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Choose your amendment wisely: Zero-valent iron nanoparticles offered no advantage over microparticles in a laboratory study on metal immobilization in a contaminated soil

Elvira A. Dovletyarova [a], Olga S. Fareeva [a], Alexander P. Zhikharev [a], Ramilla A. Brykova [a], Evgenii L. Vorobeichik [b], Marina V. Slukovskaya [c], Martina Vítková [d], Vojtěch Ettler [e], Carolina Yáñez [f], Alexander Neaman [g,*]

[a] Department of Landscape Design and Sustainable Ecosystems, Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., Moscow, 117198, Russian Federation
[b] Institute of Plant and Animal Ecology, Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russian Federation
[c] Laboratory of Nature-Inspired Technologies and Environmental Safety of the Arctic, Kola Science Centre, Russian Academy of Sciences, Apatity, Russian Federation
[d] Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 165 00, Prague – Suchdol, Czech Republic
[e] Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University, Albertov 6, 128 00, Prague 2, Czech Republic
[f] Instituto de Biología, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile
[g] Departamento de Recursos Ambientales, Facultad de Ciencias Agronómicas, Universidad de Tarapacá, Arica, Chile

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ABSTRACT

The potential use of zero-valent iron (ZVI) nanoparticles (i.e., <100 nm in size) for the remediation of metal-contaminated soils has sparked a flurry of research in recent years. However, even reading a large number of these papers cannot completely dispel doubts that ZVI nanoparticles are indeed superior to ZVI microparticles (e.g., iron powder or grit) in immobilizing metals and metalloids in soils. Our primary objective was to compare the adsorption properties of iron-based amendments (ZVI micro- and nanoparticles, natural iron oxides) supplied in a biochar matrix in soils contaminated by a copper-nickel (Cu/Ni) smelter on the Kola Peninsula in Russia. The following iron-containing amendments were added to the studied soil: a composite of ZVI nanoparticles and biochar (synthesized by pyrolysis of iron-impregnated biochar), a mixture of iron powder (i.e., ZVI microparticles) with biochar, and a mixture of iron oxides (from natural ferromanganese nodules) with biochar. Perennial ryegrass (*Lolium perenne* L.) was grown in pots on untreated and amended soils for 21 days under laboratory conditions. In our time-limited study, ZVI nanoparticles did not prove superior to ZVI microparticles or natural iron oxides at immobilizing metals in copper- and nickel-contaminated soil. In other words, ZVI particles size was irrelevant under the experimental setup of this study in its effects on exchangeable metal concentrations, foliar elemental concentrations, and plant growth.

1. Introduction

The potential use of zero-valent iron (ZVI) nanoparticles (i.e., <100 nm in size) for the remediation of metal-contaminated soils has sparked a flurry of research in recent years (e.g., Baragaño et al., 2022; Zhou et al., 2022). Many commercial ZVI nanoparticle products have already become available, and numerous studies have been carried out on the use of ZVI nanoparticles for the remediation of contaminated soils (e.g., Gil-Díaz et al., 2017; Vítková et al., 2018). However, even reading a large number of these papers cannot completely dispel doubts that ZVI nanoparticles are indeed superior to ZVI micro- and macroparticles (e.g., iron powder or grit) in immobilizing metals and metalloids in soils. After all, the effectiveness of iron powder and grit is supported by 15 years of experiments (e.g., Tiberg et al., 2016; Kumpiene et al., 2021), in which their behavior and mechanisms of action in soil have been thoroughly investigated. In the following discussion, iron powder and grit will be referred to simply as "ZVI microparticles" for the sake of fluency, regardless of the exact particle size.

* Corresponding author.
E-mail address: alexander.neaman@gmail.com (A. Neaman).

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The superior adsorption properties of nanoparticles are attributed to their small size, which is seen as an advantage over microparticles (e.g., Mueller and Nowack, 2010). However, few studies have directly compared the efficacy of ZVI micro- and nanoparticles (Zhang et al., 2017; Danila et al., 2020). So the question arises, what role does ZVI particle size play in the remediation of metal-contaminated soils?

Our study needed to focus on a specific site to answer this research question. We chose an industrial barren near the copper-nickel (Cu/Ni) smelter on the Kola Peninsula, Russia (e.g., Slukovskaya et al., 2020), because it is considered a particularly challenging location to reduce metal phytotoxicity in the soil (Tarasova et al., 2020; Neaman et al., 2021; Dovletyarova et al., 2022). As a first step, we decided to test the selected amendments under laboratory conditions, before considering a field-scale investigation.

Due to the high surface energy of ZVI nanoparticles, they tend to aggregate in soil, which may reduce their effectiveness (Sun et al., 2019; Zhou et al., 2022). To overcome this problem, we used ZVI nanoparticles exclusively as an iron-impregnated biochar composite synthesized by pyrolysis (Semerád et al., 2021). To balance the experimental design, treatments with ZVI microparticles without biochar and with biochar without ZVI microparticles were also carried out. Since iron oxides have been proven to be an effective amendment for immobilizing metals and metalloids in contaminated soils (e.g., Komárek et al., 2013), we decided to include treatments with iron oxides (from natural ferromanganese nodules) as well in this study.

Our primary objective was to compare the adsorption properties of iron-based amendments (ZVI micro- and nanoparticles, natural iron oxides) supplied in a biochar matrix in soils contaminated by a Cu/Ni smelter. In the following discussion, iron-based amendments supplied in a biochar matrix will be referred to simply as "ZVI microparticles" and "ZVI nanoparticles" for the sake of fluency. As ZVI nanoparticles can be toxic to organisms causing oxidative stress (e.g., review of Xue et al., 2018), it was also decided to evaluate the phytotoxicity of ZVI nanoparticles.

2. Materials and methods

2.1. Materials

The soil sample was taken from an industrial barren (67°55′70″ N, 32°51′50″ E) at a distance of 0.7 km from the copper-nickel (Cu/Ni) smelter located in the northern taiga subzone, near the town of Monchegorsk, Kola Peninsula, Russia (e.g., Slukovskaya et al., 2020). Peat eutrophic soil (Eutric Histosol) was sampled from 0 to 20 cm depth. A composite soil sample was collected from 10 equidistant points in the total sampling area of 400 m^2. The combined soil sample was air-dried at 20 ± 2 °C and grinded to particle size <2 mm.

The soil sample was shipped to the laboratory of the RUDN University in Moscow. Uncontaminated commercial peat (Pelgorskoe brand, Russia) was also used in our laboratory experiments for comparison, hereafter referred to as "peat" for convenience. In addition, commercially available iron powder (<100 μm in size) with a minimal amount of admixture of Mn, Ni, and Cu (0.03%, 0.02%, and 0.003%, respectively) was used (Denis A. Pankratov, personal communication, unpublished results).

Ferromanganese nodules from the Gulf of Finland were obtained from the company Olkat, Russia. A detailed description of these can be found elsewhere (Zhamoida et al., 2017). The chemical composition of the bulk Fe–Mn nodules obtained by the ICP-OES analysis of the digests (Ettler et al., 2017) showed that they contain ~12% Fe and ~15% Mn. The mineralogical composition was dominated by Fe and Mn oxides and hydroxides such as goethite (FeOOH) and birnessite (nominal composition: $MnO_2 \cdot nH_2O$) and also included some quartz, muscovite, and albite (see X-ray diffraction and micro-X-ray fluorescence results as Supplementary Fig. 1). The Fe–Mn nodules were ground in mortar before being applied to the soil.

Zero-valent iron nanoparticles (<100 νm in size) incorporated in the biochar matrix were purchased from the company LAC, Ltd. (Židlochovice, Czech Republic). Hereafter, this product will be referred to as "ZVI nanoparticles/biochar composite" or simply "ZVI nanoparticles". The composite was prepared from pine and spruce sawdust pretreated with iron precursor (hematite powder, α-Fe_2O_3) and pyrolyzed in nitrogen atmosphere at 700 °C (Semerád et al., 2021). The characteristics of ZVI nanoparticles/biochar composite were as follows (Zarzsevszkij et al., 2022): cation exchange capacity of 15 $cmol_c\ kg^{-1}$, pH (H_2O) of 11, BET specific surface area of 203 $m^2\ g^{-1}$.

For comparison, pure biochar without ZVI particles was also purchased from the same company. Its characteristics were as follows (Zarzsevszkij et al., 2022): cation exchange capacity of 4.6 $cmol_c\ kg^{-1}$, pH (H_2O) of 10, BET specific surface area of 351 $m^2\ g^{-1}$.

2.2. Evaluation of phytotoxicity of ZVI nanoparticles in uncontaminated peat

A preliminary experiment was carried out on uncontaminated commercial peat with the following amendments:

Peat + dolomite (10%);

Peat + dolomite (10%) + ZVI nanoparticles/biochar composite (4%).

Commercially available dolomitic lime (BHZ brand, Russia) was used. In all the treatments, multipurpose fertilizer (Fertika brand, Russia) was applied according to the manufacturer's recommendations for grass species (0.4 g fertilizer per 1 kg substrate). The fertilizer had the following composition of macro- and micronutrients: NH_4–N 6.6%, NO_3–N 4.4%, P_2O_5 12%, K_2O 26%, MgO 0.4%, S 0.7%, Ca 0.55%, Mn 0.16%, Cu 0.08%, B 0.09%, Fe 0.16%, Zn 0.09%, Mo 0.008%.

Amended peat was wetted weekly and allowed to dry at room temperature (20–25 °C). Specifically, for each treatment, 1 kg of peat was placed in a 5 L container and wetted weekly with ~1.5 L of distilled water. The weekly wetting-drying cycles continued for one month to allow the amendments to react in the soil.

Plant bioassays were carried out in four replicates according to a standard protocol (ISO 11269-2, 2012), as detailed in our previous studies (Tarasova et al., 2020; Neaman et al., 2021). Each replicate consisted of a pot containing 165 g of peat. The plants were irrigated daily with 90 mL of distilled water. This irrigation rate was set so no water was drained from the pots.

Elemental foliar concentrations were determined after 21 days of growth by ICP-OES following a standard procedure of dry ashing at 600 °C and extraction of elements from the ash by 2 M HCl (Kalra, 1998; Sadzawka et al., 2007). Four replicates were used for the foliar analysis. Standard reference materials (wheat, barley, rye, and peas, obtained from the Pryanishnikov All-Russian Scientific Research Institute of Agrochemistry) were used throughout the analysis, and the experimental values for the metals of interest were within 100 ± 20% of the certified values.

2.3. Preliminary experiment on dolomite dosage

Given that over-liming has been proposed to reduce the phytotoxicity of nickel in contaminated soils (e.g., Kukier and Chaney, 2000; Kukier and Chaney, 2004), a preliminary experiment was conducted to determine the dolomite dose to be used in this study. Specifically, two different doses of dolomite were tested: 3% w/w (yielding soil pH 5.8) and 20% w/w (yielding soil pH 7.2). The preliminary experiment showed that plant growth was stunted in the over-limed soil (Supplementary Fig. 2). Therefore, in the further experiments of this study, the dolomite dose was set at 3%.

Our finding that over-liming stunts plant development contradicts previous studies (e.g., Kukier and Chaney, 2000; Kukier and Chaney, 2004). However, these authors used nickel-contaminated soils, whereas the soils used in this study were contaminated by both nickel and copper. In the case of contamination by both Ni and Cu, the effect of soil pH on metal solubility is different. Specifically, it was observed that the high dolomite dose and the resulting increase in pH reduced the solubility of Ni (Supplementary Table 1), but had no effect on the solubility of Cu. Thus, the higher dolomite dose lowered the foliar concentration of Ni below the toxicity threshold of 80 mg kg^{-1} for *L. perenne* (Reuter and Robinson, 1997), but had the opposite effect on the foliar concentration of Cu, which exceeded the toxicity threshold of 39 mg kg^{-1} for that species (Verdejo et al., 2015) (Supplementary Table 2). Thus, these findings suggest that over-liming does not reduce Cu phytotoxicity in contaminated soils. This conclusion is consistent with the results of other studies that investigated increased Cu solubility in alkaline soils (e.g., Mondaca et al., 2015).

2.4. Treatments

The selected doses of Fe–Mn and iron powders were based on our previous experiments (Dovletyarova et al., 2022). The nine experimental treatments performed in this study were as follows:

Peat: uncontaminated commercial peat + dolomite (5%);

A: untreated soil;
B: soil + dolomite (3%);
C: soil + dolomite (3%) + ZVI nanoparticles/biochar composite (4%);
D: soil + dolomite (3%) + biochar (2%);
E: soil + dolomite (3%) + iron (2%);
F: soil + dolomite (3%) + biochar (2%) + Fe–Mn nodules (2%);
G: soil + dolomite (3%) + iron powder (2%);
H: soil + dolomite (3%) + biochar (2%) + iron powder (2%).

In all the treatments, multipurpose fertilizer (Fertika brand, Russia) was used according to the manufacturer's recommendations for grass species (0.4 g fertilizer per 1 kg substrate). Peat, untreated and amended soils were wetted weekly and allowed to dry at room temperature (20–25 °C). The weekly wetting-drying cycle continued for one month to allow sufficient time for the amendments to react in the soil. Four replicates were then used for plant bioassay, as detailed above.

2.5. Chemical characterization of the soils

Total elemental concentrations in soil and peat were determined by ICP-OES (Agilent, model 5110) after microwave digestion with a mixture of concentrated HNO_3 and H_2O_2. Standard reference materials (Krasnozem and Chernozem, obtained from the company Ecolan, Russia) were used throughout the analysis, and the experimental values of the target metals were within 100 ± 20% of the certified values.

The exchangeable concentrations of Cu, Ni, Zn, Mn, and Cd were also determined using ICP-OES. A solution of 0.01 M KNO_3 was used as extractant (soil/solution ratio of 1/25). The resulting suspension was shaken for 60 min and then filtered through ashless filter paper. Soil pH was measured in the same 0.01 M KNO_3 extract. The organic matter content of the soil and commercial peat was estimated by loss-on-ignition at 600 °C.

2.6. Statistical analysis

The effects of treatments on soil and plant responses were compared by one-way ANOVA tests, and the Dunnett test was used for post-hoc comparisons ($p \leq 0.05$). Statistical analysis was performed using the R package DescTools (Core Team, 2021).

3. Results and discussion

3.1. Evaluation of phytotoxicity of ZVI nanoparticles in uncontaminated peat

Several studies have shown that ZVI nanoparticles can cause oxidative stress to soil organisms (e.g., review of Xue et al., 2018). However, no phytotoxicity attributed to ZVI nanoparticles was recorded in this study. Furthermore, plant growth was similar or better in the ZVI nanoparticle-treated soil (C) compared to the dolomite treatment (B) (Fig. 1). Since the concentrations of exchangeable metals and foliar elements were practically the same in treatments B and C (data not shown), future studies to clarify the weakly stimulatory effect of ZVI nanoparticles on shoot length will be very useful (Fig. 1b).

3.2. Effect of dolomite and biochar treatments on soil and plant responses

In the studied soil, the total concentrations of Cd, Co, Cu, and Ni were several times higher than the corresponding background concentrations (i.e., in the soil without anthropogenic influence) (Table 1). The main pollutants were Cu and Ni, with concentrations two orders of magnitude higher than the corresponding background levels (Kashulina, 2017). Both Cu and Ni are essential plant micronutrients (López and Magnitski, 2011) but become toxic above a certain threshold (e.g., Santa-Cruz et al., 2021).

Since acidic conditions in the untreated soil (pH 4.5, Table 2) increase metal solubility and bioavailability (Lillo-Robles et al., 2020), it is not surprising that very high concentrations of exchangeable metals

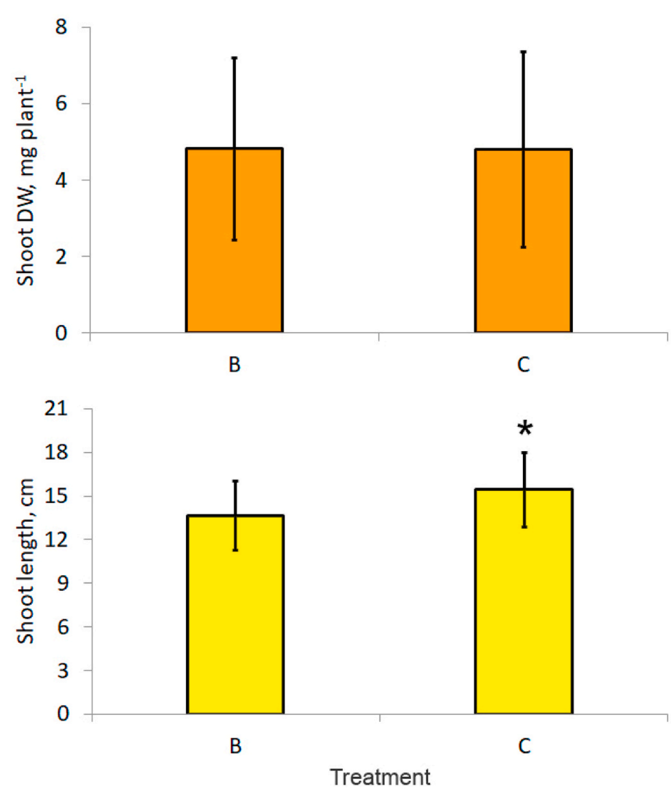

Fig. 1. Effect of different treatments on (a) shoot dry weight (DW) and (b) shoot length of ryegrass grown on uncontaminated commercial peat. Average values and standard deviations are shown (n = 4). An asterisk indicates a statistically significant difference ($p < 0.05$) between the treatments. Hereafter, percentages are for weight/weight basis. B: dolomite (10%), pH 6.9; C: dolomite (10%) + ZVI nanoparticles/biochar composite (4%), pH 7.0. All-purpose fertilizer was added to all substrates, including commercial peat, at the rate of 0.4 g fertilizer per 1 kg substrate.

Table 1
Total metal concentrations and organic matter (estimated as loss on ignition, LOI) in the soil under study and in commercial peat. The soil corresponds to Histosol (0–5 cm) from Monchegorsk (Kola Peninsula, Russia) contaminated by atmospheric emissions from a copper-nickel (Cu/Ni) smelter. Background total metal concentrations in the soils of the study area are also shown for comparison (mean ± standard deviation). Peat corresponds to uncontaminated commercial peat.

Soil property	Contaminated soil	Background[a]	Uncontaminated peat
Total Cd, mg kg^{-1}	3.5	0.22 ± 0.16	4.3
Total Co, mg kg^{-1}	77	7.4 ± 8.9	1.8
Total Cu, mg kg^{-1}	6977	12 ± 7.2	48
Total Ni, mg kg^{-1}	2580	18 ± 17	6.5
Total Zn, mg kg^{-1}	80	48 ± 0.07	14
LOI, %	71	–	90

[a] Kashulina (2017).

Table 2
Effect of treatments on soil pH determined in 0.01 N KNO_3 extract at soil/solution ratio of 1/25 (mean ± standard deviation, n = 4).

Treatment	Treatment code	pH
Untreated soil	A	4.5 ± 0.09
Dolomite (3%)	B	5.8 ± 0.04
Dolomite (3%) + ZVI nanoparticles/biochar composite (4%)	C	5.9 ± 0.01
Dolomite (3%) + biochar (2%)	D	5.9 ± 0.03
Dolomite (3%) + Fe–Mn nodules (2%)	E	5.8 ± 0.04
Dolomite (3%) + biochar (2%) + Fe–Mn nodules (2%)	F	5.8 ± 0.04
Dolomite (3%) + iron powder (2%)	G	5.9 ± 0.02
Dolomite (3%) + biochar (2%) + iron powder (2%)	H	5.9 ± 0.01

were found in the untreated soil (Table 3, treatment A) resulting in high concentrations of metals in the *L. perenne* shoots (Fig. 2, treatment A). As a consequence, shoot length and biomass of *L. perenne* were severely inhibited (Fig. 3). In contrast, dolomite-treated soil (i.e., treatments B–H) with circumneutral pH (Table 2) and lower exchangeable metal concentrations (Table 3) resulted in lower metal content in *L. perenne* shoots (Fig. 2), which favored plant growth (Fig. 3).

However, plant growth rate was slower in dolomite-treated soil than in uncontaminated peat (Supplementary Fig. 3). This may be attributed to the fact that metal toxicity remained high even after the dolomite treatment. Consistent with this argument, foliar concentrations of Ni (110 mg kg^{-1}, Table 4, treatment B) were found to be above the toxicity threshold of 80 mg kg^{-1} for *L. perenne* (Reuter and Robinson, 1997). Therefore, in the studied soils, Ni was toxic to plants even after the dolomite treatment.

Treatments with ZVI micro- and nanoparticles reduced foliar Ni concentrations below the toxicity threshold of 80 mg kg^{-1} (Fig. 2) and improved plant growth rate (Fig. 3). Similarly, foliar Zn and Cu concentrations (Table 4) were also found to be below the EC_{20} values for *L. perenne* of 560 mg kg^{-1} (Smilde, 1981) and 39 mg kg^{-1}(Verdejo et al., 2015), respectively. Thus, dolomite treatment helped to reduce Ni, Zn, and Cu toxicity to safe levels. Yet, given the presence of several metal pollutants in the soil under study, the exact cause of phytotoxicity is not immediately obvious.

For the dolomite + biochar treatment (D), the effects on exchangeable metal concentrations (Table 3), foliar elemental concentrations (Fig. 1), and plant growth (Fig. 2) were broadly similar to those for the dolomite-only treatment (B). As to biochar additions to iron-containing treatments (F and H), the effects on exchangeable metal concentrations (Table 3), foliar elemental concentrations (Fig. 1), and plant growth (Fig. 2) were essentially the same as for the corresponding iron-only treatments (E and G, respectively). Thus, biochar had no effect on the efficacy of iron-containing treatments. However, in this study we will not discuss the role of biochar *per se*, given the extensive information available on this topic (e.g., reviews by O'Connor et al., 2018; Wang et al., 2018).

Table 3
Effect of treatment on the concentration of exchangeable fraction of metals in the soil under study. The results are expressed in mg kg^{-1} of air-dry substrate. A 0.01 N KNO_3 solution with a soil/solution ratio of 1/25 was used for extraction.

Treatment	Co, mg kg^{-1}	Cu, mg kg^{-1}	Mn, mg kg^{-1}	Ni, mg kg^{-1}	Zn, mg kg^{-1}
A	13 ± 1.9	161 ± 20	111 ± 15	381 ± 49	7.3 ± 0.97
B	0.80 ± 0.15*	11 ± 1.0*	9.3 ± 1.8	17 ± 2.9*	0.6 ± 0.01*
C	0.50 ± 0.03	8.6 ± 1.6	7.0 ± 0.28	9.8 ± 1.3	0.4 ± 0.02
D	0.70 ± 0.03	12 ± 1.5*	7.9 ± 0.4	15 ± 0.5*	0.5 ± 0.02*
E	0.60 ± 0.15	14 ± 1.2*	114 ± 28*	19 ± 4.4*	0.6 ± 0.08*
F	0.50 ± 0.12	12 ± 1.6*	105 ± 22*	18 ± 3.8*	0.6 ± 0.09*
G	0.60 ± 0.03	9.4 ± 0.78	6.6 ± 0.43	11 ± 0.6	0.4 ± 0.04
H	0.50 ± 0.04	7.9 ± 1.2	6.7 ± 0.21	10 ± 0.7	0.4 ± 0.02

Exchangeable Cd concentrations were below the detection limit. An asterisk indicates a statistically significant difference compared to Treatment C ($p < 0.05$). Treatment A is shown but was not included in the statistical analysis.

3.3. Comparison of the effects of ZVI micro- and nanoparticles

In the present study, differences between iron-containing treatments (i.e., treatments C, E-H) were either very slight or not statistically significant with respect to exchangeable metal concentrations (Table 3), foliar elemental concentrations (Fig. 1), and plant growth (Fig. 2). Similarly, plant growth dynamics were similar among all iron-containing treatments (Supplementary Fig. 3). In other words, the size of ZVI particles was irrelevant under the experimental setup of this study.

Upon corrosion in the soil, ZVI particles are converted to iron oxide and oxyhydroxides such as green rust, magnetite, ferrihydrite, hematite, and goethite (e.g., review of Kumpiene et al., 2019). Iron oxides are known to have high adsorption capacity for potentially toxic metals (e.g., Cu, Zn, Pb, Cd) and metalloids (e.g., As) (e.g., Neaman et al., 2004; Neaman et al., 2008). Under the experimental settings of this study, both new iron oxides formed by corrosion of ZVI particles and the natural iron oxides from ferromanganese nodules exhibited similar metal adsorption properties.

4. Conclusion

Our main finding was that the ZVI nanoparticles did not exhibit any phytotoxicity and may thus be suitable for the remediation of metal-contaminated soils. However, our study, although limited in time, showed that ZVI nanoparticles were not superior to ZVI microparticles at immobilizing metals in copper-nickel-contaminated soil. In other words, ZVI particle size was irrelevant under the experimental setup of this study. Thus, it seems that there is no upside to following the fashionable 'nano' trend currently playing out in this field.

This is the first study to compare the adsorption properties of ZVI micro- and nanoparticles in real anthropogenically contaminated soil. This strength aside, this study is not without its limitations as it was conducted under laboratory conditions. In fact, most of the research on

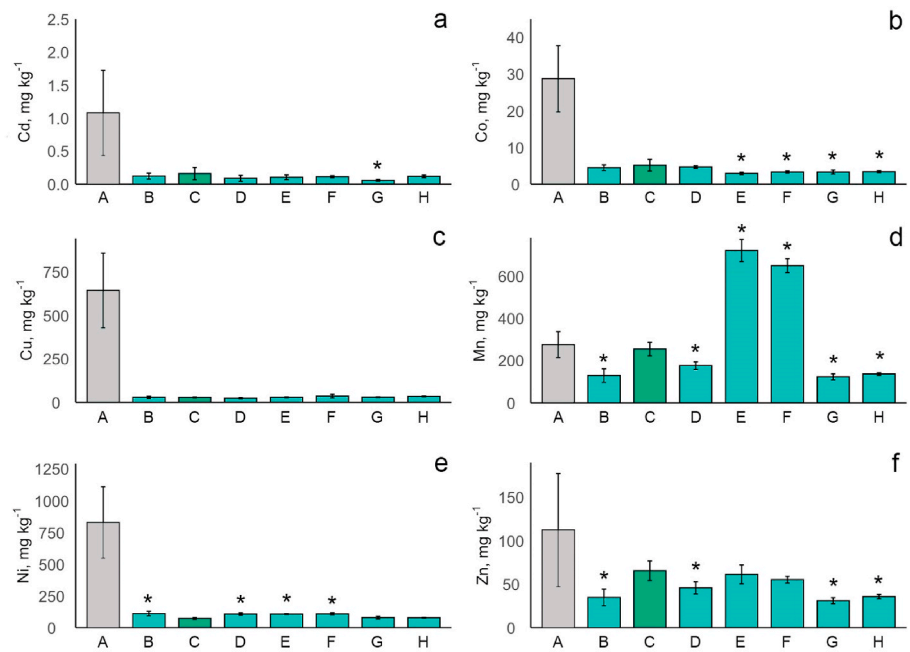

Fig. 2. Effect of treatment on the foliar concentrations of elements in ryegrass grown on metal-contaminated Histosol from Monchegorsk: (a) Cd, (b) Co, (c) Cu, (d) Mn, (e) Ni, (f) Zn. Means and standard deviations are shown (n = 4). An asterisk indicates a statistically significant difference (Dunnett test, $p < 0.05$) between a given treatment and Treatment C, i.e., a ZVI nanoparticles/biochar composite (4%). Treatment A is shown for comparison but is not included in statistical analysis. Hereafter, percentages are for weight/weight basis. A: untreated soil; B: soil + dolomite (3%); C: soil + dolomite (3%) + ZVI nanoparticles/biochar composite (4%); D: soil + dolomite (3%) + biochar (2%); E: soil + dolomite (3%) + Fe–Mn-concretions (2%); F: soil + dolomite (3%) + biochar (2%) + Fe–Mn-concretions (2%); J: soil + dolomite (3%) + iron powder (2%); H: soil + dolomite (3%) + biochar (2%) + iron powder (2%).

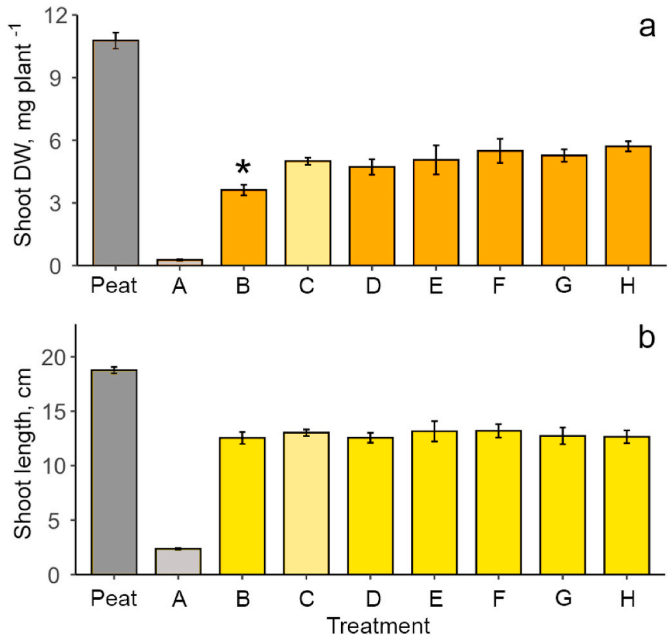

Fig. 3. Effect of different treatments on (a) shoot dry weight (DW) and (b) shoot length of ryegrass grown on Histosol (0–5 cm) from Monchegorsk (Kola Peninsula, Russia) contaminated by the atmospheric emissions from a copper-nickel (Cu/Ni) smelter. Average values and standard deviations are shown (n = 4). An asterisk indicates a statistically significant difference (Dunnett test, $p < 0.05$) between a given treatment and Treatment C, i.e., a ZVI nanoparticles/biochar composite (4%). Treatment A is shown for comparison but is not included in statistical analysis. Uncontaminated commercial peat (Peat) with 5% dolomite, pH 6.4, is also shown for comparison but is not included in the statistical analysis. Hereafter, percentages are for weight/weight basis. A: untreated soil; B: dolomite (3%); C: dolomite (3%) + ZVI nanoparticles/biochar composite (4%); D: dolomite (3%) + biochar (2%); E: dolomite (3%) + Fe–Mn-concretions (2%); F: dolomite (3%) + biochar (2%) + Fe–Mn-concretions (2%); J: dolomite (3%) + iron powder (2%); H: dolomite (3%) + biochar (2%) + iron powder (2%). All-purpose fertilizer was added to all substrates, including commercial peat, at the rate of 0.4 g fertilizer per 1 kg substrate.

Table 4
Foliar metal concentrations (mg kg^{-1}) in ryegrass grown on soils treated with 3% dolomite (Treatment B). Toxicity threshold values for foliar concentrations of metals are shown for comparison.

Metal	Foliar concentration, mg kg^{-1}	Toxicity threshold, mg kg^{-1}	Reference
Cd	0.10 ± 0.04	15	Davis et al. (1978)
Co	4.5 ± 0.78	6.0	Davis et al. (1978)
Cu	29 ± 6.4	39	Verdejo et al. (2015)
Mn	129 ± 32	>400	Reuter and Robinson (1997)
Ni	110 ± 18	80	Reuter and Robinson (1997)
Zn	35 ± 9.7	560	Smilde (1981)

the use of ZVI nanoparticles in soil is based on laboratory experiments, leaving many questions unanswered. For example, ZVI nanoparticles bound to metals and metalloids can migrate into groundwater and pose additional environmental problems (e.g., review of Lefevre et al., 2016). Therefore, data on the vertical and horizontal migration of ZVI nanoparticles are needed to predict their residence time in soil and removal rate to groundwater. Similarly, the adsorption properties of ZVI micro- and nanoparticles should be compared under different Eh conditions, including waterlogging. Thus, future long-term field studies are required to elucidate the role of ZVI particle size in the remediation of metal-contaminated soils.

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 data

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