

Modelling the Potential Effects of the Hungarian Red Mud Disaster on Soil Properties

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Abstract In this experiment, the effects of the Hungarian red mud disaster were studied in a soil column experiment focusing on element solubility. The effect of flooding with the highly alkaline red mud suspension and the effect of the percolation of precipitation water through the 10 cm thick red mud layer were modelled separately. Both scenarios affected the soil pH up to a depth of 80 cm. An increase in the total element concentration was only observed for Na and Mo, probably due to the leaching of red mud particles measuring 0.05–0.02 and <0.002 mm in the column. At the same time, the water-soluble concentrations of the potentially toxic elements As, Co, Cr, Cu, Ni, Pb, and Zn rose, at least in the top soil layer, but the concentration values remained below the limit values laid down by quality standards. Over a longer period of time, the main environmental risk raised by the disaster is the secondary salinization of the area.

Keywords Soil column · Leaching · Bauxite residue · Toxic elements · Alkaline pollution

1 Introduction

On 4 October 2010, the red mud impoundment wall at the Ajka Timföldgyár Ltd. aluminium factory collapsed (Szépvölgyi 2010). This was the most serious industrial accident ever recorded involving the release of red mud on such a scale. A total of 700,000 m³ highly alkaline (~pH 13) material flowed into the Torna creek and the surrounding area, covering more than 800 ha including settlements (Kolontár, Devecser, Somlóvásárhely). The average thickness of the red mud layer on soil surface was 5–10 cm (min, 3 cm; max, 45 cm). The removal of the red mud layer from the soil surface was begun a few weeks after the disaster but in some areas the red mud covered the soil for more than 3 months.

Red mud is the by-product of the Bayer process. This process is the production of aluminium from bauxite by digestion at high temperature with concentrated caustic soda (NaOH) (Power et al. 2011; Klauber et al. 2011). The properties of red mud, especially as regards ore composition and toxic element concentrations, may differ greatly from one factory to another (Pagano et al. 2002). The main components of red mud are Fe, Al and Si. Based on 18 red mud samples, Snars and Gilkes (2009) found that the average Fe₂O₃, Al₂O₃ and SiO₃ content of the red mud

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was 33, 20 and 16 %, respectively. The average pH value of red mud is alkaline: 11.3 ± 1 (Gräfe and Klauber 2011). Ghosh et al. (2011) found that the total extractable ($\text{HNO}_3 + \text{H}_2\text{O}_2$ soluble) metal content in fresh red mud was 41.3 ± 5.01 mg/kg Cu, 395 ± 30 mg/kg Cr, 20.2 ± 1.17 mg/kg Pb and 0.037 ± 0.009 mg/kg Cd while Ni and Zn were below the detection limit. Because of the bauxite processing method, red mud contains a high percentage of exchangeable sodium, which may be as high as 81 % (Meecham and Bell 1977). The radionuclide content of red mud may also cause problems but this may occur in the case of red mud utilisation as a building material (Somlai et al. 2008). Ninety percent of the particles in dry red mud are below $63 \mu\text{m}$ in size causing a serious health risk when inhaled. To sum up, the environmental risks associated with red mud are related to its soda content, alkalinity, heavy metal content and radioactive material (Klauber et al. 2011). Bertocchi et al. (2006) stated that in general, the main risk is the highly caustic nature of red mud. However, from the plant physiology point of view, the salt content is the main issue for soils contaminated with red mud (Ruyters et al. 2011).

Despite the risks and adverse effects, red mud can be applied to soils for environmental and agricultural purposes. It is able to decrease the mobility of elements such as As, Cd, Cu, Ni, Pb, Zn in contaminated soils. Because of its high alkalinity, it may cause metals to be precipitated as hydroxides and carbonates and its high Al and Fe contents in the form of oxides and hydroxides, provide surfaces for the adsorption of potentially toxic elements (Bertocchi et al. 2006; Gray et al. 2006; Garau et al. 2011). From the agricultural point of view, red mud improves the nutrient-holding capacity of soils by increasing the cation exchange capacity (CEC) and on sandy soils it may ameliorate the water-holding capacity (McPharlin et al. 1994; Barrow 1982). Because of its high pH, it can be used on organic soils to raise the pH and thus prevent Al toxicity (Alva et al. 2002). Furthermore, red mud can be used to prevent eutrophication due to its ability to retain phosphorus (Summers and Pech 1997). However, before agricultural or environmental use, red mud should be neutralised (e.g. using seawater) so as to reduce the toxic effects (Brunori et al. 2005).

In the case of the disaster in Hungary, the potential beneficial effects of red mud did not materialise because it was caustic and was not mixed into the soil

but covered in a solid layer. The adverse effects of the red mud disaster on soil properties may depend on numerous factors, e.g. the contact time between red mud and soil, the relief and precipitation of the relevant area, the pH, element composition and water content of the red mud and the soil properties.

The soils of the affected area are heterogeneous, because of the diverse parent materials, and the age, geomorphology and hydrogeology of the soils. According to the available data, the deepest hydro-morphic locations in the Kolontár–Devecser area are characterised by the light soil texture with a gravel layer at the depth 0–30 cm. The depth of the organic horizon exceeds 20 cm. The soil profiles are layered in the deeper horizons as a result of the Fluvisol characteristics. The profiles are carbonated from the surface; the pH is neutral or slightly alkaline. The groundwater level is within 1 m. At the time of the disaster, the soils were saturated due to the abundant precipitation in the area. The saturated soil was first thought to interfere with the leaching of potentially hazardous elements into deeper layers (Anton 2010).

A laboratory soil column experiment was setup to study the potential effects of the disaster. Two scenarios that could be important for environmental risk assessment were modelled separately. The first scenario modelled a situation where the highly alkaline red mud suspension that flowed out of the impoundment settled on a low-lying area without runoff. In this case, the most threatening factor was the extremely high pH (~pH 13). The second scenario modelled a situation where after the runoff of the liquid phase, the red mud remained as a sediment on the soil surface. This could hinder the gas exchange of the soil, causing it to become anoxic. The red mud layer could lead to an unfavourable modification of the soil water balance and rainfall could leach dissolved components into the soil.

The soil column was compiled from the typical soil profile of the area. The principal aim of the work was to investigate the mobility and potential enrichment of heavy metals and metalloids (especially As, Co, Cr, Na, Ni, Pb) in the soil profile and also the changes in the mobility of other potentially toxic elements (Cd, Cu, Mo, Zn) due to the chemical and physical changes induced by the red mud.

The investigation of these two scenarios provided exact information for the qualitative risk assessment that formed the basis of the environmental clean-up plan for the disaster area. However, the present paper

only focused on the effects of red mud cover on soil properties, and gives no information about fugitive dust lift-off after the drying of the red mud, which is a serious environmental concern in risk assessment.

2 Materials and Methods

2.1 Experimental Setup

The model soil profile for the experiment was collected from the uncontaminated arable land soil profile (0–100 cm) in Kolontár (latitude, 47° 5' 55.60"N; longitude, 17° 28' 12.96"E; elevation, 182 m). Four layers were identified according to texture and colour:

1. 0–30 cm, sandy loam with gravel
2. 30–50 cm, sand with higher gravel content
3. 50–80 cm, sand with gravel and a coherent gravel layer at 60 cm
4. 80–100 cm, sand with gravel

The chemical properties of the soil layers are shown in Table 1.

The model soil was dried and the volume of gravel was measured. The soils of each layer were homogenised, then filled into 100 cm long PVC tubes (diameter, 15 cm) according to the original sequence of the layers. The bottom of the columns was closed with a polyethylene textile. The soil was filled into the column from the top and compacted. The bulk density of each soil layer was adjusted to the same value: after the addition of each 5 cm soil layer the weight of the column was measured. Before red mud application, the soils were saturated up to the maximum water-holding capacity from the bottom of the column.

The red mud used for the experiment was collected from the disaster area on 29th October, 25 days after the collapse of the dam. At that time, the pH of the red mud had decreased from its original value (~pH 13) to

10.2. The original pH was above the limit value for qualification as hazardous waste (11.5) according to the Basel Convention (240/2005. Gov. Order). The red mud suspension could be thus classified as hazardous material. The element composition of the red mud is given in Table 2. There is no directive for red mud utilisation so the total element composition only can be compared with the Hungarian limit values for the agricultural application of sewage sludge (50/2001 Gov. Order).

The two investigated scenarios for the red mud disaster: (1) flooding with caustic red mud suspension and (2) percolation of precipitation water through the 10 cm thick red mud layer, required different treatments, resulting in two experimental setups. The differences were in the pH and water content of the red mud applied, the duration of the experiment, whether irrigation was applied and the number of soil layers investigated.

2.2 First Scenario: Flooding with Red Mud Suspension

In the flooding experiment, the red mud sample was diluted with NaOH solution in a 1:10 m/m ratio. The pH of the suspension was set to 12.5. A quantity of 3,800 ml (400 mm) suspension was poured on to the top of the column. After 30 days, the four layers of the column were separated and prepared for further analysis. The top soil layer (0–30 cm) was divided into three further layers each 10 cm thick. The trial was performed in three replications. During the 30 days, no water was added to the columns.

2.3 Second Scenario: Percolation of Precipitation Water Through Red Mud Layer

When modelling the effect of precipitation, a 10 cm red mud layer was placed on the top of the soil column, which was the average thickness of the red mud in the disaster area and this is equivalent to about 1,900 t red mud/ha. The water content of the red mud was set to 38 % in accordance with the value measured at the time of sampling. The time that elapsed after the top of the column was covered with red mud was taken as the treatment. Three periods were investigated: 30, 60 and 120 days, each in three replications. At the end of the given time period, the columns were divided into four sections according to the soil layers.

Table 1 Selected chemical properties of the soil layers in the column

Depth (cm)	pH (KCl)	Organic matter (%)	CEC (meq/100 g)
0–30	6.76	2.17	9.33
30–50	6.80	1.32	9.97
50–80	7.20	0.64	9.63
80–100	7.92	0.38	7.27

Table 2 Total (cc. HNO₃+HCl soluble) and water-soluble element concentrations in the red mud (milligrams per kilogram DW)

Fraction	Elements											
	Al	As	Cd	Co	Cr	Cu	Mo	Na	Ni	Pb	Se	Zn
Total	51,470	32.1	1.17	40.3	396	34.5	3.00	32,918	193	117	<dl	107
Water Soluble	167	2.52	0.011	0.158	1.27	1.63	5.35	3,680	0.773	0.432	<dl	0.610
Limit Value ^a		75	10	50	1,000	1,000	20		200	750	100	2,500

<dl under detection limit; the dl of Se was 0.6 mg/kg

^a Limit values for sewage sludge agricultural application, total fraction (50/2001 Gov. Order)

Further analysis was performed on these separated soil layers.

During the 120 days of the experiment, the columns were irrigated according to the precipitation observed in the disaster area (Fig. 1). The total amount of irrigation water was 51 mm (901 ml) at the end of the 30-day period, 132.8 mm (2,346 ml) after 60 days and 181.8 mm (3,212 ml) after 120 days. Thus, the cumulative amount of water added in the experiment (181.1 mm) was equivalent to about one third of the annual average precipitation in Hungary.

In both scenarios, the temperature was set to 17 °C. Chemical and physical analyses were made on the soil samples. Effluent water samples were collected in the second scenario at the end of each time period and analysed for pH and element composition.

2.4 Chemical and Physical Analysis

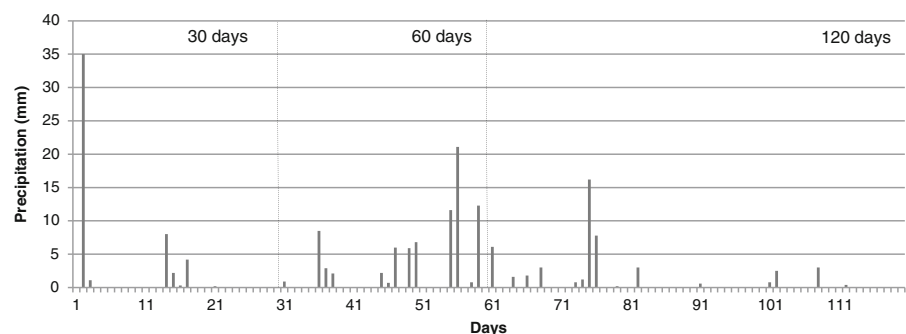
The soil samples were dried before chemical analyses. The soil pH was measured according to the Hungarian Standard (MSZ-08-0206/2:1978) in 1:2.5 soil/water and soil:1 M KCl suspensions after standing for 12 h.

The soil organic matter content was measured by oxidation with K₂Cr₂O₇ according to the method of

Tyurin (1931). Dissolved organic carbon (DOC) was measured by extraction with 0.01 M CaCl₂ in a 1:10 soil:solution ratio for 2 h (Jászberényi et al. 1994). DOC was measured using a TOC/TN analyser (Tekmar Dohrmann Apollo 9000) involving combustion (680 °C) with a platinum catalyst. The CEC values of the soils were measured by the modified method of Mehlich (1948; MSZ-08-0215 1978). Particle-size distribution was determined by the pipette method. The soil/water suspension was mixed in a sedimentation cylinder, then sampled with a pipette to collect particles of a given size (MSZ-08-0215 1978).

The total element concentrations were determined with the inductively coupled plasma-atomic emission spectrometry (ICP-AES) method after microwave Teflon bomb digestion with cc. HNO₃+HCl. The water-soluble element contents were measured in a 1:10 soil/water extract (MSZ 21470-50: 2006). The concentrations were determined by means of ICP-AES (Jobin-Yvon Ultima 2 sequential instrument), using Merck calibration standards and following the manufacturer's instructions. In each measurement session, the extract of a standard soil sample was also analysed as a control. The calibration curves were determined

Fig. 1 Irrigation of the soil columns during the period of the experiment, according to the precipitation observed in the disaster area after the collapse of the dam (second scenario)



after every 12th sample. The element composition of the effluent water was analysed according to the Hungarian Standard (MSZ 1483-3: 2006).

2.5 Statistical Analysis

The data were analysed for treatment effects using one-way analysis of variance, on the main treatments (time period, different layers). Significant differences between the treatment means were calculated by the least significant difference (LSD) test at $p < 0.05$. In the correlation analysis, the asterisks, *, ** and *** indicate significance at $P < 0.05$, 0.01 and 0.001, respectively. Statistica v.9 (StatSoft Inc.) software was used for all the statistical evaluations.

3 Results and Discussion

Among the soil properties investigated, significant changes were observed for the 0.05–0.02 and <0.002 mm particle size fractions, pH and DOC 30 days after the flooding with red mud suspension (first scenario). For the elements investigated (As, Cd, Co, Cr, Cu, Mo, Na, Ni, Pb, Zn) the cc. $\text{HNO}_3 + \text{HCl}$ and/or water-soluble concentrations of all but Cd changed significantly. Each element concentration increased significantly in the 0–10 cm surface soil layer.

The percolation of the irrigation water through the 10 cm thick red mud layer (second scenario) significantly affected the following soil properties: the 0.05–0.02, 0.005–0.002 and <0.002 mm particle size fractions, pH, DOC, total Mo and Na, and water-soluble Cr, Cu, Mo and Na concentrations.

3.1 Red Mud Properties

Changes in the properties of the red mud were only monitored in the second scenario. During the 120 days of the experiment, the pH (H_2O) of the red mud decreased significantly from 10.2 to 10.0. This contradicts the findings of Thornber and Binet (1999), who recorded no change in the solution pH during the sequential H_2O extraction of red mud. In the present experiment, the leaching of the residual alkali content of the red mud may have caused the pH change. The total and water-soluble element concentrations of the red mud are given in Table 2. Regarding the element composition, only the water-soluble As, Cu, Na and

Mo concentration diminished due to the leaching caused by precipitation (Table 3).

3.2 Soil Physical Properties

In the first scenario, the red mud suspension modified the ratio of the particle size fractions in the 0–30 cm soil layer, especially in the 0–10 cm layer (Table 4). These changes were caused by the infiltration of the liquid phase from the red mud suspension into the soil, thus washing red mud particles into the soil. The sand fractions and the 0.02–0.01 mm silt fraction remained unchanged, while changes were only observed in two silt fractions (0.01–0.005 and 0.005–0.002 mm) in the 0–10 cm soil layer. The 0.05–0.02 mm silt and <0.002 mm clay fractions of the red mud exhibited change in the whole of the 0–30 cm surface soil layer. The downward flow might have caused the change in the 0.01–0.005 mm fraction in the 0–10 cm soil layer. This change was negative, suggesting that particles of this size were not filtered out from the red mud suspension. However, the lack of changes in the 10–30 cm soil layer contradicted this assumption. Theoretically, the filtration of red mud particles into the soil may influence its element composition. Correlation analysis demonstrated that the changes in the total Mo and Na concentrations in the top soil might be connected to the downward movement of the 0.05–0.02 and <0.002 mm fractions (Table 5).

In the case of the second scenario, the extent of change in the particle fractions was almost the same as that observed after flooding with red mud suspension. In the 0–30 cm surface soil layer of the columns the silt (0.05–0.02 and 0.005–0.002 mm) and clay (<0.002 mm) fractions increased significantly even after 30 days (Table 6), but no further significant

Table 3 Changes in the pH (H_2O) and water soluble As, Cu, Na and Mo content (milligrams per kilogram) of the red mud during the time of the experiment (second scenario)

Time	pH	As	Cu	Na	Mo
Control	10.2	2.52	1.63	3,680	5.35
30 days	10.3	1.87	1.32	2,417	2.32
60 days	10.0	1.68	1.33	1,812	1.49
120 days	10.0	1.10	0.84	1,978	0.79
LSD ₅ % ^a	0.1	0.17	0.24	169	0.49

^a LSD₅ % least significant difference at $p < 0.05$

Table 4 Changes in the particle size fractions of the 0–30 cm surface soil layer 30 days after flooding with red mud suspension (first scenario)

Treatment	Sand		Silt				Clay
	2–0.25 mm (%)	0.25–0.05 mm (%)	0.05–0.02 mm (%)	0.02–0.01 mm (%)	0.01–0.005 mm (%)	0.005–0.002 mm (%)	<0.002 mm (%)
0–10 cm							
Control	29.8	41.4	7.07	4.10	3.44	2.95	11.3
Flooded	26.3	42.2	8.52	4.38	2.42	3.83	12.3
LSD ₅ %*	n.s.	n.s.	0.70	n.s.	0.61	0.87	0.9
10–20 cm							
Control	29.8	41.4	7.07	4.10	3.44	2.95	11.3
Flooded	27.3	41.9	8.01	4.26	3.14	3.24	12.1
LSD ₅ %	n.s.	n.s.	0.93	n.s.	n.s.	n.s.	0.8
20–30 cm							
Control	29.8	41.4	7.07	4.10	3.44	2.95	11.3
Flooded	27.8	41.9	7.98	4.25	2.85	3.31	11.9
LSD ₅ %*	n.s.	n.s.	0.78	n.s.	n.s.	n.s.	0.4

n.s. not significant, LSD₅ % least significant difference at $p < 0.05$

increment could be detected in the period from 30 to 120 days. The element content of these particles contributed to an increase in the total element concentration in the 0–30 cm soil layer, as in the case of the first scenario (Table 7). The total Mo and Na concentrations, which showed a significant change in the top soil layer are mostly correlated with the 0.05–0.02 mm silt and <0.002 mm clay fraction.

The changes observed in the particle size fractions are in agreement with the data published by Summers et al. (1996), Snars and Gilkes (2009) and Luo et al. (2011) who also established that the dominant particle size fractions of red mud are clay and silt. The textural classes in red mud have different chemical characteristics (Gräfe and Klauber 2011), which may explain the correlation between the changes observed in the element concentrations and particle size fractions in the soil column.

3.3 Soil Chemical Properties

In both scenarios, the soil pH rose significantly. The pH increment caused by flooding with caustic red mud suspension was the consequence of applying a pH 12.5 NaOH suspension. The pH in the 0–10 cm layer reached more than 9.5 after 30 days, while the average pH of the 0–30 cm layer was 8.06. The changes could be traced in the whole soil profile (Fig. 2).

The percolation of irrigation water through the 10 cm thick red mud layer also changed the soil pH significantly in the whole soil column, but to a lesser extent (Fig. 2). At the end of the 0–30 days period the pH of the 0–30 cm layer was 7.73, indicating that in this scenario the pH in the topsoil changed to a lesser degree than after flooding with red mud suspension. The differences in pH between the soil layers decreased over time. By

Table 5 Correlation coefficients between soil particle size fractions and the total (cc. HNO₃+HCl) Mo and Na concentration in the 0–30 cm soil layer after flooding with red mud suspension (first scenario)

Element	0.05–0.02 mm (%)	0.01–0.005 mm (%)	0.005–0.002 mm (%)	<0.002 mm (%)
Mo	0.67*	−0.60*	n.s.	0.78**
Na	0.70*	−0.76**	0.65*	0.66*

n.s. not significant

Table 6 Changes in the particle size fractions of the 0–30 cm surface soil layer under the red mud cover (second scenario)

Time	Sand		Silt				Clay
	2–0.25 mm (%)	0.25–0.05 mm (%)	0.05–0.02 mm (%)	0.02–0.01 mm (%)	0.01–0.005 mm (%)	0.005–0.002 mm (%)	<0.002 mm (%)
Control	29.8	41.4	7.07	4.10	3.44	2.95	11.3
30 Days	30.8	37.5	8.65	4.38	3.02	3.67	11.9
60 Days	28.7	40.0	8.72	4.03	3.25	3.49	11.8
120 Days	30.1	39.5	8.21	4.08	2.78	3.20	12.2
LSD ₅ %	n.s.	n.s.	0.67	0.19	n.s.	0.42	0.4

n.s. not significant; *LSD₅* % least significant difference at $p < 0.05$

the end of the experiment (after 120 days), the neutral pH of the top soil layer (6.8) became slightly alkaline (8.0). The pH changes were associated with the rise in the DOC concentration (Fig. 2). Lombi et al. (2002) also found an increase in the dissolved organic matter concentration of the soil solution after red mud application on contaminated soil. Flooding with the red mud suspension changed the DOC concentration significantly up to a depth of 50 cm after 30 days. In the 0–10 cm soil layer, it increased to five times the control value. In the case of the second scenario, a significant change in the DOC concentration in the 0–80 cm soil layer could only be detected after 120 days, while the pH increased constantly over time. The DOC release was in positive correlation with the soil pH confirming the results of earlier studies (Curtin and Smillie 1986; You et al. 1999). This relationship can be explained by various processes, such as increased organic matter solubility, increased microbial activity and the displacement of previously adsorbed DOC by other mobilised anions (Tombácz and Rice 1999; Guggenberger et al. 1994; Castro Filho and Logan 1991; Vance and David 1992).

The total Na and Mo concentrations changed significantly in both scenarios, while the total concentrations

of the other elements investigated were constant over the experimental period. These changes in the total element content were limited to the top soil (0–30 cm) and were related to the downward movement of red mud particles.

The red mud only contained 3 mg/kg aqua regia soluble Mo, which was about 10 times higher than the soil Mo concentration. Under alkaline conditions, like those in the investigated soil after red mud application, Mo is in soluble oxyanionic form, representing a serious soil and water quality issue that was studied earlier and again during the red mud disaster (Németh and Kádár 2005; Mayes et al. 2011). The total Mo content of the 0–20 cm soil layer increased to a value of ~1 mg/kg 30 days after flooding with red mud suspension. The water-soluble Mo concentration only rose significantly in the 0–10 cm soil layer. In deeper soil horizons, the Mo remained constant, with concentrations close to the detection limit (Fig. 3).

The results were similar in the columns modelling the second scenario. Due to the high pH of the 10 cm red mud layer (pH 10.2), the total Mo content of the soil may have been increased not only by the downward movement of red mud particles but also by the

Table 7 Correlation coefficients between soil particle size fractions and the total (cc. HNO₃+HCl) Mo and Na concentration in the 0–30 cm soil layer considering each sampling time of the experiment (second scenario)

Element	Particle size fractions			
	0.05–0.02 mm	0.02–0.01 mm	0.005–0.002 mm	<0.002 mm
Mo	0.78**	n.s.	n.s.	0.78**
Na	0.77**	n.s.	n.s.	0.73**

n.s. not significant

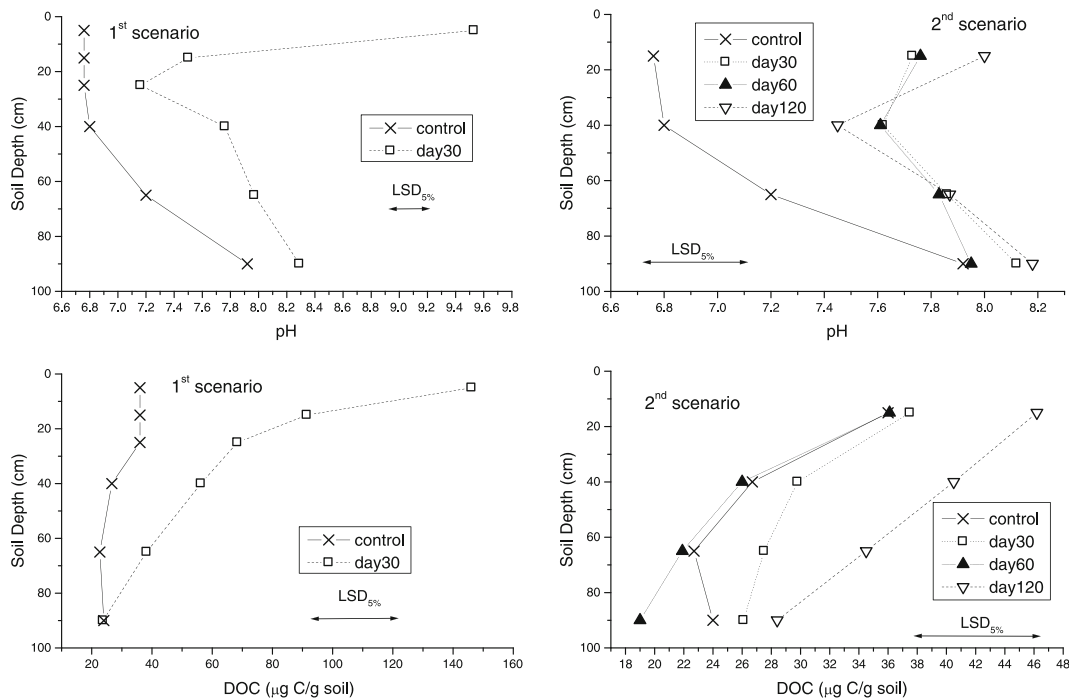


Fig. 2 Changes in pH and DOC concentrations in the soil column during the time of the experiment. 1st scenario: changes after flooding with red mud suspension. Second scenario,

changes caused by percolation of the irrigation water through the 10 cm thick red mud layer. $LSD_5\%$ least significant difference at $p < 0.05$

leaching of water-soluble Mo from the red mud (Fig. 3). This possibility was confirmed by mass balance calculations: the decrease in the water-soluble Mo content in the red mud layer (17.9 mg) exceeded the total Mo increment (8.1 mg) in the top soil layer.

Sodium is an important issue for the environmental application of red mud (Snars and Gilkes 2009). This element is highly mobile and can easily be leached to the deeper layers of the soil profile (Kádár et al. 2009). In the case of flooding with the red mud suspension, the total Na content only increased significantly in the 0–20 cm soil layer. The water-soluble Na content showed a significant increment up to a depth of 50 cm 30 days after the addition of the red mud suspension (Fig. 4).

In the case of the second scenario, both the total and water-soluble Na contents increased in the top soil layer as a result of the percolation of irrigation water through the 10 cm thick red mud layer (Fig. 4). As in the case of Mo, the decline in the water-soluble Na content of the red mud layer was sufficient to account

for the Na increment in the soil column. The total Na content only changed significantly in the top soil layer, while the water-soluble Na content increased up to a depth of 80 cm. The profile of the water-soluble Na content shows equilibration over the period of the experiment (Fig. 4). The water-soluble Na concentration in the top soil layer increased until the end of the 60 days period, while in the deeper soil layers it remained constant. By the 120th day, however precipitation leached the Na into the deeper soil horizons, causing a decrease in the water-soluble Na concentration in the 0–30 cm soil layer. Flooding with red mud suspension (first scenario) caused a higher water-soluble Na concentration in the top soil layer than leaching from the 10 cm red mud layer after 30 days. This could be attributed to the fact that more Na was dissolved in the liquid phase in the red mud suspension (made of red mud and NaOH solution, as was the case in the disaster) which may have caused the faster, more extensive change in Na concentration in the soil column (Fig. 4).

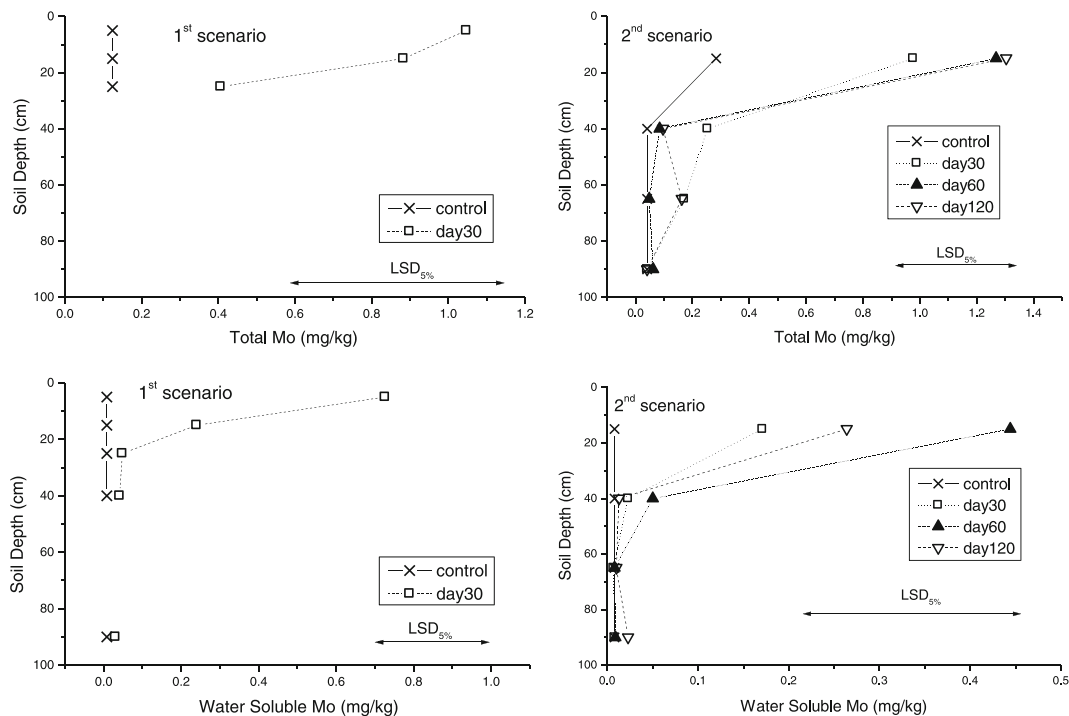


Fig. 3 Changes in total (cc. $\text{HNO}_3 + \text{HCl}$ soluble) and water-soluble Mo concentrations in the soil column during the time of the experiment. First scenario, changes after flooding with red mud suspension. Second scenario, changes

caused by percolation of the irrigation water through the 10 cm thick red mud layer. $\text{LSD}_{5\%}$ least significant difference at $p < 0.05$. The missing points of the graph denote concentrations below detection limit

The water-soluble Cu concentration was also affected in both scenarios. In the first scenario, after flooding with red mud suspension, the total Cu content in the soil profile did not change, while the water-soluble Cu content rose substantially, increasing tenfold in the 0–10 cm soil layer by 30 days after flooding (Fig. 5).

The results were similar for the second scenario. The water-soluble Cu content decreased in the 10 cm red mud layer and showed an increment in the top soil layer (Fig. 5). In the experiment of Lombi et al. (2002), a rise in the Cu concentration of soil solution was also observed on a contaminated soil after red mud treatment. Various processes could be behind this increment. One is the leaching of Cu from the red mud. The other factor that could increase the solubility of Cu is the elevated concentration of DOC. The solubility of Cu is greatly dependent on organic matter, because Cu is readily adsorbed by organic substances (Adriano 1986). The water-soluble Cu content in the soil columns significantly increased in the 0–

30 cm soil layer, but was not correlated with the DOC concentration. It thus appears that the source of the water-soluble Cu increment in the soil was the Cu content of the red mud in both scenarios.

The caustic red mud suspension caused changes in the water-soluble Cr content of the 0–20 cm soil layer. The concentration in the 0–10 cm layer increased six times reaching a value of 0.2 mg/kg while it doubled in the 10–20 cm layer to a concentration of 0.06 mg/kg. These concentrations exceeded those measured in the second scenario after 120 days; but at depths lower than 30 cm, the water-soluble Cr concentration was below the detection limit (Fig. 5).

In the second scenario, the water-soluble Cr concentration in the 0–30 cm soil layer increased almost four times due to the percolation of the irrigation water through the 10 cm thick red mud layer (Fig. 5). In the deeper layers, the water-soluble Cr content remained unchanged. Chromium exists in the environment mainly in two oxidation forms: Cr

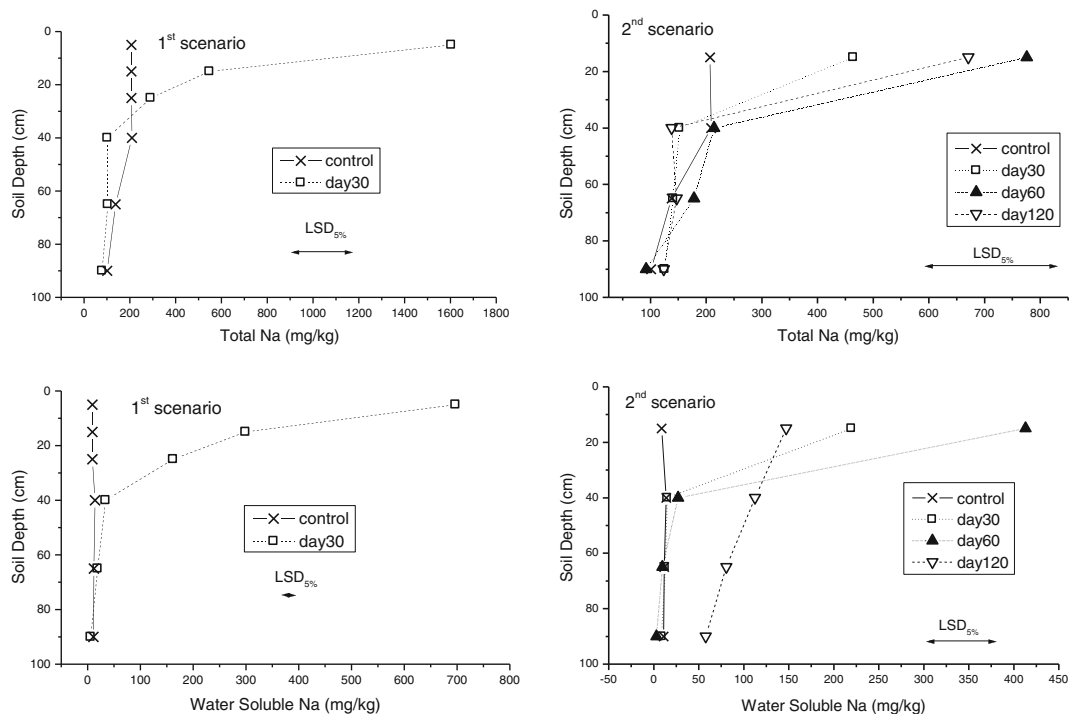


Fig. 4 Changes in total (cc. $\text{HNO}_3 + \text{HCl}$ soluble) and water-soluble Na concentrations in the soil column during the time of the experiment. First scenario, changes after flooding with red

mud suspension. Second scenario, changes caused by percolation of the irrigation water through the 10 cm thick red mud layer. $\text{LSD}_{5\%}$ least significant difference at $p < 0.05$

(VI) and Cr(III). Cr(VI) is the mobile form, while the mobility of Cr(III) depends on the low molecular weight organic molecules in the soil (Mandiwana et al. 2008). In the soil column, there was no correlation between the water-soluble Cr form and the DOC content, so the leaching of Cr was probably mostly due to the Cr(VI) content of red mud (Ghosh et al. 2011).

Directly after the disaster rumours arose concerning the risk represented by the arsenic content of red mud (Enserink 2010). The results obtained with the second scenario showed that, although the red mud contained 32 mg/kg As, it did not leach into the soil. This was due to the strong adsorption of arsenic by Al and particularly Fe oxides, which are the main components of red mud (Livesey and Huang 1981; Jacobs et al. 1970). The water-soluble As content was also constant in each soil layer throughout the period of the second scenario. However, flooding with the highly alkaline liquid red mud suspension led to a significant, more than threefold increase in the water-soluble As content

in the upper 10 cm soil layer to a value of 0.76 mg/kg while the total As concentration was unchanged (Fig. 6). Consequently, the arsenic content of red mud did not pose a direct risk to the food chain or the groundwater.

In addition, flooding with red mud suspension significantly ($P < 0.01$) increased the water-soluble Co, Ni, Pb and Zn concentrations in the 0–10 cm soil layer after 30 days, from control concentrations of 0.009, 0.07, 0.06 and 0.465 to 0.156, 0.455, 0.194 and 1.335 mg/kg, respectively. In the deeper layers, the changes were either not significant or the element concentrations were below the detection limit. The increased Zn, Ni and Pb mobility may have been caused by the increased solubility of metal–organic complexes due to the higher pH (Kabata-Pendias and Pendias 1992).

The total element concentrations in the soil column remained below the contamination limit values of the Hungarian soil quality standard (6/2009 KvVM-EüM-FVM common order) in both scenarios.

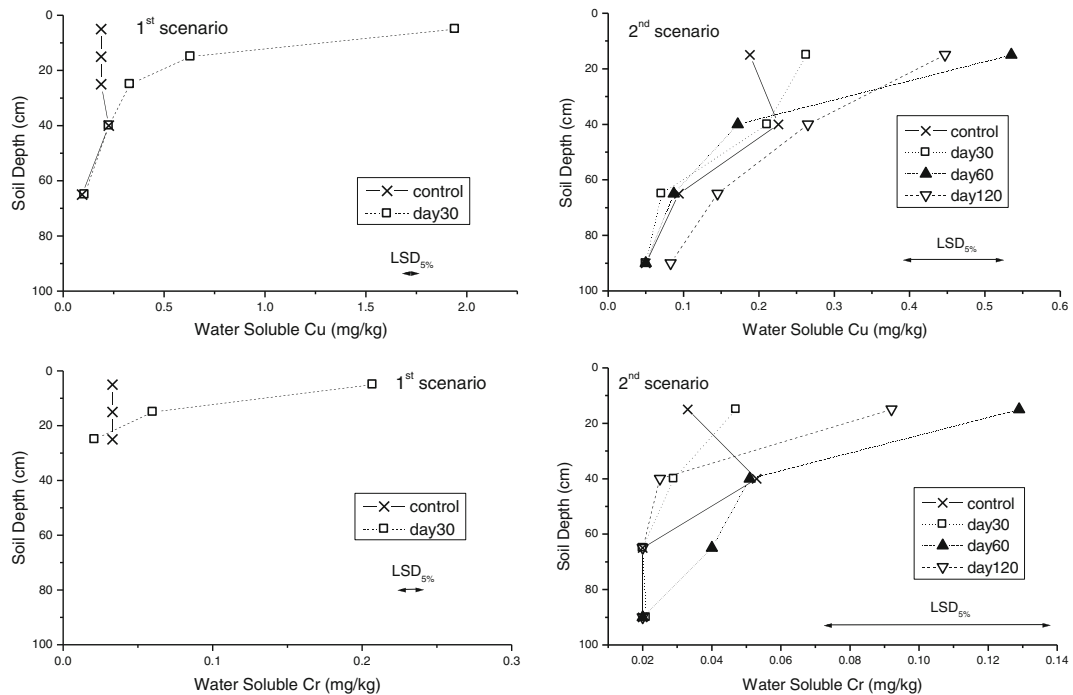


Fig. 5 Changes in water-soluble Cu and Cr concentrations in the soil column during the time of the experiment. First scenario, changes after flooding with red mud suspension. Second scenario, changes caused by percolation of the irrigation water

through the 10 cm thick red mud layer. $LSD_{5\%}$ least significant difference at $p < 0.05$. The missing points of the graph denote concentrations below detection limit

Comparing the results of the two scenarios, the following differences and similarities can be found:

- The red mud had a similar significant effect on the top soil clay and silt fractions in both scenarios.

The changes in particle size fractions resulted in modifications in the total Na and Mo concentrations of the soil.

- Flooding with the red mud suspension caused a greater change in pH. Although, this rise in pH

Fig. 6 Changes in the water-soluble As concentration in the soil column 30 days after flooding with red mud suspension (first scenario). $LSD_{5\%}$ least significant difference at $p < 0.05$

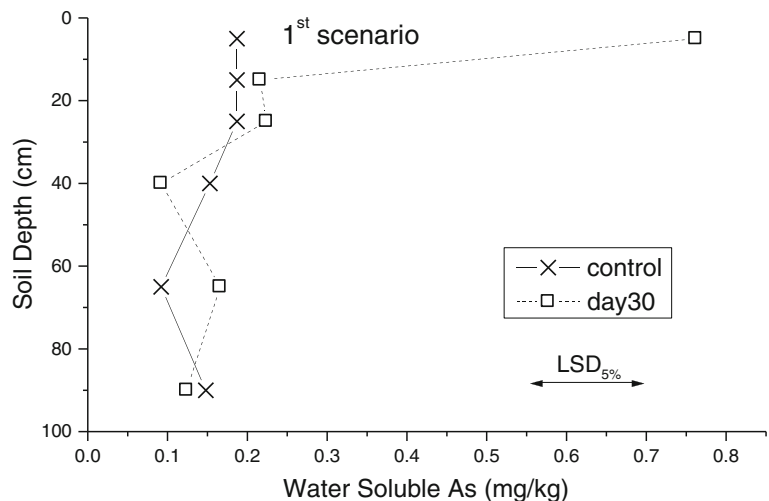


Table 8 Changes in the mass of As, Co, Cr, Cu and Na leached out the soil column during the time of the experiment (second scenario)

Period	As (μg)	Co (μg)	Cr (μg)	Cu (μg)	Na (μg)
0–30 Days	7.47	0.153	0.382	2.93	3.62
30–60 Days	2.03	0.362	0.333	4.34	4.38
60–120 Days	2.45	0.622	0.523	11.57	7.05
LSD ₅ % ^a	4.44	0.217	0.170	7.52	0.54

^a LSD₅ % least significant difference at $p < 0.05$

was limited to the soil surface, it caused a great increase in the DOC concentration.

- Flooding with the red mud suspension caused a four times greater increase in the water-soluble Mo concentration in the top soil layer after 30 days than the percolation of irrigation water through the red mud cover, but no differences could be observed in the total Mo concentration. In the case of both total and water-soluble Na and water-soluble Cu and Cr concentrations, greater increments were observed in the first scenario after 30 days.

3.4 Effluent Water

The effluent water was only analysed in the second scenario. The volume of effluent water was 736 ml at the end of the first 30-day period, 577 ml in the 30- to 60-day period and 740 ml in the 60- to 120-day period. The potentially toxic element concentrations of the effluent water did not change during the 120 days of the experiment and none of the element concentrations exceeded the limit values for underground water (6/2009 KvVM-EüM-FVM common order). At the same time, the Na concentration of the effluent increased.

Different results were obtained when the volume of the effluent water was considered. The leached amounts of Co, Cr and Cu increased significantly over the period of the experiment, while the amount of As leached from the column decreased (Table 8). These results indicated that over a period of 120 days red mud potentially toxic element content was not likely to pose a risk to the groundwater on the soil typical of the disaster area, but the Na content could cause problems for groundwater quality.

4 Conclusions

The model experiment showed that, despite the saturation of the soil, elements were leached into the soil from the red mud. Red mud caused changes in the particle size composition of the surface soil and increased the pH and the solubility of DOC. The red mud also affected the total Mo and Na concentrations of the top soil layer due to the leaching of red mud particles.

In spite of the shorter exposure time, flooding with highly caustic red mud suspension resulted in higher water-soluble element concentrations in the top soil than the percolation of irrigation water through the 10 cm thick red mud layer.

Based on the total and water-soluble element concentrations, only the top soil layer was affected by the insignificant leaching of potentially toxic elements. The element concentrations in the soil and the effluent water remained below the limit values laid down in the relevant quality standards. These results are favourable for the remediation and recultivation of the area.

The results affirmed the decisions outlined in the environmental clean-up plan for the disaster area, which envisaged the removal of the red mud layer from the soil surface. Even without consideration of fugitive dust lift-off after the drying of red mud, this intervention was definitely justified because Na content of red mud could pose the risk of salinization.

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