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Proceeding Paper

Ecotoxicity Assessment of Substrates from a Thermally Active Coal Tailing Dump Using Tests for *Daphnia magna* †

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Abstract: The aim of the study was to compare the ecotoxicity of waste materials formed from a mixture of construction materials with tailings obtained from the thermally active Ema coal tailing dump located in the city of Ostrava, Czech Republic. The ecotoxicity assessment was performed using acute lethality tests on the crustacean *Daphnia magna*. The test results are relevant for further possibilities of using technogenic substrates from tailings after mining activities and are an integral part of a comprehensive assessment of their biological effects on the environment.

Keywords: ecotoxicology; toxicity; *Daphnia magna*; coal mining; heaps; reclamation

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1. Introduction

With the growing awareness of the negative impact of human activities on the planet, it is increasingly important to monitor and assess environmental stresses. One of the key tools in this area are ecotoxicity tests, which allow the identification of potentially hazardous substances and assess their impacts on ecosystems. These tests verify the reactions of living organisms to different concentrations and types of chemicals or mixtures of chemicals, thus providing relevant information on the risk effects of these substances and their direct effects on living organisms in the environment.

One of the areas that require close monitoring for ecotoxicity is anthropogenic environments following mining and industrial activities. The environment contaminated by mining and industry induces changes not only in the stability of soil ecosystems [1–4], but also leads to erosion and other changes in the structure and composition of soil substrates down to the level of their microstructures [5–10]. All of these changes then reduce the use of these substrates in the processes of revegetation and reclamation in these areas.

The tailings occurring in the Ostrava-Karviná district (Czech Republic) were never covered in any way and were therefore exposed to chemical weathering. Since the tailings also contained large amounts of fine-grained coal mass that was difficult to separate by conventional treatment methods, thermal processes caused by oxidation or combustion of the coal mass were common in the tailings [11]. The process of spontaneous combustion of the deposited tailings is mainly influenced by their chemical properties, especially the amount of water, ash, and combustible elements (e.g., pyritic sulphur, hydrogen). The ongoing endogenous combustion is closely related to the emission of gases, the possible resuspension of dust particles, and the presence of hazardous elements that may be present in the tailings material [12–15]. Another issue closely related to thermally active tailings is their acidification. Oxidation of pyrite produces sulfuric acid, which causes a decrease in pH [16]. Due to the low content of basic rocks in Ostrava-Karviná district tailings, acid neutralization occurs very slowly. Thus, considering the low pH value, the release of hazardous metals may occur. Thermally active tailings can thus represent a significant environmental burden, especially if the stored material burns through [17–19].

Today, coal tailings, which are mainly made up of rocks, are already being used, for example, in the construction industry and in the reclamation of landscapes after the end of deep mining. Within the construction industry, tailings are used as an available and cheap aggregate for earth embankments in transport structures [20]. However, for such use, it is necessary that the tailings have appropriate properties and do not endanger the construction environment with undesirable substances. Coal gangue has a low pH value, which can affect the mobility of toxic metals. However, its pH value can be adjusted with alkaline construction material, which is currently being used as a backfill material.

The aim of this study was to evaluate the ecotoxicity of tailings from the thermally active Ema tailings impoundment that were mixed with construction wastes for further use. The aquatic crustacean genus *Daphnia magna*, a species widely used in ecotoxicological studies, was selected as the test organism.

2. Materials and Methods

2.1. Description of the Origin of the Samples

Tailings samples were taken in September 2022 at the thermally active Ema coal tailing dump, Czech Republic. Sampling was carried out in places without vegetation from a depth of about 10 cm. Sampling points were chosen so that they were distributed evenly over the unvegetated area of the tailing dump. The samples of construction and demolition waste (CDW) came from renovation work in a prefab house. The waste mainly consisted of hollow burnt bricks, lime-cement mortar, plaster, including painting, and concrete. The construction waste was freed from the remains of foreign materials (plastics, paper, etc.). The tested samples were created by mixing tailings and CDW in a ratio of 9:1, 8:2, and 7:3. The proportions were chosen to preserve a greater amount of tailings. Another condition for the selection of parameters was maintaining the pH/H2O of the mixture around 7.0. Samples of the CDW mixture and tailings were mechanically treated by crushing on a Retsch jaw crusher type BB200 WC (Haan, Germany). After homogenization, they were fine-grained through Retsch sieves with a mesh size of 2 mm and subsequently dried to a constant weight in a vacuum dryer VO29 MEMMERT (Schwabach, Germany). The dried samples were kept for further analysis in a desiccator.

2.2. Methodologies Used for Determining Physico-Chemical Parameters and Bioavailability of Selected Metals

The active pH value (pH/H_2O) and the exchangeable pH value (pH/$CaCl_2$) were determined according to the standard ČSN EN ISO 10390 (836221) [21]. According to the standard ČSN ISO 11265 (836210) [22], the determination of soluble salts (conductivity, κ) in the samples was carried out. The obtained values were assessed according to APAL (2023).

To determine the bioavailability of selected risk metals (Co, Mn, Ni, Zn, and Fe), the BCR (Community Bureau of Reference) sequential extraction analysis according to Sutherland and Tack (2007) was chosen.

2.3. Analytical Methods

The F-AAS (flame atomic absorption spectrometry) method was applied to determine the concentration of selected hazardous metals in individual fractions using an AAS contrAA® 700 atomic absorption spectrometer from Analytik Jena GmbH company (Jena, Germany).

The element composition of the samples was determined using the X-ray powder diffraction (XRD) technique. XRD patterns were obtained using a Rigaku SmartLab diffractometer (Rigaku, Tokyo, Japan) with a D/teX Ultra 250 detector. The measured XRD patterns were evaluated using PDXL 2 software (version 2.4.2.0) and compared with the PDF-2 database, 2015 release (ICDD, Newton Square, PA, USA).

2.4. 48 h Acute Toxicity Test on Daphnia magna

Acute toxicity tests were performed using the Daphnotoxkit F test kit (MicroBiotests Inc., Ghent, Belgium). This test included pearl mussel epiphytes that are allowed to hatch 72 h prior to the start of tesus. This method allows simple age determinations of the individuals used in the test and ensures that only females are present. After prior activation, pearl-eyes were exposed to the test samples. For this test, aqueous leachates of a mixture of tailings from the Ema tailings impoundment and CDW were used at a ratio of 9:1, 8:2, and 7:3. A concentration series was then formed for each sample with 100%, 50%, 10%, and 1% aqueous leachate concentrations. Standardized water, prepared according to the kit manufacturer's instructions, was used to dilute the samples. Each sample test was performed in triplicate. Five individuals and 10 mL of the test solution were added to each test well. After 24 h, the immobility and mortality of the observed guinea fowl were calculated.

3. Results and Discussion

Active pH indicates the concentration of hydrogen ions. The addition of CDW increased both the active and exchange pH values. The exchange pH is determined by the concentration of hydrogen and aluminum cations, which can be exchanged for basic ions in the presence of a neutral salt solution. Mixing CDW with tailings caused an increase in conductivity, which indicates the salinity of the soil. However, even the mixture with the highest CDW ratio did not exceed the value of 2 dS m^{-1} and is therefore still evaluated as a low salinity sample. However, regarding the composition of CDW, it is mainly alkali metals such as calcium, etc. All the values found, including their evaluation, are shown in Table 1.

Table 1. Evaluation of the results of the tested mixtures of CDW (construction and demolition waste) and tailings.

	pH/H_2O	Interpretation	pH/$CaCl_2$	Interpretation	k dS m^{-1}	Interpretation
Tailing	5.54	Moderately acidic	5.78	Moderately acidic to slightly alkaline	0.125	Low salinity
CDW	11.33	Strongly alkaline	11.15	Moderately to strongly alkaline	0.772	Low salinity
Tailing/CDW, 9:1	6.01	Moderately acidic	7.17	Moderately acidic to slightly alkaline	0.274	Low salinity
Tailing/CDW, 8:2	6.44	Moderately acidic	7.37	Moderately acidic to slightly alkaline	0.308	Low salinity
Tailing/CDW, 7:3	6.86	Slightly acidic	7.91	Moderately to strongly alkaline	0.389	Low salinity

For an objective evaluation, an elemental analysis of tailings and CDW was also performed (see Table 2). Based on the results, it can be concluded that elements such as Si (27%), Fe (25%), and Al (11%) prevailed in the tailings. Ref. [19] states in his work that, considering the percentage of silicon, it can be assumed that acidification will not occur because of its loss but as a result of the lack of basic cations during the decomposition of aluminosilicates. The content of total sulphur contained in the anhydrous sample of OKR coal is generally low, which was also confirmed by elemental analysis. The total sulphur content was around 3.38%. In general, the content of heavy metals in OKR carbonaceous rocks is low and does not exceed the background of other industrial emissions from an ecological point of view.

Table 2. Chemical composition of construction and demolition waste and tailing [19].

%	CDW	Tailing	%	CDW	Tailing	%	CDW	Tailing
Ag	0.002	<0.0002	Ge	0.0002	0.002	S	0.53	3.38
Al	8.5	12.11	Hf	0.006	0.002	Sb	<0.0003	0.001
As	0.002	0.06	Hg	<0.0001	0.0005	Se	<0.00005	0.002
Ba	0.17	0.58	I	0.0002	<0.00030	Si	45	28.75
Bi	<0.0001	0.002	K	3.4	4.21	Sn	<0.0003	0.01
Br	0.0004	0.003	La	0.022	0.02	Sr	0.05	0.07
Ca	27	1.02	Mg	0.82	0.31	Ta	0.02	0.01
Cd	<0.0002	0.001	Mn	0.19	0.20	Th	0.003	0.01
Ce	0.02	0.03	Mo	0.001	0.002	Ti	1.09	1.09
Cl	<0.0002	0.02	Nb	0.006	0.01	Tl	0.0002	0.0006
Co	0.003	0.01	Nd	0.02	0.03	U	0.0002	0.003
Cr	0.10	0.04	Ni	0.02	0.02	V	0.03	0.05
Cs	0.01	0.01	P	0.14	0.38	W	0.0002	0,002
Cu	0.01	0.02	Pb	0.008	0.05	Y	0.008	0.01
Fe	8.0	31	Pr	0.0004	<0.00020	Zn	0.27	0.07
Ga	0.005	0.01	Rb	0.02	0.05	Zr	0.29	0.06

BCR sequential extraction analysis mimics the conditions to which the material may be exposed in natural conditions to determine the bioavailability of metals. For the analysis, several leaching agents are used, the strength of which gradually increases. According to the results of the BCR analysis (see Table 3), it cannot be unequivocally stated that the addition of CDW would reduce the metal content in the bioavailable fractions.

Table 3. Results of BCR (Community Bureau of Reference) analysis.

	Co mg kg^{-1}	**Mn** mg kg^{-1}	**Ni** mg kg^{-1}	**Zn** mg kg^{-1}	**Fe** mg kg^{-1}
			EXCHANGEBLE FRACTION		
Tailing/CDW, 9:1	17	300	8	75	30
Tailing/CDW, 8:2	2	100	9	90	30
Tailing/CDW, 7:3	14	60	9	140	25
			REDUCIBLE FRACTION		
Tailing/CDW, 9:1	2.08	4 691	1.04	89	906
Tailing/CDW, 8:2	2.08	4 820	3.65	99	1 078
Tailing/CDW, 7:3	0.52	4 871	3.13	89	1 042
			OXIDIZABLE FRACTION		
Tailing/CDW, 9:1	25	269	6.5	87	179
Tailing/CDW, 8:2	30	161	13.6	92	207
Tailing/CDW, 7:3	54	215	8.7	92	136

At last, ecotoxicity tests for *Daphnia magna* were carried out for the 9:1, 8:2, and 7:3 samples of the mixture of tailings from the Ema tailings and CDW. For the purpose of this test and for better orientation, the samples were renamed 1a (9:1 ratio), 2a (8:2 ratio), and 3a (7:3 ratio). The test results were read after 24 and 48 h. The mortality results after 24 h are graphically evaluated in Figure 1a, and the number of dead individuals after 48 h in Figure 1b. After 24 h of incubation, the highest mortality rates were found for the sample containing 70% tailings and 30% CDW. The highest lethality was observed for the 100% sample concentration, while the second highest lethality was observed for the sample treated at 1% concentration. There was no significant difference between samples that contained 10% CDW (sample 1a) and 20% CDW (sample 2a). After 48 h, we observed increased mortality in each sample. Again, the highest mortality was in the sample with the highest CDW content (sample 3a). The second highest mortality after 48 h was observed in sample 1a, which contained only 10% CDW. Considering the concentration of the sample, the highest mortality was observed at 100% concentration. Here again, there is no direct proportionality between concentration and mortality; the second highest mortality percentage was found at 1% concentration.

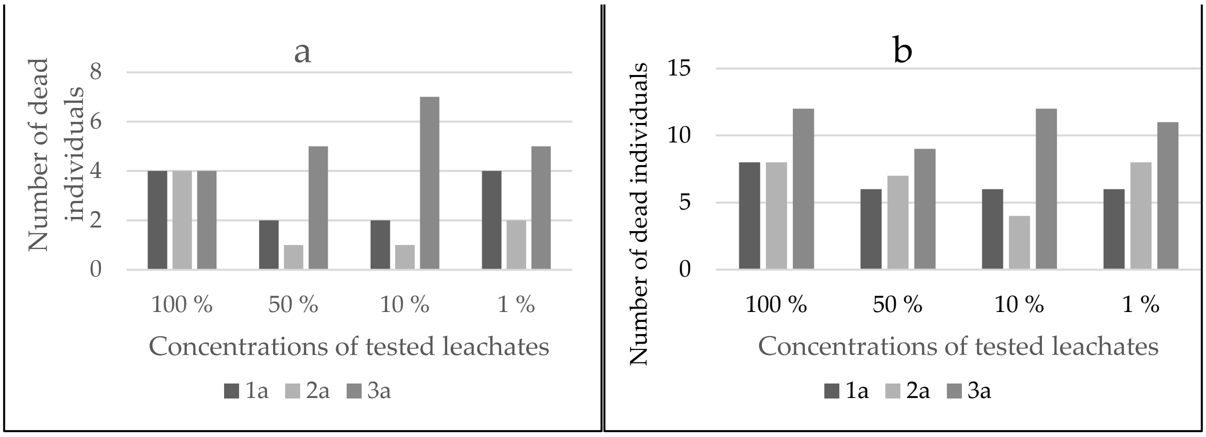

Figure 1. Graphical evaluation of mortality after 24 h (**a**: on the right) and 48 h (**b**: on the left).

The results show that the addition of CDW to the Ema tailings did not reduce toxicity to *Daphnia magna*. The increased mortality at 1% concentration was surprising. Samples could be retested at lower concentrations to determine the mechanism of action (not performed in this study due to small sample volumes).

4. Conclusions

The mixing of construction and demolition waste with the tailings of the selected tailings has been shown to influence the pH from acidic values towards neutral to slightly alkaline values, which could have a positive effect on the future development of the entire site. The increase in pH is demonstrably dependent on the amount of CDW added, so it can be said that increasing the amount will result in improved parameters.

The results of the sequential extraction analysis of BCR did not show a significant correlation between the increase in the amount of CDW added and the decrease in the content of hazardous metals in the bioavailable fractions.

Test results obtained in the acute toxicity test on *Daphnia magna* show increased negative effects in samples with higher CDW content. For a better evaluation, it is necessary to perform a larger number of tests with a larger volume of tested samples.

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