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**ACCUMULATION OF HEAVY METALS
BY *Silene vulgaris* OCCURRING ON SERPENTINE
WASTE DUMP IN GROCHOW (LOWER SILESIA)**

**AKUMULACJA METALI CIĘŻKICH PRZEZ *Silene vulgaris*
WYSTĘPUJĄCEJ NA HAŁDZIE ODPADÓW SERPENTYNITOWYCH
W GROCHOWIE (DOLNY ŚLĄSK)**

Abstract: The investigation involved serpentine waste dump in Grochow (Lower Silesia). Botanical composition of analyzed serpentine dumping ground was poor since in the areas subjected to examination there were designated only 30 vascular plant species classified mainly to three botanical families – Poaceae, Fabaceae and Asteraceae. Dominant species on dumping ground in Grochow was the only recognized species representing Caryophyllaceae – *Silene vulgaris*. Analysis of soils material proved that total contents of nickel, chromium, manganese and cobalt were higher than average quantities of these metals in soil environment. Mobile forms, available for plants, provided, in most cases, for only a small per cent of their total forms. In plant material originating from serpentine dumping ground their were recorded high concentrations of Ni, Cr and Co in comparison with their natural amounts. Concentrations of all the examined metals were higher in underground parts of *Silene vulgaris* than in aboveground parts.

Keywords: heavy metals, serpentine, spoil heaps, *Silene vulgaris*

Introduction

In Poland, the areas of surface soils featuring naturally high content of heavy metals are limited to a few calamine, ore-bearing areas and rare, specific for Lower Silesia, soils formed from serpentine rocks [1]. Serpentine rocks are to be found on the territory of Poland, covering the area of about 80 km² and they form several elevated mountain massifs in the foot of the Sudeten [2]. Polish serpentine soils occupy relatively small areas and therefore, they are not of economic value [3]. Lower Silesian serpentine rocks have been exploited for a long time as a basis of nickel and chromium mining. The

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evidence for the latter ones are old quarries, headings and mineral waste dumps with scarce vegetation growing there.

Relatively poor occurrence of plant species probably results from specific, extremely hard, unfavorable conditions typical for those places [4]. Detrital serpentine minerals characterize a number of disadvantageous properties. Low moisture, high (basic) pH, low content of nitrogen, phosphorus and calcium, high, potentially harmful concentration of manganese, nickel and cobalt provide for the disorders in plant growth and development [5, 6].

Toxic effect of heavy metals, deficit of macroelements and water in the ground, intensive insolation (especially in the case of mineral waste dumps) can favor the occurrence of plants specific for these conditions [2].

The aim of the work was determination of botanical composition of waste dump vegetation (exclusively vascular plants), as well as the degree of heavy metals accumulation in soil and plant material collected from serpentine waste dump in Grochow.

Material and methods

The area subjected to investigation is located about 70 km to the south from Wrocław, and to the south-west direction from Zabkowice Śląskie within the territory of Bardo community.

Serpentine waste dump in Grochow was formed in connection with magnesite exploitation from mineral deposit within the range of Grochow Massif.

Serpentines building this massif were created as a result of alteration of ultrabasic and basic rocks in deep facies of contact metamorphism [7].

Outer serpentine dumping ground in Grochow, subjected to the examination, covers the area of about 36 hectares and is situated in the vicinity of magnesite exploitation range, map No. 1. The material for chemical analysis were soil samples (mainly detrital minerals) and plant samples from serpentine dumping ground in Grochow. In order to compare examination data, on large territory there were distinguished four areas, diversified both as to their succession and surface constitution. The material of dumping ground, collected from surface layer from the depth of 0–15 cm, was transported to the analytical laboratory after its previous preservation. The samples underwent the assay of reaction (pH) according to potentiometric method in 1 mol KCl solution. Total content of selected heavy metals (Ni, Cr, Co, Mn, Zn, Pb and Cu) was determined due to spectrometric analysis technique, after previous samples mineralization in 70 % (per)chloric(VII) acid. Soluble forms of selected metals, after extraction in 1 mol HCl dm⁻³, were assayed by AAS method.

Plant material included above – and underground parts of *Silene vulgaris*, collected from four previously distinguished areas and preserved for further chemical analyses.

Plant material, cleaned, dried and ground, underwent dry mineralization at the temperature of 450 °C, and in the filtrates obtained there were assayed the following chemical elements Cr, Co, Mn, Zn, Pb and Cu according to AAS technique with the use of Spectra AA 220 Fast Sequential device. Inflated catchfly *Silene vulgaris* (Moench)

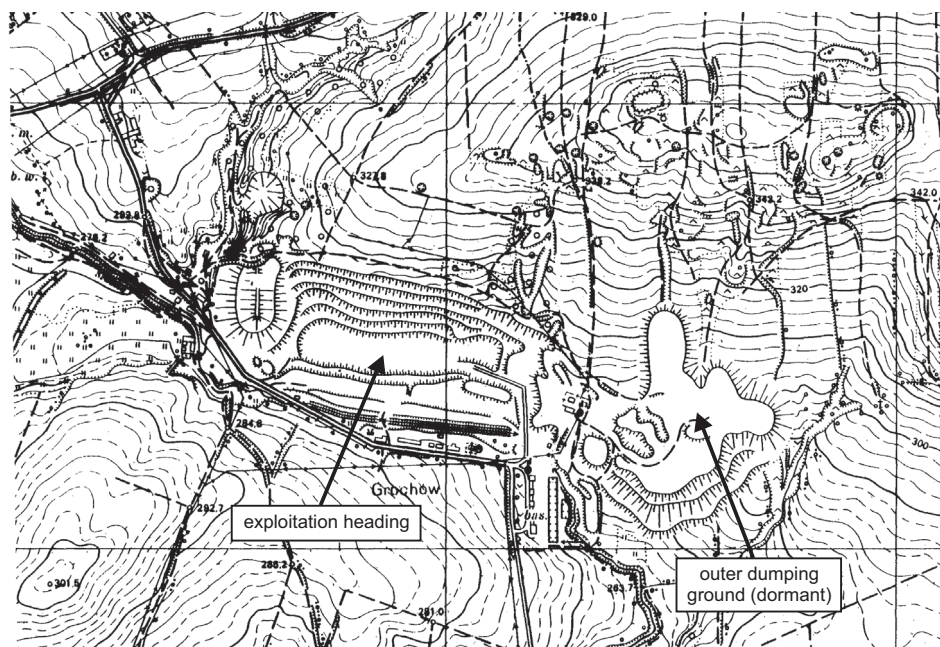


Fig. 1. Location of serpentine waste dump in Grochow (owned by Magnesite Plant "Grochow" S.A. in Grochow)

Garcke is a perennial plant belonging to Caryophyllaceae family [8]. It commonly occurs in native territories of Europe, north Africa and Asia. This species has also spread in the areas of both Americas. In Poland *Silene* species can be found on meadows, fields and forests [9], as well as on ruderal habitat sand the ones enriched with heavy metals, eg serpentine [10] or calamine waste dumps [11] as well as post-mining dumping grounds [12, 13].

Results and discussion

Botanical composition of serpentine waste dump

In the area of the examined serpentine waste ground in Grochow there were designated 30 species of vascular plants from 16 botanical families (Table 1). The presence of majority of these species on serpentine waste dump results from natural primary succession, while the remaining ones represent numerous seedlings of trees with some part of them planted within the frames of initial stage of waste dumps reclamation destined as afforested areas. Most commonly occurring botanical families on a waste dump were Poaceae and Fabaceae, as well as Asteraceae. The remaining families had their single representatives, yet very often dominating on a dumping ground, eg *Silene vulgaris* from Caryophyllaceae.

Table 1

Botanical composition of serpentine waste dump in Grochow

No.	Species	Family	Examined stand			
			1	2	3	4
1	<i>Achillea millefolium</i> L.	Asteraceae	+	–	–	–
2	<i>Anthyllis vulneraria</i> L.	Fabaceae	+	–	+	–
3	<i>Apera spica-venti</i> (L.) P.B.	Poaceae	+	+	+	+
4	<i>Betula pendula</i> Roth seedlings	Betulaceae	–	+	+	+
5	<i>Bromus erectus</i> Huds.	Poaceae	+	+	+	+
6	<i>Calamagrostis epigeios</i> (L.) Roth	Poaceae	+	+	+	+
7	<i>Campanula rotundifolia</i> L.	Campanulaceae	+	+	–	–
8	<i>Carlina vulgaris</i> L.	Asteraceae	–	–	+	+
9	<i>Centaurea stoebe</i> L.	Asteraceae	+	+	+	–
10	<i>Cirsium arvense</i> (L.) Scop.	Asteraceae	–	+	–	–
11	<i>Koeleria macrantha</i> (Ledeb.) Schultes	Poaceae	+	+	+	+
12	<i>Daucus carota</i> L.	Apiaceae	+	+	+	+
13	<i>Echium vulgare</i> L.	Boraginaceae	+	–	–	–
14	<i>Euphrasia roscoviana</i> Hayne	Scrophulariaceae	–	+	–	–
15	<i>Festuca ovina</i> L.	Poaceae	+	+	+	+
16	<i>Galium verum</i> L.	Rubiaceae	+	+	–	–
17	<i>Genista tinctoria</i> L.	Fabaceae	+	–	–	–
18	<i>Hypericum perforatum</i> L.	Hypericaceae	–	+	+	–
19	<i>Lathyrus sylvestris</i> L.	Fabaceae	–	+	+	–
20	<i>Leontodon hispidus</i> L.	Asteraceae	+	–	–	–
21	<i>Lotus corniculatus</i> L.	Fabaceae	+	+	+	+
22	<i>Melilotus alba</i> Medik.	Fabaceae	–	–	+	–
23	<i>Phleum pratense</i> L.	Poaceae	+	+	+	+
24	<i>Pinus silvestris</i> L. seedlings	Pinaceae	–	+	+	+
25	<i>Plantago media</i> L.	Plantaginaceae	+	–	–	–
26	<i>Potentilla recta</i> L.	Rosaceae	+	–	–	+
27	<i>Scabiosa ochroleuca</i> L.	Dipsacaceae	+	–	+	+
28	<i>Silene vulgaris</i> (Moench) Garcke	Caryophyllaceae	+	+	+	+
29	<i>Thymus pulegioides</i> L.	Labiatae	+	–	+	–
30	<i>Trifolium dubium</i> Sibth.	Fabaceae	–	+	–	–

On post-mining and post-industrial waste dumps spontaneous succession of plants requires a long time to take place [14]. Outer dumping of serpentine wastes in Grochow was made dormant only several years ago, which can explain its poor botanical composition. Relatively small number of plant species on serpentine dumping grounds and headings are confirmed by investigation conducted in this type of objects in Lower Silesia [10, 15].

Environmental conditions of waste dumps, effected by unfavorable properties of the ground and by exposure to intensive insolation and winds, find their reflexion not only

in poor but also specific flora. Numerously occurring species of Poaceae, Fabaceae and Asteraceae families seem to be significant of anthropogenic serpentine habitats of Lower Silesia [10, 15]. The species designated as the waste dump in Grochowa are repeatedly found on these types of objects in Naslawice, Wirki or Szklary. The species like *Silene vulgaris*, *Calamagrostis epigejos* or *Festuca ovina* are also enumerated regarding the composition of Polish natural serpentine plants communities [10, 15, 16].

Among designated in the whole examined area 30 species of vascular plants the highest number of them was found on the stand No. 1–21 species, stand. No. 2 and 3 were the site of occurrence of 19 plant species and the lowest number belonged to stand No. 4–14 species. There were recorded 9 species common for all the areas, namely: *Apera spica-venti*, *Bromus erectus*, *Calamagrostis epigejos*, *Daucus carota*, *Festuca ovina*, *Koeleria macrantha* *Lotus corniculatus*, *Phleum pratense* and *Silene vulgaris*. On some stands there were also recognized plant species which did not grow on the remaining stands. Here can be distinguished the stand No. 1 covered by thick vegetation, located in some distance from serpentine waste dumps.

The content of selected heavy metals in soils

In the analyzed soil material originating from serpentine dumping ground the highest total concentrations of heavy metals belonged to nickel, chromium and manganese – Table 2.

Table 2

Soil reaction and the content of total forms of selected heavy metals in soil collected from serpentine waste dump in Grochow

Stand	Sample number	pH [1 mol KCl · dm ⁻³]	Total forms content [mg · kg ⁻¹ of soil]						
			Ni	Cr	Mn	Co	Cu	Pb	Zn
1	1	7.9	3182	1033	1188	86.3	9.68	25.0	75
	2	7.8	2301	1088	813	64.0	8.45	28.5	53
	3	7.4	2052	984	915	64.5	13.93	36.3	73
2	4	8.7	1854	1155	1025	67.3	34.05	24.0	45
	5	8.7	1833	1229	988	65.8	28.73	21.8	45
	6	8.7	4081	1093	1075	70.0	35.98	23.3	45
3	7	8.7	1960	1285	1078	66.3	69.80	60.8	53
	8	8.6	1736	916	1035	57.8	37.36	31.5	35
	9	8.6	2058	1245	935	65.0	43.75	38.3	43
4	10	8.6	2287	1657	1018	74.3	162.80	176.3	78
	11	8.3	2314	1242	1068	70.5	148.10	102.3	60
	12	8.5	2063	1033	1028	66.5	178.80	124.3	48

Total concentration of nickel in the examined samples in the range (1736; 4081) mg · kg⁻¹ (Table 2). Most often reported admissible nickel content in soils used for forming purposes was 100 ppm [17]. According to Decree by Minister of the

Environment regarding soil quality standards and earth quality standards [18] industrial grounds or useful minerals grounds can contain maximum 300 mg Ni in kg of soil. In the soils formed from serpentine minerals nickel concentration reaches the values of thousand ppm [17]. Detected high range of total contents of nickel forms finds its confirmation in the results of examination conducted in the area of other serpentine dumping grounds subjected to investigation [19], as well as nickel ore mines connected with Lower Silesian occurrences of serpentine [20].

In the analyzed soil material there was also determined considerably high content of total chromium, ranging from 916 mg · kg⁻¹ to 1657 mg · kg⁻¹ – Table 2. For soils formed from serpentine minerals typical values range 5000 mg · kg⁻¹ (0.5 %) Cr, at the range from 1000 mg · kg⁻¹ to even 25000 mg · kg⁻¹, which depends on the amounts of scattered chromite [21]. Polish soils, in relation to their mechanical composition, contain average from 7 ppm of chromium for light soils to 24 ppm for heavy soils [17]. The content of total manganese in soil samples from serpentine waste dump in Grochow amounted to (813; 1188) mg · kg⁻¹ – Table 2. Average manganese content in sandy soils of Poland equals 240 ppm and in loamy soils it is about 570 ppm, while admissible content in cultivated soils is assumed as (1500; 3000) ppm Mn [17].

Soil samples collected from the waste dump contained elevated (as compared with average amounts in Polish soils) values of total cobalt, since they were found within the range of (57.8; 86.3) mg · kg⁻¹ – Table 2. Detected Co concentrations exceeded admissible values for grounds used for farming purposes as the latter ones equal to 30 mg · kg⁻¹ [17]. Yet the values obtained did not exceed admissible level of this chemical element for useful minerals grounds [18]. Concentrations of the remaining analyzed metals (Cu, Pb, Zn) met their natural level [17], except for the samples from stand No. 4 lead and copper contents featured slightly higher values.

The contents of soluble metals subjected to analysis, thus those of significant meaning as far as plants are concerned, proved that they constitute, except for nickel and manganese, only a small per cent of their total contents (Table 3). It was determined that concentration of nickel mobile forms ranged from 12.0 % to 25.8 % of total forms content, while in the case of available manganese it amounted from 20.5 % to 66.4 %. Concentrations of mobile forms of the remaining metals were as follows: cobalt (14.8; 24.4) mg · kg⁻¹ and chromium (1.1; 10.8) mg · kg⁻¹ (Table 3). The results obtained pointed to especially low quantity of chromium available for plants whose contribution does not exceed 1 % of total forms content. According to the literature [21], available forms of chromium in serpentine soils occur in extremely low quantities, which is expressed in scarce absorption of this metal by plants.

Our own investigation was carried out regarding four diversified fragments of serpentine dumping ground, which enabled their comparing with one another in the view of heavy metal content in the ground. Recorded total contents of selected heavy metals (Table 2) proved to be diversified and they depended both on the fragment of examined dumping ground and on chemical element analyzed.

As it results from the data of Table 3 showing the concentrations of mobile form of analyzed metals determined for particular stands, the stand No. 4 (typical dumping ground covered with poor vegetation) characterized (in the case of all the elements) the

Table 3

The content of soluble forms of selected heavy metals in soil collected from serpentine waste dump in Grochow

Stand	Sample number	Soluble forms content [$\text{mg} \cdot \text{kg}^{-1}$ of soil]						
		Ni	Cr	Mn	Co	Cu	Pb	Zn
1	1	600.5	1.3	244.0	15.8	3.29	11.7	15.5
	2	388.8	1.1	251.5	14.8	3.52	14.0	14.5
	3	353.1	1.9	305.0	17.3	4.73	19.7	27.0
2	4	425.9	5.2	644.5	26.1	11.13	6.4	10.0
	5	424.0	8.4	630.5	26.7	9.57	6.3	11.0
	6	488.7	7.6	622.0	28.3	10.61	6.7	11.0
3	7	465.8	6.0	659.0	24.4	60.33	39.0	17.0
	8	364.3	3.3	662.5	21.7	13.46	14.2	9.5
	9	500.1	7.5	620.5	28.3	22.93	20.8	12.5
4	10	573.7	10.8	648.5	27.8	42.73	132.5	27.5
	11	596.5	9.0	698.5	29.7	115.80	74.6	27.5
	12	448.0	6.4	632.0	24.0	95.30	76.3	14.0

highest values. The stand No. 1 featured the lowest contents of mobile chromium, manganese, cobalt and copper. The lowest concentrations of soluble lead and zinc were detected in detrial minerals originating from the stand No. 2. On the basis of the examinations conducted it is possible to state that soil pH amount from 7.4 to 8.7. Basic reaction constitutes a characteristic property of serpentine minerals formed from ultrabasic rocks [22].

The content of selected heavy metals in plants

Considerable accumulation of nickel in plants, ranging up to several thousands ppm Ni in dry matter can occur in some plant species growing on serpentine soils "nickel" ones [23]. Nickel concentrations, which can prove toxic, in plants ranges from 10 to 100 ppm and they depend, among others, on plant resistance or chemical form of the element [17]. Analyzed parts of *Silene vulgaris* contained from 23.7 to 161.8 mg Ni in kg d.m., yet only two samples showed Ni concentration exceeding $100 \text{ mg} \cdot \text{kg}^{-1}$ d.m. (Table 4). The content of chromium in the analyzed plant material was found within the range of $2.6\text{--}41.6 \text{ mg} \cdot \text{kg}^{-1}$ d.m. (Table 4). The value assumed as toxic for plants equals 20 ppm d.m. and it was exceeded in three samples. Chromium content in plants on serpentine waste dump in Grochow reached higher values than those detected on serpentine dumping ground in Wirki [10]. Sample analysis of *Silene vulgaris* showed manganese content meeting the range $49.6\text{--}127.7 \text{ mg} \cdot \text{kg}^{-1}$ d.m. (Table 4). Manganese concentration in plants most often amounts several tens ppm in dry matter, but it can range from several to even several thousands ppm Mn, according to plant species and properties of the ground [23]. Cobalt concentration in a plant was between $1.80\text{--}6.62 \text{ mg} \cdot \text{kg}^{-1}$ d.m. (Table 4). Natural Co content in plants is usually much lower than the one detected in the examined plant material [24]. Higher concentration of

Table 4

The content of selected heavy metals in *Silene vulgaris* from serpentine waste dump in Grochow

Stand	Sample number	Plant parts	Heavy metals content [mg · kg ⁻¹ d.m.]							
			Fe	Ni	Cr	Mn	Co	Cu	Pb	Zn
1	1	aboveground	938.0	60.5	5.7	60.5	2.94	5.32	6.70	22.45
	2		481.5	40.0	2.6	60.5	2.30	3.89	4.30	16.85
	3	underground	1056.5	63.0	7.2	77.6	3.34	32.65	7.00	32.35
2	4	aboveground	597.0	30.5	10.1	81.4	2.14	3.76	4.30	17.60
	5		453.0	23.7	5.4	78.2	1.96	4.81	4.50	21.65
	6	underground	1818.0	87.1	29.1	100.9	4.31	6.53	4.20	20.70
3	7	aboveground	829.5	47.4	10.5	62.4	2.56	7.70	7.65	18.60
	8		397.5	24.2	5.5	49.6	1.80	10.01	6.70	24.70
	9	underground	2892.0	159.2	41.6	122.2	6.01	29.05	15.90	23.65
4	10	aboveground	1488.0	88.0	16.1	70.0	3.68	15.97	7.80	15.00
	11		453.0	22.8	4.0	57.8	2.10	12.42	9.50	9.14
	12	underground	3011.5	161.8	37.1	127.7	6.62	25.89	21.30	24.88

cobalt can be explained by absorption of this element in the amounts proportional to its soluble forms occurring in the ground [17]. Assumed toxic level for plants is higher than 15–50 ppm [17]. Concentrations of the remaining heavy metals (Cu, Pb, Zn) remained within their natural range or even relatively low, in the case of zinc [17]. Elevated concentrations of nickel, chromium and cobalt in plants can be justified by the character of serpentine ground, which was rich in those elements [2, 25]. The estimation of heavy metals in above- and underground parts of plants makes it possible to state that plant roots accumulated markedly higher quantities of analyzed elements (Table 4). The tendency in plants to accumulate metals in underground parts protects plants organs important for their functioning (flowers, fruits), yet it is not a rule governing plants higher tolerance of excessive amounts of metals [26].

Conclusions

1. There were designated 30 species of vascular plants on serpentine waste dump in Grochow.
2. Most numerous represented botanical families were Poaceae, Fabaceae and Asteraceae.
3. There were recorded high contents of total form so Ni, Cr, Mn and Co (as compared with a natural one) in soil material originating from serpentine waste dump.
4. Soluble forms of analyzed metals (generally) provided for only an insignificant per cent of their total forms.
5. In plant material (*Silene vulgaris*) coming from serpentine waste dump there were recorded high concentrations of Ni, Cr and Co in comparison with natural ones. In all the examined plants concentrations of the metals examined were higher in underground plant parts than in aboveground parts.

6. The reaction of soil material subjected to examination, collected from serpentine dumping ground was basic.

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AKUMULACJA METALI CIĘŻKICH PRZEZ *Silene vulgaris* WYSTĘPUJĄCEJ NA HAŁDZIE ODPADÓW SERPENTYNITOWYCH W GROCHOWIE (DOLNY ŚLĄSK)

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Abstrakt: Badaniem objęto hałdę odpadów serpentynitowych w Grochowie (Dolny Śląsk). Skład florystyczny analizowanego zwałowiska był ubogi. Na badanych powierzchniach stwierdzono jedynie 30 gatunków roślin naczyniowych, należących głównie do trzech rodzin botanicznych – Poaceae, Fabaceae, Asteraceae.

Gatunkiem dominującym na zwałowisku w Grochowie był jedyny rozpoznany na jego obszarze przedstawiciel Caryophyllaceae – *Silene vulgaris*. Analiza materiału glebowego wykazała, że ogólne zawartości niklu, chromu, manganu i kobaltu były wyższe od przeciętnych ilości tych metali w środowisku glebowym.

Formy mobilne, dostępne dla roślin stanowiły we wszystkich przypadkach tylko niewielki procent ich form całkowitych. W materiale roślinnym pochodzącym ze zwałowiska stwierdzono wysokie w porównaniu z naturalnymi zawartości Ni, Cr i Co. Koncentracje wszystkich analizowanych metali były wyższe w częściach podziemnych *Silene vulgaris* niż w częściach nadziemnych.

Słowa kluczowe: metale ciężkie, hałda, serpentynit, *Silene vulgaris*