Revista
Brasileira de
Ciência do Solo

Division – Soil Use and Management | Commission – Soil and Water Management and Conservation

Field experiment pitting magnetite nanoparticles against microparticles: Effect of size in the rehabilitation of metal-contaminated soil

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Received: February 28, 2023

Approved: June 07, 2023

How to cite: Smorkalov IA, Vorobeichik EL, Dzeranov AA, Pankratov DA, Dovletyarova EA, Yáñez C, Neaman A. Field experiment pitting magnetite nanoparticles against microparticles: Effect of size in the rehabilitation of metal-contaminated soil. Rev Bras Cienc Solo. 2023;47:e0230017
https://doi.org/10.36783/18069657rbcs20230017

Editors: José Miguel Reichert and Yuri Jacques Agra Bezerra da Silva.

ABSTRACT: A significant portion of the current knowledge regarding the use of iron nanoparticles for remediating metal-contaminated soils is derived from laboratory experiments, leaving several unanswered questions. This article presents a field experiment comparing the efficacy of magnetite nanoparticles and microparticles for the immobilization of metals and the growth of plants in metal-contaminated soils. This study aimed to investigate the effects of magnetite particle size on metal immobilization and plant growth in soils exposed to airborne pollution from the Middle-Urals Copper Smelter in the southern taiga subzone near Revda, Russia, 50 km from Ekaterinburg. Magnetite nano- and microparticles were added to forest litter at a 4 % w/w dose. The total metal contents in litter from the study plots were 1-2 orders of magnitude higher than background metal concentrations. The magnetite nanoparticle treatment was found to decrease the concentration of exchangeable copper in soil and improve the growth of red fescue (*Festuca rubra L.*) on polluted soil compared to the control. In contrast, magnetite microparticles did not show any statistically significant effects. These findings are in line with laboratory results that demonstrated the superior metal adsorption properties of magnetite nanoparticles compared to microparticles. However, this study was limited in duration (2 months), and longer field studies would be necessary to confirm the role of iron particle size in the rehabilitation of metal-contaminated soils.

Keywords: heavy metals, iron oxides, nanomaterials, nanotechnology, nano, micro.

INTRODUCTION

The term “metal immobilization in soils” refers to the reduction of the bioavailable metals[1] in the soil solution by adding amendments (Mench et al., 2000). In other words, the amendments do not extract the metals from the soil but convert them into less soluble or insoluble forms via mechanisms such as adsorption, complexation, or co-precipitation (Kumpiene et al., 2008). As the solubility of the metals decreases, they become less accessible to plants and soil organisms.

Iron oxides have been found to be effective amendments for immobilizing metals in contaminated soils (Komárek et al., 2013) due to their high adsorption capacity for toxic metals like Cu, Zn, Pb, and Cd (Neaman et al., 2008, Neaman et al., 2004). Some researchers prefer to use iron oxide precursors, such as zerovalent iron particles (e.g., iron powder or grit), which convert to iron oxides[2] upon corrosion in soil (Kumpiene et al., 2019).

A thorough review of the literature suggests that both iron oxides and their precursors, such as zerovalent iron particles, are valuable materials for *in situ* metal immobilization in soils. Notably, in a study by Dovletyarova et al. (2022b) it was discovered that iron oxides formed through the corrosion of zerovalent iron particles and the natural iron oxides originating from ferromanganese nodules exhibited comparable metal adsorption properties in soils polluted by a copper smelter. Similarly, Zhang et al. (2010) demonstrated that zerovalent iron nanoparticles did not present any discernable benefits over magnetite nanoparticles in terms of immobilizing arsenic in soils.

In recent years, the possibility of using iron-containing nanoparticles, which are less than 100 nm in size, for the remediation of metal-contaminated soils has generated a surge of research interest (Liang et al., 2022). Iron-containing nanoparticles are believed to possess superior adsorption characteristics compared to microparticles due to their smaller size and larger surface area (Mueller and Nowack, 2010). However, our scrutiny of the literature on this topic did not completely resolve concerns about the advantages of nanoparticles over microparticles in immobilizing soil metals. For instance, nanoparticles can be harmful to organisms by inducing oxidative stress (Xue et al., 2018).

Given the limited number of studies that have directly compared iron micro- and nanoparticles (Danila et al., 2020), it is pertinent to inquire whether particle size contributes to the efficient remediation of metal-contaminated soils. In light of this, the question arises: what role does the size of iron-containing particles play in the remediation of metal-contaminated soils?

Our study focused on a specific type of iron-containing particles to answer our research question through a field experiment. We selected magnetite (Fe_3O_4), a mixed oxide composed of both Fe(III) and Fe(II), for several reasons. Firstly, magnetite has an advantage over other iron oxides as it is a magnetically separable adsorbent. Magnetic separation is significant in the field of water treatment (Linley et al., 2013). Some authors have suggested that magnetite with adsorbed metals can be extracted from the soil by magnets (Duan et al., 2022; Fu et al., 2021; Ji et al., 2022). Secondly, the synthesis of magnetite is straightforward (Pomogailo et al., 2011), requiring only one step, which enables the preparation of large quantities of magnetite for a field experiment. Lastly, commercial magnetite nanoparticle products are widely available (Huang et al., 2018).

Much of the knowledge on using iron-containing nanoparticles in soil remediation is derived from laboratory experiments, which leaves numerous questions unanswered. To clarify the role of iron particle size in the rehabilitation of metal-contaminated soils, it is imperative to compare the adsorption properties of iron-containing micro- and

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[1] For brevity, metalloids (e.g., arsenic) will be referred to as “metals” in the following discussion.
[2] For brevity, oxyhydroxides (e.g., goethite) will be referred to as “oxides” in the following discussion.

nanoparticles in field studies. Thus, our study was designed to focus on a specific location to address our research question. We selected the area surrounding the Middle-Urals Copper Smelter (56° 51′ 0.8″ N, 59° 54′ 25.6″ E), situated in the southern taiga subzone near Revda, Russia, which has been exposed to air-borne pollution since 1940 (Prudnikova et al., 2020). The smelter emissions did not affect the acidity of the litter; the pH values (pH <5.0) were typical for both polluted and unpolluted areas surrounding the smelter (Prudnikova et al., 2020). In acidic conditions, metals tend to be more soluble (Sposito, 2016), thereby inducing high phytotoxicity (Adriano, 2001). As a result, the area under investigation had sparse herbaceous vegetation (Vorobeichik et al., 2014).

Plants are commonly employed as bioindicators to assess the reduction of metal toxicity in polluted soils following the addition of amendments (Lwin et al., 2018). The current study aimed to assess the impact of magnetite particle size on both metal immobilization and plant growth in soils contaminated by a copper smelter.

MATERIALS AND METHODS

Magnetite synthesis and characterization

Magnetite nanoparticles were synthesized via a stoichiometric 1:2 coprecipitation reaction of iron salts (II and III) in the presence of alkali (Pomogailo et al., 2011). The resulting paste contained 25 % magnetite nanoparticles. To produce magnetite microparticles, the solution was cooled to 4 °C, wrapped in aluminum foil to maintain a constant temperature, and agitated continuously (100 rpm) for 2 h after adding 10 % NaOH. The resulting particles were then dried at 40 °C, resulting in a powder form.

The phase composition of the particles was determined using a Mössbauer spectrometer MS1104EM with ^{57}Co in Rh matrix, ensuring a noise/signal ratio of no more than 2 %. A detailed procedure for this can be found in our previous study (Yurkov et al., 2022). Additionally, X-ray diffraction diagrams were recorded using an X-ray diffractometer Diffray-401 (Scientific Instruments, Russia) with Bragg-Brentano focusing and Cr-Kα radiation (wavelength 0.22909 nm) at room temperature. Diffraction images were identified using the PDF-2 database of the International Center for Diffraction Data. The coherent scattering domain size was calculated using the method of Waseda et al. (2011).

A JEM 2100 transmission electron microscope (Jeol, Japan) was utilized with an acceleration voltage of 200 kV to estimate the crystallite size of nanoparticles. The powder was diluted with isopropyl alcohol and dispersed in an ultrasonic bath for 5 min. The resulting solution was then dropped onto a copper mesh coated with an amorphous carbon film. Conversely, for microparticles, a JSM-6700F scanning electron microscope (Jeol, Japan) was employed.

In addition, dynamic light scattering analyses were conducted using a NanoBrook Omni particle analyzer equipped with a solid-state He-Ne laser at 633 nm and scattering angles of 15 and 25°. To achieve a concentration of 0.1 g L^{-1}, the samples were appropriately diluted and adjusted to a pH of 6.9 before analysis. All measurements were taken at consistent intervals. Following dispersion in an ultrasonic bath for 10 s, a period of 100 s was allowed for the system to reach equilibrium.

Specific surface areas of the samples was determined by measuring them at a temperature of liquid nitrogen (77 K) using a Sorbtometr-M (Katakon, Russia). The surface area measurements were based on adsorption isotherms and were calculated using the well-established Brunauer-Emmett-Teller (BET) method, following a standard procedure (Neaman et al., 2003).

Experimental field conditions

In this study, forest litter was chosen as the experimental substrate over mineral soil, as metal concentrations in the litter in the study area are one order of magnitude higher than in mineral soil (Prudnikova et al., 2020). This results in higher toxicity in the litter, which inhibits the development of herbaceous vegetation in the study area (Vorobeichik et al., 2014).

Soil pH impacts metal immobilization by iron oxides (O'Reilly and Hochella, 2003; Tiberg et al., 2016). Changes in the surface chemistry of iron oxides are pH-dependent (Kosmulski, 2001), with higher pH values resulting in a higher negative surface charge. However, at higher pH values, metals may precipitate as insoluble compounds, masking the effects of iron oxides. In preliminary laboratory experiments using soils from the study area, the effect of zerovalent iron microparticles was not evident in limed soils (Dovletyarova et al., 2022a). Therefore, lime was deliberately not added to the litter in the present study to isolate the effects of iron oxides on metal immobilization.

Experimental design

The experiment was conducted in a native spruce-fir forest, located approximately 3 km from the copper smelter (56° 49' 49.9" N, 59° 52' 02.9" E). The soils in the study area were classified as silt loam Retisols (IUSS Working Group WRB, 2015). Fifteen 0.50 × 0.50 m test plots were allocated on June 22-23, 2022, with three treatments (control, magnetite-micro, magnetite-nano) distributed across five blocks. The plots were spaced 1-3 m apart within each block and located no closer than 1 m from large trees (>0.30 m in diameter). The blocks were separated by distances of 3-5 m. The plots were established in a relatively uniform forest patch, free from dense vegetation or visible signs of soil disturbance, and with a mean litter thickness of 5.2±0.9 cm (mean ± standard deviation, n = 15). The mean dry weight of the litter was 1.05 ± 0.22 kg plot^{-1}, and the mean bulk density was 83 ± 20 kg m^{-3}.

A composite litter sample weighing approximately 50 g (fresh weight) was collected from each plot. The sample was air-dried at room temperature for approximately three days and subsequently ground for chemical analysis. Carbon content of the litter was determined to be 38 ± 2.6 % using the 2100 CN analyzer (Analytik Jena).

To implement the treatment, the litter layer was removed from each plot, and cones, large branches, and roots were extracted. The litter was mixed thoroughly to ensure homogeneity and a portion of the litter was collected for chemical analysis. Additionally, a 6 mm thick polypropylene mesh was positioned over the mineral soil horizon to ensure that only the litter was sampled at the end of the growing season, with no inclusion of the mineral soil horizon.

The treatments used in the experiment were prepared as follows:

1) Control treatment consisted of 300 mL distilled water and 0.8 g fertilizer.

2) Magnetite micro treatment consisted of 40 g magnetite powder, 300 mL distilled water, and 0.8 g fertilizer.

3) Magnetite nano treatment consisted of 160 g magnetite paste (equivalent to 40 g magnetite powder since paste contained 25 % magnetite nanoparticles), 180 mL distilled water (equivalent to 300 mL of water since paste contained 75 % water), and 0.8 g fertilizer.

Magnetite nanoparticles and microparticles were added to the forest litter at an equal dose of 4 % w/w, considering the mean dry weight of the litter (1.05 ± 0.22 kg plot^{-1}). Furthermore, equal amounts of water were added to all the treatments. Fertilizer composition for all treatments comprised N (12 %), P_2O_5 (8 %), K_2O (14 %), MgO (2 %), S (8 %), B (0.1 %), Cu (0.1 %), Fe (0.1 %), Mn (0.2 %), Mo (0.01 %), and Zn (0.1 %). To avoid cross-contamination, separate containers were utilized for each treatment, and the litter was hand-mixed with different gloves for each sample before returning it to the plot, where it was placed on top of the mesh.

On June 28, five days after the treatments were applied, 3 g of red fescue (*Festuca rubra* L.) seeds were sown per plot. This species was chosen for the experiment as it is a common native species in the study area (Rafikova and Veselkin, 2022) and is frequently used for remediating metal-contaminated soils (Winterhalder, 1996; Slukovskaya et al., 2019).

Laboratory analysis indicated a high seed germination rate of 92 %. However, due to dry weather conditions, each plot was irrigated with 2 L of water on August 16 and 23, 2022. On September 1-2, 2022, composite litter samples (~50 g fresh weight) were also collected from each plot. The entire aboveground biomass of fescue was collected from each plot using scissors, which corresponded to a growth duration of approximately two months. Notably, the duration of this experiment, which spanned two months, is consistent with that of a previous laboratory study conducted by Danila et al. (2020).

Laboratory studies and statistical analysis

Total metal concentrations in the pre-treatment litter samples were determined by atomic absorption spectroscopy using the ContrAA 700 instrument from Analytik Jena. Prior to the analysis, a microwave digestion process was carried out with concentrated HNO_3 in accordance with the manufacturer's instructions for the Berghof microwave system. Standard reference materials, including CRM-482 lichen and CRM-100 beech leaves obtained from the Community Bureau of Reference (BCR) of the Commission of the European Communities, were used throughout the analysis. The experimental values for the target metals were within 100 ± 20 % of the certified values. The litter pH was determined for both pre-treatment and end-of-season samples using a KNO_3 0.01 mol L^{-1} solution with a litter/solution ratio of 1/25.

In recent decades, numerous studies have attempted to predict the "phytoavailable" metal fraction by correlating plant responses with various soil metal pools. It is generally believed that metal soluble fractions extracted by chemically non-aggressive neutral salts are useful in assessing metal phytotoxicity in contaminated soils (Kabata-Pendias, 2004; McBride et al., 2009). Our recent study with soils near a copper smelter in central Chile (Lillo-Robles et al., 2020) suggests that the exchangeable copper fraction was the best indicator of metal phytotoxicity in the soil. Therefore, we determined the exchangeable forms of metals in the end-of-season litter samples using a 0.01 mol L^{-1} KNO_3 extract at a litter/solution ratio of 1/20. Atomic absorption spectroscopy was employed for metal determinations.

While 0.01 mol L^{-1} $CaCl_2$ is often considered the most appropriate agent for extracting exchangeable metals from metal-polluted soils, it should be noted that divalent cations, such as Ca^{2+}, can promote the flocculation of dissolved organic carbon in the soil solution (Sauvé, 2002). This mechanism may lead to underestimating the exchangeable metal fraction when using 0.01 mol L^{-1} $CaCl_2$, as metals with a strong affinity for dissolved organic carbon can precipitate out (Neaman et al., 2009). For this reason, we prefer to use 0.01 mol L^{-1} KNO_3 for exchangeable metal extraction, which is also widely used for exchangeable metal extraction from metal-contaminated soils (Almas et al., 2000; Luo et al., 2006; Moreno-Caselles et al., 2000; Perez-Esteban et al., 2013).

All aboveground fescue biomass was meticulously washed using a sequential process comprising tap water, 0.1 mol L^{-1} HCl, distilled water, 0.05 mol L^{-1} EDTA, and distilled water (twice). Subsequently, the fescue biomass was dried at 70 °C and weighed using an analytical balance with an accuracy of 0.0001 g. The metal concentrations in the fescue samples were determined as previously described for the litter samples.

Statistical analyses were performed using R, version 4.1.2. The statistical unit was the sample area (plot) in all cases. Prior to analysis, metal contents were log-transformed. A one-way analysis of variance was conducted, and differences among treatments were assessed using Tukey's test with the *multcomp* package (Hothorn et al., 2008).

RESULTS AND DISCUSSION

Magnetite characterization

The data obtained from Mössbauer spectroscopy revealed that the samples of magnetite nano- and microparticles were composed solely of Fe_3O_4. Similarly, X-ray diffraction analysis confirmed the presence of only the magnetite phase, Fe_3O_4, in both samples of magnetite nano- and microparticles. In addition, Mössbauer spectroscopy data indicated that the magnetic domain size was smaller in the nanoparticles than in the microparticles. Furthermore, the diffraction maxima of the X-ray diffraction pattern of the nano sample were notably broader, indicating that the size of Fe_3O_4 crystallites in the nano sample was smaller than that in the micro-sample.

There is no universally accepted method for determining the particle size of a material (Pankratov and Anuchina, 2019). However, the use of various techniques yielded comparable results (Table 1). Specifically, the sizes of the magnetic domain, coherent scattering domain, and crystallites were all on the same order of magnitude for the nano sample (Table 1). While the hydrodynamic diameter of the nano sample was an order of magnitude larger, this is typical for magnetite nanoparticles due to aggregation (Bondarenko et al., 2020). Similarly, the crystallite size and hydrodynamic diameter of the micro-sample were in agreement with each other. It is worth noting that each microparticle contains multiple magnetic and coherent scattering domains (Liu et al., 2010; Waseda et al., 2011). Nevertheless, all of the methods employed consistently indicated a significantly smaller size for the studied nanoparticles than the microparticles. Correspondingly, the BET surface area was found to be greater for the nanoparticles in comparison to the microparticles (Table 1).

Litter characterization

The litter collected from the study plots (Table 2) exhibited total metal contents that were 1-2 orders of magnitude greater than the background metal contents in litter obtained from unpolluted regions located roughly 30 km away from the copper smelter (Prudnikova et al., 2020). However, such elevated metal contents are typical in soils near metal smelters (Vorobeichik, 2022).

Table 1. Characteristics of magnetite nano- and microparticle samples

Sample characteristic (method)	Fe_3O_4 nano	Fe_3O_4 micro
Magnetic domain size(1), (nm)	16±0.2	19±0.2
Coherent scattering domain size(2) (nm)	6.0±2.9	210±74
Crystallite size(3) (nm)	12±3.2	5000±1900
Hydrodynamic diameter(4) (nm)	270±33	5400±1500
Specific surface area(5) (m^2 g^{-1})	130	11

(1) Mössbauer spectroscopy. (2) X-ray diffraction. (3) Electron microscopy. (4) Dynamic light scattering. (5) Nitrogen adsorption, BET method.

Table 2. Mean and standard deviation (n = 5) of total metal content and pH in litter samples before amendment application across different treatments. No statistically significant differences were found among the treatments. Additionally, the mean and standard deviation (n = 5) of litter pH at the end of the growing season are presented, and no statistically significant differences were observed among the treatment

Treatment	Cu	Zn	Pb	Cd	Fe	Mn	pH(1)	
	mg kg^{-1}				%		Initial	Final
Control	2097±651	1673±522	839±360	25±8	1.5±0.35	0.38±0.11	5.0±0.1	5.0±0.1
Magnetite, micro	2161±220	1482±158	774±181	36±6	1.5±0.34	0.26±0.06	4.8±0.3	4.9±0.1
Magnetite, nano	1565±654	1595±248	685±320	24±8	1.1±0.42	0.32±0.07	5.0±0.2	5.0±0.1
Background(2)	56	182	72	1.5	nd	nd	na	na

(1) The analysis was carried out using a litter-to-solution ratio of 1:20 in 0.01 mol L^{-1} KNO_3. (2) Background metal contents in forest litter from unpolluted areas located approximately 30 km away from the copper smelter (Prudnikova et al., 2020). nd: not determined; na: not available for the litter-to-solution ratio of 1:20.

Each plot had a high degree of variability in total metal concentrations, which is customary for the area under investigation (Vorobeichik and Pozolotina, 2003). Nonetheless, it should be emphasized that no statistically significant differences were found in total metal contents or in the initial pH of the litter (i.e., before the application of the amendment) in the plots designated for different treatments (Table 2). This implies that differences in litter properties in the various plots did not impact plant responses.

Effects of amendments

Application of the amendment did not alter the pH of the litter (Table 2). Nonetheless, compared to the control (Table 3), the amendment of magnetite nanoparticles led to a reduction in the exchangeable copper concentrations in the litter, typically regarded as the most bioavailable (Lillo-Robles et al., 2020). The findings of Tiberg et al. (2016) suggest that in the soil treated with magnetite, copper was sequestered via bidentate inner-sphere complexes with magnetite. However, further research is warranted to decipher the precise binding mechanisms of copper by magnetite in the context of this field experiment.

Due to copper immobilization in the litter, the dry biomass of fescue shoots exhibited a significant increase in plots treated with magnetite nanoparticles compared to the control (Figure 1). Although there was only a marginally significant difference in copper contents in fescue shoots between the plots treated with magnetite nanoparticles and the control (Table 3; p=0.052), the trend indicated a reduction in metal phytoavailability in the litter due to the use of nanoparticles.

Table 3. Mean and standard deviation (n = 5) of exchangeable metal forms in litter samples and metal content in plant biomass across different treatments. Different letters for exchangeable copper indicate significant differences among the treatments (Tukey test, p≤0.05). No statistically significant differences were found among the treatments for all other cases

Treatment	Cu	Zn	Pb	Cd	Fe	Mn
	mg kg^{-1}					
	Exchangeable forms of metals in litter samples					
Control	10±2 a	27±5	1.2±1.8	0.23±0.08	8.9±1.8	63±6
Magnetite, micro	12±2 a	24±9	1.7±0.8	0.20±0.13	12±1.6	67±9
Magnetite, nano	7±1 b	20±6	1.8±0.6	0.20±0.08	17±4.2	57±22
	Metal content in plant biomass					
Control	113±72	132±51	24±16	1.8±1.4	970±486	140±67
Magnetite, micro	85±45	86±41	28±21	1.1±1.7	1347±840	118±90
Magnetite, nano	52±18	98±19	14±10	1.4±0.5	786±294	86±26

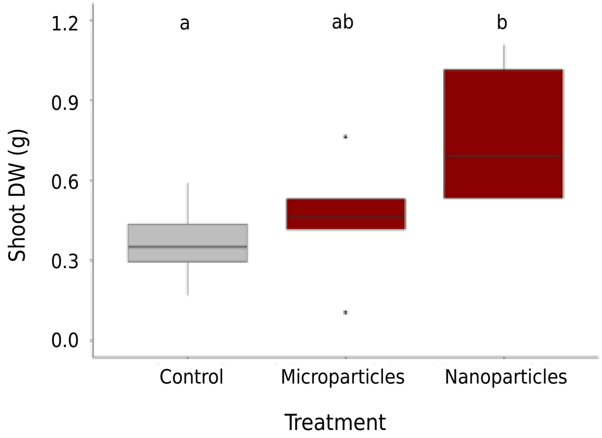

Figure 1. Dry shoot biomass of red fescue (shoot DW) under different treatments. 0: control; 1: magnetite microparticles; 2: magnetite nanoparticles. Box plots show the lower, median, and upper quartile, with whiskers indicating the most extreme data points and dots indicating outliers. Significant differences among treatments (Tukey test, $p \leq 0.05$) are denoted by different letters.

In contrast, applying magnetite microparticles did not elicit any statistically significant effect on the concentrations of exchangeable metals in the litter or the metal concentrations in fescue shoots (Table 3). Of significant note, fescue growth was not improved with the application of magnetite microparticles compared to the control. Our finding is in line with previous laboratory results demonstrating superior metal adsorption properties of magnetite nanoparticles relative to microparticles (Ajmal et al., 2020).

Restoring vegetation cover in metal-polluted areas, as demonstrated in this study, has several practical benefits, such as reducing soil erosion (Bienes et al., 2016), improving air quality (Terzaghi et al., 2017), minimizing metals transport (Tordoff et al., 2000), decreasing the impact of metal-rich dust on human health (Bierkens et al., 2011), and enhancing the aesthetic value of the land (Ivanova et al., 2020).

CONCLUSIONS

Magnetite nanoparticles performed better than microparticles in remediating metal-contaminated soils. Specifically, the application of magnetite nanoparticles resulted in a significant reduction in soil exchangeable copper concentrations and enhanced the growth of red fescue in polluted soils. Conversely, the application of magnetite microparticles did not produce any statistically significant effects. These findings align with previous laboratory studies demonstrating that magnetite nanoparticles possess superior metal adsorption properties compared to their micro-sized counterparts.

However, despite the growing interest in using iron nanoparticles to remediate metal-contaminated soils, much of the available knowledge is derived from laboratory experiments. This study, which is the first to compare the effectiveness of magnetite nanoparticles with microparticles in field conditions, contributes to filling this knowledge gap. Nevertheless, the study is limited by its short duration and drought conditions that affected plant growth. To address these limitations, longer field studies and ongoing monitoring of the effects of iron particles on plant growth in different weather conditions are recommended.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://www.rbcsjournal.org/wp-content/uploads/articles_xml/1806-9657-rbcs-47-e0230017/1806-9657-rbcs-47-e0230017-suppl01.pdf.

ACKNOWLEDGEMENTS

This study was supported by the Russian Foundation for Basic Research (grant 20-54-26012, fieldwork and analysis, manuscript writing), the FONDECT 1200048 project (granted to Alexander Neaman, manuscript writing), and the RUDN University Strategic Academic Leadership Program (granted to Elvira A. Dovletyarova, fieldwork, and analysis, manuscript writing). D.A. Pankratov's work was funded by the government allocation project 122040600057-3 (awarded to Lomonosov Moscow State University). The research team acknowledges Kamila A. Kydralieva for magnetite synthesis and Elmira Akhunova for chemical analyses. The authors would like to express their utmost gratitude to Andrei Tchourakov, of Vancouver, BC, Canada, academic editor and translator, for the English editing of this paper.

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