



Research article

Organic amendments potentially stabilize metals in smelter contaminated Arctic soils: An incubation study

Polina Tregubova^{a,b,*}, Galina Koptsik^{a,**}, Andrey Stepanov^a, Sergey Koptsik^c, Graeme Spiers^{a,d}^a Faculty of Soil Science, Lomonosov Moscow State University, Moscow, Russian Federation^b Center for Computational and Data-Intensive Science and Engineering, Skolkovo Institute of Science and Technology, Moscow, Russian Federation^c Faculty of Physics, Lomonosov Moscow State University, Moscow, Russian Federation^d Laurentian University, 935 Ramsey Lake Road, Sudbury, ON, P3E 2C6, Canada

ARTICLE INFO

Keywords:

Soil remediation

Heavy metals

Carbon stock regulation

ABSTRACT

The long-term emission impacts of the nickel processing industry in the Kola Peninsula, the largest source of sulfur dioxide and heavy metals emissions in Northern Europe, have created vast technogenic barrens near the mineral industry complexes. The pace of rehabilitation using the improved remediation technologies to enhance sustainable environmental management and regional economic development is of crucial social and economic importance. In a 120-day incubation experiment, we evaluated the prospects for the restoration of two soils at different degradation stages via carbon pool regulation comparing to mineral ameliorants – NPK fertilizer, and liming agent. Organic additives used included a humic preparation based on an alkaline brown coal extract, wood-derived biochar, and peat-derived gel, supplied by mycorrhizae fungi. The results demonstrate that the selected organic amendments are suitable for restoration of acidic metal contaminated soils. Specifically, the treatments provided a measurable increase in soil carbon content, a marked decrease in acidity, a decrease in extractable metal contents, together with an enhanced nutrient uptake and vegetative growth. A stabilization effect increased from biochar to peat-gel, liming agent and humic preparation, with an accompanying increase in soil pH. Although biochar showed a reduced ability to metal stabilization, the associated treatments were the most productive. The most effective amendments in multi-metallic contaminated soils need to be able to stabilize bioavailability of metals, adjust pH to the optimum for plant growth, and regulate nutrient consumption.

1. Introduction

The intensification of anthropogenic activities such as industry and mining (Kozlov and Zvereva, 2007; Gascó et al., 2019), agriculture (Liu et al., 2015), urbanization (Ciarkowska et al., 2019) driven by the expansion of the needs of the burgeoning human population has led to a wide spread increase in levels of potentially toxic metals and metalloids (HMs) in all natural environmental media during last decades. Current research documenting the behavior and influence of HMs in the environment and their influence on biotic and abiotic ecosystem components is of great interest to the scientific and regulatory community (Bolan et al., 2014; Jia et al., 2018). Although organic pollutants can be biogeochemically degraded over time, inorganic contaminants can be neither degraded or decomposed, with footprints of human mining activity from Paleolithic times still being measurable in selected

environmental media even today (Nriagu, 1996; Bolan et al., 2014; Monge et al., 2015). The incorporation of HMs into the soil leads to a transformation of soil properties with rapid incorporation into biological cycles. These soil property transformations lead to suppression of critical soil ecosystem functions that support primary production and maintain microbiological communities, sustain biodiversity, promote sequestration of greenhouse gases, provide water and promote nutrient supply (Ding et al., 2018).

Modern policy-makers consider soil as a non-renewable natural resource of high importance that links atmospheric, subsurface and aquatic media to minimize release of wastes and emissions (EC, 2006; EEA, 2017) and support development of monitoring (Tóth et al., 2016) and remediation programs (Martino et al., 2016). However, input of pollutants into soils is still increasing, commonly reaching toxic levels, with examples on the planet where industrial activity has

* Corresponding author.

** Corresponding author.

E-mail addresses: tregubova.polin@gmail.com (P. Tregubova), koptsig@mail.ru (G. Koptsik).<https://doi.org/10.1016/j.heliyon.2021.e06022>

Received 5 June 2020; Received in revised form 23 September 2020; Accepted 14 January 2021

2405-8440/© 2021 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

catastrophically affected soil cover and destroyed ecosystems (Kozlov and Zvereva, 2007; Koptsik et al., 2016; Campbell et al., 2017).

Landscape severely impacted by technogenic activity require remediation – the application of complex techniques that promote an improvement of both soil quality and health, especially by decreasing of bioavailable forms of potentially toxic HMs in the environment to levels compatible with normal functioning of biota (Adriano et al., 2004; Osman, 2014). As soil is a complex heterogeneous multifunctional system, each contaminated site has specific issues that depend on soil properties, climatic conditions, landscape and geology of both the biogeoclimatic region territory and actual nature of the anthropogenic

contamination. Today the traditional costly smaller site environmentally damaging excavation techniques to remove the contaminated surficial materials, with the associated construction of new soil cover layers that bury the potentially toxic material at depth (Yao et al., 2012) are being replaced by less invasive, *in-situ* remediation techniques (Onwubuya et al., 2009; Yin and Zhu, 2016).

The current research highlights one approach, namely the application of organic amendments, for the remediation of highly contaminated soils. This practice possibly could aid in remediation of soil cover layers by the restoration of soil functions through the soil carbon pool regulation, thus providing the enhancement of one of the major factors responsible for

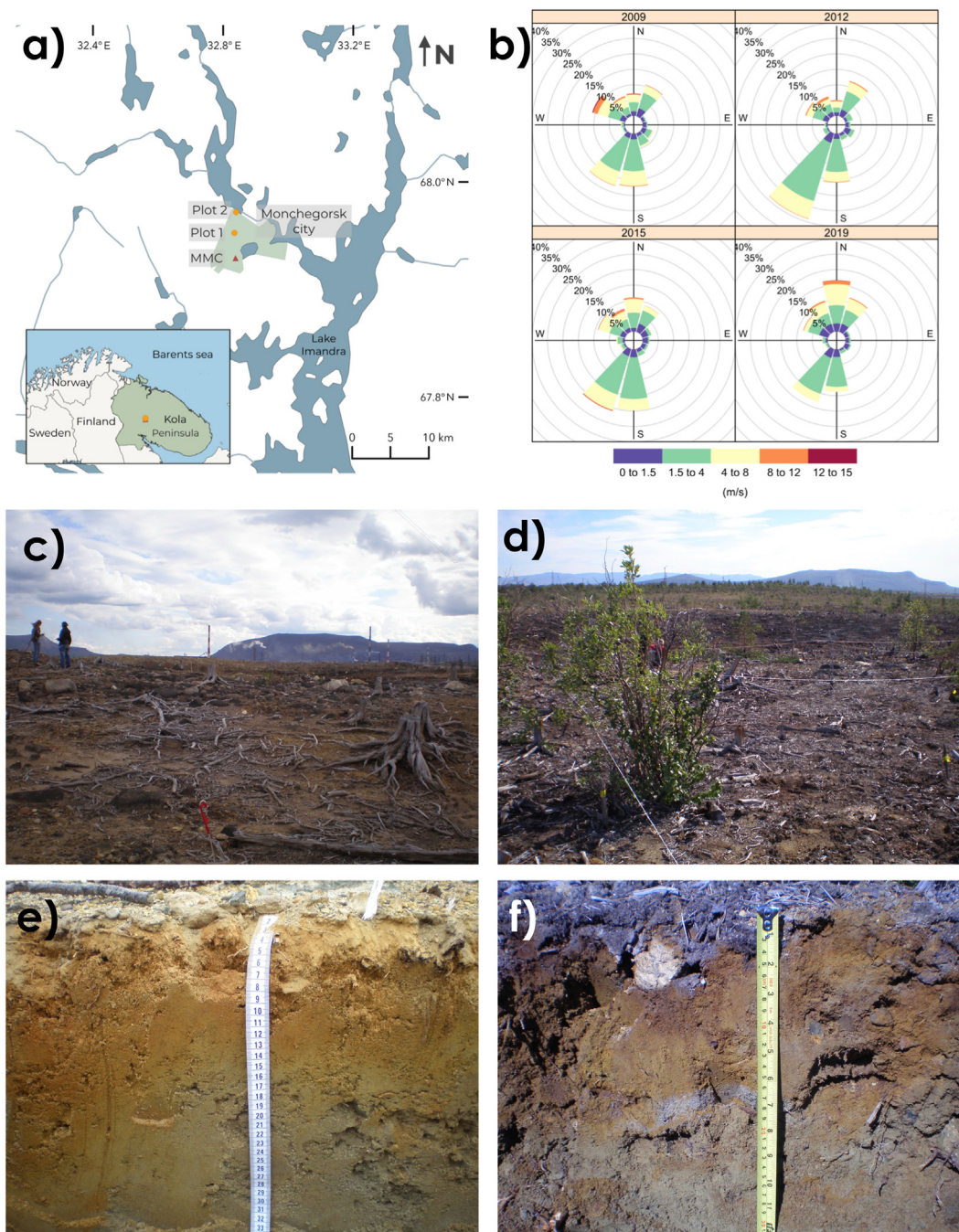


Figure 1. Object of research: a) location of the research site; b) averaged wind rose diagram for 2009, 2012, 2014 and 2019. The points represent the study plots situated in 2 and 5 km from the Monchegorsk industrial complex. Wind speed and direction data measured on height of 10–12 m above the ground were collected by the Monchegorsk weather station, located in 6 km to the North of the smelter. Industrial barren landscapes surrounding the copper-nickel industrial complex (c, d) and the sampled eroded Entic Podzol (e) and Histic Albic Podzol (f) near Monchegorsk, the Kola Peninsula, Russia.

sustainable soil function (Park et al., 2011; Lal, 2016). The variety of potential organic additives includes agricultural waste (green waste, manure), forestry by-products, composts, biosolids, and humics-based materials (Park et al., 2011; Bolan et al., 2014). Recent data demonstrate excellent prospects for use of humics-based materials in remediation of metal(loid) contaminated soils (Perminova, 2019). Biochar, a porous carbon-enriched substance obtained by the thermal destruction of biomass in an oxygen-limited environment, has been increasingly considered a useful multifunctional material for contaminant removal/immobilization from soil and water and energy applications (Lehmann and Joseph, 2015; O'Connor et al., 2018).

The objectives of the study were to compare the effects of specific organic amendments, coal-humate, peat-gel, biochar, with and without mycorrhizal inoculation, with agricultural lime (CaCO_3) and mineral fertilizers (NPK) on the chemical and biological properties of degraded soils in an incubation experiment. The study results highlight main drivers promoting stabilization of HMs and plant growth. We hypothesized the application of organic amendments would positively influence the stabilization of mobile HMs and promote plant growth by enhancing plant nutrition. We further hypothesized the soil improvements may vary significantly because of the structural and functional properties of treatments irrespective of application rate, with greater effects at lower different contamination levels.

2. Material and methods

2.1. Study area

Soil samples were collected from above the Polar Circle in the technogenic barren lands surrounding the enterprises of the Kola Mining and Metallurgical Company (MMC) (Murman'sk region, Russia), the largest nonferrous industrial complex in the Northern Europe (Figure 1a and b).

The average temperatures in the coldest month, January, range from -8° to -13°C , while the average temperature for July, the warmest month, rarely rise above $+13$ – 15°C , with periodic frosts. The annual precipitation is ~ 490 mm, with predominant wind direction being from the south and south-west. Most of the area is covered by glacial tills with coarse texture. The till mineralogy is generally characterized by slowly weathered primary minerals, represented by mainly quartz and feldspars (mostly plagioclase) derived from gneisses and granites. Podzol is the most common soil type (Koptsik et al., 2003). The natural vegetation of the region consists of shunted coniferous and parvifoliate forests dominated by Siberian spruce (*Picea obovata*), Scots pine (*Pinus sylvestris*) and European white birch (*Betula pubescens*), with a ground cover of dwarf shrubs, mosses and lichens.

The adverse environmental impacts of sulfur dioxide and metallic emissions high in Ni and Cu, especially as surface soils contaminants, on the landscapes and watersheds surrounding the industrial complex of the MMC have been detected up to 250–300 km from the industrial complexes as widely discussed in scientific literature for decades (Reimann et al., 1998; Barcan, 2002; Evdokimova et al., 2011; Koptsik et al., 2016; Lyanguzova et al., 2016; Kashulina, 2017). The industrial barrens created by emissions of the MMC extend for 5–7 km depending

on the wind direction, with areas in the prevailing N and S wind being most impacted. The acidic soils of the smelter emission impacted barren lands have high contents of heavy metals in soil surface layers and are characterized by the absence of vegetation leaving the upper potentially fertile soil layers prone to wind and water erosion (Tregubova et al., 2019). Content of Ni and Cu in barren soils exceeds both median regional (Reimann et al., 1998) and background (Kashulina, 2018) concentrations by 15–50 times (Table 1). These combined negative industrial impacts on the ecosystems, coupled with the low natural ability of ecosystems to self-restore given the natural harsh climate conditions, short annual vegetative growth periods, and slow rate of pedogenic biogeochemical processes.

Soil samples were collected from two sites (Figure 1c and d) exhibiting different stages of degradation at distances of two and five km north from the smelter, with the ongoing atmospheric contaminant emissions being deposited on the landscape surface. The resultant secondary pollution, soil erosion, and accumulated levels of contaminant metals in topsoils inhibit the recovery of vegetation near the complex. The horizon sequence of **Soil 1** (location N $67^\circ 56.457$, E $032^\circ 50.074$), an eroded Entic Podzol (Phytotoxic) situated two kilometers from the industrial complex was BF-BC-C. The horizon sequence of **Soil 2** (location N $67^\circ 57.901$, E $032^\circ 50.37$), an eroded Histic Albic Podzol (Phytotoxic) situated 5 km from the industrial complex, was (Oe)-(Ee)-BF-B-C (Koptsik et al., 2016). Samples of BF horizons representative of the surface soil layers exposed at both sites due to erosion were used for incubation study. The sand textured horizons are low in organic matter, acidic (pH 4.9 in S1 and 5.6 in S2), and have significant total metal contents of 270 mg Ni, 350 mg Cu and 86 mg Ni, 140 mg Cu kg^{-1} in S1 and S2, respectively.

2.2. Experimental design

The experiment was conducted in a climate controlled growth chamber (Binder) at temperature, humidity and lighting conditions (Figure 2) representing summer months from the Monchegorsk meteorological station (<https://www.ncdc.noaa.gov/cdo-web/datatools/finderstation>) and imitating the polar day.

Four replicates of the experimental treatments were set up as follows: 1) control (C), NPK (16:16:16); 2) CaCO_3 (L), application rate variable to neutralize acidity, with commercial mycorrhizae fungi (*Glomus sp.*), (F) "BioSannie" (The Netherlands) – obtained due to pyrolysis of wood residues; 3) coal-humate "Extra" (HS) – K–Na dry salt of alkali extracted brown coal, a Russian commercial preparation; 4) (G) peat-gel "Humic-Land" – gel from gridding peat dispersed in water, a Lithuanian commercial preparation; 5) HSF, coal-humate with addition of mycorrhizae fungi; 6) GF, peat-gel with addition of mycorrhizae fungi; 7) biochar "BioSannie" (B), a commercial product from The Netherlands. Organic treatments were applied at rates to increase carbon contents of the study soils by 0.5%.

The homogenized individual soil and treatment replicates were incubated for 30 days in the climate chamber to achieve an equilibrium state. After that, *Festuca rubra*, a common component of universal grass-

Table 1. Total content of HMs – Ni, Cu, Co, Zn, Fe, Cr, Cd – in B horizons of soils in the study sites, S1 and S2, mg/kg, comparing reported background values and regional HM concentrations expressed as contamination factor (C_f).

Site	Ni	Cu	Co	Cd	Fe	Cr	Zn
Soil 1, 2 km from the source, N	271	347	17.8	0.6	26410	73.6	37.2
Soil 2, 5 km from the source, N	86.0	143	11.4	29.4	18990	48.8	0.4
Northern Finland, median for background areas (Kashulina, 2018)	5.5	9.6	16.3	NA	NA	NA	24.7
Central Barents Region, median (Reimann et al., 1998)	16.1	10.5	5.7	25.5	23500	35.2	0.04
Contamination factor ($C_f = C_{\text{on site}}/C_{\text{background}}$)							
C_f Soil 1	49	36	1.1	NA	NA	NA	1.5
C_f Soil 2	16	15	0.7	NA	NA	NA	0.02

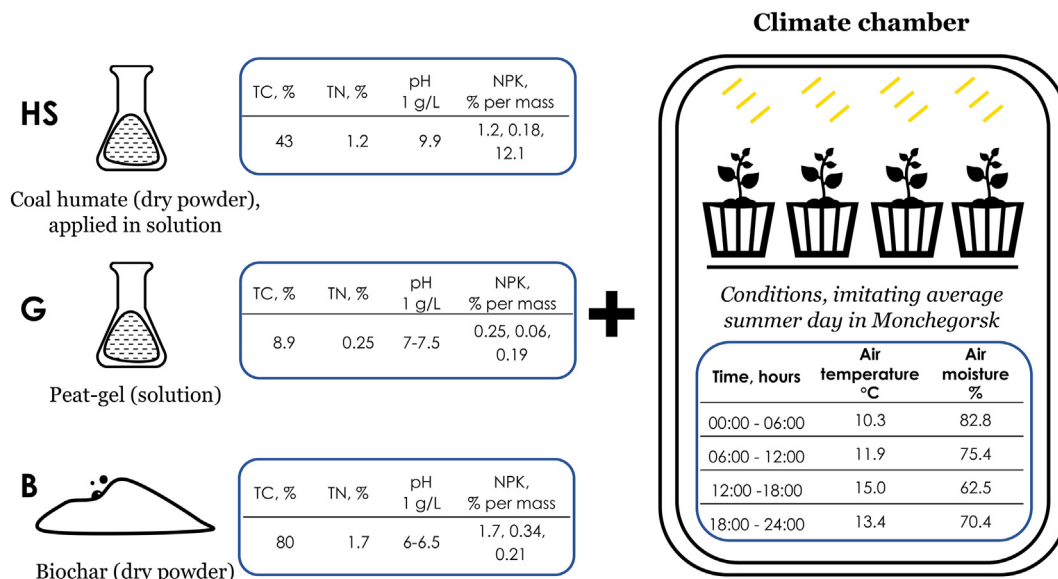


Figure 2. Details of the study: characteristics of organic amendments and climate chamber conditions during the experiment.

mixtures suitable for Far North climate conditions with a 98% germination rate, was sown and grown for 90 days prior to harvest.

2.3. Methods

Soil water extracts (1:10 soil:water) for sub-samples from all replicates were characterized for pH with an InLab Expert Pro-ISM S220-Kit (Mettler Toledo), dissolved organic carbon (DOC) and dissolved nitrogen (DN) on TOC-analyzer (Shimadzu), content of water-extractable elements (Ca, Mg, K, P, Ni, Cu, Co, Cd, Zn, Mn, Fe, Al) by inductively-coupled plasma mass-spectrometry using an ICP-MS 7500A (Agilent). Content of total carbon (TC) and nitrogen (TN) in the soils was measured by dry combustion using a CHNS-analyzer Thermo Flash 2000. Infra-red spectra (FTIR) of the organic amendments as crushed powders were obtained with a Tensor II infrared spectrometer (NETZSCH GmbH). Microbial biomass carbon was determined using the fumigation-extraction technique (Vance et al., 1987).

Basal respiration was measured on collected samples after 24 h additional incubation at 22° by gas chromatography (Schinner et al., 1996). At the end of experiment plants from each pot were visually inspected, with above and below ground plants being cleaned and weighed, then dried at 40°, and weighed once again. After drying shoots and roots were blended by treatment, digested with HNO₃ (c) with addition of H₂O₂ at 180–185° in Milestone microwave (EPA3050). The plant digests were analyzed by ICP MS 7500A for concentration of Ni, Cu, Co, Cd, Zn, Mn, Fe, Al, Ca, Mg, K, and P. All methods were thoroughly validated, with trueness, accuracy and precision being continuously monitored.

2.4. Statistical analysis

Analytical data were processed and visualized in RStudio using libraries Hmisc, ggplot. To perform multiple pairwise comparison of obtained properties between variants of the experiment ANOVA was applied. Correlation analysis and visualization was completed using the corrplot library (FactoMineR and factoextra).

Principal component (PC) analysis (PCA) and ordination of properties completed in accordance with ter Braak (1987). The PCA diagrams display the first two principal components to characterize soil treatments as a whole and the different soil properties having direct concentration sense (total carbon, pH, water-extractable C, N, S, P, K, Ca, Mg, Ni, Cu, Co, Cd, Zn, Mn, Fe, Al) within the variants of experiment respectively.

Environmental, vegetation-related (above- and below-ground phytomass, shoot elements concentrations) and microbial (microbial biomass carbon, basal respiration rate) properties were treated as external variables. The signs of PCs were chosen in accordance with the success of revegetation, so that correlation of phytomass with PCs is positive. The usual Euclidian distance between two points on the treatment diagrams describes similarity of variants within normalized variables, with the cosine of angle between the vectors on the diagram approximating the correlation coefficient between the corresponding properties. Standard deviation was used for scaling of variables before analysis. Other details of PCA and ordination implementation in Matlab environment were described elsewhere (Koptsik et al., 2003).

3. Results

3.1. Characteristics of applied organic amendments

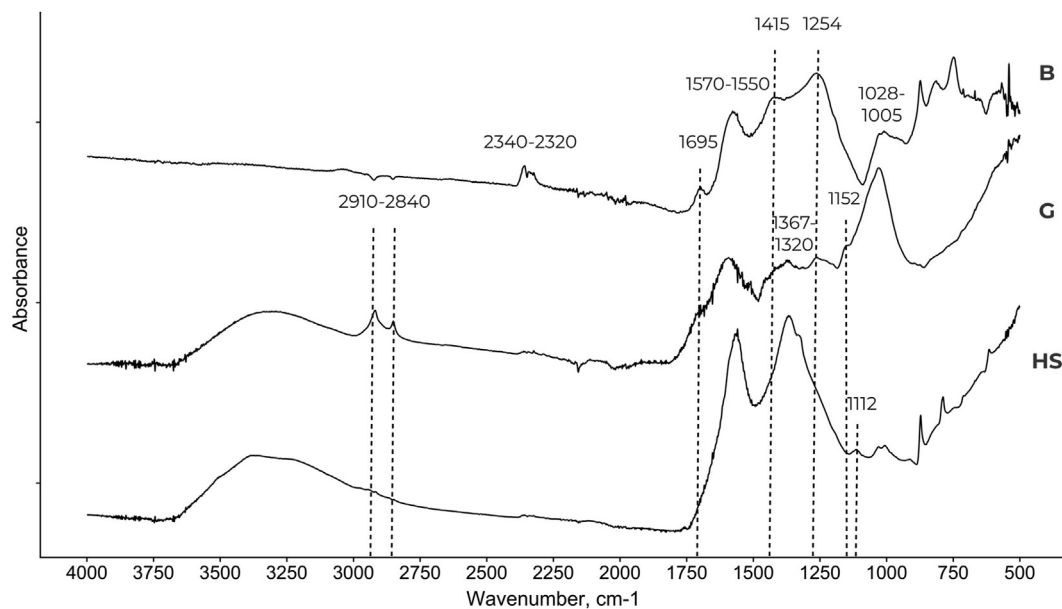
Examination of the FTIR spectra obtained for the used organic amendments indicated the presence of peaks of the covalent vibrations of O–H alcohol groups (Figure 3), and, possibly, C–O groups of polysaccharides in the 1000 to 1100 cm⁻¹ spectral region.

The presence of broad peaks centered in range from 1500 to 1660 cm⁻¹ is common to all organic amendments also, corresponding to the absorption bands of NH- and COO⁻ groups of primary amides, C=N, aromatic C=C groups (Pedersen et al., 2011; Parolo et al., 2017).

The presence of a shoulder peak at wavenumber 1380 cm⁻¹ in the spectrum for HS may be attributable to the range of groups, namely –OCOCH₃, –COCH₃, –C(CH₃)₃, >C(CH₃)₂. This peak, although broader, is also present in the spectrum for G, the ‘peat gel’ material. The broad absorption band in the 3000 to 3600 cm⁻¹ spectral region indicates presence of OH functional groups and hydration water.

The FTIR spectrum of G, the ‘peat gel’, when compared with HS and B, the ‘coal humates’ and ‘biochar’, has a strong absorption band maximum at 1100 cm⁻¹, a feature common to all spectra obtained in this study. Other amendment materials, namely G, HS and B, also have a well-defined shoulder at 1152 cm⁻¹. The spectrum for soil amendment B, a biochar, exhibits a wide peak attributable to carboxyl – C=O and, partly, – OH groups, with a maximum at 1254 cm⁻¹. The spectrum for G, the ‘peat gel’, has two vibrational bands corresponding to C–H bonds of aliphatic CH₂, CH₃ groups with maxima at 2840 cm⁻¹ and 2910 cm⁻¹.

Another distinctive feature of B spectrum is the presence of additional peak maximum at 1695 cm⁻¹ attributable to valence vibrations of groups



$\sim \text{cm}^{-1}$	Proposed assignment	HS	G	B
<800	Aromatic C-H	+		+
1000		+		+
1030	C-O, OH	+	+	+
1100		+		
1150	C-O, OH, COO ⁻		+	
1250			+	+
1320	OH	+		
1380	-OCOCH ₃ , -COCH ₃ , -C(CH ₃) ₃ , >C(CH ₃) ₂	+	+	
1415	CH, COO ⁻ , OH			+
1570-1600	NH of primary amides, aromatic C=C, >C=N	+	+	+
1695	C=C, COO ⁻ of amides			+
2340	CO ₂			+
2840	-O-H, -C-H of CH ₂ , CH ₃		+	
2910	-O-H, -C-H of CH ₂ , CH ₃		+	

Figure 3. FTIR spectra of organic treatments applied to the BF horizon soil samples in the growth chamber study with assignment to structure groups documented in the literature: HS – coal humate, G – peat gel and B – biochar.

containing nitrogen and/or oxygen, namely C=O groups in primary amides and COO⁻ groups. The peak maximum at 2340 cm⁻¹ is related to a CO₂ band. Peaks distributed in the spectral region below 1000 cm⁻¹ may be contributed either by undefined organic groups or by the ash content/mineral components of the amendments. The spectral peaks in the 800 to 700 cm⁻¹ range are out-of-plane vibrations of C-H bonds of aromatic rings (Meng et al., 2017). These latter features are also present in the HS spectrum but absent in G spectrum.

3.2. Soil properties at the experiment completion

3.2.1. Chemical and microbiological properties of soils

The different amendments all had a significant impact on the biochemical properties of the treated soils, as highlighted in Table 2. The pH of the soil solution increased significantly for all treatments, apart from B, comparing to control or have an expressed tendency in cases of G/GF application to abrazem soil. The organic treatments (HS, G, B) significantly increased the total carbon content in both soils, S1 and S2, by approximately 0.5%. Dissolved organic carbon in the soil-water

extracts and basal respiration increased with the HS/HSF treatments, the increases being 10–25% more for DOC and 20–30% more for basal respiration in both S1 and S2 samples. An increase in basal respiration rate was also observed with the G/GF treatment for soil S2. There was decreased dissolved nitrogen content with treatment B for both soils (S1 and S2), with the decrease being significant with the blending of LF with S2. There are no measurable differences in amounts of microbial biomass carbon for any of the six treatments on either soil.

The addition of treatments change content of water-extractable macroelements in soils as well (Table S1). HS and G induced an increase in levels of water-extractable K for both S1 and S2, with LF causing an increase in extractable Ca enrichment. The addition of LH, on the other hand, induced a decrease in water-extractable K in both soils, whereas this effect was only observed for the application of amendment B to the S2 soil.

3.2.2. Influence of amendments on bioavailability of metals in soils

The pH adjustment resulting from the application of both the LF and organic amendments induced significant changes in the levels of water-

Table 2. Chemical and microbiological properties of the amended soils S1 and S2 at the termination of the 90 days growth experiment – means and 95% confidence intervals.

Treatment	pH	TC %	DOC	DN mg/kg	Cmicro	Resp mg CO ₂ /m ² /h
S1						
C	4.8 ± 0.04	1.4 ± 0.1	63 ± 3.7	254 ± 41	178 ± 27	11 ± 5.3
LF	6.2 ± 0.1*	1.8 ± 0.2	65 ± 5.8	233 ± 6.8	147 ± 53	18 ± 7.0*
HS	6.3 ± 0.2*	2.1 ± 0.1*	109 ± 16*	236 ± 18	168 ± 67	27 ± 2.0*
G	5.5 ± 0.2*	1.9 ± 0.4*	75 ± 45	309 ± 248	175 ± 99	25 ± 15*
HSF	6.3 ± 0.1*	1.8 ± 0.3	88 ± 20*	246 ± 20	198 ± 25	28 ± 12*
GF	5.6 ± 0.3*	1.9 ± 0.2*	65 ± 10	239 ± 87	174 ± 41	29 ± 18*
B	4.9 ± 0.04	2.0 ± 0.6*	55 ± 5.4*	114 ± 14*	171 ± 21	19 ± 11
S2						
C	5.6 ± 0.4	0.97 ± 0.07	65 ± 11	228 ± 10	172 ± 51	9.5 ± 8.8
LF	6.5 ± 0.1*	1.0 ± 0.08	69 ± 1.7	199 ± 20*	133 ± 52	17 ± 7.6
HS	6.5 ± 0.1*	1.3 ± 0.03*	84 ± 9.1*	213 ± 10	229 ± 27	20 ± 12
G	6.1 ± 0.1*	1.5 ± 0.08*	57 ± 9.0	210 ± 14	185 ± 35	26 ± 8.7*
HSF	6.3 ± 0.2*	1.3 ± 0.1*	87 ± 21*	229 ± 21	202 ± 54	11 ± 3.9
GF	6.4 ± 0.0*	1.3 ± 0.2*	61 ± 3.1	205 ± 21	189 ± 82	35 ± 11*
B	6.2 ± 0.2*	1.8 ± 0.2*	62 ± 5.5	133 ± 29*	165 ± 103	27 ± 4.3*

Bolded values marked by * -symbol significantly differ from the control at $p < 0.05$ according to control-amendment ANOVA. The symbols are: TC – total carbon, DOC – dissolved organic carbon, DN – dissolved nitrogen, Cmicro – microbial biomass carbon, Resp – basal respiration of soils. Treatments are: C – NPK as control, LF – CaCO₃, HS – K–Na coal humate, G – peat-gel, B – biochar, F – mycorrhizae fungi.

extractable metals quantified in the soil water extracts (Figure 4). The non-amended control treatments of S1 and S2 have high contents of water-extractable metals, with mean values of Ni, Cu, Co, Zn, Mn, Fe and Al being 8, 29, 0.5, 0.8, 4.8, 5.6, 13.7 mg/kg in S1, and 5, 6, 1.1, 1.2, 15, 3.6, 7.5 mg/kg respectively in S2. The concentrations of water-extractable Ni, Cu, Fe and Al in non-amended soil S2 was 1.5–2 times lower, except from Cu, which levels in S2 was 5 times lower.

The individual treatments have no significant impact on water-extractable Zn levels for S1, with variable effects being observed on S2 treatments ranked in decreasing order HS/HSF = LF > G ~ GF > B. There are also no significant differences in content of water-extractable Mn in S1 soils, apart from the higher content in HSF and the lower in B. In S2 all variants demonstrated lower content of Mn comparing to the control, expressed more in LF and B.

On the contrary, concentrations of water-extractable Co, Cd, Zn in S2 were quite the same, while concentration of Mn was significantly higher.

The extractable levels of Ni, Cu, Co, Cd and Al from the treated samples followed the same pattern, but with significantly decreased concentrations in amended samples, namely 60–70% lower with HS and LF and ~20% lower with G and B.

There is no significant suppression difference of water extractable levels of Ni, Cu, Co, Cd and Al following the application of G to either the S1 and S2 soils, with the suppression effect of B being less in the more highly contaminated S1 soil. The concentrations of water-extractable Fe between the treatments do not appear to exhibit a clear pattern, except for the application of LF, which induces an increase in extractable Fe levels.

3.3. Plant growth results

The root systems in the control samples for S1 and S2 were poorly developed 3 months after seedling germination. Root development varied with the addition of the organic amendments to S1, with maximum development being observed with the addition of LF and B, followed by HS, and G (Figure 5A). The G/GF treatments induced a suppression in development of root systems.

Root biomass increased by approximately a factor of two for S2 amended soils, with differences observed between the treatments. Total

above- and below-ground plant biomass decreased in range B > LF > G > HS.

The leaves of seedlings of both the S1 control and G treated amendments were pale and yellow from the very outset, with decreased chlorosis expression for seedlings in other amendments on S1 noticeable by the end of experiment. The only seedlings displaying chlorosis for S2 amendment series were those of the control treatment from the outset, with limited chlorosis development being observed for the HS treatment towards the end of the experimental growth period.

There is no apparent pattern in P consumption by the seedlings across the amendments, with the highest level (~2 mg/kg) being observed for amendment B (Figure 5B). The distribution of K (Figure 5C) in plant tissues shows a distinct difference in patterns across treatments to those observed for Ca and Mg (Figure S1), with levels being lowest in the S1 and S2 control soils and highest in the HS treatment. The higher levels of K in the tissues grown on the HS is indicative of an increased uptake of K as result of increased K supply to the soils from the HS amendment, with K levels varying from 35 to 50 mg/kg (dry weight) for seedlings across all amendments. These K levels are approximately twice those obtained for plants grown in the C(control) soils, being between 18–29 mg K/kg on dry weight basis.

We expected that application of mycorrhizae fungi would promote development of the root system and enhance nutrient uptake. Under the conditions of this experiment the expected enhancement of root system development was not observed, with seedlings grown on the F treatment having both a lower growth rate and nutrient accumulation.

The phytomass of the plants at the end of the experimental period exhibits a non-linear relationship to the decreasing concentrations of water-extractable HMs in soils. The levels of water-extractable HMs in S1 and S2 is significantly different in both control soils, with the plants exhibiting a poor overall growth response, a poorly developed root-system and a high accumulation of metals (Figure 5E–H) in both above and below-ground tissues. The metal concentrations in the S1 seedlings are two to four times higher than in S2, except for the reverse in S2 for Co, Cd, Mn and Zn with an accumulation of 1.2–3 times more.

The effect of amendments applied to the S1 and S2 soils exhibited marked differences, with amendment applications to S1 being effective in suppressing the accumulation of metals in the seedlings in descending

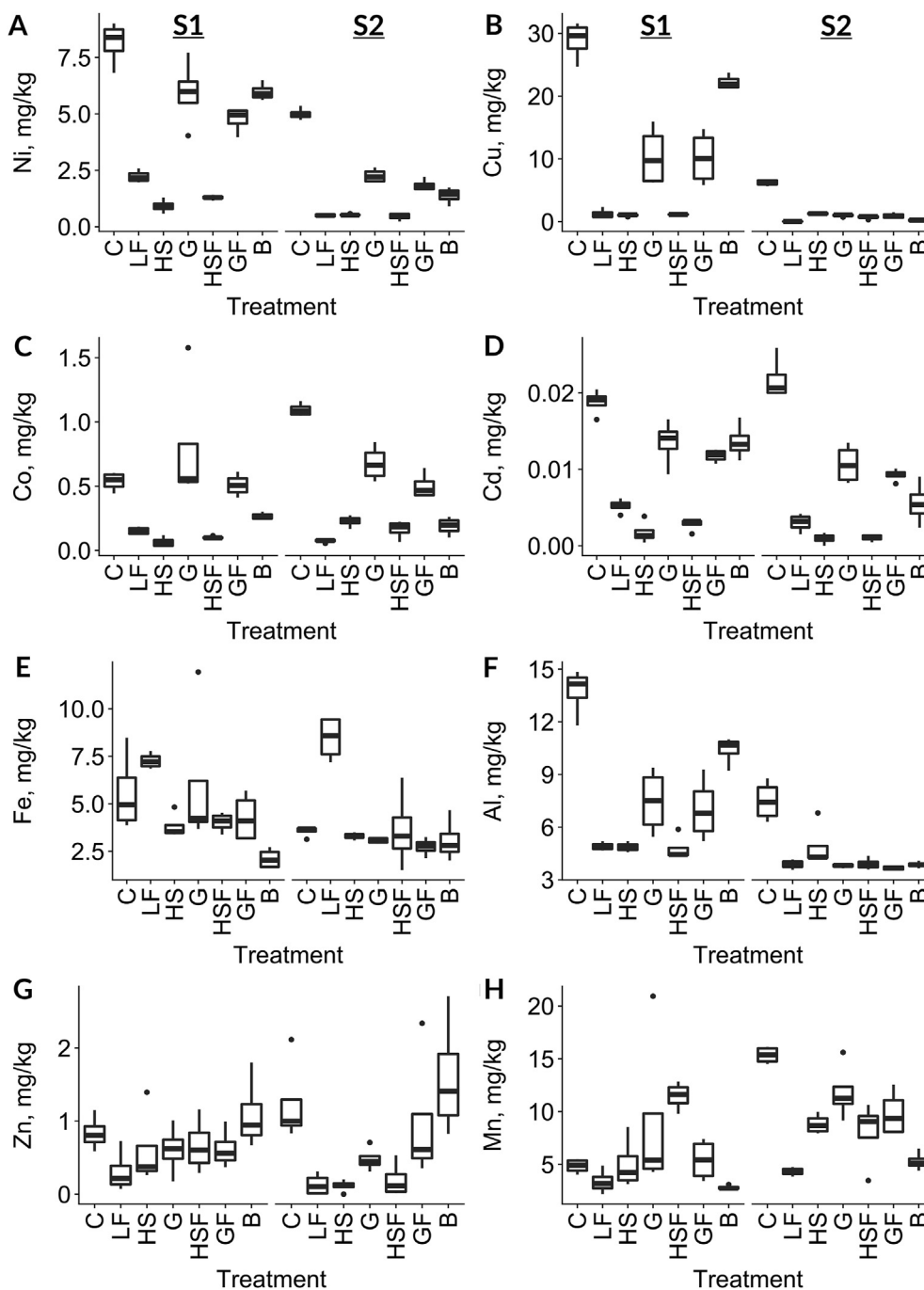


Figure 4. Content of water-extractable metals in soils in the end of the experiment: A-H – Ni, Cu, Co, Cd, Fe, Al, Zn, Mn, respectively. The dots on the box plots mark outliers.

order from $HSF \geq LF \geq HS \geq B$, with the metal content being 10–30 times lower than observed in the control soils, with the G/GF application being only 2–3 times lower. The Zn levels were similar in plants grown in most treatments. The application of all amendments led to an increase in the Mn uptake by shoots. For S2 group the HSF treatment suppressed the accumulation of metals, with the measured levels in the plant tissues for other treatments being in the following descending order, $HS > LF > G \sim B \geq GF$. All treatments prevent accumulation of Ni, Cu, Co (Figure 5E–G) and partly Fe and Al (Figure S1e, S1f) in the shoots, with minimal effect on Mn, Cd and Zn (Figure 5D, H, S1d) uptake into the experimental plants.

Accurate evaluation of root uptake is not possible because of poor development in the control soils. However, the content of metals in roots of S1 seedling groups was 2–4 times higher than for the S2 soil, with the exception of the seedling roots in the HS treatment. The lowest accumulation of metals in plants grown on the S1 soil was observed for the HS/HSF treatments, with the highest levels of Ni, Cu, Co and Zn being measured on the B and GF treatments, and for Al and Fe in the LF treatment. The highest metal accumulation levels exceeded the lowest by 2–3 times, with accumulation of Zn in roots in BF variant being 10 times higher. The observed pattern of metal accumulation for the S2 soils and treatments was similar, with the lowest accumulation of metals being in

roots with the HS/HSF treatment and the highest being in the B and G treatments. The GF addition exhibits at lower level of metal accumulation. The results above suggest threshold water-extractable uptake levels of potentially toxic HMs for seedlings grown in the highly contaminated S1 soil is low when compared to uptake levels in untreated controls, being 2.2, 1.2, 0.2 and 5 mg/kg for Ni, Cu, Co and Al respectively.

4. Discussion

4.1. Functional characteristics of organic treatments

Application of organic treatments to facilitate soil remediation of metal contaminated soils is a well-known approach (Park et al., 2011). It is supported by the idea of high environmental importance of organic carbon, regulating all ecosystem functions of soils. Organic matter is considered to have two main effects, namely immobilization (Alvarenga

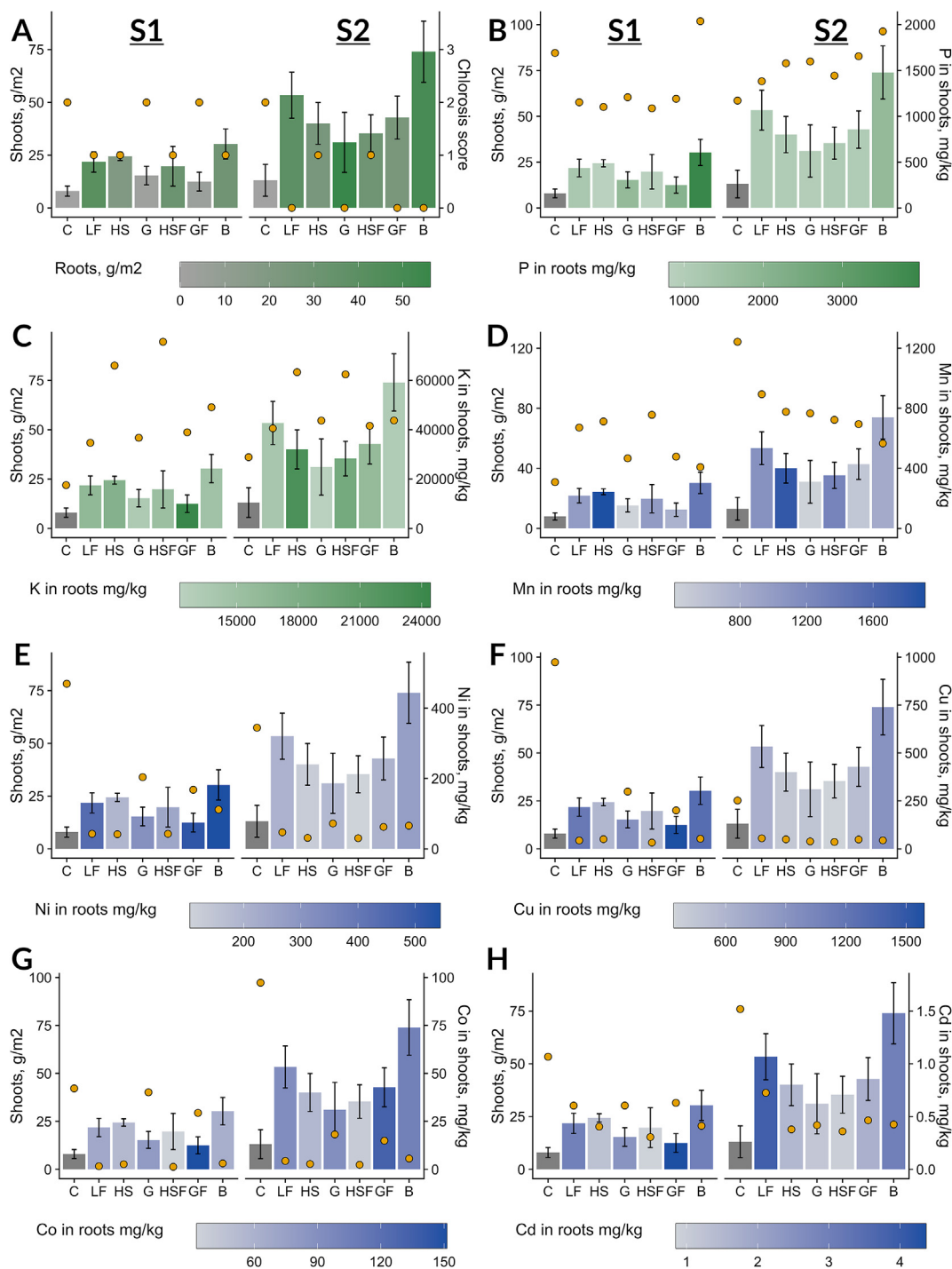


Figure 5. Test culture state, roots and shoots, in the end of experiment: A – shoots phytomass, colored by roots phytomass, orange points represent chlorosis score from 0 – no evidence, 1 – occurred by the end of experiment, 2 – expressed from the beginning; B–H – content of P, K, Mn, Ni, Cu, Co, and Cd in shoots (represented by orange points) and roots (expressed by color) in mg/kg.

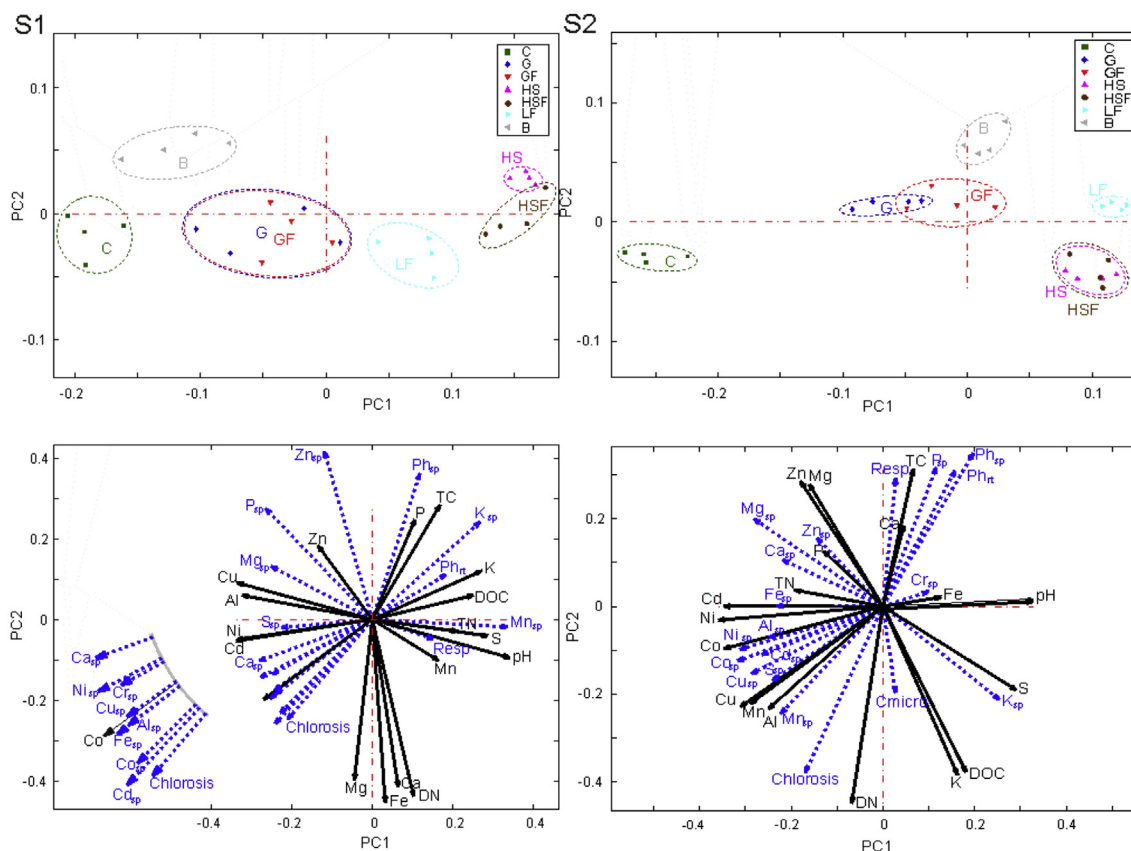


Figure 6. Ordination of treatments (above) and soil properties (below, black solid arrows) for S1 and S2; chemical symbols denote content of water-extractable elements in soils in the end of the experiment. External variables (blue dashed arrows) are above- (Ph_{sp}) and below- (Ph_{rt}) ground phytomass; Chlorosis, microbial biomass (Cmicro), soil respiration (Resp); chemical symbols denote concentrations of elements in *Festuca rubra* shoots.

et al., 2009; Bolan et al., 2014) and mobilization (Hernandez-Soriano, Jimenez-Lopez, 2012) of various metal species in soil solutions available to living organism after supplementation by diverse exogenic organic matter materials. Stabilization procedures have key advantages, such as reduced impact on environmental media and prevention or reduction of contamination spread through migration of pollutants in groundwater or plant uptake (Bolan et al., 2014). The effectiveness of organic amendment applications such as brown coal derivatives (Kwiatkowska-Malina, 2018), biochar (Xu et al., 2018), and peat derivatives (Pukalchik et al., 2018) examined in this current remediation research is still open to question.

In this study we document the structural characteristics of HS, G and B to enable changes in functional groups within the organic amendments utilized to be correlated with properties of soils and plants after experimental completion. We choose FTIR analysis, a non-destructive and non-invasive analytical method, and not acid-base extraction procedures suitable only for removal of soluble components of applied amendments whilst causing chemical undesirable alterations in the analyzed materials (Kögel-Knabner, Rumpel, 2018). Further, although the organic amendments were applied to give the same levels of initial soil carbon in the experimental microcosms, we suspect varying influence of applications to soils and experimental plants due to their unequal biogeochemical property influence.

As the absorption band below 1000 cm^{-1} is related to the presence of aromatic structures (Figure 3), the spectra suggest a more aromatic character for B and HS, with an associated larger saturation of G by aliphatic structures. Nevertheless, the functional groups (such as carboxylic, phenolic and aromatic) in all applied organic amendments are characterized by an affinity to pH-dependent metal ion binding behavior. This binding behavior could explain lower ability of B to bind metal ions

in S1 experimental soils, while neutralization of soil solution with the HS amendment application may be a key factor for metal ion stabilization in our experiments. Although carboxyl groups have higher metal ion binding affinity (Chen et al., 2015; Huang et al., 2018), aromatic functional groups are characterized by higher binding capacity (Xu et al., 2013). However, in this experiment, the metal stabilization mechanism remains unclear, perhaps occurring both through binding metal ions in soil-water insoluble complexes by HS and G, though sorption by G, and also by precipitation with the adjustment of soil pH to neutral. The pH changed in the experimental treatments from moderately acidic (below 6.0) to slightly acidic (6.1–6.5). Although still acidic, the pH range for precipitation HM may be below 7, with Cu, for example, being commonly in 5.4–6.9 range and Ni in the 6.7–8.2 (Kabata-Pendias, 2011).

4.2. Influence of organic treatments on changing soil toxicity with multi-metallic contamination

All applied organic matter rich amendments changed overall system biological and chemical properties relative to S1 and S2 soil controls (Figure S3). Although the distance between two plots is relatively small, there are several important distinctions such as the higher pH of S2 than S1, the lower carbon content, and different total and water-extractable metal levels between them.

For control samples only amended with NPK-fertilizer, the content of water-extractable Ni, Cu, Co and Al is relatively high. However, official soil health standards normally evaluate only total or strong acid extractable metal levels (e.g. Assessment levels for Soil, Sediment and Water, 2010), thus ignoring the plant root important bioavailable levels forms. The interaction of a series of pollutant metals enhances their

potentially toxic effects, with none to the plots in severe climate conditions being suitable for optimal plant growth.

All applied amendments, organic and LF, in this study have demonstrated a stabilization effect, increasing from B < G/GF < LF < HSF/HS, with an accompanying increase in measured soil pH. Although the stabilization effect was enhanced from S1 to S2, the improvement of plant physiological state was not straightforward. High concentrations of metals in soil solution are known to suppress the protective and regulating abilities of root system (Kabata-Pendias, 2011). An excess of some nutrients in comparison to others decreases the possible positive effect of an amendment, such as is observed for potassium in the HS/HSF treatments. In a short-term dynamic incubation experiment maize silage pyrolysis char, a mostly inert material, did not impact overall soil microbial activity and microbial abundance (Lanza et al., 2016). The observed significant increase of respiration rate in our experiments is still extremely low and corresponds to that documented for highly degraded ecosystems (Kadulin, Koptsik, 2013). The respiration rate increase does not reflect a microbial biomass growth stimulation.

4.3. Integral analysis of application of organic treatments: correlations and PCA

Our previous findings (Koptsik et al., 2016), supported by recent research (Kashulina, 2017), have shown that bioavailable metal levels along with enhanced nutrient depletion in an acidic environment suggest the investigated soils of the Kola Region barren lands unsuitable for vegetation. Thus, without additional remediation efforts, the above-ground and below-ground parts of components of plants normally observed in the natural conditions of the Kola Peninsula are not able to develop on soils of the technogenic barrens near the Monchegorsk industrial site.

The measured concentrations of water-extractable Ni, Cu, Co, Cd, Al and Zn, but not Fe and Mn, show a strong negative correlation with pH (Figure S2). Growth of shoots and roots is inversely correlated with content of water-extractable Cu, Al, Ni, Cd and Co, suggesting that water-extractable metal concentrations are strongly related to overall soil phytotoxicity. Content of Zn and Mn in shoots has positive correlation with shoots development, with that content of Mn is in antagonism with content of Ni, Cu, Fe, which may indicate a deficiency of Mn as an essential microelement in contaminated soils. Phytomass development positively related to the accumulation of K in shoots, which is negatively correlated with accumulation of metals and Ca in shoots. Inefficient uptake of K, Ca and P by growing plants may lead to the weakened development of plant tissues even if water-extractable potentially toxic metals in soils are essentially undetectable. The high levels of accumulation of metals by plants in control soils may reflect stress conditions, with low soil pH and poor root development impacting the sorption of critical metal micronutrients into the plant.

Although B showed a reduced ability to metal stabilization, the associated treatments were the most productive, and also had a higher P uptake. We can conclude that most effective amendments in multi-metallic contaminated soils need to be able to both stabilize bioavailability of metals, regulate pH to the optimum for plant growth, and regulate nutrient consumption.

Using the full suite of available soil data from these experiments we performed PCA by each soil group separately. The treatment ordination diagrams (Figure 6) exhibit a clustering of the organic matter treatments in the experiments for both soils, except for the G/GS for S1 and the HS/HSF treatments for S2. All the experimental treatments are noticeably separated from control samples by soil properties for the two soils. The best separation was achieved for HS/HSF and LF-treated soils, promoting the conclusion that they are highly suitable for application in remediation practice in field conditions.

The PCA plots are similar visually, with the first two components explaining almost 61% of the data variability in both soils. In S1, pH, water-extractable Cd, Ni, Cu, and, to a lesser extent, Al and S content contribute significantly to PC1, while Fe, DN, Ca, Mg, TC and P content contribute dominantly to PC2. For soil S2, these same variables, namely Ni, Co, Cd, pH, Cu, and S content, contribute heavily to PC1, with DN, K, DOC, TC, Zn and Mg content contributing to PC2.

For both experimental soils, the observed changes in the above- and below-ground phytomass in our experiments depended on TC, being also linked with water-extractable P and K in the most damaged soil S1. The phytomass and soil respiration rate were negatively correlated with concentrations of water-extractable Ni, Cu, Co, Cd and Al in soils. In the ordination, the shoot concentrations of pollutant metals were positively linked with their measured contents in soils. The bioavailable forms of Ni, Cu, Co and Cd, together with the experimental carbon enrichment, are the main factors that will control the success of revegetation in field conditions.

5. Conclusions

This focused study documents an assessment of the potential utility for the application of diverse organic amendments of varying compositions derived from different sources for the remediation of sensitive soils. The soils selected for this study were impacted by over 80 years of acidic precipitation containing both soluble and fine metal-rich particulates in the technogenic barren landscapes of the Kola Arctic Region of Northwestern Russia. Incubation experiments highlighted the variable impacts of the applied amendments, with the results of the coal humate applications promoting such improved soil conditions that we recommend their use for highly metal contaminated sites. The application of biochar also promotes enhanced plant growth in the acidic metal contaminated soils, with the 'raw' peat-gel inducing positive plant responses on the acidic soils with lower metal loadings. Thus, from the results of these experiments, we recommend the application of complex organic amendments with high contaminant metal absorption characteristics for use in land remediation efforts in sub-Polar landscapes impacted by technogenic metal smelter emissions. The containment and stabilization of the potentially mobile contaminant metals following organic amendment incorporation has economic, social and environmental benefits including suppression of soluble metal release to surface and ground waters and, more critically perhaps, enhancement of soil carbon sequestration capacity.

Of importance, land application of complex organic amendments must be experimentally tested in the specific receptor ecosystems to ensure there are no antagonistic impacts on nutrient bioavailability to the soil-plant system that may induce suppression of plant growth, or even prevent seed germination. The results from this study provide valuable additional detailed biogeochemical and structural chemistry information to add to the developing research database documenting the suitability of potentially useful, yet diverse, soil organic amendments for use in critical land reclamation applications in sensitive physiographic regions of the planet.

Declarations

Author contribution statement

P. Tregubova: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

G. Koptsik: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

A. Stepanov: Contributed reagents, materials, analysis tools or data.

S. Koptsik: Analyzed and interpreted the data.

G. Spiers: Analyzed and interpreted the data; Wrote the paper.

Funding statement

This work was supported by RFBR Research Project No. 18-04-01028.

Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at <https://doi.org/10.1016/j.heliyon.2021.e06022>.

References

- Adriano, D.C., Wenzel, W.W., Vangronsveld, J., Bolan, N.S., 2004. Role of assisted natural remediation in environmental cleanup. *Geoderma* 122, 121–142.
- Alvarenga, P., Palma, P., Gonçalves, A.P., Fernandes, R.M., de Varennes, A., Vallini, G., Duarte, E., Cunha-Queada, A.C., 2009. Organic residues as immobilizing agents in aided phytostabilization: (II) Effects on soil biochemical and ecotoxicological characteristics. *Chemosphere* 74, 1292–1300.
- Barcan, V., 2002. Nature and origin of multicomponent aerial emissions of the copper-nickel smelter complex. *Environ. Int.* 28, 451–456.
- Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B., Scheckel, K., 2014. Remediation of heavy metal(loid)s contaminated soils – to mobilize or to immobilize? *J. Hazard Mater.*
- Campbell, D., Stewart, K., Spiers, G., Beckett, P., 2017. Growth and metal uptake of canola and sunflower along a thickness gradient of organic-rich covers over metal mine tailings. *Ecol. Eng.* 109, 133–139.
- Chen, W., Habibul, N., Liu, X.Y., Sheng, G.P., Yu, H.Q., 2015. FTIR and synchronous fluorescence heterospectral two-dimensional correlation analyses on the binding characteristics of copper onto dissolved organic matter. *Environ. Sci. Technol.* 49, 2052–2058.
- Ciarkowska, K., Gambus, F., Antonkiewicz, J., Koliopoulos, T., 2019. Polycyclic aromatic hydrocarbon and heavy metal contents in the urban soils in southern Poland. *Chemosphere* 229, 214–226.
- Department of Environment and Conservation, 2010. Assessment Levels for Soil. Sediment and Water.
- Ding, K., Wu, Q., Wei, H., Yang, W., Séré, G., Wang, S., Echevarria, G., Tang, Y., Tao, J., Morel, J.L., Qiu, R., 2018. Ecosystem services provided by heavy metal-contaminated soils in China. *J. Soils Sediments* 18, 380–390.
- Ec-European Commission, 2006. Thematic Strategy for Soil protection, 231. Com.
- European Environment Agency, 2017. Air Quality in Europe — 2017 Report No 13/2017, EEA Technical Report.
- Evdokimova, G.A., Kalabin, G.V., Mozgova, N.P., 2011. Contents and toxicity of heavy metals in soils of the zone affected by aerial emissions from the Severonikel Enterprise. *Eurasian Soil Sci.* 44, 237–244.
- Gascó, G., Álvarez, M.L., Paz-Ferreiro, J., Méndez, A., 2019. Combining phytoextraction by *Brassica napus* and biochar amendment for the remediation of a mining soil in Riotinto (Spain). *Chemosphere* 231, 562–570.
- Hernandez-Soriano, M.C., Jimenez-Lopez, J.C., 2012. Effects of soil water content and organic matter addition on the speciation and bioavailability of heavy metals. *Sci. Total Environ.* 423, 55–61.
- Huang, M., Li, Z., Huang, B., Luo, N., Zhang, Q., Zhai, X., Zeng, G., 2018. Investigating binding characteristics of cadmium and copper to DOM derived from compost and rice straw using EEM-PARAFAC combined with two-dimensional FTIR correlation analyses. *J. Hazard Mater.* 344, 539–548.
- Jia, Z., Li, S., Wang, L., 2018. Assessment of soil heavy metals for eco-environment and human health in a rapidly urbanization area of the upper Yangtze Basin. *Sci. Rep.* 8, 3256.
- Kabata-Pendias, A., 2011. Trace Elements in Soils and Plants, fourth ed.
- Kadulin, M.S., Koptsik, G.N., 2013. Emission of CO₂ by soils in the impact zone of the Severonickel smelter in the Kola Subarctic region. *Eurasian Soil Sci.* 46 (11), 1107–1116.
- Kashulina, G.M., 2017. Extreme pollution of soils by emissions of the copper-nickel industrial complex in the Kola Peninsula. *Eurasian Soil Sci.* 50, 837–849.
- Kashulina, G.M., 2018. Monitoring of soil contamination by heavy metals in the impact zone of copper-nickel smelter on the Kola Peninsula. *Eurasian Soil Sci.* 51, 467–478.
- Kögel-Knabner, I., Rumpel, C., 2018. Advances in molecular approaches for understanding soil organic matter composition, origin, and turnover: a historical overview. In: *Advances in Agronomy*, pp. 1–48.
- Koptsik, G.N., Koptsik, S.V., Smirnova, I.E., 2016. Alternative technologies for remediation of technogenic barrens in the Kola Subarctic. *Eurasian Soil Sci.* 49, 1294–1309.
- Koptsik, S., Koptsik, G., Livantsova, S., Eruslankina, L., Zhmelkova, T., Vologdina, Zh., 2003. Heavy metals in soils near the nickel smelter: chemistry, spatial variation, and impacts on plant diversity. *J. Environ. Monit.* 5, 441–450.
- Kozlov, M.V., Zvereva, E.L., 2007. Industrial barrens: extreme habitats created by non-ferrous metallurgy. In: *Life in Extreme Environments*, pp. 69–97.
- Kwiatkowska-Malina, J., 2018. Functions of organic matter in polluted soils: the effect of organic amendments on phytoavailability of heavy metals. *Appl. Soil Ecol.* 542–545.
- Lal, R., 2016. Soil health and carbon management. *Food Energy Secur.* 5, 212–222.
- Lanza, G., Rebensburg, P., Kern, J., Lentzsch, P., Wirth, S., 2016. Impact of chars and readily available carbon on soil microbial respiration and microbial community composition in a dynamic incubation experiment. *Soil Tillage Res.* 164, 18–24.
- Lehmann, J., Joseph, S. (Eds.), 2015. *Biochar for Environmental Management: Science, Technology and Implementation*, second ed. Earthscan – Routledge, London & N.-Y.
- Liu, M., Yang, Y., Yun, X., Zhang, M., Wang, J., 2015. Concentrations, distribution, sources, and ecological risk assessment of heavy metals in agricultural topsoil of the Three Gorges Dam region, China. *Environ. Monit. Assess.* 187, 147.
- Lyanguzova, I.V., Goldvirt, D.K., Fadeeva, I.K., 2016. Spatiotemporal dynamics of the pollution of Al-Fe-humus podzols in the impact zone of a nonferrous metallurgical plant. *Eurasian Soil Sci.* 49, 1189–1203.
- Martino, L.E., Dona, C.L., Dicerbo, J., Hawkins, A., Moore, B., Horner, R., 2016. Green and sustainable remediation practices in Federal Agency cleanup programs. *Environ. Earth Sci.* 75, 1407.
- Meng, F., Yuan, G., Wei, J., Bi, D., Wang, H., 2017. Leonardite-derived humic substances are great adsorbents for cadmium. *Environ. Sci. Pollut. Res.* 24, 23006–23014.
- Monge, G., Jimenez-Espejo, F.J., García-Alix, A., Martínez-Ruiz, F., Mattioli, N., Finlayson, C., Ohkouchi, N., Sánchez, M.C., De Castro, J.M.B., Blasco, R., Rosell, J., Carrión, J., Rodríguez-Vidal, J., Finlayson, G., 2015. Earliest evidence of pollution by heavy metals in archaeological sites. *Sci. Rep.* 5, 1–9.
- Nriagu, J.O., 1996. A history of global metal pollution. *Science* 272 (5259), 223–224.
- O'Connor, D., Peng, T., Zhang, J., Tsang, D.C.W., Alessi, D.S., Shen, Zh., et al., 2018. Biochar application for the remediation of heavy metal polluted land: a review of in situ field trials. *Sci. Total Environ.* 619–620, 815–826.
- Onwubuya, K., Cundy, A., Puschenreiter, M., Kumpiene, J., Bone, B., Greaves, J., Teasdale, P., Mench, M., Tlustos, P., Mikhailovsky, S., Waite, S., Friesl-Hanl, W., Marschner, B., Müller, I., 2009. Developing decision support tools for the selection of “gentle” remediation approaches. *Sci. Total Environ.* 407, 6132–6142.
- Osman, K.T., 2014. *Soil Degradation, Conservation and Remediation*. Springer.
- Park, J.H., Lamb, D., Paneerselvam, P., Choppala, G., Bolan, N., Chung, J.W., 2011. Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *J. Hazard Mater.* 185, 549–574.
- Parolo, M.E., Savini, M.C., Loewy, R.M., 2017. Characterization of soil organic matter by FT-IR spectroscopy and its relationship with chlorpyrifos sorption. *J. Environ. Manag.* 196, 316–322.
- Pedersen, J.A., Simpson, M.A., Bockheim, J.G., Kumar, K., 2011. Characterization of soil organic carbon in drained thaw-lake basins of Arctic Alaska using NMR and FTIR photoacoustic spectroscopy. *Org. Geochem.* 42, 947–954.
- Perminova, I.V., 2019. From green chemistry and nature-like technologies towards ecoadaptive chemistry and technology. *Pure Appl. Chem.* 91 (5), 851–864.
- Pukalchik, M., Panova, M., Karpukhin, M., Yakimenko, O., Kydralieve, K., Terekhova, V., 2018. Using humic products as amendments to restore Zn and Pb polluted soil: a case study using rapid screening phytotest endpoint. *J. Soils Sediments* 18, 750–761.
- Reimann, C., Ayraç, M., Chekushin, V.A., Bogatyrev, I., Boyd, R., de Caritat, P., Dutter, R., Finne, T.E., Halleraker, J.H., Jæger, Ø., Kashulina, G., Niskavaara, H., Lehto, O., Pavlov, V., Räisänen, M.L., Strand, T., Volden, T., 1998. Environmental geochemical atlas of the central barents region. NGU-GTK-CKE special publication, Trondheim.
- Schinner, F., Ohlinger, R., Kandeler, E., Margesin, R., 1996. *Methods in Soil Biology*.
- Tóth, G., Hermann, T., Da Silva, M.R., Montanarella, L., 2016. Heavy metals in agricultural soils of the European Union with implications for food safety. *Environ. Int.* 88, 299–309.
- ter Braak, C.J.F., 1987. Ordination. In: Jongman, H.J., ter Braak, C.J.F., van Tongeren, O.F.R. (Eds.), *Data Analysis in Community and Landscape Ecology*. Pudoc, Wageningen, pp. 91–173.
- Tregubova, P., Koptsik, G., Stepanov, A., 2019. Remediation of degraded soils: effect of organic additives on soil properties and heavy metals' bioavailability. *IOP Conf. Ser. Earth Environ. Sci.* 368, 012054.
- Vance, E.D., Brookes, P.C., Jenkinson, D.S., 1987. An extraction method for measuring soil microbial biomass C. *Soil Biol. Biochem.*
- Xu, H., Yu, G., Yang, L., Jiang, H., 2013. Combination of two-dimensional correlation spectroscopy and parallel factor analysis to characterize the binding of heavy metals with DOM in lake sediments. *J. Hazard Mater.* 263, 412–421.
- Xu, Y., Seshadri, B., Sarkar, B., Wang, H., Rumpel, C., Sparks, D., Farrell, M., Hall, T., Yang, X., Bolan, N., 2018. Biochar modulates heavy metal toxicity and improves microbial carbon use efficiency in soil. *Sci. Total Environ.* 621, 148–159.
- Yao, Z., Li, J., Xie, H., Yu, C., 2012. Review on remediation technologies of soil contaminated by heavy metals. *Procedia Environ. Sci.* 16, 722–729.
- Yin, H., Zhu, J., 2016. In situ remediation of metal contaminated lake sediment using naturally occurring, calcium-rich clay mineral-based low-cost amendment. *Chem. Eng. J.* 285, 112–120.