI amendment with 180% WHC. \* indicates significant differences ( $p < 0.05$ ) of the extracted Cd or Mn between +nZVI and -nZVI soils based on the independent *t*-test.

yellow (80–193%) and black soils (19–48%) with additional nZVI were higher than those in the respective control soils. An increasing  $Mn^{2+}$  content with nZVI amendment in soils was also observed previously (Vitkova et al., 2018). Moreover, the available Mn content significantly increased as the soil moisture level increased from 30% to 180% WHC. Because of the high standard electrode potentials of Mn, Mn oxides were dissolved under the reductive conditions (Vitkova et al., 2018). In addition, the nZVI application increased the available Mn concentration from 0.9 to 7.9  $mg\ kg^{-1}$  with 180% WHC; however, it had no effect on the available Mn concentration at the other two soil moisture levels in the cinnamon soil.

The stabilization rate of Cd by nZVI increased with increasing soil moisture content in the yellow and black soils, whereas nZVI had limited effect on the available Cd in the cinnamon soil (Fig. 2a). Moreover, the efficiency of the amendments was different with the same soil moisture content in the yellow and black soils. That is, compared with those of the control soils, the Cd-stabilization efficiencies of the yellow soil increased by 4.7%, 11.8%, and 28.9% under the low, middle, and high soil moisture conditions, respectively, whereas those of the black soil increased by 3.0%, 4.6%, and 19.4%, respectively. On one hand, Cd availability is known to be related to the increase in the number of negatively charged sites for  $Cd^{2+}$  sorption with increasing pH (Mele et al., 2015; Xue et al., 2018). The differences among the soils described above are likely due to the amount of  $OH^-$  released by nZVI corrosion, which is larger in the yellow soil than in the black soil (Fig. S2), producing a higher negative charge on the surfaces of the Fe oxides in the former (Li et al., 2020a). On the other hand, it is likely that the higher content of poorly crystalline Fe(II) mineral phases that formed during nZVI oxidation caused the difference. It is well known that Fe oxides have large surface areas and active adsorption sites for  $Cd^{2+}$  (Tessier et al., 1979). And the conversion of Fe mineral crystallinity led to the regeneration of Cd compounds by providing fresh reactive sites (Muehe et al., 2013b; Randall et al., 1999). Moreover, the increase in poorly

crystalline Fe(II) compounds resulted in Cd stabilization and compensated for Cd dissolution by the reduction of Mn oxides. Significant negative correlations ( $p < 0.05$ ) were found between the amount of available Cd and the physicochemical characteristics of the soils, including the pH and amounts of available Mn and poorly crystalline Fe (II) (Fig. S5), regardless of soil moisture content, highlighting the key roles of pH, Mn oxides, and nZVI corrosion products in Cd availability in soils.

To confirm the specific transformations of Fe, Mn, and Cd by nZVI amendment further, the five-step extraction method of Tessier was used to investigate the differences in Cd, Mn (Fig. 3), and Fe (Table S4) species in the soils with and without nZVI with 180% WHC treatment. nZVI treatment significantly increased the levels of all Fe species in the three soils, except that of the residual Fe species, which was mainly due to the nZVI corrosion products and their redistribution. In addition, nZVI application increased the exchangeable and carbonate species of Mn but decreased the Fe/Mn-oxide-bound and residual Mn species in all three soils, which was due to the reduction of Mn oxyhydroxides into ions (Fan et al., 2014; Long et al., 2019). Specifically, nZVI amendment increased the organically bound Mn in the black soil but had no significant effect on the organically bound Mn present in the yellow and cinnamon soils. The fractions of SOC in the different soils varied considerably in their structure and chemical composition, which could further affect their affinity to Mn (Sun et al., 2013; Zhang et al., 2019). On the other hand, the variations in the Cd species differed markedly among all three soils. In the yellow soil, the nZVI treatment decreased the amount of exchangeable species of Cd from 53.4% to 50.3%; however, it increased the amounts of the Cd species bound to carbonates and bound to Fe/Mn oxides by 7.7% and 14.8%, respectively. Black soil amendment with nZVI decreased the level of exchangeable Cd species from 60.2% to 57.8% and increased those of the Cd species bound to Fe/Mn oxides and organic compounds by 16.9% and 22.1%, respectively. Due to the increased dissolution of Mn oxides by nZVI amendment, the increased



**Fig. 4.** Correlations between (a) the increase in poorly crystalline Fe(II) content ( $\Delta$  poorly crystalline Fe(II), concentration of poorly crystalline Fe(II) with nZVI treatment minus that without nZVI treatment in yellow, black, and cinnamon soil) and (b) pH variation by nZVI amendment and the stabilization of Cd ( $\Delta$  available Cd, concentration of available Cd with nZVI treatment minus that without nZVI treatment in yellow, black, and cinnamon soil).

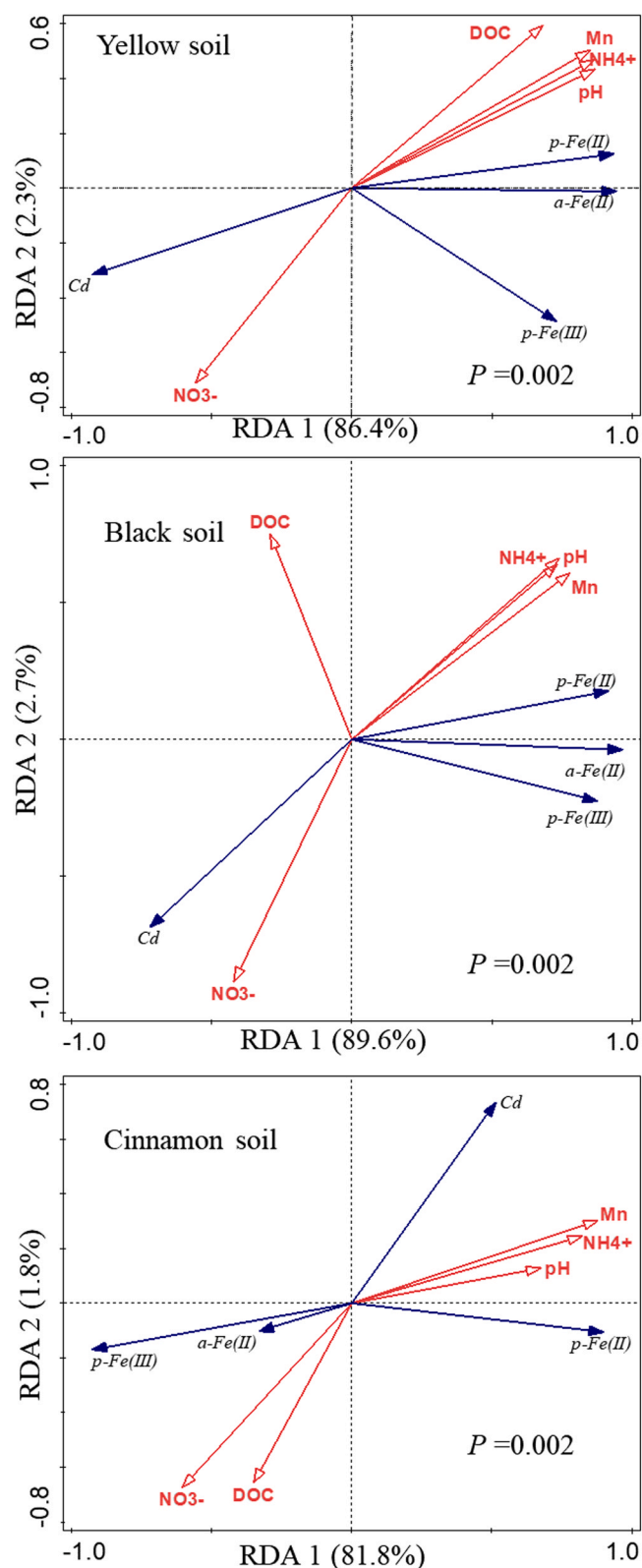


Fig. 5. RDA of soil samples with different soil moisture conditions with or without nZVI treatment. a-Fe(II), p-Fe(II), and p-Fe(III) represent amorphous/adsorbed Fe, poorly crystalline Fe(II), and poorly crystalline Fe(III), respectively; Mn and Cd correspond to the available Mn and Cd, respectively.

Cd stabilization was attributed to the binding of Cd to Fe oxyhydroxides (Danila et al., 2020) or the formation of surface complexes comprising of Cd-humic substances and Fe oxyhydroxides (Muehe et al., 2013a). Cd bound to Fe/Mn oxides and organic materials, as well as residual Cd, represent the less accessible forms of Cd for uptake by plants, suggesting that nZVI addition may decrease Cd bioavailability in yellow and black soils. On the other hand, the amendment of cinnamon soil with nZVI increased its amount of exchangeable Cd by 4.1% and decreased its amount of Cd bound to Fe/Mn oxides by 10.4%. The release of Cd was attributed to the reduction of Mn oxides (Fulda et al., 2013). With the opposite trend in Fe/Mn oxide-bound Cd and Mn in yellow and black soils, it seems that Fe oxides rather than Mn oxides dominated the Cd solubility by nZVI amendment in soils.

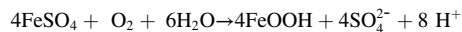
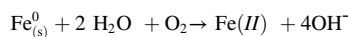
#### 3.4. Relationships among pH, Fe solid phases, and Cd solubility

The increase in poorly crystalline Fe(II) mineral phases had a significant positive correlation with the decrease in extractable Cd in soils, whereas pH variation had a limited effect on the Cd solubility changes by nZVI amendment regardless of the soil types and soil moisture contents (Fig. 4). The results further indicate that the poorly crystalline Fe (II) mineral phases are an important factor for facilitating the nZVI-based stabilization of Cd in soils. The relative abundance of the poorly crystalline Fe mineral phases accounted for 11–13% of the poorly and highly crystalline Fe phases in both the yellow and black soils and merely 0.01% of that in the cinnamon soil. This characteristic may be the main reason for the large difference in Cd stabilization between the cinnamon soil and the yellow soil, as well as black soil. Therefore, the low poorly crystalline Fe content may limit the applicability of nZVI treatment for Cd stabilization in soil.

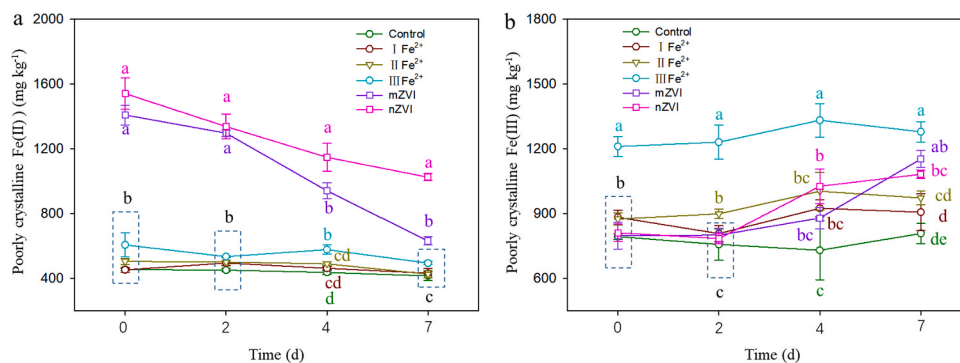
RDA was subsequently performed to analyze the potential connection between the changes in soil physicochemical properties and the crystallinity of the solid phases of Fe (Fig. 5). The concentrations of poorly crystalline Fe(II) and Fe(III) were positively correlated to the soil pH and  $\text{NO}_3^-$  in the yellow soil, available Mn and  $\text{NO}_3^-$  in the black soil, and available Mn in the cinnamon soil. These results further indicate that the increase of poorly crystalline Fe(II) mineral phases was related to the interaction between nZVI and the active compounds in the soils. The concentration of available Cd was negatively correlated with that of amorphous/adsorbed Fe, as well as poorly crystalline Fe(II) and Fe (III). Fe(II) released via nZVI corrosion was noted to be involved in Fe cycling coupled to the cycling of other elements, such as Mn, N, and C, as well as the transformation of heavy metal species (Muehe et al., 2013b; Yu et al., 2016). These results further confirm that the biogeochemistry processes of nZVI contribute to the stabilization of Cd.

#### 3.5. Specific function of nZVI on Fe transformation

To assess the distinct effects of nZVI on Cd stabilization in soil and Fe oxide transformation, the effects of nZVI, mZVI, and Fe(II) on redox-sensitive compounds and solid-phase Fe in soil were investigated. On day 7, the soil pH with nZVI and mZVI treatment significantly increased from 4.84 to 5.14 and 4.99, respectively, whereas with the  $\text{FeSO}_4$  treatment, the soil pH significantly decreased by 0.06–0.38 units (Fig. S6a). The opposite trend of the change in soil pH upon ZVI or  $\text{FeSO}_4$  addition was attributed to its rapid reactions with the soil constituents such as  $\text{H}_2\text{O}$  and  $\text{O}_2$  according to the following equations (Komarek et al., 2013):



The available Mn concentration in soil increased after 7 days from 52.16 to 91.10, 114.56, and 156.29  $\text{mg kg}^{-1}$  with increasing amount of  $\text{FeSO}_4$ , whereas it increased to 64.97 and 75.88  $\text{mg kg}^{-1}$  with nZVI and



**Fig. 6.** Poorly crystalline Fe(II) and Fe(III) mineral phases in soil with different treatments throughout the 7-day incubation process. The different small letters indicate significant differences ( $p < 0.05$ ) among the treatments at the same sampling time, whereas the boxes indicate treatments with no significant difference ( $p > 0.05$ ).

mZVI treatment, respectively (Fig. S6b). The huge difference in the available Mn concentration between the ZVI and  $\text{Fe}^{2+}$  treatments indicates that Mn was reduced by the generation of Fe(II) from the core  $\text{Fe}^0$  corrosion. In addition, the Fe oxide shell could prevent direct contact of  $\text{Fe}^0$  with Mn (Mu et al., 2017). The nano-effect was observed for nZVI, as indicated by the slower release of amorphous/adsorbed Fe and higher amount of poorly crystalline Fe(II) minerals compared to those with mZVI after 7-day incubation (Fig. 6, Fig. S7). At the beginning of incubation, the 0.5 M HCl-extractable Fe(II) included both poorly crystallized Fe(II) and the core  $\text{Fe}^0$ . Meanwhile, the concentration of 0.5 M HCl-extractable Fe(II) upon mZVI and nZVI treatment decreased over time after the initial introduction. The decrease in the amount of 0.5 M HCl-extractable Fe(II) indicates different oxidization rates of poorly crystallized Fe(II) or core  $\text{Fe}^0$  between mZVI and nZVI. The heatmap analysis of the physicochemical properties of the soil and Fe solid phase demonstrated that nZVI and mZVI formed one group, whereas the control and  $\text{Fe}^{2+}$  treatments (except for  $\text{III Fe}^{2+}$  treatment) formed another group (Fig. S8). These results also show a nanosize-specific effect and further confirm the specific mechanism of Cd stabilization by nZVI.

#### 4. Conclusions

The treatment with nZVI under flooding conditions resulted in the most efficient Cd stabilization. The nanosize-specific effect of nZVI on solid Fe phase transformation showed that the rapid oxidation of nZVI considerably affected the concentration of Fe oxide species in the soil, as well as Cd solubility. Further, we demonstrated that the variation in the Cd stabilization efficiency by nZVI among different soil types and moisture contents is attributable to the poorly crystalline Fe(II) compounds, rather than the changes of soil pH. The addition of nZVI to the cinnamon soil did not induce any Cd-stabilization effect in any of the investigated controlled soil-moisture regimes because of the extremely low background concentration of poorly crystalline Fe mineral phases. Therefore, the applicability of nZVI for Cd stabilization can be limited by the soil type. Further research is required to identify the factors that affect the nZVI corrosion products, which could further affect Cd stabilization efficiency.

#### CRedit authorship contribution statement

**Mengjiao Liu:** Conceptualization, Methodology, Writing – original draft. **Meng Xu:** Conceptualization, Methodology. **Xin Zhang:** Visualization. **Jingjie Zhou:** Visualization. **Qingxu Ma:** Supervision, Writing – review & editing. **Lianghuan Wu:** Supervision, Conceptualization, Funding acquisition.

#### 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.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.ecoenv.2021.112616](https://doi.org/10.1016/j.ecoenv.2021.112616).

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