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The Potential Use of Solid Waste and Mine Water for Land Rehabilitation of the Coal Mine-Affected Area in Slovenia

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Abstract: The rehabilitation of post-mining sites is crucial due to the severe environmental impacts of mining, including land degradation, heavy metal pollution, and loss of biodiversity. Effective reclamation strategies are essential to reverse these impacts and enable sustainable land use. This study presents the possibility of the rehabilitation of a post-mining area in Velenje, Slovenia, using artificial soils made from combustion by-products amended with lignite and organic compost, and explores the potential of lignite mine water for irrigation. This approach introduces an innovative solution that differs from the traditional methods of rehabilitating degraded areas. Physicochemical and phytotoxicity tests were conducted to determine the quality of the soil substitutes. The analysis revealed that the pH, salinity, and chemical composition of soils positively impacted *Sinapis alba* growth as a test plant, with the most promising compositions containing 20–30% of lignite by weight as a replacement for organic compost. Irrigation water quality parameters, such as electrical conductivity (0.87 dS/m), the sodium absorption ratio (2.09 meq/L), and boron content (0.05 mg/L), indicated a low soil dispersion risk, while the residual sodium carbonate (3.02 meq/L) suggested a medium risk. Although, the concentration of toxic elements did not exceed the threshold limits; the long-term irrigation with mine water requires the monitoring of the molybdenum levels. These results suggest the potential for using artificial soils and mine water in post-mining land reclamation but highlight the need for the monitoring of their quality.

Keywords: artificial soils; post-mining areas; land rehabilitation; irrigation; circular economy approach

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1. Introduction

The reclamation of post-coal mine sites faces global challenges, including degraded soil quality, heavy metal pollution, and the loss of biodiversity. Conventional land rehabilitation techniques, such as topsoil cover, are costly and have limited effectiveness, particularly for areas affected by mining activities. Using solid waste for mine ecological restoration not only utilizes it but also reduces costs and provides conditions to promote plant growth [1].

The combustion of coal and lignite in thermal power plants generates a large amount of coal combustion by-products (CCPs), including fly ash, bottom ash, boiler slag, and waste from the removal of sulfur dioxide (SO_2) in the flue gas desulfurization process. Approximately 150 million tons of CCPs are estimated to be produced annually in European countries [2], with more than 70% produced being fly ash [3] CCPs can be used as major components in cement and ceramics, in the manufacturing of aggregates, in mining applications, in the backfilling of excavations, or as mineral fillers [4]. It is also known for its use in the production of zeolites [5] and geopolymers [6] Fly ash is also an effective adsorbent for the removal of organic compounds and heavy metals from wastewater or solid waste leachates [7–9] The most effective removal of heavy metals from wastewater has been carried out at pH values between 6 and 8 [10]. The utilization of CCPs for land reclamation in post-mining areas has been practiced for many years [3,11]. In accordance with data from the European Coal Combustion Products Association [12], in 2016, the use of CCPs in European countries for land reclamation and restoration accounted for approximately 41.5% of total production, while their use as a soil amendment represented only 0.1%.

The implementation of the circular economy concept suggests that the further development of these applications is still necessary, and that the recovery of waste from the mining industry is one of the priority goals of the European Parliament, according to Directive 2006/21/EC [13]. Studies have reported that a combination of coal fly ash and a lime-stabilized biosolid may be beneficial for the reclamation of acid mine spoils [14]. The pH of fly ash can vary from 4.5 to 12.0 and depends on the source of coal and its sulfur content [15,16]. Strongly alkaline fly ash (pH 10–12) [17] is beneficial for neutralizing soil acidity. Coal fly ash is also a source of macro- and micronutrients (e.g., Ca, Mg, K, P, S, B, Cu, Fe, Mo, and Zn), essential for plant growth and development [18]. However, the potential for using coal combustion residues for soil reclamation is limited due to their high content of heavy metals and technologically enhanced naturally occurring radioactive materials [19]. Although the application of CPPs to soil improves its physical properties, including pH, bulk composition, and nutrient availability, the long-term disposal of combustion mining waste leads to the contamination of the land and groundwater by toxic heavy metals such as As, B, Cu, Co, Cr, Hg, Mn, Mo, Ni, Pb, and Zn [20].

The use of CCPs as soil components, mainly fly ash, can lead to an increase in soluble ions such as Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2+} in the soil–water mixture, which are responsible for soil salinity [19]. High salinity levels in soil leachates are toxic to plants and lead to the formation of surface runoff during atmospheric precipitation and water erosion. Furthermore, CCPs are deficient in organic matter, which is essential for soil fertility, structure, water retention, and buffering capacity [21]. Soil amendments with high organic matter content may be delivered from agriculture, livestock manure, forestry, or urban waste, such as sewage and municipal sludge [22]. However, brown coal may be one of the sources of organic material used for reclaiming land. Research has shown that the amendment of lignite in contaminated soils effectively reduces heavy metals' bioavailability through adsorption, complexation with humic acids, and pH buffering [23–25]. This work explores a novel approach to developing artificial soils to restore coal mine-affected areas in Velenje, located in Slovenia's northeastern region. Our study proposes using lignite combustion by-products, including fly ash, slag, and gypsum, generated in the local power plant. This product's mixture has been used to prevent subsidence and land deformation. However, it needs to be converted into a soil substitute for the biological reclamation of areas degraded by mining activity.

The specific goal of this research was to use lignite coal as an organic amendment to enhance the properties of soil substitutes. This innovative approach efficiently uses locally available material rich in organic matter and plant nutrients. This study introduces a comprehensive solution to address the challenges of artificial soils being safe for the environment and human and animal health. Additionally, the research explores the novel use of industrial water from a Slovenian lignite mine for irrigation purposes, further enhancing the rehabilitation process's sustainability and circular economy potential. This methodology emphasizes waste minimization and reuse, contributing to advancements in sustainable land reclamation practices.

2. Materials and Methods

2.1. Area for Land Rehabilitation

The research focused on a coal mine degraded area located in Velenje, the northeastern region of central Slovenia (Figure 1). The study site covers an area of 0.5 km^2 and is surrounded by two artificial lakes, Družmirje and Velenjsko, created as a result of underground coal lignite excavation in the PVM. Long-term underground coal excavation in PVM has adverse environmental effects, resulting in numerous areas of land subsidence [26]. In 2016, the volume of subsidence hollows between Lake Družmirje and Lake Velenje exceeded 150 million m^3. Surface movements and deformations are monitored at over 300 measurement points, both within and around the mining area, using the mine's geodetic monitoring system. To prevent surface damage, the product of lignite combustion, called soil stabilizer (ST), has been used to prevent subsidence in areas of active remediation, land deformation, and water leakage from Velenje Lake to Družmirje Lake.

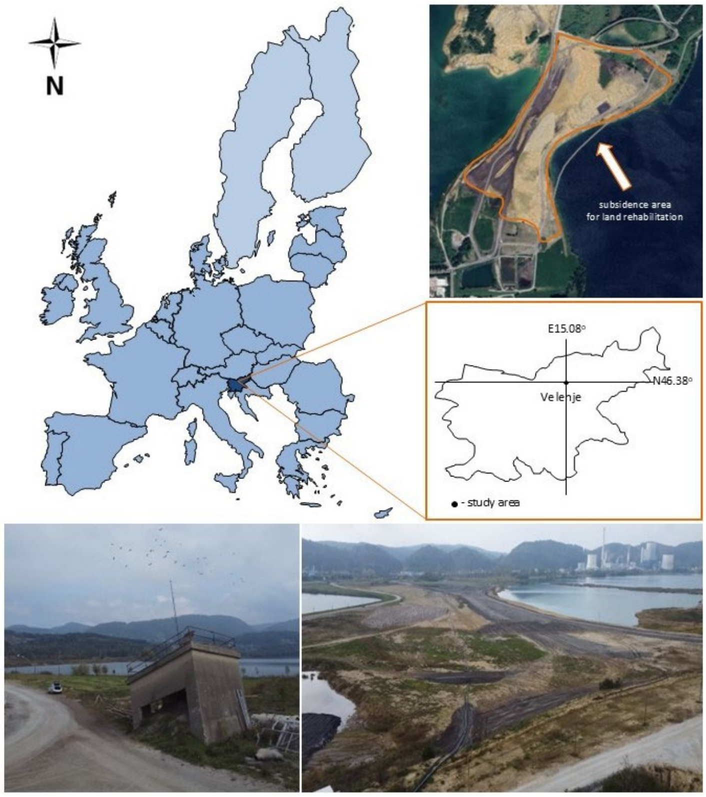


Figure 1. Map of the land subsidence area in Velenje, Slovenia (adapted from Google Maps Data), and an example of subsidence at the surface.

2.2. Combustion By-Products and Organic Materials

A combustion by-product, called soil stabilizer (ST), which is a mixture of fly ash, gypsum, and slag, was collected from Unit 6 (600 MWe) of the Šoštanj Power Plant in Velenje, Slovenia. Soil stabilizer is a by-product of combustion lignite from PVM and has been used to fill the subsidence between Lakes Družmirje and Velenje. The fly ash and slag were by-products of coal combustion, while the gypsum was from the flue gas desulfurization. Another combustion by-product, sludge (SG), was collected from the pool in which technological water was processed from the Šoštanj Power Plant (Figure 2).

Figure 2. Šoštanj Power Plant pool with technological water.

Organic materials, including lignite (CL) and green compost (GC) from the biological manufacturing process, were delivered by PVM and an industrial composting facility (Sosnowiec, Poland), respectively.

An average of 20 kg of laboratory samples of CCPs and organic materials were transported to the Central Mining Institute in Poland and stored in a laboratory at ambient temperature before analysis. After moisture removal, samples were crushed and sieved through a mesh with a 2 mm pore size to remove particles of other impurities. Finally, each sample was thoroughly mixed to guarantee that it was a representative sample for physicochemical analysis.

2.3. *Physicochemical Analysis of Soil Substitutes and Their Components*

All physicochemical analyses were conducted in accredited laboratories in the Department of Environmental Monitoring at the Central Mining Institute. The research equipment and apparatus used in this study were regularly calibrated following the laboratory procedures.

The ash content was determined by the weight method, involving the combustion of soil samples at 815 °C in a laboratory furnace (HT 16/16 with a P310 controller, Nabertherm GmbH, Lilienthal, Germany). The contents of primary elements, including Al_2O_3, CaO, K_2O, MgO, Na_2O, P_2O_5, SO_3, SiO_2, and TiO_2, were determined via wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) provided by Rigaku Analytical Devices Inc. (Rigaku ZSX Primus, Wilmington, NC, USA). The concentration of trace elements (As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn) was measured via inductively coupled plasma optical emission spectroscopy (ICP–OES) after mineralization in aqua regia (Perkin Elmer Optima 5300DV ICP-OES analyzer, Perkin Elmer Inc., Waltham, MA, USA). The mercury (Hg) content was analyzed using cold-vapor atomic absorption spectrometry (CV-AAS) by SMS 100, PerkinElmer Inc., Waltham, MA, USA. The infrared spectroscopy method (ELTRA CHS, Eltra GmbH, Haan, Germany) was used to analyze the content of total organic carbon (TOC) and total sulfur (TS), while the Kjeldahl method was applied to determine the total nitrogen (TN).

2.4. *Analysis of Soil Substitute Leachates and Mine Water for Irrigation*

The contents of metals and nonmetals (As, Ba, Ca, Cd, Cr, Cu, K, Mg, Mn, Mo, Na, Ni, Pb, and Zn) in the water extracts of the soil substitutes were determined via the ICP–OES method (Perkin Elmer Optima 5300DV ICP-OES analyzer, Perkin Elmer Inc., Waltham, MA, USA). The content of Cl^-, SO_4^{2-}, NO_3^-, and PO_4^{3-} anions was analyzed using ion chromatography (DIONEX ICS-5000, Thermo Fisher Scientific, Waltham, MA, USA), and the concentrations of sulfide (S^{2-}) and ammonium (NH_4^+) ions were measured via flow analysis with spectrophotometric detection (FIA, MLE Gmbh Dresden, Germany). High-temperature combustion with CV-AA detection was used to determine the Hg concentration (SMS 100, PerkinElmer Inc., Waltham, MA, USA). An elemental analyzer with infrared detection (TOC-L CPH, Shimadzu, Kyoto, Japan) was used to determine the content of dissolved organic carbon (DOC), while the total nitrogen content was determined via high-temperature infrared chemiluminescence detection (TNM-L, Shimadzu, Kyoto, Japan). The pH value and electrical conductivity (EC) of the water extracts were measured with a pH meter with a combination electrode (CPC-411 and IJ44AT, Elmetron, Zabrze, Poland). The water extracts were prepared by mixing soil substitutes with deionized water at a soil-to-water ratio of 1:10 (dry weight), as specified in European Standard EN 12457-2:2004 [27]. After being shaken on a rotary mixer (ROTAX 6.8, Velp Scientifica Srl, Usmate, Italy) at 40 rpm for 8 h, the samples were centrifuged at 15000 rpm for 10 min (Centrifuge 5810, Eppendorf, Hamburg, Germany) and filtered through Whatman 0.45 µm filters (GE Healthcare, Chicago, IL, USA).

The chemical composition of the mine water from PVM was determined via the same methods as those used for the leachate samples.

2.5. Assessment of Mine Water Quality

Two parameters were calculated to determine the suitability of mine water for the irrigation of soil substitutes. The potential risk of soil degradation due to sodium was assessed by the sodium absorption ratio (SAR). The SAR value of mine water for irrigation soil substitutes was calculated via Formula (1) [28]:

$$\mathrm{SAR} = \mathrm{Na}^{+} / \sqrt{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)} / 2 \tag{1}$$

where Na^{+}, Ca^{2+}, and Mg^{2+} represent the concentrations in milliequivalents per liter (meq/L) of the respective ions.

The residual sodium carbonate and bicarbonate ion concentrations (RSCs) indicate the potential for water to cause soil alkalinity or salinity issues over time when used for irrigation. The RSC value of mine water for irrigation, expressed in meq/L, was calculated according to Formula (2) [28]:

$$\mathrm{RSC} = \left(\mathrm{CO}_3^{2-} + \mathrm{HCO}_3^{-}\right) - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right) \tag{2}$$

The classification of irrigation water for the SAR and RSC values is presented in Table 1.

Table 1. Classification of water irrigation by the SAR and RSC indicators [28,29].

Parameter	Range (meq/L)	Water Class
Sodium absorption ratio (SAR)	<10	Excellent
	10–18	Good
	18–26	Doubtful
	<26	Unsuitable
Residual sodium carbonate (RSC)	<1.25	Good
	1.25–2.5	Doubtful
	<2.5	Unsuitable

2.6. Phytotoxicity Tests

To assess the toxicity of soil substitute leachates and their potential impact on irrigation with mine water, white mustard (*Sinapis alba* L.) was used as a test organism. The effects of toxicity were evaluated according to a modified procedure based on the European Standard EN ISO 18763:2020 [30]. The samples of the soil substitutes were placed in Petri dishes

(9.0 cm diameter) and mixed with distilled or mine water from the PVM. Each dish was lined with filter paper (87 g/m^2) and allowed to absorb moisture until saturated. Then, 15 tested seeds of *Sinapis alba* L. were placed on filter paper and closed with a lid. To determine the effect on germination, the seeds were incubated in a laboratory incubator (POL-EKO, CLW 32, Wodzislaw Slaski, Poland) at 25 ± 1 °C for 72 h with no access to light. The length of the roots was measured as the primary parameter, with an accuracy of ±0.1 cm.

2.7. Pot Test of the Soil Substitutes

The effect of biomass growth on soil substitutes irrigated with distilled and coal mine water was investigated under laboratory conditions under a constant temperature (22 ± 1 °C) for the entire day, controlled humidity (40 ± 5%), and lighting parameters (70 W, 4900 lm, and 6000 K).

Ecotoxicity tests involving *Sinapis alba* were carried out to determine the toxic effects of mine water on plant growth.

2.8. Statistical Analysis

Statistica 13.3 (StatSoft Polska, Cracow, Poland) was used for all the statistical analyses; the limit of statistical significance was set at $p < 0.05$. The existence of correlations between different variables was tested by calculating the Pearson rank coefficients.

One-way analysis of variance (ANOVA) was performed to determine the differences among the experimental groups. The significance of differences between groups was tested via the post hoc Tukey HSD test ($p \leq 0.05$).

3. Results and Discussion

3.1. Physicochemical Analysis of the Components of the Soil Substitutes

The chemical properties of the CCPs and organic materials used for the elaboration of the soil substitutes are presented in Table 2. Among all the investigated components, two organic materials, CL and GC, contained much higher amounts of organic carbon (426.1 and 173.8 g/kg, respectively) and nitrogen (8.4 and 15.6 g/kg, respectively), with relatively low concentrations of mineral oxides, except for 461.3 g/kg of SiO_2 in GC. The high content of mineral oxides such as SiO_2, Al_2O_3, and CaO in CCPs was typical of fly ash from lignite combustion and suggested the presence of calcium-based compounds. A higher amount of Fe_2O_3 in mineral samples (90.3 g/kg for ST and 90.1 g/kg for SG), compared to the organic samples (31.4 g/kg for CL and 18.1 g/kg for GC), showed the mineralogical nature of CCPs. The typical mineral composition of ST and SG samples was reflected in the higher concentrations of MgO and K_2O. Moreover, a higher content of P_2O_5 (6.3 mg/kg) in GC was likely due to the organic nature of the sample.

The analysis revealed that the total sulfur (S_t) concentration varied from 2.6 g/kg in the GC to 49.3 g/kg in the SG. The reason for the greater amount of S_t in the CCPs was the amount of gypsum generated in the flue gas desulfurization process.

Moreover, the chemical analysis showed that the concentrations of trace elements in CCPs were greater than those in organic materials. However, the highest amounts of Zn (624 mg/L) and Pb (108 mg/L) were observed in the GC. The highest concentration of molybdenum in the components was observed in CL and ST, whereas the highest amount of As (39 mg/L) was detected in the ST sample. Notably, high concentrations of toxic metals in soils may reduce sprouting and biomass yields and have harmful effects on plant growth [31].

Table 2. Chemical analysis (±uncertainty) of the components for preparation of soil substitutes.

Parameter	**Unit**	**CCPs**		**Organic Material**	
		ST	**SG**	**CL**	**GC**
A	%	92.82 ± 3.71	88.86 ± 3.55	244.1 ± 9.8	60.37 ± 2.41
TOC	g/kg	4.6 ± 0.9	8.4 ± 1.7	426.1 ± 85.2	173.8 ± 34.8
S_t		45.0 ± 4.5	49.3 ± 0.49	21.6 ± 2.2	2.6 ± 0.4
N_t		0.75 ± 0.1	0.05 ± 0.1	8.4 ± 1.3	15.6 ± 2.3
SiO_2		345.1 ± 20.7	334.3 ± 20.1	104.3 ± 6.3	461.3 ± 27.7
Al_2O_3		168.0 ± 10.1	136.9 ± 8.2	51.9 ± 3.1	23.1 ± 1.4
F_2O_3		90.3 ± 5.4	90.1 ± 5.4	31.4 ± 1.9	18.1 ± 1.1
CaO		159.1 ± 15.9	157.0 ± 15.7	24.5 ± 2.5	61.1 ± 6.1
MgO		18.3 ± 1.8	18.7 ± 1.9	4.8 ± 0.5	8.6 ± 0.9
Na_2O		3.3 ± 0.4	4.9 ± 0.6	1.1 ± 0.4	3.3 ± 0.4
K_2O		16.7 ± 1.7	17.2 ± 1.7	5.5 ± 0.6	11.2 ± 1.1
SO_3		98.6 ± 14.8	114.0 ± 17.1	17.5 ± 2.6	8.2 ± 1.2
TiO_2		7.5 ± 0.8	5.5 ± 0.06	1.9 ± 0.2	1.6 ± 0.2
P_2O_5		1.9 ± 0.3	1.9 ± 0.03	0.6 ± 0.1	6.3 ± 0.9
As	mg/kg	39.0 ± 7.8	23.0 ± 4.6	21.0 ± 4.2	4.0 ± 1.4
Ba		249.0 ± 49.8	261.0 ± 52.2	281.0 ± 56.2	146.0 ± 29.2
Cd		2.0 ± 0.7	1.0 ± 0.35	4.0 ± 1.4	5.0 ± 1.75
Co		11.0 ± 2.2	7.0 ± 2.45	10.0 ± 2.0	4.0 ± 1.4
Cr		85.0 ± 17.0	95.0 ± 19.0	79.0 ± 15.8	26.0 ± 5.2
Cu		36.0 ± 7.2	46.0 ± 9.20	49.0 ± 9.8	48.0 ± 9.6
Hg		0.11 ± 0.04	0.11 ± 0.04	0.06 ± 0.02	0.06 ± 0.02
Mn		867.0 ± 173.4	817.0 ± 163.4	1260.0 ± 252.0	360.0 ± 72.0
Mo		35.0 ± 7.0	27.0 ± 5.4	37.0 ± 7.4	2.0 ± 0.7
Ni		59.0 ± 11.8	45.0 ± 9.0	42.0 ± 8.4	16.0 ± 3.2
Pb		23.0 ± 4.6	28.0 ± 5.6	37.0 ± 7.4	108.0 ± 21.6
Zn		104.0 ± 20.8	219.0 ± 43.8	159.0 ± 31.8	624.0 ± 124.8

ST—soil stabilizer, SG—sludge from the sedimentation tank; CL—coal lignite, GC—green compost; A—content of ash; TOC—total organic carbon.

3.2. Preparation and Analysis of the Soil Substitutes

The soil substitute samples were prepared via the weight method based on the results of the physicochemical analysis of the CCPs and organic materials. A list of the component materials and their percentage ranges for the preparation soil substitutes (M1-M6) is presented in Figure 3.

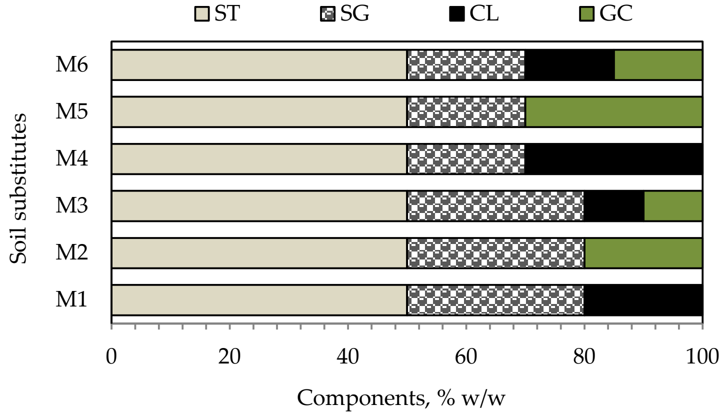


Figure 3. Composition of soil substitutes for land rehabilitation in subsidence areas.

The main component of each mixture was the ST used to prevent subsidence in the post-mining area, with a 50% w/w content. The amount of SG ranged from 20 to 30% w/w, whereas the percentages of CL and GC were between 0 and 30% w/w. The purpose of this blending process was to ensure that the soil had appropriate parameters, including low salinity, a balanced content of essential nutrients, a low concentration of toxic metals, and an optimal structure.

The results of the trace elements analysis in soil substitutes, along with their permissible thresholds for limit, warning, and critical concentrations in soils according to the

Official Journal of the Republic of Slovenia [32,33] and their contents in soil substitutes are presented in Table 3.

Table 3. The concentration (±uncertainty) of trace elements in soil substitutes and the limit values of dangerous substances in soils in Slovenia [32,33].

Parameter	**Soil Substitute (mg/kg)**						**Permissible Thresholds (mg/kg)**		
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**Limit**	**Warning**	**Critical**
As	23 ± 5	22 ± 4	22 ± 4	20 ± 4	20 ± 4	23 ± 5	20	30	55
Ba	220 ± 44	208 ± 42	216 ± 43	191 ± 38	202 ± 40	200 ± 40	N/A	N/A	N/A
Cd	1 ± 0.3	2 ± 0.7	1 ± 0.3	1 ± 0.3	2 ± 0.7	2 ± 0.7	1	2	12
Co	8 ± 2.8	7 ± 2.4	7 ± 2.4	7 ± 2.4	9 ± 3.2	8 ± 2.8	20	50	240
Cr	53 ± 11	53 ± 11	53 ± 11	53 ± 11	54 ± 11	55 ± 11	100	150	380
Cu	29 ± 6	32 ± 6	29 ± 6	25 ± 5	33 ± 7	30 ± 6	60	100	300
Hg	0.11 ± 0.04	0.11 ± 0.04	0.06 ± 0.02	0.06 ± 0.02	0.11 ± 0.04	0.11 ± 0.04	0.8	2.0	10.0
Mn	878 ± 176	893 ± 179	888 ± 178	851 ± 170	834 ± 167	858 ± 167	N/A	N/A	N/A
Mo	30 ± 6	30 ± 6	30 ± 6	28 ± 6	26 ± 5	28 ± 6	10	40	200
Ni	28 ± 6	28 ± 6	28 ± 6	28 ± 6	26 ± 5	30 ± 6	50	70	210
Pb	40 ± 8	40 ± 8	29 ± 6	23 ± 5	55 ± 11	33 ± 7	85	100	530
Zn	125 ± 25	180 ± 36	145 ± 29	100 ± 20	234 ± 47	168 ± 34	200	300	720

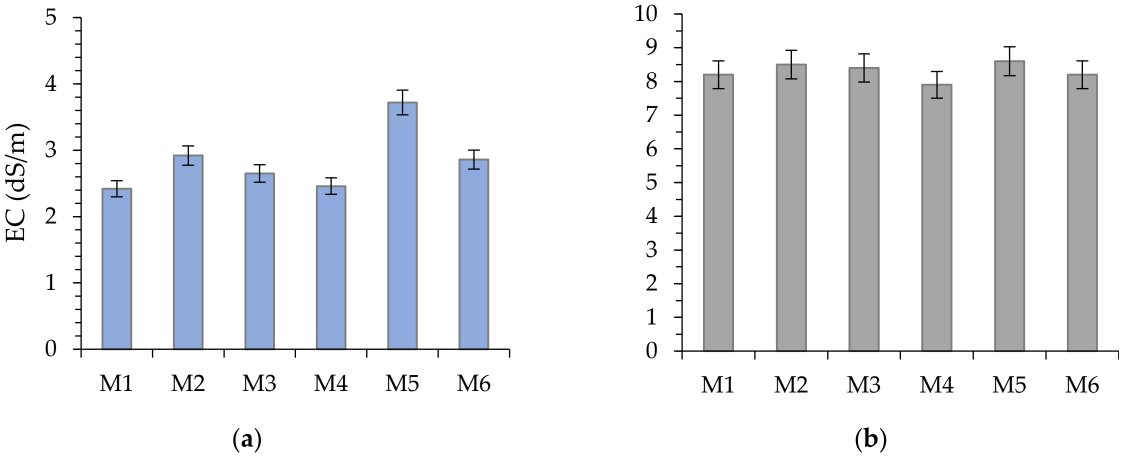
N/A—not applicable.

According to the regulations in Slovenia [32], the permissible thresholds for dangerous substances are classified into three categories: (i) the limit value indicates the soil load where living conditions for plants and animals are ensured and groundwater quality and soil fertility do not deteriorate. The effects or impacts on human health or the environment are still acceptable at this value; (ii) the warning value is the density of an individual hazardous substance in the soil, indicating a probability of harmful effects or impacts on human health or the environment in particular land use; (iii) the critical value determines the concentrations at which, due to harmful effects or impacts on humans and the environment, contaminated soil is not suitable for producing plants intended for human or animal consumption.This study demonstrates that the concentrations of arsenic (>20 mg/kg) and molybdenum (>10 mg/kg) in soil substitutes exceeded their respective limit values. Additionally, a warning concentration of cadmium (>2 mg/kg) was detected in samples M2, M5, and M6. However, it is essential to highlight that soil substitutes should be applied only in areas degraded by industry, with no plans to carry out agricultural activities. In that case, the use of mixtures that slightly exceed the limit values for the biological reclamation of post-mining areas is safe for the environment. It poses an acceptable risk to human and animal health, as well as to plant growth.

3.3. Analysis of Water Leakage from the Soil Substitutes

The measured parameters for the soil substitute leachates (M1-M6) are shown in Figure 4.

According to the general classification [34], the measured salinity of soil substitutes M1-M6, expressed as electrical conductivity, can be classified as slightly alkaline soils (2.0–4.0 dS/m). In this approach, the sprouting and biomass growth of sensitive plants, such as Sinapis alba, may be restricted. However, the literature data [31] reported that most crops prefer growing in EC between 2.0 and 3.5 dS/m. The highest EC (3.72 dS/m) measured in sample M5 may restrict water availability to plants, as increased soil salinity induces osmotic stress. In response to such conditions, plants may reduce their growth rate or change their root structure to increase water absorption [35].



(**a**) (**b**)

Figure 4. Parameters in aqueous leachates from soil substitutes: (**a**) electrical conductivity; (**b**) pH.

Based on the general interpretation of the pH value [36], the leachates of the soil substitutes were moderately alkaline (pH 7.9–8.4) and strongly alkaline (pH 8.5–9.0). The solubility of metals in aqueous soil solutions depends on their pH value. Many studies have concluded that the solubility of Fe, Cu, Zn, Mn, and Co decreases in alkaline solutions [37]. At pH levels above 7, a reduced bioavailability of Al and Mn is observed due to the formation of insoluble hydroxy salts such as $Al(OH)_3$ and $Mn(OH)_2$, respectively. Conversely, higher pH values increase the mobility of molybdenum and arsenic in the form of anions $MoO_4{}^{2-}$ and $AsO_4{}^{3-}$, which are weakly adsorbed by alkaline soils [38]. More stable and less mobile alkaline conditions lead to the formation of insoluble hydroxyl complexes or compounds with organic substances [39]. The chemical parameters of soil substitute leachates, including the concentrations of nutrients and trace elements, are listed in Table 4.

Table 4. Chemical characteristics of aqueous leachates from soil substitutes (mg/L).

Parameter	**Soil Substitutes**					
	M1	**M2**	**M3**	**M4**	**M5**	**M6**
Al	1.07 ± 0.13	1.47 ± 0.18	1.55 ± 0.19	0.31 ± 0.07	1.79 ± 0.22	0.65 ± 0.14
As	0.032 ± 0.008	0.018 ± 0.004	0.027 ± 0.007	0.043 ± 0.011	0.030 ± 0.007	0.038 ± 0.009
Ba	0.061 ± 0.016	0.072 ± 0.019	0.064 ± 0.017	0.056 ± 0.015	0.077 ± 0.020	0.074 ± 0.019
Cd	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cu	<0.005	<0.005	<0.0005	<0.005	0.011 ± 0.003	<0.005
Cr	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Hg	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Mn	0.056 ± 0.012	0.011 ± 0.003	0.027 ± 0.007	0.16 ± 0.03	0.022 ± 0.006	0.082 ± 0.017
Mo	0.64 ± 0.14	0.86 ± 0.18	0.70 ± 0.15	0.58 ± 0.12	0.80 ± 0.17	0.65 ± 0.14
Ni	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Pb	<0.00	<0.005	<0.005	<0.00	<0.005	<0.005
Zn	0.033 ± 0.009	0.023 ± 0.06	0.013 ± 0.003	0.24 ± 0.05	0.059 ± 0.015	0.022 ± 0.006
K^+	20.9 ± 2.6	228 ± 28	113 ± 14	17.5 ± 2.1	447 ± 55.0	171 ± 21
Na^+	55.6 ± 6.8	50.4 ± 6.2	50.1 ± 6.1	65.3 ± 8.0	64.8 ± 7.9	50.2 ± 6.1
Ca^{2+}	625 ± 76	620 ± 76	591 ± 72	612 ± 75	654 ± 80	632 ± 77
Mg^{2+}	24.5 ± 3.0	20.2 ± 2.5	19.9 ± 2.4	37.1 ± 4.5	42.6 ± 3.71	35.5 ± 4.3
NH^{4+}	0.83 ± 0.1	1.00 ± 0.1	0.90 ± 0.11	0.82 ± 0.01	0.89 ± 0.11	1.10 ± 0.1
Cl^-	9.0 ± 1.1	77 ± 9.4	42 ± 5.1	9.7 ± 1.2	144 ± 18	60 ± 7.3
$PO_4{}^{3-}$	0.027 ± 0.01	0.12 ± 0.01	0.07 ± 0.01	0.012 ± 0.001	0.18 ± 0.02	0.13 ± 0.02
$SO_4{}^{2-}$	1590 ± 190	1560 ± 190	1510 ± 180	1510 ± 180	1760 ± 210	1600 ± 200
$S_2{}^-$	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
DOC	17.0 ± 2.8	12.0 ± 2.0	8.5 ± 1.4	12 ± 2.0	49 ± 8.1	14 ± 2.3
N_t	2.5 ± 0.4	16.0 ± 2.6	7.8 ± 1.3	2.5 ± 0.4	29.0 ± 4.8	11.0 ± 1.8

DOC—dissolved organic carbon.

Sample M5 is characterized by the highest EC (3.72 dS/m), which corresponds with the highest concentrations of K^+ (447 mg/L), Cl^- (144 mg/L), and $SO_4{}^{2-}$ ions (1760 mg/kg). More K^+ (228 mg/L) and Cl^- ions (77 mg/L) were detected in sample M2, corresponding to a salinity of 2.92 dS/m. The highest contents of N_t (29 mg/L) and DOC (49 mg/L) were observed in M5, whereas the concentrations of other nutrients, such as Ca^{2+} (591–654 mg/L), Mg^{2+} (19.9–42.6 mg/kg), and Na^{+} (50.1–65.3 mg/kg), were comparable for all the samples. Dissolved organic carbon is a parameter that indicates the presence of organic nutrients in the soil–water solution. It acts as a primary energy source for soil microorganisms, thereby supporting biogeochemical cycles and enhancing nutrient availability to plants. Elevated DOC concentrations can influence metal mobilization by forming organic complexes that increase their solubility [40].

The use of CCPs as soil components, mainly fly ash, can lead to an increase in soluble ions such as Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2+} in the soil–water mixture, which are responsible for soil salinity [19]. When present at high concentrations, sulfate and chloride ions may hinder proper plant growth and development. 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 concentrations of toxic metals such as Cr, Cd, Cu, Hg, Ni, and Pb were below the detection limit, whereas the highest content of trace elements was recorded for Mo (0.58–0.86 mg/L).The levels of nutrients (Ca, Mg, P, K, N, and Na) in all leachates indicate that these amounts may be sufficient to support plant growth. According to the literature, the primary nutrients N, P, and K are responsible for biomass build-up, the development of plant root systems, and internal water management [41–43]. Nevertheless, a relatively high concentration of K may cause strong soil salinity and reduce green biomass production.

3.4. Composition of Water from the Velenje Coal Mine

The quality of irrigation water and its detrimental effects on soil properties were assessed via several parameters, such as EC, SAR, RSC, and the content of boron (B), and classified into four risk criteria according to the Standard Guidelines for Irrigation Water [44] as presented in Table 5.

Table 5. Soil dispersion risk after irrigation with PVM water [44].

Parameter	Unit	Result	Risk Criteria			
			Low	Medium	High	Very High
Electrical Conductivity (EC)	dS/m	0.87	<1.5	1.5–3.0	3.0–6.0	>6.0
Sodium Absorption Ratio (SAR)	meq/L	2.09	<10	10–18	18–26	>26
Residual Sodium Carbonate (RSC)	meq/L	3.02	<1.5	1.5–3.0	3.0–6.0	>6.0
Boron (B)	mg/L	0.05	<1.0	1.0–2.0	2.0–4.0	>4.0

The results suggest that the risk of irrigation with PVM water is low, according to the EC, SAR, and B concentrations. However, the calculated value of the RSC (3.02 meq/L) indicates that the risk of applying water for irrigation is medium or even high. Based on this classification (Table 1), waters containing more than 2.5 meq/L of RSC are considered unsuitable for irrigation [28]. However, a literature study revealed that to neutralize the RSC of irrigation water to over 2.5 meq/L, the addition of acid or gypsum to the soil structure is recommended [45]. A study carried out by Kumar et al. [46] indicated that the application of gypsum to soil with a high RCS water index decreases the pH of the soil, resulting in an increased crop yield. The pH decreased due to the removal of sodium carbonate and bicarbonate after the gypsum treatment.

The compositions of the water samples from the PVM and the recommended quality standards for irrigation water, adapted from the Food and Agriculture Organization of the United Nations Standards [47], are presented in Table 6.

Table 6. Soil dispersion risk after irrigation with PVM [47].

Parameter		Unit	Usual Range in Irrigation	Result	Degree of Restriction Range
Salinity	EC	dS/m	0–3	0.869 ± 0.04	0.7–3.0 (a)
	TDS	mg/L	0–2000	666 ± 67	450–2000 (a)
Cations and anions	Ca^{2+}	meq/L	0–20	2.337 ± 0.234	N/A
	Mg^{2+}	meq/L	0–5	1.875 ± 0.187	N/A
	Na^{+}	meq/L	SAR (0–9)	2.091 ± 0.209	SAR < 3 (b)
	$CO_3{}^{2-}$	meq/L	0–0.1	0.050 ± 0.005	N/A
	Cl^{-}	meq/L	0–30	0.310 ± 0.031	<4 (b)
	$SO_4{}^{2-}$	meq/L	0–20	2.062 ± 0.206	N/A
Nutrients	$P\text{-}PO_4{}^{3-}$	mg/L	0–2	0.67 ± 0.10	N/A
	$N\text{-}NH_4{}^{+}$	mg/L	0–5	2.00 ± 0.20	N/A
	$N\text{-}NO_3{}^{-}$	mg/L	0–10	0.77 ± 0.08	<5.0 (b)
	K^{+}	mg/L	0–2	3.93 ± 0.79	N/A
Miscellaneous effects	B	mg/L	0–2	0.048 ± 0.012	<0.7 (b)
	$HCO_3{}^{-}$	meq/L	0–10	7.180 ± 0.718	1.5–8.5 (a)
	pH	1–14	6.5–8.5	7.600 ± 0.2	N/A
Infiltration	SAR	meq/L	0–40	2.091	SAR 0–3

EC—electrical conductivity, TDS—total dissolved solids, SAR—sodium absorption ratio; (a) slight to moderate; (b) no restriction; N/A—not applicable.

The EC and TDS of treated mine water were 0.869 dS/m and 666 mg/L, respectively, which classified the water as slightly to moderately suitable for irrigation, according to the guideline interpretations [47]. The EC and pH values indicate the neutral and nonsaline characteristics of the PVM water, with negligible toxicity effects on plant growth. However, for water used for long-term irrigation, values of EC lower than 0.7 dS/m are needed to avoid soil salinization [48]. The results demonstrated that the concentrations of cations and anions responsible for the salinity were below the threshold values. Additionally, the presence of sodium and chloride ions indicated that the irrigation water could be used without restrictions. The salinity of PVM water is caused mainly by $SO_4{}^{2-}$ ions, which are less harmful than chloride and sodium ions to plants in terms of osmotic stress. As a result of osmotic stress, plants have a reduced ability to take up water through their roots, resulting in dry and wilting leaves and overall weakening. However, research on osmotic stress in an indicator plant (*Zea mays*) has shown that sulfate ions ($SO_4{}^{2-}$) can act to buffer osmotic stress to some extent, meaning that they can help reduce its adverse effects on plants [49].

The calculated SAR value (2.091 meq/L) is the relative percentage of sodium to Ca^{2+} and Mg^{2+} ions in water. High Na^{+} concentrations in irrigation water can also affect calcium and potassium deficiencies in soils with low contents of these nutrients. In general, high levels of SAR in water for irrigation can reduce soil stability, decrease the rate of water infiltration, and increase the risk of sodium accumulation to toxic levels in plants [50]. According to the classification of water irrigation by the sodium absorption ratio (Table 1), the PVM water may be categorized as excellent (SAR < 10) [28].

The results for the bicarbonate ($HCO_3{}^{-}$) ion content classified the PVM water's irrigation quality as slight to moderate. Higher concentrations of $HCO_3{}^{2-}$ ions in the presence of dissolved Ca^{2+} or Mg^{2+} ions can lead to the formation of insoluble calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$), the precipitation of which increases the risk of sodium hazards affecting plant growth [51].

A comparison of the concentrations of the biogenic forms revealed that the contents of nutrient ions ($P\text{-}PO_4{}^{3-}$, $N\text{-}NH_4{}^{+}$, and $N\text{-}NO_3{}^{-}$) were within the range suitable for irrigation, whereas the amounts of $N\text{-}NO_3{}^{-}$ (<5 mg/L) and boron (<0.7 mg/L) suggest that the water for irrigation can be used with no restrictions. The concentration of K^{+} ions was 3.93 mg/L, which was above the usual range for irrigation water (<2 mg/L). However, the water quality guidelines [47] do not indicate limit values for the potassium content. The reason is that potassium is one of the essential nutrients for plant growth, and the excessive content of K$^+$ ions has a much less negative effect on the physical properties of soils than Na$^+$ ions have. According to the literature data, the harmful impact of the potassium content in irrigation water was estimated to be approximately one-third of the sodium concentration [52]. In conclusion, an antagonistic interaction exists between potassium and sodium contents, and the K$^+$/Na$^+$ ratio in saline soils is positively correlated with biomass weight and nutrient accumulation [53].

The water suitability of irrigation water is also assessed by the concentration of trace elements, excessive amounts of which can lead to reduced plant growth. According to water quality guidelines [47], the toxicity limits of trace elements for long and short-term irrigation, and the results of the analysis of PVM water are presented in Table 7.

Table 7. Analysis of PVM water and maximum concentrations of trace elements (mg/L) in irrigation water.

Trace Element	**Result**	**Threshold**	
		For Long Use	**For Short Use**
LiFe	0.025 ± 0.006	2.5	N/A
	0.400 ± 0.080	5.0	20
Mn	0.034 ± 0.009	0.2	10
Al	0.160 ± 0.040	5	20
As	0.009 ± 0.002	0.10	2
Be	<0.001	0.1	0.5
Cd	<0.001	0.01	0.05
Co	<0.001	0.05	5.0
Cr	0.001	0.1	1.0
Cu	<0.003	0.2	5.0
Hg	<0.001	0.001	N/A
Mo	0.013 ± 0.003	0.01	0.05
Ni	<0.002	0.2	2.0
Pb	<0.005	5.0	10.0
Se	0.006 ± 0.001	0.02	0.02
V	<0.002	0.1	1.0
Zn	0.061 ± 0.015	2.0	10.0

N/A—not applicable.

The concentrations of metals varied in the following order: Fe > Al > Zn > B > Li > Mn > Mo > As > Se > Cu > V > Cr. They did not exceed the permissible thresholds for irrigation water for long-term use. The exception was the content of molybdenum (0.013 mg/L), which slightly exceeded the threshold for long-term use. The availability of molybdenum to plants in the soil solution is determined by increasing the soil pH and the contents of available phosphorus and organic carbon [54]. In acidic soils (pH < 5.5), molybdenum is rarely available for plant roots but increases in alkalinity at a pH in the range between 7.5 and 8.5 pH > 7.5 [55]. As shown in Table 6, the PVM water is slightly alkaline (pH = 7.6). Considering that the pH of soil substitutes ranges between 7.9 and 8.5 (Table 4), the mobility of molybdenum can decrease after irrigation [56]. Moreover, it should be taken into account, that in European countries, including Slovenia, there is a possibility of acid rain (acid deposition) from regional air pollution caused by sulfur and nitrogen emissions. Typical pH values of occurring acid rain may range from 3.5 to 5.0 [57]. For this reason, the risk of the intensive bioavailability of Mo in soil substitute solutions will be decreased. Results showed that the concentrations of dissolved metals such as Be, Cd, Co, Hg, Ni, and Pb in PVM water were below the detection limit; therefore, the risk of the dispersion of these elements in the soil can be considered very low. However, long-term irrigation with PVM water, due to its low alkalinity, may affect the availability of heavy metals, which show elevated concentrations in the soil substrates (As and Cd). The reduction in soil substrate pH as a result of mine water irrigation can also increase the bioavailability of cadmium and decrease the bioavailability of arsenic [58] This effect may be intensified in the presence of acid rain.

3.5. Phytotoxicity Tests of the Soil Substitutes

The experimental data indicated various levels of phytotoxicity of the tested soil substitutes. The soils saturated with distilled water presented slightly greater root growth than the samples saturated with PVM water. The average root length for the soil substituted with distilled water ranged from 17.27 to 41.10 mm, whereas the measured root length for the soils treated with PVM water ranged from 13.84 to 40.16 mm. High toxicity was observed for the soil substitute M5, which contained 30% *w/w* of green compost. In contrast, the most effective soil substitutes were M1 and M4, which contained 20 to 30% *w*/*w* of coal lignite, i.e., 38.65 and 41.10 mm for distilled water and 36.20 and 40.16 mm for PVM water, respectively.

The analysis of variance (ANOVA) between the groups of soil substitutes revealed a significant difference for *S. alba* early growth, both for samples irrigated with distilled water ($p < 0.001$; $R^2 = 0.94$, $R^2_{adj} = 0.86$; F = 22.16) and those treated with PVM water ($p < 0.001$; $R^2 = 0.95$, $R^2_{adj} = 0.93$; F = 43.25). The results of the *S. alba* root length and the significance of the difference between the groups are presented in Figure 5.

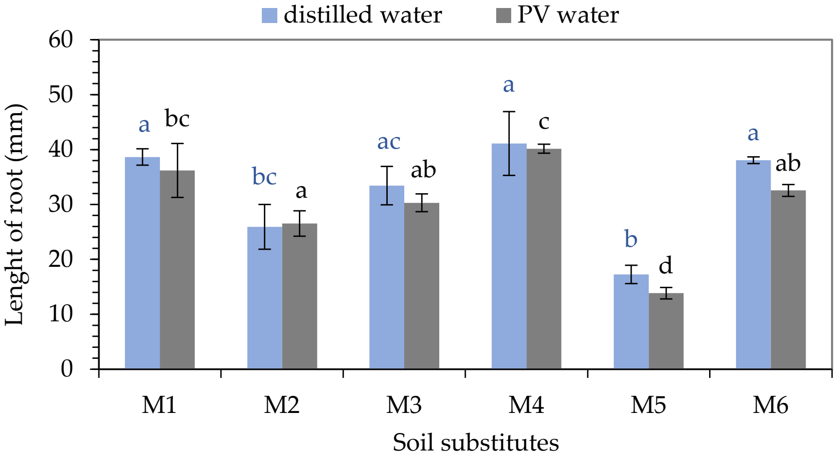
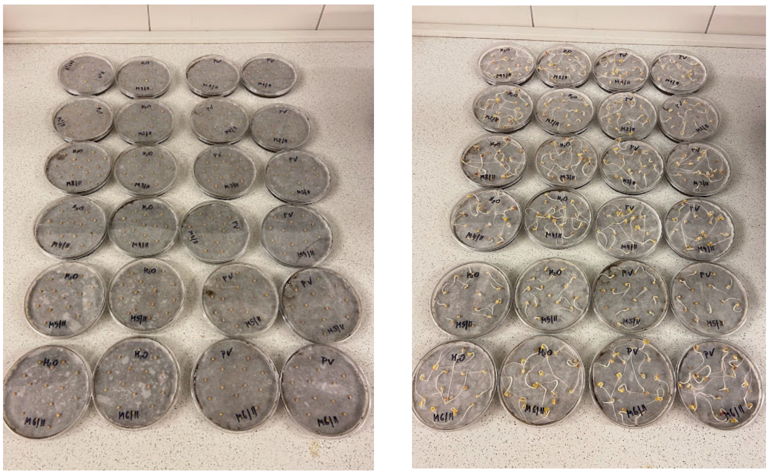


Figure 5. Root growth of *Sinapis alba* on soil substitutes irrigated with distilled water and PV water. The data are expressed as the means ± SD (n = 3). Different letters on the bars indicate significant differences among the groups.

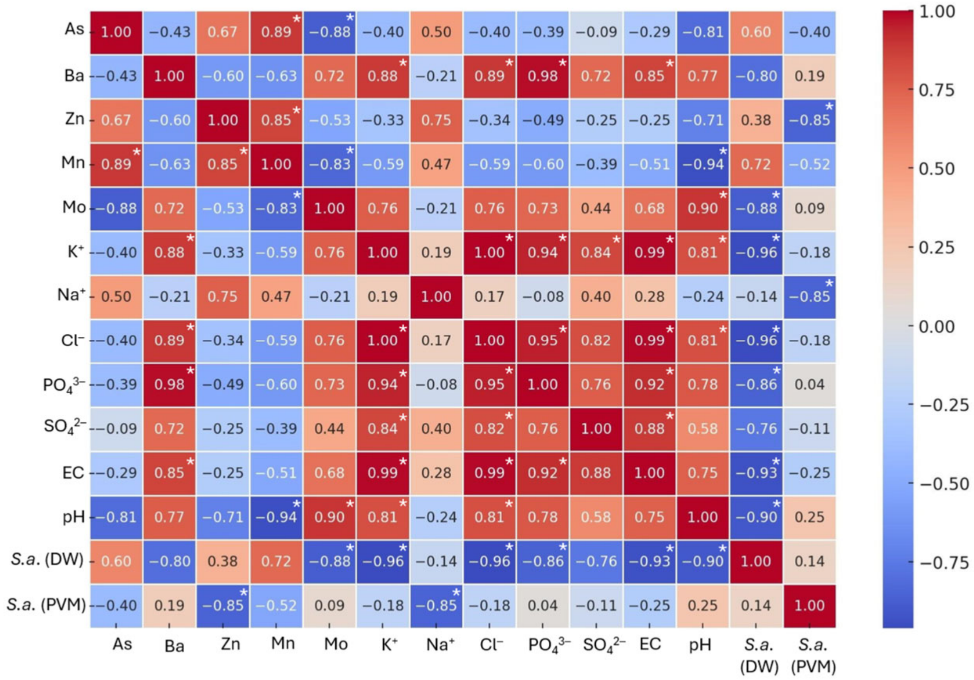
The phytotoxic effects of *Sinapis alba* root growth on Petri dishes are presented in Figure 6.



(**a**) (**b**)

Figure 6. Petri dishes with soil substitutes and *Sinapis alba* seeds: (**a**) before germination; (**b**) after 72 h of germination.

These results indicate that the pH and EC of soil substitutes can have an inhibitory effect on the early growth of *Sinapis alba*, indicating the length of the seedling root. The results of the Pearson analysis of the physicochemical parameters of the soil substitutes saturated with distilled water and the phytotoxicity parameters of white mustard are presented in Figure 7.



	As	Ba	Zn	Mn	Mo	K^+	Na^+	Cl^-	PO_4^{3-}	SO_4^{2-}	EC	pH	*S.a.* (DW)	*S.a.* (PVM)
As	1.00	−0.43	0.67	0.89*	−0.88*	−0.40	0.50	−0.40	−0.39	−0.09	−0.29	−0.81	0.60	−0.40
Ba	−0.43	1.00	−0.60	−0.63	0.72	0.88*	−0.21	0.89*	0.98*	0.72	0.85*	0.77	−0.80	0.19
Zn	0.67	−0.60	1.00	0.85*	−0.53	−0.33	0.75	−0.34	−0.49	−0.25	−0.25	−0.71	0.38	−0.85*
Mn	0.89*	−0.63	0.85*	1.00	−0.83*	−0.59	0.47	−0.59	−0.60	−0.39	−0.51	−0.94*	0.72	−0.52
Mo	−0.88	0.72	−0.53	−0.83*	1.00	0.76	−0.21	0.76	0.73	0.44	0.68	0.90*	−0.88*	0.09
K^+	−0.40	0.88*	−0.33	−0.59	0.76	1.00	0.19	1.00*	0.94*	0.84*	0.99*	0.81*	−0.96*	−0.18
Na^+	0.50	−0.21	0.75	0.47	−0.21	0.19	1.00	0.17	−0.08	0.40	0.28	−0.24	−0.14	−0.85*
Cl^-	−0.40	0.89*	−0.34	−0.59	0.76	1.00*	0.17	1.00	0.95*	0.82	0.99*	0.81*	−0.96*	−0.18
PO_4^{3-}	−0.39	0.98*	−0.49	−0.60	0.73	0.94*	−0.08	0.95*	1.00	0.76	0.92*	0.78	−0.86*	0.04
SO_4^{2-}	−0.09	0.72	−0.25	−0.39	0.44	0.84*	0.40	0.82*	0.76	1.00	0.88*	0.58	−0.76	−0.11
EC	−0.29	0.85*	−0.25	−0.51	0.68	0.99*	0.28	0.99*	0.92*	0.88	1.00	0.75	−0.93*	−0.25
pH	−0.81	0.77	−0.71	−0.94*	0.90*	0.81*	−0.24	0.81*	0.78	0.58	0.75	1.00	−0.90*	0.25
S.a. (DW)	0.60	−0.80	0.38	0.72	−0.88*	−0.96*	−0.14	−0.96*	−0.86*	−0.76	−0.93*	−0.90*	1.00	0.14
S.a. (PVM)	−0.40	0.19	−0.85*	−0.52	0.09	−0.18	−0.85*	−0.18	0.04	−0.11	−0.25	0.25	0.14	1.00

Figure 7. Pearson's correlation between the parameters of the soil substitute leachates and the root length of the *Sinapis alba* seedlings watered. * correlation significant at $p < 0.05$; *S.a.* DW–watered with distilled water; *S.a.* PVM = watered with mine water.

The analysis of the samples irrigated with distilled water revealed a significant negative correlation between the length of the roots of *Sinapis alba* and the pH of the soil substitutes (r = −0.90). A significant negative correlation was detected between the results of the phytotoxicity tests and the salinity parameters, i.e., EC (r = −0.93), K^+ (r = −0.96), Cl^- (r = −0.96), and PO_4^{3-} (r = −0.86). The results of this study confirmed that an increased salt level in the soil limits seed germination and reduces the osmotic activity of plants, thereby preventing them from transporting water and nutrients to their roots [59].

The Pearson analysis indicated that the increased content of Mo (r = −0.88) in the soil–water mixtures led to a decrease in *Sinapis alba* root growth. A negative but non-significant correlation was also observed for plant growth and the contents of Ba (r = −0.80) and SO_4^{2-} (r = −0.76). The availability of Mo (r = 0.90) for plant roots in soil solutions increases with an increasing soil pH (r = 0.90), as verified by the literature data [55,56]. The opposite effect was observed between pH values and other trace elements, i.e., Mn (r = −0.94), Zn (r = −0.74), and As (r = −0.81). The availability of some plant nutrients is strongly affected by soil pH and has been widely confirmed by other studies [37,60].

The analysis of soil substitutes irrigated with PVM water revealed that the most significant and negative correlation with the early growth of *S. alba* was observed for the concentration of Na^+ ions (r = −0.85). A strong negative significant correlation was also detected between *S. alba* root growth (*S.a.* PVM) and the content of Zn (r = −0.85). However, the literature results suggest that white mustard growth on zinc-contaminated soils is likely due to the accumulation of this metal in plant stems, which supports its potential for the phytoremediation of soils with high contents of Zn [61]. In contrast to soil substitutes watered with distilled water, samples with mine water (*S.a.* PVM) presented a weak and insignificant correlation between EC ($r = -0.25$) and K^+ and Cl^- ions ($r = -0.18$). This means that PVM water may reduce the negative impact of the increased salinity of soil substitutes on the early growth of *Sinapis alba*. The reason summarized in Table 6 may be the greater abundance of Ca^{2+} (2.337 mEq/L) and Mg^{2+} (1.875 mEq/L) ions in PVM water compared to Cl^- ions (0.310 mEq/L).

Both calcium and magnesium are essential nutrients for plants, playing critical roles in plant growth and being required in relatively large amounts [62]. Calcium in the soil improves its structure, increasing permeability and aeration. It is crucial for the formation of cell walls, the proper functioning of cell membranes, and cell division processes [63]. However, magnesium is a key component of chlorophyll and is vital for photosynthesis [64]. The high content of these ions in PVM water for irrigation can be beneficial to the proper growth of plants; however, excessive levels of these nutrients can lead to more alkaline soil, which reduces the uptake of other important nutrients. The contents of calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$) in soils can increase their pH to 7.8 [36]. Therefore, monitoring and maintaining appropriate levels of calcium and magnesium in the soil are important to ensure optimal conditions for plant growth and ensure the applicability of the phytoremediation process [65,66].

3.6. Pot Test

The results for the shoot length and biomass growth of *Sinapis alba* in the pot test with soil substitutes treated with distilled water or mine water (PVM) are presented in Table 8.

Table 8. Comparison of the growth of *Sinapis alba* after seven days of growth in the pot test analysis of PVM water and the maximum concentrations of trace elements (mg/L) in irrigation water.

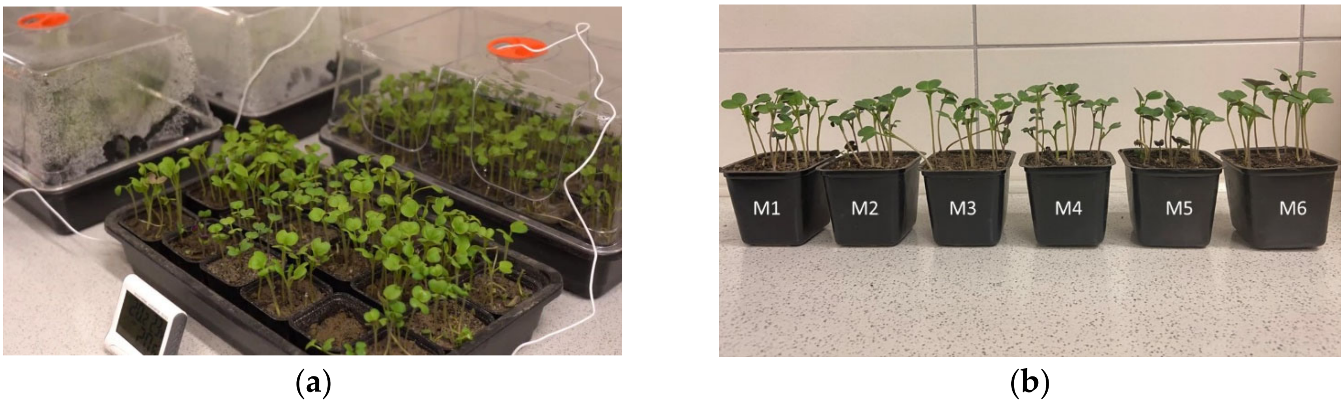
Soil Substitutes	**Germination (%)**		**Average ± SD**			
			Shoot Length (mm)		**Weight of Biomass (g)**	
	Distilled Water	**PVM Water**	**Distilled Water ***	**PVM Water ****	**Distilled Water ***	**PVM Water *****
M1	94	94	34.45 ± 4.69	35.00 ± 1.69 b	1.27 ± 0.14	1.16 ± 0.08 a
M2	78	92	30.14 ± 2.71	32.86 ± 4.31 ab	0.99 ± 0.24	1.11 ± 0.03 a
M3	97	58	31.07 ± 1.60	25.50 ± 4.77 a	1.36 ± 0.16	0.78 ± 0.12 b
M4	97	81	32.43 ± 0.94	31.37 ± 3.74 ab	1.33 ± 0.10	1.16 ± 0.10 a
M5	86	92	30.81 ± 1.19	28.06 ± 1.55 ab	1.29 ± 0.05	1.11 ± 0.04 a
M6	89	83	32.43 ± 4.00	31.14 ± 0.93 ab	1.36 ± 0.21	1.19 ± 0.15 a

SD—standard deviation (n = 3). Values with different letters are significantly different at $p \leq 0.05$ according to Tukey's test; * $p > 0.05$; ** $p < 0.05$; *** $p < 0.01$.

The phytotoxicity test revealed little difference between the pots watered with distilled water and those treated with PVM mine water after seven days of growth. The average length of the shoots in the pots with distilled water ranged from 30.14 mm (M2) to 34.45 mm (M1), whereas that of the samples with PVM water ranged from 25.5 mm (M3) to 35.0 mm (M1). The highest mean shoot length was obtained for the soil substituted with 20% *w*/*w* of coal lignite.

The average weight of the fresh biomass of *Sinapis alba* on the tested soil substitutes was comparable and ranged between 1.27 and 1.39 g (pots with distilled water) and between 1.11 and 1.19 g (pots with PVM water). Only two soil substitutes, watered with PVM water (M2 and M3), presented lower biomass weights, 0.99 and 0.78 g, respectively. A lower germination of *Sinapis alba* in this treatment was also observed (78% for M2 and 58% for M3).

One-way ANOVA for the soil samples irrigated with PVM water revealed significant differences in shoot elongation ($p = 0.0387$) and biomass weight ($p = 0.0038$). Significantly less biomass was obtained on soil substrate M3. The shoot length ($p = 0.5035$) and biomass weight ($p = 0.1130$) did not differ significantly among the soil substrates treated with distilled water. In addition, no plant necrosis or other changes were observed, indicating a negative impact of the soil substitute and irrigation with mine water on plant growth. The images of the growth of the *Sinapis alba* samples at the end of the experiment during the pot test are presented in Figure 8.



(**a**) (**b**)

Figure 8. Pots with soil substitutes and *Sinapis alba* seeds: (**a**) biomass growth after seven days of germination; (**b**) results of *Sinapis alba* growth depending on the type of soil substitute (M1−M6).

Research on mine water quality and its environmental impact has been carried out worldwide. For example, the use of mine water containing a large amount of sulfide compounds for the irrigation of crops was investigated in South Africa [67]. These results showed that gypsiferous waters do not seem to have any deleterious effects on the soil environment.

Another study in southern India reported that the quality of water collected from lignite mine channels was suitable for both domestic use and irrigation. The analysis revealed very minor concentrations of trace elements, and the calculated values of SAR and RSC revealed that the mine water samples fell under the excellent category [68]. However, studies carried out in Portugal indicated that the samples of water from coal mines were unsuitable for land irrigation due to high concentrations of iron, manganese, bicarbonates, magnesium, and potassium [29]. Considering the results from the physicochemical analysis and phytotoxicity tests, it is feasible to conclude that the application of mine water from the PVM for irrigation is possible in degraded areas.

The results of our study suggest that producing soil mixtures from CCP amendment with lignite can be a crucial component of a long-term mine management strategy and a cost-effective method for rehabilitating and maintaining post-mining land.

However, to assess the long-term irrigation of biologically reclaimed areas, further research is needed.

4. Conclusions

The results demonstrate that the most promising soil substitutes for further land rehabilitation in post-mining areas include coal and lignite at concentrations ranging from 20 to 30% w/w. The use of this organic material has proven to be more beneficial than the addition of green compost from the biological manufacturing process. The results of the chemical analysis of soil substitutes show that the concentrations of dangerous substances for human and animal health (As, Cd, Co, Cr, Hg, Ni, Pb, and Zn) are below or within the limit values. This indicates that using these mixtures in post-mining areas with no plans to carry out agricultural activities is environmentally safe.

The experimental data suggest that the pH, salinity, and chemical composition of artificial soil had a positive effect on the germination and early growth of sensitive test plants, such as *Sinapis alba*, whose development is inhibited by contact with toxic soil.

This study demonstrates that using lignite mine water for irrigation under laboratory conditions can increase the organic matter and nutrients in soil substitutes, thereby benefiting plant growth and development. The content of ions responsible for salinity (SO_4^{2-}, Cl^-, Na^+, and K^+) indicates that the water is not excessively contaminated with residual salts. It was also observed that the concentrations of trace elements do not exceed the permissible thresholds for irrigation, whether used for the long or short term. The use of mine water can even reduce the negative effects of increased salinity (caused by Na^+) in developed soil substrates in the early stages of vegetation growth.

The only exception was molybdenum, whose availability in soil may increase with an increasing pH. To avoid toxic effects on plants, the mine water for irrigation should be used only periodically, and the irrigated soil should be continuously monitored.

The current study's data showed that using coal lignite with its combustion products to develop ecologically friendly soil substitutes suitable for plant growth is possible. Nevertheless, further research is needed to assess the long-term development of vegetation in reclaimed subsidence areas, particularly under field conditions. The primary limitation of this approach should include examining the bioaccumulation of heavy metals in plants. Additionally, the impact of long-term irrigation with PVM water on the bioavailability of cadmium in the soil substrates should also be explored. Considering the physicochemical properties of the soil mixture and mine water for irrigation, the risk of a significant toxic effect on plant growth is relatively low. However, when conducting further studies in field conditions, it is essential to consider the physicochemical parameters of local atmospheric precipitation, which may contribute to the formation of acid rain. Another limitation of our research is the lack of information on the amounts of naturally occurring radioactive materials in soil substitutes and mine water, such as ^{238}U, ^{226}Ra, ^{210}Pb, and ^{40}K. However, the long-term research on CCPs conducted by the Šostanj Power Plant in the air shows that the emission of radioactive contamination is below the limit levels, according to Slovenian regulations.

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Abbreviations

The following abbreviations are used in this manuscript:

CCPs	Coal combustion by-products
PVM	Premogovnik Velenje d. o. o. mine
ST	Soil stabilizer
SG	Sludge from the sedimentation tank
CL	Coal lignite
GC	Green compost
M1-M6	Soil substitutes
SAR	Sodium absorption ratio (meq/L)
RSC	Residual sodium carbonate (meq/L)
EC	Electrical conductivity (dS/m)
S. alba (*S.a.*)	White mustard (*Sinapis alba* L.)

References

1. Wu, X.; Xing, C.; Ju, Q.; Su, S.; Zhang, X.; Zhu, T. Research Progress in Mining Ecological Restoration Technology. *J. Ind. Saf.* **2024**, *1*, 100004. [CrossRef]
2. Strzałkowska, E. Fly Ash—A Valuable Material for the Circular Economy. *Miner. Resour. Manag.* **2021**, *37*, 49–62. [CrossRef]
3. Jala, S.; Goyal, D. Fly Ash as a Soil Ameliorant for Improving Crop Production—A Review. *Bioresour. Technol.* **2006**, *97*, 1136–1147. [CrossRef] [PubMed]
4. Siddique, R. Utilization of Coal Combustion By-Products in Sustainable Construction Materials. *Resour. Conserv. Recycl.* **2010**, *54*, 1060–1066. [CrossRef]
5. Białecka, B.; Cempa, M.; Adamczyk, Z.; Świnder, H.; Krawczyk, P. Cost-Effectiveness Analysis and Cost-Benefit Analysis for X-Type Zeolite Production from Fly Ash. *Miner. Resour. Manag.* **2022**, *38*, 83–103. [CrossRef]
6. Chindaprasirt, P.; Rattanasak, U.; Jaturapitakkul, C. Utilization of Fly Ash Blends from Pulverized Coal and Fluidized Bed Combustions in Geopolymeric Materials. *Cem. Concr. Compos.* **2011**, *33*, 55–60. [CrossRef]
7. Ahmaruzzaman, M. Role of Fly Ash in the Removal of Organic Pollutants from Wastewater. *Energy Fuels* **2009**, *23*, 1494–1511. [CrossRef]
8. Mohan, S.; Gandhimathi, R. Removal of Heavy Metal Ions from Municipal Solid Waste Leachate Using Coal Fly Ash as an Adsorbent. *J. Hazard. Mater.* **2009**, *169*, 351–359. [CrossRef]
9. Aigbe, U.O.; Ukhurebor, K.E.; Onyancha, R.B.; Osibote, O.A.; Darmokoesoemo, H.; Kusuma, H.S. Fly Ash-Based Adsorbent for Adsorption of Heavy Metals and Dyes from Aqueous Solution: A Review. *J. Mater. Res. Technol.* **2021**, *14*, 2751–2774. [CrossRef]
10. Cho, H.; Oh, D.; Kim, K. A Study on Removal Characteristics of Heavy Metals from Aqueous Solution by Fly Ash. *J. Hazard. Mater.* **2005**, *127*, 187–195. [CrossRef]
11. Park, J.H.; Edraki, M.; Mulligan, D.; Jang, H.S. The Application of Coal Combustion By-Products in Mine Site Rehabilitation. *J. Clean. Prod.* **2014**, *84*, 761–772. [CrossRef]
12. European Coal Combustion Products Association ECOBA Statistics. Available online: https://www.ecoba.com/ecobaccpprod.html (accessed on 19 February 2025).
13. European Communities Directive 2006/21/EC of the European Parliament and of the Council of 15 March 2006 on the Management of Waste from Extractive Industries and Amending Directive 2004/35/EC. *Off. J. Eur. Communities* **2006**. Available online: https://eur-lex.europa.eu/eli/dir/2006/21/oj/eng (accessed on 28 March 2025).
14. Abbott, D.E.; Essington, M.E.; Mullen, M.D.; Ammons, J.T. Fly Ash and Lime-Stabilized Biosolid Mixtures in Mine Spoil Reclamation: Simulated Weathering. *J. Environ. Qual.* **2001**, *30*, 608–616. [CrossRef] [PubMed]
15. Jaworek, A.; Sobczyk, A.T.; Czech, T.; Marchewicz, A.; Krupa, A. Recovery of Cenospheres from Solid Waste Produced by Coal-Fired Power Plants. *Clean. Waste Syst.* **2023**, *6*, 100109. [CrossRef]
16. Kishor, P.; Ghosh, A.K.; Kumar, D. Use of Fly Ash in Agriculture: A Way to Improve Soil Fertility and Its Productivity. *Asian J. Agric. Res.* **2010**, *4*, 1–14.
17. Matsi, T.; Keramidas, V.Z. Fly Ash Application on Two Acid Soils and Its Effect on Soil Salinity, pH, B, P and on Ryegrass Growth and Composition. *Environ. Pollut.* **1999**, *104*, 107–112. [CrossRef]
18. Shaheen, S.M.; Hooda, P.S.; Tsadilas, C.D. Opportunities and Challenges in the Use of Coal Fly Ash for Soil Improvements—A Review. *J. Environ. Manag.* **2014**, *145*, 249–267. [CrossRef]
19. Ram, L.C.; Masto, R.E. An Appraisal of the Potential Use of Fly Ash for Reclaiming Coal Mine Spoil. *J. Environ. Manag.* **2010**, *91*, 603–617. [CrossRef]

20. Minister of Environment. *Regulation of 5 September 2016 on the Manner of Conducting Assessment of Land Surface Pollution*; Law Gazette of the Republic of Poland: Warsaw, Poland, 2016; pp. 1–86.
21. Pérez-Gimeno, A.; Navarro-Pedreño, J.; Almendro-Candel, M.B.; Gómez, I.; Jordán, M.M. Environmental Consequences of the Use of Sewage Sludge Compost and Limestone Outcrop Residue for Soil Restoration: Salinity and Trace Elements Pollution. *J. Soils Sediments* **2016**, *16*, 1012–1021. [CrossRef]
22. Larney, F.J.; Angers, D.A. The Role of Organic Amendments in Soil Reclamation: A Review. *Can. J. Soil Sci.* **2012**, *92*, 19–38. [CrossRef]
23. Król-Domańska, J.; Smolińska, B. Advantages of Lignite Addition in Purification Process of Soil Polluted by Heavy Metals. *Biotechnol. Food Sci.* **2012**, *76*, 51–58.
24. Symanowicz, B.; Toczko, R. Brown Coal Waste in Agriculture and Environmental Protection: A Review. *Sustainability* **2023**, *15*, 13371. [CrossRef]
25. Di, J.; Ruan, Z.; Zhang, S.; Dong, Y.; Fu, S.; Li, H.; Jiang, G. Adsorption Behaviors and Mechanisms of Cu^{2+}, Zn^{2+} and Pb^{2+} by Magnetically Modified Lignite. *Sci. Rep.* **2022**, *12*, 1394. [CrossRef] [PubMed]
26. Špeh, N.; Plut, D. Sustainable Landscape Management in Slovenia: Environmental Improvements for the Velenje Coal Mining Community 1991–2000. *GeoJournal* **2001**, *55*, 569–578. [CrossRef]
27. *EN 12457-2*; Characterisation of Waste-Leaching-Compliance Test for Leaching of Granular Waste Materials and Sludges—Part 2. European Committe for Standarization: Brussels, Belgium, 2002.
28. Richards, L.A. Diagnosis and Improvement of Saline and Alkali Soils. In *Agricultural Handbook 60*; United States Department of Agriculture: Washington, DC, USA, 1954.
29. Mansilha, C.; Melo, A.; Flores, D.; Ribeiro, J.; Rocha, J.R.; Martins, V.; Santos, P.; Marques, J.E. Irrigation with Coal Mining Effluents: Sustainability and Water. *Water* **2021**, *13*, 2157. [CrossRef]
30. *EN ISO 18763*; Soil Quality. Determination of the Toxic Effects of Pollutants on Germination and Early Growth of Higher Plants. International Organization for Standardization: Geneva, Switzerland, 2020.
31. Ociepa-Kubicka, A.; Ociepa, E. Toxic Effect of Heavy Metals on Plants, Animals and Humans. *Eng. Environ. Prot.* **2012**, *15*, 169–180.
32. *Official Gazette of the Republic of Slovenia No. 68/96 Decree on the Limit, Warning and Critical Concentration Values of Dangerous Substance in Soil*; The Government of the Republic of Slovenia: Ljubljana, Slovenia, 1996.
33. Gregorauskiene, V. Overview of the Quality Criteria for Soil in the East European Countries. *Pol. Geol. Inst. Spec. Pap.* **2008**, *24*, 45–54.
34. Miller, R.; Donahue, R. *Soils in Our Environment: An Introduction to Soils and Plant Growth*, 7th Revised ed.; Cambridge University Press: Cambridge, UK; Prentice-Hall: Saddle River, NJ, USA, 1995.
35. Acosta-Motos, J.R.; Ortuño, M.F.; Bernal-Vicente, A.; Diaz-Vivancos, P.; Sanchez-Blanco, M.J.; Hernandez, J.A. Plant Responses to Salt Stress: Adaptive Mechanisms. *Agronomy* **2017**, *7*, 18. [CrossRef]
36. Bruce, R.; Rayment, G. *Analytical Methods and Interpretations Used by the Agricultural Chemistry Branch for Soil and Land Use Surveys*; Bulletin QB82004; Queensland Department of Primary Industries: Brisbane, Australia, 1982.
37. Reitsma, K.D.; Clay, D.E.; Carlson, G. Soil Fertility. In *Alternative Practices for Agronomic Nutrient and Pest Management in South Dakota*, I ed; Darrell Deneke, South Dakota State University, College of Agriculture and Biological Sciences: Brookings, SD, USA, 2011; pp. 1–57, Chapter 2.
38. Yu, H.; Li, C.; Yan, J.; Ma, Y.; Zhou, X.; Yu, W.; Kan, H.; Meng, Q.; Xie, R.; Dong, P. A Review on Adsorption Characteristics and Influencing Mechanism of Heavy Metals in Farmland Soil. *RSC Adv.* **2023**, *13*, 3505–3519. [CrossRef]
39. Golia, E.E.; Kantzou, O.D.; Chartodiplomenou, M.A.; Papadimou, S.G.; Tsiropoulos, N.G. Study of Potentially Toxic Metal Adsorption in a Polluted Acid and Alkaline Soil: Influence of Soil Properties and Levels of Metal Concentration. *Soil Syst.* **2023**, *7*, 16. [CrossRef]
40. Gmach, M.R.; Cherubin, M.R.; Kaiser, K.; Cerri, C.E.P. Processes That Influence Dissolved Organic Matter in the Soil: A Review. *Sci. Agric.* **2020**, *77*, e20180164. [CrossRef]
41. Lee, M.S.; Wycislo, A.; Guo, J.; Lee, D.K.; Voigt, T. Nitrogen Fertilization Effects on Biomass Production and Yield Components of *Miscanthus* × *Giganteus*. *Front. Plant Sci.* **2017**, *8*, 544. [CrossRef] [PubMed]
42. Grzebisz, W.; Gransee, A.; Szczepaniak, W.; Diatta, J. The Effects of Potassium Fertilization on Water-Use Efficiency in Crop Plants. *J. Plant Nutr. Soil Sci.* **2013**, *176*, 355–374. [CrossRef]
43. Shen, Q.; Wen, Z.; Dong, Y.; Li, H.; Miao, Y.; Shen, J. The Responses of Root Morphology and Phosphorus-Mobilizing Exudations in Wheat to Increasing Shoot Phosphorus Concentration. *AoB Plants* **2018**, *10*, ply054. [CrossRef] [PubMed]
44. Bhavan, M.; Shah, B.; Marg, Z. Guidlines for the Quality of Irrigation Water. Bureau Indian Standards IS:11624-1986 New Delhi, 1986, (Reaffirmed 2001). pp. 1–12. Available online: https://law.resource.org/pub/in/bis/S06/is.11624.1986.pdf (accessed on 19 February 2025).

45. Hopkins, B.G.; Horneck, D.A.; Stevens, R.G.; Ellsworth, J.W.; Sullivan, D.M. *Managing Irrigation Water Quality for Crop Production in the Pacific Northwest*; Oregon State University Extension Service: Washington, DC, USA, 2007. Available online: https://extension.oregonstate.edu/sites/extd8/files/documents/pnw597.pdf (accessed on 19 February 2025).
46. Kumar, M.; Kar, A.; Singh, R. Interventions of High Residual Sodium Carbonate Water-Degraded Soils Amelioration Technology in Indian Thar Desert and Farmers' Response. *Natl. Acad. Sci. Lett.* **2016**, *39*, 245–249. [CrossRef]
47. Ayers, R.; Westcot, D. *Water Quality For Agriculture*; Food and Agriculture Organization of the United Nations: Rome, Italy, 1985.
48. Beltrán, J.M. Irrigation with Saline Water: Benefits and Environmental Impact. *Agric. Water Manag.* **1999**, *40*, 183–194. [CrossRef]
49. Conde, S.; Azuara, P. Osmotic and Specific Effects of Magnesium Sulphate on the Mineral Content of Zea Mays. *Plant Soil* **1980**, *55*, 121–131. [CrossRef]
50. Sattari, M.T.; Farkhondeh, A.; Patrick Abraham, J. Estimation of Sodium Adsorption Ratio Indicator Using Data Mining Methods: A Case Study in Urmia Lake Basin, Iran. *Environ. Sci. Pollut. Res.* **2018**, *25*, 4776–4786. [CrossRef]
51. Hannam, K.D.; Kehila, D.; Millard, P.; Midwood, A.J.; Neilsen, D.; Neilsen, G.H.; Forge, T.A.; Nichol, C.; Jones, M.D. Bicarbonates in Irrigation Water Contribute to Carbonate Formation and CO_2 Production in Orchard Soils under Drip Irrigation. *Geoderma* **2016**, *266*, 120–126. [CrossRef]
52. Smith, C.J.; Oster, J.D.; Sposito, G. Potassium and Magnesium in Irrigation Water Quality Assessment. *Agric. Water Manag.* **2015**, *157*, 59–64. [CrossRef]
53. Patel, S.; Mohanty, P.; Baral, J.; Mohanta, A.; Jena, D. Effects of Potassium and Saline Water Irrigation on Growth of Maize Plant. *J. Pharmacogn. Phytochem.* **2022**, *11*, 195–201. [CrossRef]
54. Rutkowska, B.; Szulc, W.; Spychaj-Fabisiak, E.; Pior, N. Prediction of Molybdenum Availability to Plants in Differentiated Soil Conditions. *Plant Soil Environ.* **2017**, *63*, 491–497. [CrossRef]
55. Kabata-Pendias, A.; Pendias, H. *Biogeochemistry of Trace Elements*; Polish Scientific Publisher PWN: Warsaw, Poland, 1999.
56. Velazquez-Gonzalez, R.S.; Garcia-Garcia, A.L.; Ventura-Zapata, E.; Barceinas-Sanchez, J.D.O.; Sosa-Savedra, J.C. A Review on Hydroponics and the Technologies Associated for Medium-and Small-Scale Operations. *Agriculture* **2022**, *12*, 646. [CrossRef]
57. Menz, F.C.; Seip, H.M. Acid Rain in Europe and the United States: An Update. *Environ. Sci. Policy* **2004**, *7*, 253–265. [CrossRef]
58. Shen, B.; Wang, X.; Zhang, Y.; Zhang, M.; Wang, K.; Xie, P.; Ji, H. The Optimum PH and Eh for Simultaneously Minimizing Bioavailable Cadmium and Arsenic Contents in Soils under the Organic Fertilizer Application. *Sci. Total Environ.* **2020**, *711*, 135229. [CrossRef]
59. Bojović, B.; Delić, G.; Topuzović, M.; Stanković, M. Effects of NaCl on Seed Germination in Some Species from Families Brassicaceae and Solanaceae. *Kragujev. J. Sci.* **2010**, *32*, 83–87.
60. Truog, E. Soil Reaction Influence on Availability of Plant Nutrients. *Soil Sci. Soc. Am. J.* **1947**, *11*, 305–308. [CrossRef]
61. Repkina, N.; Nilova, I.; Kaznina, N. Effect of Zinc Excess in Substrate on Physiological Responses of *Sinapis alba* L. *Plants* **2023**, *12*, 211. [CrossRef]
62. Bradley, L.; Hosier, S. Guide to Symptoms of Plant Nutrient Deficiencies. *Univ. Arizona Coop. Ext.* **1999**, *AZ1106*, 1–3.
63. Demidchik, V.; Shabala, S.; Isayenkov, S.; Cuin, T.A.; Pottosin, I. Calcium Transport across Plant Membranes: Mechanisms and Functions. *New Phytol.* **2018**, *220*, 49–69. [CrossRef]
64. Tripathi, D.; Singh, V.; Chauhan, D.; Prasad, S.; Dubey, N. Improvement of Crops in the Era of Climatic Changes. In *Role of Macronutrients in Plant Growth and Acclimation: Recent Advances and Future Prospective*; Springer: New York, NY, USA, 2014; Volume 2. [CrossRef]
65. Su, R.; Ou, Q.; Wang, H.; Dai, X.; Chen, Y.; Luo, Y.; Yao, H.; Ouyang, D.; Li, Z.; Wang, Z. Organic–Inorganic Composite Modifiers Enhance Restoration Potential of *Nerium oleander* L. to Lead–Zinc Tailing: Application of Phytoremediation. *Environ. Sci. Pollut. Res.* **2023**, *30*, 56569–56579. [CrossRef]
66. Su, R.; Ou, Q.; Wang, H.; Luo, Y.; Dai, X.; Wang, Y.; Chen, Y.; Shi, L. Comparison of Phytoremediation Potential of Nerium Indicum with Inorganic Modifier Calcium Carbonate and Organic Modifier Mushroom Residue to Lead–Zinc Tailings. *Int. J. Environ. Res. Public Health* **2022**, *19*, 10353. [CrossRef] [PubMed]
67. Annandale, J.G.; Beletse, Y.G.; Stirzaker, R.J.; Bristow, K.L.; Aken, M.E. Is Irrigation With Coal-Mine Water Sustainable? In Proceedings of the International Mine Water Association, Pretoria, South Africa, 19–23 October 2009; pp. 337–342.
68. Anjali, R.; Krishnakumar, S.; Thivya, C.; Kasilingam, K.; Suresh Gandhi, M.; Selvakumar, S.; Satheesh Herbert Singh, D.; Magesh, N.S. Assessment of Mine Water Quality for Domestic and Irrigation Purposes, Neyveli Coal Mine Region, Southern India. *Total Environ. Res. Themes* **2023**, *6*, 100047. [CrossRef]