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Using industrial waste to reclaim acidic, heavy metal-contaminated soils in Arctic areas

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Abstract

This study evaluates the effectiveness of industrial waste-based ameliorants for the phytoremediation of disturbed lands. To conduct an experiment surface soil samples characterized by an acidic pH, polymetallic contamination, and heavy physical and mechanical composition were collected from industrial wastelands in the Arctic region. Lime and industrial waste, such as smelter slag, pulp and paper mill (PPM) ash, and ash from the combustion of alternative fuels based on municipal solid waste (MSW), were used to neutralize these samples. To assess the efficiency of soil neutralization and detoxification following the application of various ameliorants, the pH of aqueous and salt extracts of the original soil and the soil mixtures, as well as the content of mobile and water-soluble forms of heavy metals, were determined. A pot experiment with Indian mustard (*Brassica juncea*) was conducted to comprehensively assess soil mixtures availability for phytoremediation, followed by an assessment of the biometric parameters of its aboveground biomass and a determination of the rate of heavy metal accumulation in plant shoots and roots. *Brassica juncea* demonstrated high tolerance to polymetallic contamination, with good germination and survival. Phytostabilization was also found to be the primary mechanism for reducing of soil pollution levels. The studied industrial wastes demonstrated a high potential for neutralizing acidic soils contaminated with heavy metals, compared to traditional ameliorants. A decrease in soil acidity and an improvement in their physical and mechanical properties and elemental composition were observed. To obtain productive soil mixtures, the application rates of the studied industrial wastes into acidic soils contaminated with heavy metals, as well as the duration of the treatment period, were experimentally determined: 16-33 g/kg of slag (8-week neutralization), 7-14 g/kg of MSW ash, and 20-39 g/kg of PPM ash (3-4 weeks neutralization). Future research will explore the synergistic effects of adding humic and fulvic acids into contaminated soils.

Keywords

phytoremediation; phytotoxicity; acidic soil; heavy metals; Indian mustard (*Brassica juncea*); industrial waste; slag; ash; Arctic region

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Introduction

Pedogenesis in Arctic and Subarctic regions proceeds under harsh climatic conditions influenced by permafrost and associated cryogenic processes. Weakly developed pedogenic features, shallow profile thickness, poor structural organization, a pronounced gleyic horizon, and deformations resulting from the displacement of water-saturated soil material during freeze-thaw cycles characterize these soils [1, 2]. Among the most hazardous contaminants in Arctic soils are heavy metals, due to their high toxicity, environmental persistence, and capacity for biogenic migration. Currently, chemical methods such as leaching and transformation of metals into immobile forms are used to remediate soils of these elements. However, these approaches do not always yield the desired results and are often expensive [3, 4].

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Chemical pollution of Arctic soils is often accompanied by desertification and intensive erosion processes. Findings from studies conducted by Russian and international researchers [5-7], indicate that natural recovery of industrial wastelands in the Arctic is impossible. Apart from the high contamination levels and severe transformation of ecotopes due to anthropogenic activity, a major obstacle to such recovery is the lack of seed sources for both pioneer and late-successional plant species – a consequence of the severe climatic conditions, the vast extent of disturbed areas, and the limited dispersal capacities of these species.

However, there are many studies demonstrating the possibilities of using phytotechnologies for the reclamation of disturbed lands under Arctic conditions [8-10]. For example, at the Zapolyarny test site (Murmansk Region), works were carried out to establish an artificial phytocoenosis on technogenic substrate, using thermovermiculite and amendments derived from mining waste containing serpentine and other minerals, with planting of perennial grasses (*Elymus trachycaulus*, *Festuca rubra* and *Phleum pratense*) [11]. In the vicinity of Norilsk, long-term experiments on biological reclamation of disturbed lands were conducted, involving planting of cuttings of various willow species, several of which demonstrated high survival rates and good growth [12]. At experimental plots located within the zone of industrial wastelands near Monchegorsk (Murmansk Region), remediation of disturbed lands was performed by planting deciduous woody shrubs (willows and birches) and sowing perennial grasses, followed by long-term monitoring of the vegetation dynamics [13, 14]. The use of phytoremediation technologies for the restoration and decontamination of polluted and disturbed soils in Arctic territories remains a relevant and promising approach.

Soils with high levels of polymetallic contamination typically also exhibit an acidic reaction, which represents a significant limiting factor for their phytoremediation [15, 16]. Therefore, the restoration of such lands requires neutralization, which, in addition to reducing soil acidity, may also improve the physical and mechanical properties of the soil and reduce the mobility of heavy metals, thereby decreasing their hazard to plants. One of the most common and effective methods for neutralizing acidic soils is liming [17, 18]. Ground limestone (limestone flour) is one of the principal ameliorants used for liming. Natural calcareous fertilisers also include ground dolomite, marl, chalk, burnt lime (quicklime and slaked lime), calcareous tufa (spring lime), and alm (lake lime) [19].

Of great interest for the implementation of resource-saving technologies, reduction of accumulated waste and lowering the cost of reclamation measures is the use of industrial by-products for liming acidic soils. Among the already known and widely applied liming materials are wastes generated from the combustion of oil shale (oil-shale ash) and peat (peat ash), from the production of domestic gas in chamber furnaces (shale coke), as well as wastes from aluminum production (belite sludge), cement plants (cement dust), and sugar-beet processing (defecation lime) [20-22]. Less studied, but equally widespread and potentially suitable for liming, are ash from municipal solid waste (MSW) incineration, ash from pulp and paper mill (PPM) waste incineration, and smelter slag. The use of these residuals for the restoration of disturbed lands in the Arctic area is particularly relevant given the presence of metallurgical enterprises in the region (the Kola Mining and Metallurgical Company, Norilsk Nickel) and a major pulp and paper mill (the Arkhangelsk PPM). To address the problem of MSW disposal, which is especially acute in the Arctic area, Russian scientists are actively developing waste-to-energy (W2E) technologies [23-25]. Along with energy, thermal waste processing yields by-products, including ash, which can be used as a neutralizing soil amendment.

The main objective of this study was to examine the influence of neutralizing ameliorants based on industrial by-products on the effectiveness of phytoremediation of disturbed lands, and to determine the optimum application doses through the analysis and integration of biometric parameters and elemental composition data for Indian mustard (*Brassica juncea*) cultivated on polluted soils in the Arctic region.

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Methods

To conduct the research, soil samples were collected from the surface horizon of low-humus contaminated podzolic soils. These soils exhibit the characteristic features typical of man-made wastelands in the Arctic region, namely high levels of heavy metals, an acidic reaction, and a considerable proportion of physical clay (particles < 0.01 mm). All collected samples were thoroughly mixed to obtain a composite (averaged) model soil sample, which was then cooled and stored at +4 °C. A representative laboratory sample was subsequently taken from this model soil sample for further analyses at the Laboratory for Monitoring and Restoration of Arctic Ecosystems, Saint Petersburg Mining University.

Particle-size distribution was determined in accordance with the Russian State Standard GOST 12536-2014. Soil sample preparation for chemical analysis was performed in accordance with GOST 17.4.4.02-2017. The sample was air-dried, ground in an agate mortar, and sieved through a 1 mm mesh sieve. Soil moisture content was measured using a thermogravimetric analyzer TGA 701 (Leco, USA) in accordance with GOST 28268-89. The total content of metals, as well as their mobile and water-soluble forms, were determined following the certified analytical procedure M-MVI-80-2008 using an inductively coupled plasma optical emission spectrometer ICPE-9000 (Shimadzu, Japan). Mobile forms were extracted with an ammonium acetate buffer solution at pH 4.8. The pH values were measured in both aqueous and salt soil suspensions in accordance with GOST 26423-85 and GOST 26483-85, respectively. To calculate the required doses of neutralizing amendments, hydrolytic acidity was determined by the Kappen method according to GOST 26212-2021.

For an integrated assessment of the contamination of the model soil sample with heavy metals, the total contamination level indicator was calculated in accordance with Sanitary Rules and Regulations SanPiN 1.2.3685-21:

$$Z_c = \sum K_c - (n - 1),$$

where K_c – metal concentration coefficient, mg/kg; n – number of evaluated ingredients.

The concentration coefficient for each metal was calculated as the ratio of its actual concentration in the soil to the established regulatory maximum permissible concentration (MPC) or approximate permissible concentration (APC).

To neutralize the model soil sample, the following materials were applied: ground limestone (particle size ≤ 1 mm), used as a conventional ameliorant, and three industrial residuals relevant to the Arctic zone, namely smelter slag (particle size ≤ 1 mm), PPM ash and MSW ash. For each ameliorant, the neutralizing capacity was determined in accordance with ISO 20978:2020.

The designated dose of calcium carbonate required to neutralize the model soil sample was calculated using the formula:

$$D_{CaCO_3} = N_g \cdot 0.5,$$

где N_g – the value of hydrolytic acidity of the soil according to Kappen, mg·eq/100 g; 0.5 – the coefficient for converting milligrams to grams; the calculated dose D_{CaCO_3} = 7.85 g/kg.

The application rate of each type of ameliorant in physical mass was calculated using the formula:

$$D_{f.m} = (D_{CaCO_3} \cdot 10^6) / (N(100 - W)\,(100 - K),$$

где N – $CaCO_3$-equivalent neutralizing capacity of the ameliorant, %; W – ameliorant moisture, %; K – the number of particles larger than 1 mm, %.

At the first stage of the research, the effects of half and double doses were investigated in addition to the calculated full doses of the ameliorants. Because the model soil sample was characterized by a significant content of particles smaller than 0.01 mm, high density, and poor drainage, its physical and mechanical properties were improved by adding 10 wt.% of ground vermiculite (particle

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size ≤5 mm), a major deposit of which is located in the Murmansk Region (northwestern Russia). To carry out the neutralization process and prepare for the pot experiment, 1000 g of the prepared soil mixture with a moisture content equal to 50 % of the total field capacity, 100 g of ground vermiculite, and half, single, and double doses of the ameliorants were placed into 13 containers (in total 12 experimental variants). One sample was used as a blank control, with no neutralizing ameliorant added. The neutralization process was conducted over one month, with periodic watering of the samples with demineralized water. After incubation, the contents of each container were thoroughly mixed and homogenized. A representative sample was collected from each resulting soil mixture to determine the pH of aqueous and salt soil suspensions, as well as the content of mobile and water-soluble forms of metals, as described above.

Brassica juncea was selected for the pot experiment due to a number of reasons:

• based on the literature review, Indian mustard exhibits high tolerance to contamination and is recognized as a hyperaccumulator of a number of heavy metals [26, 27];

• it is suitable for cultivation in poor soils with a slightly acidic to alkaline pH range, is frost-hardy and drought-resistant, and is capable of growing under the harsh climatic conditions of the Arctic zone [28];

• it is recognized as a green manure crop, meaning it can enrich the soil with nutrients and improve its structure, which will subsequently has a beneficial effect on soil health and promotes natural revegetation of disturbed lands while minimizing erosion processes [29, 30];

• it is characterized by rapid growth and biomass accumulation, and is capable of intensively accumulating heavy metals as early as the juvenile stage of development, which is crucial for the short growing season of the Arctic zone [31].

To set up the pot experiment, 100 g portions of the resulting soil mixtures were placed into cell trays, with 9 replicates for each variant. A universal potting soil was used as a reference; the pH of aqueous and salt suspensions and metal content were also determined for this reference sample as described above. Indian mustard was sown at a rate of 9 seeds per cell, which corresponded to the recommended seeding rate of 250 g per 10 m^2. The trays were placed in a closed climate-controlled grow box equipped with ventilation and intense artificial lighting. The air temperature within the working zone of the box was maintained at +15 °C during the day and +8 °C at night, with a relative humidity of 37 and 85 %, respectively. The photoperiod was set at 12 h. Periodic watering was performed using low-mineralized water.

For the pot experiment, natural (continuous) phytoextraction was selected as the most accessible technology compared to induced phytoextraction, as it does not require the application of additional expensive amendments [32]. Due to the high content of mobile and water-soluble forms of heavy metals in the model soil sample, additional stimulation of their transition into bioavailable forms was not required. Fertilization was also omitted in order to assess the feasibility of reclaiming disturbed lands with minimal costs and minimal external impact on fragile Arctic ecosystems.

After 6 weeks of cultivation, the plants were harvested by cutting the aboveground parts, after which the root systems were carefully extracted and thoroughly rinsed with distilled water. Biometric parameters of the aboveground biomass (shoot length and weight) were measured for each individual cell, and the data were then averaged. Subsequently, the collected plants were air-dried (shoots with leaves and roots separately) and ground in an agate mortar. From the resulting samples, 0.1 g aliquots were taken and subjected to wet digestion using concentrated nitric acid (2 ml) and hydrogen peroxide (2 ml) in a microwave digestion system Multiwave 3000 (Anton Paar, Austria). After cooling, the digests were quantitatively transferred into 20 ml polyethylene volumetric tubes and made up to volume with distilled water. All samples were run in duplicate, and blank solutions were prepared using the same reagents. The resulting solutions were analyzed by inductively coupled plasma atomic emission spectrometry on an ICPE-9000 (Shimadzu, Japan). To assess the intensity of heavy metal

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accumulation under the conditions of each resulting soil mixture, the bioaccumulation coefficient (BAC) was calculated as the ratio of the pollutant concentration in the air-dry biomass of the plants to the concentration of their mobile forms in the substrate. The BAC was calculated separately for plant shoots and roots. To evaluate the efficiency of element transport from underground to above-ground plant organs, the translocation factor T_F was calculated as the ratio of the pollutant concentration in the shoots to that in the roots.

An important characteristic of the successful neutralization of acidic soils is the durability of the ameliorative effect [33]. Therefore, following the pot experiment, the pH values for the water and salt extracts from the soil mixtures were redetermined. Based on the results obtained after the first stage of the research, a second stage of the experiment was designed to evaluate the application of 1/4, 1/8, and 1/16 of the calculated doses of industrial waste-based ameliorants, totaling 9 variants. The pre-neutralization time was increased to two months.

Discussion of results

Based on the particle size distribution analysis, and taking into account the podzolic type of soil formation, the studied model soil sample was classified as medium loam according to Kachinsky's classification. The predominant fraction was medium silt (39 %), followed by coarse silt (24 %). The pH values measured in aqueous and salt extracts from the model soil sample were pH_{H_2O} = 4.71 and pH_{KCl} = 3.52, respectively, indicated that the studied sample could be characterized as strongly acidic. The hydrolytic acidity determined by the Kappen method was 15.7 mg·eq/100 g. The results of determining the main metal content in the model soil sample are presented in Table 1.

According to the data presented in Table 1, the values of the total contamination index Z_c = 42 for the total metal content and 187 for their mobile forms, the pollution degree of the studied soil sample falls into the hazardous and extremely hazardous categories, respectively. Notably, the content of essential nutrients (K, Ca, and Mg) was low.

Table 1

Average values of the elemental profile in a model soil sample

Element	Total content[1], mg/kg / MPC (APC)[2]	Mobile form[1], mg/kg / MPC (APC)[2]	Water-soluble form[1], mg/kg
Al	36396 / n/s[3]	218 / n/s	4.7
Ba	402 / n/s	18 / n/s	0.25
Ca	12060 / n/s	199 / n/s	50
Cd	13 / 1.0	2,5 / n/s	0.12
Co	71 / n/s	1,8 / 5.0	0.12
Cr	595 / n/s	1,0 / 6.0	0.036
Cu	1595 / 66	427 / 3.0	7.2
Fe	47392 / n/s	23 / n/s	3.4
K	8458 / n/s	24 / n/s	5.3
Mg	12287 / n/s	165 / n/s	21
Mn	962 / 1500	64 / 60	3.7
Na	9251 / n/s	5,6 / n/s	4.6
Ni	255 / 40	8,4 / 4.0	0.41
Pb	128 / 65	2,1 / 6.0	0.13
Sr	141 / n/s	1,9 / n/s	0.42
Zn	784 / 110	377 / 23	13

Notes: 1. In accordance with the certified analytical procedure M-MVI-80-2008, the analytical error for all element forms and all elements was 30 %.
2. In accordance with SanPiN 1.2.3685-21.
3. Is not standardized.

The results of the neutralizing capacity determination, as well as the calculated application rates of the neutralizing ameliorants, are presented in Table 2.

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Table 2

Neutralizing capacity of liming materials and calculated application rates

Ameliorant	CaO, %	$CaCO_3$, %	$D_{f.m}$, g/kg
Lime, $d \leq 1$ mm	22.2	39.6	19.8
Slag, $d \leq 1$ мммм	6.7	12.0	65.6
MSW ash	7.8	13.9	56.4
PPM ash	5.6	10.0	78.5

The results of the study of the model soil samples after neutralization are presented in Fig.1. In the blank control (soil + vermiculite without a neutralizing ameliorant), no significant changes in acidity or the content of water-soluble and mobile forms of metals were detected compared to the initial model soil sample. In all soil mixtures with the addition of ameliorants (Fig.1), a significant increase in pH value occurred, and the resulting soil mixtures were within the range from moderately acidic to alkaline. In this regard, MSW and PPM ashes proved to be the fastest and strongest neutralizers. Even a half dose of these ameliorants led to excessive soil alkalization, which is likely associated with the fine particle size and the fact that the neutralizing agents they contain are in hydroxide form. The positive effect from the application of PPM ash to the soil may also be due to an increase in the content of P, N, and organic C contained in this type of waste. Furthermore, an increase in the water-holding capacity was noted in the soil mixtures amended with these ameliorants, which is also a favorable factor. Slag turned out to be the weakest neutralizer; the application of its single dose was sufficient to obtain a soil mixture with a neutral acidity level. The application of a half dose of slag allowed neutralizing the model soil sample to a moderately acidic level. Lime showed better neutralization results compared to slag: a half dose application was sufficient to obtain a soil mixture with a neutral acidity level. When assessing the duration of maintaining the neutralization effect, an increase in pH was noted in all soil mixture samples after the pot experiment, with the most significant pH increase observed in the samples where slag was applied as the neutralize.

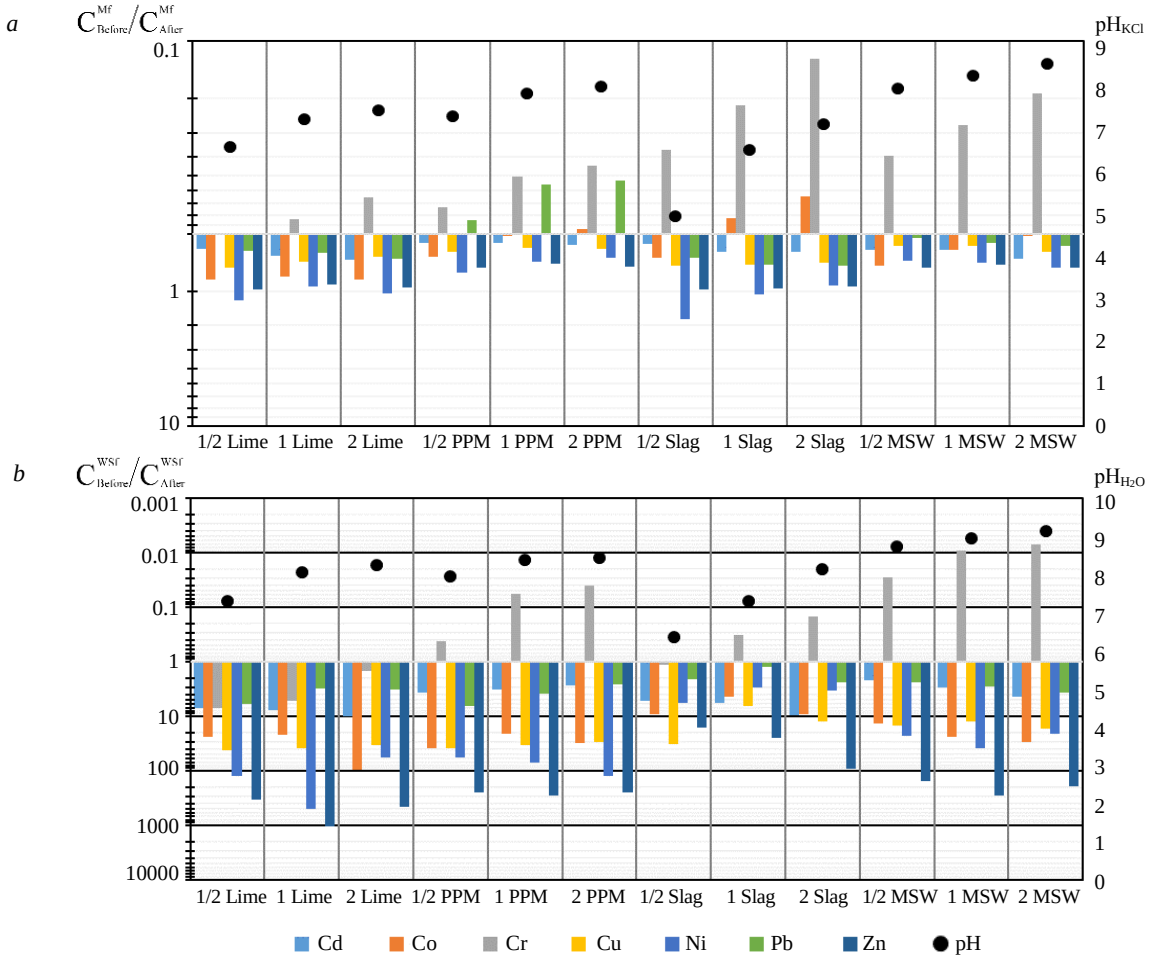


Fig.1. Ratio of mobile (*a*) and water-soluble (*b*) forms of heavy metals in soil samples before and after neutralization (C^{Mf}, C^{WSf}) and pH values of aqueous and salt suspensions (Experiment 1)

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In addition to acidity, the content of mobile and water-soluble forms of heavy metals is an important factor for the successful cultivation of plants on contaminated soils. As can be seen from Fig.1, *a*, the decrease in the content of mobile metal forms is negligible, while the concentration of mobile Cr forms increased in all resulting soil mixtures, with a clear upward trend correlating with the rise in pH value. The highest increase in mobile Cr forms was observed when slag and MSW ash were added to the soil. In certain soil mixture variants, a slight increase in mobile forms of Co and Pb was also noted. This is likely due to the content of these elements in the ameliorants themselves. It is important to note that even in these cases, the concentrations of mobile Cr, Pb, and Co forms in the resulting soil mixtures do not exceed the MPC according to SanPiN 1.2.3685-21. Meanwhile, a downward trend in migratory ability can be observed observed for all water-soluble forms of heavy metals, except for Cr (Fig.1, *b*). In all soil mixtures obtained after neutralization, the content of water-soluble Zn, Co, Ni, and Cu forms decreased most significantly (by 10-1000 times), which may favorably affect the germination and survival rates of the planted crops.

The results of the second experiment with adjusted application rates and durations of preliminary neutralization of the soil mixtures are presented in Fig.2.

As can be seen from Fig.2, due to the longer duration of preliminary soil neutralization, even 1/16 of the calculated slag application rate is sufficient to obtain soil with a slightly acidic reaction. However, in this case, the efficiency of heavy metal binding decreases significantly, and the amount of their water-soluble forms increases sharply compared to the soil mixtures obtained by applying 1/8 and 1/4 of the slag rates. A similar situation is observed with the application of PPM ash. In the remaining soil mixture variants, as in the first experiment, a decrease in all water-soluble and mobile metal forms was noted, except for Cr.

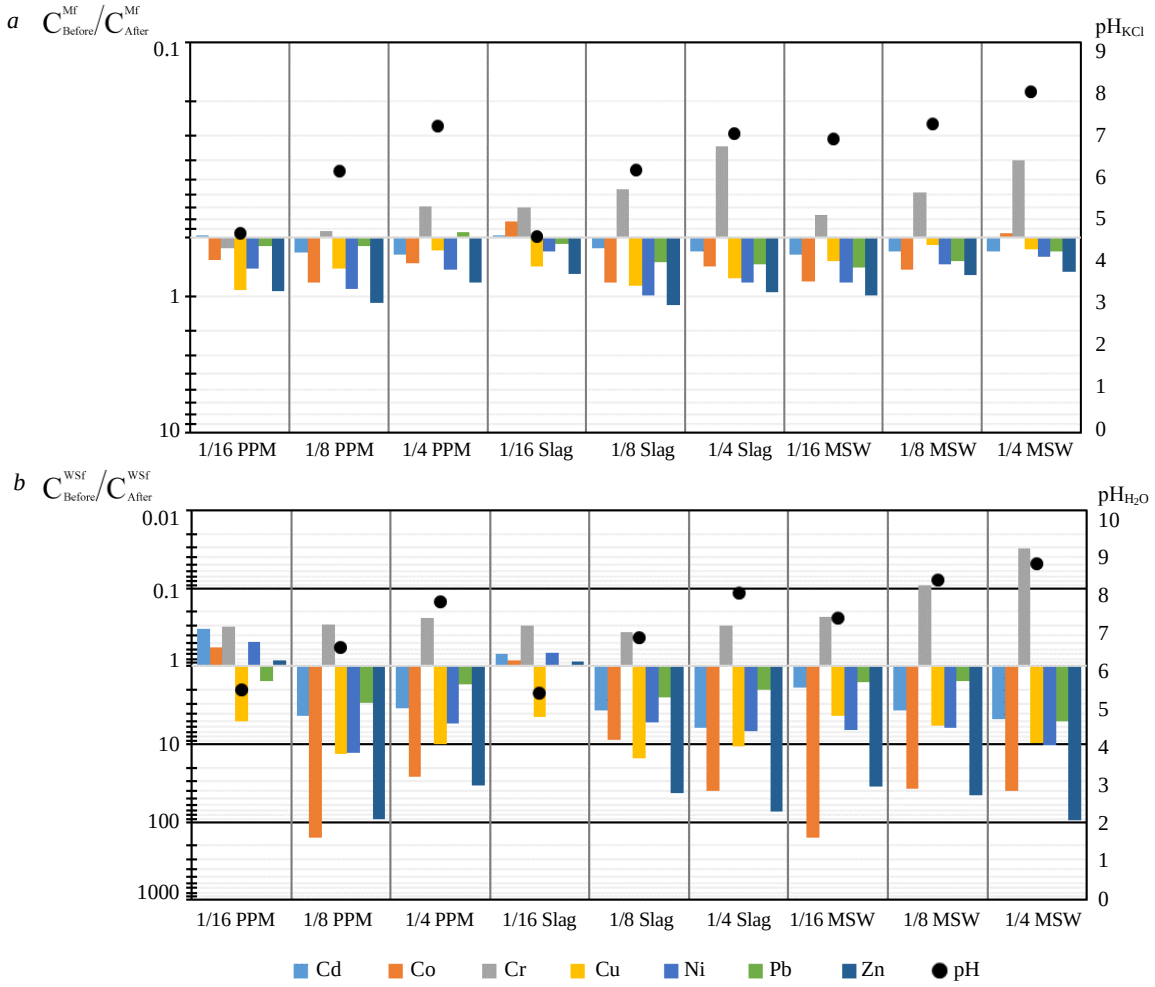


Fig.2. Ratio of mobile (*a*) and water-soluble (*b*) forms of heavy metals in soil samples before and after neutralization (C^{Mf}, C^{WSf}) and pH values of aqueous and salt suspensions (Experiment 2)

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In the first experiment, in all experimental variants, except for the blank control (soil + vermiculite without a neutralizing ameliorant), the seeds germinated on the 4th day after planting. The average germination rate was 75 %. In the blank control experiment, seedlings emerged on the 7th day after planting, but no further plant development occurred. In all other variants, a developmental delay was noted compared to the reference: true leaves appeared later and were smaller, shoots were shorter, and internodes were reduced. After 5 weeks, the flowering stage began in plants grown in model soil samples amended with PPM and MSW ashes, as well as in the reference sample of universal potting soil. For plants grown in model soil samples with the addition of slag and lime, flowering was recorded 6 weeks after sowing. This trend is likely associated with the enrichment of the soil with nutrients contained in the ashes, which favorably affects plant development.

In the second pot experiment with lower ameliorant application rates, a similar pattern was observed. However, with the application of 1/16 rate of the slag and 1/16 rate of the PPM ash, a decrease in the germination rate to 60 %, a delay in seedling emergence (only on the 5-6th day after planting), and a subsequent cessation of their development were noted. This is consistent with the chemical analysis data of the resulting soil mixtures (Fig.2), according to which an elevated content of mobile and water-soluble forms of heavy metals are observed in the variants under consideration.

The results of measuring the biometric parameters of the aboveground plant biomass are presented in Table 3.

Table 3

Average biometric parameters of above-ground plant biomass for 9 replicates

Sample	Average shoot length, cm	Average shoot mass, g	Reaching the generative stage
Reference (universal potting soil)	29	2.7250	Yes
1/2 Lime	11	0.7735	Yes
1 Lime	11	0.8319	Yes
2 Lime	12	0.9069	Yes
1/16 Slag	1	0.0851	No
1/8 Slag	8	0.6698	No
1/4 Slag	9	0.7041	Yes
1/2 Slag	10	0.7338	Yes
1 Slag	10	0.8406	Yes
2 Slag	11	0.8865	Yes
1/16 MSW	7	0.5512	No
1/8 MSW	8	0.5584	Yes
1/4 MSW	10	0.6155	Yes
1/2 MSW	10	0.6287	Yes
1 MSW	9	0.6129	Yes
2 MSW	8	0.6038	Yes
1/16 PPM	1	0.0602	No
1/8 PPM	10	0.8656	No
1/4 PPM	11	0.9985	Yes
1/2 PPM	12	1.0356	Yes
1 PPM	10	0.8110	Yes
2 PPM	9	0.7211	Yes

As shown in Table 3, a decrease in biological productivity was observed for all prepared soil mixture samples compared to the universal potting soil. However, the attainment of the generative stage by plants in most experimental variants indicates the high potential of the obtained soil mixtures, as well as of *Brassica juncea*, for creating an anti-erosion cover in the disturbed areas of the Arctic zone. As noted above, the low productivity of the soil mixtures prepared with the application of 1/16 rate of the slag and 1/16 rate of the PPM ash is associated with the high toxicity of these samples. The decline in plant biological parameters and the absence of flowering 6 weeks after sowing in the remaining samples with reduced ameliorant application rates are likely due to the soil mixture structure and a low amount of nutrient components, which is consistent with the assumption regarding the combined effect of the selected ameliorants. The maximum biomass values were observed in the experimental variants with

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the application of 1/2 calculated rate of the PPM ash. This is explained, on the one hand, by the optimal pH value of the resulting soil mixture and, on the other hand, by the improvement of its physical and mechanical properties and increased nutritional value due to valuable macro-, micro-, and organic elements contained in the ash, as well as by the reduction in toxicity, owing to the decreased migration ability of heavy metals.

MSW ash proved to be the most potent ameliorant; even 1/16 of its calculated application rate is sufficient to adjust soil acidity and reduce the bioavailability of heavy metals. However, its application demonstrated lower efficacy compared to the other studied ameliorants. On the one hand, the application of high doses of MSW ash leads to excessive soil alkalinization and an increase in the content of bioavailable forms of Cr originating from the ameliorant. On the other hand, low application rates do not provide the necessary improvement in the physical and mechanical properties of the soil or an increase in its nutritional content.

The results of measuring the pH values of the soil mixtures after the pot experiment are presented in Fig.3.

As can be seen from Fig.3, *a*, *b*, a significant increase in pH is observed after completion of the first experiment in the soil mixtures prepared by adding slag, which is consistent with the assumption of its prolonged effect. Meanwhile, the increase in the pH value in the remaining samples is insignificant. With an increase in the duration of preliminary neutralization from 1 to 2 months, the process proceeds more completely (Fig.3, *c*, *d*), which allows for the adjustment of the slag application rate [34].

The results of calculating the biological accumulation coefficients (BAC) of heavy metals by *Brassica juncea* and the translocation factors are given in Table 4. Due to the insignificant biomass of roots and shoots in the soil mixture amended with 1/16 rate of PPM ash, as well as roots in the soil mixture amended with 1/16 rate of slag, the heavy metal content in them was not determined.

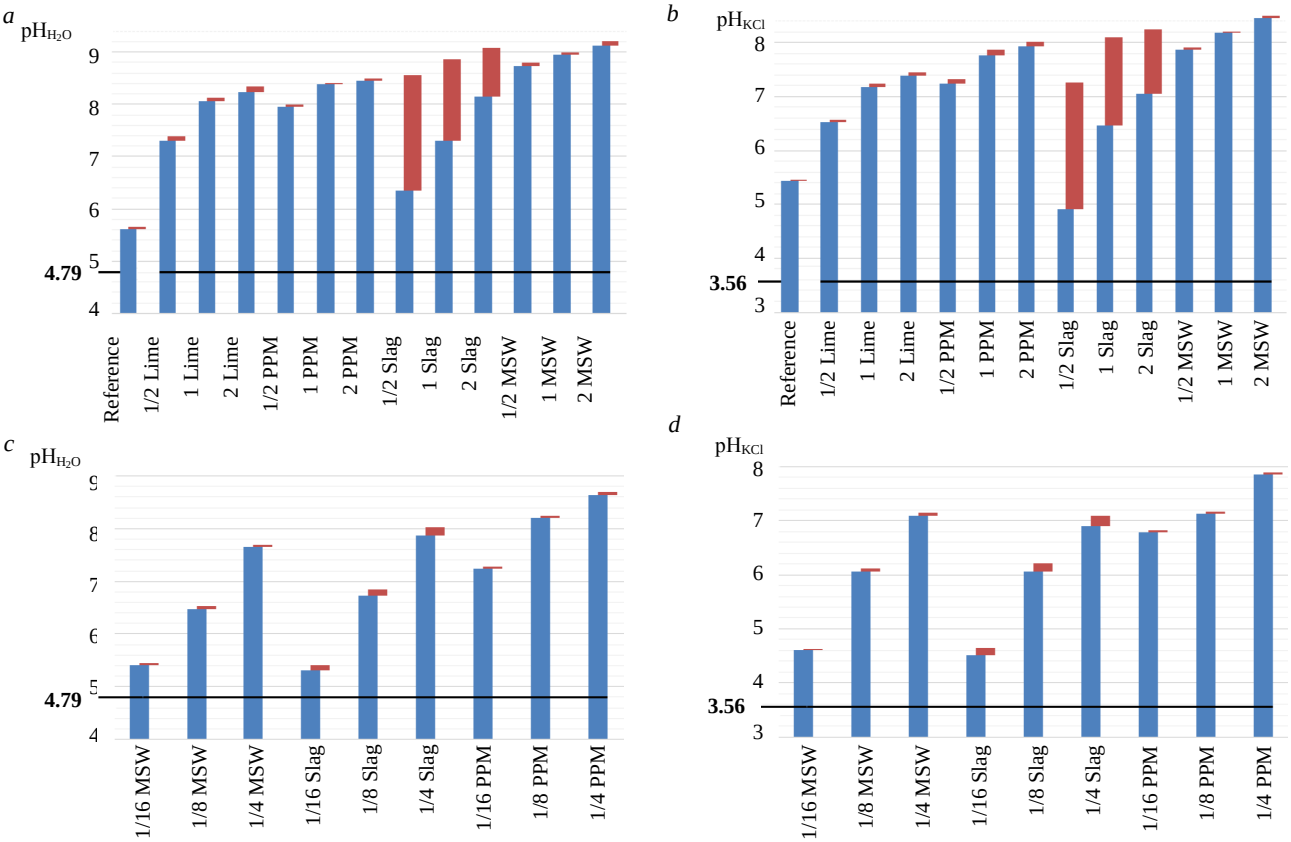


Fig.3. Dynamics of pH changes in soil mixtures after the pot experiment:
a – pH values of aqueous suspensions; *b* – pH values of salt suspensions (Experiment 1);
c – pH values of aqueous suspensions; *d* – pH values of salt suspensions (Experiment 2)
4,79 (3,56) – initial pH value of the model soil sample before neutralization, – pH value of the soil samples before pot experiment;
– pH value of the soil samples after pot experiment

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Table 4

Biological accumulation coefficients of heavy metals in shoots and roots of *Brassica juncea* from soil mixtures and the reference soil sample

Sample / Element	BAC Shoots/Roots ‖ T_F						
	Cd	Co	Cr	Cu	Ni	Pb	Zn
Reference	13/28 ‖ 0.46	7/40 ‖ 0.18	28/114 ‖ 0.22	5/101 ‖ 0.05	24/105 ‖ 0.23	2 / 7 ‖ 0.29	10 / 12 ‖ 0.83
1/2 Lime	4.4/7.1 ‖ 0.62	0.25/8.7 ‖ 0.36	2.0/45 ‖ 0.04	0.08/1.6 ‖ 0.05	0.72/16 ‖ 0.05	0.42/7.8 ‖ 0.05	0.78/1.1 ‖ 0.71
1 Lime	4.9/7.4 ‖ 0.66	0.15/6.7 ‖ 0.02	1.1/20 ‖ 0.06	0.09/1.1 ‖ 0.08	0.52/12 ‖ 0.04	0.58/7.5 ‖ 0.08	0.65/0.94 ‖ 0.69
2 Lime	5.0/6.8 ‖ 0.74	0.18/6.6 ‖ 0.03	1.6/26 ‖ 0.06	0.09/1.1 ‖ 0.08	1.6/16 ‖ 0.1	0.76/9.4 ‖ 0.08	0.60/0.92 ‖ 0.65
1/16 Slag	4.0/ – ‖ –	5.7/ – ‖ –	17/ – ‖ –	1.9/ – ‖ –	8.9/ – ‖ –	9.3/ – ‖ –	3.4/ – ‖ –
1/8 Slag	4.1/5.1 ‖ 0.80	2.3/7.0 ‖ 0.33	0.71/17 ‖ 0.04	0.32/2.4 ‖ 0.13	1.4/58 ‖ 0.02	0.85/9.1 ‖ 0.09	0.94/1.4 ‖ 0.67
1/4 Slag	3.5/5.4 ‖ 0.65	1.0/7.2 ‖ 0.14	0.88/29 ‖ 0.03	0.34/2.8 ‖ 0.12	1.1/36 ‖ 0.03	0.7/8.2 ‖ 0.09	1.1/1.3 ‖ 0.85
1/2 Slag	3.1/5.4 ‖ 0.57	0.38/7.6 ‖ 0.05	1.1/29 ‖ 0.04	0.11/2.0 ‖ 0.06	1.4/24 ‖ 0.06	0.66/8.5 ‖ 0.08	0.91/1.5 ‖ 0.61
1 Slag	2.4/2.6 ‖ 0.92	0.15/2.3 ‖ 0.07	0.6/10 ‖ 0.06	0.08/0.88 ‖ 0.09	1.1/12 ‖ 0.09	0.57/10.0 ‖ 0.06	0.58/0.89 ‖ 0.65
2 Slag	2.1/2.6 ‖ 0.81	0.05/1.7 ‖ 0.03	0.2/4.4 ‖ 0.05	0.08/1.0 ‖ 0.08	1.0/11 ‖ 0.09	0.50/6.5 ‖ 0.08	0.52/0.86 ‖ 0.60
1/16 MSW	6.8/8.0 ‖ 0.85	0.72/6.8 ‖ 0.11	1.0/13 ‖ 0.08	0.28/2.4 ‖ 0.12	0.76/6.6 ‖ 0.12	1.6/11 ‖ 0.15	1.2/1.5 ‖ 0.80
1/8 MSW	6.3/7.2 ‖ 0.88	0.42/6.1 ‖ 0.07	1.7/15 ‖ 0.11	0.32/1.9 ‖ 0.17	0.56/7.8 ‖ 0.70	1.6/10 ‖ 0.16	0.71/1.0 ‖ 0.71
1/4 MSW	4.1/6.9 ‖ 0.59	0.43/5.5 ‖ 0.08	2.2/28 ‖ 0.08	0.34/2.1 ‖ 0.16	0.70/7.5 ‖ 0.09	1.3/9.3 ‖ 0.16	0.69/1.2 ‖ 0.58
1/2 MSW	3.5/6.8 ‖ 0.51	0.25/5.5 ‖ 0.05	2.0/38 ‖ 0.05	0.11/1.2 ‖ 0.09	0.58/11 ‖ 0.05	0.82/9.7 ‖ 0.08	0.43/1.1 ‖ 0.39
1 MSW	2.7/5.1 ‖ 0.53	0.25/4.5 ‖ 0.06	2.0/40 ‖ 0.05	0.12/1.0 ‖ 0.12	0.59/10 ‖ 0.06	0.90/8.4 ‖ 0.11	0.42/0.87 ‖ 0.48
2 MSW	2.1/4.2 ‖ 0.50	0.18/2.7 ‖ 0.07	1.8/39 ‖ 0.05	0.10/0.86 ‖ 0.12	0.81/7.1 ‖ 0.11	0.27/6.9 ‖ 0.04	0.47/0.79 ‖ 0.59
1/8 PPM	9.2/10 ‖ 0.92	0.86/11 ‖ 0.08	2.0/27 ‖ 0.07	0.32/3.0 ‖ 0.11	0.91/11 ‖ 0.08	2.0/17 ‖ 0.12	1.3/2.1 ‖ 0.62
1/4 PPM	8.8/8.9 ‖ 0.99	0.47/6.8 ‖ 0.07	1.8/25 ‖ 0.07	0.27/2.9 ‖ 0.09	0.94/10 ‖ 0.09	1.6/14 ‖ 0.11	0.88/2.2 ‖ 0.40
1/2 PPM	4.9/9.3 ‖ 0.53	0.32/7.0 ‖ 0.05	3.5/33 ‖ 0.11	0.06/1.2 ‖ 0.05	1.0/13 ‖ 0.08	0.45/9.3 ‖ 0.05	0.43/1.1 ‖ 0.39
1 PPM	5.3/8.9 ‖ 0.60	0.16/4.6 ‖ 0.03	1.3/32 ‖ 0.04	0.08/2.1 ‖ 0.04	0.43/9.5 ‖ 0.05	0.32/6.9 ‖ 0.05	0.51/1.2 ‖ 0.43
2 PPM	5.6/11 ‖ 0.51	0.18/4.2 ‖ 0.04	1.3/31 ‖ 0.04	0.11/1.2 ‖ 0.09	0.43/9.1 ‖ 0.05	0.34/6.2 ‖ 0.05	0.65/1.2 ‖ 0.52

According to Table 4, the accumulation intensity of the heavy metals under consideration by *Brassica juncea* from the unpolluted soil sample (reference) is 5-20 times higher than from the soil mixtures with an extremely hazardous pollution level. This is explained by the functioning of the plant's ecoprotective mechanism under conditions of polymetallic stress. For all studied elements, the translocation factor was less than one ($T_F < 1$), and their distribution within the plant organs followed an acropetal pattern, which also indicates the high tolerance of *Brassica juncea* to heavy metal contamination of the substrate [34]. At the same time, the root system, acting as the primary buffer zone of the plants, exhibits intensive accumulation of all considered heavy metals. Only Cd and Cr, as well as partially Ni (its intensive accumulation in shoots was noted only in certain soil mixture variants), can be classified as elements of strong accumulation in shoots. The remaining metals accumulated in the *Brassica juncea* shoots are classified as elements of medium uptake. Among the studied heavy metals, the most efficient translocation from roots to aboveground organs was noted for Zn and Cd (geochemical analogues) [35]. Notably, the intensity of Cd accumulation is approximately an order of magnitude higher than that of Zn.

A trend toward an increase in the intensity of heavy metal accumulation by plants can be noted with a decrease in the application rate of the neutralizing ameliorant. This is due to an increase in the content of bioavailable forms of metals in the soil mixtures as their acidity rises, as well as an enhanced bioaccumulation capacity of the plants with a decrease in the medium pH [36]. A decrease in the application rate of the neutralizing ameliorant leads to a decline in the productivity of the soil mixtures (Table 4), and consequently, to a reduction in the total amount of extracted heavy metals. In the case of applying 1/16 of the calculated rate of slag and PPM ash, the plants exhibit very poor development of the root system, which prevents the formation of an antierosion cover. It is likely that the application of low doses of neutralizing amendments will also require more frequent periodic liming to maintain the neutral acidity of the soil mixtures.

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Conclusion

Based on the results obtained, the following conclusions can be formulated, and a plan for further research on the restoration of disturbed Arctic lands using phytotechnology can be outlined.

• A high potential of the studied industrial wastes (slag, MSW ash and PPM ash) for neutralization of acidic soils contaminated with heavy metals was established in comparison with the traditional ameliorant (lime). Their application not only changes soil acidity but also improves its physical and mechanical properties and elemental composition. Secondary contamination of the treated soils from the industrial waste application is insignificant, owing to the reduced mobility of heavy metals due to an increase in pH. All variants of the resulting soil mixtures showed an increase in mobile and water-soluble forms of Cr, as well as a slight increase in the content of mobile forms of Pb and Co, with the addition of PPM ash and slag, respectively. At the same time, the total soil pollution level decreased, and the soils were enriched with nutrients such as Ca, Mg, K, and Na, and, in the case of PPM ash addition, enrichment with P, N, and organic C was also observed.

• It was established that the main limiting factor in the remediation of the studied acidic soil sample contaminated with heavy metals is its phytotoxicity, namely the content of mobile and water-soluble (bioavailable) forms of metals, which decreases with increasing the pH of the soil mixture. Moreover, the efficiency of phytoextraction is inversely proportional to the pH of the soil mixture. In order to obtain productive soil mixtures that ensure normal development of the plant root system and enable them to reach the generative stage, while at the same time promoting effective phytoextraction, the following application-rate ranges for the studied industrial wastes were identified: 1/4-1/2 of the calculated dose of slag (16-33 g/kg); 1/8-1/4 of the calculated dose of MSW ash (7-14 g/kg) and 1/4-1/2 of the calculated dose of PPM ash (20-39 g/kg).

• MSW ash proved to be the strongest ameliorant. However, its application showed lower effectiveness compared with the other studied ameliorants (see Table 3). On the one hand, the application of high doses of MSW ash leads to excessive soil alkalization and an increase in the content of bioavailable forms of Cr, which is its component; on the other hand, low application rates do not provide the necessary improvement in the soil's physical and mechanical properties or its nutrient status, which affects the productivity of the resulting soil mixtures. To improve the productivity of such soil mixtures, additional application of organomineral fertilisers is possible. Slag proved to be a long-acting ameliorant, requiring approximately 8 weeks for preliminary neutralization, whereas the MSW ash and PPM ash require only 3-4 weeks, which is due to their different composition and, above all, the particle size of the studied wastes.

• *Brassica juncea* demonstrated high tolerance to polymetallic contamination and good germination and survival across a wide range of soil pH, confirming its potential for use in creating erosion-resistant vegetation on disturbed lands. Despite the intense accumulation of all the heavy metals considered (Cd, Co, Cr, Cu, Ni, Pb, Zn) in the root system, their translocation to the aboveground plant organs was low, suggesting that phytostabilization will be the primary mechanism for reducing the risk associated with contaminated soils in this case. Combined with the green manure properties of *Brassica juncea* and its short growing season, this may facilitate the rapid establishment of pioneer vegetation in contaminated areas, as well as the improvement of the soil ecosystem and increased fertility for the subsequent restoration of natural succession.

• Further research on the restoration of disturbed Arctic lands using phytotechnology also includes the study of induced phytoextraction. This involves studying the effects of adding humic and fulvic acids to contaminated soils. These acids, on the one hand, bind heavy metals in the soil into stable complexes and help stabilize soil acidity, thereby performing a bioprotective function, and, on the other hand, intensify the uptake of metals from contaminated soil by plants.

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