



Leveraging the competitive advantages of  
end-of-life underground coal mines to  
maximise the creation of green and quality jobs

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## **Deliverable 3.2**

Soil substitutes for restoration

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## 1 Executive summary

This Deliverable presents the results of the development of artificial soil substitutes for rehabilitating coal mine-affected areas in the northeastern region of Slovenia (Velenje).

The artificial soil substitutes for land reclamation were prepared based on by-products from lignite coal combustion: fly ash, gypsum from desulfurization, and sludges from technological water. The components' high pH, high salinity and low organic matter level are responsible for the lack of plant sproutings.

To improve the conditions for plant growth, lignite coal and green compost from biological manufacturing were tested as additives to the mixture. The optimal composition of artificial soil was developed based on the results of the physicochemical and phytotoxicity analyses.

Sufficient plant growth was obtained; however, concentrations of some toxic metals could slightly exceed warning values according to the regulations in the Republic of Slovenia (As, Cd, Mo and Zn). An additional review of the local laws has to be done to ensure that final products can be used in the reclamation processes.

Based on the results of the physicochemical analyses and phytotoxicity test, the possibility of using mining water from the Premogovnik Velenje coal mine to irrigate vegetation was confirmed. However, salinity and the concentration of molybdenum in that water slightly exceed the recommended threshold for prolonged irrigation use. The concentration of soluble salts and molybdenum and the possible toxic effects on plants and soil organisms should be monitored in areas where long-time irrigation was applied.



## 2 Introduction

Within Work Package 3, Task 3.2 assesses the possibility of land rehabilitation of coal mine-affected areas in northeastern Slovenia (Velenje) using soil substitutes. For this purpose, the artificial soils were investigated at a laboratory scale using coal combustion by-products from Šoštanj Thermal Power Plant, coal lignite from coal mine Premogovnik Velenje and one organic material called green compost from an industrial composting facility. Components and elaborated soil substitutes were tested in the Laboratories of the Central Mining Institute in Poland for physicochemical parameters and phytotoxicity tests.

Preparing soil substitutes was to restore the high subsidence post-mining area in Velenje and transform it into a green surface for recreational use.

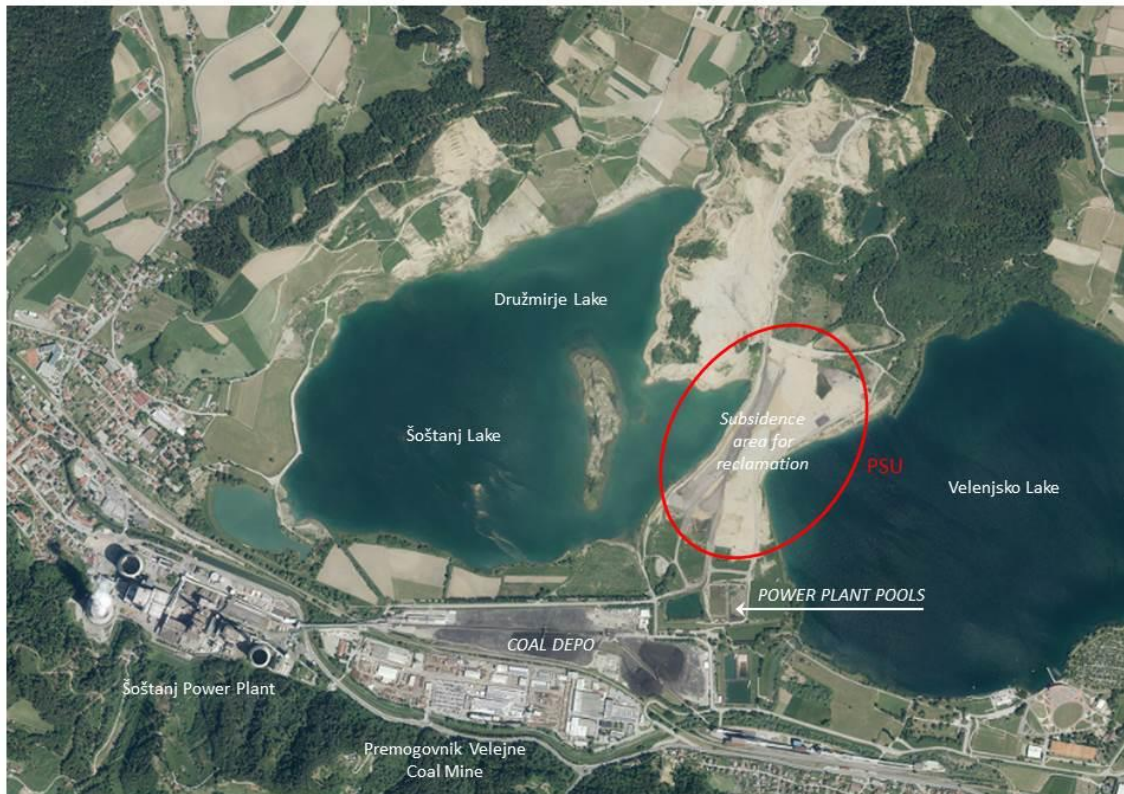
The specific objectives of Task 3.2 were:

- a) to select coal combustion by-products from local power plants and organic materials,
- b) to convert mineral and organic components into usable soil substitutes for environmental reclamation of post-mining degraded areas,
- c) to study the physicochemical parameters of soil substitutes and their water leachates,
- d) to assess the germination and growth of testing plants on soil substitutes in laboratory conditions,
- e) to study the physicochemical parameters of mining water from coal mine Premogovnik Velenje,
- f) to assess the phytotoxicity test of soil substitutes after using mining water from coal mine Premogovnik Velenje for plant irrigation in laboratory conditions.

The results from this task will be considered for assessing circular economy technologies for land rehabilitation and ecological restoration of coal mining-affected areas and creating a potential for new jobs.

### 3 Study area

The Velenje mining site is located in the northeastern region of central Slovenia. The study site covers a surface of 0.5 km<sup>2</sup> and is surrounded by two artificial lakes, Šoštanj-Družmirje and Velenjsko. Artificial lakes were created as a result of underground excavation of coal lignite. Lake Velenje is the largest and reached a size of 145 hectares (Figure 3-1).



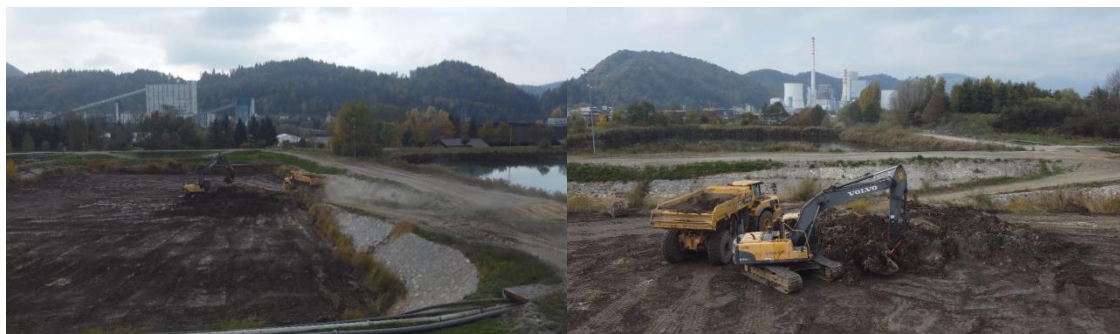
**Figure 3-1. Location of subsidence area for land reclamation in Velenje, Slovenia**

The land subsidence rehabilitation area (PSU) in Velenje, Slovenia, was built up with Stabilizat from Šoštanj Power Plant, official name Termoelektrarna Šoštanj d.o.o. (TEŠ). The plant operates six lignite and natural gas-fueled generating units. Two (blocks 5 and 6) are lignite-fueled thermal units retrofitted with new technology according to EU environmental requirements. The blocks can produce 345 and 600 MWe, respectively [1]. The fuel for TEŠ is supplied from a local coal lignite mine, Premogovnik Velenje (PV). The Power Plant and Coal Mine in Velenje are presented in Figure 3-2.



**Figure 3-2. Drone photos: a) Šoštanj Power Plant, b) Premogovnik Velenje coal mine**

As it was signed in Figure 3-1, there are also two pools in which process technological water goes from power plant TEŠ. This water is used in a closed circuit (Figure 3-3).



**Figure 3-3. Šoštanj Power Plant pool with technological water**

Due to the underground longwall coal mining method, PV causes subsidence of the surface above the mine pits. Surface movements and deformations are observed at more than 300 measurement points in and around the mining area using the mine's geodetic monitoring system. The subsidence at the PSU develops gradually as the coal is extracted within the area of influence of the mined coal panel. The example of subsidence building in the study area is presented in Figure 3-4.



**Figure 3-4. Example of subsidence of the surface caused by lignite excavation in Premogovnik Velenje coal mine**

As a result of coal mine extraction, the appearance of the subsidence area is changing (Figure 3-5). In 2016, the volume of subsidence hollows exceeded 150 million m<sup>3</sup>, and the lakes cover an area of more than 7 km<sup>2</sup>, about a third of the exploitation area (2.5 km<sup>2</sup>) [2].



**Figure 3-5. Drone photos of the subsidence area for land rehabilitation in Velenje**

The extent of the mining area depends on the size, shape and number of excavation fields, the depth and method of excavation of lignite, and the number, position and shape of the safety pillars. Maximum subsidence of terrain occurs directly above the longwall faces. Due to the large number of mining horizons lying beneath each other and the influence of longwall faces on each other, the surface is prone to repeating and long-lasting subsidence. Impacts on the surface can be seen as surface subsidence and horizontal terrain displacements, reflected in the form of cracks and small landslides. Following the mining legislation, the PV must ensure safety within the mining area and carry out the degraded area's land remediation. In the PV mining area, temporary land remediation and recultivation on the broader impact area are carried out, as well as filling the subsidence in the area of active remediation between Lake Šoštanj and Lake Velenje (PSU).

Subsiding terrain between lakes (PSU) are constantly filled with "Stabilizat" and other suitable materials like construction excavations. The PSU area is between Velenje Lake and Družmir Lake and measures approximately 52 hectares.

Stabilizat is a by-product of burning lignite from PV in the nearby thermal power plant and can be used to fill subsidence based on Slovenian Technical Approval. Stabilizat is a composite of fly ash and gypsum, which is used to fill the subsidence between lakes with up to about 700.000 t/year. By filling the PSU area, the initial elevation of the terrain is maintained to prevent leakage of water from Velenje Lake, whose surface level is 366.5 meters above sea level, to the lower-lying Družmirje Lake, with water surface level at 360.0 meters above sea level.

The course of remediation activities, temporary reclamation and maintenance of the area between lakes is performed based on the prognosis of surface subsidence and calculations of the required quantities of material for maintaining the terrain at appropriate elevations. Mining projects and a plan for the production of lignite in the Velenje Coal Mine pits are the basis for the prognosis of subsidence and the quantities needed to fill the subsidence between lakes. Most of the fill material on the PSU is Stabilizat, which is transported from the temporary dump with dumpers to the installation site (Figure 3-6). The stabilizer is then unfolded and straightened in layers with bulldozers and consolidated with a roller.







**Figure 3-6 Filling the subsidence area in Velenje using Stabilizat**




PSU surfaces that will not be damaged for a long time are covered with a layer of earth and compacted to prevent dust from rising and regular landscaping.

#### 4 Components for the development of soil substitutes

Four coal combustion by-products from TEŠ (blocks 5 and 6) and two organic materials, such as coal lignite from PV and green compost from the Composting Facility, were used in the current investigation. The list of selected materials tested as components for artificial soil preparation is presented in Table 4-1.

**Table 4-1. Set of coal by-products and substrates for soil substitutes**

No	Wastes and substrates	Description	Symbol	Origin
1		Fly ash from coal lignite combustion	FA	Šoštanj Power Plant Velenje, Slovenia
2		Gypsum from the desulfurization process	GY	Šoštanj Power Plant Velenje, Slovenia
3		Mud from technological water process (sludges from sedimentation tank)	MD	Šoštanj Power Plant Velenje, Slovenia
4		Stabilizat mixture of: fly ash (45-75 %), gypsum (10-55 %), slag (0-20 %), sludge (0-2 %)	ST-I	Šoštanj Power Plant Velenje, Slovenia (block 6)

5		<p>Stabilizat  mixture of:  fly ash (29-30 %),  gypsum (20-24 %),  slag (0-14 %),  sludge (1-2 %)</p>	ST-II	<p>Šoštanj  Power Plant  Velenje,  Slovenia  (block 5)</p>
8		Coal lignite	CL	<p>Premogovnik  Velenje  Coal Mine,  Velenje,  Slovenia</p>
6		<p>Green compost from  the biological  manufacturing process</p>	GC	<p>Industrial  Composting  Facility  (Sosnowiec,  Poland)</p>

## 5 Methods of physicochemical analysis

All physical and chemical analyses were conducted in an accredited Laboratory of Solid Wastes Analysis and Laboratory of Water and Wastewater Analysis (GIG Research Institute, Katowice, Poland).

### 5.1 Analysis of soil samples

The ash content of the sample was determined by weight method at 815°C in a laboratory muffle furnace. The content of primary nutrients (Ca, Mg, K, Na, P, S), heavy metals (As, Cd, Cr, C, Ni, Mo, Pb, Se, Zn) and other elements in solid samples were determined by wavelength-dispersive X-ray fluorescence spectrometry method (WDXRF) and inductively coupled plasma optical emission spectroscopy (ICP-OES). The amount of total organic carbon (TOC) and total sulfur (TS) were determined by an elemental analyzer with infrared detection, whereas the total nitrogen content (TN) was determined by the Kjeldahl method.

### 5.2 Analysis of water sample and leachates

The content of metals and non-metals (As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Se, Zn) in water extracts was determined by the ICP-OES method. The content of nonorganic anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ) was determined by ion chromatography, whereas sulfide and ammonium ions were determined by flow analysis with spectrophotometric detection (FIA). High-temperature combustion with CV-AAs detection determined the mercury concentration (Hg). An elemental analyzer with infrared detection determined the content of dissolved organic carbon (DOC), whereas the total nitrogen was determined by high-temperature infrared chemiluminescence detection. The pH value and electrical conductivity (EC) of water extracts were measured by the pH meter with the combination electrode.

The water extracts were made by mixing components materials or soil substitutes with deionized water in a soil-to-water ratio of 1:10 (on dry weight) according to standard [3]. After being shaken on a rotary mixer at 40 rpm for 8 hours, the samples were centrifuged at 15,000 rpm for 10 minutes and filtered using Whatman 0.45  $\mu\text{m}$  filters.

The chemical composition of the leachates was determined using the same methods as for the water samples.

### 5.3 Phytotoxicity tests

The tests were performed according to the modified procedure based on the European standard [4]. To determine the phytotoxicity of the coal by-products, waste components, and soil substitutes, two test organisms were chosen, i.e., white mustard (*Sinapis alba* L.) and garden cress (*Lepidium sativum* L.). Pot test of soil substitutes.



The effect of biomass growth on soil substitutes watered with distilled water or coal mine water was carried out in laboratory conditions under constant temperature ( $22 \pm 1$  °C) for the entire day, controlled humidity ( $40\% \pm 5\%$ ) and lighting parameters (70 W, 4900 lm, 6000 K). To determine the toxic potency of coal mine water on plant growth, *Sinapis alba* and a mixture of grass were selected.

## 6 Results of component materials analysis for soil substitutes

### 6.1 Physicochemical analysis of component materials

The chemical composition of the materials for soil substitutes is presented in Table 6-1.

**Table 6-1. Chemical analysis of components for elaboration soil substitutes**

Parameter	Unit	Components for soil substitutes						
		ST-I	ST-II	MD	FA	GY	CL	GC
M	%	10.62	12.08	23.4	<0.1	22.41	28.15	38.83
A	%	93.24	92.82	88.86	>99	78.9	24.41	60.37
TC	%	0.21	0.55	1.19	0.21	0.14	42.7	17.74
TOC	%	0.09	0.46	0.84	0.21	0.08	42.61	17.38
TS	%	0.64	4.50	4.93	0.64	>13.7	2.16	0.26
TN	%	<0.10	<0.15	<0.10	<0.1	0.14	0.84	1.56
SiO <sub>2</sub>	%	35.83	34.51	33.43	46.57	1.52	10.43	46.13
Al <sub>2</sub> O <sub>3</sub>	%	16.07	16.80	13.69	22.02	0.69	5.19	2.31
F <sub>2</sub> O <sub>3</sub>	%	9.5	9.03	9.01	12.22	0.24	3.14	1.81
CaO	%	15.59	15.91	15.7	10.25	36.84	2.45	6.11
MgO	%	1.89	1.83	1.87	2.24	0.21	0.48	0.86
Na <sub>2</sub> O	%	0.57	0.33	0.49	0.52	<0.01	0.11	0.33
K <sub>2</sub> O	%	1.89	1.67	1.72	2.44	0.07	0.55	1.12
SO <sub>3</sub>	%	10.43	9.86	11.4	1.45	40.77	1.75	0.82
TiO <sub>2</sub>	%	0.57	0.75	0.55	0.77	0.03	0.19	0.16
P <sub>2</sub> O <sub>5</sub>	%	0.24	0.19	0.19	0.29	0.03	0.06	0.63
As	ppm	21	39	23	44	<1	21	4
Ba	ppm	242	249	261	330	11	281	146
Cd	ppm	1	2	1	1	<1	4	5
Co	ppm	8	11	7	12	<1	10	4
Cr	ppm	75	85	95	97	4	79	26
Cu	ppm	35	36	46	52	3	49	48
Hg	ppm	0.10	0.11	0.11	0.03	0.28	0.06	0.06
Mn	ppm	1330	867	817	1420	18	1260	360
Mo	ppm	25	35	27	36	1	37	2
Ni	ppm	44	59	45	58	9	42	16
Pb	ppm	18	23	28	35	<1	37	108
Sb	ppm	<1	3	2	2	<1	2	2
Se	ppm	5	4	43	6	3	5	<2
Sn	ppm	<1	1	1	2	<1	2	3
Zn	ppm	130	104	140	219	6	159	624

M-moisture, TOC-total organic carbon, A-content of ash

The sample of stabilizat ST-II from block 6 characterized higher content of TOC and heavy metals (As, Co, Cr, Mo, Ni, Pb) compared with ST-I from block 5. However, the measured concentrations of Mn and Zn in the ST-II sample were much lower than in ST-I. Among all investigated components, only GC and CL could be considered rich in organic matter, 17.38 and 42.61%, respectively. The content of TOC in the rest of the components ranged from 0.08 to 0.46 %. It was observed that the amount of total sulphur (TS) excluding GY (>13.7 %) varied from 0.26 to 4.93 %. The fly ash sample detected the highest concentrations of metals such As, Ba, Co, Cr, Cu, Ni, Mn, Mo, Pb and Zn (FA). However, the highest amount of Zn (624 ppm) was observed in green compost (GC). It should be pointed out that high concentrations of heavy metals in soil may reduce the sprouting and biomass yields and exhibit a series of harmful effects on plant growth [5]. The highest concentration of selenium that could reduce the negative effect of heavy metals on plant growth was observed in mud from the technological water process (MD).

In all soil substitutes, the levels of nutrients (Ca, Mg, P, K, N, Na) indicate that these amounts may be sufficient for supporting plant growth. According to the literature data, primary nutrients N, P, and K are responsible for biomass build-up, development of plant root systems or internal water management [6] [7] [8] [9]. Nevertheless, a higher concentration of K may cause strong soil substitute salinity, reducing green biomass production.

The chemical composition of water extracts from coal by-products and organic materials used for composing soil substitutes is presented in Table 6-2.

The obtained result showed that water leachates' content of main macronutrients (Ca, Mg, K, Na, P, N) varied widely. The highest calcium content was observed in mineral coal by-products and ranged between 581 to 645 mg/l. Three tested components exhibited magnesium content above 10 %, two typical organic materials, CL and GC and one coal by-product from the desulphurization process, GY. GC was characterized by a very high amount of potassium (915 mg/l) and total nitrogen (150 mg/l), with a low content of ammonium ions 0.63 mg/l. Nitrogen in soil is available directly to plants in the forms of ammonium, nitrate and nitrite; the excess amount of these ions can reduce biomass quality. The phosphorus content in the form of  $PO_4^{3-}$  did not exceed 0.1 mg/l, except for GC (13 mg/l). It is crucial to know that excess of N and P in soil-water solution is a cause of the eutrophication of water bodies.

The content of toxic heavy metals (As, Cr, Cd, Cu, Hg, Ni, Pb, Zn) was low. Higher concentrations of Mo were observed at coal combustion by-products, i.e., FA, ST-I and ST-II (0.72-1.72 mg/l), than in organic materials GC and CL.

**Table 6-2. Chemical analysis of water leaches of components for elaboration soil substitutes**

Parameter	Unit	Components for soil substitutes						
		ST-I	ST-II	MD	FA	GY	CL	GC
Ca	mg/l	623	591	645	581	614	93.0	37.5
Mg	mg/l	5.07	4.69	9.19	0.41	36.0	21.7	14.1
K	mg/l	67.3	49.6	6.8	94.3	5.67	5.63	915
Na	mg/l	62.9	49.4	3.61	76.6	6.67	66.5	27.9
N <sub>t</sub>	mg/l	1.3	1.3	0.91	3.4	2.0	4.6	150
As	mg/l	0.027	nd	0.0089	0.014	<0.002	0.039	0.053
Ba	mg/l	0.095	0.085	0.026	0.46	0.051	0.041	0.042
Cr	mg/l	0.015	0.019	<0.003	0.033	<0.003	<0.003	<0.003
Zn	mg/l	0.0082	0.0056	0.011	0.0099	0.019	0.023	0.4
Cd	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	0.0006	<0.0005	0.0032
Mn	mg/l	<0.005	<0.005	0.0062	<0.005	0.072	0.38	0.1
Cu	mg/l	0.0058	<0.005	<0.005	0.005	<0.005	<0.005	0.063
Mo	mg/l	0.72	1.03	0.17	1.72	0.036	0.006	0.051
Ni	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.01
Pb	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	0.036
Hg	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Se	mg/l	0.015	0.009	0.083	0.0085	0.042	<0.005	<0.005
Fe	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	0.015	1.18
NH <sub>4</sub> <sup>+</sup>	mg/l	0.43	0.34	0.4	4.6	0.56	4.8	0.63
Cl <sup>-</sup>	mg/l	39	29	<5	<5	15	<5	302
PO <sub>4</sub> <sup>3-</sup>	mg/l	0.044	<0.1	0.027	0.03	0.014	<0.01	13
SO <sub>4</sub> <sup>2-</sup>	mg/l	1530	1440	1460	1040	1470	386	202
S <sup>2-</sup>	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	<0.05
TOC	mg/l	2.7	2.6	2.2	2.7	2.3	50	270

Comparing the chemical composition of two organic materials (GC and CL), GC's total organic carbon content was five times higher than CL. However, GC is characterized by a high concentration of chloride ions (302 mg/l) responsible for soil-water solution salinity.

The basis of criteria of soil salinity expressed as electrical conductivity (EC) is listed in Table 6-3.

Table 6-3. Classifications for saline soils [10]

Degree of salinity	EC (mS/cm)	Hazard to plant growth	Plant responses
Non-saline	0-2	Very low	Salinity effects negligible
Slightly saline	2-4	Low	Sprouting, biomass and yields of sensitive plants may be restricted
Moderately saline	4-8	Medium	Sprouting, biomass and yields of many plants are restricted
Strongly saline	8-16	High	Only tolerant plants develop satisfactory biomass and yields
Very strongly saline	> 16	Very high	Only very tolerant plants develop satisfactory biomass and yields

The result of EC, indicative of the salinity of used materials and pH values, was presented in Figure 6-1.

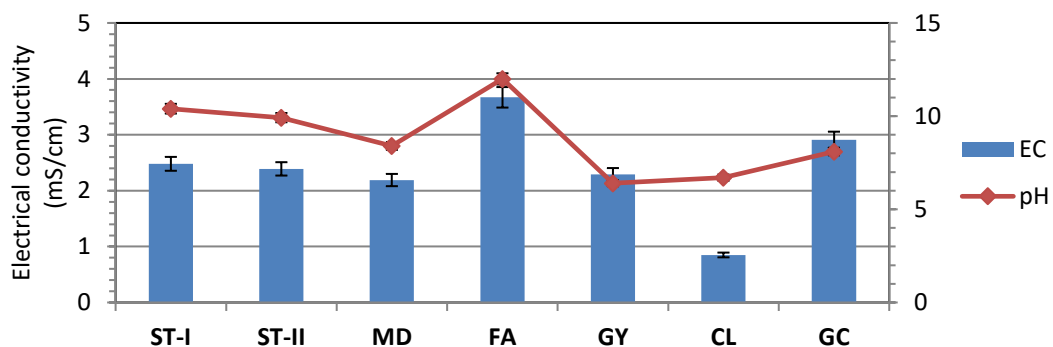


Figure 6-1. Electrical conductivity and pH of components materials used for soil substitutes

The salinity values may be classified into two groups: non-saline for coal lignite (0.85 mS/cm) and slightly saline for the rest of the components (2.19-3.75 mS/cm).

Increased salinity of artificial soil substitutes may reduce the sprouting and biomass yields and exhibit harmful effects on plant growth and development.

Based on the general interpretation of pH value, the components for elaboration soil substitutes varied in ranges [11]:

- slightly acid (pH 6.5-6.1) for GY,
- neutral (pH 6.6-7.3) for CL,
- moderately alkaline (pH 7.9-8.4) for GC and MD,
- extreme alkaline (pH >9.0) for ST-I, ST-II and FA.

Most plant species prefer to grow in pH between 6-8. A higher pH level could also negatively affect plant growth, especially for unadapted species.

## 6.2 Phytotoxicity tests of component materials

Figure 6-2 Figure 6-3 show the results of phytotoxicity tests conducted with two test organisms: the white mustard (*Sinapis alba*) and garden cress (*Lepidium sativum*).

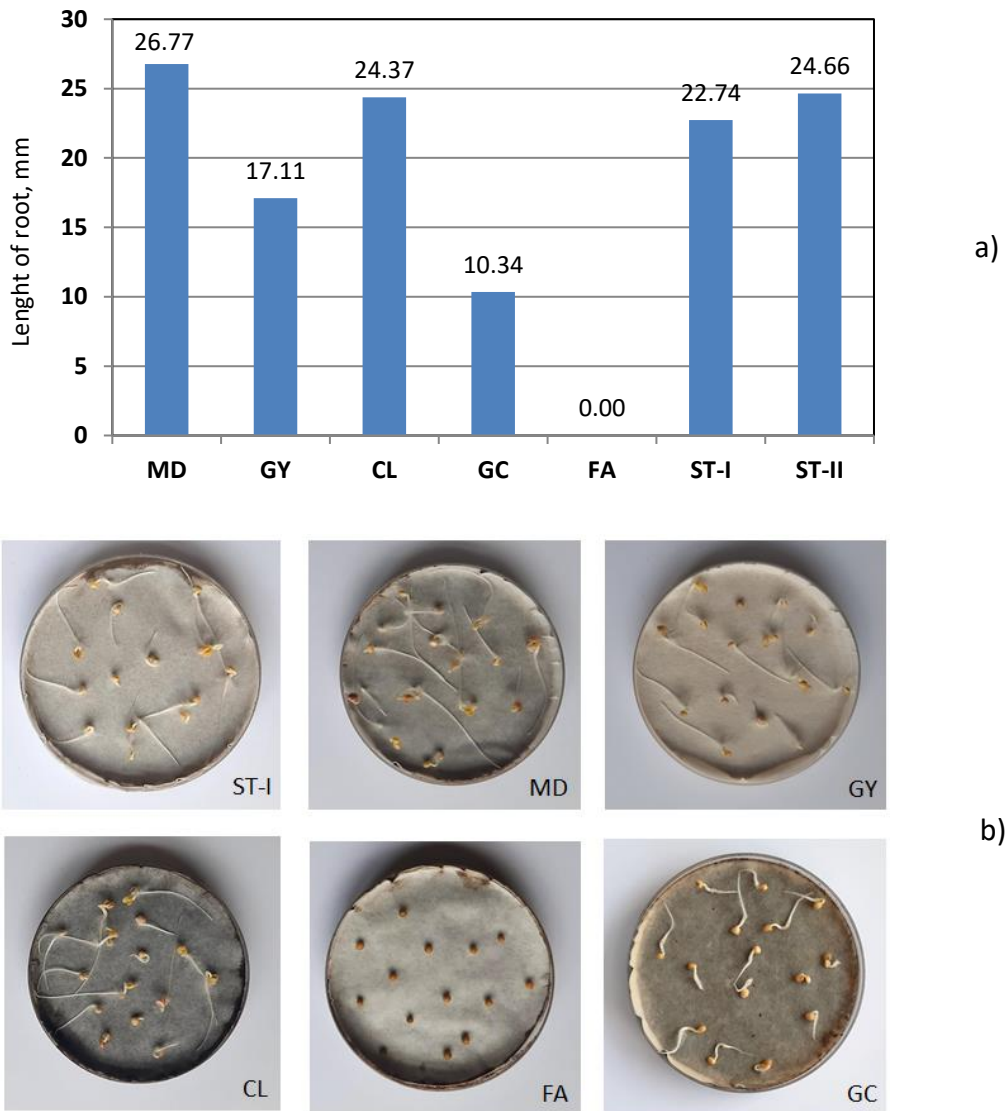
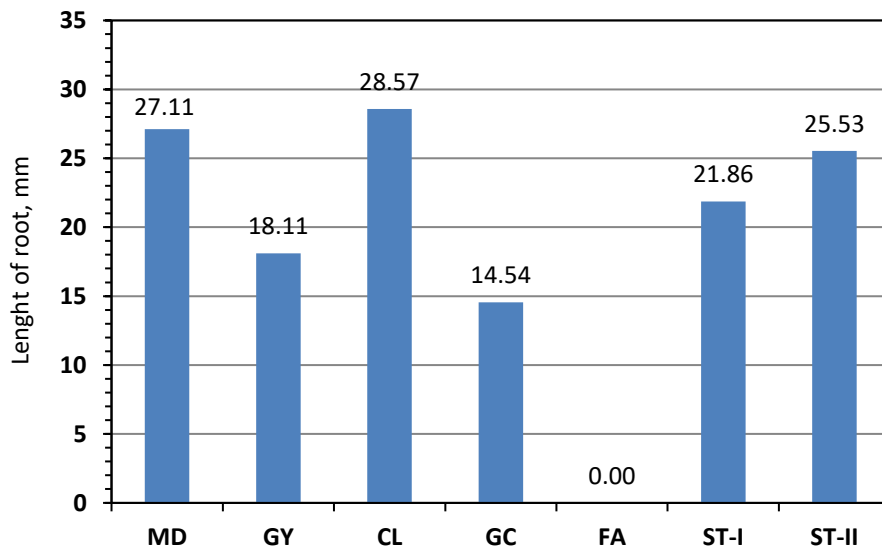
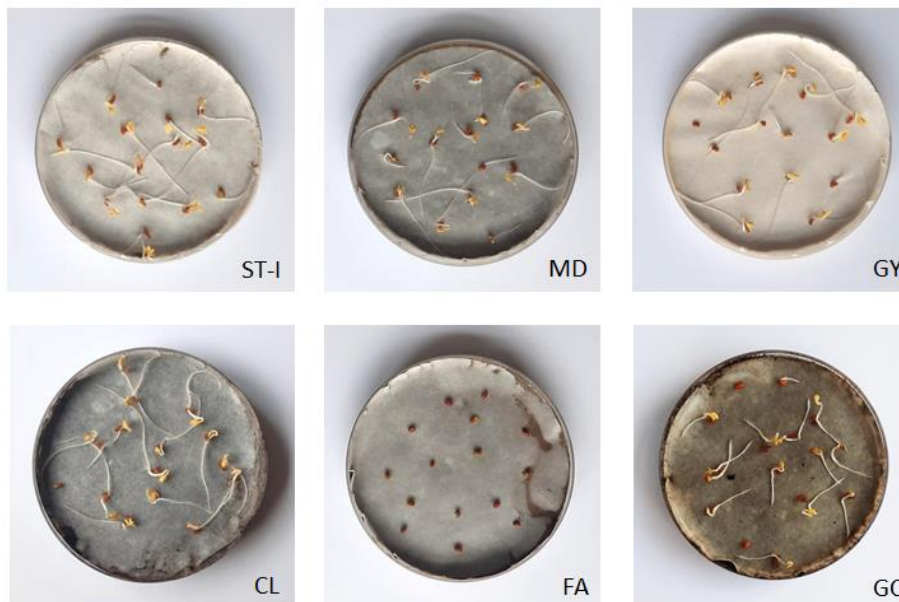


Figure 6-2. Phytotoxicity test of *Sinapis alba*: a) the average length of root, b) photos of Petri dishes after germination of seeds on component materials



a)



b)

**Figure 6-3. Phytotoxicity test of *Lepidium sativum*: a) the average length of root, b) photos of Petri dishes after germination of seeds on component materials**

The experiment indicated the high toxicity of FA due to the salinity and extreme alkalinity (pH 12). The best results of *Sinapis alba* and *Lepidium sativum* growth were shown for MD (24.37 and 28.57 mm) and two stabilizat materials, ST-I (22.74 and 21.86 mm) and ST-II (24.66 and 25.53 mm), respectively. A positive effect on plant growth was noticed for CL (24.37 and 28.57 mm). The lowest length of roots was observed for GC (10.34 and 14.54 mm).

Correlation coefficients between basic parameters of water leachates from components and early growth of test plants are reported in Table 6-4.

**Table 6-4. The Pearson analysis between physicochemical parameters of components and early growth of test plants**

	ΣMe	Ca	K	Mg	N <sub>t</sub>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	DOC	EC	pH	S.a.	L.s.
ΣMe	1.00	0.26	0.07	-0.77	-0.03	0.27	-0.01	-0.02	0.09	-0.10	0.78	0.93	-0.65	-0.73
Ca	0.26	1.00	-0.66	-0.24	-0.70	-0.34	-0.65	-0.69	0.97	-0.81	0.34	0.43	0.12	-0.08
K	0.07	-0.66	1.00	-0.04	0.99	-0.20	0.99	0.99	-0.67	0.97	0.34	-0.06	-0.41	-0.29
Mg	-0.77	-0.24	-0.04	1.00	0.04	-0.07	0.01	0.04	-0.13	0.09	-0.50	-0.90	0.18	0.26
N	-0.03	-0.70	0.99	0.04	1.00	-0.20	0.99	1.00	-0.70	0.99	0.26	-0.17	-0.36	-0.22
NH <sub>4</sub> <sup>+</sup>	0.27	-0.34	-0.20	-0.07	-0.20	1.00	-0.30	-0.23	-0.48	-0.11	-0.13	0.13	-0.41	-0.35
Cl <sup>-</sup>	-0.01	-0.65	0.99	0.01	0.99	-0.30	1.00	0.99	-0.63	0.97	0.28	-0.13	-0.31	-0.19
PO <sub>4</sub> <sup>3-</sup>	-0.02	-0.69	0.99	0.04	1.00	-0.23	0.99	1.00	-0.69	0.98	0.27	-0.16	-0.35	-0.22
SO <sub>4</sub> <sup>2-</sup>	0.09	0.97	-0.67	-0.13	-0.70	-0.48	-0.63	-0.69	1.00	-0.80	0.17	0.29	0.32	0.13
RWO	-0.10	-0.81	0.97	0.09	0.99	-0.11	0.97	0.98	-0.80	1.00	0.13	-0.25	-0.30	-0.15
EC	0.78	0.34	0.34	-0.50	0.26	-0.13	0.28	0.27	0.17	0.13	1.00	0.72	-0.77	-0.84
pH	0.93	0.43	-0.06	-0.90	-0.17	0.13	-0.13	-0.16	0.29	-0.25	0.72	1.00	-0.44	-0.55
S. a.	-0.65	0.12	-0.41	0.18	-0.36	-0.41	-0.31	-0.35	0.32	-0.30	-0.77	-0.44	1.00	0.98
L.s.	-0.73	-0.08	-0.29	0.26	-0.22	-0.35	-0.19	-0.22	0.13	-0.15	-0.84	-0.55	0.98	1.00

ΣMe – the sum of metals (As, Cr, Cd, Cu, Hg, Mo, Ni, Pb, Zn), S.a. –*Sinapis alba* root length, L.s.- *Lepidium sativum* root length

The study results showed a significant negative correlation between the root length of test plants and parameters responsible for the salinity EC, i.e., *Sinapis alba* ( $r=-0.77$ ) and *L. sativum* ( $r=-0.84$ ). A negative non-significant correlation in water leachates was also observed between the results of the phytotoxicity tests and the total metals content (As, Cr, Cd, Cu, Hg, Mo, Ni, Pb, Zn), i.e. *Sinapis alba* ( $r=-0.65$ ) and *L. sativum* ( $r=-0.73$ ).



### 6.3 Underground water analysis from Premogovnik Velenje

A water sample from a PV coal mine was delivered to the GIG laboratory to assess the possibility of using the mine water to irrigate vegetation in reclaimed areas. Table 6-5 presents the physicochemical water quality parameters, including pH, electrical conductivity (EC), dissolved organic carbon (DOC), 5-day biochemical oxygen demand (BOD<sub>5</sub>), chemical oxygen demand (COD<sub>Cr</sub>), the concentration of metals, non-metals and main anions. Threshold in Table 6-5 means the limit value of contaminant introduced with industrial waste into soil and surface water bodies according to Polish Regulation [12], and the recommended maximum concentrations of trace elements in irrigation water are presented in Table 6-6.

**Table 6-5. Physicochemical parameters of water from Premogovnik Velenje coal mine and threshold limits for discharge of wastewater into the ground**

Parameter	Unit	Result	Threshold	Parameter	Unit	Result	Threshold
Ca	mg/l	93.50	*	Al	mg/l	0.16	3
Mg	mg/l	45.00	*	As	mg/l	0.009	0.1
Na	mg/l	69.80	800.00	B	mg/l	0.048	1
K	mg/l	3.93	80.00	Be	mg/l	<0.001	1
Ba	mg/l	0.05	*	Cd	mg/l	<0.001	0.2
Sr	mg/l	0.58	*	Co	mg/l	<0.001	1
Li	mg/l	0.03	*	Cr	mg/l	0.001	0.5
Fe	mg/l	0.40	*	Cu	mg/l	0.002	0.5
Mn	mg/l	0.03	*	Hg	mg/l	<0.001	0.03
N <sub>t</sub>	mg/l	4.20	30.00	Mo	mg/l	0.013	1
N-NH <sub>4</sub> <sup>+</sup>	mg/l	2.00	10.00	Ni	mg/l	<0.002	0.5
N-NO <sub>3</sub> <sup>-</sup>	mg/l	0.77	30.00	Pb	mg/l	<0.005	0.5
N-NO <sub>2</sub> <sup>-</sup>	mg/l	0.26	1.00	Sb	mg/l	<0.050	0.3
SO <sub>4</sub> <sup>2-</sup>	mg/l	198.00	500.00	Se	mg/l	0.005	1
S <sup>2-</sup>	mg/l	<0.01	0.20	Sn	mg/l	<0.005	2
CO <sub>3</sub> <sup>2-</sup>	mg/l	<3.00	*	V	mg/l	0.002	2
HCO <sub>3</sub> <sup>2-</sup>	mg/l	438.00	*	Zn	mg/l	0.061	2
NO <sub>3</sub> <sup>-</sup>	mg/l	3.40	*	Zr	mg/l	<0.001	*
NO <sub>2</sub> <sup>-</sup>	mg/l	0.86	*	BOD <sub>5</sub>	mg/l O <sub>2</sub>	5.800	25.00
PO <sub>4</sub> <sup>3-</sup>	mg/l	0.67	*	COD <sub>Cr</sub>	mg/l O <sub>2</sub>	10.00	125.00
Cl <sup>-</sup>	mg/l	11.00	1000.00	DOC	mg/l	2.00	30.00
Br <sup>-</sup>	mg/l	0.17	*	Alkalinity	mmol/l	7.18	*
I <sup>-</sup>	mg/l	<0.30	*	EC	μS/cm	869.00	*
F <sup>-</sup>	mg/l	0.09	25.00	pH		7.6	6.5-9.0

\*not applicable, DOC-dissolved organic carbon, BOD<sub>5</sub>-Biochemical Oxygen Demand (5-day), COD-Chemical Oxygen Demand

**Table 6-6. Recommended maximum concentrations of trace elements in irrigation water**

Parameter	Unit	Result	Threshold for long use	Threshold for short use	Remarks
EC	µS/cm	869.00	750	2000	PV water has a low concentration of sodium (Na <sup>+</sup> ) and chloride ions (Cl <sup>-</sup> ), which cause more significant osmotic stress on plant roots compared to sulfate (SO <sub>4</sub> <sup>2-</sup> ).
pH		7.6	6.5-9.0		Threshold for prolonged use is not exceeded
N <sub>t</sub>	mg/l	4.20	≤ 15.0		
Li	mg/l	0.03	2.5		
Fe	mg/l	0.40	5.0	20	
Mn	mg/l	0.03	0.2	10	
Al	mg/l	0.16	5	20	
As	mg/l	0.009	0.10	2	
B	mg/l	0.048	0.75	2	
Be	mg/l	<0.001	0.01		
Cd	mg/l	<0.001	0.01	0.05	
Co	mg/l	<0.001	0.05	5	
Cr	mg/l	0.001	0.1		
Cu	mg/l	0.002	0.2	5	
Hg	mg/l	<0.001	0.001		
Mo	mg/l	0.013	0.01	0,05	It can be toxic to plants in soils with high levels of available molybdenum. The availability of molybdenum in the soil increases together with increasing pH.
Ni	mg/l	<0.002	0.2	2	Threshold for prolonged use is not exceeded
Pb	mg/l	<0.005	5	10	
Se	mg/l	0.005	0.02	0.02	
V	mg/l	0.002	0.1	1	
Zn	mg/l	0.061	2.0		

The pH and EC values 7.6 and 869 µS/cm, respectively, indicate the neutral and non-saline character of the water sample with negligible toxicity effects on plant growth. The sulphate ions are dominated. However, the content of SO<sub>4</sub><sup>2-</sup>, as well as sodium, chloride and potassium ions, responsible for water salinity, were below the threshold limits for wastewater. It shows that the water is not excessively contaminated with residual salts. PV coal mine exceeds limit standards for water quality for long-term irrigation use (EC>750 µS/cm). However, the salinity of analysed water is caused mainly by sulphate. On the other hand, sulfates are much less harmful than chloride and sodium ions to plants in terms of osmotic stress, and they can even act to buffer osmotic stress to some extent, meaning they can help reduce its adverse effects on plants [18]. Excess sulfate

concentration in the soil leads to osmotic stress in plants, which means that plants have restricted access to water due to the high salt concentration, hindering their ability to take up water through the roots. As a result, plants may exhibit symptoms of dry and wilting leaves and overall weakening. The concentrations of a biogenic form of nitrogen (N-NH<sub>4</sub><sup>+</sup>, N-NO<sub>3</sub><sup>-</sup>, N-NO<sub>2</sub><sup>-</sup>) ranged from 0.26 to 2 mg/l and were low as compared with the threshold limits for wastewater standard (1-30 mg/l) and total nitrogen (N<sub>t</sub>) not exceeds the standards for prolonged irrigation use (<15mg/l).

It was observed that concentrations of metals varied in the following order: Al>Zn>B>Pb>Sb>Mo>As>Se>V>Cu>Cr>Hg>Ni>Co>Cd>Zr>Be and did not exceed the permissible thresholds for wastewater standard. The dissolved metal concentrations (Be, Cd, Co, Hg, Ni, Pb, Sb, Sn Zn) were below the detection limit. Considering the recommended maximum concentrations of trace elements in irrigation water, the molybdenum (Mo) concentration slightly exceeds the threshold for prolonged use.

The results showed that BOD<sub>5</sub> and COD<sub>Cr</sub> levels did not exceed the permissible limits, confirming that the mine water has a low organic matter content and the measured value of dissolved organic carbon was only 2 mg/l.

## 7 Results of soil substitute analysis

### 7.1 Preparation of soil substitutes

Based on previous research, five components were selected for the elaboration of artificial soils for land reclamation of degraded areas in Slovenia:

- stabilizat (ST-I or ST-II), including fly ash, gypsum, slug and sludge;
- mud from water pool (MD);
- coal lignite (CL), and
- green compost (GC).

Soil substitute samples were prepared using the weight method, identified as M1/I-M6/I with stabilizat ST-I and M1/II-M6/II with ST-II. A list of component materials and their percentage range for elaborated soils was presented in Table 7-1.

The reason for such a blending process was to ensure appropriate soil parameters such as low salinity, adequate content of nutrients, low content of toxic metals or the optimal structure of soil (loose and clumpy).

In addition, the estimated annual production of soil substitute components (stabilizat – 245 000 t and mud from water pool – 11 000 m<sup>3</sup>) was also considered.

**Table 7-1. List of components materials and their percentage range for soil substitutes**

Soil substitutes	Component materials for soil substitutes				
	ST-I	ST-II	MD	CL	GC
M1/I	50	-	30	20	0
M2/I	50	-	30	0	20
M3/I	50	-	30	10	10
M4/I	50	-	20	30	0
M5/I	50	-	20	0	30
M6/I	50	-	20	15	15
M1/II	-	50	30	20	0
M2/II	-	50	30	0	20
M3/II	-	50	30	10	10
M4/II	-	50	20	30	0
M5/II	-	50	20	0	30
M6/II	-	50	20	15	15

## 7.2 Physicochemical analysis of soil substitutes

### 7.2.1 Chemical composition of soil substitutes

The limit, warning and critical concentration of dangerous substances in the soil in Slovenia, according to the Official Journal of the Republic of Slovenia [13], was presented in Table 7-2.

**Table 7-2. The concentration of dangerous substances in the soil in Slovenia**

Parameter	Permissible thresholds (mg/kg)		
	Limit value	Warning value	Critical value
Arsenic and its compounds, expressed as As	20	30	55
Cadmium and its compounds, expressed as Cd	1	2	12
Cobalt and its compounds, expressed as Co	20	50	240
Chromium total, expressed as Cr	100	150	380
Copper and its compounds expressed as Cu	60	100	300
Mercury and its compounds, expressed as Hg	0.8	2	10
Molybdenum and its compounds, expressed as Mo	10	40	200
Nickel and its compounds, expressed as Ni	50	70	210
Lead and its compounds, expressed as Pb	85	100	530
Zinc and its compounds, expressed as Zn	200	300	720

The chemical composition of soil substitutes M1-M6/I and M1-M6/II are presented in Tables 7-3 and 7-4.

The concentrations of the elements for soil substitutes based on ST-I showed upper limit values concerning arsenic (21-23 mg/kg), cadmium (1 mg/kg), molybdenum (23-26 mg/kg) and zinc (236 mg/kg for M5/I). Warning values were observed concerning cadmium (2 mg/kg for M5/I).

Data shows that the concentration of arsenic and molybdenum in soil substitutes M1-M6/II exceeded the limit value (20-23 mg/kg and 26-30 mg/kg, respectively). In addition, it was observed that the cadmium content for soils M1, M3 and M4/II was above the limited value (1 mg/kg), whereas for M2, M5 and M6/II, the warning value (2 mg/kg).

Table 7-3. Composition of soil substitutes based on stabilizat ST-I

Parameter	Unit	Soil substitutes					
		M1/I	M2/I	M3/I	M4/I	M5/I	M6/I
TOC	g/kg	9.10	3.78	6.23	11.97	5.74	9.38
TS		4.43	4.34	4.54	0.32	3.75	3.44
TN		0.28	0.34	0.31	0.32	0.47	0.42
SiO <sub>2</sub>		28.58	35.89	32.14	27.53	36.16	32.31
Al <sub>2</sub> O <sub>3</sub>		13.13	12.81	12.96	12.71	11.71	12.06
F <sub>2</sub> O <sub>3</sub>		8.27	8.08	8.12	7.76	7.29	7.47
CaO		13.40	13.96	13.92	12.34	12.58	12.21
MgO		1.55	1.62	1.59	1.44	1.52	1.45
Na <sub>2</sub> O		0.38	0.41	0.39	0.37	0.36	0.37
K <sub>2</sub> O		1.46	1.72	1.60	1.40	1.75	1.57
SO <sub>3</sub>		9.46	9.08	9.42	8.67	7.80	8.21
TiO <sub>2</sub>		0.49	0.48	0.48	0.46	0.43	0.44
P <sub>2</sub> O <sub>5</sub>		0.20	0.30	0.25	0.19	0.33	0.26
As*	mg/kg	23	23	23	22	22	21
Ba		191	198	202	193	198	199
Cd*		1	1	1	1	2	1
Co*		8	8	8	8	8	8
Cr*		57	55	58	56	57	55
Cu*		28	37	32	31	44	31
Hg*		0	0	0	0	0	0
Mn		1030	1035	1060	1030	1020	1020
Mo*		26	25	26	25	23	24
Ni*		32	32	31	32	31	30
Pb*		16	36	25	16	56	29
Sb		2	1	2	2	2	2
Se		21	19	21	15	14	16
Sn		2	2	1	2	2	2
V		92	86	90	88	82	86
Zn*		106	187	159	103	236	172

\* Dangerous substances in soil in Slovenia [13]

	Upper Limit Value
	Upper Warning value

Table 7-4. Composition of soil substitutes based on stabilizat ST-II

Parameter	Unit	Soil substitutes					
		M1/II	M2/II	M3/II	M4/II	M5/II	M6/II
TOC	g/kg	10.27	4.64	7.14	13.37	8.88	9.83
TS		6.31	6.30	6.46	5.88	4.92	5.84
TN		0.28	0.33	0.28	0.30	0.59	0.37
SiO <sub>2</sub>		23.70	23.79	26.05	21.20	29.77	25.20
Al <sub>2</sub> O <sub>3</sub>		10.34	11.49	10.40	10.26	8.84	9.75
F <sub>2</sub> O <sub>3</sub>		6.44	7.14	6.49	6.23	5.48	6.07
CaO		15.16	16.21	15.65	14.10	13.79	14.64
MgO		1.29	1.36	1.35	1.19	1.26	1.25
Na <sub>2</sub> O		0.36	0.38	0.35	0.32	0.37	0.34
K <sub>2</sub> O		1.22	1.31	1.35	1.08	1.48	1.26
SO <sub>3</sub>		12.73	14.09	12.74	12.39	10.63	12.13
TiO <sub>2</sub>		0.36	0.43	0.40	0.38	0.36	0.38
P <sub>2</sub> O <sub>5</sub>		0.28	0.19	0.26	0.16	0.35	0.23
As*	mg/kg	23	22	22	20	20	23
Ba		220	208	216	191	202	200
Cd*		1	2	1	1	2	2
Co*		8	7	7	7	9	8
Cr*		53	53	53	53	54	55
Cu*		29	32	29	25	33	30
Hg*		0	0	0	0	0	0
Mn		878	893	888	851	834	858
Mo*		30	30	30	28	26	28
Ni*		28	28	28	28	26	30
Pb*		40	40	29	23	55	33
Sb		2	2	2	2	1	2
Se		20	21	19	14	15	17
Sn		1	2	1	1	2	2
V		90	88	89	85	76	85
Zn*		125	180	145	100	234	168

\* Dangerous substances in soil in Slovenia [13]

	Upper Limit Value
	Upper Warning value

The limited concentration of dangerous substances on the ground surface, according to the Polish Regulation of the Minister of Environment [14], is presented in Table 7-5.

**Table 7-5. Concentration of trace elements in soil according to Polish Regulation**

Trace elements	Permissible thresholds (mg/kg)		
	Group II-1 agricultural areas	Group III wooded and shrub lands as well as green areas	Group IV industrial lands and mining grounds
As	10	50	100
Cd	2	10	15
Cr	150	500	1000
Cu	100	300	600
Ni	100	300	500
Pb	100	500	600
Zn	300	1000	2000

The concentrations of trace elements in soil substitute M1/I-M6/I and M1/II-M6/II varied in the order Zn>Cr>Cu>Ni>Pb>As>Co>Cd and Zn>Cr>Pb>Cu>Ni>As>Co>Cd, respectively. According to the Polish Regulation of the Minister of Environment, the respective amounts did not exceed the permissible limits for soils classified as Group III for As (20-23 mg/kg). The concentration of rest elements such as Cd (1-2 mg/kg), Co (7-9 mg/kg), Cr (53-58 mg/kg), Cu (28-44 mg/kg), Ni (26-32mg/kg), Pb (16-56 mg/kg) and Zn (103-236 mg/kg) did not exceed the permissible limits for the Group II-1.

### 7.2.2 Characteristics of water leaches

Studies on the composition of soil substitute leachates were conducted to identify pollutants and assess the risk of land contamination after their deposition.

The chemical characteristic of soil substitute leachates based on stabilizat ST-I is summarized in Table 7-6.



**Table 7-6. Analysis of soil substitute leaches based on stabilizat ST-I**

Parameter	Unit	Soil substitutes					
		M1/I	M2/I	M3/I	M4/I	M5/I	M6/I
As	mg/l	0.045	0.025	0.036	0.055	0.038	0.049
Ba	mg/l	0.054	0.061	0.062	0.060	0.067	0.068
Cr	mg/l	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Zn	mg/l	0.250	0.056	0.048	0.04	0.016	0.280
Al	mg/l	0.055	0.260	0.210	0.083	0.150	0.061
Cd	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Mg	mg/l	35.6	33.5	33.9	43.6	46.6	48.4
Mn	mg/l	0.30	0.03	0.11	0.43	0.05	0.24
Cu	mg/l	0.0057	0.0091	0.0064	<0.005	0.0099	0.0064
Mo	mg/l	0.35	0.44	0.40	0.36	0.44	0.36
Ni	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
K	mg/l	26	21	127	33	345	180
Hg	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Se	mg/l	0.038	0.057	0.048	0.033	0.04	0.036
Na	mg/l	49.0	43.3	45.9	64.4	57.5	65.4
Ca	mg/l	610	592	612	622	600	611
NH <sub>4</sub> <sup>+</sup>	mg/l	0.60	0.19	0.41	0.76	0.63	0.55
Cl <sup>-</sup>	mg/l	23	76	53	22	112	72
PO <sub>4</sub> <sup>3-</sup>	mg/l	0.049	0.26	0.17	0.065	0.66	0.31
SO <sub>4</sub> <sup>2-</sup>	mg/l	1570	1710	1680	1610	1800	1780
S <sup>2-</sup>	mg/l	<0.05	<0.05	<0.05	<0.05	<0.005	<0.05
DOC	mg/l	12	31	20	15	49	33
N <sub>t</sub>	mg/l	2.9	19	9.5	3.2	28	15
EC	mS/cm	2.52	3.00	2.79	2.61	3.39	3.06
pH		7.8	8.3	8.1	8.0	8.2	8.0

The pH of leachates ranged from 7.8 to 8.3 and demonstrated that the water extracts were mildly alkaline (7.4-7.8) and moderately alkaline (pH 7-9-8.4). The content of Ca (592-622 mg/l) and Mg (33.5-48.4 mg/l) were in a similar range for all samples. However, the concentration of K in samples M3/I (127 mg/l), M5/I (345 mg/l) and M6/I (180 mg/l) was several times higher than in samples M1/I, M2/I and M4/I (21-33 mg/l). The result showed that the sample M5/I characterized the highest concentration of Cl<sup>-</sup> (112 mg/l) and SO<sub>4</sub><sup>2-</sup> ions (1800 mg/kg), which corresponded with the highest electrical conductivity (3.39 mS/cm) of this sample. The lowest concentration of total nitrogen (N<sub>t</sub>) was observed for M1 (2.9 mg/l) and the highest for M5/I (28 mg/l). The highest dissolved organic carbon (DOC) concentrations were registered in sample M5 (49 mg/l).

The amount of toxic metals such as Cr, Cd, Hg, Ni, and Pb was below the detection limit, whereas the alkaline pH decreases the mobility of most heavy metals in soil-water

solution. Relatively low metal concentrations suggest that leachate is not a significant hazard to trace elements. The highest concentrations were recorded for trace elements Mo and Mn, and the lowest was observed for As, Al, Ba, Cu and Zn.

Chemical characteristics of soil substitute leachates based on stabilizat ST-II are summarized in Table 7-7.

**Table 7-7. Analysis of soil substitute leaches based on stabilizat ST-II**

Parameter	Unit	Soil substitutes					
		M1/II	M2/II	M3/II	M4/II	M5/II	M6/II
As	mg/l	0.032	0.018	0.027	0.043	0.03	0.038
Ba	mg/l	0.061	0.072	0.064	0.056	0.077	0.074
Cr	mg/l	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Zn	mg/l	0.033	0.023	0.013	0.24	0.059	0.022
Al	mg/l	1.07	1.47	1.55	0.31	1.79	0.65
Cd	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	0.0006	<0.0005
Mg	mg/l	24.5	20.2	19.9	37.1	42.6	35.5
Mn	mg/l	0.056	0.011	0.027	0.16	0.022	0.082
Cu	mg/l	<0.005	<0.005	<0.0005	<0.005	0.011	<0.005
Mo	mg/l	0.64	0.86	0.70	0.58	0.80	0.65
Ni	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	mg/l	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
K	mg/l	20.9	228	113	17.5	447	171
Hg	mg/l	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Se	mg/l	0.043	0.041	0.037	0.026	0.037	0.038
Na	mg/l	55.6	50.4	50.1	65.3	64.8	50.2
Ca	mg/l	625	620	591	612	654	632
NH <sub>4</sub> <sup>+</sup>	mg/l	0.83	1.00	0.90	0.82	0.89	1.10
Cl <sup>-</sup>	mg/l	9	77	42	10	144	60
PO <sub>4</sub> <sup>3-</sup>	mg/l	0.027	0.12	0.068	0.012	0.18	0.13
SO <sub>4</sub> <sup>2-</sup>	mg/l	1590	1560	1510	1510	1760	1600
S <sup>2-</sup>	mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
DOC	mg/l	17	12	8.5	12	49	14
N <sub>t</sub>	mg/l	2.5	16.0	7.8	2.5	29.0	11.0
EC	mS/cm	2.42	2.92	2.65	2.46	3.72	2.86
pH		8.2	8.5	8.4	7.9	8.6	8.2

The pH of leachates ranged from 7.9 to 8.6 and demonstrated that the samples were moderately alkaline (pH 7.9-8.4) and strongly alkaline (8.5-9.0). The sample M5/II is characterized by the highest concentration of K (447 mg/l), Cl<sup>-</sup> (144 mg/l) and SO<sub>4</sub><sup>2-</sup> ions (1760 mg/kg), which corresponded with the highest electrical conductivity (3.72 mS/cm). A higher amount of K (228 mg/l) and Cl<sup>-</sup> ions (77 mg/l) were detected in sample

M2/II, corresponding to a 2.92 mS/cm salinity. The highest content of  $N_t$  (29 mg/l) and DOC (49 mg/l) was observed in M5/II, whereas the amount of other nutrients such as Ca (591-654 mg/l), Mg (19.9-42.6 mg/kg) or Na (50.1-65.3 mg/kg) were comparable for all samples.

The sulphate and chloride ions in higher concentrations may exert a harmful effect on plant sprouting and growth. Excessive amounts of  $SO_4^{2-}$  and  $Cl^-$  ions increase the concentrations of  $H^+$  ions in soils, leading to their acidification. However, since chlorides and sulfates do not possess significant buffering capabilities, their influence on soil pH is typically short-lived and limited.

The concentration of toxic metals such as Cr, Cd, Cu, Hg, Ni, and Pb was below the detection limit, whereas the highest content of trace elements was recorded for Mo (0.58-0.86 mg/l).

### 7.3 Phytotoxicity tests of soil substitutes

#### 7.3.1 Germination and root growth of *Sinapis alba*

The effect of phytotoxicity of soil substitutes was assessed based on white mustard's physiological and morphological traits (germination and root length). Samples of soil substitutes were placed in sterile plastic Petri dishes (9 cm diameter) and mixed with distilled or coal mine water from Premogovnik Valenje d.o.o. Each dish was lined with 87 g/m<sup>2</sup> filter paper and left until saturated with moisture. Then, 15 tested plant seeds were placed on filter paper and closed with the lid. To determine the effect on germination, the seeds were incubated in darkness at  $25 \pm 1$  °C for 72 hours. The length of roots was measured as the main parameter of the growth of the plants with an accuracy of  $\pm 0.1$  cm. The test was conducted with three repetitions. The phytotoxic effect of *Sinapis alba* on petri dishes is presented in Figure 7-1.

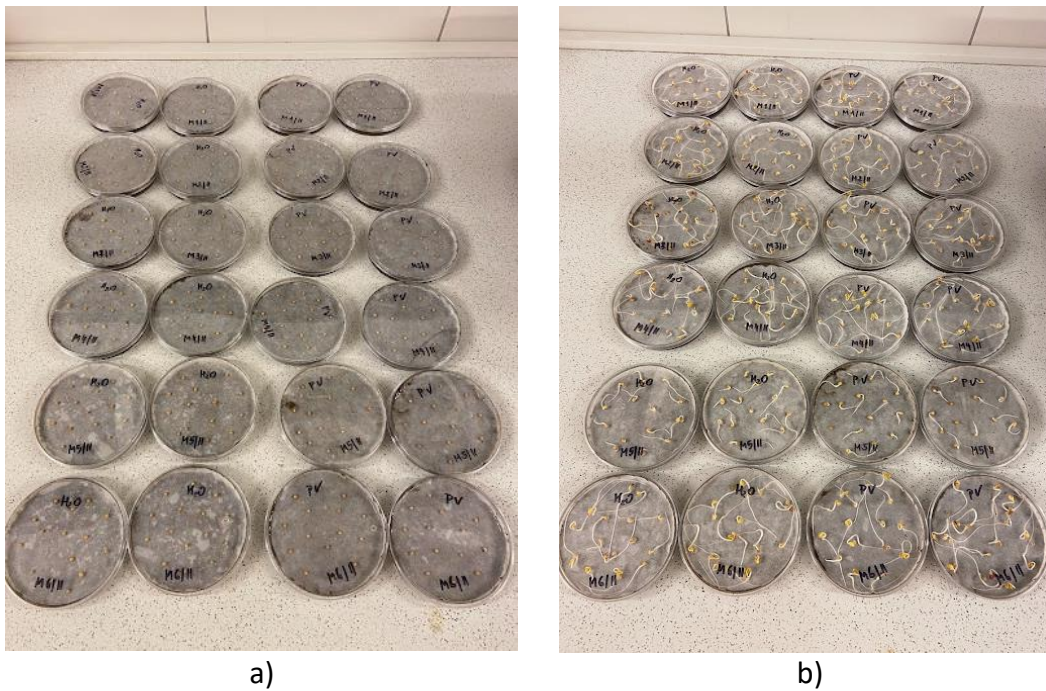


Figure 7-1. Petri dishes with soil substitutes and *Sinapis alba* seeds: a) before germination, b) after 72 hours of germination

The result of the phytotoxicity test is presented in Figure 7-2 and Figure 7-3.

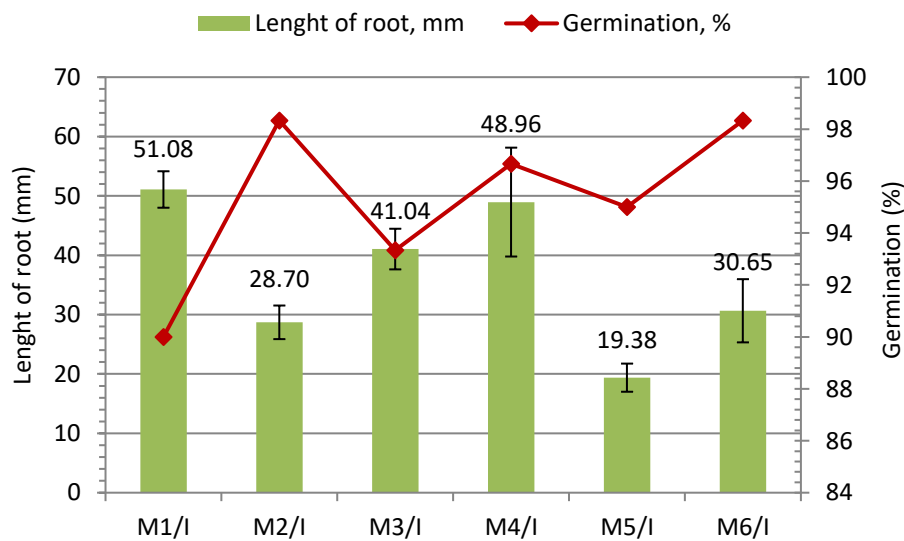
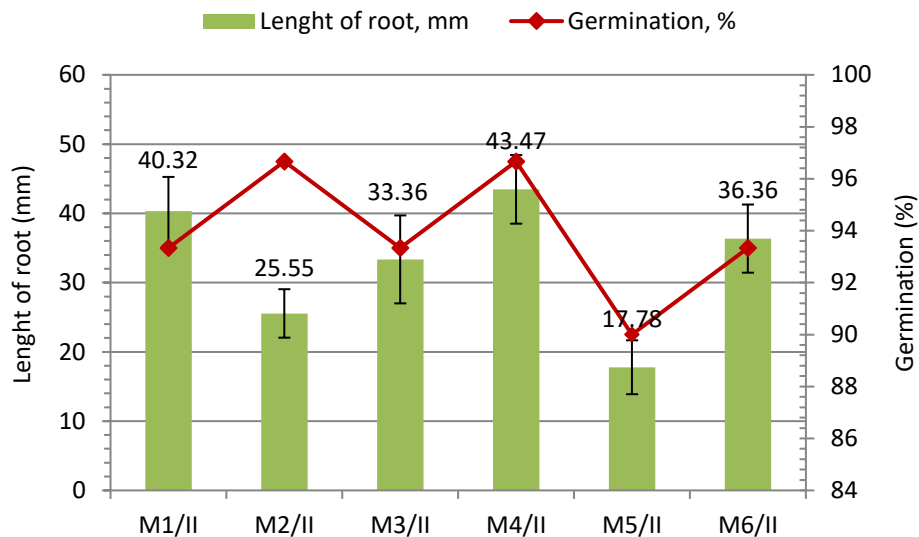


Figure 7-2. Germination and root growth of *Sinapis alba* on soil substitutes based on ST-I

The best result of *Sinapis alba* germination was observed for artificial soil substitutes M2/I (98%), M6/I (98%) and M4/I (97%). The average root length on the tested soil ranged from 19.38 mm for M5/I to 51.08 mm for M1/I. It was observed that better root

growth in soils with higher content of coal lignite (M1/I and M4/I), while soil substitutes with higher green compost content lead to lower root growth.



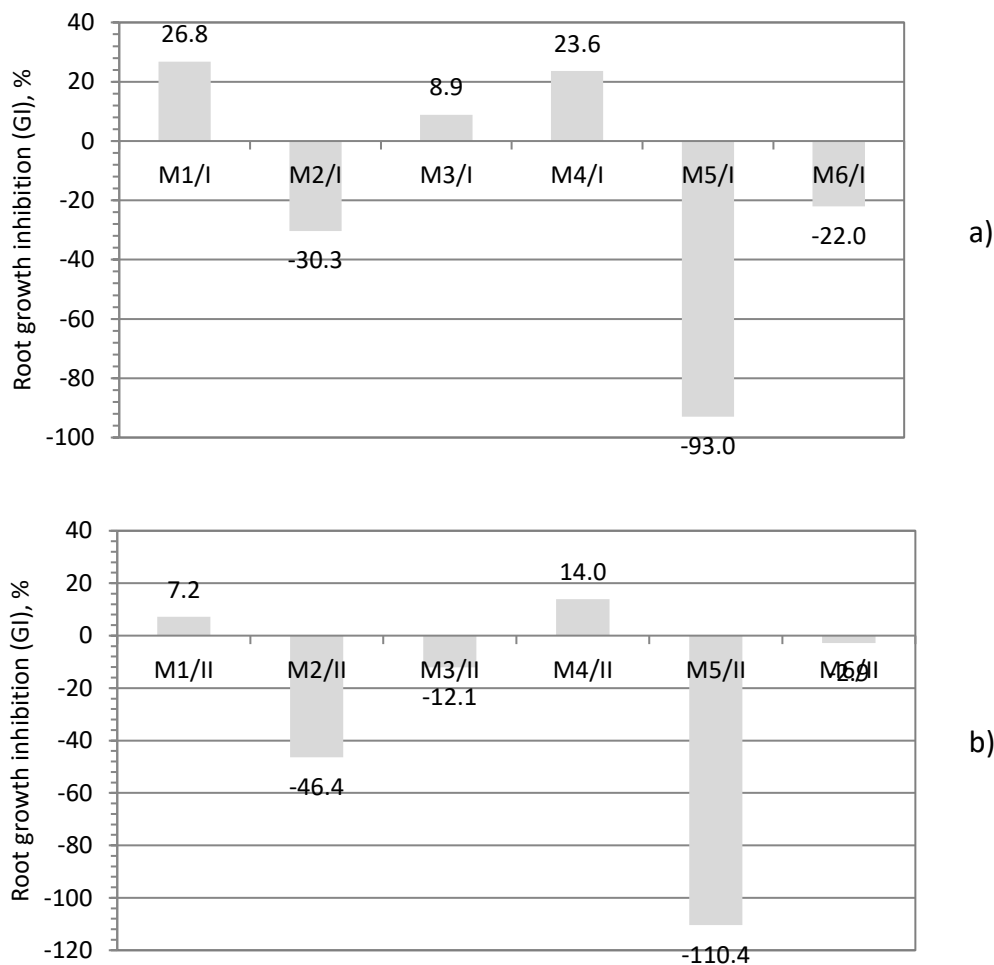
**Figure 7-3. Germination and root growth of *Sinapis alba* on soil substitutes based on ST-II**

*Sinapis alba*'s germination and root growth in soil based on ST-II were comparable to those based on ST-I. The best result of sprouting was observed for artificial soil substitutes M2/II and M4/II (97%), while 90% was observed in soil M5/II with 30% green compost sharing. The soils M1/II, M4/II and M6/II, with high content of carbon lignite, showed higher root growth at 40.32 mm, 43.47 mm and 36.36 mm, respectively. It could be assumed that the pH and EC of the rest of the soils could have been hampering the sprouting process.

Figure 7-4 shows the percentage of root growth inhibition (GI) calculated with the formula:

$$GI = \frac{R_s - R_c}{R_s} \cdot 100\%$$

where  $R_s$  is the average length of roots on the tested sample, and  $R_c$  is the average length of roots on the control soil, defined as a mixture of 75% fine quartz sand (50% particles 0.05–0.2 mm), 20% kaolin clay (kaolinite content preferably above 30%) and 5% finely ground, according to the standard EN 18763 [4].



**Figure 7-4. Per cent of root growth inhibition of *Sinapis alba* on tested soil substitutes: a) based on stabilizat ST-I, b) based on stabilizat ST-II**

The lowest GI and growth stimulation effect was observed for soil substitutes with a high content of green compost, i.e., -30,0 % for M2/I, -46.4 % for M2/II, -93.0 for M5/I and -110.4 % for M5/II.

Adding 20 % by weight of coal lignite in samples M1/I and M1/II increased the GI to 26.8 % and 7.2 %, respectively. Soil substitutes M4/II and M4/II contained 30 % by weight of carbon lignite, but lower mud content from the sedimentation tank showed a GI of 23.6 % and 14.0 %, respectively.

Decrease of growth inhibition was observed for soil substitutes M3/II, M6/I and M6/II with the equal content of coal lignite and green compost (from 10 to 15 % by weight).

The study results (Table 7-8) showed a significant negative correlation between *Sinapis alba*'s root length and soil substitutes' pH ( $r=-0.78$ ). A negative significant correlation in water leachates was also observed between the results of the phytotoxicity tests and parameters responsible for the salinity, i.e. EC ( $r=-0.78$ ),  $K^+$  ( $r=-0.83$ ),  $Cl^-$  ( $r=-0.90$ ),  $PO_4^{3-}$  ( $r=-0.65$ ) and  $SO_4^{2-}$  ( $r=-0.60$ ). A negative significant correlation was indicated between *Sinapis alba*'s growth and Ba's content ( $r=-0.76$ ), whereas a positive correlation for the concentration of Mn ( $r=0.71$ ).

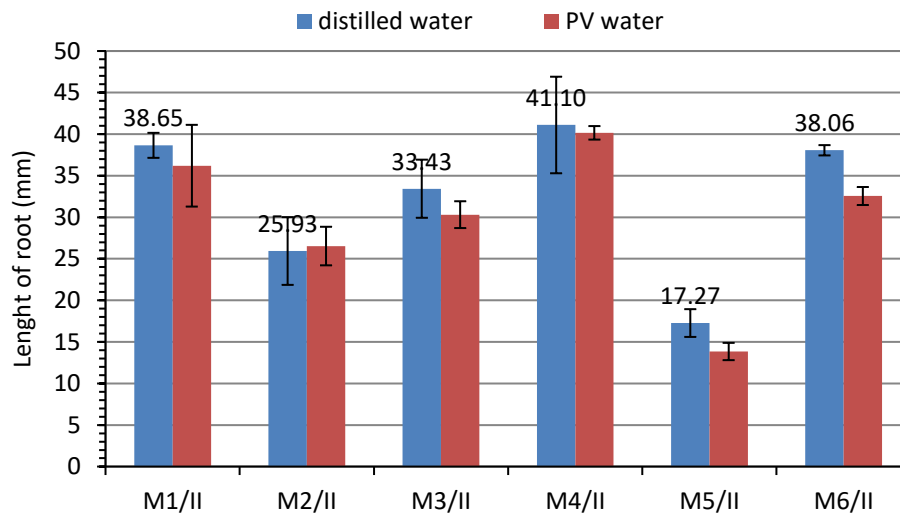
**Table 7-8. Pearson analysis between physicochemical parameters of soil substitutes and early growth of *Sinapis alba***

	As	Ba	Zn	Mn	Mo	K	Na	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	EC	pH	S.a.
As	1.00	-0.39	0.54	0.89	-0.72	-0.26	0.55	-0.12	-0.36	-0.01	0.11	-0.24	-0.81	0.57
Ba	-0.39	1.00	-0.42	-0.50	0.60	0.83	0.13	0.46	0.77	0.31	0.41	0.75	0.75	-0.76
Zn	0.54	-0.42	1.00	0.50	-0.43	-0.27	0.37	-0.24	-0.28	-0.14	-0.01	-0.22	-0.68	0.36
Mn	0.89	-0.50	0.50	1.00	-0.68	-0.44	0.39	-0.14	-0.49	-0.24	-0.10	-0.40	-0.76	0.71
Mo	-0.72	0.60	-0.43	-0.68	1.00	0.42	0.00	0.72	0.28	-0.27	-0.32	0.21	0.78	-0.47
K <sup>+</sup>	-0.26	0.83	-0.27	-0.44	0.42	1.00	0.27	0.28	0.91	0.57	0.60	0.91	0.62	-0.83
Na	0.55	0.13	0.37	0.39	0.00	0.27	1.00	0.30	0.08	0.04	0.20	0.20	-0.15	-0.07
NH <sub>4</sub> <sup>+</sup>	-0.12	0.46	-0.24	-0.14	0.72	0.28	0.30	1.00	-0.04	-0.36	-0.48	-0.06	0.31	-0.06
Cl <sup>-</sup>	-0.36	0.77	-0.28	-0.49	0.28	0.91	0.08	-0.04	1.00	0.67	0.74	0.99	0.66	-0.90
PO <sub>4</sub> <sup>3-</sup>	-0.01	0.31	-0.14	-0.24	-0.27	0.57	0.04	-0.36	0.67	1.00	0.81	0.68	0.14	-0.65
SO <sub>4</sub> <sup>2-</sup>	0.11	0.41	-0.01	-0.10	-0.32	0.60	0.20	-0.48	0.74	0.81	1.00	0.80	0.17	-0.60
EC	-0.24	0.75	-0.22	-0.40	0.21	0.91	0.20	-0.06	0.99	0.68	0.80	1.00	0.59	-0.87
pH	-0.81	0.75	-0.68	-0.76	0.78	0.62	-0.15	0.31	0.66	0.14	0.17	0.59	1.00	-0.78
S.a.	0.57	-0.76	0.36	0.71	-0.47	-0.83	-0.07	-0.06	-0.90	-0.65	-0.60	-0.87	-0.78	1.00

S.a. –*Sinapis alba* root length

### 7.3.2 Toxicity of coal mine water to *Sinapis alba* - petri dish test

Soil substitutes based on ST-II stabilizer were used for the study. The result of root growth of *Sinapis alba* in Petri dishes on soil substitutes M1-M6/II is presented in Figure 7-5.



**Figure 7-5. Effect of coal mine water (PV) treatment on root growth of *Sinapis alba* – Petri dish test**

The obtained experimental data indicate varied levels of phytotoxicity of the tested soil substitutes. Soils with distilled water showed slightly more significant root growth than samples saturated with PV water.

The average root length for soil substitutes with distilled water ranged from 17.27 to 41.10 mm, whereas the measured root length for soils treated with coal mine water (PV) was 13.84 to 40.16 mm.

High toxicity was observed for soil M5/II, whereas the most effective soil substitutes were M1/II (38.65 mm for distilled water and 36.20 mm for PV water) and M4/II (41.10 mm for distilled water and 40.16 mm for PV water) containing 20 and 30 % by weight coal lignite, respectively.

### 7.3.3 Toxicity of coal mine water to *Sinapis alba* - pot test

The shoot length and biomass growth of *Sinapis alba* were conducted in pots. The seeds of test plants (*Sinapis alba* or grass mixture) were placed at a depth of 1 cm in plastic plant pots with soil substitutes. Each pot was watered once a day with distilled water or coal mine water (Premogovnik Valenje d.o.o.) and exposed to white light for 12 hours a day. The analysis was carried out by measuring the increase in the biomass of plants.

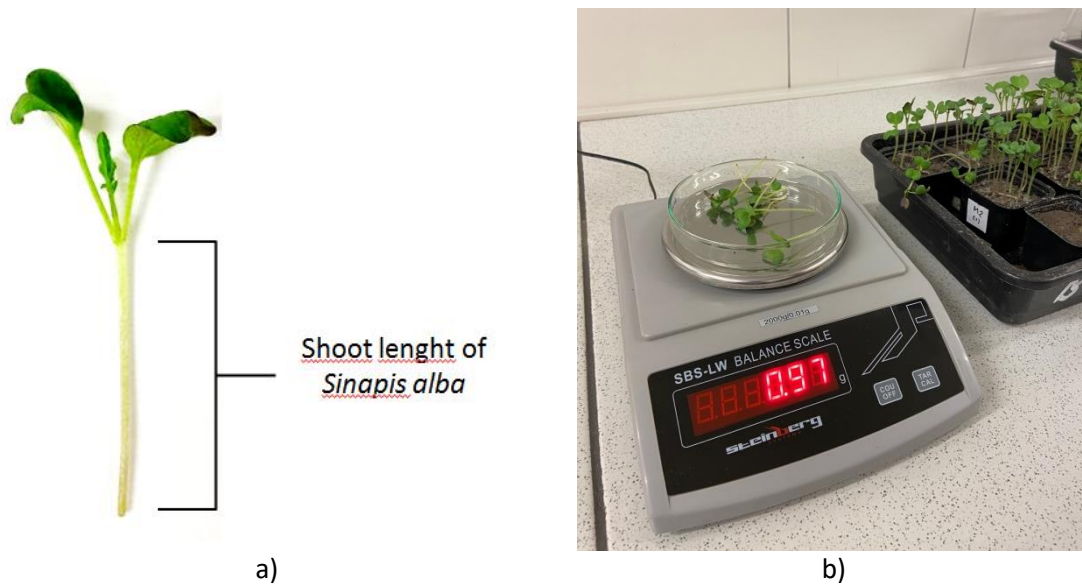


After seven days, the sprouted plants of *Sinapis alba* were carefully harvested and weighed. The test was conducted with three repetitions. The phytotoxic effect of *Sinapis alba* on the pot test is presented in Figure 7-6.



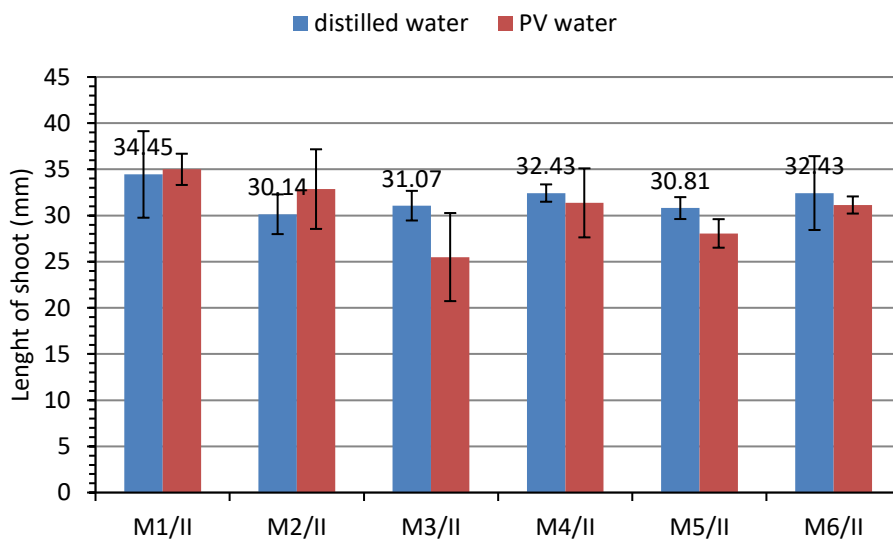
a) b)  
Figure 7-6. Pots with soil substitutes and *Sinapis alba* seeds: a) before germination, b) after seven days of germination

The methods of measuring shoot length and biomass weight of *Sinapis alba* are shown in Figure 7-7.



**Figure 7-7. Measurement of *Sinapis alba* shoot after seven days of sowing in pots: a) shoot length, b) biomass weight**

The result of the shoot length measurements for the examined sprouts of *Sinapis alba* is illustrated in Figure 7-8.



**Figure 7-8. Effect of coal mine water treatment on shoot growth of *Sinapis alba* –pot test**

After seven days of growing, the phytotoxicity test showed little difference between pots watered with distilled water and pots watered with PV coal mine water.

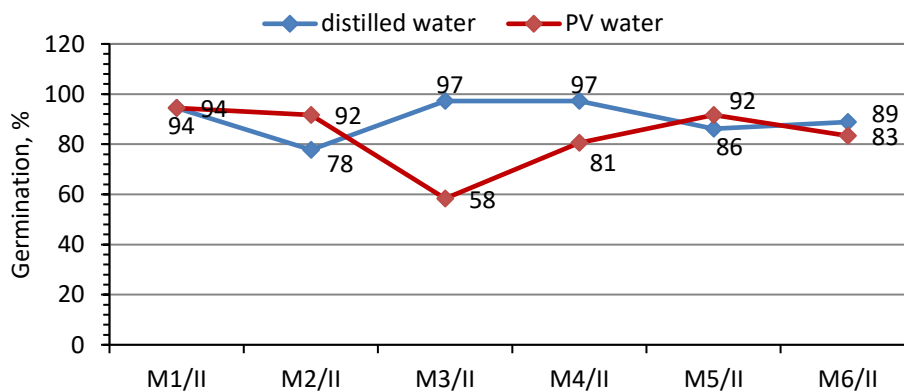
The average length of shoots for pots with distilled water was in a range from 30.14 (M2/II) to 34.45 (M1/II) mm, whereas the measured length of shoot for pots treated with coal mine water (PV) was from 25.5 (M3/II) to 35.0 mm (M1/II).

The result of the biomass weight of *Sinapis alba* shoots after harvesting is presented in Table 7-9. Table 7-9. *Sinapis alba* biomass after seven days of growing

**Table 7-9. *Sinapis alba* biomass after seven days of growing during the pot test**

Pot symbol	Weight of biomass (g) for soil substitutes					
	M1 /II	M2/II	M3/II	M4/II	M5/II	M6/II
<b>treated with distilled water</b>						
A	1.15	0.72	1.26	1.4	1.34	1.14
B	1.43	1.08	1.28	1.22	1.29	1.55
C	1.24	1.17	1.55	1.38	1.24	1.4
<b>Average</b>	<b>1.27</b>	<b>0.99</b>	<b>1.36</b>	<b>1.33</b>	<b>1.29</b>	<b>1.36</b>
SD	±0.14	±0.24	±0.16	±0.10	±0.05	±0.21
<b>treated with coal mine water</b>						
A	1.19	1.13	0.72	1.07	1.08	1.27
B	1.22	1.12	0.96	1.26	1.15	1.02
C	1.07	1.07	0.66	1.16	1.09	1.28
<b>Average</b>	<b>1.16</b>	<b>1.11</b>	<b>0.78</b>	<b>1.16</b>	<b>1.11</b>	<b>1.19</b>
SD	±0.08	±0.03	±0.12	±0.10	±0.04	±0.15

The average biomass weight on soil substitutes was comparable and ranged between 1.27 to 1.39 g (pots treated with distilled water) and from 1.11 to 1.19 g (pots watering with PV water). Only two soil substitutes, M2/II and M3/II, showed lower biomass weight, 0.99 and 0.78 g, respectively. The reason for that was less germination of *Sinapis alba*, as illustrated in Figure 7-9.



**Figure 7-9. Germination of *Sinapis alba* during pot test**

Additionally, no necrosis of the plants and any other changes indicating a negative impact of soil substitute and coal mine watering on the plant growth was observed after the test (see Figure 7-6 b).

### 7.3.4 Toxicity of coal mine water to *grass mixture* - pot test

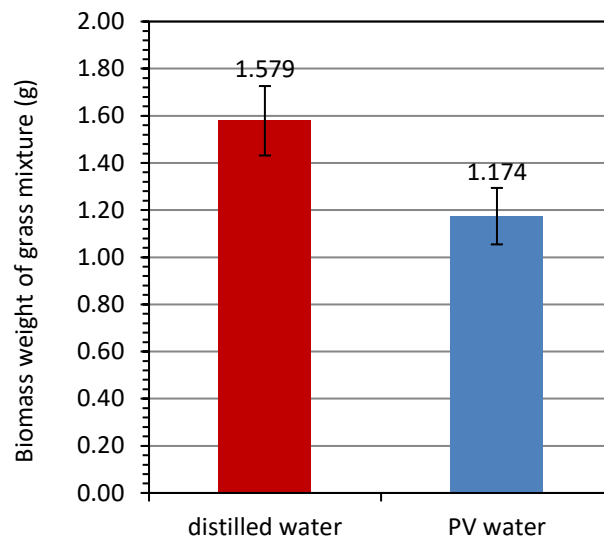
The effect of biomass growth of grass mixture treated with PV water was conducted in pot tests in laboratory conditions (Figure 7-10).



**Figure 7-10. Example of pots with grass mixture during the tests in laboratory conditions**

A weight of 0.5 g seeds of grass mixture (30 % of *Lolium perenne*, 30 % *Festuca rubra-Dipper*, 10% of *Festuca rubra-Adio*, 10 % of *Festuca rubra-Capriccio*, 15 % of *Poa pratensis-Lincolnshire*, 15 % of *Festuca arundinacea-Starlett*) was placed at the depth of 1 cm in plastic plant pots (9x9 cm) with soil substitute. Each pot was watered with distilled or PV water and exposed to white light for 12 hours daily. The sprouted grass mixture was carefully harvested and weighed after 21 days. The aboveground part of the plant's biomass was measured. The test was conducted with three repetitions.

Additionally, one garden soil was used as a reference soil for the potting tests to determine the growth potential of the soil substitutes. The reference soil has been selected as the typical garden soil with appropriate pH, organic matter and N, P, and K content. The result of the test with grass mixture on reference soil, treated with distilled or PV water, was presented in Figure 7-11.



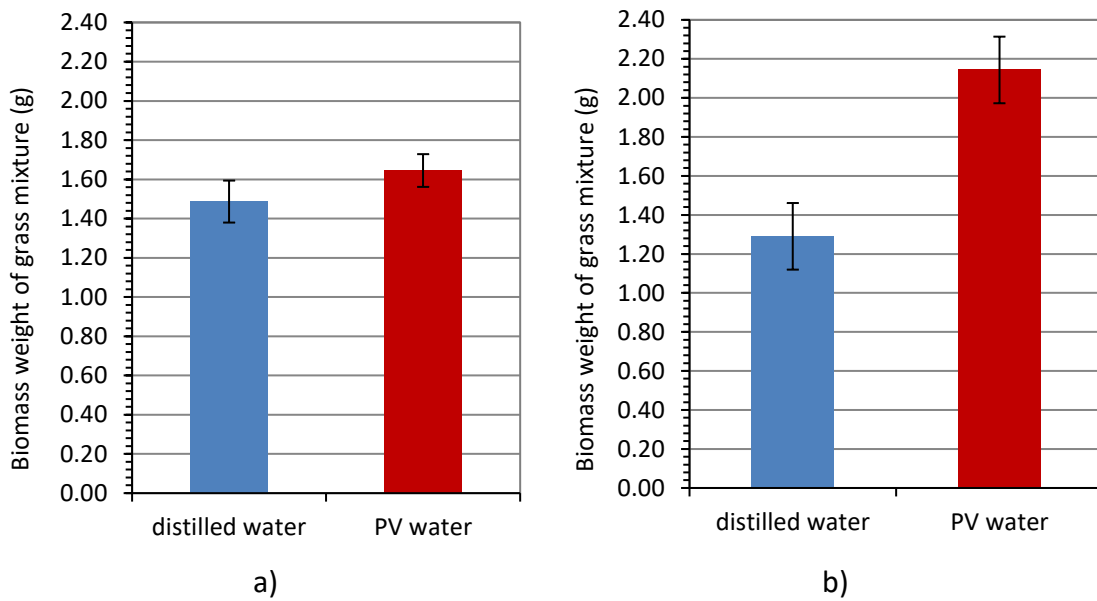
**Figure 7-11. Biomass weight of mixture grass after 21 days of growing on reference soil**

The phytotest result revealed that the average biomass weight for reference soil treated with distilled water was 25 % higher than for pots treated with water delivered by coal mine PV. The effect of growing grass mixture after 21 days is presented in Figure 7-12.



**Figure 7-12. Effect of growing mixture grass after on reference soil treated with: a) distilled water, b) PV water**

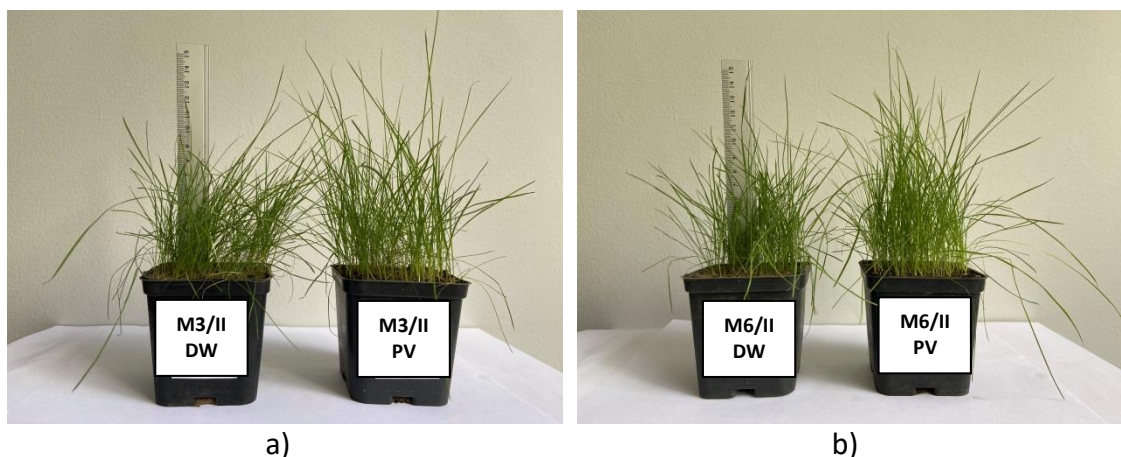
Figure 7-13 shows the result of the phytotoxicity test on two soil substitutes, M3/II and M6/II. The lowest biomass weight was observed for samples treated with distilled water (1.49 g for M3/II and 1.29 g for M6/II) in comparison with samples treated with PV water (1.64 g for M3/II and 2.14 g for M6/II).



**Figure 7-13. Biomass weight of grass mixture treated with distilled water and PV water**  
 a) soil substitute M3/II, b) soil substitute M6/II

In addition, a better increase in biomass was noticed for soil substitutes M6/II, which contained a higher content of organic materials (15 % CL and 15% GC).

The conducted pot test of the increase of the grass mixture on artificial soils enriched with PV water did not affect discolouration or necrosis of grass stalks or other changes, indicating a negative impact of water PV on plant growth. Moreover, the plants on the soils amended with PV water were characterized by higher biomass weight and stalk length (Figure 7-14).



**Figure 7-14. Effect of growing mixture grass after 21 days on soil substitutes a) treated with distilled water, b) treated with PV water**

## 8 Conclusions & lessons learnt

The research outlines a new approach to developing artificial soils to restore coal mine-affected areas in Velenje, in the northeastern region of Slovenia. The main aim is to transform degraded and subsidence terrain into a good ecosystem before installing photovoltaic or wind renewable energy infrastructure.

As the components for artificial soils, industrial by-products generated in a local coal mine (Premogovnik Velenje) and a local coal-fired power plant (Šoštanj Power Plant) were used. The study included the following industrial by-products: fly ash from coal lignite combustion, gypsum from desulfurization, mud from the technological water process, and stabilizat. Stabilizat is a mixture of fly ash, gypsum, slag, and sludge used to fill subsidence in Velenje to prevent surface movements, land deformation, and water leakage from Velenje Lake to Družmirje Lake. For this reason, the stabilizat is the essential component of developed artificial soil substitutes. Due to the chemical composition of the stabilizat and its high mineral content, two organic products, such as coal lignite from Premogovnik Velenje and green compost from the biological manufacturing process, were used as additives to improve habitat conditions for plant growth.

The components of soil mixtures were analyzed in the GIG laboratories to determine their physicochemical parameters, including chemical composition, pH and electrical conductivity. In addition, water leachate tests were performed to show the concentration of macro- and micronutrients in bioavailable forms and toxic metals for proper plant growth and development.

Furthermore, the conventional phytotoxicity procedure was used to determine seed germination and early growth of two test organisms, i.e., white mustard (*Sinapis alba*) and garden cress (*Lepidium sativum*). The specific concept of the phytotoxic micro biotest under laboratory conditions allows direct measurements of root and shoot length and morphological characteristics of early plant stages.

Observations and data obtained from tests of components showed three parameters that are responsible for the lack of sproutings, i.e., high pH, high salinity and low organic matter level.

Fly ash was found to be the most harmful component of soil substitutes for plant germination. For this reason, it is essential to avoid raising its amount in the stabilizat.

Based on the results of the physicochemical and phytotoxicity analyses, the compositions of artificial soil, using different combinations of industrial by-products with coal lignite and organic waste, were proposed. The study of adding coal lignite and green compost to the stabilizat and mud from the technological water process showed a positive effect on the germination and growth of *Sinapis alba* seeds.

Results revealed that the amounts of organic carbon and macronutrients (N, P, K, Ca, Mg) in prepared soil substitutes were sufficient to support plant growth. Moreover, according to Polish Regulation, the content of toxic metals (As, Cd, Cr, Cu, Ni, Pb and Zn) in artificial soils did not exceed the permissible thresholds for soils classified as wooded, shrubby, and green areas. However, as reported in the Official Journal of the Republic of Slovenia, concentrations of toxic metals (As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb and Zn) for soil substitutes based on stabilizat and green compost may slightly exceed the limit values for As, Cd, Mo and Zn. Therefore, during soil substrate development, the range of substances that could cause environmental risk must be identified and checked against local legal conditions to ensure that the final products can be used in reclamation processes.

Based on the data gathered throughout phytotoxicity tests of soil substitute leaches, the results showed a promising opportunity for implementing the tested soils in the potentially acidic coal mine-affected areas. The pH values indicate soils' mildly or moderately alkaline character with negligible toxicity effects on plant growth and development.

The electrical conductivity of soil substitutes shows slight salinity values with low hazard for plant growth. However, sprouting, biomass and yields of sensitive plants such as *Sinapis alba* may be restricted. The salinity of soil-water solutions is determined by the content of sulfate ions, which have a less harmful effect on plant sprouting and growth.

The obtained experimental data indicated varied levels of phytotoxicity of the tested soil substitutes using *Sinapis alba*. The best root and shoot length result was observed for artificial soils containing coal lignite. The results of phytotoxicity tests on soil substitutes based on two stabilizats, from block five and block six, were comparable.

The analysis of phytotoxicity of coal mine water from Premogovnik Velenje for germination and plant growth indicated slightly lower root and shoot growth of *Sinapis alba* compared to samples treated with distilled water.

Coal mine water's pH and EC values have the neutral and non-saline character with negligible toxicity effects on plant growth. The content of ions responsible for salinity ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) shows that the water is not excessively contaminated with residual salts. The salinity of the PV water is determined mainly by sulfate ions that are less harmful than chloride, potassium, and sodium ions to plants. However, prolonged use of mine water for irrigation purposes, especially during long rain-free periods, could negatively affect plant growth.

According to the Polish Regulation of contaminants introduced with industrial waste into soil and surface water bodies,  $\text{BOD}_5$ ,  $\text{COD}_{\text{Cr}}$ , and toxic metal concentrations were below the threshold. The trace elements in the mine water do not exceed the recommended maximum concentrations for irrigation water. The exception is



molybdenum, which slightly exceeds the threshold for prolonged irrigation use. The availability of molybdenum in the soil increases together with increasing pH. It means that extensive use of mine water for irrigation vegetation, especially on soil with neutral and alkaline reactions, could harm living organisms. The concentration of molybdenum and its toxic effects on plants and soil organisms must be monitored in prolonged-irrigated areas.

The result showed that using mine water for plant growth on soil mixtures can positively increase organic matter and nutrients in a form available to plant growth and development. Nevertheless, mine water should only be used to irrigate degraded areas periodically to avoid salinization and exceed molybdenum concentration in the soil and surface waters.

Data from the current study showed that using coal lignite with its combustion products to develop soil substitutes that are ecologically friendly and suitable for plant communities is possible. Further research is needed to evaluate the long-term development of vegetation communities in reclaimed subsidence areas.

Regarding the laboratory tests, the main lessons learnt were as follows:

- Due to its high organic matter content, coal lignite from PV Coal Mine is a valuable component of soil substituent. However, to improve soil characteristics such as texture, fertility, water-holding capacity and structure, it is essential to apply other organic materials in the form of ecologically friendly compost from a biological manufacturing process.
- Before developing soil substitute mixtures, exploring the local market for suppliers of green compost, a material rich in organic matter and low content of toxic metals, is essential.
- The most critical parameters for the water extract of tested components can be limited to pH, electrolytic conductivity, primary ions and main heavy metals.
- Industrial products and organic waste with the lowest possible pH and electrolytic conductivity should be qualified for further testing and analysis.
- Fly ash is the most harmful component of stabilizat for germination and plant growth. For this reason, it is essential to avoid raising its amount for soil substitute production.
- Mine water is suitable for periodic vegetation irrigation in post-mining reclamation areas.

## 9 Glossary

GIG – Central Mining Institute

PV – Premogovnik Velenje Coal Mine

TEŠ – Termoelektrarna Šoštanj d.o.o.

PSU – Land subsidence rehabilitation area

EC – Electrical conductivity

ST-I – Stabilizat (coal by-product from TEŠ, block 6)

ST-II – Stabilizat (coal by-product from TEŠ, block 5)

FA – Fly ash from coal lignite combustion

MD – Mud from technological water process

GY – Gypsum from the desulfurization process

CL – Coal lignite

GC – Green compost from the biological manufacturing process

M1-M6/I – soil substitutes based on ST-I

M1-M6/II – soil substitutes based on ST-II

TOC – total organic carbon, %

DOC – dissolved organic carbon, mg/l

EC-electrical conductivity, mS/cm

BOD<sub>5</sub> – Biochemical Oxygen Demand, mg/l O<sub>2</sub>

COD – Chemical Oxygen Demand, mg/l O<sub>2</sub>

GI – root growth inhibition, %

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