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## RESEARCH ARTICLE

# Rehabilitation of Industrial Barren in Arctic Region Using Mining Wastes

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### Abstract:

#### Background:

This work has explored the possibility of applying mining waste-based ameliorants for the remediation of soil that has been transformed by copper-nickel smelter emissions by means of forming artificial phytocenosis.

#### Objective:

The aim of our work was to propose, develop and approbate a technique for the preservation of dumps polluted by heavy metals and prevention of their erosion by creating dense grass covers with the use of wastes from mining and processing enterprises to form a supporting substrate for herbaceous plants.

#### Methods:

The vegetative cover was cultivated on a supporting medium, consisting of mining waste, with a hydroponic vermiculite substrate and a mix of graminaceous plant seeds, indigenous to the study area and resistant to heavy metal pollution. The mining wastes, used in the experiment, contained acid-neutralizing minerals such as calcium and magnesium carbonate and hydrous magnesium silicate.

#### Results:

It is shown that, due to a large pool of Ca and Mg, these mineral substrates are alkaline (pH 8.4 – 9.2) and can perform successfully in optimizing of edaphic conditions for the plant communities grown on industrial barrens. In a pilot experiment without a proposed supporting medium, the plants did not form a stable grass cover and had died out by the beginning of the third growing season, whereas the experimental plots with a proposed supporting medium (waste-based substrate) developed a high-quality grass cover by the end of second vegetation seasons.

#### Conclusion:

The resulting plant communities grown on a proposed supportive medium is found to be resistant to aerotechnogenic pollutants and capable of independent survival, representing the initial stage of progressive succession in the presence of on-going pollution.

**Keywords:** Rehabilitation, Copper-nickel smelter, Industrial barren, Mining wastes, Ameliorant, Phytoremediation.

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## 1. INTRODUCTION

It is well-known that the industrial mining and processing of natural resources damages the biogeosystems adjacent to industrial sites (Crawford 1995, Remon *et al.* 2005). Some of the examples are the technogenic geochemical anomalies that have developed in some parts of North-West Russia in the immediate vicinity of large sources of pollution, such as enterprises of non-ferrous metallurgy (Dauvalter *et al.* 2011).

Any metallurgical production is accompanied by voluminous emissions of toxic compounds into the atmosphere (acid-causing substances, Heavy Metal (HM) compounds, *etc.*) (Ali *et al.* 2015). Being present in the soil in a labile form and migrating and/or transforming into phytoavailable forms, these toxicants become a source of prolonged environmental pollution, creating extreme conditions for the biota survival phytoavailable (Zhou *et al.* 2007). This situation leads to technogenic wasteland formation – area with dead vegetation and eroded soils with significantly elevated concentration of heavy metals. For example, in the Sudbury mining and smelting region in Canada, large areas have been contaminated with heavy metals around the industrial plants, where the plant impact zones have turned into industrial barrens (Adamo *et al.* 1996). It is noted that the improvement of air quality does not result in full recovery of vegetation under significantly reduced emissions and even under closed production.

Northern ecosystems are most vulnerable to anthropogenic contamination (Moiseenko *et al.* 2006). Destruction of the upper soil layers dramatically affects the local climate, which becomes evident in the increasing wind velocity, deeper frost penetration in winter, earlier thaws in spring, earlier summer droughts, and a more intensive heat penetration during the summer (Kozlov *et al.* 2006). The lack of forest leaf litter (a storage of heavy metals), fresh leaf and plant shedding, combined with mineralization of the earlier accumulated organic matter, causes the soil to degrade and fail to provide mineral nutrition for the plants, leading to the loss of the entire vegetation cover (Kozlov *et al.* 2006) and the soil horizon (Kashulina *et al.* 2010).

These degradation processes, combined with the on-going aerotechnogenic pollution and severe climatic conditions, hinder the natural progressive succession, or totally inhibit it (Kalabin, Yevdokimova and Gorny 2010). Remediation of such areas requires developing of innovative methods taking into account the regional specifics.

International experience on the remediation of derelict lands around copper-nickel smelters (Singh and Prasad 2011) has revealed that the restoring of the vegetation cover cannot be achieved through mere improvement of the quality of atmospheric air, significant reducing of emissions, or even the shutting down of the contaminating plants. The main factor limiting the vegetation recovery on industrial barrens is the irreversible degradation of soil (Vangronsveld, Assche and Clijsters 1995).

The authors (Kabata-Pendias and Pendias 1989) believe that the soil contamination by HM is stable, “eternal”. In this case the natural anthropogenic objects are incapable of self-purification so that the soil will remain permanently contaminated, resisting all the attempts of remediation. Nonetheless, the problem of soil detoxification from HM is being actively explored (Bernardino *et al.* 2016); much research is devoted to biomelioration due to the inefficiency of engineering technologies in this case.

Generally, there are two remediation strategies: cleanup and containment (Koptsik 2014). The first one is to reduce total concentration of pollutants to a maximum allowed level. The second one is to reduce pollutant mobility and bioavailability. In this case, soil can be treated in two ways: *ex situ* (off-site) and *in situ* (on the site).

The most common *in situ* remediation methods include strict remediation (chemical washing and cementation) and mild (passive) remediation. Mainly, there are such mild remediation methods as phytoextraction, phytostabilization and immobilization. (Koptsik 2014) Phytoextraction method requires plants-hyperaccumulators, but there are no such plants applicable in case of Cu-Ni contamination under strong climatic conditions of industrial wastelands. Therefore, the purpose of this research is to introduce and test an original method for creating stable grass cover on heavy-metal poisoned soils.

The methods of immobilization of the pollutants are widespread and can include creation of plant cover (for the aim of phytostabilization and as the initial stage of succession at the territory where plant cover absents).

After analysis of technologies applicable for the detoxification of the HM contaminated soil media and technogenic soil on impact zones of copper-nickel smelters, we have opted for the phytostabilization that allows converting the contaminants into a less active form at the junction of plant roots and the soil (Padmavathiamma and Li 2007). This technology is preferable for large areas, where the recovery of toxic components is economically unviable (Singh and

Prasad 2011).

According to Adamo *et al.* (2015), the conditions for plant cultivation on areas with highly degraded ecosystems should be created by using soil-forming materials and simulating soil conditions. In the polar latitudes, a rehabilitation of technogenically disturbed areas are easiest achieved through an improvement of the soil horizon with ameliorants, including those consisting of mining wastes.

In fact, by forming a layer of mineral substrates we precipitate pedogenesis (the initial stage of the soil formation) (Androkhanov, Ovsyannikova and Kurachev 2000). High Ca and Mg contents in ameliorants can become a favourable factor, as those elements reduce the toxicity of HM (Viehweger 2014), contained in the technogenic soil and accumulated in the ameliorants as a result of aerotechnogenic emissions. In the course of its development, the artificial phytocenosis promotes accumulation of the organic matter, which may change the migration status of HM due to the formation of organo-mineral complexes (Lockwood *et al.* 2015). Alkaline properties of the ameliorants facilitate anchoring of the pollutants.

It is not inconceivable that the employment of the mining waste phytoameliorants following the innovative method of accelerated phytocenosis validated on the Kola peninsula (Slukovskaya *et al.* 2014), will enable a successful recultivation of industrial barrens in the Arctic and Subarctic zones (Nikonov and Lukina *et al.* 2003). This study extends the original integrated technique of technogenic soil phytostabilization developed by Kotelnikov and Ivanova (2011).

## 2. MATERIALS AND METHODS

The study was conducted during the period from 2010 to 2014 on the impact zone of a copper-nickel smelter (*Kolskaya Mining and Metallurgical Company JCS*, Monchegorsk industrial site) in the Murmansk region, Russia, which is situated at the territory of the Kola peninsula. The experimental site was presented by a plot with mineral soil, devoid of vegetation, located 1.5 km away from the industrial area (67°56.403'N, 32°50.287'E). On the surrounding area, sparse sporadic specimens of the *Salix* genus were reported.

The soil of the industrial barren was eroded down to the illuvial horizon; its chemical composition is given in the work (Slukovskaya *et al.* 2013). Note the high content of phytoavailable Cu and Ni (on the average, Cu - 400 mg kg<sup>-1</sup>, Ni - 20 mg kg<sup>-1</sup>) and low concentrations of phytoavailable Ca (15-75 mg kg<sup>-1</sup>) and Mg (2-10 mg kg<sup>-1</sup>). For comparison, the concentrations of phytoavailable elements on a plot, located in the same region but having a sustainable herbaceous soil covering, were (mg kg<sup>-1</sup>): Cu 100-500, Ni 300-700, Ca 1300-2500, Mg 140-360 (Vangronsveld *et al.* 1995). It is interesting that high Ca and Mg concentrations can improve the conditions for plant growth on contaminated soil at comparable (for Cu), and even higher (for Ni) heavy metal contents.

### 2.1. Climatic Features At The Experimental Sites

The agroclimatic conditions of the Kola peninsula are characterized by a short vegetation season, low average monthly temperatures, a short frost-free season, frost occurrences even in June, and nutrient-poor soils. Due to transpolar location, the day length in the region varies between 0 (during the polar night, in winter) and 24 hours (the polar day, in summer). All these factors create unfavourable conditions for plant cultivation (Gontar *et al.* 2010).

During the research period, the average monthly temperature varied within 9.4-14.4°C in June, 13.0-16.4°C in July, 11.0-15.2 °C in August and 7.7-9.3°C in September. The most favourable weather conditions were observed in 2011 and 2013.

### 2.2. Experimental Design

In 2010, 15 plots, 1×1 m each, were laid on the experimental site. Two types of mining wastes were used in the experiment: Carbonatite Wastes (CW) and Serpentine Magnesite (SM). The experimental design included three variants with 5 replications for each one. The variant 1 represented a control (nil treatment) plot without mineral substrates. In the experimental plots, the barren surface was covered by a 5-cm layer of mineral growing medium, including of SM and CW for Variants 2 and 3, respectively. The amount of growing media was 770 t ha<sup>-1</sup> for CW and 600 t ha<sup>-1</sup> for SM.

The artificial phytocenosis was formed following a patented hydroponic express-method for the creation of high-quality plant communities, proposed for improving of northern environment (the Kola peninsula) (Kotelnikov and

Ivanova 2011) The method incorporates vermiculite from Kovdor mines and local populations of perennial herbaceous plants (*Festuca rubra* L., *F. pratensis* Huds., *Bromus inermis* Leyss., *X Festulolium* F. Aschers. et Graebn.), the seeds of which were taken in the weight ratio 4:3:1:1. The resulting vegetation cover was fertilized with azophospka (NPK) every year, once in the growing season at a ratio of 20 g m<sup>-2</sup>.

### 2.3. Methods of Analysis

Chemical analyses of the soil, ameliorant and plant samples were performed in specialized accredited laboratories of the I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials and the Institute of the Industrial Ecology Problems of the North of the Kola Science Centre of the Russian Academy of Sciences (Apatity, Murmansk region, Russia).

The total amount of elements in the soil was determined after an autoclave microwave digestion in a SW4 system with DAK 100 autoclaves (Berghof) using a concentrated acid mix (47% fluoric acid and 65% nitric acid). The concentrations of phytoavailable forms of elements in the soil and in the mineral substrates were determined using a standard procedure involving an acetate-ammonium buffer solution (pH 4.65) (Ure 1996). The obtained solutions were analysed using the mass spectrometry with inductively coupled plasma on an ELAN 9000 DRC-e (Perkin Elmer). The pH was determined using a standard procedure with the aid of an I-160 M ionometer.

### 2.4. Collection and Preparation of Soil and Plant Samples for Analysis

The soil samples were taken from different horizons (0-5, 5-10 and 10-15 cm) on completion of the second and third growing seasons, three samples from each horizon. The samples were dried to the air-dry state in a special laboratory compartment at the temperature of 18±2°C and relative humidity of 70-80% and sieved through a mesh screen of 1 mm to remove all residual vegetation and gravel.

The grass sod samples for biometrical studies were collected from the control plot and two experimental plots throughout the period of experiment (2014 – 2010) using the monolithic method in three replications. The following parameters of the vegetation mantle were determined: the projective cover (%), the height (cm) and mass of above-ground organs (gm<sup>-2</sup>), the rooting depth (cm), the degree to which the plants have invaded the mineral substrate layer (%), and the root mat thickness (cm). The plant samples were dried until air-dry in the same conditions as the soil samples, and then ground in a blender.

### 2.5. Statistical Analysis

Microsoft Excel 2010 was used for the data processing, calculations and graphic illustrations. The averaged numerical data are presented with mean deviations of characteristics values.

## 3. RESULTS

### 3.1. The Characteristics of Mineral Substrates from Mining Wastes

The CW sample was taken from the dressing tailings dump of *Kovdorsky mining and processing works* JSC (Murmansk region, Russia), where the wastes are stored after reextraction of valuable components. The volume of tailings, accumulated for many years of the plant's operation, currently amounts to 120 mln t. In mineral composition, the tailings consist of (wt. %): calcite, dolomite (30-40), forsterite (25-35), apatite (10-15), magnetite (0-2), other minerals (2-8). In grain size, the CW is by 73% represented by particles of less than 0.1 mm, the remaining 22% and 5% being, respectively, the fractions of 0.1-0.25 mm and 0.25-2 mm. So, in terms of grain size composition, this growing medium can be classified as fine sand.

The SM mineral substrate is basically the overburden rock from the Khalilovsky magnesium deposit, manufactured by *Litosfera* CJSC (Orenburg region, Russia). The rock is being mined and processed for magnesite as a target product, which yield is about 5%. The bulk of the mined rock (95%) is composed by serpentinite magnesite. The reserves of serpentinite rock within the Khalilovsky ore district are practically unlimited. In our experiments, the SM sample had a particle size of less than 20 mm, which corresponds to the gravel-sand fraction. The average content of minerals in the serpentinite magnesite is, wt. %: serpentine 80, magnesite 15, calcite 2, magnetite 2.5, chromite 0.5.

Due to the presence of calcium carbonate, magnesium carbonate, and magnesium hydrous silicates in the substrates, the reaction of pore solutions is alkaline. The pH value for CW is 9.2; for SM it is 8.4 (Table 1). The pH value is

consistent with the total content of phytoavailable Ca and Mg, which is an order of magnitude higher in CW than in SM (Table 1).

Most of the Ca (about 85% of the total content) in the tailings is present in the phytoavailable form as carbonate minerals. The wastes contain much phytoavailable Mn (about 10% and 40% of the total content in CW and SM, respectively). Fe, Cu and Ni convert to the available form to a lesser degree. The microelements, present in the substrates in proportions sufficient for plant nutrition (Kabata-Pendias & Pendias 1989), are represented by the following groups: S, P, Mn, Zn, Cu for CW, and Mn, Fe, Cu, Zn for SM. Since the mineral substrates contain little amounts of nutrient elements, the deficit of the latter in the experiment was compensated for by a complex fertilizer containing nitrogen, phosphorus and potassium.

**Table 1. Content components in the phytoavailable form ( $C_{avail}$ ) (mean  $\pm$  standard deviation,  $n = 3$ ) and the ratio  $C_{avail}/C_{total}$  ( $C_{total}$  - total content) in ameliorants (CW, SM)**

Component	CW pH – H <sub>2</sub> O 9.2 $\pm$ 0.1		SM pH – H <sub>2</sub> O 8.4 $\pm$ 0.1	
	$C_{avail}$ mg kg <sup>-1</sup>	$C_{avail}/C_{total}$ %	$C_{avail}$ mg kg <sup>-1</sup>	$C_{avail}/C_{total}$ %
K	18 $\pm$ 3	-	10 $\pm$ 2	-
P	89 $\pm$ 9	-	15 $\pm$ 5	-
Ca	123021 $\pm$ 485	87.3	2931 $\pm$ 112	83.7
Mg	1821 $\pm$ 121	1.1	26211 $\pm$ 625	11.7
Fe	530 $\pm$ 49	1.2	24 $\pm$ 7	0.1
Mn	153 $\pm$ 17	9.6	159 $\pm$ 18	31.8
Zn	3 $\pm$ 2.3	-	1 $\pm$ 0.9	-
S	35 $\pm$ 4.3	-	18 $\pm$ 2	-
Cu	7 $\pm$ 4.5	1.8	0.2 $\pm$ 0.1	0.0
Ni	6 $\pm$ 4.2	6.0	25 $\pm$ 9.3	1.5

*n* - number of measurements, CW - carbonatite wastes, SM - serpentinite magnesite

Chemically, the experimental growing media can be referred to ameliorants, that is, the materials capable of creating favourable conditions for vegetation. On impact areas of copper-nickel smelters, the ameliorants can neutralize the acidic components and diminish the heavy metals toxicity.

### 3.2. The Growth and Development of Plants in Artificial Phytocenosis

The observation results of the growth and development of plants in the control and the two experimental plots are presented in Table (2). In all the variants of the field experiment the seeds of graminaceous plants shot up on the 5-7th day. By the end of the 2010 growing season half of the seedlings in the control plot had died, the projective cover degree made up 50%, the height of the surviving plants was 5 $\pm$ 0.5 cm, and no penetration of the roots into the soil layer was observed (Table 2). In the experimental plots, the plants were approximately two times higher than in the control one, the root systems of 45% of the plants invaded the 5-cm ameliorant layer, and some roots penetrated into the technogenically transformed soil to the depth of 1-2 cm. The projective cover degree in the experimental plots made up 100%. The above-ground organs' mass was almost three times greater in the experimental plots than in the control one.

**Table 2. Biometrical parameters (mean standard  $\pm$  deviation) of vegetation mantle growth.**

Variant	Years	Plant Height, cm <i>n</i> = 20	Ameliorant Invasion by the Roots, %	Root Penetration Depth into Technogenic Layer, cm <i>n</i> = 3	Above-ground Organ Biomass, g m <sup>-2</sup> <i>n</i> = 3	Thickness of Root Mat, cm <i>n</i> = 3	Projective Cover, %
CW	2010	10.1 $\pm$ 1.0	45	2.0 $\pm$ 0.1	51.2 $\pm$ 3.0	2.0 $\pm$ 0.1	100
	2011	27.0 $\pm$ 1.3	100	2.6 $\pm$ 0.1	83.3 $\pm$ 3.1	4.3 $\pm$ 0.2	100
	2012	27.4 $\pm$ 1.1	100	3.1 $\pm$ 0.2	395.5 $\pm$ 20.2	7.5 $\pm$ 0.2	100
	2013	30.0 $\pm$ 2.1	100	4.0 $\pm$ 0.1	600.4 $\pm$ 23.4	8.5 $\pm$ 0.1	100
	2014	33.7 $\pm$ 2.0	100	4.3 $\pm$ 0.3	672.1 $\pm$ 31.4	7.0 $\pm$ 0.3	100
Pearson Correlations with Control		-0.64631	--	--	-0.77396	-0.97488	--

(Table 4) contd....

Variant	Years	Plant Height, cm n = 20	Ameliorant Invasion by the Roots, %	Root Penetration Depth into Technogenic Layer, cm n = 3	Above-ground Organ Biomass, g m <sup>-2</sup> n = 3	Thickness of Root Mat, cm n = 3	Projective Cover, %
Spearman Correlations with Control		-0.78262	--	--	-0.89443	-0.89443	--
Kendall Correlations with Control		-0.59761	--	--	-0.83667	-0.83667	--
SM	2010	10.4 ± 1.1	45	1.0 ± 0.1	48.0 ± 2.4	2.1 ± 0.1	100
	2011	25.8 ± 1.2	100	2.1 ± 0.1	126.2 ± 12.0	4.0 ± 0.1	100
	2012	25.3 ± 2.3	100	2.8 ± 0.2	375.8 ± 19.8	6.8 ± 0.2	100
	2013	24.3 ± 1.7	100	3.7 ± 0.2	475.6 ± 23.2	8.0 ± 0.2	100
	2014	28.0 ± 2.1	100	3.9 ± 0.1	701.2 ± 27.9	7.1 ± 0.2	100
Pearson Correlations with Control		-0.52783	--	--	-0.77657	-0.95242	--
Spearman Correlations with Control		-0.1118	--	--	-0.89443	-0.89443	--
Kendall Correlations with Control		-0.11952	--	--	-0.83667	-0.83667	--
Control	2010	5.0 ± 0.5	-	0	17.4 ± 1.2	1.0 ± 0.1	50
	2011	5.8 ± 0.1	-	0	4.7 ± 0.9	0.7 ± 0.1	10

*n* - number of measurements, CW - Carbonatite Wastes, SM - Serpentinite Magnesite

In the spring of 2011, the control plot showed a massive plant mortality and poor development of the plants, whereas the experimental plots were noted for an intensive spring aftergrowing. Plant roots in the control plot remained on the surface. The root mat thickness had reduced compared to the previous year, and the above-ground organs' biomass was considerably less than that in the experimental plots (Table 2). In the experimental plots, a 100% invasion of the ameliorant layer by the plant roots and their massive penetration into the technogenic soil to a depth of 2.1 – 2.6 cm was reported. An intensive root mat growth was observed as well.

By the beginning of the third growing season (2012), all vegetation in the control plot had died. In the experimental plots, the invasion of the technogenically polluted soil by the roots continued. All the parameters of the plant growth were higher in the CW variant than in the SM variant.

During the fourth growing season (2013), the ameliorants continued their positive influence on the plants' biometrical parameters. Similarly to 2012, better results were observed in the plot with the CW ameliorant: the plants were taller (by 5.7 cm) and had a greater biomass (by 125 g m<sup>-2</sup>) than for the SM variant. The plant roots in experimental plots had penetrated into the soil to a depth of 3.7 – 4.0 cm (Table 2).

In 2014, an intensive growth of the vegetation mantle was observed: the plants passed to the earing phase. By the end of the season, the biometrical characteristics of the plant formation in the experimental plots had levelled off. The trend of increase in the average plant height is maintained, the value of this index was 33.7 ± 0.1 cm for the CW and 28.0 ± 2.1 cm for SM; the root mat thickness was 7.0±0.3 for CW and 7.1±0.2 cm for SM. The above-ground organs' biomass had increased by 226 g m<sup>-2</sup> in the SM plot and only by 72 g m<sup>-2</sup> in the CW plot compared to the previous season.

### 3.3. Chemical Composition of The Ameliorants and The Soil in The Experiment

In the experiment, we assessed chemical composition of both the ameliorants and soil samples beneath the ameliorants. The results of 2011/2012 after two and three growing seasons under the experiment are presented in Table (3).

### 3.4. Chemical Composition of The Plants

The plant content in terms of some elements is shown in Table 4. The elements are divided into several groups according to their inflow in plants. Plant food elements' content (nitrogen, phosphorus, potassium) from the background side is higher than in the experimental samples. There is a substantial deficit of calcium, while the magnesium content

exceeds (ameliorant – SM) the concentration, or there is no magnesium in the control sample (CW variant). The greatest differences were recorded for toxic metals – nickel, copper, cobalt.

**Table 3. Content components in the form available for plants ( $\text{mg kg}^{-1}$ ) in ameliorants (CW, SM) and soil samples (the slash represent the data for 2011/2012).**

Variant	Analyzed Growing Medium	Ca	Mg	Ni	Cu	S
CW	Initial ameliorant	123000	1800	6	7	35
	Ameliorant after 3 growing seasons (2012)	26090	1130	20	220	1350
	Soil layer 0-5 cm	5130/190	234/20	9/5	250/310	310/700
	Soil layer 5-10 cm	460/60	215/10	2/2	240/280	430/860
	Soil layer 10-15 cm	170/50	20/10	3/3	170/200	230/420
SM	Initial ameliorant	2870	25630	25	1	20
	Ameliorant after 3 growing seasons (2012)	1580	4320	14	30	280
	Soil layer 0-5 cm	300/170	450/310	5/6	180/200	330/560
	Soil layer 5-10 cm	110/50	50/130	4/4	160/160	290/510
	Soil layer 10-15 cm	100/2	20/50	3/3	160/100	160/680

CW - carbonatite wastes, SM - serpentinite magnesite

**Table 4. Chemical composition of plants.**

Group of Elements	Element	Composition, mg/kg		
		SM	CW	Background
Fertilizer elements	N	21280	22000	27720
	P	3090	2140	3440
	K	13600	12570	26960
Ameliorant components	Ca	1320	2400	4240
	Mg	2430	1100	1460
Major elements	Si	2120	1940	1630
	Al	270	140	125
	Na	240	90	90
	Fe	710	830	450
	Mn	165	140	25
Toxic metals	Ni	425	355	5
	Cu	255	215	6
	Co	10	9	0,2
Trace elements	Zn	11	13	38
	Cr	15	11	8
	Pb	3	3	0,2

The results of biometrical analysis show that vegetation conditions for plants growing on the CW are more favorable than those on the SM. The Mann–Whitney  $U$  test was performed for the statistical data analysis of the plant height in 2013 and 2014. In 2013 the difference between the vegetation covers for the SW and CW is significant ( $U = 37$  at the critical value  $U_{\text{crit}} = 56$ ,  $p \leq 0.01$ ) but in 2014 the discrepancy became negligible ( $U = 665$  at  $U_{\text{crit}} = 499$ ,  $p \leq 0.01$ ).

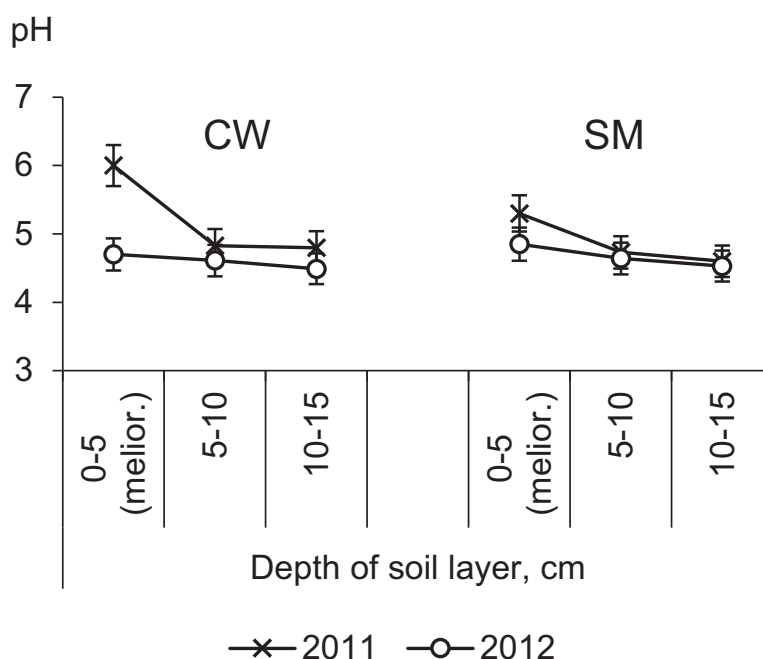
In both experimental plots, the process of canopy closure between the plots was observed due to the natural self-seeding of the species. Besides, the plant biomass accumulated as a result of an intensive leaf formation and tillering. The totality of characteristics of the created plant formation indicated a high quality of the artificial phytocenosis formed on the basis of the ameliorants.

#### 4. DISCUSSION

The greater part of the new vegetation root system was found to concentrate in the CW and the SM ameliorant layer. Chemical analyses of the technogenic soil and ameliorants, performed three years after the beginning of the experiment,

revealed that in conditions of on-going aerotechnogenic emissions of the copper-nickel smelter, the Ca and Mg compounds continued to migrate from the ameliorants into the technogenic soil (Table 3), the data are given without error estimation). For example, the concentration of phytoavailable forms of these components in the ameliorants dropped, whereas in the technogenic soil it went up, which was especially evident in the data for 2011, that is after two growing seasons. The process of Ca incoming into the soil in the CW plot was more intensive compared to the SM one, due to a higher concentration of phytoavailable Ca in CW.

The above mentioned processes contributed to a change in the actual acidity of the technogenic soil (Fig. 1). In 2011, the highest pH values were recorded in the top soil layer. At the same time, the pH value in the top soil layer of the CW variant was near-optimal (6.0) and higher than in the SM plot (5.3). According to (Yagodin, Zhukov and Kobzarenko 2002), the pH values, at which the soil produces no negative influence on the plants, lie within the range of 6.1-7.4.



**Fig. (1).** The pH dynamic pattern as per the soil depth according to the ameliorant type (CW - carbonatite wastes, SM - serpentinite magnesite).

In 2012, a reduction in the concentration of phytoavailable Ca in the technogenic soil in both experimental plots was observed (Table 3). This affected the actual acidity level of the soil (Fig. 1). In the same period, a similar reduction was observed in the concentration of phytoavailable Mg in the experimental plots.

Besides the soil acidity, another important factor to be taken into account in plant cultivation is the concentration of phytotoxic elements. It is known that the thresholds for Ni and Cu phytotoxicity are  $100 \text{ mg kg}^{-1}$  and  $60\text{-}125 \text{ mg kg}^{-1}$ , respectively (Kabata-Pendias and Pendias 1989). On the experimental plots, the flow of gas-dust toxic compounds into the soil surface layer has resulted in accumulation in the ameliorants of the main pollution components: S, Cu and Ni (Table 3). In the course of the experiment, the concentration of phytoavailable S increased compared to the initial substrate by  $1315 \text{ mg kg}^{-1}$  in the CW plot and by  $260 \text{ mg kg}^{-1}$  in the SM one; of phytoavailable Cu – by  $213 \text{ mg kg}^{-1}$  in the CW plot and by  $29 \text{ mg kg}^{-1}$  in the SM one; of phytoavailable Ni – by  $14 \text{ mg kg}^{-1}$  in the CW plot. The conclusion we can draw is that the CW growing medium, containing higher concentrations of alkaline components, is more effective in the anchoring of toxic metals compared to the SM substrate. It is also important to note that the concentration of phytoavailable Cu is 1-2 orders of magnitude higher than that of Ni. The concentration of phytoavailable Ni does not exceed the toxicity threshold, whereas for Cu it is exceeded by 2-3 times. The obtained results are consistent with the



knowledge of the geochemical mobility of these elements (Kabata-Pendias and Pendias 1989).

Nevertheless, both the growth and the development parameters of the plant formation are indicative of the fact that despite the high heavy metal concentrations in the ameliorants, the edaphic conditions of these substrates remained favourable for plant development throughout the experiment. This can be explained by high concentrations of phytoavailable Ca and Mg in the ameliorants (Yagodin, Zhukov and Kobzarenko 2002). By migrating into the technogenic soil, Ca and Mg reduce the soil toxicity thus favouring the penetration of plant roots.

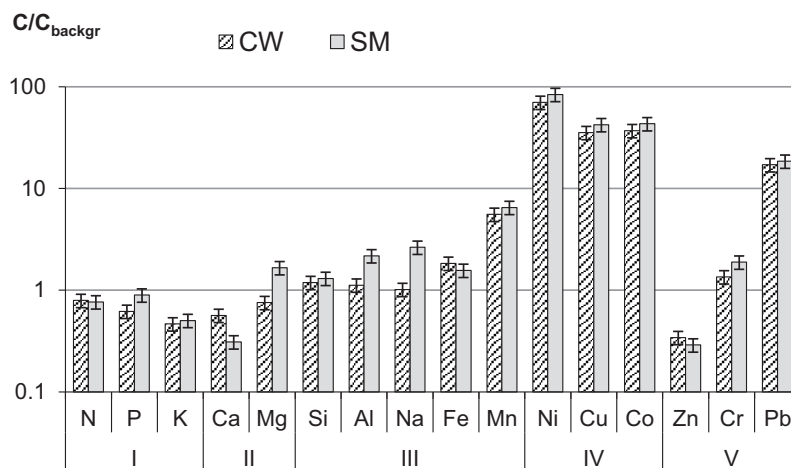
We suggest that the difference in the development of phytocenosis for the two substrates is caused by a significant excess of phytoavailable magnesium over calcium in the SM. Both elements play an important role in the biochemical processes in plants and influence their productivity, but calcium concentration in the soil solution should be higher than that of magnesium (Yagodin, Zhukov and Kobzarenko 2002). The ratio of the mass contents of phytoavailable Ca and Mg is 68 for the CW and 0.11 for the SM. However, magnesium is leached out faster than calcium from the SM and slower than calcium from the CW. After two years of the field experiments the Ca and Mg ratio reduced to 23 in the CW and increased to 0.37 in the SM. An improvement of this factor for the SM has been reflected in the biometrical characteristics of the plants.

The results of monitoring of the plant formation on an experimental site in the course of three growing seasons have shown that the ameliorants used in the soil reclamation area create favourable conditions for the formation of plant communities resistant to the existing stress factors. Intensive growth of the plant above-ground organs, the tillering process, and the biomass increase ensure a 100% projective covering of the formed vegetation cover. Gradual penetration of the plant roots into the technogenic soil, the successful development of the root mat and vegetational sod and increased species diversity as a result of colonization of the plots with indigenous species (*Equisetum arvense* L., *Trifolium repens* L.) suggest the formation of a self-supporting phytocenosis as the initial stage of succession (Fig. 2).



**Fig. (2).** View of the experimental site. In the foreground, there is a vegetation cover as the initial stage of succession, in the back - a wasteland and a metallurgical plant.

The concentrations of chemical elements in the plants reflect their specific growth conditions in the setting of air pollution with the gas-dust emissions of the copper-nickel smelter. Fig. (3) shows the results of normalization of the chemical composition in the plants, belonging to the artificial phytocenosis, as opposed to the same species cultivated on the background territory.



**Fig. (3).** The ratio ( $C/C_{backgr}$ ) of the metal concentration in the experimental plants ( $C$ ) to its background level ( $C_{backgr}$ ) (CW - carbonatite wastes, SM - serpentinite magnesite, I – fertilizer elements, II – ameliorant components, III – major elements, IV – toxic metals, V – trace elements).

The concentrations of K, P, Ca, and Zn in the plants of the artificial phytocenosis were lower compared to the background plants. The deficient phosphorus and potassium values indicate the need of nutritional support with mineral fertilizers. The concentrations of Al, Mg, Si, Cr, Fe and Na were twice as high as the background values. We note a significant difference in the values of Ca and Mg concentrations in the plants cultivated on different ameliorants. Higher concentrations of Ca and Mg in the plants taken from, respectively, the CW and SM plots correlate with the concentrations of phytoavailable forms of these elements in the ameliorants.

The accumulation of toxic elements in the plants is more intensive, the  $C/C_{backgr}$  ratio for Co, Cu and Ni ranging within 50-100. Our findings suggest that experimental plants can accumulate heavy metals without damage to the phytocenosis cultivated under the extreme conditions of the northern latitudes using the proposed technology.

## CONCLUSION

Northern ecosystems are highly vulnerable when affected by emissions of metallurgical enterprises playing a key role in the economy of northern regions, including the Kola peninsula on the north-west of Europe. The side effect of industrial development is a contamination of vast land and water areas, formation dumps of overburden rock and tailing storages. Unlike the more southward regions, these technogenically transformed areas are incapable of self-restoration, while the existing reclamation technologies are uneconomical due to consumption of sizable volumes of natural resources (land, peat, etc.). Our research has revealed the remediation capacity of carbonatite and serpentinite wastes for highly contaminated technogenic landscapes of the Arctic region. Due to the alkaline reaction of the growing medium and a large pool of essential elements, the wastes have proved effective in improving the edaphic conditions of industrial barren.

As demonstrated by the full-scale experiment, the vegetation cover formed using the local populations of perennial herbaceous graminoids (*Festuca rubra*, *F. pratensis*, *Bromus inermis*, *X Festulolium*), vermiculite from Kovdor mines and ameliorants, obtained from carbonatite and serpentinite wastes, has a capacity for self-survival and creation of the initial stage of progressive succession in the impact zone of copper-nickel smelters (Fig. 2). The formation of an artificial phytocenosis with the use of mining wastes for remediation of derelict land in conditions of on-going industrial emission reduces the intensity of heavy metals migration by anchoring them in the soil top layer. Presumably, the created plant formations will trigger the natural progressive succession in the examined industrial barren.

The ecological effect of this method is resulted in the emergence of native plant species and the establishment of the plant community on the industrial barren on the one hand and the decrease of HM-migration and the formation of primary soil - on the other hand. This effect we observe at present.

The effect of physical sorption of copper and nickel by the particles of substrate take place for the mineral wastes used in the experiment. Vermiculite has the properties of ion exchange due to its structure. The both effect was observed in the wide range of pH and Cu/Ni-concentration. It allows decreasing HM-migration in changing soil conditions and avoiding the secondary pollution.

The great current significance of the results is confirmed by the long-term (for already 7 years) sustainable development of plant community. This is reflected in biomass and litter generation, seed formation, cessation of erosion processes at the experimental plot of the industrial barren. There isn't another cost-effective rehabilitation technology for this territory at present. The results of this experiment instantiated that "mild" remediation *in situ* is one of the best techniques for industrial barrens and wastelands.

## CONSENT FOR PUBLICATION

Not applicable.

## CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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