

# The Red Mud Accident in Ajka (Hungary): Plant Toxicity and Trace Metal Bioavailability in Red Mud Contaminated Soil

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 Supporting Information

**ABSTRACT:** The red mud accident of October 4, 2010, in Ajka (Hungary) contaminated a vast area with caustic, saline red mud (pH 12) that contains several toxic trace metals above soil limits. Red mud was characterized and its toxicity for plants was measured to evaluate the soil contamination risks. Red mud radioactivity (e.g., <sup>238</sup>U) is about 10-fold above soil background and previous assessments revealed that radiation risk is limited to indoor radon. The plant toxicity and trace metal availability was tested with mixtures of this red mud and a local noncontaminated soil up to a 16% dry weight fraction. Increasing red mud applications increased soil pH to maximally 8.3 and soil solution EC to 12 dS m<sup>-1</sup>. Shoot yield of barley seedlings was affected by 25% at 5% red mud in soil and above. Red mud increased shoot Cu, Cr, Fe, and Ni concentrations; however, none of these exceed toxic limits reported elsewhere. Moreover, NaOH amended reference treatments showed similar yield reductions and similar changes in shoot composition. Foliar diagnostics suggest that Na (>1% in affected plants) is the prime cause of growth effects in red mud and in corresponding NaOH amended soils. Shoot Cd and Pb concentrations decreased by increasing applications or were unaffected. Leaching amended soils (3 pore volumes) did not completely remove the Na injury, likely because soil structure was deteriorated. The foliar composition and the NaOH reference experiment allow concluding that the Na salinity, not the trace metal contamination, is the main concern for this red mud in soil.

## INTRODUCTION

On October 4, 2010, the western dam of the red mud reservoir of an alumina plant in Ajka (Hungary) collapsed. About 700,000 m<sup>3</sup> of the red mud/water mixture with a pH of about 12 was released from the reservoir to the valley of the Torna river, and flooded the lower parts of the city Devecser and villages Kolontár and Somlóvásárhely. The flood killed 10 persons, more than hundred persons were injured and some houses were irreversibly damaged. Along with this human tragedy, rivers and land have been contaminated with red mud. It is estimated that about 800 ha of agricultural land, of which 300 ha of grassland, 310 ha of tilled area, 150 ha of corn, 30 ha of alfalfa, and 15 ha of sorghum, have been covered by a red mud layer of 5–10 cm. The flood is the largest ecological disaster for Hungary ever (<http://redsludge.bm.hu>). Inhalation of resuspended red mud dust is a human health risk as reported in an accompanying paper.<sup>1</sup> This resuspension may be alleviated by incorporating the red mud in soil, potentially after removal of the largest deposits at the surface. An industrial accident of this size has never happened before with red mud. This study assesses the risk of incorporating the red mud on the quality of the local soil.

Red mud is the by-product of the alkaline aluminum (Al) extraction from bauxite ores via the Bayer process. For each ton of alumina (Al<sub>2</sub>O<sub>3</sub>) produced, 0.5–2 tons (on a dry weight basis)

of red mud is produced yielding an estimated global production of about 90 million tons of red mud per year.<sup>2</sup> Red mud is generally deposited in reservoirs or dumped in the sea. Red mud has an alkaline pH (9–12), contains residual minerals, such as hematite, goethite, boehmite, and quartz, and has a fine particle size distribution (mostly < 10 μm). The concentrations of residual minerals, trace elements (e.g., As, Cr, Cd, Ni, Pb, Zn), and radioactivity depend on the composition of the bauxite ore.<sup>3</sup> Red mud has a large acid neutralizing capacity (ANC) between pH 12 and 7, and this is primarily attributed to the dissolution of tricalciumaluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>) and Na,Al-silicate (NaAlSiO<sub>4</sub>) and to the neutralization of Al(OH)<sub>4</sub><sup>-</sup>, NaOH, and NaCO<sub>3</sub><sup>-</sup> in the pore water.<sup>4</sup>

The high sodium (Na) content and fine structure of the red mud deteriorate soil structure. In addition, the salinity and alkalinity of the red mud can affect plant growth on the short term. These factors primarily determine the adverse effect of red mud on soil quality. Leaching by rainwater decreases salinity and the pH generally decreases upon storage,<sup>5,6</sup> likely because of

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carbonation. The presence of high-soluble Al concentrations in the alkaline red mud additionally affects plant growth as confirmed in independent solution culture studies at alkaline pH.<sup>7</sup> Field trials have shown that bauxite residues can be vegetated by a combination of amendments with sand, compost, and gypsum, leaching and equilibration, and the use of salt or Al tolerant plants.<sup>8,9</sup> Gypsum applications improve the red mud structure and gradually reduce the red mud pH to about pH = 8, likely due to the formation of calcite.<sup>10–12</sup> Revegetation of red mud accelerates the pH neutralization, probably because of enhanced carbonation in rooted zones.

Red mud may contain trace metals at concentrations above regulatory soil limits and this has created public concern in the Hungarian accident. However, several studies have shown successful effects of red mud application for remediation of trace metal contaminated soil.<sup>13–15</sup> Typical soil applications are 1–5% (w w<sup>-1</sup>). The remediation successes are related to the adsorption of toxic metals on the Fe and Al oxyhydroxides in the red mud.<sup>16–18</sup> In addition, red mud acts as a liming material by which metals are increasingly adsorbed or precipitated in soil.<sup>16</sup> Acidification of red mud amended metal contaminated soils showed that Cu, Zn, and Cd were irreversibly fixed by red mud application to soil, likely because of solid-phase diffusion or migration into micropores.<sup>17</sup> Red mud has also found application to adsorb P and reduce P emission to sensitive waterways<sup>19</sup> and has been successfully used as soil liming material at doses of 40 ton ha<sup>-1</sup> (about 5% w w<sup>-1</sup>) in Australian acid pastures.<sup>20</sup>

The direct toxicity of red mud in soil is surprisingly rarely assessed in soil–red mud mixtures, likely because an acute spill as in Hungary is unprecedented. It is predictable that adverse effects depend on the final salinity of the mixture and on the soil cation exchange capacity (CEC) as this determines the exchangeable sodium percentage (ESP) at a given red mud dose. Soil structure decreases in the so-called sodic soils at ESP > 15%.<sup>21</sup> In addition, soil pH buffer capacity and the acid neutralizing capacity of the red mud determines final soil pH. Pot trial studies with mixtures of red mud and artificial substrates, that is, potting mixture, peat, or perlite revealed only moderate toxicity with growth inhibition only at 100 g red mud dm<sup>-3</sup> substrate (perlite) to 1000 g red mud dm<sup>-3</sup> substrate (potting mixture, peat).<sup>22</sup> The lower toxicity in the peat compared to the perlite was attributed to the larger pH buffer capacity of the peat.

The objective of this study was to monitor the short and potential long-term effects of the red mud from the Hungarian accident on soil quality. More specifically, effects of red mud on plant growth and plant composition was analyzed in mixtures of soil and red mud. An uncontaminated soil near the red mud contaminated area was mixed with increasing red mud doses with or without leaching the mixtures with artificial rainwater. The trace metal uptake in seedlings was assessed as a surrogate for crop uptake in the field. It was hypothesized that plant growth is inhibited by increasing red mud doses because of (i) alkalinity, (ii) salt (Na) toxicity, or (iii) trace metal toxicity. A NaOH reference treatment was included to identify the contribution of trace metals to the toxicity. Leaching the soil mixtures was included to simulate the effect of rain on removing the salt toxicity on the long term.

## MATERIALS AND METHODS

**Soil and Red Mud Sampling and Soil Treatments.** Red mud (RM) was sampled on 15 October 2010 in flooded grassland in

Devecser (Hungary; 17°6′13″ N, 17°26′56″ E), and uncontaminated topsoil (0–30 cm) was sampled in a nonflooded grassland nearby (17°6′25″ N, 17°25′00″ E). Two additional red mud samples were collected in Somlóvásárhely. Red mud and soil were stored in closed plastic containers. Experiments started 4 days after sampling.

Uncontaminated soil was sieved (<8 mm) to remove stones and plant residues, and air-dried. The red mud of Devecser is a slurry (44% dry weight) and was mixed into the soil to final weight fractions of 0, 0.3, 1, 3, 10, and 30% wet red mud in air-dry soil corresponding to 0, 0.1, 0.5, 1.4, 4.9 and 16.5% oven dry weight fractions. Below, only reference is made to dry weight fractions. Treatments were divided in two series: one unleached series and one series leached with three pore volumes of artificial rainwater. Leaching was performed as described by.<sup>23</sup> In short, the soils were added to plastic pots with a perforated bottom that was covered by a filter cloth (mesh size 140–150 μm). The pots were put in a bucket with artificial rainwater (ARW; 5 × 10<sup>-4</sup> M CaCl<sub>2</sub>·2H<sub>2</sub>O, 5 × 10<sup>-4</sup> M Ca(NO<sub>3</sub>)<sub>2</sub>, 5 × 10<sup>-4</sup> M MgCl<sub>2</sub>, 10<sup>-4</sup> M Na<sub>2</sub>SO<sub>4</sub>, 10<sup>-4</sup> M KCl; pH 5.9), and water was added to the bucket until the water level in the pot was about 1 cm above the soil surface. The water saturated soils were left to equilibrate overnight and pore volume was subsequently determined as the weight difference of dry soil and saturated soil. The appropriate amount of ARW was poured gently over the soil surface and the soil was allowed to drain. Leachate volume was monitored and a subsample was membrane filtered (0.45 μm) and acidified (100 μL HNO<sub>3</sub> 5 M per 5 mL sample) before analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Perkin-Elmer Optima 3300 DV). The water saturated soils were subsequently air dried.

The NaOH reference treatments were prepared by mixing soils with a 1 M NaOH solution at 12, 21, and 49 mmol NaOH kg<sup>-1</sup> soil dry weight. These three doses were selected to mimic final soil pH of the three highest red mud doses based on soil titration data. The total Na application at the highest red mud dose, that is, real total Na in the red mud multiplied with red mud weight fraction, is equivalent to 300 mmol Na kg<sup>-1</sup> soil dry weight. This means that the NaOH reference treatment does not match the total Na dose as in the red mud dose range. However, not all Na in the red mud is exchangeable as it is present in minerals such as cancrinite. Soil CaCl<sub>2</sub> extracts of soil–red mud mixtures (see Results) show that exchangeable Na in the NaOH amended soils was 60–70% of corresponding red mud amended soils. Along the same lines, plant Na (see Results) concentrations suggest that the available Na in NaOH dosed soils was 75% of the corresponding red mud amended soils.

Nutrients were added to all soil treatments at (100 mg N, 50 mg P and 240 mg K kg<sup>-1</sup> soil dry weight) through KH<sub>2</sub>PO<sub>4</sub> and KNO<sub>3</sub> stock solutions. Distilled water was added to obtain a final soil moisture content of 25%.

**Soil and Red Mud Characterization.** Oven-dried (105 °C) and crushed soil and red mud samples were analyzed in parallel. Soil and red mud digests were made to obtain real total (concentrated HNO<sub>3</sub>, HClO<sub>4</sub> and HF followed by dissolution in HCl 2.5 M) and aqua regia soluble (concentrated HCl and HNO<sub>3</sub>) elements. Each sample was digested in duplicate. The elements in digests were determined by ICP-OES. Certified reference materials BCR-142R (uncontaminated light sandy soil, Institute for Reference Material Measurement, Joint Research Center, European Commission) and BCR-143R (sewage sludge contaminated soil, Institute for Reference Material

Table 1. Selected Properties of Red Mud and Uncontaminated Soil<sup>a</sup>

	pH <sup>b</sup>	EC <sup>c</sup> (dS m <sup>-1</sup> )	EC <sup>d</sup> (dS m <sup>-1</sup> )	DOC (mg L <sup>-1</sup> )	radioactivity (Bq kg <sup>-1</sup> )				CEC (mmol <sub>c</sub> kg <sup>-1</sup> )	texture (%)			pH buffer capacity (pH range given) (mmol <sub>c</sub> kg <sup>-1</sup> )
					<sup>238</sup> U	<sup>232</sup> Th	<sup>137</sup> Cs	<sup>40</sup> K		sand (>63 m)	silt	clay	
red mud	12	20.2	2.4	36.2	550	640	5.5	250	nd	nd	nd	nd	520 (pH 12–7.0)
soil	6.8	-	0.05	3.1	34	49	13	540	182	34	33	25	160 (pH 7.2–11)

<sup>a</sup> Soil pH, dissolved organic carbon (DOC), acid neutralizing capacity (ANC; 2 h equilibration), and radioactivity were determined on wet red mud (44% dry weight) and moist soil (80% dry weight). Cation exchange capacity (CEC) and texture were measured on air-dried samples. All values (except EC and DOC) are expressed on oven dry weight basis. nd not determined. <sup>b</sup> In water at 1:1 solid/liquid ratio (RM) or in 10<sup>-2</sup> M CaCl<sub>2</sub> at 1:10 ratio (soil). <sup>c</sup> EC of the liquid red mud phase. <sup>d</sup> EC of 1:5 red mud/water or soil/water extraction.

Measurement, Joint Research Center, European Commission) were included in duplicate for both analyses, and GBW7311 (sediment, National Research Center for Certified Reference Materials, China) was included in duplicate for real total analysis. Real total analyses (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) were all within 15% of the certified value except for Co (145%) and Ni (142%) for BCR-142R, Co (127%) for BCR-143R, and Ni (185%) and P (154%) for GBW7311. Aqua regia digests were all within 15% of the certified values. The determination of Hg in the red mud was directly performed on the wet sample with thermal decomposition–amalgamation and atomic absorption spectroscopy (Milestone, DMA 80). The determination of hexavalent chromium was performed on an alkaline extract (20 mM NaHCO<sub>3</sub>) of the wet sample with ion chromatography with spectrophotometric detection (IC, Dionex, DX-120). Red mud and soil-red mud mixtures were extracted with CaCl<sub>2</sub> 0.01 M (2.5 g soil or red mud fresh weight; 25 mL solution) and shaken end-over-end for 2 h. Soils were extracted after plant growth and 2 pots were sampled per treatment, each extracted in duplicate. One replicate was allowed to settle for 0.5 h and soil pH was measured. The other replicate was 0.45 μm filtered, and the dissolved organic carbon (DOC) content (catalytic combustion with infrared detection; Multi N/C 2100, AnalyticJena) and soluble metal concentrations (acidified subsample; ICP-OES) were determined.

Radioactivity was determined on fresh red mud and soil with a Canberra HPGe detector with 10 000 s measuring time. Peaks of <sup>137</sup>Cs, <sup>40</sup>K, <sup>228</sup>Ac (911 keV for <sup>232</sup>Th-series), and <sup>214</sup>Bi (609 keV for <sup>238</sup>U-series) were considered.

Soil pH buffer capacity was determined by gradually adding 1 M NaOH to 20 g soil in 25 mL CaCl<sub>2</sub> 10<sup>-3</sup> M and shaken end-over-end for 2 h to equilibrate. The short-term red mud acid neutralizing capacity (ANC) was determined by amending a 1:1 volume ratio of red mud and 10<sup>-3</sup> M CaCl<sub>2</sub> with various aliquots of 1 M HCl and shaking end-over-end for 2 h. The red mud ANC was defined as the amount of acid required (mol kg<sup>-1</sup>) to reduce the pH to 7.0. The silver-thiourea method<sup>24</sup> was used to measure the cation exchange capacity (CEC) at soil pH, and silver concentrations in the extracts were determined by ICP-OES. Particle size distribution was measured according to ISO 11277 (E) guidelines.

**Plant Assays.** The barley root elongation assay ISO 11269-1 used spring barley (*Hordeum vulgare* L. cv. Mauritia) as test species. The soil was divided in 75 g (wet weight basis) subsamples and loaded in cylindrical pots of 2.8 cm in diameter and 11 cm height. Three replicates were used per treatment. Barley seeds were pregerminated at 20 °C in darkness. Three seeds with a radicle length lower than 2 mm were planted in each pot approximately 10 mm beneath the soil surface. Planted

pots were placed in a growth cabinet (Weiss, 18' SP/+5 Ju-Pa; growing conditions: 12 h/12 h light/darkness cycle, 20 °C during light hours and 16 °C during night time, 70% humidity). Light intensity at canopy height was 650 μmol photons m<sup>-2</sup> s<sup>-1</sup>. The soil surface was covered with a thin layer of polyethylene beads to prevent excessive moisture loss. After 4 days of growth, soil was gently taken out of the pots. Shoot roots were washed preventing root damage, and the length of the longest root per seedling was measured. The end point of this assay is the mean length of the longest roots per pot.

The barley plant growth assay ISO 11269-2 was performed using spring barley (*Hordeum vulgare* L. cv. Mauritia) as test species. The soil was divided in 500 g (wet weight basis) sub samples and loaded in cylindrical pots with a top diameter of 95 mm of which the bottom was perforated and covered with a filter cloth (mesh size 140–150 μm). Four replicates were used per treatment. Twenty seeds were uniformly sown 0.5–1 cm under the soil surface. Planted pots were placed in a growth cabinet with plant growth conditions as mentioned above. The soil surface was covered with a thin layer of polyethylene beads to prevent excessive moisture loss. Water loss of the pots was restored daily with deionized water. Five days after 50% of the control seedlings emerged, emergence of all pots was assessed and the seedlings were thinned to five uniformly distributed seedlings per pot. Plants were harvested 14 days after thinning (i.e., 19 days after emergence of the control seedlings) by cutting the above ground part of the plant and the fresh shoot yield per pot was determined. Plants were dried at 65 °C for 36 h and the dry plant yield per pot was determined. Plant material was crushed, digested (50–200 mg plant material in 2 mL boiling 65% HNO<sub>3</sub>) and analyzed for total metal content (ICP-OES). Three reference materials were included: BCR-100 (beech leaves, Institute for Reference Materials and Measurements, Joint Research Center, European Commission), BCR-281 (rye grass, Institute for Reference Materials and Measurements, Joint Research Center, European Commission), and NIST SRM-1573a (tomato leaves, National Institute of Standards and Technology, Gaithersburg, Germany) to have at least two certified values per element. Recoveries differed less than 20% from the certified values except for Ca (122% for NIST SRM1573a and 126% for BCR-100) and Al (70% for BCR-100).

## RESULTS AND DISCUSSION

**Red Mud Composition and Its Reaction in Soil.** Selected properties of red mud and soil are given in Tables 1 and 2. The wet red mud is alkaline (pH 12) and has 4.3% Na, typical for bauxite residues of the Bayer process.<sup>3</sup> The mineralogy of this red mud is dominated by hematite, cancrinite calcite, and hydrogarnet.<sup>1</sup>

**Table 2. Elemental Composition of Red Mud and Soil Determined as Real Totals, Aqua Regia Soluble Elements, and 0.01 M CaCl<sub>2</sub> Extractable Elements<sup>a</sup>**

	real total (%)		aqua regia (%)			0.01 M CaCl <sub>2</sub> extracts (mg L <sup>-1</sup> )			
	RM	soil	RM	soil	limits	RM	soil	soil +16.5% RM without leaching	soil +16.5% RM with leaching
Al	7.5	5.5	nd	nd		36	0.22	0.12	0.10
Ca	6.0	0.76	5.3	0.53		190	270	210	220
Fe	20	2.4	nd	nd		<0.002	0.1	<0.002	<0.002
K	0.42	1.5	0.19	0.44		15	4.6	7.3	8.8
Mg	0.46	0.63	nd	nd		<0.008	19	8.7	7.7
Mn	0.30	0.079	nd	nd		<0.001	0.004	<0.001	<0.001
Na	4.3	0.57	3.8	0.080		400	2.1	140	110
P	0.095	0.072	nd	nd		0.06	0.10	0.03	0.03
S	0.30	0.034	nd	nd		32	0.51	10	2.2
Ti	2.3	0.24	nd	nd		nd	nd	nd	nd

	real total (mg kg <sup>-1</sup> )		aqua regia (mg kg <sup>-1</sup> )			0.01 M CaCl <sub>2</sub> extracts (μg L <sup>-1</sup> )			
	RM	soil	RM	soil	limits	RM	soil	soil +16.5% RM without leaching	soil +16.5% RM with leaching
As <sup>b</sup>	140	8.8	5.0	7.1	15	20	14	16	14
Ba	100	340	nd	nd	250	nd	nd	nd	nd
Cd	nd	nd	1.3	0.23	1.0	<1.0	<1.0	<1.0	<1.0
Co	98	14	64	13	30	<1.0	<1.0	<1.0	<1.0
Cr	620	64	560	37	75	3.9	<1.0	<1.0	<1.0
Cr(VI) <sup>c</sup>	<0.1	nd	nd	nd		nd	nd	nd	nd
Cu	52	19	52	19	75	210	12	<3.0	<3.0
Hg	1.7	nd	nd	nd	0.50	nd	nd	nd	nd
Ni	290	39	270	32	40	2.8	16	1	1
Pb	160	26	160	18	100	<5.0	<5.0	<5.0	<5.0
V	870	77	nd	nd		nd	nd	nd	nd
Zn	130	61	110	55	200	<1.0	17	14	26
pH						11	6.8	8.3	8.3
DOC <sup>d</sup>						36	3.1	3	3.7

<sup>a</sup> Concentrations are all oven dry weight based, except CaCl<sub>2</sub> extract data that are expressed on a solution volume basis. Hungarian soil limits for toxic trace metals<sup>32</sup> are added. <sup>b</sup> Indicative value, see Results and Discussion section. <sup>c</sup> Alkaline extract. <sup>d</sup> In mg L<sup>-1</sup>.

The liquid phase has an EC of 20 dS m<sup>-1</sup>, equivalent to about 0.2 mol<sub>c</sub> L<sup>-1</sup>, and contains about 0.015 M SO<sub>4</sub><sup>2-</sup> (details not shown), the remainder being CO<sub>3</sub><sup>2-</sup>, OH<sup>-</sup>, and Al(OH)<sub>4</sub><sup>-</sup>, since Cl<sup>-</sup>, HPO<sub>4</sub><sup>-</sup> or NO<sub>3</sub><sup>-</sup> were all <0.001 M. The ANC (2 h, pH 7.0) between pH 12–7.0 is 500 mmol kg<sup>-1</sup>; this ANC is about a factor 2 below long-term values (>30 days) reported elsewhere, likely related to the difference in equilibration time used.<sup>4</sup> The soil and red mud titration curves, with 2 h equilibration time, predict that the 16.5% red mud dose raises soil pH to 7.9, in close agreement with the observed pH 8.3 of this mixture after 3 weeks plant growth.

Aqua regia soluble trace metal concentrations in red mud are above the Hungarian soil limits for Co, Cr, Ni, and Pb. At the 4.9% and 16.5% red mud dose, *aqua regia* soluble trace metal concentrations exceed the Hungarian limits for Ni and only at 16.5% for Cr. No detectable Cr (VI) was present. Trace metals of the two other red mud samples differed not more than 20% from the values reported in Table 2. The University of Pannonia sampled 14 red mud samples directly after the accident and reported that trace metal concentrations varied within a factor 2 from the mean value except for Ni in 1 sample (details not shown).

Real total elements in the red mud are maximally 2-fold above corresponding *aqua regia* soluble ones except for As (Table 2).

No certified soil standards were used for *aqua regia* soluble As, but PACS2 (marine sediment, National Research Council of Canada) was used as an alternative reference sample for *aqua regia* soluble As. The recovery was 80% of the certified real total value. Comparing the real total and *aqua regia* results suggests that As is poorly dissolved by *aqua regia* digestion from the red mud and strongly occluded in the red mud matrix as also suggested by the trace As (20 μg L<sup>-1</sup>) in the red mud CaCl<sub>2</sub> extracts. The CaCl<sub>2</sub> extractable elements (dissolved metals) in red mud were logically large for Al at that pH and were large for Na and K. The red mud pH in CaCl<sub>2</sub> (11) was lower than the pH of the liquid phase of red mud (12), likely because of calcite precipitation in the extracts. Trace metal concentrations in the CaCl<sub>2</sub> extracts of red mud were low, except Cu that might be solubilized as Cu(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup> or as a complex with DOC. This already suggests that most trace metals and As were strongly fixed in the red mud as suggested before.<sup>17</sup>

Red mud application to soil increased the CaCl<sub>2</sub> extractable Na 70-fold compared to the control, but did not affect any CaCl<sub>2</sub> extractable trace metal except Fe (Supporting Information Table SI 1). These trends in composition were comparable to those of NaOH amended soils (Supporting Information Table SI 1)

**Table 3. Root Length and Yield of Barley Shoots (Dry Matter Yield) Grown on Soil with Increasing Red Mud Doses before or after Soil Leaching with Artificial Rain Water<sup>a</sup>**

red mud dose (%)	root elongation (mm)		barley yield (g pot <sup>-1</sup> )	
	without leaching	with leaching	without leaching	with leaching
0	6.6 ab	4.9 b	0.65 b	0.51 a
0.1	8.2 a	4.7 b	0.71 b	0.37 b
0.5	6.5 b	6.8 a	0.83 a	0.52 a
1.4	7.6 ab	7.1 a	0.63 b	0.49 a
4.9	7.5 ab	7.3 a	0.48 c	0.35 b
16.5	6.2 b	1.0 c	0.50 c	0.37 b
effect dose		***		***
leaching		***		***
dose × leaching		***		**

NaOH dose (mmol kg <sup>-1</sup> )	root elongation (mm)		barley yield (g pot <sup>-1</sup> )	
	without leaching	with leaching	without leaching	with leaching
0	6.6 a	4.9 b	0.65 a	0.51 a
12	5.2 a	4.7 b	0.49 bc	0.37 b
21	6.4 a	6.8 a	0.44 c	0.52 a
49	5.3 a	7.1 a	0.54 b	0.49 a

<sup>a</sup> A NaOH reference treatment (no red mud application) was included. Significant differences of means within the same columns are indicated (Duncan test; different letters indicate significantly different values at  $p < 0.05$ ). Significance of effects of two-way ANOVA are added ( $p < 0.001$ , \*\*\*;  $p < 0.01$ , \*\*).

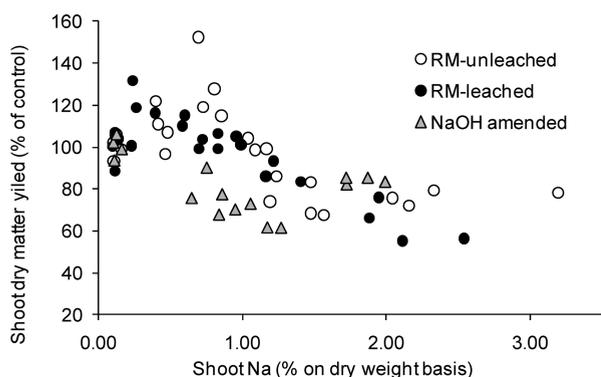
suggesting that increased Na and increased pH were the main factors changing soil solution chemistry in red mud amended soils. Extractable Al concentration in red mud sharply decreased when mixed in soils as a result of the pH neutralization (Table 2). Trace metal concentrations in 0.01 M CaCl<sub>2</sub> soil extracts may underestimate in situ (soil solution) concentration due to a lower concentration of dissolved organic matter.<sup>25</sup> The DOC concentrations in CaCl<sub>2</sub> extracts were not only lower than in corresponding in situ soil solutions due to dilution but, in Na dominated solution, also due to added Ca<sup>2+</sup> that reduces organic matter solubility.<sup>26</sup> Indeed, the DOC concentrations in soil percolates collected during leaching soils with artificial rainwater (not shown) increased from 25 to 180 mg C L<sup>-1</sup> with increasing red mud dose and these leachates were more strongly yellow colored, in contrast with the CaCl<sub>2</sub> soil extracts (Supporting Information, Table SI 1). Analysis of the percolates confirmed that the red mud application increased the mobility of Cu, Fe, Mn, and Cr by up to a factor 10, that is, trace metals with a DOC controlled solubility between pH 7–8. The CaCl<sub>2</sub> extracts allow estimating the ESP of soils (Supporting Information, Table SI 1). The ESP at the soil moisture content in planted pots was derived with the Na, Ca, and Mg concentrations in the 0.01 M CaCl<sub>2</sub> soil extracts and the Gapon cation exchange equation<sup>21</sup> after correcting for the dilution factor and the Ca added with the CaCl<sub>2</sub> extract. The ESP in the pots increased from <1% at zero loading to 12% at the 4.9% red mud dose and 30% at the largest dose, that is, soil structural problems (ESP > 15%) are predicted from the ESP as also visually observed. This likely explains the unsuccessful effect of leaching on reducing soil sodicity. Analyses of leachates showed that maximally 7 mmol Na kg<sup>-1</sup> (dry) soil was removed by leaching, that is, only about 10% of the exchangeable Na in the soil mixtures (data not shown). The CaCl<sub>2</sub> soil extracts and the ion exchange model predict that soil solution Na concentrations at the highest red mud dose decreased from 0.06 M before leaching to about 0.04 M after 3 pore

volumes leaching. Most likely, the poor soil structure in the amended soils did not allow passage of water through the entire pore volume.

The <sup>40</sup>K and <sup>137</sup>Cs activity concentrations in the red mud are about 4-times lower than in soil (Table 1), roughly in proportion to the total elemental K (Table 2). The <sup>238</sup>U and <sup>232</sup>Th activities, here measured as <sup>214</sup>Bi and <sup>228</sup>Ac gamma activities, are 5–10-fold above the soil background values and correspond to activities detected in several Hungarian red mud samples (200–600 Bq kg<sup>-1</sup> for each isotope). The EU project INTAILRISK has evaluated radiation risks from red mud in Hungary and concluded that the main (but limited) contribution to the dose received by the surrounding population could come from indoor radon.<sup>27</sup> Radon concentrations in the gas phase of Hungarian red mud deposits may reach 300 kBq m<sup>-3</sup>, about 10-fold background values.<sup>28</sup> A mixture of red mud with normal soil increases the radon concentration in the soil, yielding an increased risk from indoor radon exposure. This suggests that buildings on the contaminated land may require an assessment of radon inhalation risks, that is, indoor radon measurements.

**Plant Growth and Composition.** Low red mud doses (<1%) stimulated the barley root elongation and barley plant yield for unknown reasons (Table 3). At the 4.9% and 16.9% red mud doses, barley plant yield decreased significantly and effects did not disappear with leaching (Table 3). Unexpectedly, barley root elongation was almost completely inhibited at the largest red mud dose after leaching. A two-way ANOVA revealed a significant interaction between leaching and red mud dose indicating that high doses combined with leaching have strongest effects on plant yield. Leaching the soils at high red mud doses deteriorated soil structure and created local anaerobic zones as witnessed by blue-gray spots in soil aggregates of planted soils.

Trace element concentrations in plant shoots (Cu, Cr, Ni, B and Fe) increased significantly with increasing red mud dose (Supporting Information Table SI 2), but such increases are also



**Figure 1.** Shoot Na concentrations of barley grown in red mud (RM) amended soils, with or without leaching after amendment, and in NaOH amended soils. Literature (NaCl dosed soils) suggests 0.8% Na as the toxic threshold. Linear regression analysis on all data reveal a significant trend ( $R^2 = 0.38$ ,  $p < 0.001$ ).

found in NaOH dosed soils, except for B. Shoot Cd and Pb concentrations either decreased with increasing red mud dose (Supporting Information Figure SI 1) or were unaffected (Supporting Information Table SI 2), which may reduce concerns regarding food chain risk of these elements if crops are grown in the red mud contaminated soils. Proper matrix matched standards (high Na) were included during ICP analysis for Cd and Pb to exclude analytical effects in these trends.

None of the shoot concentrations of Al, Cd, Cr, Cu, Mn, Ni, and Zn were above foliar concentrations toxic to plants.<sup>29</sup> This suggests that trace elements in red mud are unlikely the reason for growth inhibition effects. Increased shoot concentrations of Cu, Cr, Ni and Fe in red mud or NaOH amended soils may reflect increased mobility by DOC in these soils as suggested by composition of soil percolates (see above). This means that the increased soil pH in either treatment did not induce micronutrient deficiency. Shoot P decreased with increasing red mud and not with increasing NaOH (Supporting Information Table SI 2) suggesting that sorption reactions on oxyhydroxides are involved. Shoot P decreased below the 0.2% P deficiency limit<sup>30</sup> in leached soils only, suggesting that P deficiency may be a long-term side effect of the red mud contamination. The red mud and NaOH dosing increased shoot Na and decreased shoot Ca and Mg (Supporting Information Table SI 2). Barley is classified as relatively salt tolerant compared to several other grasses such as wheat. Salinity responses of barley in NaCl or CaCl<sub>2</sub> dosed soils showed about 25% shoot yield reduction at a soil solution EC (at field capacity) of about 10 dS m<sup>-1</sup>.<sup>31</sup> The EC of the red mud is 20 dS m<sup>-1</sup>, and a simple dilution model predicts a pore water EC of 16 dS m<sup>-1</sup> at the largest red mud dose if no precipitates are formed. The electrical conductivity (EC) measured in 1:5 soil extracts increased from 0.05 to 0.6 dS m<sup>-1</sup> (details not shown) which, corrected for dilution suggests a soil solution EC increasing up to 12 dS m<sup>-1</sup>, that is, salinity stress is most likely affecting barley yield. Shoot Na concentrations (Supporting Information Table SI 2) in red mud or NaOH dosed soils are 0.11–2.4% dry weight. Barley grown in NaCl dosed soils showed that 1% Na in shoot results in 20–50% shoot yield reduction depending on variety<sup>31</sup> while other references denote 0.8% as the toxic Na threshold in whole shoots.<sup>30</sup> The yield reduction of all red mud and NaOH treatments correlated well with shoot Na (Figure 1) suggesting that the Na salt injury is the prime reason for toxic effects. The hint of largest toxicity in the leached soils (Figure 1) may indicate

that adverse effects of soil structure on plant growth increase with leaching because of mixing and breaking of aggregates.

**Implications for Soil Recovery and Remediation.** Overall, yield data and plant composition suggest that salt injury is the main concern for red mud contaminated soils. Trace metal deficiency due to the pH increase is not a factor involved at the short-term, while incipient P deficiency suggests that P fertilization may be required. Actions must be taken to remove the salinity in soils contaminated by red mud. Natural leaching will do this only gradually as suggested by the weak effects of leaching on extractable Na or plant Na in our trials. Gypsum application to restore soil structure is the recommended remediation as shown in several red mud revegetation tests.<sup>8</sup> Gypsum application temporarily increases Na<sub>2</sub>SO<sub>4</sub> salinity, but a better soil structure will accelerate the Na leaching and a concomitant reduction of the ESP. Soil pH is likely to decrease by carbonation with increasing aging, as also confirmed in long-term data of revegetated red mud impoundments in the field.<sup>6</sup> No data are available to suggest that the fixed metals in the red mud may be released on the long-term, even no release of these fixed metals has been found under acidifying conditions.<sup>17</sup> A precautionary approach may be to monitor crop composition in the first years after red mud incorporation to remove all concerns.

## ■ ASSOCIATED CONTENT

**Supporting Information.** The composition of the soil CaCl<sub>2</sub> extracts and the plant composition in all treated soils. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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