Trace and rare earth element dispersal downstream of the Ajka red mud spill, Hungary

Will M. Mayes[1], Adam P. Jarvis[2], Ian T. Burke[3], Melanie Walton[1], Katalin Gruiz[4]

[1]*Centre for Environmental and Marine Sciences, University of Hull,YO11 3AZ, UK, w.mayes@hull.ac.uk;*
[2]*School of Civil Engineering and Geosciences, Newcastle University, NE1 7RU, UK a.p.jarvis@ncl.ac.uk;*
[3]*School of Earth and Environment, University of Leeds, LS2 9JT, UK, i.t.burke@leeds.ac.uk;*
[4]*Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, 1111 Budapest, St. Gellert sq. 4, Hungary, gruiz@mail.bme.hu.*

Abstract Between 600,000—700,000m^3 of caustic (pH>13) red mud suspension were released from the Ajkai Timfoldgyar Zrt alumina plant on the 4th October 2010. This study highlights the dispersal of key red mud-derived contaminants in downstream fluvial sediments from surveys undertaken within two months of the spill. Source samples contain abundant V (>1000mg/kg), Cr (>800mg/kg), Ni (>250mg/kg) and As (>80mg/kg). Red mud-affected samples are also particularly enriched above reference sites in rare earth elements which include Ce (>400mg/kg), La, Nd and Pr (all >100mg/kg). The combined signal of these provides a useful tracer of red mud dispersion in the 3076km^2 Marcal catchment. A comparison of the bulk physico-chemical properties of the spill material at Ajka is made with other notable tailings failures elsewhere. The implications for system management and recovery along with the effects of emergency management (e.g. gypsum dosing) on metal availability downstream of the site are also discussed.

Key Words red mud, bauxite processing residue, rare earth, trace metal, alkaline

Introduction

Up to 120 million tonnes of bauxite processing residue (the fine fraction of which is referred to as red mud) are produced globally each year (Power *et al.* 2009). The storage or disposal of red mud provides challenges because of its caustic nature (alkalinity >20,000 mg/L as equivalent $CaCO_3$), high sodium concentration (>50g/kg) and fine grained nature (Johnston *et al.* 2010). While multiple afteruses for red mud have been developed in recent years (e.g. Somlai *et al.* 2008; Zijlstra *et al.* 2010), these do not yet prevent disposal of large volumes of red mud via conventional means (e.g. stockpiling, drying and revegetation: Courtney *et al.* 2005). The failure of the north-western corner of Cell × of the Ajkai Timfoldgyar Zrt alumina plant red mud depository in October 2010, led to the catastrophic release of caustic red mud suspension which engulfed the downstream villages of Kolontár, Devecser and Somlóvásàrhely in western Hungary. While there have been other examples of sudden release of caustic wastes to river systems, notably at fly ash disposal ponds on the Clinch River, Virginia, USA (pH 12.0—12.7: Cairns *et al.* 1972) and at the Sebastião das Águas Claras red mud disposal site upstream of Belo Horizonte in Brazil (Younger *et al.* 2002), the disaster at Ajka is unprecedented given both the scale of the release and the type of material involved. The disaster response has focussed on removal of red mud from residential areas and in some cases the ploughing of thin surface deposits into underlying soils to minimise dust-blow hazards (Gruiz 2010; Gelenscer *et al.* 2011). Water management has seen ongoing acid dosing of waters in addition to gypsum dosing throughout the Torna Creek and the Marcal and Rába rivers (Gruiz 2010).

Initial scientific studies from the site have suggested that salinity as opposed to trace element enrichment is the key constraint to plant growth on red mud affected floodplain sediments (Ruyters *et al.* 2011), while the hazard to human health from fugitive red mud dusts has been suggested to be equivalent to, or less than that of urban dusts (Gelenscer *et al.* 2010). Preliminary studies on the fluvial sediment contamination have highlighted the abundance of vanadium, chromium, nickel and arsenic from the red mud spill (Mayes *et al.* 2011). This study provides a broader overview of contaminant dispersal through the Torna Creek and Marcal River after the spill at Ajka. Surveys were undertaken within two months of the spill and detail physico-chemical characteristics of the spill material which are contrasted with reports from other tailings failures worldwide. The implications for management and recovery of the Marcal river are discussed.

Methods

Study site

Sample locations along the course of the Torna Creek, Marcal, Rába and Mosoni-Duna rivers are shown in Figure 1. Land cover across the catchments is dominated by agriculture, with principal urban areas at Ajka, Pápa, and towards the confluence with the Mosoni-Duna around the spa town of Győr. Bedrock geology in the upper catchment

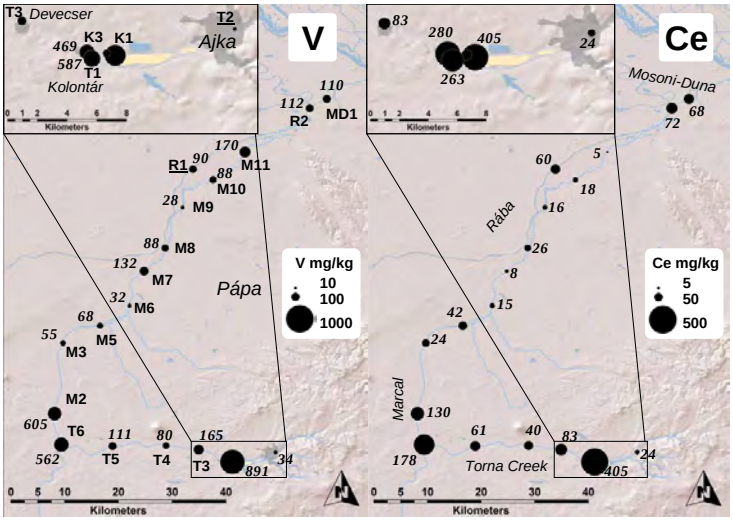

Figure 1 *Distribution of V (left image) and Ce (right) downstream of the Ajka spill (Nov 11). Each sample station shows mean of 3 samples. Selected concentrations (mg/kg) annotated next to proportional symbols.*

is dominated by dolomites and limestones of Triassic age which lie beneath a sequence of fluvial marls, slates and interbedded sands of Miocene age (Reeves *et al.* 2011). Superficial Pleistocene and Holocene deposits consist of alluvial silts and sands along the valley floor of the Torna Creek (Reeves *et al.* 2011). Relief downstream of the spill site is generally slight, with peak elevation (431.8m AOD) associated with a conical basaltic intrusion north of Somlóvásàrhely. The Torna, Marcal and Rába are all extensively channelised with levees minimising floodplain extent.

Experimental

Triplicate bulk (≈ 500g) sediment samples were collected by aggregating three randomly collected sub-samples from a 12m^2 area of stream bed at each sample station. Spot samples of transported red mud from floodplain deposits at Somlóvásàrhely, flyash (that formed the dam wall), stock-piled gypsum and gypsum-affected fluvial sediments were also taken at selected sites. Sediments were homogenized, air-dried, disaggregated and sieved (2mm aperture) in the laboratory prior to microwave-assisted total digestion (aqua regia and HF) following USEPA (1996). Elemental concentrations in digests were analysed using a Perkin Elmer Elan DRCII inductively Coupled Plasma-Mass Spectrometer (ICP-MS; As, Cr and Mo) and an Optima 5300 DV ICP-OES (all other elements). Principal Component Analysis (PCA) was undertaken on standardized sediment element concentration data using Minitab v15.

Results and Discussion

Red mud physico-chemical composition

Table 1 compares the key chemical characteristics of spill material at Ajka (taken from sample location K1 and reference sites) with those from recent major tailings failures elsewhere. The red mud samples at Ajka are enriched in a range of trace elements (As, Co, Cr, Mo, Ni and V in particular) and rare earth elements (REE) above reference sites. REE have been widely documented to be enriched in red mud (Akinci and Artur 2008) and 15 of the 17 REE were found above detection limits in the Ajka spill material with Ce being the most abundant followed by La then Nd and Pr (Table 2). Although relatively little data exists on the toxicity of REE, in situations where excess REE are released to the environment, their low solubility usually results in widespread adsorption to sediments and limits potential bioavailability (Yang *et al.* 1999).

The pH of the spill material at Ajka is a particular characteristic of the red mud. While caustic industrial wastes are produced from numerous industries (e.g. steel-making, cement production, coal-fired electricity generation, paper mills), catastrophic spills have been rarely documented. The pH of the material can itself provide constraints to growth, or cause toxicity in waters (Wilkie and Wood 1996), however, a key concern of hyperalkalinity is the greater mobility of oxyanionic trace elements such as As, Cr, Mo, V (Langmuir 1997). Studies at an abandoned pit lake in western Poland filled with red mud have highlighted the presence and mobility of such contaminants in concentrations of 2—5 mg/L at high pH (Czop *et al.* 2011), while other investigations of hyperalkaline sites have found similar concerns (e.g. Mayes *et al.* 2009). The mobility of these in leachate waters at the site and subsequent attenuation of in-stream loadings (Mayes *et al.* 2011) is reflected in the relative enrichment in the deposited sediments.

The most notable potential contaminants in the Ajka red mud solid samples are As, Cr, Ni and V (Table 1). The presence of less frequently encoun-

Table 1 *Comparison of selected contaminant concentrations of spill material at a series of major tailings failures. All concentrations show maxima reported in mg/kg.*

Site (year of spill)	Facility	pH	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
Ajka, Hungary (2010), site K1[1]	Alumina plant	13.1	79	4.0	97	811	60	14.4	292	80	891	173
Ajka, Hungary (2010) ref sites[1]	Alumina plant	8.5	3	0.1	8	29	15	5.2	8	3	34	27
Aznalcóllar, Spain (1998)[2]	Cu/Pb/Zn mines	7.0	442	14.8	54	32	521	-	124	3332		3997
Baia Mare, Romaina (2000)[3]	Cu/Pb/Zn mines	4.8	562	9.7	-	11	1020	-	28	897	-	1500
Chenzu, China (1985)[4]	Pb/Zn mine	4.7-8.0	1227	11.1	14	6	149	-	32	1444	-	1252
Little Bay Arm, Canada (1989)[5]	Cu mine	-	44	0.4	742	219	5045	-	76	30	236	3574
Porco mine, Bolivia (1996)[6]	Ag/Zn/Pb/ Sn mine	-	7200	190.0	-	-	1400	-	-	1700	-	10000
TEL[7]			6	0.6	-	37	37	-	18	35	-	123
PEL[7]			17	3.5	-	90	197	-	36	91	-	315
Background[7]			-	-	10	-	-	-	-	-	50	-

[1] this study; [2]Cabrera et al. (2008); [3] Soldan et al. 2001; [4] Liu et al. 2005; [5] Veinott et al. 2003; [6] Hudson-Edwards et al. 2001; [7] TEL is Threshold Effects Level; PEL is Predicted Effects Level; Background represents global baseline concentrations. All from Buchmann 1997.

Table 2 *Concentrations of REE in K1 (source) and reference (M1, T2) samples in mg/kg.*

Sample	Ce	Er	Eu	Gd	Ho	La	Lu	Nd	Pr	Sc	Sm	Tb	Tm	Y	Yb
K1	404.5	19.0	6.7	74.0	9.3	149.2	8.7	133.4	106.7	89.1	29.3	4.3	9.2	90.1	16.6
M1	20.9	1.3	<1	4.2	1.4	9.7	2.0	5.8	5.6	4.1	2.9	<1	<1	7.1	<1
T2	21.9	2.7	<1	4.8	2.6	10.8	1.5	6.8	11.5	5.2	<1	<1	<1	9.3	1.3

tered contaminants (e.g. V, Co and Mo) makes widespread evaluation against prescribed quality guidelines and intervention thresholds (e.g. Buchmann 1997; Macklin *et al.* 2003) more difficult at Ajka than at other sites with more commonly encountered trace pollutants (e.g. Cd, Pb, Zn). Comparison with regional or global background concentrations suggest considerable enrichment in source samples (K1) of V, Ni, Cr and As in concentrations at least an order of magnitude above unaffected reference sites (Table 1). Sequential extraction data (see Mayes *et al.* 2011) however show that the bulk of As, Cr, Ni, V are associated with hard-to-leach residual phases (e.g. crystalline haematite) in source samples and the downstream sediments, or phases only likely to be remobilised under highly alkaline conditions (e.g. where sorbed oxyanions could be re-solubilised) which are unlikely to be encountered in environmental settings. In some areas, there is an association of V and As in particular with carbonate or Fe/Mn oxide phases, where some future mobility could be envisaged (Mayes *et al.* 2011).

Most major tailings failures are usually associated with metalliferous, potentially acidic and sometimes cyanide-rich spills (e.g. Baia Mare). In such cases, the key contaminants of concern are typically Cd, Cu, Pb and Zn. These are not present in concentrations appreciably elevated above reference samples in the Ajka catchment as would be anticipated given the typical composition of red mud deposits. Only at source samples (K1) do Cd, Cu and Zn exceed either Threshold Effects Level (TEL) or Predicted Effects Level (PEL) concentrations deemed by consensus-based research to pose a potential risk to freshwater systems (Buchmann 1997; Mayes *et al.* 2011).

Another key feature of the material is the fine-grained nature of the red mud. Laser particle sizing and SEM microscopy suggest that the red mud is comprised of two groups of particles: aggregates of nano-particulate haematite (median size of 0.7µm), and slightly larger cancrinite phases (median size of 1.3 µm; Mayes *et al.* 2011). In studies of major tailings failure elsewhere, sediment-borne contaminants have been found to be associated primarily with size fractions of the order of 10—500 µm (Hudson-Edwards *et al.* 2003). The deposition of such coarser material can form secondary hotspots of potential future contamination in affected river systems that can remain for several years after the spill (Macklin *et al.* 2003).

Downstream dispersal of red mud

The key contaminants present in the Ajka red mud show rapid dilution in fluvial sediments with distance downstream as shown in the PCA in Figure 2. Elevated Na, Al and enrichment in a suite of trace elements and REE characterise the source

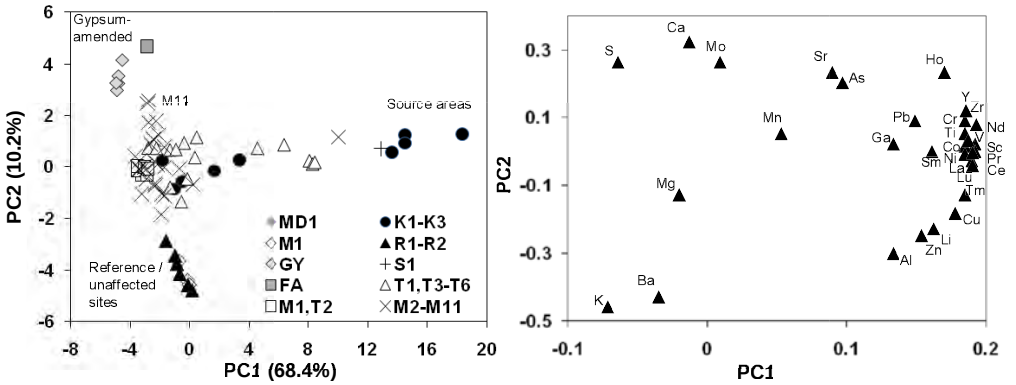

Figure 2 *Principal Component Analysis of sediment elemental composition data. Ordination of sample sites by the first two principal components on the left. Variable loading on the first two principal components on the right. FA; flyash; GY: gypsum amended; S1: floodplain sample adjacent to T4.*

material. PCA axis 1, which accounts for 68.4% of the sample variance, highlights a gradient of dilution from source material (K1 on the right) to largely unaffected sites towards the left of the image (e.g. M1, T2). The reference sites are themselves characterised by relative enrichment in elements indicative of solid and superficial deposits in the catchment such as K, Ba and Mg. The downstream patterns do not show a systematic decline in concentrations from source with dilution. Hotspots of deposition are apparent (Figure 1) which correspond with reaches in the lower Torna Creek (e.g. T6) and upper Marcal (M2), where stream velocity reduces and channel planform changes from a straight channelised form, to a lowland meandering planform more conducive to particulate settlement. Vanadium was shown to be the most mobile contaminant in the aqueous phase downstream of the site, due to it's presence as vanadate (VO_4^{3-}) from high pH source areas to circum-neutral pH conditions that characterise the remainder of the catchment (Mayes *et al.* 2011). Despite this aqueous mobility, V concentrations in sediments are shown to fall towards reference site concentrations by around 70km downstream of the source (Figure 1). REE show similar trends in dilution and deposition, albeit with a lesser extent of elevation in concentration above reference sites as shown with the example data for Ce (Figure 1). This may be a feature of the lesser solubility of Ce compared to V under the alkaline to hyperalkaline conditions encountered. The relative enrichment of Ce in reference and downstream samples (R1-MD1) are likely to reflect diffuse urban sources of Ce (e.g. the signal of Ce automotive catalysts in highways runoff) around Győr.

One clear feature in the downstream sediments is the influence of gypsum dosing on the bulk composition of the sediments. Sample M11 falls towards the upper left of the PCA characterised by enrichment in Ca and S in particular. These samples were collected from lowland reaches of the Marcal River where the streambed was blanketed in gypsum-rich sludges and secondary carbonate precipitates. The addition of gypsum as an ameliorant for red mud Na-OH dominated leachates and soils has been widely used (Courtney *et al.* 2005); the excess Ca^{2+} encouraging the precipitation of calcium carbonate, thus consuming sample alkalinity. In the case of Ajka, the gypsum dosing may have played a role in neutralisation of the leachate slug and the secondary stream deposits do suggest some modest uptake of trace elements compared to stockpiled samples (Table 3). However, there may be potential issues of calcareous hard-panning under low flow given the extensive smothering of benthic habitats. These have been shown to be detrimental to aquatic macrophytes at other sites receiving hyperalkaline drainage (e.g. Mayes *et al.* 2009).

Table 3 *Range in contaminant concentrations (mg/kg) in stockpiled gypsum and gypsum-amended fluvial sediments (n = 3 for each).*

Site	As	Cr	Cu	Mo	Ni	V	Zn
Stockpiled gypsum	12.4-14.1	<4	1.6-1.8	<2.5	<3	1.5-1.9	6.1-6.5
Secondary instream calcareous deposits	21.1-45.0	<4-6.9	0.9-2.3	6.4-9.3	<3-3.4	4.0-5.3	8.2-10.3

Conclusions

The material released at Ajka is characterised by its caustic nature, fine grain size and enrichment of various trace contaminants and REE. The geochemical signature of the spill is apparent throughout the Torna Creek and upper reaches of the Marcal river system principally with elevated Al, V, As and Mo and various REE. Although concentrations of some trace elements exceed aquatic life standards (where prescribed) in fluvial sediments (As, Cr, Ni), the spatial extent of these is limited. The rapid dilution of the red mud from source areas reflect the management efforts to minimise red mud release after the initial spill (e.g. check dams, treatment of residual leachates using settlement lagoons, acid dosing and an informal flyash PRB) and the fine grained nature of the material which is readily transported downstream and diluted. The relatively limited spatial extent of high concentrations of trace elements downstream of the site and the preponderance of residual phases is encouraging in terms of the longer term recovery of the downstream river systems. Although the caustic nature of the released material caused acute water pollution issues in the immediate aftermath of the spill, the physicochemical nature of the spill material is unlikely to be as persistent a problem as those found in rivers affected by tailings failures associated with base / precious metal mining. Studies on the potential future mobility of V and As in particular, which characterise some hotspots of deposition are taking place. These will offer a more detailed prognosis on the likely long-term effects of the spill on the aquatic environment.

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