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Use of material from poor vermiculite-serpentine ores for remediation of urban soils and agrosoils in the Arctic zone of Russia

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Abstract

The problem of waste disposal in the mining industry is urgent for the Arctic zone of Russia. Significant volumes of overburden rocks from the Kovdor phlogopite deposit, represented by poor vermiculite-sungulite ores, require the development of environmentally safe methods for their integration into economic circulation. The aim of the study is to assess the potential of vermiculite-serpentine concentrate (VSC) obtained from overburden rocks for the remediation of anthropogenically disturbed soils. The prospect of using VSC for improving soil properties is due to its favourable mineral composition (serpentine 30-35, vermiculite 28-31 wt.%). Laboratory experiments prepared mixtures of VSC with agrosoil (10-60 wt.%) and samples of urban soils from three cities in the Murmansk Region (Apatity, Kirovsk, and Monchegorsk) (20 wt.%), differing in the level of anthropogenic impact. The content of chemical elements in two mobile fractions was studied, phytotesting was carried out with French marigolds (*Tagetes patula*). VSC has an alkaline reaction (pH_{H_2O} 8.9) due to the presence of minerals in the composition capable of concentrating Ni; the gross content of this component is 730 mg/kg. It was found that the introduction of VSC increases the alkalinity of soil mixtures and the content of mobile forms of Ca and Mg. In slightly contaminated agrosoil, the content of mobile nickel when adding 10-50 % VSC increases from 1.5 to 2.5 mg/kg, with a content of more than 60 % it decreases below background values. Phytotesting showed that in the range of 10-60 % VSC, the root mass increased from 0.09-0.1 to 0.13-0.18 g/plant, there were no signs of phytotoxicity. For soils of Monchegorsk, characterized by a high level of anthropogenic contamination with nickel and copper, the introduction of concentrate, on the contrary, led to a steady decrease in the content of mobile forms of both metals. Vermiculite-serpentine concentrate can be recommended as a meliorant for soil remediation, poor in macroelements and contaminated with heavy metals.

Keywords

vermiculite; serpentine; nickel; soil remediation; urban soils; phytotesting; Murmansk Region

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Introduction

The problem of waste disposal in the mining industry is urgent for the Arctic zone of the Russian Federation. Significant volumes of poor vermiculite-sungulite ores are stockpiled in the Kovdor area of the Murmansk Region during the development of the phlogopite quarry of Kovdorslyuda LLC [1]. The stockpile of vermiculite-sungulite ores occupies an area of 74,200 m^2, and the amount of such ore mass is approximately 400 thousand t. Currently, both poor vermiculite-sungulite ores and their dressing products are not used at an industrial scale.

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Sungulite is a common name for serpentinite formed as a result of vermiculite weathering, with lizardite, a serpentine mineral, predominating in the mineral composition. A characteristic feature of poor ores is the presence of vermiculite-sungulite intergrowths, which significantly reduces the efficiency of traditional dressing methods [2, 3]. At the same time, the mineral composition of this raw material determines its potential suitability for use as agronomic ores in the design of soil substrates for various purposes. Vermiculite-serpentine materials can be in demand for regulating acid-base and hydrophysical properties, as well as immobilizing heavy metals in anthropogenically disturbed areas [4, 5].

Serpentine minerals are widely distributed in the Earth's crust, forming serpentine provinces with specific vegetation in certain regions [6, 7]. Similar to clay minerals, serpentinites can be considered as environmentally safe materials [8]. Serpentine minerals belong to magnesium hydrosilicates with the stoichiometric formula $Mg_3Si_2O_5(OH)_4$ [9, 10]. The combination of silicon-oxygen tetrahedral and magnesium-containing octahedral layers gives rise to a layered structure, and the mismatch in layer geometry leads to the existence of several polymorphic modifications – lizardite, chrysotile, and antigorite. The chemical composition of serpentines varies due to isomorphic substitutions in the octahedral and tetrahedral layers: in the M position (octahedron), besides Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Mn^{2+}, and Zn^{2+} can occur, while in the T position (tetrahedron) – Si^{4+}, Al^{3+}, Fe^{3+}; the generalized formula is $Mg_{3-x}(M)_xSi_{2-y}(T)_yO_5(OH)_4$ [11-13]. Owing to their well-developed layered structure, high specific surface area, and ion exchange capacity, serpentines exhibit sorption properties toward heavy metals, which makes them promising natural materials for environmental and industrial applications, including wastewater treatment and remediation of contaminated areas [14, 15]. Metal sorption by serpentine minerals can occur through surface adsorption [16], incorporation into the mineral structure [17], and precipitation of poorly soluble compounds in an alkaline medium [18].

Vermiculite belongs to the group of layered aluminosilicates of the hydromica type and is characterized by a layered crystal structure formed by tetrahedral silicon-oxygen and octahedral magnesium-iron layers, between which exchangeable cations and water molecules are located [19]. The approximate chemical formula of vermiculite can be represented as $(Mg, Fe^{2+}, Fe^{3+})[(Si\ A1)_4,O_{10}][OH]_2 \cdot 4H_2O$, where the interlayer cations and water determine the swelling and ion exchange capacity of the mineral [20-22]. Thermal treatment causes a sharp increase in the interlayer distance and the formation of a highly porous structure with a developed specific surface area, which significantly enhances the adsorption properties of the mineral [23]. Due to these features, vermiculite possesses a high cation exchange capacity and effectively sorbs ions of heavy and rare earth metals, as well as is used for the elimination of oil contamination. The sorption process involves both ion exchange in the interlayer positions and surface adsorption on hydroxyl and silicate groups [24-26].

Mineral and processing properties and practical experience in using vermiculite and serpentines in remediation make it possible to consider the use of Kovdor raw materials as agronomic ores. Expanding the scope of application of poor vermiculite-sungulite ores for their utilization involves studying the effect of materials containing vermiculite and sungulite on phytotoxicity and the concentration of nutrient elements and potentially toxic metals in soil solutions. Since serpentine minerals and vermiculite are natural concentrators of nickel, special attention is paid to the behaviour of this metal.

The aim of the study is to assess the potential of vermiculite-serpentine concentrate (VSC) obtained from overburden rocks for the remediation of anthropogenically disturbed soils. The objectives of the study are to examine the effect of various doses of VSC (10-60 wt.%) on the physicochemical properties, the content of mobile forms of macroelements (Ca, Mg, Si, P) and heavy metals (Ni, Cu) when introduced into agrosoil and urban soils with different levels of anthropogenic impact; to identify the biological response of the test plant (*Tagetes patula*) and microbial community (cellulolytic activity) to the introduction of VSC into the soil.

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Materials and methods

VSC was obtained by screening the fraction larger than 20 mm from poor vermiculite-sungulite ore, which was then crushed and sorted to obtain a fraction smaller than 0.5 mm. The serpentine content in VSC is 30-35 wt.%, vermiculite – 28-31 wt.%, the remainder being predominantly pyroxene minerals, as well as dolomite, calcite, and apatite. VSC is an alkaline material with pH_{H_2O} 8.9 and pH_{KCl} 7.8.

In accordance with the mineral composition, Mg and Si predominate in the gross chemical composition of VSC (Table 1); Fe – 10.7, Al – 2.5, Ca – 2.1, K and P – less than 1 wt.% are also present. Metal content: Cu – 30, Zn – 140, Ni – 730 mg/kg.

Table 1

Chemical composition of VSC

Components	Gross content	Potentially mobile fraction (0.2 N HCl)	Actually mobile fraction (0.01 N HCl)
Si, wt.%	21.5	0.58	0.055
Mg, wt.%	18.9	1.59	0.12
Ca, wt.%	2.1	2.04	0.50
K, wt.%	0.1	0.1	0.1
P, wt.%	0.5	0.35	0.0045
Cu, mg/kg	30	12	0
Ni, mg/kg	730	81	2
Zn, mg/kg	140	18	2

The agrosoil, sampled in an agricultural enterprise near Apatity, is neutral, with pH_{H_2O} 6.9 and pH_{KCl} 6.3. Urban soil samples were collected in settlements of the Murmansk Region with different anthropogenic impact – in Kirovsk (series K samples), Apatity (series A), and Monchegorsk (series M). Soil sampling at a depth of 0-15 cm was carried out in two land use zones: recreational (parks and squares), samples A1, A7, M13, M15; and public (dividing strips and lawns along roadsides), samples A3, A5, K9, K11, M17, M19. The general properties of soil samples, as well as the analysis of the relationship between carbon, nitrogen forms, and metal content, are presented in [27].

Experimental design. Effect of VSC on agrosoil properties. Mixtures of agrosoil with VSC were prepared with a concentrate content from 10 to 60 % by mass; pure agrosoil (0 % variant) and pure VSC (100 % variant) were used as control series. Phytotesting experiments were performed in triplicate. Cotton fabric was placed at the bottom of the vessel, soil mixtures were moistened and kept for 14 days, then marigold seedlings were planted. Seedlings of French marigolds (*Tagetes patula*), cultivar "Red King", were obtained using thermal vermiculite from vermiculite concentrate (Kovdor, Murmansk Region). Vermiculite fraction 0.45-2 mm was fired in an electric modular-trigger furnace designed by A.I.Nizhegorodov [28].

The French marigolds were chosen due to their high tolerance to contaminated urban substrates and the proven ability of this plant to accumulate heavy metals (Zn, Cu, Pb) [29, 30]. The adaptive potential to the main stress factors (moisture and light deficiency, low temperatures, high concentrations of heavy metals) along with rapid development of a powerful root system makes French marigolds ideal candidates for restoration of contaminated lands, since roots provide systematic removal of toxicants [31]. In addition, *Tagetes patula* is widely used for landscaping in northern cities.

In the Arctic zone, in particular in the Murmansk Region, the use of seedlings is a common practice determined by the climatic features of the region, primarily the short growing season. In greenhouses, expanded vermiculite is among the materials used for seedling production. Plants were grown for 28 days; at the end of the experiment, morphological and biometric parameters (number of leaves and stems, air-dry biomass of root systems, leaves, stems, buds, and flowers) were determined. Soil mixtures were then dried to an air-dry state, sieved through a 2 mm mesh, and analysed.

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Effect of VSC on properties of urban soils of various composition. Mixtures of VSC with urban soil samples were prepared at a VSC content of 20 wt.%; phytotesting of the soil mixtures was carried out similarly to the experiment with agrosoil.

Research methods. For measuring pH of aqueous and salt suspensions (KCl solution with a concentration of 1 mol/l), a liquid analyser pH-meter-ionometer "Expert-001" with a glass laboratory electrode ESL-63-07SR and a reference laboratory silver chloride electrode EVL-1M3.1 was used. The aqueous extract for pH measurement was prepared at a solid-to-liquid ratio (S:L) of 1:5, with mixing and settling for 3 and 5 min in accordance with GOST 26423-85[1]. The salt (KCl) extract for pH measurement was prepared at S:L = 1:25, mixed on a laboratory shaker for 1 h in accordance with GOST 26483-85[2].

The gross composition of soil samples was determined using an ELAN-9000 DRC-e inductively coupled plasma mass spectrometer (Perkin Elmer, USA) after autoclave acid digestion. Concentrated acids HF, HNO_3, HCl of ultrapure grade were used in a ratio of (2:2:1). Digestion of 1 g samples was carried out in DAK-100 autoclaves made of PTFM material with a volume of 100 ml, withstanding a maximum pressure of 100 bar at temperatures up to 195 °C in an MW 4 microwave system (Berghoff, Germany). A multi-element standard solution Multi-element ICP-MS Calibration STD – N 1 (Perkin Elmer, USA) was used for instrument tuning; multi-element standard solutions IV-STOK-21, IV-STOK-28, and IV-STOK-29 (Inorganic Ventures, USA) with a mass concentration of determined elements of 10 mg/dm^3 and an error not exceeding 0.5 % at P = 0.95 were used for calibration. A 2 % HNO_3 solution was used as the background solution for sample dilution. The accuracy of measurements was assessed using standard reference materials: GSO 902-76 (SP-2 – Moscow sod-podzolic soil), GSO 903-76 (SP-3 – Caspian light-chestnut soil), NIST SRM-SOIL-A (High purity standards, USA).

Concentrations of mobile components in VSC and soil samples were determined by the method of parallel leaching with HCl solutions at concentrations of 0.01 mol/l (actually mobile fraction, C1) and 0.2 mol/l (potentially mobile fraction, C2). Soil samples (10 g) were filled with acid solution (100 ml) and left for 24 h; then the solution was separated from the solid phase by centrifugation for 30 min at 4000 rpm. The resulting solution was filtered through a MFAS-OS-2 membrane filter ("Vladipor", Vladimir) with a pore size of 0.45 μm and analysed by atomic emission spectrometry on an ICPE-9000 instrument (Shimadzu, Japan).

Cellulolytic activity of soil (CAS) was determined by the application method using cotton fabric [32]. Upon completion of the experiment, samples were extracted, cleaned, and dried. Quantitative assessment of the degree of cellulose material destruction was carried out based on the analysis of digital images of residual fabric fragments. The area of samples after the experiment was estimated using ImageJ software.

The bulk density of materials was determined according to GOST 19440-94[3], and the maximum moisture-holding capacity – according to GOST 32632-2014[4]. Carbon and nitrogen content was determined on a EuroVector EA 3000 analyser.

Ammonium and nitrate nitrogen were determined using ion-selective electrodes. Ammonium nitrogen was extracted with distilled water (50 ml per 20 g of soil mixture) for 5 min; the resulting suspension was centrifuged. Nitrate nitrogen was extracted with a 1 % aluminium-potassium alum solution at the same S:L ratio. The suspensions were shaken for 30 min on a PE-6410M mixing device

[1] GOST 26423-85. Soils. Methods for determining the specific electrical conductivity, pH, and dry residue of a water extract.
[2] GOST 26483-85. Soils. Preparation of a salt extract and determination of its pH by the CINAO method.
[3] GOST 19440-94. Metallic powders. Determination of bulk density. Part 1. Method using a funnel. Part 2. Scott volumeter method.
[4] GOST 32632-2014. Methods for testing chemicals hazardous to the environment.

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and centrifuged. Centrifugation of suspensions for separation of the liquid phase from the solid was performed on a DM 0636 laboratory centrifuge (DLAB Scientific Co., Ltd, Beijing, China, 2022) for 30 min at 4000 rpm. The supernatant was additionally passed through a MFAS-OS-2 membrane filter (pore size 0.45 μm, "Vladipor") using a vacuum pump (NVM-5). The resulting solution was analysed using a liquid analyser "Expert-001".

The results were processed by methods of mathematical statistics using MS Excel 2016 software; estimations of the least significant difference for a 5 % significance level ($LSD_{0.5}$) were performed on the simple-statistics.ru website.

Discussion

Effect of VSC application on agrosoil properties. With increasing VSC content, the alkalinity of experimental soil mixtures consistently increases (Fig.1). Linear correlation coefficients of soil mixture parameters with VSC content are as follows: pH_{H_2O} 0.93, pH_{KCl} 0.77, Ca 0.72, Mg 0.15, P –0.90, Si –0.77, Ni –0.54. The decrease in the correlation coefficient between VSC content and pH_{KCl} indicates the occurrence of exchange reactions with soil mixture components. At high VSC contents in the range of 40-100 wt.%, the pH of the aqueous suspension exceeds 8, while in the salt suspension the medium reaction changes insignificantly – within 7.7-7.9.

The concentration of Ni in the agrosoil in the mobile fraction is 1.5 mg/kg; in the VSC content range of 10-50 %, the transition of Ni to the mobile fraction leads to an increase in this parameter to 2.5 mg/kg. At higher VSC contents, the concentration of Ni in the mobile fraction decreases to values below the background (1.5 mg/kg). This behaviour of Ni can be explained by secondary reactions of magnesium-nickel silicate formation in an alkaline medium at pH above 8. The occurrence of such reactions is also indicated by the extremal dependence of mobile Mg on pH with a maximum at pH 8 (Fig.2, *a*).

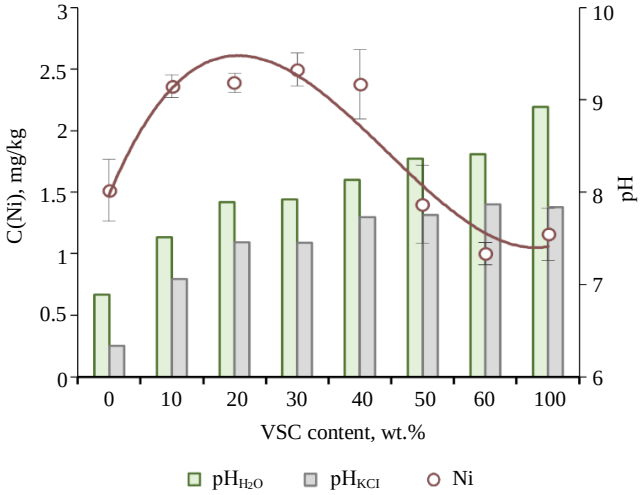


Fig.1. Effect of soil mixture composition on pH and Ni concentration in the mobile fraction

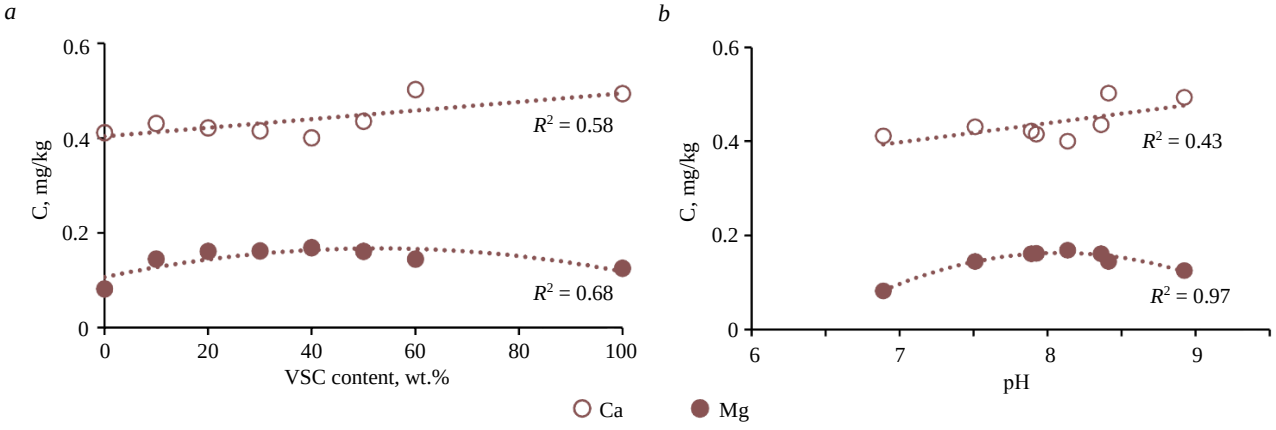


Fig.2. Dependence of mobile forms of magnesium and calcium concentrations on the amount of VSC (*a*) and pH (*b*) of soil mixtures

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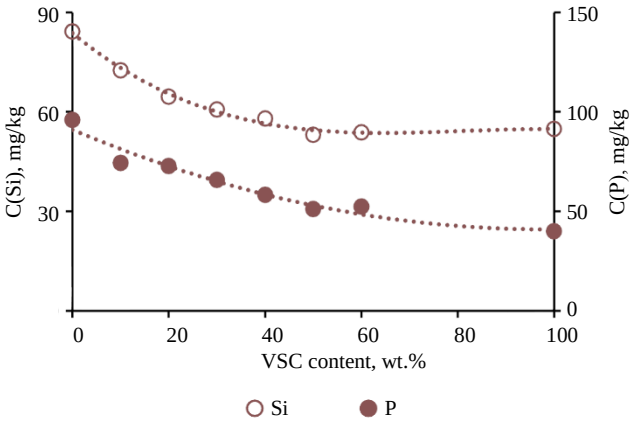


Fig.3. Dependence of concentrations of mobile forms of silicon and phosphorus on the amount of VSC in soil mixtures

Among the chemical components, mobile Ca has the highest linear correlation coefficient with VSC content; a linear dependence with a coefficient of determination R^2 = 0.58 is observed between the parameters (Fig.2, *a*). For Mg, the coefficient is significantly lower, and its value (0.15) indicates the absence of a linear dependence. The effect of VSC content on the concentration of mobile Mg is approximated by an extremal dependence (Fig.2, *a*). The active participation of VSC components in acid-base reactions is indicated by a similar relationship between pH_{H_2O} and the concentration of Ca and Mg in the mobile fraction (Fig.2, *b*).

In the agrosoil, the concentration of mobile Si and P is higher than in VSC; their transition to the soluble fraction decreases synchronously as the VSC content in the soil mixtures increases (Fig.3). The level of mobile silicon stabilizes in the VSC content range of 50-100 wt.%.

Properties of urban soils. Depending on the location, urban soils differ significantly in such properties as bulk density and field moisture, gross carbon and nitrogen content, and content of mobile nitrogen forms (Table 2).

Table 2

Physicochemical properties of urban soils

Properties	Samples									
	A1	A3	A5	A7	K9	K11	M13	M15	M17	M19
Bulk density, kg/dm^3	0.81	0.63	0.61	0.94	1.07	1.06	0.96	0.23	1.01	0.64
Field moisture, %	76	96	111	65	45	49	34	280	51	64
C, wt.%	4.63	8.35	8.92	2.90	3.36	4.28	1.26	27.86	3.54	4.64
N, wt.%	0.25	0.26	0.49	0.17	0.23	0.23	0.03	1.20	0.20	0.25
NH_4, mg/kg	11	1	4	3	9	2	3	15	2	10
NO_3, mg/kg	24	22	82	35	111	18	59	79	253	120
pH_{H_2O}	6.57	6.23	5.92	6.85	7.06	6.68	6.65	5.07	6.78	6.75
pH_{KCl}	4.89	4.60	4.49	5.69	6.58	5.27	5.55	4.00	5.94	5.86

The bulk density of soils varies from 0.23 kg/dm^3 in a park zone with a high content of organic matter (sample M15) to 1.07 kg/dm^3 on a lawn near a road of predominantly mineral composition (K9). Field moisture also depends on the ratio of organic and mineral components and varies in the range of 45-280 %. The content of carbon and nitrogen demonstrates similar heterogeneity: maximum concentrations were recorded in sample M15 (27.86 wt.% C and 1.20 wt.% N), indicating the presence of organic matter.

The content of ammonium (NH_4^+) and nitrate (NO_3^-) forms of nitrogen also varies greatly. The highest content of nitrate nitrogen was found in sample M17 (253 mg/kg), the lowest – in sample K11 (18 mg/kg). The acidity of aqueous soil suspensions corresponds to slightly acidic and near-neutral conditions. In KCl solution, the studied samples show a decrease in pH due to ion exchange of potassium for H_3O^+ cations of the soil absorption complex [33].

Effect of VSC application on the content of mobile forms of metals in mixtures with urban soils. Soils of Monchegorsk have elevated concentrations of Ni and Cu, while in Apatity and Kirovsk their content is significantly lower. The concentration of the actually mobile (C1) form of Ni in Monchegorsk soils reaches 180 mg/kg (M15), Cu – 110 mg/kg (M19), which significantly exceeds background values and indicates a high degree of anthropogenic contamination. In one sample from

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Apatity, the content of C1(Cu) reaches 320 mg/kg; in Kirovsk, soils are not contaminated with metals, and concentrations of both forms are 1-5 mg/kg.

The use of background values of heavy metal content instead of maximum permissible concentrations (MPC) for assessing the degree of soil contamination is due to the need to account for the regional geochemical features of the study area. MPC is a sanitary-hygienic standard uniform for the entire country and does not account for natural anomalies. Comparison with the regional background allows assessing specifically the anthropogenic load on the soil, excluding the natural variability of its chemical composition. This approach corresponds to standard methods of geoenvironmental monitoring[5].

The introduction of VSC into the soil reduces the content of both forms of Cu in all samples from Apatity and Monchegorsk (Fig.4, *a*, *b*). For Ni, both an increase and a decrease in concentrations in the experimental series compared to the control are observed (Fig.4, *c*, *d*). At C1(Ni) in the initial soil up to 10 mg/kg (and C2(Ni) < 100 mg/kg), the addition of VSC leads to an increase in the content of metal forms in the soil mixtures. For highly contaminated soils (C1 > 10 mg/kg, C2 > 400 mg/kg), the concentrations of mobile forms of Ni decrease. In the range of C2(Ni) 100-400 mg/kg, no significant change in C2 occurs.

As is known, the toxicity of multicomponent solutions depends not only on the concentration of ecotoxicants but also on the content of macroelements, which prevent the penetration of metals into cellular structures of biological entities [34].

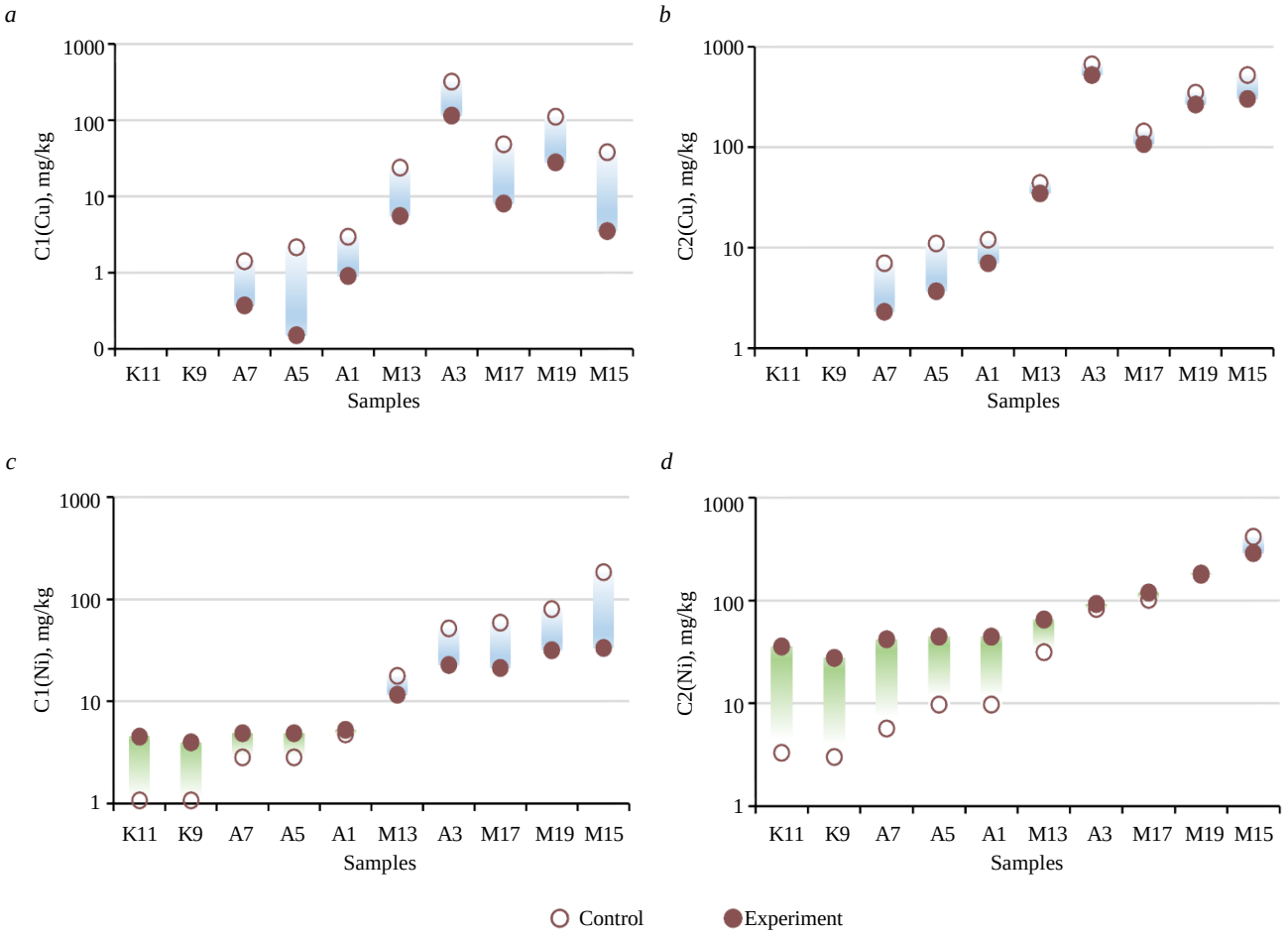


Fig.4. Content of Cu (*a*, *b*) and Ni (*c*, *d*) in soil samples in actually (C1) and potentially (C2) mobile forms in control and experimental series

[5] RD 52.18.885-2019. Methodological guidelines. Determination of regional background concentrations of organic contaminating substances in soils (introduced by Order of Roshydromet dated 30.12.2019 N 844).

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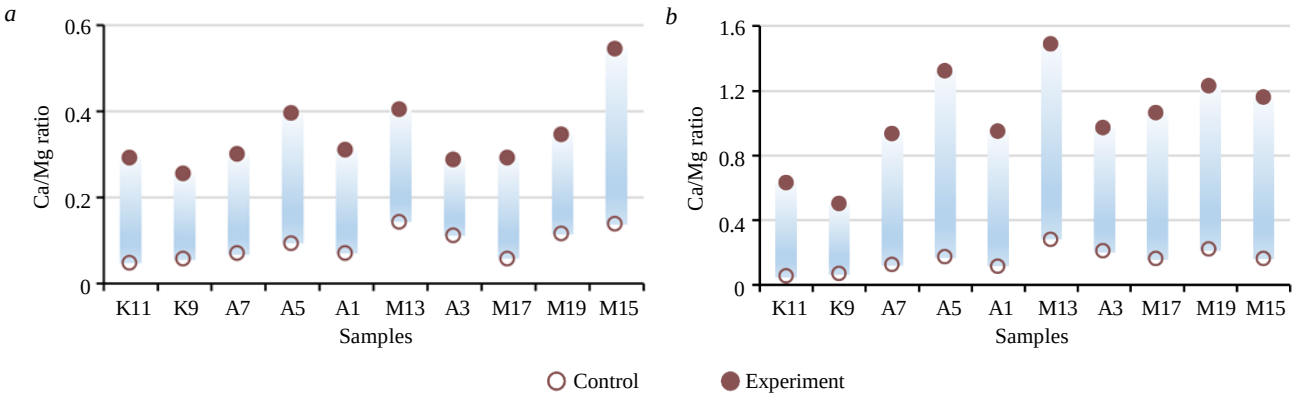


Fig.5. Ratio of actually (*a*) and potentially (*b*) mobile forms of Ca to Mg upon VSC application in soils with different composition

Effect of VSC application on the content of mobile forms of macroelements in urban soils. The content of the actually mobile form of Mg increases statistically significantly in all experimental variants (Fig.5, Table 3). In the initial soils, C1(Mg) is 0.14-0.69 g/kg; after VSC application, it reaches 0.9-1.9 g/kg. For Ca, the same parameter changes to a lesser extent and amounts to C1(Ca) in the control group of 1.33-5.03 g/kg, in the experimental one, 2.58-3.56 g/kg. More significant changes are observed for the potentially mobile (C2) form of macroelements, the content of which increases by an order of magnitude for Mg and 2-3 times for Ca. The concentration of Ca in both forms in all variants exceeds the concentration of Mg, which is a favourable factor for plants (Fig.5).

Table 3

Content of actually and potentially mobile forms of Mg and Ca upon VSC application to soils with various composition

Component	Component form	Parameter	Samples									
			K11	K9	A7	A5	A1	M13	A3	M17	M19	M15
Mg	C1	Control	0.14	0.22	0.20	0.20	0.19	0.19	0.22	0.20	0.31	0.69
		Experiment	0.90	0.90	1.00	1.26	1.01	1.04	0.88	1.00	1.00	1.90
		$LSD_{0.5}$	0.15	0.03	0.05	0.15	0.06	0.10	0.10	0.16	0.07	0.26
	C2	Control	0.27	0.34	0.43	0.45	0.42	0.43	0.69	0.63	0.79	1.16
		Experiment	6.15	4.63	7.20	8.61	7.30	7.60	6.75	8.78	8.93	13.81
		$LSD_{0.5}$	0.45	0.93	0.64	1.09	0.92	1.25	0.67	0.30	0.40	1.58
Ca	C1	Control	2.98	4.02	2.98	2.13	2.73	1.33	1.98	3.45	2.72	5.03
		Experiment	3.08	3.56	3.36	3.21	3.29	2.58	3.08	3.43	2.89	3.50
		$LSD_{0.5}$	0.60	0.50	0.39	0.52	0.29	0.33	0.32	0.31	0.29	0.22
	C2	Control	5.93	5.59	3.71	2.73	3.69	1.54	3.44	4.09	3.73	7.29
		Experiment	9.84	9.24	7.76	6.51	7.76	5.11	6.96	8.28	7.31	11.96
		$LSD_{0.5}$	1.16	1.23	0.72	0.37	0.36	1.02	0.51	0.63	1.22	2.07

According to the classification [35], a high degree of soil silicon supply corresponds to a content of the actually mobile form of > 0.04 g/kg, potentially mobile > 1 g/kg. For Monchegorsk soils, these values are lower; they are characterized by a medium level of silicon supply, and an increase in the content of acid-soluble forms of silicon upon VSC application is observed, while in other variants either a decrease or no change in silicon concentration occurs (Fig.6, *a*, *b*).

Similar processes of component content stabilization are also observed for phosphorus (Fig.6, *c*, *d*). At a P content in the potentially mobile fraction (Kirsanov extract) of C2 < 1 g/kg, a slight increase is observed after VSC application, while at higher values – a decrease in this parameter. As for the actually mobile form, its concentration decreases in all variants. This effect is consistent with the well-studied properties of silicate minerals (including vermiculite and serpentine), which can retain phosphates through surface sorption, formation of poorly soluble compounds, and changes in the acid-base and ionic balance of the soil [36-38].

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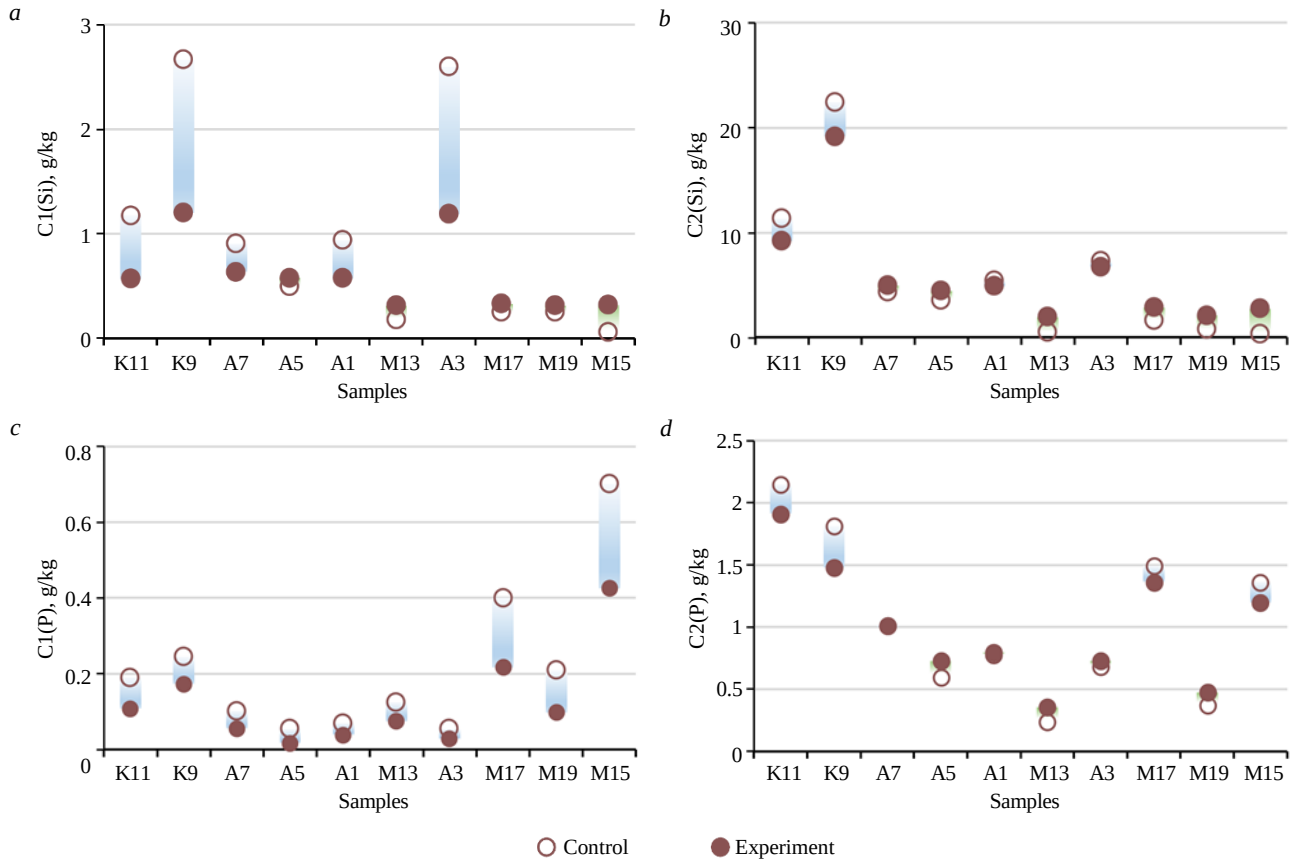


Fig.6. Acid-soluble forms of silicon and phosphorus in VSC mixtures with different soils

Phytotesting of VSC mixtures with agrosoil and urban soils. In soil mixtures with agrosoil, with increasing VSC content, a linear decrease in CAS from a high value for agrosoil (0.95) to its absence in VSC is observed (Fig.7, *a*). The mass of the underground part (UP) of the plant at the extreme points of the experimental dependence is practically the same and amounts to 0.09-0.1 g/plant, but at a VSC content of 10-60 wt.%, an increase to 0.13-0.18 g/plant is observed. The lowest value of the aboveground part (AP) biomass was recorded for the experiment with 100 % VSC (1 g/plant); in the 0-50 wt.% VSC mass range, the AP mass changes insignificantly (5-5.5 g/plant) and decreases at a 60 wt.% VSC mass content to 3.8 g/plant. The total biomass and the number of leaves of plants differed statistically significantly ($p < 0.05$) from other variants only when growing plants on pure VSC (Fig.7, *b*).

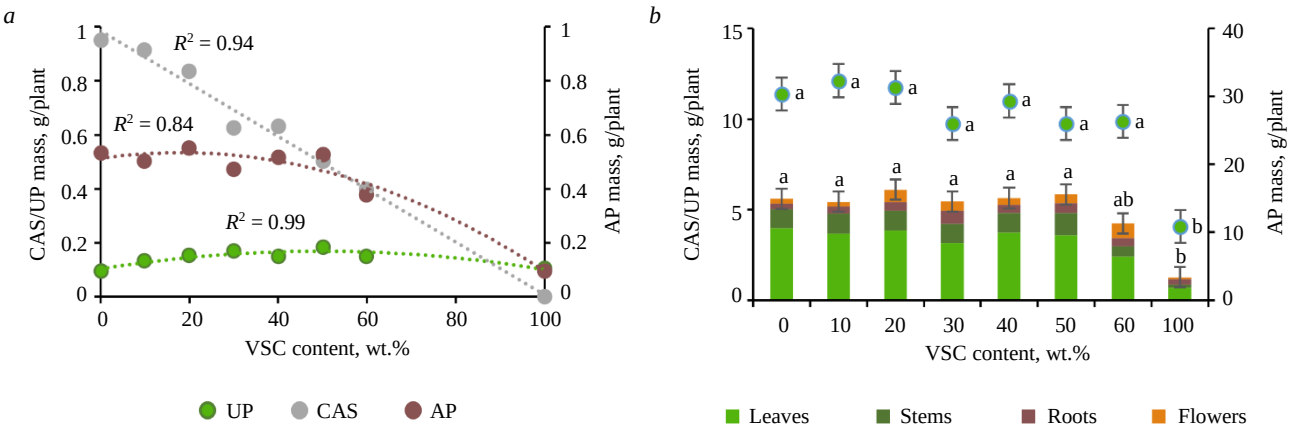


Fig.7. Effect of VSC application on cellulolytic activity (*a*) and biometric parameters of test plants (*b*)

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The number of leaves slightly decreases (from 30 to 26) in the range of 0-60 % VSC by mass and drops sharply to 10 leaves in the experiment with 100 % VSC by mass (Fig.7, *b*). A similar effect was noted for the number of stems, but it was less pronounced. Despite a significant decrease in the nutritional status of soil mixtures, as reflected by CAS, within the VSC content range of 0-50 % by mass, the weight of the aboveground part of plants practically does not change, while that of the underground part increases.

The increase in the root system mass of marigolds at 100 % VSC compared to the initial agrosoil is an adaptive response to a substrate with a high content of actually and potentially mobile forms of metals under conditions of their low availability [39]. In all experimental variants and in the control (100 % VSC), a high content of mobile forms of calcium and magnesium is maintained. The low content of available forms of nickel and the high content of macroelements create optimal conditions for root system development, which is confirmed by the results for root system mass in variants with a 60-100 % VSC content. The use of high doses of concentrate does not exert a toxic effect on the development of marigolds, which is important when using VSC as a prolonged source of Ca and Mg for plants in urban areas.

The results of short-term phytotesting of VSC mixtures with urban soils using marigolds did not reveal differences between experimental variants, which confirmed the described results. The introduction of VSC into urban soil contaminated with nickel exerts an integrated positive effect, allowing the adaptive mechanisms of marigolds to be fully realized. On the one hand, the sorption properties of the material and its ability to increase soil pH reduce the availability of potentially toxic metals. This is important, since marigolds in the active growth phase are sensitive to high concentrations of available Ni [34]. On the other hand, enrichment of the soil with calcium and magnesium improves mineral nutrition, which is especially relevant given the ability of nickel to inhibit the transport of these elements. As a result of stress reduction and nutrition optimization, plants accumulate biomass and can effectively implement their species-specific strategy toward nickel.

Recent studies confirm that marigolds can act as effective accumulators of nickel under certain soil conditions, and their antioxidant system allows neutralizing residual oxidative stress [40]. Thus, the combined use of a mineral sorbent and marigold culture represents a promising approach for phytostabilization and phytoextraction of nickel in contaminated urban areas.

Conclusion

Using the example of agrosoil and soil samples collected in cities with different levels of anthropogenic impact, we showed that the introduction of vermiculite-serpentine concentrate to soils increases the content of acid-soluble forms of calcium and magnesium and optimizes the Ca/Mg ratio. Simultaneously, stabilization of the content of mobile forms of silicon and phosphorus occurs.

The application of VSC exerts a differentiated effect on the content of the actually mobile fraction of heavy metals. The content of mobile copper decreases significantly in all studied samples regardless of the level of anthropogenic impact. For nickel, a dependence on the initial contamination level was observed: in slightly contaminated agrosoil at a VSC content of 10-50 wt.%, the mobility of Ni increases from 1.5 to 2.5 mg/kg, and at doses above 60 % drops below background values; in Monchegorsk soils with a high level of contamination (actually mobile Ni up to 180 mg/kg), VSC application leads to a steady decrease in mobile forms of nickel.

We found out that the introduction of VSC into soils does not exert a toxic effect on test plants (*Tagetes patula*). The absence of phytotoxicity is confirmed by an increase in root system mass in the VSC content range of 10-60 % from 0.09-0.1 to 0.13-0.18 g/plant, which indicates adaptive responses of plants to a substrate with a high content of potentially mobile forms of metals under conditions of their low actual availability.

The practical significance of the work lies in substantiating the possibility of using large-tonnage waste from the mining industry – poor vermiculite-sungulite ores – for the remediation of disturbed lands in the Arctic zone of the Russian Federation. The fraction smaller than 20 mm, the content of

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which is 80 wt.% of poor ores, is advisable to use for revegetation in areas with zero biological productivity [5], and the fraction larger than 20 mm can be used to obtain vermiculite-serpentine concentrate with a high content of vermiculite and serpentine. This will reduce the application rate of the material for targeted use at local sites. Vermiculite-serpentine concentrate can be recommended as a meliorant for the remediation of urban degraded soils characterized by a low content of macroelements and contamination with heavy metals.

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