

# Environmental Toxicity Assessment of the Spilled Ajka Red Mud in Soil Microcosms for Its Potential Utilisation as Soil Ameliorant

Éva Ujaczki<sup>1</sup>\*, Orsolya Klebercz<sup>1</sup>, Viktória Feigl<sup>1</sup>, Mónika Molnár<sup>1</sup>,  
Ádám Magyar<sup>1</sup>, Nikolett Uzinger<sup>2</sup>, Katalin Gruiz<sup>1</sup>

Received 26 November 2014; accepted after revision 23 February 2015

## Abstract

After the red mud spill in Hungary one of the risk reduction measures was to remove the deposits from the soil surface. The residual thin red mud layer was ploughed into the soil. The aim of the present 8-month-long lab-scale microcosm experiment was to estimate the red mud amount with no adverse effects on the soil as natural habitat and to assess the mid-term environmental risk of red mud mixed into the soil. The red mud ratio mixed into the soil ranged between 0–40 %. The experiments were monitored by physico-chemical, biological and ecotoxicological methods. Mixing of 5 % red mud into the soil significantly increased the total As, Cr, Ni, Pb and Na content of the soil, but it did not exceed the Hungarian soil quality criteria. The microcosms containing 5 % red mud did not show any adverse effects on the testorganisms. Overall, 5 % red mud could be mixed into the soil without any mid-term adverse effects.

## Keywords

red mud, Ajka red mud spill, soil amendment, ecotoxicology, soil microcosm

## 1 Introduction

At present the global demand for aluminium metal is increasing because of its use for packaging and construction, from the fabrication of fuselages and car parts to disposable containers and various consumer durables [1]. For that very reason the amount of red mud, the industrial by-product of bauxite processing to aluminium via the Bayer process, is increasing, and its appropriate management is an environmental concern, as an estimated 2.7 billion tonnes of red mud is produced worldwide every year and this amount will be increasing probably by approximately 120 million tonnes per annum [1]. Red mud is the slurry by-product generated from the treatment of bauxite with concentrated NaOH under elevated temperature and pressure by Bayer process [2]. Therefore it is highly alkaline with a pH usually ranging from 10 to 13 [3,4].

Previously there were only two main red mud disposal methods: marine discharge and lagooning on land. Marine disposal caused adverse effects on the aquatic environment, which inspired new approaches to residue management [5]. The land-based disposal method traditionally adopted was one of wet disposal where red mud (15–30 % solids) is deposited on the land surface with additional construction of dams. The management of leachate water is necessary due to the high risk of seepage of alkaline solution to groundwater and it takes many years for the deposit to consolidate [6].

The risks associated with alkalinity are reduced in case of dry stacking methods, where the red slurry is stored in solids phase (48–50 % solid content) in storage areas [7]. A special way of dry disposal is the dry cake method, where a dry cake with solid's content of 65 % is produced prior to disposal by filtration [8].

About one million cubic meters of highly alkaline (pH=13) red mud flooded three Hungarian villages on October 4, 2010, after the wall of the dam of a red mud reservoir in Ajka, degraded by the corrosive alkaline red mud, had failed [9,10]. The red mud reservoir of the Ajka alumina plant stored 3–4 million m<sup>3</sup> of red mud wherefrom 800.000 m<sup>3</sup> of slurry was released into the environment [11].

The spilled alkaline slurry affected several environmental elements, including the surface layers of the soil, the surface

<sup>1</sup> Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics  
H-1111 Budapest, Szent Gellért square 4, Hungary

<sup>2</sup> Institute for Soil Sciences and Agricultural Chemistry, Centre for Agricultural Research, Hungarian Academy of Sciences,  
H-1022 Budapest, Herman Ottó street 15, Hungary

\* Corresponding author, e-mail: [ujaczki.eva@mail.bme.hu](mailto:ujaczki.eva@mail.bme.hu)

waters and their sediments [9]. As an immediate emergency measure the red mud layer was removed from the soil surface in residential areas and the surface water was neutralised by acid dosing (acetic, hydrochloric, nitric) [12]. Following the catastrophe the immediate assessment of the short-term environmental risk of red mud was required, given its high alkalinity and elevated Na content. According to previous studies on the risks associated with red mud the toxic metals and radioactive isotopes were also considered. Burke et al. [13] found that the high alkalinity has mobilized some of the toxic metals, typically As, Cr, Ni, Se and V. Assessing the long term risk of the high Na-concentration Gruiz et al. [9] found that it increased the risk of sodification. According to Grundy et al. [14] the red mud exposure does not appear to have posed any immediate genotoxic hazard on inhabitants after the Ajka red mud spill.

Apart from its highly alkaline pH (pH=11 on the average) and high sodium content owing to the digestion step of the Bayer process, red mud is a recyclable and reusable material with beneficial properties [15]. Utilization of red mud has environmental and economic importance because of its composition and annually generated amount [16,17]. Some attempts have been made to apply red mud for soil improvement. Red mud has been applied in agriculture for the improvement of acid sulfate soils [18,19]. It is proven to be effective in raising the pH of soils with high organic matter content [20] and low pH [21]. Red mud can also be applied for chemical stabilization of metal contaminated soils [22,23,24,25,26,27]. However, no combinations of afteruses are currently sufficient to avoid terrestrial disposal of the majority of red mud arisings globally.

Further to the 2010 red mud spill the topsoil in the affected residential and grassland areas was overlain by 3–45 cm thick red mud deposits [28], wherefrom the alkali solution infiltrated into the underlying soil [9]. The red mud deposit was recovered and the (>5 cm) residual red mud layers were ploughed into the soil, since the available mechanical tools could not remove the very thin red mud layers from the soil surface [9, 29]. Soil microcosm experiments have been conducted to determine the maximum proportion of red mud which may be mixed into the soil with no adverse effect on the soil as natural habitat. The experiments were monitored by an integrated approach, combining physical, chemical, microbiological and eco-toxicological methods. The aim of our experiment was to predict the red mud amount that poses no risk on the mid-term to the environment when mixed into the soil in view of its potential utilisation as soil ameliorant in the future. Studying of the mid-term effect of red mud mixed into soil is novel as compared to other studies conducted so far [28,25,30]. These studies have focused on the relatively short term effect of red mud on the soil surface, while the effect of mixing red mud into the soil was studied only by Ruyters et al. [31]. In addition, our study targets potential utilisation of red mud as soil ameliorant.

## 2 Materials and methods

### 2.1 Experimental set-up

The red mud (RM) samples for laboratory experiments were collected from an area flooded by red mud along the Torna-creak (47° 6' 53.1072"N, 17° 23' 5.1792"E), approximately 15 km West from the source of the spill 4 months after the catastrophe. By the time of sampling the pH of the spilled red mud had already decreased to 10.2 from 13.0 which was the average pH of the red mud in the Ajka red mud storage facility. The red mud was mixed with sandy soil (S) at 0 w/w % (untreated control), 5 w/w %, 10 w/w %, 20 w/w %, 30 w/w % and 40 w/w %, respectively. The sandy soil sample (S) was taken from the red mud flooded grassland between Somlóvásárhely and Devecser (47° 6' 48.2178", 17° 24' 20.3112") 4 months after the accident. By that time the red mud had been removed from its surface and, the alkalinity had already been washed off by snowmelt and rain as shown in Table 1 [9]. The soil is characteristically of light texture (pebbly sand, sand or loamy sand), though silty or clayey intrusions occur in some places [28]. The experimental setup included also a reference, uncontaminated soil (R), collected from a grass-land nearby Ajka (47° 6' 43.4448", 17° 23' 35.3646"), not affected by the 2010 red mud spill.

The soil / red mud mixtures and the untreated soil (S) were placed into 2 kg flowerpots (microcosms). Triplicate experiments were performed as a check on data reproducibility.

The microcosms were open and their moisture content was set to 60 % of their maximum water holding capacity. The microcosms were irrigated with tap water to their initial water content, every second week. The soil microcosms were maintained at room temperature (25 °C) for 8 months. Samples were taken from the static solid phase microcosms after the first, the second and the eighth month.

### 2.2 Integrated methodology for soil characterisation and monitoring

We monitored the effects of different red mud doses on the soil ecosystem with a complex methodology that integrates physical, chemical, biochemical analysis and ecotoxicity testing [32, 33].

#### 2.2.1 Chemical analysis

The total metal concentration was measured after aqua regia digestion (3:1 hydrochloric acid–nitric acid ratio; 1:4 soil extractant ratio; 2 hrs at 25 °C; microwave digestion) by ICP-AES (Jobin-Yvon Ultima 2 sequential instrument), according to Hungarian Standard 21470-50:2006. To predict the mobile (water-soluble) metal concentrations we analyzed the distilled water extract of the samples (pH 7.0; 1:10 soil extractant ratio; agitation for 4 hrs at 25 °C, HS 21978-9:1998). The pH was determined according to the Hungarian Standard (MSZ-08-0206/2-1978) at a 1:2.5 soil:water suspension after 12 hours.

## 2.2.1 Experimental design of biological and ecotoxicological measurements

The microbiological and ecotoxicological tests were carried out in three replicates. The environmental toxicity tests measured the integrated adverse effects on testorganisms from three trophic levels: *Aliivibrio fischeri* (luminescent bacterium), *Sinapis alba* (plant) and *Folsomia candida* (animal).

The number of aerobic living cells in soil was determined in each soil sample by colony counting after cultivation of microorganisms occurring in soil suspensions [34]. Soil suspension was prepared as follows: 1 g fresh soil was placed into 9 ml sterilized tap water (sterilized in an autoclave, 10 min at 121 °C) and was shaken for 30 minutes at 200 rpm, then from the soil suspension decimal dilution series were prepared. For the cultivation 100 µl from each dilution was pipetted into Petri-dishes. The nutrient agar was Peptone-Glucose-Meat extract (PGM) and it was sterilized for 10 min at 121 °C. 10 ml agar was effused into each Petri-dish and was incubated at 30 °C for 48 hours. Finally, the number of developed colonies (Colony Forming Units –CFU) was counted and the cell-concentration in the soil was calculated.

The *Aliivibrio fischeri* bioluminescence inhibition test was carried out based on the protocol described by Leitgib et al. [35]. 2 g of dry powdered soil (ground and sieved through a 2 mm sieve) was suspended in 2 ml 2 % NaCl solution, and then a five-step dilution series was prepared. The reference luminescence intensity was measured with a luminometer (Lumac Biocounter M 1500 1) at the beginning of the test (t=0 min), then 50 µl of the soil dilution series was added to the 200 µl inoculums. The luminescence was measured after 30 minutes of contact time. The inhibition percentage (H %) of luminescence intensity were calculated compared to reference soil. The inhibition percentage (H %) values were plotted against the soil doses and then the effective dose values (ED20 and ED50 – Effective Dose 20 and Effective Dose 50, dose causing 20 % and 50 % inhibition) were determined from the dose-response curve (inhibition percent values of different dilutions) after sigmoidal fitting of data by ORIGIN 8.5 software. For better interpretation of the results we worked out the “Copper Equivalent Method” for the soil sample containing toxic metals. The 20 % inhibition of soil is given in Cu equivalent ( $\Sigma\text{Cu}_{20}$  (mg Cu kg<sup>-1</sup> soil)), which means the Cu concentration that would cause the identical toxicity as the actual pollution in the soil. The concentration of Cu equivalent is determined from the Cu-calibration curve considering the same % of inhibition or other effect of the soil [35].

The *Sinapis alba* (white mustard) root and shoot growth inhibition test was carried out according to the Hungarian Standard 21976-17:1993 modified to direct contact with soil as described by Leitgib et al. [35]. *Sinapis alba* seeds (20 pieces) were placed onto 5 g dry powdered soil (ground and sieved through a 2 mm sieve) in a Petri-dish, wetted with 3.5 ml water and incubated at 20 °C for 3 days in darkness.

For the determination of the inhibition effect of soil samples the lengths of roots and shoots was measured.

The *Folsomia candida* inhibition test is an international standardized test method (ISO/TC 190SC4, WG2, [36]). The test was carried out in a 200 cm<sup>3</sup> volume closed glass container. We used 10±12 days old juveniles. To carry out the test 20 animals were placed onto 10 g of dry powdered (ground and sieved through a 2 mm sieve) soil and incubated at room temperature for 7 days in darkness. The food and water supplying were 5 ml water and dried yeast powder added at the beginning of the test. At the end of the period of exposure to the control and treated soils, water was added and, following thorough stirring, the animals floated to the top of the suspension where they were counted.

## 2.3 Statistical analysis

To determine if the added amounts of red mud had a significant effect on the measured chemical parameters, we performed an analysis of variance (ANOVA) using StatSoft® Statistica 11. We established the level of significance to p<0.05. Fisher’s least significant difference test was used for the comparison of the effects of various red mud amounts mixed into the soil.

## 3 Results and discussion

### 3.1 Metal content of the red mud and of the soil

The metal content of the reference (R) and of the untreated soil (S) samples was compared with the metal content of the red mud treated soil. The Mo and Na contents in the aqua regia digest of the untreated soil (S) were significantly higher than in the reference soil (R) (Table 1). This may be due to leaching of these metals into the soil from the red mud deposit on the soil surface (S), as observed also by Rékási et al. [30], in a column experiment modelling the leaching into the soil of metals from a 10 cm red mud layer.

The water soluble metal contents of the reference (R) and untreated (S) soils in our experiment indicated a similar process with significantly elevated Al, Ba, Cr, Cu, Na, Ni, Pb and Se concentrations in the untreated soil compared to the reference soil. Rékási et al. [30] observed an increase only in the water soluble Cu, Cr and Na concentrations and in the plant-available (NH<sub>4</sub>-acetate + EDTA soluble) Cu, Pb, Na and Mo concentrations. The total amount of Zn in the reference soil (R) was higher than in the untreated soil (S), but this might be due to local differences in parent material.

Although others have found soluble vanadium in red mud leachates [37], we omitted the vanadium analyses because there is no Hungarian standard for vanadium.

The total metal content of the untreated and of the reference soil was below the Hungarian quality criteria for soil (Hungarian 6/2009 (IV. 14.) KvVM-EüM-FVM decree) shown in the first column of Table 1. The aqua regia-soluble metal content of the red mud was also below the Hungarian limit for sewage sludge (from

**Table 1** Total (aqua regia digests) and water soluble metal content of the red mud and the soils

Element	HQC for soil*	HQC for sewage sludge**	Red mud		Untreated soil		Reference soil	
			Total (Aqua regia extract)	Water soluble	Total (Aqua regia extract)	Water soluble	Total (Aqua regia extract)	Water soluble
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Al	-	-	60183	-	9629a	69.5 a	11770 a	29.5 b
As	15	75	28.7	2.98	4.23a	0.31a	4.20 a	0.340 a
Ba	250	-	68.1	<DL	62.4 a	0.398 a	61.5 a	0.158 b
Cd	1	10	1.26	<DL	0.125 a	0.007	0.165 a	<DL
Co	30	50	53.8	0.087	4.29 a	0.029	4.38 a	<DL
Cr	75	1000	590	0.800	15.9 a	0.129 a	20.6 a	0.058 b
Cu	75	1000	24.0	1.23	10.7 a	0.688 a	6.83 a	0.163 b
Hg	0.5	10	<DL	<DL	<DL	0.043 a	<DL	0.052 a
Mo	7	20	0.345	10.1	1.45 a	0.285	0.171 b	<DL
Na	-	-	44845	-	642 a	328 a	142 b	40.0 b
Ni	40	200	279	0.448	8.33 a	0.133 a	8.55 a	0.059 b
Pb	100	750	128	0.180	10.3 a	0.204 a	10.1 a	0.099 b
Se	1	100	<DL	0.311	<DL	0.369 a	<DL	0.196 a
Sn	30	-	22.4	-	<DL	-	<DL	-
Zn	200	2500	101	<DL	26.0 a	0.632 a	30.4 b	0.320 a
pH				10.2		7.5		6.0

<DL below detection limit; -: not measured

\* Hungarian Quality Criteria for soil based on KvVM-EüM-FVM Joint Decree No. 6/2009

\*\* Hungarian Quality Criteria for sewage sludge from waste water treatment for agricultural applications based on Government Decree No. 50/2001

wastewater for agricultural applications (Hungarian 50/2001 (IV. 3.) Government decree) except for two metals (Co and Ni).

The Co concentration was only 7.6% higher than the limit value, but the Ni concentration exceeded the limit value by 39.5 %.

Numbers marked with the same letter are significantly not different ( $p < 0.05$ ). LSD, Least significant difference. The total metal and the water soluble metal contents of the untreated and the reference soils were compared separately.

### 3.2 Effect of red mud on the soil pH and on the metal content

The pH of the untreated soil (0 % red mud) was moderately alkaline (pH 7.5). Following the application of red mud, the soil pH had increased: the addition of 5 % red mud increased the pH of the soil by 1.7 units; 10 % by 2.1 units; 20 % by 2.3 units; 30 % and 40 % by 2.5 units (Table 2). This is in accordance with the results of Lombi et al. [25] who observed an approximately 1.4 units increase of the soil pH (from pH 6.4 to pH 7.8) after the addition of 2 % red mud.

The total metal content and the water soluble metal content of the soils increased with the red mud loading. We monitored the concentrations of As, Cr, Cu, Ni, Mo, Na and Pb in each soil

microcosm. The As, Cr and Ni concentrations in the red mud mixed soils (Table 2) exceeded the Hungarian quality criteria for soil (Hungarian 6/2009 (IV. 14.) KvVM-EüM-FVM decree) as shown in the first column of Table 1.

The Mo and Na concentrations were higher in the untreated soil than in the reference.

Our results (Table 2) showed that the red mud loading had a significant ( $p < 0.05$ ) effect on both the total and the water soluble As, Cr, Cu, Ni, Mo and Na content. There was no significant effect on the water soluble Pb content. At 10 % red mud dose the total As, Cr and Ni concentration exceeded the Hungarian quality criteria for soil, similarly to the findings of Ruyters et al. [31]. According to Ruyters et al. [31] 4.9 % and 16.5 % red mud dose in a similar soil type resulted that the aqua regia extractable Ni concentrations exceeded the Hungarian quality criteria, while 16.5 % red mud dose caused exceedance of the Hungarian quality criteria for Cr. Based on the chemical analysis of the microcosm samples we found that at 5 % red mud dose the concentrations of the examined toxic metalloids did not exceed the Hungarian quality criteria for soil.

The red mud has high Na content, typical for bauxite residues of the Bayer process [38]. High Na-concentration in the soil increases the risk of sodification. Gruiz et al. [9] recommended

**Table 2** Total (aqua regia extract) and water-soluble element concentrations in the red mud mixed soil (at the beginning of the experiment)

Elements/red mud (RM) amount in soil	As (mg/kg)		Cr(mg/kg)		Cu(mg/kg)		Mo (mg/kg)	
	Total	Water soluble	Total	Water soluble	Total	Water soluble	Total	Water soluble
Untreated soil (S)	4 a	0.31 a	16 a	0.13 a	11 a	0.69 a	1.5 a	0.29 a
S + 5% RM	11 b	0.31 ab	59 b	0.32 a	10 a	0.61 ab	2.2 b	0.39 b
S + 10% RM	19 c	0.50 ab	107 c	0.63 b	13 a	1.00 ca	2.3 b	0.52 c
S + 20% RM	32 c	0.83 b	216 d	0.97 b	22 b	1.57 dc	3.0 c	0.69 d
S + 30% RM	35 d	0.88 c	238 e	1.10 c	22 b	1.70 e	3.2 c	0.83 e
S + 40% RM	35 e	1.04 c	267 f	1.37 d	25 b	1.84 e	2.5 b	0.99 f

Elements/red mud (RM) amount in soil	Na (mg/kg)		Ni (mg/kg)		Pb (mg/kg)		pH
	Total	Water soluble	Total	Water soluble	Total	Water soluble	
Untreated soil (S)	641 a	328 a	8 a	0.13 a	10 a	0.20 a	7.5 a
S + 5% RM	3773 b	575 b	28 b	0.24 a	22 b	0.12 a	9.2 b
S + 10% RM	7192 c	725 cb	52 c	0.39 b	33 c	0.23 a	9.6 c
S + 20% RM	16088 d	1114 dc	101 d	0.60 b	63 d	0.19 a	9.8 d
S + 30% RM	18212 e	1230 e	110 e	0.66 c	70 e	0.27 a	10.0 e
S + 40% RM	21025 f	1438 f	126 f	0.77 c	80 f	0.45 a	10.0 e

Values followed by the same letters, indicate no significant differences at the level of  $p=0.05$ . LSD, Least significant difference

Na: 900 mg/kg concentration as site specific screening value for the soil of the Ajka region. We found that this value had already been exceeded in the 5 % red mud containing soil. Red mud loading in soil had significantly increased the total and the water soluble Na content compared to the untreated soil (Table 2).

The same pattern was found by Ruyters et al. [31]. The salinity of red mud may affect plant growth on the short term. However, depending on the salinity of the soils (Table 3) at 5 %, 10 % and 20 % red mud dose the soils became slightly saline according to Stefanovits [39], therefore, the growth of only some very salt-sensitive crops would be inhibited. The 30 % and 40 % red mud dose resulted in moderately saline soil, inhibiting the growth of most cultivated crops, but the growth of salt-tolerant crops would be undisturbed. According to salt content of the soil samples we found a tolerable inhibition of plant growth at below 20 % red mud dose.

**Table 3** Salinity of red mud mixed soils

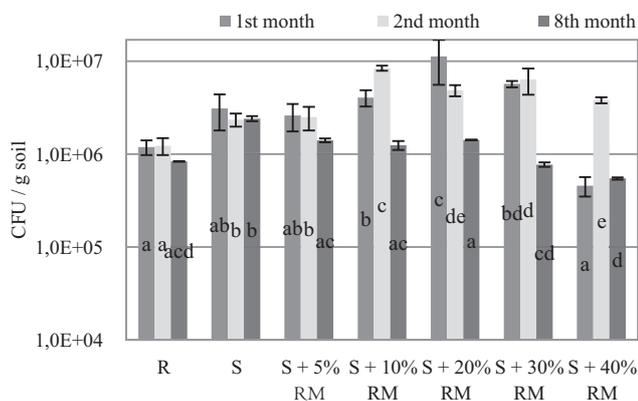
	Total salt content [%]	Salt content*
R	0.00	not saline
S	0.05	not saline
S + 5% RM	0.11	low salinity
S + 10% RM	0.12	low salinity
S + 20% RM	0.19	low salinity
S + 30% RM	0.27	moderate salinity
S + 40% RM	0.34	moderate salinity

\* Stefanovits [39]

### 3.3 Influence of red mud on soil microorganisms and ecotoxicity

The characterization of soil microbiological activity and its quality as habitat was based on the determination of bacterial cell concentration in the soil (Fig. 1). In the short experimental run (during two months) the concentration of colony forming cells increased compared to the reference soil (R) and untreated soil (S) in case of 10 %, 20 % and 30 % red mud dose. The number of aerobic heterotrophic living cells did not increase at 5 % red mud dose compared to the untreated soil and decreased at 40% red mud dose, however in the latter case the cells adapted to the medium by the second month. The number of microorganisms decreased during the experiment in the treated microcosms and also in the reference soil on the mid-term. Castaldi et al. [40], who treated with red mud acidic soil contaminated with Pb, Zn and Cd, found that red mud had significant short term positive effect on the soil microbial cell number. Lombi et al. [25] also observed an increase in the microbial biomass volume in metal contaminated soil after red mud application. Examining the fluvial sediments in the Marcal river after the Ajka's red mud spill Klebercz et al. [41] concluded that red mud appears to stimulate aerobic heterotrophic microbial populations, resulting a 10–100 times increase in microbial colonies in the red mud containing samples over reference samples.

The results of the *Aliivibrio fischeri* bioluminescence inhibition test are shown in Fig. 2, where the smaller ED20 values (Effective Dose causing 20 % inhibition) mean higher toxicity. The reference soil was used as control for the calculation of the inhibition percentage. The untreated soil was not toxic therefore no ED20 values could be determined, as the bioluminescence inhibition was below 10 % at the highest soil dose. Based on the ED20 values the soil containing 5 % red mud was the least toxic of all. The inhibition in Cu equivalent ( $\Sigma\text{Cu}20$ )

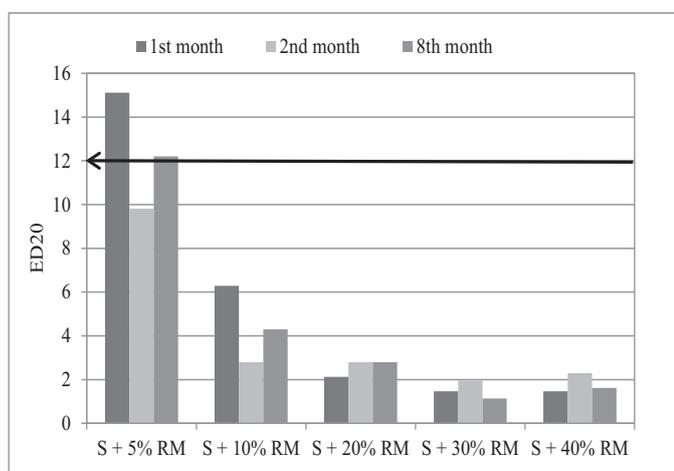


**Fig. 1** The number of colonies formed by aerobic heterotrophic cells (Colony Forming Unit - CFU) in 1 g soil. Values followed by the same letter indicate no significant differences at the level of  $p=0.05$  at each sampling. LSD, Least significant difference. (S: untreated soil, R: reference soil, RM: red mud)

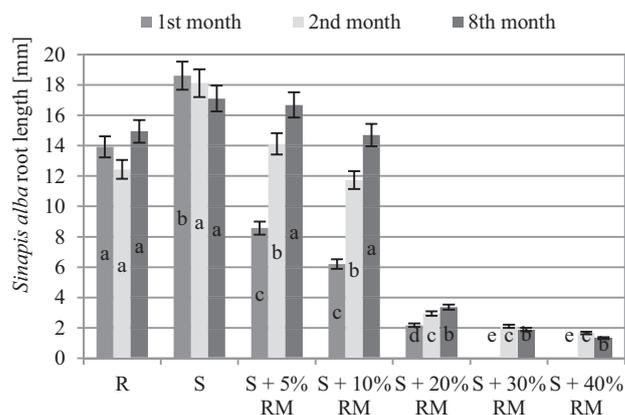
was determined based on the ED20 values to ensure the comparability of data and it showed that the toxicity was very high at above 5 % red mud treatment. The 20 % inhibition expressed in Cu equivalent at 5 % red mud dose was 1238 mg Cu  $\text{kg}^{-1}$  soil in the first month (very toxic), 144 in the second (slightly toxic) and 8 mg Cu  $\text{kg}^{-1}$  soil in the eighth month (non toxic). The borderline of the tolerable harmful effect on the testorganism is shown in Fig. 2.

The inhibiting effect of the 5 % red mud dose shows a decreasing trend during the 8 months of the experiment: very toxic during the first month and non-toxic by the eighth month. Within the 20–40 % red mud dose range the samples showed approximately the same toxicity during the experiment.

According to the experiments performed by Rékási et al. [30], the bioluminescence inhibition did not change significantly after the red mud treatment of the soils, but the untreated alkaline red mud was toxic to *Aliivibrio fischeri*.

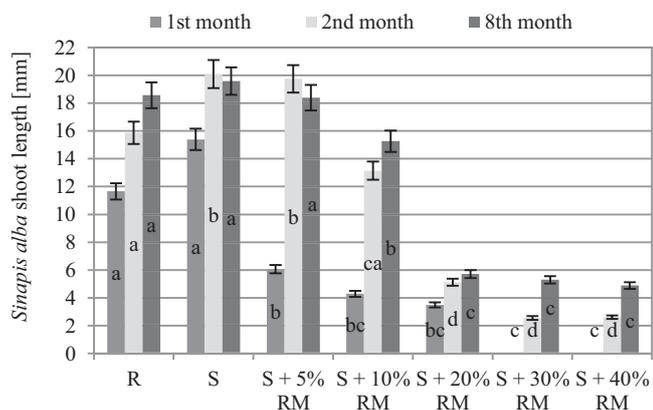


**Fig. 2** ED20 (Effect Dose resulting in 20 % inhibition of luminescence) by *Aliivibrio fischeri* bioluminescence inhibition test. Borderline indicates the tolerable adverse effect on the testorganism.

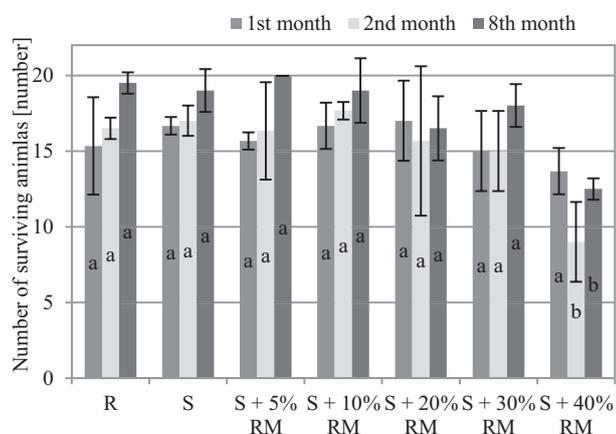


**Fig. 3** *Sinapis alba* root length. Values followed by the same letter indicate no significant differences at the level of  $p=0.05$  at each sampling. LSD, Least significant difference. (S: untreated soil, R: reference soil, RM: red mud)

The *Sinapis alba* root length is shown in Fig. 3. With the increase of the red mud loading in most cases we found significant decrease in the root length as compared to the untreated soil (0 % red mud). At 5 % and 10 % red mud dose the root length decreased significantly during the first and the second month, but after eight months of incubation the difference disappeared. Ruyters et al. [31] found that low red mud doses (<1 %) stimulated the barley root elongation and barley plant yield for unknown reasons, but they also found significant decrease at 4.9 % and 16.9 % red mud doses in barley plant yield. In our experiment there was no difference between 5 % and 10 % red mud doses, neither between 20 %; 30 % and 40 % doses (except for the first month, where 30 % and 40 % red mud dose caused 100% inhibition in root growth: root length 0.0 mm). These results are similar to those of the *Sinapis alba* shoot lengths (Fig. 4). However, there was no significant difference in shoot growth of the untreated and of the 5% red mud treated soil in the second and the eighth months. The 10 % red mud treatment resulted in a significant decrease in shoot growth at each sampling time compared to the untreated. At 20 %, 30 % and 40 % red mud dose there was no significant difference in the effect of the above doses during the second and the eighth months. At 30 % and 40 % red mud addition into the soil the *Sinapis alba* root and shoot length decreased drastically during the first month but it had improved in time. However, 20 %, 30 % and 40 % red mud dose resulted in significantly smaller root and shoot growth, compared to the untreated soil, and to the 5 % and the 10 % red mud treatment. Assessing both the root and the shoot growth results we concluded that 5 % red mud application did not have any significant harmful effect on the soil on the mid-term. Lombi et al. [25] reported positive effect of red mud on crops and they found that red mud addition reduced the toxic effect of Cd, Cu, Ni, Pb and Zn in the contaminated soil. Rékási et al. [30] also stated that the length of 3-day-old *Sinapis alba* roots and shoots increased by 131 % and 64 % after 120 days.



**Fig. 4** *Sinapis alba* shoot length during the experiments. Values followed by the same letters, indicate no significant differences at the level of  $p=0.05$  at each sampling. LSD, Least significant difference. (S: untreated soil, R: reference soil, RM: red mud)



**Fig. 5** Number of surviving animals (*Folsomia candida*). Values followed by the same letters, indicate no significant differences at the level of  $p=0.05$  at each sampling. LSD, Least significant difference. (S: untreated soil, R: reference soil, RM: red mud)

The *Folsomia candida* (Collembola) lethality test (Fig. 5) results showed that the red mud loading of the soil did not cause any inhibition in the testorganism compared to the untreated soil except for 40 % red mud loading. At 40 % red mud loading of the soil the number of surviving animals decreased with 18% (in the 1st month), 50 % (in the 2nd month) and 30 % (in the 8th month). Rékási et al. [30] found that the mortality was 7 % in the top soil layer (0–30 cm) and 13.3 % in the 30–50 cm layer after 120 days.

Winkler [42] have analysed the collembolan community structure and species abundance distributions in the red mud polluted areas in Western Hungary. Their study demonstrated that there was no adverse effect in Collembola abundance on the soil fauna revitalisation and recolonisation.

The results of this study underline and demonstrate the need of toxicity test-battery application, which is able to measure different responses and interactions. Bioassays are influenced by the physico-chemical characteristics of the soil. Each

toxicity test method has particular uses and limitations, and no single test has universal applicability. Different testorganisms dispose various sensitivities so it is not possible to give a general recommendation for the application of the toxicity tests. In this study the most sensitive direct contact tests were *Aliivibrio fischeri* bioluminescence test, followed by *Sinapis alba* root and shoot growth inhibition test and *Folsomia candida* lethality test. *Aliivibrio fischeri* is very sensitive to alkalinity and heavy metals; *Sinapis alba* is sensitive to wide range of toxic substances contrast to the *Folsomia candida* which is mostly sensitive to the dermal adsorption and volatile substances. Because of this very important to combine ecotoxicity tests in a ‘battery of tests’, that is diversified enough to characterize different types of toxicants and different trophic levels.

Our mid-term laboratory study applied a complex monitoring methodology including biological, toxicological and analytical measurement methods. Based on the results we found conformity between the test methods. The toxic metal analysis showed that 5% red mud in soil resulted still an acceptable metal content. The soil toxicity measurements and the soil microflora activity analysis proved that 5 % red mud did not cause any adverse effects on the soil as habitat.

#### 4 Conclusion

The effect of different red mud doses on the soil affected by the red mud disaster in 2010 at Ajka, Hungary was modelled in mid-term laboratory microcosm experiments. The aim of the study was to assess the red mud/soil proportion at which the soil as natural habitat is not adversely affected in view of the potential utilisation as soil ameliorant. Mixing 5 w/w % red mud into sandy soil from the area affected by the spill has caused an increase in the total amount of As, Cr, Mo, Ni, Pb and Na, and in the water soluble fractions of Mo and Na. However, at 5 w/w % red mud dose the total metalloid amounts in the soil did not reach the Hungarian quality criteria for soil and the soil was classified as low salinity soil. 5 w/w % red mud loading shifted the pH of the moderately alkaline soil to the highly alkaline domain. At 10 w/w % red mud dose in the soil the total As, Cr and Ni concentrations exceeded the Hungarian quality criteria for soil.

The ecotoxicological test results showed that 5 w/w % red mud had no significant adverse effect on the *Sinapis alba* shoot and root growth and on the *Aliivibrio fischeri* bioluminescence on the mid-term and neither on the number of living *Folsomia candida*, while at more than 10 w/w % red mud dose both *Sinapis alba* plant growth and the *Aliivibrio fischeri* luminescence was significantly inhibited. For *Folsomia candida* only the 40 w/w % red mud dose caused significant inhibition. The conclusion of our experiment is that red mud could be mixed at up to 5 % into the soil without any mid-term adverse effect on the soil as natural habitat.

## Acknowledgement

The financial supports of the National Innovation Office (TECH\_09-A4-2009-0129, SOILUTIL project) and the New Hungary Development Plan (TÁMOP-4.2.1/B-09/1/KMR-2010-0002) are greatly acknowledged. We are grateful to the ISSAC CAR HAS (Institute for Soil Sciences and Agricultural, Chemistry, Centre for Agricultural Research, Hungarian Academy of Sciences) for the chemical analysis. We thank Emese Vaszita for her contribution to writing and language editing of the manuscript.

## References

- [1] Power, G., Gräfe, M., Klauber, C. "Bauxite residue issues: I. Current management, disposal and storage practices." *Hydrometallurgy*. 108 (1-2). pp. 33–45. 2011. DOI: [10.1016/j.hydromet.2011.02.006](https://doi.org/10.1016/j.hydromet.2011.02.006)
- [2] Gräfe, M., Klauber, C. "Bauxite residue issues: IV. Old obstacles and new pathways for in situ bioremediation." *Hydrometallurgy*. 108 (1-2). pp. 46–59. 2011. DOI: [10.1016/j.hydromet.2011.02.005](https://doi.org/10.1016/j.hydromet.2011.02.005)
- [3] Summers, R. N., Pech, J. D. "Nutrient and metal content of water, sediment and soils, amended with bauxite residue in the catchment of the Peel Inlet and Harvey Estuary, Western Australia." *Agric Ecosystems Environ.* 64 (3). pp. 219–232. 1997. DOI: [10.1016/S0167-8809\(97\)00040-6](https://doi.org/10.1016/S0167-8809(97)00040-6)
- [4] Liu, Y., Lin, C., Wu, Y. "Characterization of red mud derived from a combined Bayer Process and bauxite calcination method." *Journal of Hazardous Materials*. 146 (1-2). pp. 255–261. 2007. DOI: [10.1016/j.jhazmat.2006.12.015](https://doi.org/10.1016/j.jhazmat.2006.12.015)
- [5] Dauvin, J. C. "Towards an impact assessment of bauxite red mud waste on the knowledge of the structure and functions of bathyal ecosystems: The example of the Cassidaigne canyon (north-western Mediterranean Sea)." *Marine Pollution Bulletin*. 60 (2). pp. 197–206. 2010. DOI: [10.1016/j.marpolbul.2009.09.026](https://doi.org/10.1016/j.marpolbul.2009.09.026)
- [6] Jones, B. E. H., Haynes, R. J., Phillips, I. R. "Addition of an organic amendment and/or residue mud to bauxite residue sand in order to improve its properties as a growth medium." *Journal of Environmental Management*. 95 (1). pp. 29–38. 2012. DOI: [10.1016/j.jenvman.2011.09.014](https://doi.org/10.1016/j.jenvman.2011.09.014)
- [7] Cooling, D. J. "Developments in the disposal of residue from the alumina refining industry." In: Campbell, P. G. (ed): *Light Metals*. Halifax: TMS. 1989.
- [8] Riemer, H., Oeberg, N., Perchthaler, H., Murgia, P., Noriega, M. "Verfahren zur Entwässerung und Waschung von Rot schlamm." (Red mud dewatering and washing process.) *Patentscope*. WO/1996/011737. 1996. (in German)
- [9] Gruiz, K., Vaszita, E., Feigl, V., Klebercz, O., Ujaczki, É., Anton, A. "Environmental risk assessment of red mud contaminated soil in Hungary." *Proceedings Aquaconsoil 2013*. 2013. Available from: <http://www.aquaconsoil.org/Previous/AquaConSoil2013/Proceedings.html>. [Accessed: 29th May 2014]
- [10] Fügedi, U., Szentpétery, I., Kalmár, J., Kovács-Pálffy, P., Kónya, P., Vatai, J. "Geokémiai és ásványtani folyamatok a kolontári gáttán." (Geochemical and mineralogical processes in red mud dam of Kolontár.) In: *Conference Proceedings, Conference on red mud, Budapest: Hungarian Academy of Sciences Subcommittee of Environmental Geochemistry*. 2011. (in Hungarian)
- [11] Mayes, W. M., Jarvis, A. P., Burke, I. T., Walton, M., Feigl, V., Klebercz, O., Gruiz, K. "Dispersal and attenuation of trace contaminants downstream of the Ajka bauxite residue (red mud) depository failure, Hungary." *Environmental Science & Technology*. 45 (12). pp. 5147–55. 2011. DOI: [10.1021/es200850y](https://doi.org/10.1021/es200850y)
- [12] Renforth, P., Mayes, W. M., Jarvis, A. P., Burke, I. T., Manning, D. A. C., Gruiz, K. "Contaminant mobility and carbon sequestration downstream of the Ajka (Hungary) red mud spill: The effects of gypsum dosing." *Science of the Total Environment*. 421–422. pp. 253–259. 2012. DOI: [10.1016/j.scitotenv.2012.01.046](https://doi.org/10.1016/j.scitotenv.2012.01.046)
- [13] Burke, I. T., Mayes, W. M., Peacock, C. L., Brown, A. P., Jarvis, A. P., Gruiz, K. "Speciation of Arsenic, Chromium, and Vanadium in Red Mud Samples from the Ajka Spill Site, Hungary." *Environmental Science & Technology*. 46 (6). pp. 3085–3092. 2012. DOI: [10.1021/es3003475](https://doi.org/10.1021/es3003475)
- [14] Grundy, S., Farkas, Gy., Székely, G., Kásler, M. "No short-term cytogenetic consequences of Hungarian red mud catastrophe." *Mutagenesis*. 28 (1). pp. 1–5. 2013. DOI: [10.1093/mutage/ges042](https://doi.org/10.1093/mutage/ges042)
- [15] Wang, P., Liu, D. Y. "Physical and Chemical Properties of Sintering Red Mud and Bayer Red Mud and the Implications for Beneficial Utilization." *Materials*. 5 (10). pp. 1800–1810. 2012. DOI: [10.3390/ma5101800](https://doi.org/10.3390/ma5101800)
- [16] Klauber, C., Gräfe, M., Power, G. "Bauxite residue issues: II. options for residue utilization." *Hydrometallurgy*. 108 (1-2). pp. 11–32. 2011. DOI: [10.1016/j.hydromet.2011.02.007](https://doi.org/10.1016/j.hydromet.2011.02.007)
- [17] Maddocks, G., Lin, C., McConchie, D. "Effects of Bauxsol™ and biosolids on soil conditions of acid-generating mine spoil for plant growth." *Environmental Pollution*. 127 (2). pp. 157–167. 2004. DOI: [10.1016/j.envpol.2003.08.001](https://doi.org/10.1016/j.envpol.2003.08.001)
- [18] Zijlstra, J. J. P., Dessi, R., Peretti, R., Zucca, A. "Treatment of percolate from metal sulfide mine tailings with a permeable reactive barrier of transformed red mud." *Water Environment Research*. 82 (4). pp. 319–327. 2010. DOI: [10.2175/106143009x12487095236432](https://doi.org/10.2175/106143009x12487095236432)
- [19] Rios, C. A., Williams, C. D., Roberts, C. L. "Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites." *Journal of Hazardous Materials*. 156 (1–3). pp. 23–35. 2008. DOI: [10.1016/j.jhazmat.2007.11.123](https://doi.org/10.1016/j.jhazmat.2007.11.123)
- [20] Alva, A. K., Huang, B., Paramasivam, S., Sajwan, K. S. "Evaluation of root growth limiting factors in Spodic horizons of Spodosols." *Journal of Plant Nutrition*. 25 (9). pp. 2001–2014. 2002. DOI: [10.1081/pln-120013290](https://doi.org/10.1081/pln-120013290)
- [21] Summers, R., Guise, N., Smirk, D., Summers, K. "Bauxite residue (red mud) improves pasture growth on sandy soils in Western Australia." *Australian Journal Soil Research*. 34 (4). pp. 569–581. 1996a. DOI: [10.1071/sr9960569](https://doi.org/10.1071/sr9960569)
- [22] Feigl, V., Uzinger, N., Gruiz, K. "Chemical stabilisation of toxic metals in soil microcosms." *Land Contamination & Reclamation*. 17 (3–4). pp. 483–494. 2009 DOI: [10.2462/09670513.954](https://doi.org/10.2462/09670513.954)
- [23] Summers, R., Bolland, M., Clarke, M. "Effect of application of bauxite residue (red mud) to very sandy soils on subterranean clover yield and P response." *Australian Journal Soil Research*. 39 (5). pp. 979–990. 2001. DOI: [10.1071/sr02140](https://doi.org/10.1071/sr02140)
- [24] Summers, R. N., Rivers, M. R., Clarke, M. F. "The use of bauxite residue to control diffuse phosphorous pollution in Western Australia — a win-win-win outcome." In: *Proceedings of the 6th International Alumina Quality*. Brisbane. 2002.
- [25] Lombi, E., Zhao, F. J., Zhang, G., Sun, B., Fitz, W., Zhang, H., McGrath, S. P. "In situ fixation of metals in soils using bauxite residue: chemical assessment." *Environmental Pollution*. 118 (3). pp. 435–443. 2002a. DOI: [10.1016/s0269-7491\(01\)00294-9](https://doi.org/10.1016/s0269-7491(01)00294-9)
- [26] Lombi, E., Zhao, F. J., Zhang, G., Wieshammer, G., Zhang, H., McGrath, S. P. "In situ fixation of metals in soils using bauxite residue: biological effects." *Environmental Pollution*. 118 (3). pp. 445–452. 2002b. DOI: [10.1016/s0269-7491\(01\)00295-0](https://doi.org/10.1016/s0269-7491(01)00295-0)
- [27] Sanderson, P., Naidu, R., Bolan, N. "Ecotoxicity of chemically stabilised metal(loid)s in shooting range soils." *Ecotoxicology and Environmental Safety*. 100. pp. 201–208. (2014) DOI: [10.1016/j.ecoenv.2013.11.003](https://doi.org/10.1016/j.ecoenv.2013.11.003)

- [28] Anton, A., Rékási, M., Uzinger, N., Széplábi, G., Makó, A. "Modelling the Potential Effects of the Hungarian Red Mud Disaster on Soil Properties." *Water, Air, Soil, Pollution*. 223 (8). pp. 5175-5188. 2012. DOI: [10.1007/s11270-012-1269-3](https://doi.org/10.1007/s11270-012-1269-3)
- [29] Lehoux, A. P., Lockwood, C. L., Mayes, W. M., Stewart, D. I., Mortimer, R. J., Gruiz, K., Burke, I. T. "Gypsum addition to soils contaminated by red mud: implications for aluminium, arsenic, molybdenum and vanadium solubility." *Environmental Geochemistry and Health*. 35 (5). pp. 643-56. 2013. DOI: [10.1007/s10653-013-9547-6](https://doi.org/10.1007/s10653-013-9547-6).
- [30] Rékási, M., Feigl, V., Uzinger, N., Gruiz, K., Makó, A., Anton, A. "Effects of leaching from alkaline red mud on soil biota: modelling the conditions after the Hungarian red mud disaster." *Chemistry and Ecology*. 29 (8). pp. 709-723. 2013. DOI: [10.1080/02757540.2013.817568](https://doi.org/10.1080/02757540.2013.817568)
- [31] Ruyters, S., Mertens, J., Vassilieva, E., Dehandschutter, B., Poffijn, A., Smolders, E. "The Red Mud Accident in Ajka (Hungary): Plant Toxicity and Trace Metal Bioavailability in Red Mud Contaminated Soil." *Environmental Science & Technology*. 45 (4). pp. 1616-1622. 2011. DOI: [10.1021/es104000m](https://doi.org/10.1021/es104000m).
- [32] Gruiz, K., Vaszita, E., Siki, Z. "Environmental risk management of mining sites with diffuse pollution." In: Annokkée, G. J., Arendt, F., Uhlmann, O. (eds.), *Conference proceedings CD of 9th international FZK/TNO conference on soil-water systems*. 3-7 October 2005, Karlsruhe: Forschungszentrum Karlsruhe. Bordeaux, France, pp. 2568-2574. 2005.
- [33] Gruiz, K., Molnár, M., Feigl, V. "Measuring adverse effects of contaminated soil using interactive and dynamic test methods." *Land Contamination & Reclamation*. 17 (3-4). pp. 443-459. 2009b. DOI: [10.2462/09670513.952](https://doi.org/10.2462/09670513.952)
- [34] Benedetti, A., Dilly, O. "Introduction." In: Bloem, J., Hopkins, D. W., Benedetti, A. (eds), *Microbial methods for assessing soil quality*. Wallingford: CABI Publishing. 2006.
- [35] Leitgib, L., Kálmán, J., Gruiz, K. "Comparison of bioassays by testing whole soil and their water extract from contaminated sites." *Chemosphere*. 66 (3). pp. 428-434. 2007. DOI: [10.1016/j.chemosphere.2006.06.024](https://doi.org/10.1016/j.chemosphere.2006.06.024)
- [36] Wiles, J. A., Krogh, P. H. "Tests with the Collembolans *Isotoma viridis*, *Folsomia candida* and *Folsomia fimetaria*." In: Lokke, H., Van Gestel, C. A. M. (eds), *Handbook of soil invertebrate toxicity tests*. Chichester: John Wiley & Sons. 1998.
- [37] Burke, I. T., Mayes, W. M., Peacock, C. L., Brown, A. P., Jarvis, A. P., Gruiz, K. "Speciation of Arsenic, Chromium, and Vanadium in Red Mud Samples from the Ajka Spill Site, Hungary." *Environmental Science & Technology*. 46 (6). pp. 3085-3092. 2012. DOI: [10.1021/es3003475](https://doi.org/10.1021/es3003475)
- [38] Wang, S. B., Ang, H. M., Tade, M. O. "Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes." *Chemosphere*. 72 (11). pp. 1621-1635. 2008. DOI: [10.1016/j.chemosphere.2008.05.013](https://doi.org/10.1016/j.chemosphere.2008.05.013)
- [39] Stefanovits, P. "*Talajtani*." (Soil Science.) Budapest: Mezőgazda Publisher. 1999. (in Hungarian)
- [40] Castaldi, P., Melis, P., Silvetti, M., Deiana, P., Garau, G. "Influence of pea and wheat growth on Pb, Cd, and Zn mobility and soil biological status in a polluted amended soil." *Geoderma*. 151 (3-4). pp. 241-248. 2009. DOI: [10.1016/j.geoderma.2009.04.009](https://doi.org/10.1016/j.geoderma.2009.04.009)
- [41] Klebercz, O., Mayes, W. M., Anton, Á. D., Feigl, V., Jarvis, Á. P., Gruiz, K. "Ecotoxicity of fluvial sediments downstream of the Ajka red mud spill, Hungary." *Journal of Environmental Monitoring*. 14 (8). pp. 2063-2071. 2002. DOI: [10.1039/C2EM30155E](https://doi.org/10.1039/C2EM30155E).
- [42] Winkler, D. "Collembolan response to red mud pollution in Western Hungary." *Applied Soil Ecology*. 83. pp. 219-229. 2013. DOI: [10.1016/j.apsoil.2013.07.00](https://doi.org/10.1016/j.apsoil.2013.07.00)