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Research Paper

Nano zero-valent iron-induced changes in soil iron species and soil bacterial communities contribute to the fate of Cd

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ABSTRACT

Nano zero-valent iron (nZVI) is used for soil remediation; however, the impact of nZVI on soil solid iron phases and its interactions with soil microorganisms in relation to the fate of Cd in soil remains unclear. In the current study, we investigated the mechanisms underlying the change in mobility of Cd in exogenous Cd-contaminated soil with nZVI and γ radiation treatments. The results showed that nZVI treatment decreased Cd availability but also increased the soil pH and dissolved Mn and poorly crystalline Fe contents. However, the increased poorly crystalline Fe(II) levels contributed to a reduction in Cd availability in soils treated with nZVI by immobilizing Cd associated with Fe oxides, rather than by increasing pH or Mn oxide levels. Moreover, Cd stabilization efficiency was higher in γ-irradiated soils than in non-irradiated soils regardless of the Cd level, with noticeable differences in bacterial community composition between the non-irradiated and irradiated soils. The genera *Bacillus*, *Pullulanibacillus*, and *Alicyclobacillus* are important in the redox of poorly crystalline Fe(II)-containing minerals in non-irradiated soil. This research provides a new method for further improving the Cd stabilization efficiency of nZVI in combination with microbial iron oxidization inhibitors.

1. Introduction

Cd, which is widely present in agricultural soils, is toxic to humans. A national survey found that 7% of soil samples collected in China were contaminated with Cd (The Ministry of Environmental Protection and The Ministry of Land and Resources, 2014). Dietary intake accounts for nearly 90% of the total Cd exposure in non-smoking populations (Clemens et al., 2013). Cd enters the food chain and causes human health issues by inducing kidney damage or by decreasing bone density (Huang et al., 2021). A number of environmental remediation methods have been trialed that attempt to reduce the transfer of Cd from soil to cereals by reducing the mobility and bioavailability of Cd in the soil (Chen et al., 2018). The mobility of Cd in soil is determined by its speciation, which is related to soil pH, the presence of organic matter, and Fe/Mn oxides (Tessier et al., 1979). Generally, exogenous additions (e.g., mineral fertilization) alter soil properties and the solubility of Cd (Rizwan et al., 2017).

Nano zero-valent iron (nZVI) is an environmentally friendly material that has been used to reduce the mobility and bioavailability of Cd in contaminated soils because of its strong capacity for adsorption (Huang et al., 2018; Tang et al., 2019) and its high reactivity (Vítková et al., 2017). nZVI usually comprises an Fe^0 core and a thin Fe oxide shell (Calderon and Fullana, 2015). The core acts as an electron donor and promotes the reduction of sensitive compounds, such as carbon (Nurmi et al., 2005), nitrogen (Hwang and Shin, 2013), and manganese (Mitzia et al., 2020). The Fe oxide shells provide large surface areas and active surface sites that can bind to Cd(II) via surface adsorption and co-precipitation mechanisms (Mu et al., 2017; Yuan et al., 2019). Moreover, nZVI oxidizes rapidly on exposure to the soil environment. It has been reported that nZVI incubated in soils is oxidized into magnetite

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Abbreviations: DOC, Dissolved organic carbon; nZVI, Nano zero-valent iron; OUT, Operational taxonomic units; WHC, Water-holding capacity.

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and goethite (Wu et al., 2019). Previous research has demonstrated that Fe oxide shells play a major role in the remediation performance of nZVI in aquatic environments (Mu et al., 2017). However, the relationship between Fe oxides formed from nZVI corrosion and the mobility of Cd in soil has not yet been reported. It is consequently essential to consider the transformation of Fe oxides by nZVI during soil remediation.

Various factors control the solubility and stability of Cd in soils. Soil pH is a key factor that affects the solubility of Cd and the transformation of Fe oxides (Vítková et al., 2018; Li et al., 2020). During its interactions with active compounds such as O_2 and NO_3^-, nZVI donates electrons, which results in an increase in pH (Komárek et al., 2013). Numerous studies have reported similar increases in pH following nZVI treatment in soils (Di Palma et al., 2015; Mitzia et al., 2020; Hiller et al., 2021). At higher pHs, the precipitation of carbonate minerals is considered a sink for dissolved Cd (Rinklebe et al., 2016; Zhu et al., 2016); however, the negative surface charges on Fe/Mn oxides are altered as a result of the changes in soil pH, and this can also affect Cd adsorption (Nassar, 2012). Studying the variations in pH can help determine the role of pH in Cd stabilization during nZVI treatment. Moreover, release of Mn has been reported during nZVI treatment (Vítková et al., 2018; Mitzia et al., 2020), and Mn oxide has been shown to be efficient at Cd adsorption by inner- or outer-sphere surface complexation (Huang et al., 2017; Zhou et al., 2020). Therefore, it is also necessary to investigate changes in Mn species in soil that have been ameliorated with nZVI treatments.

The morphology and content of soil Fe oxides are affected by both abiotic and biotic factors, which have major effects on the fates of soil nutrients and contaminants (Hansel et al., 2011). Soil microorganisms also play important roles in Fe transformation (Fe cycling) and in the fate of heavy metals in soil (Yu et al., 2016a). Furthermore, exogenous additions such as nZVI and Cd can alter microbial communities (Anza et al., 2019) and, consequently, affect soil element cycling (Xi et al., 2021). Several studies have shown that exposure to nZVI significantly changes the structure and composition of soil bacterial community (Fajardo et al., 2012; Saccà et al., 2014). Investigating the impact of microorganisms on the transformation of solid-phase Fe oxides and on the fate of Cd may aid with improvements to the efficiency of Cd stabilization by nZVI treatment. However, the effects of nZVI treatment on Fe mineral phase transformation by microorganisms, as well as on the fate of soil Cd, are not well understood.

Consequently, in this study, we aimed to explore the relationships between Fe solid phases and Cd availability with nZVI treatment and to determine the contributions of pH, Mn, and bacterial-influenced nZVI corrosion on the fate of Cd in soil. Batch experiments were designed (I) to investigate the effects of exogenous Cd and bacteria on the efficiency of nZVI for Cd stabilization in soils; (II) to explore the impacts of nZVI on Fe solid phases, soil physicochemical properties, and bacterial community structures; and (III) to analyze the effect of nZVI on Fe mineral phase transformation by microorganisms and on the fate of soil Cd, which is an area of research that has not been previously addressed in the literature.

2. Materials and methods

2.1. Preparation of materials

The nZVI particles were purchased from Xuzhou Jiechuang New Material Technology Co., Ltd. (Guangzhou, Guangdong, China). Detailed characterization of the nZVI used in this study is shown in Fig. S1. Agricultural soil samples (0–20 cm) were collected from Jinhua, Zhejiang (29°01′ N, 119°28′ E) in China and were classified as a sandy loam soil according to the United States Department of Agriculture triangle method. The collected soil samples were air-dried and crushed to a particle size of < 2 mm.

Soil was slightly polluted with Cd (0.42 mg kg^{-1}) according to GB15618-2018 (State Standard of the People's Republic of China, Standardization Administration of the People's Republic of China, Beijing, China), which was defined as low-Cd soil.

To investigate the influence of exogenous Cd on soil Fe transformation, part of the soil was spiked with the desired amount of Cd $(NO_3)_2$ solution (0.13%, w/v), homogeneously mixed, and stabilized at a water-holding capacity (WHC) of 60–70% for 6 months at 25 °C and 60% humidity. Then the soil was air-dried and sieved to a particle size of < 2 mm prior to further experiments. The final Cd concentration was 13.7 mg kg^{-1}, which was defined as high-Cd soil.

The basic physicochemical characteristics of both the original soil and the spiked soil are summarized in Table S1.

2.2. Batch experiments

To test both the influence of soil microbial communities on soil Fe transformation and the presence of exogenous Cd on these processes under nZVI treatment conditions, both low-Cd soil and high-Cd soil were treated with γ radiation (^{60}Co source at a dose of 25 kGy, 6.25 Gy min^{-1}), resulting in a total of eight groups (low-Cd soil without nZVI treatment, low-Cd soil with nZVI treatment, high-Cd soil without nZVI treatment, and high-Cd soil with nZVI treatment; each with and without γ radiation). Compared with other sterilization methods, γ radiation has little effect on soil physical and chemical properties but can modify the soil microbial community (Wu et al., 2019). For the treatments, 500 g of dry non-irradiated soil or γ-irradiated soil was used with or without 0.1% nZVI (w/w), thoroughly mixed, and placed in plastic pots that had been sterilized with 75% v/v alcohol. Treatments were prepared in triplicates, and sterilized ultrapure water was added to bring the soil moisture content to 60% WHC. All pots were covered with a ventilated film and incubated in a controlled chamber (sterilized with 75% v/v alcohol and stored at 25 °C and 70% relative humidity under dark conditions) for 7 days. During this period, soil moisture was maintained with sterilized ultrapure water through gravimetric determination every 3 days.

2.3. Soil physicochemical analysis

Soil samples were collected at the end of the 7-day incubation period. Fresh soil samples were immediately extracted for nitrate-N (NO_3^--N) and ammonium-N (NH_4^+-N) analyses. The remaining soil samples were freeze-dried for further physicochemical analyses.

Soil pH was measured (1:2.5, w/v in distilled water) using a pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China). The soil dissolved organic carbon (DOC) was extracted with distilled water at a 1: 5 soil: solution ratio for 1 h (25 °C, 200 rpm) following the methods of Meng et al. (2018) and was measured using a TOC/TN analyzer (Multi N/C 2100, Analytik Jena, Jena, Thuringia, Germany). NO_3^--N and NH_4^+-N were extracted with 0.5 M K_2SO_4 at a 1:5 soil:solution ratio for 0.5 h (25 °C, 200 rpm) after passing the fresh soil through a 3 mm sieve (Ma et al., 2020). The available Cd and Mn were conducted by one-step extraction method using 0.01 M $CaCl_2$ at a 1:10 soil:solution ratio for 2 h (25 °C, 120 rpm), as previously described (Pueyo et al., 2004). A sequential Fe extraction procedure was used to determine solid-phase Fe content (Liu et al., 2021). Briefly, a centrifuge tube with 2 mL of 1 M anoxic Na acetate (pH 5) was loaded with 1 g homogenized freeze-dried soil, and the mixture was incubated under dark conditions for 24 h. After centrifugation at 11,000 × *g* for 6 min, the supernatant was decanted and stabilized with 1 anoxic M HCl (1:9 v/v). The remaining solids were added to 2 mL of 0.5 M anoxic HCl, mixed, and incubated under dark conditions for 24 h. After centrifugation, the supernatant was preserved for future analysis, and the remaining solids were used for extraction in the next step. The remaining Fe solid phases were extracted using 2 mL of 6 M anoxic HCl and incubated for 24 h. The Fe solid phase was divided into three types of fractions: 1) Fe adsorbed on Fe(III) oxyhydroxides and/or Fe from poorly crystalline carbonates and Fe^{2+} from FeS, 2) poorly crystalline Fe minerals, and 3) highly crystalline Fe minerals. The Fe^{2+} and Fe^{3+} concentrations in the supernatant were quantified using the colorimetric phenanthroline method at 510 nm (Li et al., 2020). The carbonate-bound and Fe/Mn-oxide-bound phases of Cd, Mn, and Fe were extracted with 1 M sodium acetate (pH 5.0) and 0.4 M $NH_2OH \cdot HCl$ (25% HOAc), respectively, using the sequential extraction procedure (Guha et al., 2020). The extracted Cd, Fe, and Mn concentrations were quantified using inductively coupled plasma mass spectrometry (PerkinElmer NexION 300X, USA). All extracted supernatants described above were centrifuged and were filtered through 0.22 μm pore size filters prior to analyses. The Cd stabilization efficiency was calculated from the available Cd by $CaCl_2$ extraction using the following equation:

$$Cd \quad stabilization \quad efficiency \quad = (C_0 - C_n)/C_0 \times 100\%$$

where C_n (mg kg^{-1}) is the available Cd concentration with nZVI treatment and C_0 (mg kg^{-1}) is the available Cd concentration without nZVI treatment.

2.4. Determination of nZVI

A 20 mL serum bottle with 1 g soil was purged with nitrogen to remove the air from the headspace and sealed using butyl rubber and an aluminum cap. Then, 2 mL of 6 M HCl was added to the bottle with a syringe, and the mixture was incubated on a rotary shaker for 4 h at 180 rpm. The H_2 content in the headspace was measured using gas chromatography (GC; SP-6800A; Lunan Instrument Co., Tengzhou City, Shandong, China). The Fe^0 content was calculated using the following equation:

$$Fe^0_{(s)} + 2HCl \rightarrow FeCl_2 + H_{2(g)}$$

2.5. Soil DNA extraction

Fresh samples were stored at −80 °C prior to DNA extraction. Soil samples (0.5 g) were used to extract DNA with a FastDNA Spin Kit (MP Biomedicals, Irvine, CA, USA) according to the manufacturer's protocols. The concentration and quality of the extracted DNA were estimated using a NanoDrop-2000 spectrophotometer (Thermo Scientific, Waltham, MA, USA). The primers 515F (5′-GTGCCAGCMGCCGCGGTAA-3′) and 806R (5′-GGACTACVSGGGTATCTAAT-3′) were used to determine the V4 region of the 16S rRNA of bacteria (Lin et al., 2021). Barcoded 16S rRNA gene amplicons were sequenced on an Illumina NovaSeq-PE250 platform (Guangdong Magigene Biotechnology Co. Ltd., Guangzhou International Bio Island, Guangzhou, China). To acquire high-quality data, a series of operational procedures were conducted to produce each representative sequence, as described previously (Lin et al., 2021; Tang et al., 2021; Yang et al., 2021). Briefly, raw data were filtered, and sequences with lengths of < 200 bp were removed. The USEARCH tool (V10, http://www.drive5.com/usearch/) was used to remove chimeric sequences. Then, representative sequences were clustered into operational taxonomic units (OTUs) based on > 97% similarity. OTU taxonomic information was annotated based on the SILVA database (https://www.arb-silva.de/) and used for subsequent analyses.

2.6. Statistical analysis

Data are expressed as means ± standard deviations. The Shapiro–Wilk test was used to assess variable normality among treatments prior to a one-way analysis of variance with Tukey's test. The significance was set at $p < 0.05$. Spearman's correlation was applied to selected physicochemical characteristics and bacterial abundances at the phylum and genus levels, and a heat map was generated using RStudio. A principal coordinate analysis, together with an unweighted pair group method with arithmetic mean analysis, was performed using the R package 'Vegan'.

3. Results

3.1. Effects of nZVI on Cd and Mn availability

As shown in Fig. 1A and B, although radiation had no significant effect on soil-available Cd, it significantly increased the concentration of available Mn compared with that of non-irradiated low-Cd and high-Cd control soils. Treatment with nZVI significantly decreased the concentration of available Cd but significantly increased the concentration of available Mn. In non-irradiated soils, treatment with nZVI significantly decreased the available Cd content by 10.9% and 9.3% in low-Cd and high-Cd soils, respectively, but increased the available Mn content by 53.2% and 55.6% in low-Cd and high-Cd soils, respectively, compared with those of the corresponding unamended soil. Moreover, in γ-irradiated soils, the available Cd content decreased by 18.3% and 14.7% with nZVI treatment in low-Cd and high-Cd soils, respectively, whereas the available Mn content was increased by 43.4% and 78.5% with nZVI treatment in low-Cd and high-Cd soils, respectively, compared with those of the corresponding unamended soils (Fig. 1B).

3.2. Effects of nZVI on solid-phase Fe transformation

After 7 days of incubation, approximately, 27.06 mg kg^{-1} nZVI was found in soils (Fig. S2) with nZVI treatment, whereas Fe^0 was not detected in control soils. Consequently, only 3.6% Fe^0 remained compared with the initial addition. This suggests that the majority of nZVI added to the soil was oxidized to Fe oxides. Furthermore, a similar content of Fe^0 was found among nZVI treatments, regardless of Cd level and γ irradiation (Fig. S2). Treatment with nZVI significantly increased the levels of both Na acetate and 0.5 M HCl-extractable Fe, as well as those of 6 M HCl-extractable Fe(II), among all treatment groups. In all treatments, Na acetate-extracted Fe was in the reduced state Fe(II). In the non-irradiated soils, the adsorbed Fe content in low-Cd and high-Cd soils treated with nZVI was 14.04 and 11.05 mg kg^{-1}, respectively, which was significantly higher than that in the corresponding control soils (1.92 and 1.87 mg kg^{-1}, respectively) (Fig. S3). A similar trend in increased concentrations of adsorbed Fe was observed in the irradiated soils with nZVI treatment (Fig. S3).

Fig. 1C and D show the concentrations of poorly crystalline Fe and highly crystalline Fe in soils. In both non-irradiated and γ-irradiated soils, the poorly crystalline Fe(II) and Fe(III) contents significantly increased with nZVI treatments, compared with those of the corresponding control soils. In soils with nZVI and γ radiation treatments, the contents of poorly crystalline Fe(II) were 0.6- and 0.7-fold higher than those in non-irradiated low-Cd and high-Cd soils, respectively. However, radiation had no significant effect on the concentration of poorly crystalline Fe(II) in either low-Cd or high-Cd soils. In the non-irradiated soils, the concentrations of poorly crystalline Fe(II) with nZVI treatment were 0.9- and 1.0-fold higher than those in the low-Cd and high-Cd control soils, respectively. In the γ-irradiated soils, the concentrations of poorly crystalline Fe(II) with nZVI treatments were 1.8- and 2.0-fold higher than those in the low-Cd and high-Cd control soils, respectively. Treatment with nZVI significantly ($p < 0.05$) increased the concentration of highly crystalline Fe(II) mineral fractions by 21.8–34.8% in all treatment groups. Additionally, the presence of exogenous Cd had no significant effect on the composition of soil solid Fe phases by nZVI treatment in high-Cd soil versus low-Cd soil, under both non-irradiated and γ-irradiated conditions.

3.3. Effects of nZVI on soil pH and inorganic N contents and its relationships with solid-phase Fe content and Cd availability

As shown in Fig. 2A, soil pH increased with nZVI treatment, and soil pH was higher in the γ-irradiated soils than in the non-irradiated soils. For the non-irradiated soils, nZVI treatment increased the pH by 0.11 and 0.16 in low-Cd and high-Cd soils, respectively. For the γ radiation

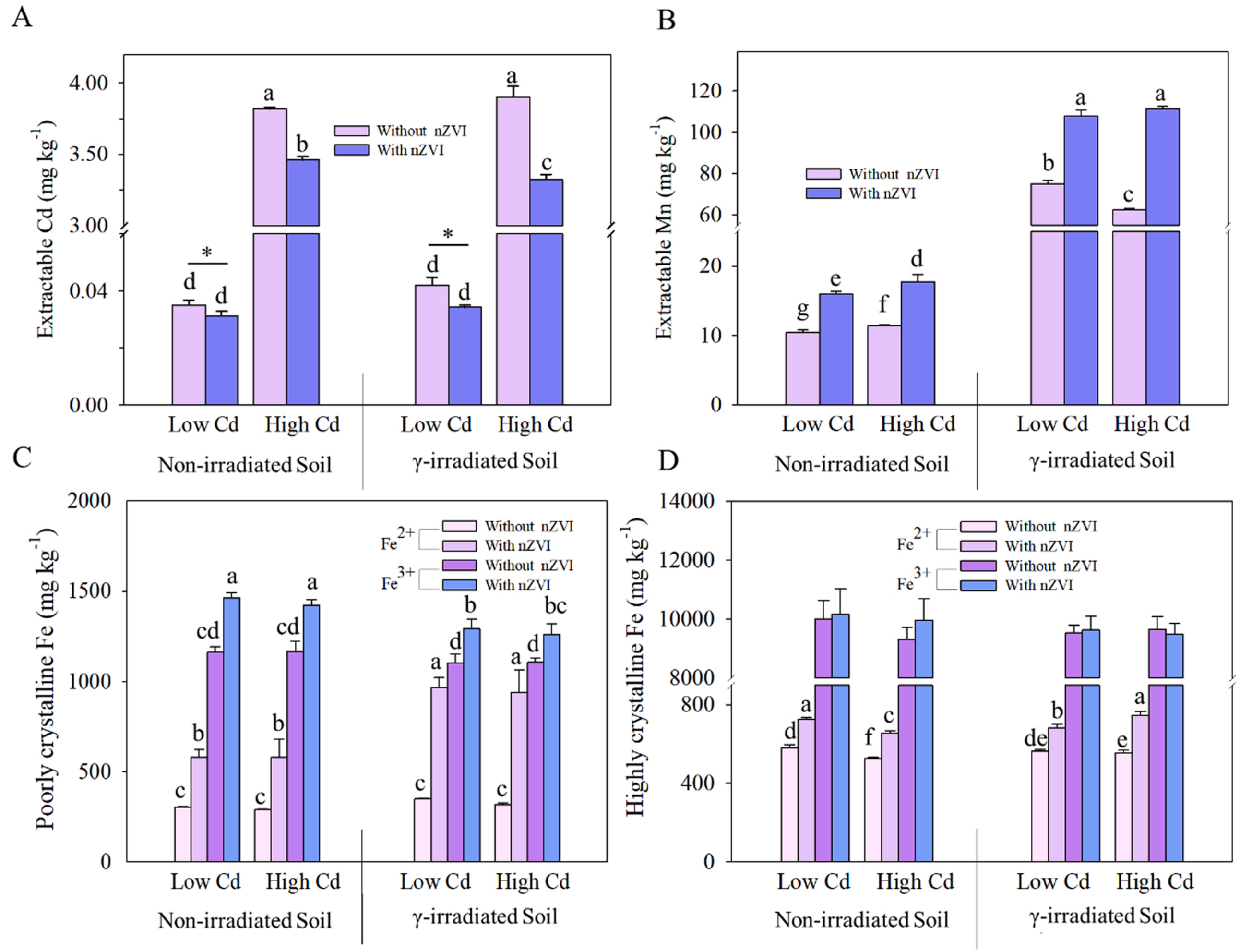

Fig. 1. Concentration of $CaCl_2$-extractable Cd (A) and Mn (B) in different treatment groups. Soil poorly crystalline Fe (C) and highly crystalline Fe (D) levels with different treatments. Different small letters indicate significant differences ($p < 0.05$) among treatments. * Indicates significant differences ($p < 0.05$) among samples with or without nZVI treatment, based on an independent *t*-test.

treatment group, nZVI treatment increased the pH by 0.25 and 0.34 in low-Cd and high-Cd soils, respectively.

The combination of nZVI treatment and γ radiation significantly decreased soil NO_3^--N content, whereas it significantly increased soil NH_4^+-N content (Fig. 2B). Treatment with nZVI significantly decreased NO_3^--N content by 30.9% and 16.0% in low-Cd and high-Cd soils, respectively, with γ radiation treatment. No significant change in NO_3^--N content with nZVI treatment was observed in the non-irradiated treatment group. Furthermore, nZVI treatment significantly increased soil NH_4^+-N content in all treatment groups but had no significant effect on soil DOC content in all treatment groups (data not shown).

The Spearman's correlation between the levels of available Cd and Fe solid phases, as well as soil properties, is shown in Fig. 2C and D. The available Cd content in low-Cd soils showed a significantly negative correlation with poorly crystalline Fe(III) ($p < 0.01$) and highly crystalline Fe(II) ($p < 0.01$) contents, regardless of γ radiation treatment, whereas the available Cd content in high-Cd soils showed a significantly negative correlation with pH ($p < 0.05$), adsorbed Fe(II) content ($p < 0.001$), poorly crystalline Fe content ($p < 0.01$), and highly crystalline Fe(II) content ($p < 0.001$), regardless of γ radiation. Furthermore, increased poorly crystalline Fe(II) levels positively correlated ($p < 0.05$) with a decrease in extractable Cd levels in both non-irradiated soils and γ-irradiated soils with nZVI treatment (Fig. 3). By contrast, decreased extractable Cd levels showed no significant correlation with increased pH or available Mn content (Fig. S4).

3.4. *Effects of nZVI on Cd, Fe, and Mn phase redistribution in soil*

The levels of the carbonate-bound phases of Cd, Fe, and Mn increased significantly (except carbonate-bound Cd in low-Cd soil) with treatment with nZVI, with or without γ radiation (Figs. 4 and S5). The levels of the Fe/Mn-oxide-bound phases of Cd and Fe also increased with nZVI treatment regardless of radiation treatment and Cd level (the levels of Fe/Mn-oxide-bound phases of Cd in low-Cd soil were too low to be detected). However, the levels of Fe/Mn-oxide-bound phases of Mn markedly decreased with nZVI treatment. The levels of carbonate-bound and Fe/Mn-oxide-bound phases of Cd, Fe, and Mn in the high-Cd soils were higher than those in the low-Cd soils. Radiation had no significant effect on the Cd and Fe fractions in both the carbonate-bound and the Fe/Mn-oxide-bound phases but significantly increased the levels of carbonate-bound Mn and decreased the levels of Fe/Mn-oxide-bound Mn. In high-Cd soils, the levels of Fe/Mn-oxide-bound phases of Cd, Fe, and Mn were considerably higher than those of the corresponding carbonate-bound phases.

3.5. *Effects of nZVI on bacterial community structure and composition*

Changes in the diversity of bacterial communities among treatments were supported by the diversity indices (Fig. S6). Treatment with nZVI had no significant effect on the α-diversity indices. Radiation generally had no negative effect on α-diversity after a 7-day incubation period,

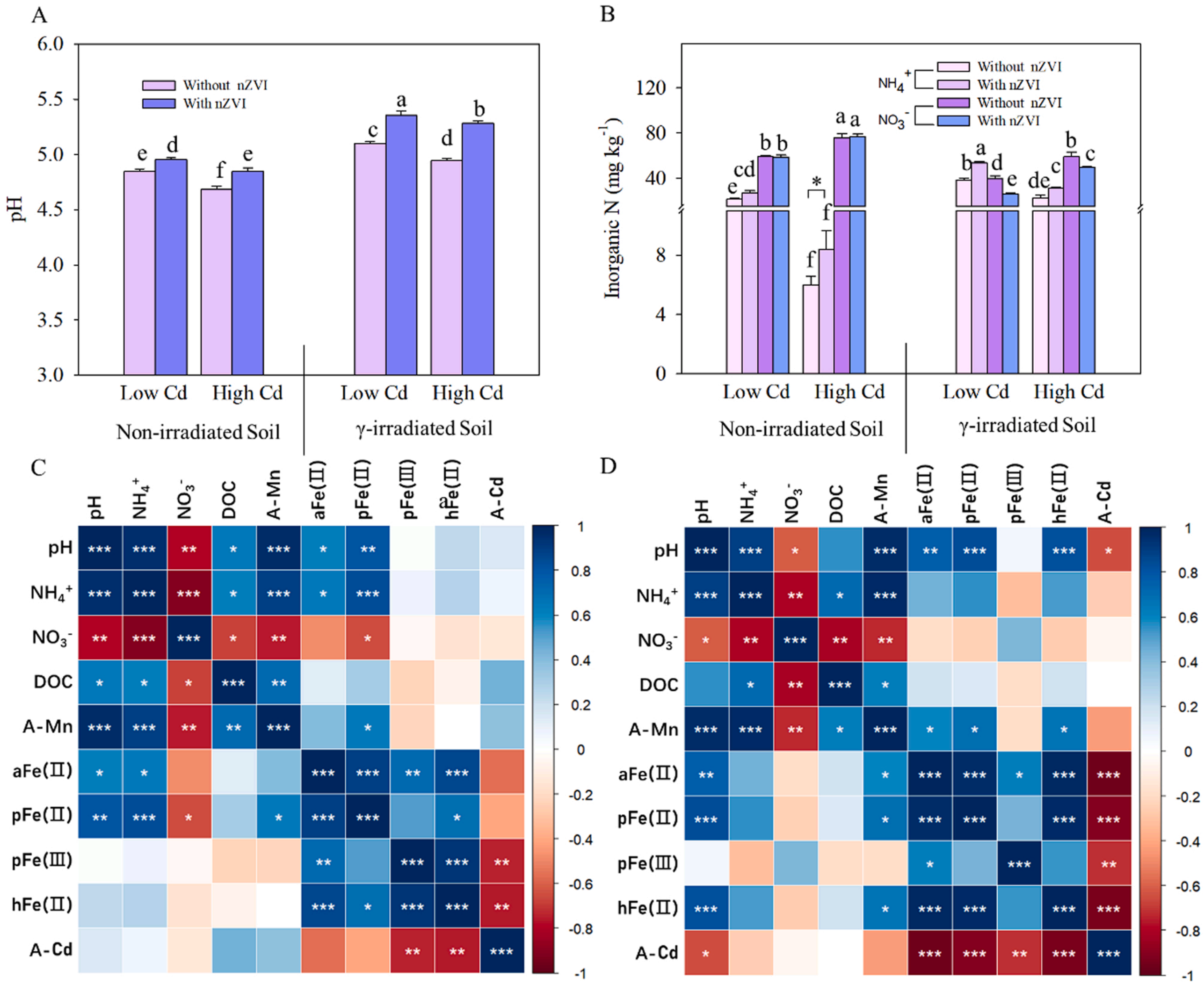

Fig. 2. Soil pH (A) and NH_4^+/NO_3^- content (B) for different treatments. Bars with the same letters indicate non-significant differences ($p > 0.05$) in NH_4^+-N or NO_3^--N content among different treatments. * Indicates significant differences ($p < 0.05$) among samples with or without nZVI treatment, based on an independent *t*-test. Matrix of correlations between Fe solid phase levels and soil properties in low-Cd soil (C) and high-Cd soil (D) groups. Bars with the same letters indicate non-significant differences ($p > 0.05$) among different treatments (A, B). * Indicates significant differences ($p < 0.05$) among samples with or without nZVI treatment, based on an independent *t*-test. *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$. A-Mn, A-Cd, aFe(II), pFe(II), pFe(III), and hFe(II) denote available Mn, available Cd, adsorbed Fe, poorly crystalline Fe(II), poorly crystalline Fe(III), and highly crystalline Fe(II), respectively.

except that the high-Cd soil with γ radiation had lower α-diversity than that in the other treatment groups. The OTU rank abundance curves also indicated a lower α-diversity in the high-Cd soil with γ radiation treatment (Fig. S6B).

Differences in bacterial community structures were analyzed using principal coordinate analysis (Fig. 5A). The projections of soils with and without nZVI treatments on the horizontal axis were relatively close, suggesting that the 0.1% nZVI treatment did not have a negative effect on the soil bacterial community structure. However, γ-irradiated soils separated from the non-irradiated soils, indicating that γ radiation induced differentiation in the bacterial community structures. Furthermore, Cd spiking induced differentiation in the bacterial community structures between low-Cd and high-Cd soils, for non-irradiated soils. However, the projection of γ radiation on the horizontal axis was similar, regardless of Cd level.

As shown in Fig. S7, γ radiation treatment had a significant effect on the relative abundance of the bacterial community at the phylum level but nZVI treatment did not. The most abundant phyla were Proteobacteria (39.5%), Acidobacteria (19.2%), and Firmicutes (10.1%) in the non-irradiated groups, whereas the dominant abundant phyla were Firmicutes (64.6%), Proteobacteria (12.5%), and Actinobacteria (7.5%) in the γ-irradiated groups. γ radiation significantly decreased the relative abundance of Proteobacteria, Acidobacteria, and Gemmatimonadetes, but significantly increased the abundance of Firmicutes. Exogenous Cd significantly decreased the relative abundance of Proteobacteria and increased the abundance of Acidobacteria and Actinobacteria. At the genus level, *Mizugakiibacter* was the most abundant genus (8.74%) in non-irradiated soils, whereas *Bacillus* was the most abundant genus (41.95%) in γ-irradiated soils (Fig. 5B). γ radiation decreased the relative abundance of some genera, such as *Mizugakiibacter* and *Lysobacter*, whereas it increased the relative abundance of other genera, such as *Bacillus* and *Tumebacillus*. Furthermore, treatment with 0.1% nZVI increased the relative abundance of *Bacillus* and *Paenibacillus* but decreased the relative abundance of *Pullulanibacillus* and *Tumebacillus*.

3.6. *Relationships among bacterial community makeup, soil physicochemical properties, and iron phases*

We hypothesized that changes in solid Fe phases, particularly for Fe

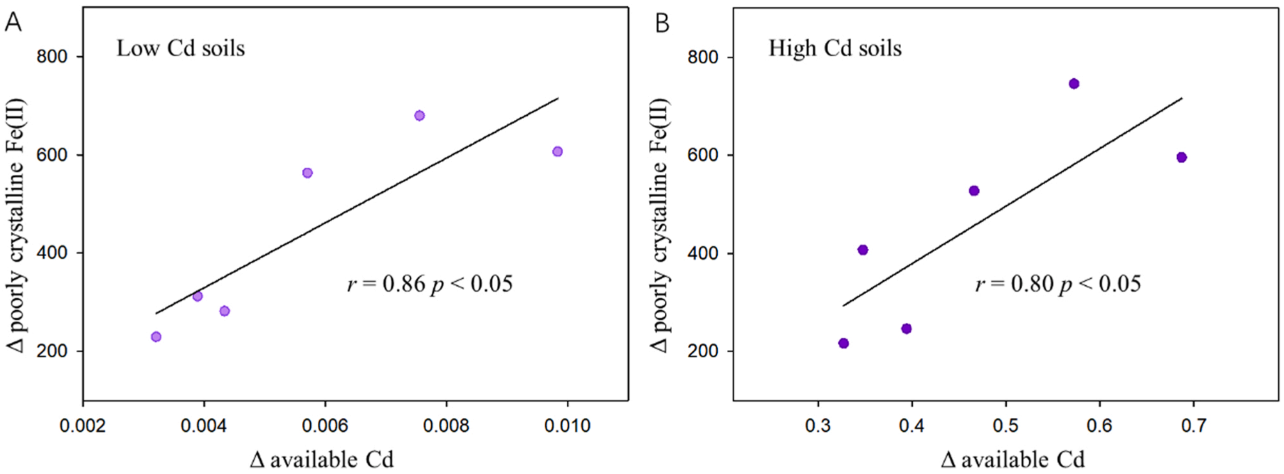

Fig. 3. Correlation between Cd stabilization (Δ available Cd, concentration of available Cd without nZVI treatment minus that treated by nZVI) and increased poorly crystalline Fe content (Δ poorly crystalline Fe(II), concentration of poorly crystalline Fe(II) treated by nZVI minus that without nZVI treatment) in low-Cd (A) and high-Cd (B) soils.

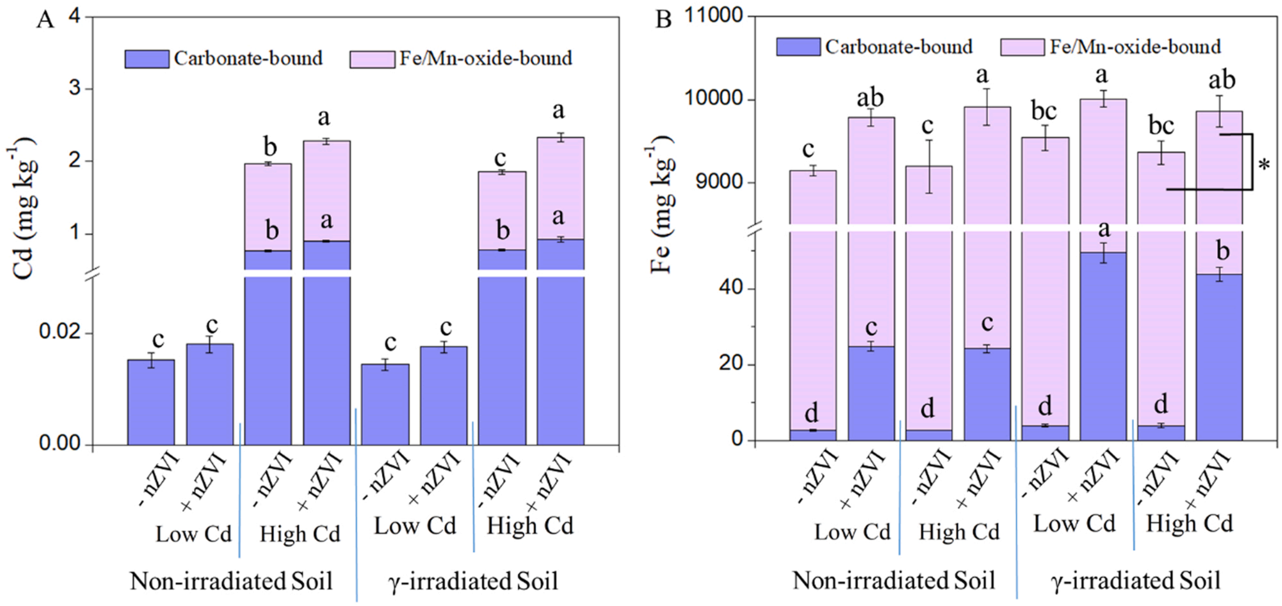

Fig. 4. Distributions of Cd (A) and Fe (B) speciation in different treatments. Bars with the same letters indicate non-significant differences ($p > 0.05$) for carbonate-bound or Fe/Mn-oxide-bound Cd/Fe among different treatments. * Indicates significant differences ($p < 0.05$) among samples with or without nZVI treatment, based on an independent *t*-test.

(II)-containing minerals in soil treated with nZVI, could be affected by the changes in bacterial communities induced by treatment with nZVI. To test this hypothesis, Spearman's correlation analysis was used to interpret the relationships among bacterial communities, soil physicochemical properties, and Fe phases. At the phylum level, the Fe phase fractions did not show any significant correlation with the abundance of bacterial communities (data not shown). Furthermore, at the genus level, poorly crystalline Fe(II) content correlated positively with the abundance of *Bacillus* ($p < 0.05$) but correlated negatively with the abundance of *Pullulanibacillus* ($p < 0.05$) and *Alicyclobacillus* ($p < 0.05$) in non-irradiated soils (Fig. 6). Poorly crystalline Fe(III) content maintained an increasing trend with changes in the relative abundance of *Bryobacter*, *Massilia*, *Candidatus-Solibacter*, and *Paenibacillus*. Additionally, the relative abundance of *Paenibacillus* was significantly positively correlated with soil pH and NH_4^+ levels, whereas the relative abundance of *Tumebacillus* was significantly negatively correlated with soil pH and NH_4^+ levels. In γ-irradiated soils, poorly crystalline Fe(II) levels were significantly positively correlated with the abundance of *Paenibacillus* but were negatively correlated with the abundance of *Pullulanibacillus* and the bacterium Ellin6067.

4. Discussion

4.1. The effect of changes in soil physicochemical characteristics on Cd redistribution under nZVI treatment

Generally, the stabilization mechanism of nZVI-Cd can be described by adsorption and/or precipitation (Xue et al., 2018). However, soil is a complex system that has solid, liquid, and gas phases, and the mobility of Cd is related to environmental factors, particularly pH (Huang et al., 2019) and Fe-Mn oxide levels (Wang et al., 2019; Li et al., 2021a). nZVI, which has a strongly reducing nature and large number of active sites, has a significant effect on soil pH (Mitzia et al., 2020) and redox-sensitive trace metals such as Mn and Fe (Li et al., 2020). In this

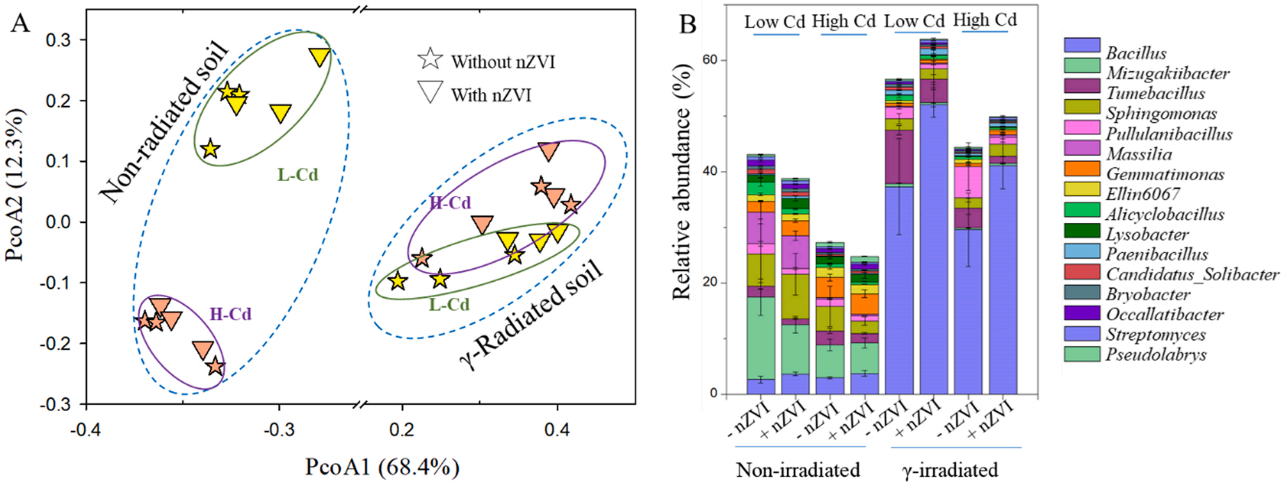

Fig. 5. Principal coordinate analysis (PCoA) analysis of the bacteria community for different treatments (A) and the relative abundances of 16 genera from the bacterial community for different treatments (B). L-Cd, low-Cd soil; H-Cd, high-Cd soil; −nZVI, without nZVI treatments; +nZVI, with nZVI treatments.

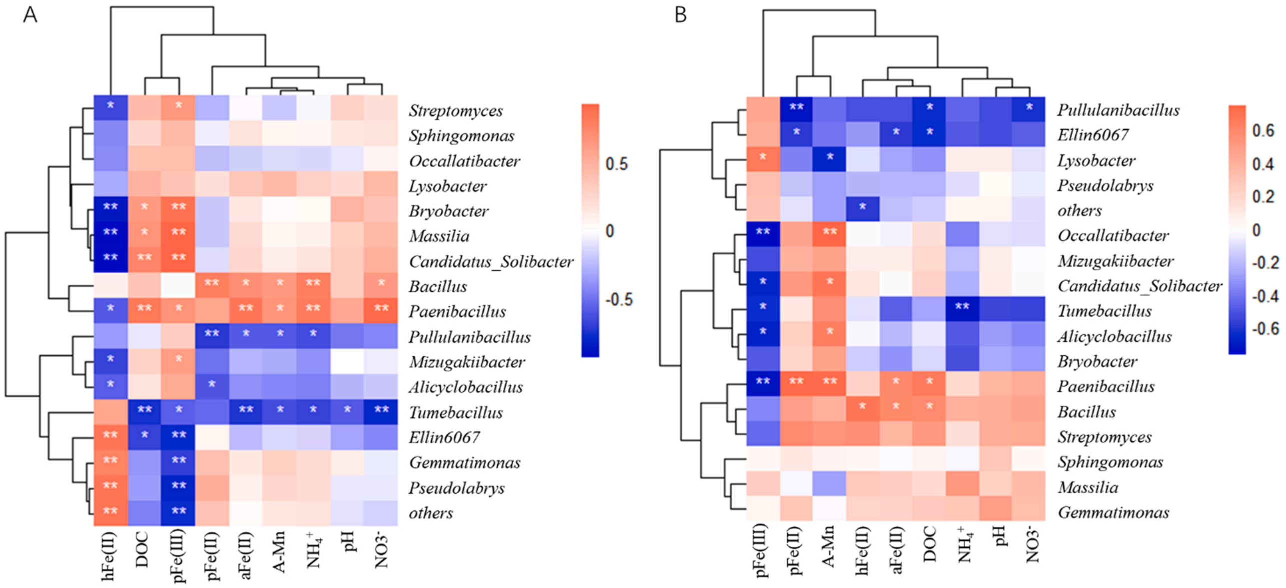

Fig. 6. Heat maps of Spearman's rank correlations coefficients and cluster analysis between the physicochemical indexes and relative abundances of bacterial genera in non-irradiated soils (A) and γ-irradiated soils (B). $*p < 0.05$, $**p < 0.01$, $***p < 0.001$. A-Mn, A-Cd, aFe(II), pFe(II), pFe(III), and hFe(II) denote available Mn, available Cd, adsorbed Fe, poorly crystalline Fe(II), poorly crystalline Fe(III), and highly crystalline Fe(II), respectively.

study, treatment with nZVI significantly increased soil pH and poorly crystalline Fe mineral and available Mn contents but also reduced the content of available Cd in soils. These results suggest that treatment with nZVI has a significant impact on soil characteristics and on the chemical form of Cd. Treatment with nZVI significantly increased soil pH owing to its rapid reaction with water and oxygen in the soil (Komárek et al., 2013). Carbonate-bound metals are susceptible to changes in pH (Tessier et al., 1979). Treatment with nZVI increased the levels of carbonate-bound Cd, Fe, and Mn in soils.

Moreover, the available Mn content also significantly increased with the reduction of Mn oxides by nZVI corrosion (Liu et al., 2021). By contrast, the levels of Fe/Mn-oxide-bound Cd and Fe increased with nZVI treatment, but the levels of Fe/Mn-oxide-bound Mn decreased. The decrease in Fe/Mn-oxide-bound Mn content correlated with the increase in Fe/Mn-oxide-bound Cd content in high-Cd control soils (Figs. 4 and S5), which suggests that a small proportion of the Cd present in the soil was released from Mn oxide dissolution (Muehe et al., 2013a). Although dissolved Mn oxides induced some solubility in Cd through nZVI treatment, other compounds offset the Cd migration risk, as evidenced by the decreased available Cd content.

Soil pH is considered a key factor in controlling the mobility of Cd in soil (Tack et al., 2006; Huang et al., 2017). However, there was no correlation between a decrease in available Cd content and any increase in pH (Fig. S4), which suggests that variation in soil pH has limited effect on Cd speciation with nZVI treatment. In this study, with 0.1% nZVI treatment, soil pH increased by only 0.11–0.34 units, which is far less than the reported one unit (Chen et al., 2018). The limited pH variation and increased Fe oxide content observed due to the 0.1% nZVI treatment might be the main reason for the inconsistencies between the results of the present study and previous reports, such as the observation that soil pH controls the mobilization of Cd (Wang et al., 2019). These inconsistencies are further discussed below.

4.2. Role of Fe oxides on Cd stabilization by nZVI treatment

Fe fractions are responsible for variability in Cd bioavailability in soils (Yu et al., 2016b; Li et al., 2020, 2021b). Interestingly, there was a significantly positive correlation between increased poorly crystalline Fe(II) levels and decreased extractable Cd levels (Fig. 3), which indicates that the shift in Cd mobility is affected by the formation of new Fe (II)-containing minerals from nZVI (Liu et al., 2021). The Cd content of the Fe/Mn-oxide-bound fractions was considerably higher than that of carbonate-bound fractions with nZVI treatment (excluding Cd content in low-Cd soils), further confirming that carbonates played a minor role in Cd stabilization with nZVI treatment and that Fe(II)-containing minerals were responsible for Cd stabilization (Muehe et al., 2013a). Owing to their large surface areas and abundant functional groups, Fe (hydr)oxides adsorb nutrients and heavy metals onto their surfaces (Schultz et al., 1987), and the newly formed secondary Fe(II)-containing minerals can supply abundant hydroxyl groups to immobilize Cd^{2+} (Li et al., 2016).

In the present study, well-mixed nZVI in soil (0.1%, w/w) was rapidly oxidized to Fe oxides within 4 h (Fig. S8), and only 0.03‰ (w/w) Fe^0 remained in the soil. Additionally, there was a significant correlation between Cd availability and poorly crystalline Fe and highly crystalline Fe levels, which suggests that Fe oxides formed from the corrosion of nZVI contributed to the stabilization of Cd.

Corrosion of nZVI increased the soil pH, which provided more sorption sites on the surface of Fe/Mn oxides for Cd^{2+} bonding (Liu et al., 2021). However, during the formation and transformation of Fe-containing minerals from the corrosion of nZVI, the chemical form of Cd is altered (Suda and Makino, 2016). This is indicated by the higher content of Fe/Mn-oxide-bound Cd in nZVI-treated soil than that of non-amended soil.

Aged nZVI has been reported to contain both Fe(II) and Fe(III) minerals (Pullin et al., 2017; Bae et al., 2018). Additionally, poorly crystalline Fe(II)-containing minerals were most likely Fe_3O_4 (magnetite or rust). It has been reported that Fe_3O_4 is one of the aging products of nZVI (Reinsch et al., 2010; Wu et al., 2019) and can be extracted using 0.5 M or 6 M HCl (Muehe et al., 2013a).

4.3. Soil bacterial composition correlates to soil solid-phase Fe transformation and to the fate of Cd under nZVI treatment

Soil Fe cycling involves biological and chemical oxidation processes (Frierdich et al., 2011; Marshall et al., 2014). A similar amount of Fe^0 remained in both non-irradiated and γ-irradiated soils that had been treated with nZVI, which suggests that Fe^0 may be initially oxidized via chemical reactions (Mu et al., 2017). A comparison of solid-phase Fe in non-irradiated and γ-irradiated soils can reveal the effect of soil bacteria on the transformation of nZVI aging products.

In the present study, γ radiation induced significant differences in bacterial structure and diversity to that of non-irradiated soils. For the first time, we showed that soil bacteria play a critical role in the transformation of the nZVI aging products as evidenced by the change in the poorly crystalline Fe(II) levels, which were significantly higher than those in non-irradiated soils, due to nZVI treatment in γ-irradiated soils. The relative abundance of *Bacillus*, *Pullulanibacillus*, and *Alicyclobacillus* strongly correlated with poorly crystalline Fe(II) levels, which suggests that these bacterial genera may be involved in the transformation of Fe (II)-containing minerals. It is well known that *Bacillus* has the capacity for Fe reduction (Wang et al., 2017). Some bacteria that have a high level of resistance to γ radiation may rapidly grow in population and may therefore become the dominant bacterial genus, such as *Bacillus* in the present study. This might explain why iron-oxidizing bacteria were not active in the γ-irradiated soil, as evidenced by the high poorly crystalline Fe(II) levels.

It has been reported that the oxidization of poorly crystalline Fe(II) is primarily influenced by iron-metabolizing bacteria (Wen et al., 2018), and that secondary Fe oxide formation during iron redox cycling mediated by microorganisms is usually accompanied by metal release or metal incorporation (Mitsunobu et al., 2013; Muehe et al., 2013b). Interestingly, our results suggested that the oxidization of Fe (II)-containing minerals reduced their capacity for Cd immobilization, as indicated by the lower Cd stabilization efficiencies observed with nZVI treatment in non-irradiated soils than those in γ-irradiated soils.

A previous study emphasized that the presence and aging of nZVI altered soil microbial communities (Wu et al., 2019). By contrast, treatment with 0.1% nZVI had a limited, negative effect on bacterial structure and diversity. This could be due to the soil type and the low dose of nZVI used in this study, compared with the high doses (10–100 g kg^{-1}) used in previous studies (Lefevre et al., 2016). However, treatment with 0.1% nZVI altered the relative abundance of some genera by regulating soil pH, contents of soil nutrients, and metal bioavailability (Zeng et al., 2016; Wang et al., 2021), as shown by the abundance of some key bacteria associated with pH and inorganic N, C, and Fe cycling (Fig. 6). The coupling effects observed between soil redox-sensitive elements and bacterial communities affect Cd mobility (Ding et al., 2014; Mejia et al., 2016; Schaedler et al., 2018). Furthermore, exogenous Cd altered the soil bacterial community structure, which was attributed to changes in the presence of metal-sensitive and metal-resistant species (Austruy et al., 2016). However, exogenous Cd did not decrease the ability of iron-oxidizing bacteria to transform the poorly crystalline Fe(II)-containing minerals, as evidenced by the similar content of poorly crystalline Fe(II) in low-Cd and high-Cd soils.

Combined with the results of solid-phase Fe, bacterial community structure and diversity, and available Cd content, treatment with nZVI was found to promote poorly crystalline Fe(II) oxidization by increasing the relative abundance of *Bacillus*, while decreasing the relative abundance of *Pullulanibacillus* and *Alicyclobacillus*. The oxidization of poorly crystalline Fe(II) minerals with a consequent decrease of Cd stabilization efficiency with nZVI treatment suggests a coupling effect of nZVI and bacteria on Cd stabilization.

5. Conclusions

This study revealed that treatment with 0.1% nZVI had a substantial effect on Cd stabilization and limited negative effects on soil bacterial community structures and diversity. Treatment with nZVI increased the soil pH, which had a slight impact on Cd stabilization. However, nZVI treatment caused Cd dissolution by the reduction of Mn oxides. The secondary Fe(II)-containing minerals formed by the nZVI treatment, particularly Fe_3O_4, made an important contribution to the stabilization of Cd by providing more adsorption sites. However, the presence of some genera associated with Fe(II)-containing mineral transformation was attributed to the decreased Cd stabilization efficiency caused by nZVI in non-irradiated soils, compared with that of γ-irradiated soils. Exogenous Cd had no negative effect on the function of these genera, including *Bacillus*, *Pullulanibacillus*, and *Alicyclobacillus*, which contributed to the transformation of poorly crystalline Fe(II)-containing minerals. Future research could focus on methods to improve Cd stabilization efficiency with nZVI treatment in combination with the inhibition of iron-oxidizing bacteria.

CRediT authorship contribution statement

Mengjiao Liu: Conceptualization, Data curation, Writing – review & editing. **Jun Wang:** Visualization, Writing – review & editing. **Meng Xu:** Visualization, Writing – review & editing. **Sheng Tang:** Visualization. **Jingjie Zhou:** Visualization. **Wankun Pan:** Methodology. **Qingxu Ma:** Supervision, Writing – review & editing. **Lianghuan Wu:** Supervision, Writing – review & editing.

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. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.127343.

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