RESEARCH PAPER

CHALLENGES IN REDUCING PHYTOTOXICITY OF METALS IN SOILS AFFECTED BY NON-FERROUS SMELTER OPERATIONS

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ABSTRACT. Lime is one of the effective agents for reducing the phytoavailability of metals in contaminated acidic soils. However, previous studies have shown that lime alone cannot reduce metal phytotoxicity to the desired extent in such soils. The goal of this study was to evaluate the effect of different amendment combinations (lime with and without Fe- and/or Mn-based amendments) on plant growth. A sample of Histosol (0-5 cm) was collected around a Cu/Ni smelter near Monchegorsk, Murmansk region, exhibiting total Cu and Ni concentrations in the soil of 6418 and 2293 mg kg^{-1}, respectively. Likewise, a sample of forest litter (0-15 cm) was collected around a Cu smelter near Revda, Sverdlovsk region, exhibiting total Cu concentration in the soil of 5704 mg kg^{-1}. Fe-Mn oxides were sourced from ferromanganese nodules in the Gulf of Finland, and iron powder was used as a precursor for iron oxides. Perennial ryegrass was grown in pots for 21 days under controlled laboratory conditions. Two dolomite doses were tested: 5% w/w (giving a soil pH of 6.5) and 20% w/w (giving a soil pH of 7.4). Over-liming stunted plant growth; therefore, the dolomite dose was set at 5% in the further experiments of the study. Importantly, the addition of 0.5% and 1% of Fe-Mn-oxides or iron powder did not improve the efficacy of the lime amendment in promoting plant growth in the soils. Therefore, the issue of reducing plant exposure to metals remained unresolved in the soils under study.

KEYWORDS: heavy metals; phytoremediation; phytostabilization; Lolium perenne; phytotoxicity

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INTRODUCTION

Environmental issues associated with long-term operation of non-ferrous smelters are a global concern (e.g., Ettler 2016). Soil acidification caused by smelter emissions is known to increase metal solubility and mobility, resulting in higher metal toxicity in the soil (e.g., Ginocchio 2000, Korkina and Vorobeichik 2021). Note that what is referred to as “metals” or “potentially toxic metals” in this study was previously referred to as “heavy metals”. However, the International Union of Pure and Applied Chemistry no longer recommends the use of the term “heavy metals” (Duffus 2002).

Polluted areas in the vicinity of non-ferrous metal smelters can act as secondary contamination sources (Luo et al. 2014). Indeed, due to the prolonged accumulation of pollutants and the deterioration of the soil cover, these areas lose their ability to bind metals and thus become uncontrolled sources of air and water pollution. One way to control metal mobility is to bind metals *in situ* by applying various additives to the soil to reduce the concentration of metals in the soil solution. Although this method does not eliminate metals from the soil, it does allow them to be converted into less soluble forms. The key criterion for evaluating the success of metal immobilization in soil is whether the toxic effects of metals on plants and soil organisms have been reduced (Lwin et al. 2018, Mahar et al. 2016).

A useful agent in reducing metal phytoavailability in acidic contaminated soils is lime (e.g., Pardo et al. 2018), which acts either by forming new solid phases – through precipitation or co-precipitation of metals – or by promoting metal adsorption on soil particles (e.g., Ma et al. 2006). For instance, lime was used in field trials at a rate of 2 t ha^{-1} to restore vegetation cover on soils in the vicinity of a Cu/Ni smelter on the Kola Peninsula, Russia (e.g., Ganicheva et al. 2004). However, our preliminary studies demonstrated that lime had not been sufficient to achieve a meaningful metal phytotoxicity reduction in soils from that site (Neaman et al. 2021, Tarasova et al. 2020). Specifically, we found that plants grown in the amended soils showed signs of metal phytotoxicity, suggesting that further experiments with combinations of multiple amendments would be required. Soil treatment with Fe- and/or Mn-based amendments has proven to be an effective technique for immobilizing metals and metalloids in contaminated soils (e.g., Komarek et al. 2013) due to the high adsorption capacity of iron oxide for potentially toxic metals (e.g., Cu, Zn, Pb, Cd) and metalloids (e.g., As) (e.g., Neaman et al. 2008, Neaman et al. 2004). Another effective method is to use iron oxide ‘precursors’ derived from iron powder (e.g., Kumpiene et al. 2019). As these zero-valent iron particles corrode in the soil, they produce iron oxides and hydroxides such as green rust, magnetite, ferrihydrite, hematite, and goethite (e.g., Tiberg et al. 2016).

This study was based on the hypothesis that the use of Fe- and/or Mn-based amendment additives could increase the efficacy of lime in promoting plant growth in the vicinity of non-ferrous smelters. The objective was therefore to determine the effect of different amendment combinations on plant growth in soils affected by long-term non-ferrous smelting operations. As a first step, we decided to test the selected amendments under laboratory conditions, as we have done in our previous studies (Neaman et al. 2021, Tarasova et al. 2020), before considering a field-scale investigation.

MATERIALS AND METHODS

Materials

The Soil 1 sample was taken in the industrial wasteland (67º55’70” N, 32º51’50” 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, Murmansk region, Russia (e.g., Slukovskaya et al. 2020) (Fig. 1). Hereafter, this smelter will be referred to as “the Cu/Ni smelter” or “the Monchegorsk site” for convenience. Peat eutrophic soil – Dystric Rheic Hemic Histosol (Toxic) (Slukovskaya et al. 2021) – was sampled from the depth of 0-5 cm. The soil was collected from 10 equidistant points of the total site area of 400 m^2. The composite soil sample was air-dried at a temperature of 20 ± 2 ºC and sieved with a 1.25 mm mesh.

The Soil 2 sample was taken in fir-spruce (*Abies sibirica* and *Picea obovata*) forests at a distance of 1-3 km from the copper smelter (56°51’0.8” N 59°54’25.6” E), located in the southern taiga subzone, near the town of Revda, Sverdlovsk region, Russia (e.g., Dubrovina et al. 2021) (Fig. 1). Hereafter, this smelter will be referred to as “the Cu smelter” or “the Revda site” for convenience. The O soil horizon (hereafter “forest litter”) (Dulya et al. 2019) was collected in 9 sampling plots of 25x25 m^2 at 10 random points within each plot. The

Fig. 1. Geographical locations of the study areas: (1) copper-nickel smelter located near the town of Monchegorsk, Murmansk region, and (2) copper smelter near the town of Revda, Sverdlovsk region

thickness of the litter was ~15 cm. The soils in the sampling plots are classified as Albic Retisols (Toxic), Stagnic Retisols (Toxic), and Skeletic Stagnic Retisols (Toxic) (Vorobeichik and Kaigorodova 2017). The litter samples were air-dried at room temperature and then homogenized. Coarse items (e.g., conifer cones) were thoroughly removed by hand.

Both soil samples were transferred to the laboratory of the RUDN University in Moscow. In our laboratory experiments, we also used uncontaminated eutrophic peat (Pelgorskoe brand, Russia). Hereafter, it will be referred to as "peat" for convenience. The pH of the peat was 4.0. When 10% dolomite was added to the peat, the pH increased to 6.2 ± 0.09. In addition, commercially available iron powder (<100 mm 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).

Finally, ferromanganese nodules (~24% Fe_2O_3 and ~14% MnO) from the Gulf of Finland were provided by the Olkat company, Russia. The industrial extraction of these nodules from marine shallow waters and processing is described by Zhamoida et al. (2017). The mineralogical composition (determined by X-ray diffraction analysis, PANalytical X'Pert Pro diffractometer) was dominated by goethite (FeOOH) and birnessite (nominal composition: $MnO_2 \cdot nH_2O$) with quartz, muscovite, and albite as other important components (Vojtěch Ettler, personal communication, unpublished results). The nodules were ground in mortar before being applied to the soil. Hereafter, the material resulting from the grinding process will be referred to as "Fe-Mn-oxides" for convenience.

Preliminary experiment on dolomite dosage

It can be argued that pH values >7 would be most appropriate for reducing metal uptake in the Monchegorsk histosol given the low concentrations of ammonium acetate-extractable metals at these pH values in that study area (e.g., Slukovskaya et al. 2018). However, ryegrass grows better in a slightly acidic pH environment (Spurway 1941). Therefore, a preliminary experiment was conducted to determine the appropriate dolomite doses to be used in the study. Two doses were tested: 5% w/w (giving a soil pH of 6.5) and 20% w/w (giving a soil pH of 7.4). The preliminary experiment showed that over-liming stunts plant growth (Fig. 2). Therefore, the dolomite dose was set at 5% in the further experiments of the study.

The higher dolomite dose lowered the foliar concentrations of Ni, Zn, and Cd, but had the opposite effect on the foliar concentrations of Cu and Co (Table 1). The fact that over-liming did not reduce Cu and Co uptake by ryegrass in our study is consistent with the results of other studies that investigated increased Cu solubility in alkaline soils with high dissolved organic carbon (e.g., Mondaca et al. 2015). We are inclined to think that Co uptake by ryegrass would show a similar trend, but future studies would be required to clarify this issue.

Treatments

The dosages of Fe-Mn-oxides and iron powder were based on our previous experiments (Goecke et al. 2011). The six experimental treatments performed in the present study were as follows:
Treatment 0: untreated soil;
Treatment 1: dolomite (5%);
Treatment 2: dolomite (5%) and Fe-Mn-oxides (0.5%);
Treatment 3: dolomite (5%) and Fe-Mn-oxides (1%);
Treatment 4: dolomite (5%) and iron powder (0.5%);
Treatment 5: dolomite (5%) and iron powder (1%).

Commercially available dolomitic lime (BHZ brand, Russia) was used. 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 of 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%.

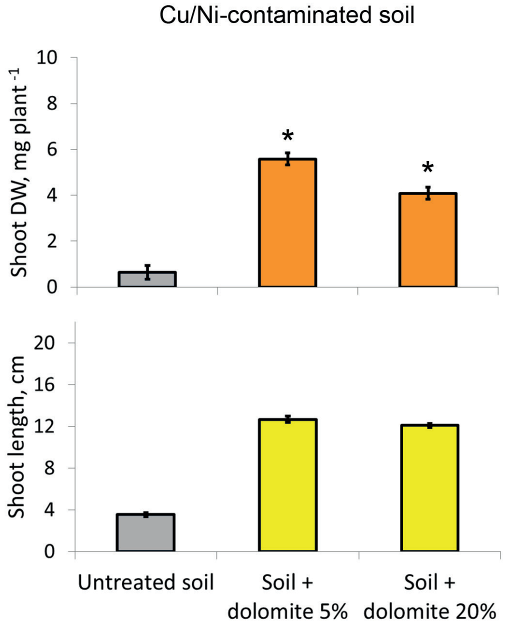

Fig. 2. Effect of different doses of dolomite (5% w/w and 20% w/w) on shoot dry weight (DW) and shoot length of ryegrass grown on Cu/Ni-contaminated soil (Histosol from Monchegorsk). Means and standard deviations are shown (n = 4). Untreated soil is also shown for comparison. Asterisks indicate a statistically significant difference between different doses of dolomite with respect to plant responses ($p < 0.05$). All-purpose fertilizer was added in all cases at a rate of 0.4 g fertilizer per 1 kg substrate

Table 1. Effect of different doses of dolomite (5% w/w and 20% w/w) on foliar metal concentrations in ryegrass grown on the Monchegorsk Histosol. The values of pH (in 0.01 N KNO^3) were 6.5 and 7.4, respectively. An asterisk indicates that the concentration of a particular metal is statistically higher in a given soil sample than in another soil sample ($p < 0.01$)

Metal	Foliar concentration, mg kg^{-1}	
	Dolomite 5%	Dolomite 20%
Cd	1.1±0.06*	0.62±0.12
Co	7.3±0.46	10±0.87*
Cu	47±17	130±7.5*
Ni	92±5.4*	74±4.3
Zn	149±7.4*	98±7.4

Peat, untreated and amended soils were wetted weekly and allowed to dry at room temperature (20-25 ºC). 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 below.

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 HNO3 and H_2O_2. Standard reference materials (Krasnozem and Chernozem, obtained from the Ecolan company, 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 Ca, Mg, Cu, Ni, Mn, Co, 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). This extractant is widely used for the extraction of exchangeable metals from metal-polluted soils (e.g., Almas et al. 2000, Luo et al. 2006, Moreno-Caselles et al. 2000, Perez-Esteban et al. 2013). Although chemically aggressive extractants, such as ammonium acetate buffer and 0.1 N HNO_3, are widely used (e.g., Slukovskaya et al. 2020), metal fractions extracted with chemically non-aggressive neutral salts are preferrable for assessing potential exposure of roots to metals in contaminated soils (e.g., Altimira et al. 2012, Kabata-Pendias 2004, McBride et al. 2009). The resulting suspension was shaken for 60 minutes and then filtered through ashless filter paper.

Soil pH was measured in the same extract of 0.01 M KNO_3 used for the determination of exchangeable metals. The approach of using the same extract for different purposes increases work efficiency and was used in our previous studies (e.g., Lillo-Robles et al. 2020). Furthermore, our previous study (Bustos et al. 2015) demonstrated a strong correlation (R^2 = 0.94) between pH values measured in KNO_3 extracts and those measured in soil solution obtained by Rhizons (Rhizosphere Research Products, Wageningen, Netherlands).

The organic matter content of the soil and commercial peat was estimated by loss-on-ignition at 600 °C. The following values were obtained: 87% for Soil 1 (Histosol from Monchegorsk), 62% for Soil 2 (forest litter from Revda), and 90% for commercial peat.

Plant bioassays

Plant bioassays were performed according to a standard protocol (ISO 11269-2 2012), as detailed in our previous studies (Neaman et al. 2021, Tarasova et al. 2020). Foliar elemental concentrations were determined after 21 days of growth by ICP-OES following a standard procedure of dry ashing at 600ºC 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.

Statistical analysis

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

RESULTS AND DISCUSSION

Although both smelters have reduced their emissions in recent years (Eeva et al. 2012), there is so far no evidence that the metal content of the topsoil has decreased. In the soil from the Monchegorsk study area, the total concentrations of copper, nickel, cadmium, and cobalt were several times higher than the corresponding background concentrations (i.e., the concentrations of metals in the soil that has not been affected by anthropogenic influences) (Table 2). Copper and nickel were the main pollutants, with concentrations two orders of magnitude higher than the corresponding background levels reported in the Kashulina (2017) study. Copper and nickel are essential plant micronutrients (López and Magnitski 2011) but become toxic above a certain threshold.

It should be noted that ecotoxicological studies of metal toxicity in soil are usually based on the use of uncontaminated soils that have been progressively enriched with metals in the form of soluble salts. This approach is complicated by the difficulty of extrapolating laboratory results to actual soils exposed to decades of contamination. This is because metal toxicity depends, among other factors, on the residence time of the metals in the soil (e.g., Santa-Cruz et al. 2021b). Although many studies emphasize the importance of using actual anthropogenically contaminated soils for toxicity bioassays, the number of studies actually conducted based on this premise is relatively small.

In the soils from the Monchegorsk study area, the total concentrations of both copper and nickel exceeded the EC50 values (50% effective concentration) for phytotoxicity of metals of 987 mg kg^{-1} and 1710 mg kg^{-1}, respectively (Santa-Cruz et al. 2021a). Due to the inconsistent data on the comparative phytotoxicity of copper and nickel, and the lack of data on the phytotoxicity of cadmium and cobalt in actual anthropogenically contaminated soils (Santa-Cruz et al. 2021a), it is hard to pinpoint the exact cause of phytotoxicity in Soil 1 under study.

Meanwhile, the total concentrations of copper, zinc and cadmium in the soil from the Revda study area were several times higher than the corresponding background levels (Table 2). Copper was the main pollutant, with the concentration two orders of magnitude higher than the corresponding background reported in the study by Prudnikova et al. (2020).

Table 2. Total metal concentrations in the soils under study and in commercial peat. Background total metal concentrations in the study areas are also shown for comparison. All values are expressed in mg kg^{-1}

Metal	Soil 1	Background, Soil 1 (Kashulina 2017)	Soil 2	Background, Soil 2 (Prudnikova et al. 2020)	Peat
Cu	6418	12	5704	56	48
Ni	2293	18	57	-	6.5
Zn	82	48	2692	182	14
Cd	2.9	0.22	20	1.5	4.3
Co	77	7.4	19	-	1.8

The pH values of untreated soils were acidic (4.6 and 5.3, Monchegorsk and Revda, respectively, Table 3). Since acidic conditions make metals more soluble, thus increasing their availability (Lillo-Robles et al. 2020), we observed very high exchangeable metal concentrations in the untreated soils (Appendix A) and high metal concentrations in the shoots of *L. perenne* (Figs. 1 and 2, treatment 0). As a result, shoot length and biomass of *L. perenne* were severely inhibited in the untreated soil (Fig. 5).

In both soils, the dolomite treatments (i.e., treatments 1-5) resulted in higher pH values (Table 3) and thus lower exchangeable metal concentrations in the studied soils (Appendix A) and lower metal content in *L. perenne* shoots (Fig. 3 and 4), which was beneficial for plant growth (Fig. 5).

It is important to emphasize, however, that plant growth was slower in the dolomite-treated soil from Monchegorsk compared to the uncontaminated peat (Fig. 6A). This may be due to the fact that the metal toxicity remained high even after the dolomite treatment. Consistent with this argument, we found foliar Ni concentrations in L. perenne plants grown in Soil 1 to be above the toxicity threshold of 80 mg kg^{-1} (Table 4) for this species (Reuter and Robinson 1997). Likewise, foliar Co concentrations in L. perenne plants grown in Soil 1 were above the toxicity level for barley of 6 mg kg^{-1} (Davis et al. 1978). Thus, it is likely that Ni and Co had a toxic effect on plant growth in Soil 1 even after the dolomite treatment.

In Soil 2 treated with dolomite, foliar Zn concentration in *L. perenne* (329 mg kg^{-1}, Table 4) was higher than the lowest observed effective concentration of 221 mg kg^{-1} reported by Davis and Beckett (1978) for this species, but lower than the EC$_{20}$ for foliar Zn concentration of 560 mg kg^{-1} reported by Smilde (1981). On the other hand, our previous study reported an EC$_{50}$ (effective concentration 50%) value of 39 mg kg^{-1} for foliar concentration of Cu in *L. perenne* (Verdejo et al. 2015). In the present study, the foliar concentration of Cu in plants grown in Soil 2 after the dolomite treatment (Table 4) was higher than the reported EC$_{50}$ value. Therefore, it is likely that Cu toxicity played a role in inhibiting plant growth in Soil 2 even after the dolomite treatment. Zinc toxicity is not expected in Soil 2 because zinc is known to exert an mitigating effect on copper phytotoxicity (e.g., Stuckey et al. 2021).

Table 3. The effect of treatments on soil pH determined in 0.01 M KNO$_3$ extract at soil/solution ratio of 1/25

Treatment	Code	pH in 0.01 M KNO$_3$	
		Soil 1	Soil 2
Untreated soil	0	4.6±0.04	5.3±0.08
Dolomite (5%)	1	6.5±0.05	6.2±0.13
Dolomite (5%) and Fe-Mn-oxides (0.5%)	2	6.5±0.08	6.1±0.04
Dolomite (5%) and Fe-Mn-oxides (1%)	3	6.5±0.10	6.2±0.21
Dolomite (5%) and iron powder (0.5%)	4	6.5±0.04	6.2±0.17
Dolomite (5%) and iron powder (1%)	5	6.4±0.07	6.3±0.02

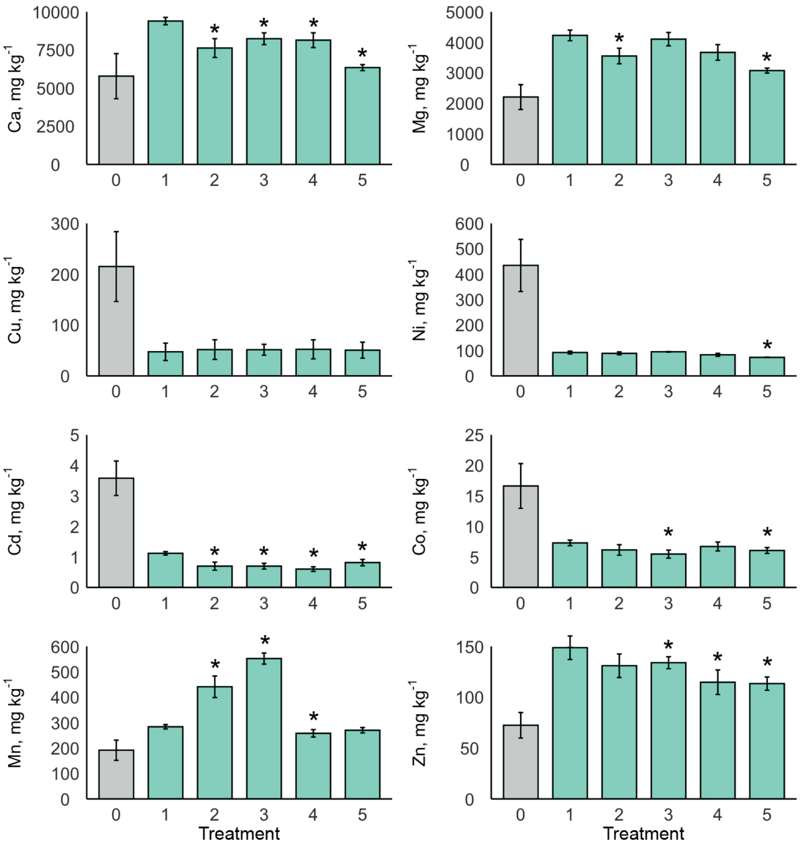

Fig. 3. Effect of treatment on the foliar concentrations of elements in ryegrass grown on Histosol from Monchegorsk, Kola Peninsula. An asterisk indicates a statistically significant difference between a particular treatment and Treatment 1 (Dunnet test, $p < 0.05$). Treatment 0 is shown but was not included in the statistical analysis

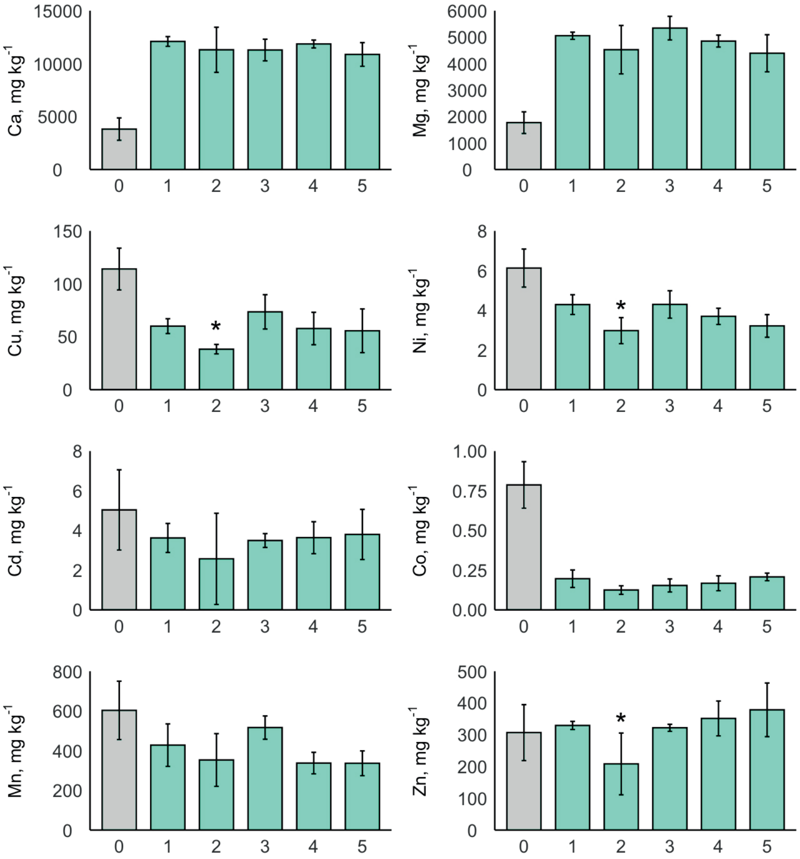

Fig. 4. Effect of treatment on the foliar concentrations of elements in ryegrass grown on forest litter from Revda. An asterisk indicates a statistically significant difference between a particular treatment and Treatment 1 (Dunnet test, $p < 0.05$). Treatment 0 is shown but was not included in the statistical analysis

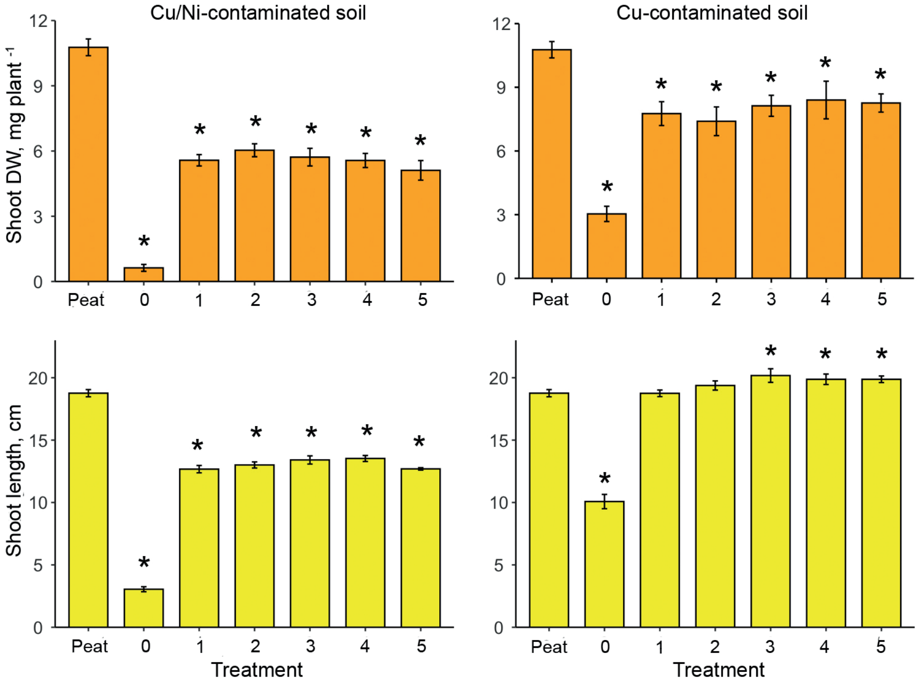

Fig. 5. Plant response to amendments. DW means dry weight. Cu/Ni-contaminated soil: Histosol from Monchegorsk; Cu-contaminated soil: forest litter from Revda). Average values and standard deviations are shown (n = 4). An asterisk indicates a statistically significant difference between a particular treatment and uncontaminated commercial peat (Dunnet test, $p < 0.05$). 0: untreated soil; 1: dolomite (5%); 2: dolomite (5%) and Fe-Mn-oxides (0.5%); 3: dolomite (5%) and Fe-Mn-oxides (1%); 4: dolomite (5%) and iron powder (0.5%); 5: dolomite (5%) and iron powder (1%). All-purpose fertilizer was added to all substrates, including commercial peat, at the rate of 0.4 g fertilizer per 1 kg substrate

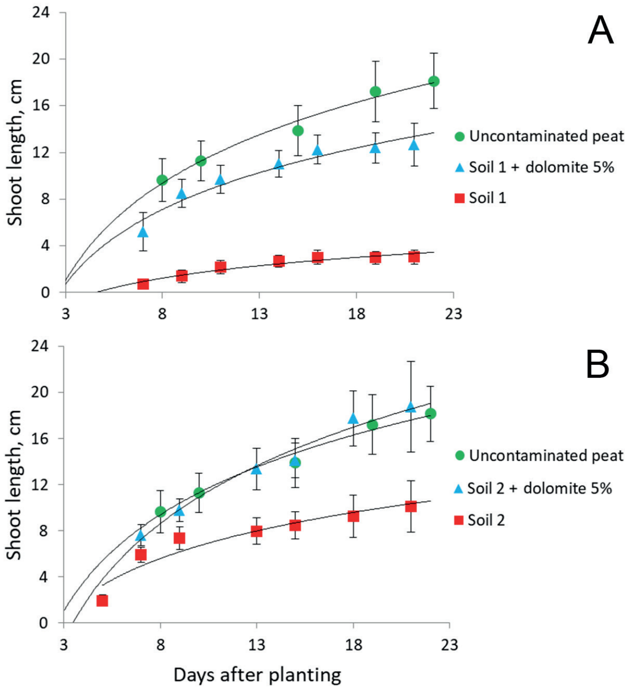

Fig. 6. Shoot length of *Lolium perenne* as a function of growth time in Soil 1 (A) and Soil 2 (B). Results are shown for untreated soil and dolomite-treated soil. Uncontaminated commercial peat is shown for comparison. The remainder of the treatments are not shown to simplify the figure and improve clarity and understanding

Table 4. Comparison of foliar metal concentrations in plants grown on soils treated with 5% dolomite. Means and standard deviations are shown (n = 4). Soil polluted with Cu and Ni corresponds to Histosol from Monchegorsk. Soil polluted with Cu corresponds to forest litter from Revda. An asterisk indicates that the concentration of a particular metal is statistically higher in a given soil sample than in another soil sample ($p < 0.01$). Toxicity threshold values for foliar concentrations of metals are also shown for comparison

Metal	Foliar metal concentrations, mg kg^{-1}		Toxicity threshold, mg kg^{-1}	Reference
	Cu/Ni-polluted soil	Cu-polluted soil		
Cu	47±17	60±7.0	39	Verdejo et al. (2015)
Ni	92±5.4*	4.3±0.5	80	Reuter and Robinson (1997)
Zn	149±8	329±13*	560	Smilde (1981)
Co	7.3±0.46*	0.2±0.05	6.0	Davis et al. (1978)
Cd	1.1±0.06	3.6±0.73*	15	Davis et al. (1978)

Finally, in our previous study (Goecke et al. 2011), treatment of contaminated soil with iron powder at 0.5% and 1% resulted in a significant reduction in copper solubility, which improved plant growth. In the present study, however, the difference between Treatment 1 (without Fe- and/or Mn-based amendments) and Treatments 2-5 (with Fe- and/or Mn-based amendments) was either not statistically significant ($p > 0.05$) or not substantial in terms of exchangeable metal concentrations in soil (Appendix A), metal concentrations in shoots (Fig. 3 and 4), and plant growth (Fig. 5). We are inclined to think that higher doses of Fe- and/or Mn-based amendments would improve the efficacy of the lime treatment in promoting plant growth in soils from the vicinity of non-ferrous smelters.

CONCLUSION

Many large metallurgical enterprises are located on the territory of Russia and the problem of soil pollution by emissions from such companies is therefore of particular concern to Russia. Therefore, the topic of the article is relevant and timely.

The addition of 0.5% and 1% of Fe-Mn-oxides or iron powder did not improve the efficacy of the lime amendment in promoting plant growth in soils from the vicinity of a Cu/Ni or Cu smelter. Thus, the challenge of reducing plant metal exposure remained unresolved in the soils studied. However, it is important to publish the results of unsuccessful studies, as negative results are also an important part of the scientific community's knowledge base.

In future studies, we plan to investigate other Fe- and/or Mn-based amendments, such as zero-valent iron nanoparticles, which have been proven to be effective metal sorbents (e.g., Mitzia et al. 2020). Likewise, higher application rates of iron amendments should be considered in future studies.

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Appendix A. Effect of treatment on the concentration of exchangeable cations in Histosol from Monchegorsk (Soil 1) and forest litter from Revda (Soil 2). A 0.01 N KNO_3 solution with a soil/solution ratio of 1/25 was used for extraction.

Treatment	Ca_{exch}	Mg_{exch}	Cu_{exch}	Ni_{exch}	Zn_{exch}	Mn_{exch}	Co_{exch}	Cd_{exch}
	mg kg^{-1} of air-dry substrate							
Soil 1								
0	522±53	203±15	65±5	150±15	13±1.5	53±5.3	6±0.59	0.1±0.02
1	**1579±120**	**720±30**	**13±0.5**	**16±0.9**	**2±0.37**	**11±0.8**	**0.7±0.05**	**bdl**
2	1536±67	641±29*	13±1.0	15±0.6	2.1±0.44	41±1.8*	0.6±0.03	bdl
3	1534±33	681±11	12±0.9	16±0.6	4.8±3.31	57±1.8*	0.6±0.02*	bdl
4	1547±81	673±14	11±0.7*	14±0.5*	4.7±4.7	11±0.5	0.7±0.02	bdl
5	1496±124	640±49	11±1.5	14±1.1	3.8±5.85	11±1.0	0.7±0.06	bdl
Soil 2								
0	567±89	147±25	14±12	0.4±0.09	34±6.3	67±16	0.1±0.03	0.8±0.11
1	**1268±128**	**295±21**	**8.0±0.8**	**0.2±0.03**	**11±1.0**	**10±3.3**	**bdl**	**0.3±0.03**
2	1124±47	275±15	9.0±2.0	0.3±0.1	8.9±0.71	15±6.5	bdl	0.2±0.04
3	1238±15	324±5.0	8±0.7	0.2±0.02	8.4±0.07*	16±2.8	bdl	0.2±0.01*
4	1266±77	298±21	8±1.1	0.2±0.02	8.5±0.83	7.0±2.0	bdl	0.2±0.02
5	1151±26	282±6.0	8±1.9	0.2±0.03	7.6±0.56*	6.0±1.4	bdl	0.2±0.01*

An asterisk indicates a statistically significant difference compared to Treatment 1. Treatment 0 is shown but was not included in the statistical analysis. bdl means below the detection limit.