Evaluation of trace metal contamination from the Baia Sprie mine tailings impoundment, Romania

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Summary

The tailings management operation for the Baia Sprie mine has the potential substantially to impact aquatic ecosystems as a result of the metals discharged. Mining operations involve the beneficiation of sulfidic ores using a flotation plant. Liquid effluents from this operation and from drainage of the mine are discharged direct to the Sasar River and have resulted in degradation of environmental quality which has been documented by the regulatory authorities, principally from excessive levels of zinc.

Tailings from the flotation operation are transferred by pipeline to a tailings pond located at a downriver site close to the village of Tautii de Sus. Settled effluent from this pond is discharged to a stream bounding the site and thence to the Sasar River, together with leachate intercepted by the stream. Analysis of samples collected at the site indicate that the tailings pond is a significant source of metals to the Sasar River, both from the discharged effluent and from leachate derived from the site.

Ongoing management of the site needs to be emplaced with two objects in mind. Firstly, emissions from continuing operations to wider systems need to be eliminated and the site configured to operate on a zero-discharge basis. There is an urgent need for suitable treatment and interception systems to be brought into operation. If this cannot be done immediately, consideration should be given to suspending operations until such times as the technology is installed. Secondly, management needs to be conducted in order to assure the long term stability of the tailings pond together integral operation of the tailings piping system. In devising such a scheme, full consideration needs to be given to the inevitable need for a duty of care in the long term to protect the environment from impacts of the tailings impoundment as a chronic source of metals to the environment and from impacts caused by catastrophic events. This duty of care will need to extend to the acid mine drainage waters which will continue to be generated after mining operations have been abandoned.

Introduction

EM Baia Sprie, a mining operation under the aegis of the Romanian State owned mining company Compania Nationala REMIN S.A. is located on the Sasar River in the Somes hydrographical basin in northwestern Romania towards the border with the Ukraine (see: Fig 1). The mine is responsible for the extraction and subsequent processing of non-ferrous sulfidic ores, to produce flotation concentrates mainly of copper but also for lead, zinc and precious metals. Some 200,000 tons of material are processed annually. Tailings, in slurried form are piped to a tailings pond located close to the village of Tautii de Sus, downstream of the mining operation. The tailings pond currently contains an estimated 13.5 million tons with total surface area of 48.6 ha. Some 27.5 ha are still available for tailings containment.

Operation of the mine and flotation plant results in substantial discharges of wastewaters (including acid mine drainage) to the river. These have resulted in documented degradation of water quality in the River Sasar. It is planned that in the future, mine drainage water will be collected and treated with flotation plant effluents and conveyed with the tailings, either to the pond at Tautii de Sus or to another tailings impoundment, for example the Bozinta pond, west of Baia Mare.

The impact of the tailings operation as a source of toxic trace metals has not been evaluated to date. The tailings pond although not regarded as currently unstable, has the potential to become a high risk operation. Current concerns largely attach to the safe operation of the tailings pipelines and these are considered to require replacement. This will involve substantial financial investment. Over time, the discharge of tailings onto the flat, river flood plain area has resulted in a raised area of wastes, bounded by a leachate collection channel. Together with the liquid phase separated from the tailings and discharged *via* pipeline, the leachate is discharged to the main river. Accordingly, the tailings operation has the potential to be a significant source of toxic trace metals into the wider environment.

Quite apart from any local impacts of the mine operations and tailings management, the river system ultimately feeds into the River Tisza and thereafter into the River Danube. Hence, a catastrophic failure of the tailings pond impoundment would be of great significance for this system, with its extensive wetland areas, while chronic inputs are also of potential significance given the multiple identified inputs to the upstream catchments from other active and abandoned mining operations and associated tailings.

Accordingly, this study was designed to evaluate the potential of the Baia Sprie tailings operation as a potential source of toxic trace metals. The results of this preliminary study are reproduced below.

Methods and Materials

a) Sample Collection

A total of ten samples were taken from the tailings operation and its vicinity. A description of the samples together with their designated numbers is given in Table 1 below. These comprised a mixture of sediments/soils, surface waters and direct discharges from the operation.

b) Sample Analysis

All chemicals were of High Purity Aristar Grade. All glassware was cleaned in detergent, rinsed with tap water and deionised water, soaked in 10% nitric acid overnight, rinsed with deionised water and dried in an oven.

i) Solid Samples

Samples were air dried until weighing readings became constant (approx. 5 days). They were then crushed using a pestle and mortar until homogenous and sieved through a 2-mm mesh. 0.5 g of sample was weighed into a glass 100 ml boiling tube and to this 10 ml of deionised water was added, followed by 7.5 ml of concentrated hydrochloric acid and 2.5 ml of concentrated nitric acid. The samples were digested at room temperature overnight prior to being placed onto a Gerhardt Kjeldatherm digestion block (40 space) connected to a Gerhardt Turbosog scrubber unit (filled with 10% w/v sodium hydroxide). The samples were then refluxed at 130°C for four hours.

After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed. With the batch of samples, a blank sample and two Standard Reference Materials were prepared; BCR143, trace elements in a sewage sludge amended soil, as certified by Commission of the European Communities, Brussels and CMI7004, loam with elevated analyte levels, as certified by the Czech Meteorological Institute. All were prepared in 15% v/v hydrochloric acid and 5% v/v nitric acid.

ii) Aqueous samples

On arrival, 100ml of sample was transferred to a clean glass bottle and acidified with nitric acid (10% v/v). 50 ml of this solution was subsequently transferred to a 100ml boiling tube, placed onto the Gerhardt Kjeldatherm digestion block, and refluxed at 130°C for four hours. After cooling to ambient temperature, the digests were filtered into volumetric flasks, diluted with deionised water, made up to a volume of 50 ml and mixed.

Sample Number	Sample Description	Sample Location
CEE02038	Sediment	Stream around boundary of tailings pond, leachate entry point
CEE02039	Wastewater	Liquid sample directly from tailings pond
CEE02040	Sediment	Sediment sample direct from tailings pond as for CEE02039
CEE02041	Sediment/soil	Sample from blocked pipe running from tailings pond to dam base
CEE02042	Sediment/soil	From stream around boundary of tailings pond, leachate entry point
CEE02043	Sediment	Stream around boundary of tailings pond, flowing away from pond towards river
CEE02044	Sediment	Stream around boundary of tailings pond, leachate entry point
CEE02045	Wastewater	Pipe running from top of tailings pond to stream around boundary of pond
CEE02046	Sediment	"Control" sample 400m downstream of point where boundary stream discharges to the Sasar River
CEE02047	Sediment	"Control" sample 450-500m upstream of point where boundary stream discharges to the Sasar River.

Table 1. Description of samples collected from Baia Sprie mine tailings impoundment, near the village of Tautii de Sus, Romania. Samples were taken from the tailings pond, from the stream running around the boundary of elevated tailings "dam" and from Sasar River, the recipient for effluents from this operation via the boundary stream.

iii) Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Following preparation, samples were analysed by ICP-AES, using a Varian Liberty-100 Sequential Spectrometer. The following metals were quantified directly: manganese, chromium, zinc, copper, lead, nickel, cobalt and cadmium. A multi-element instrument calibration standard was prepared at a concentration of 10 mg/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid). The calibration was validated using a quality control standard (8 mg/l), prepared internally from different reagent stocks. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Mercury (Hg) was determined using Cold Vapour Generation ICP-AES. Hg (II) was reduced to Hg (0) i.e. a vapour, following reduction of the samples with sodium borohydride (0.6% w/v), sodium hydroxide (0.5% w/v) and hydrochloric acid (10 molar). The vapour was carried in a stream of argon into the spectrometer. Two calibration standards were prepared, at 10 ug/l and 100 ug/l, matrix matched to the samples (i.e. in 15% v/v hydrochloric acid and 5% v/v nitric acid for solid samples or 10% v/v nitric acid for aqueous samples). The calibration was validated using a quality control standard (80 ug/l), prepared internally from different reagent stock. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Results & Discussion

Results of instrumental analysis for heavy metals are tabulated in Table 2 below.

On the basis of the analytical determinations it is clear that both the liquid present in the tailings pond (Sample CEE02039) and in the sedimented tailings (Sample CEE02040) are contaminated with a variety of trace metals of environmental concern. The sample of wastewater taken from the discharge pipe running from the top of the dam (CEE02045) confirms that significant quantities of these trace metals are being released from the tailings pond into external aquatic systems. Moreover, results from the sediments taken from the boundary stream indicate that a pervasive contamination problem exists associated with the leaching of metals from the tailings management system. The degree to which these releases may be impacting on the river is unclear. The sediment samples taken at points both upstream and downstream (CEE02046 & CEE02047) of the tailings pond operation in the Sasar River show that sediment upstream of the operation is somewhat more contaminated than the sample taken downstream. This apparently anomalous finding can be explained by discharges from the operation of the flotation plant at the mine site, together with the acidic, metal rich, effluent generated by drainage of the mine. A further possible factor is the different nature of the sediments at the two locations sampled.

The sample set includes two samples of liquid effluent associated with the tailings operation, both of which are significantly contaminated with trace metals. These are samples CEE02039 taken directly from the body of the ponds and CEE02045 taken from a pipeline from the pond to the boundary stream/collector channel. The trace metal concentrations in both samples are similar, confirming that the composition of the liquid in the pond is representative of the composition of the effluents discharged to the receiving river system.

Sample number	CEE02038	CEE02039	CEE02040	CEE02041	CEE02042
Description	Sediment	Wastewater	Sediment	Sediment	Sediment
Location	Boundary Stream	Tailings Pond	Tailings Pond	Blocked Pipe	Boundary Stream
Metals	mg/kg	ug/l	mg/kg	mg/kg	mg/kg
Arsenic (As)	-	-	-	-	-
Cadmium (Cd)	130	219	35	9	3
Chromium (Cr)	39	<20	22	16	28
Cobalt (Co)	13	224	45	66	10
Copper (Cu)	369	<20	578	787	267
Iron (Fe)	35638	23539	116833	73607	77042
Lead (Pb)	560	642	2039	1065	939
Manganese (Mn)	873	105444	10693	3042	694
Mercury (Hg)	2.8	<2	3.0	1.2	1.2
Nickel (Ni)	10	133	11	18	10
Zinc (Zn)	950	68622	7236	3337	3586

Sample number	CEE02043	CEE02044	CEE02045	CEE02046	CEE02047
Description	Sediment	Sediment	Wastewater	Sediment	Sediment
Location	Boundary Stream	Boundary Stream	Discharge Pipe	Sasar River downstream	Sasar River upstream
Metals	mg/kg	mg/kg	ug/l	mg/kg	mg/kg
Arsenic (As)	-	-	-	-	-
Cadmium (Cd)	40	142	241	<1	7
Chromium (Cr)	191	28	34	57	31
Cobalt (Co)	56	17	259	12	17
Copper (Cu)	2058	697	<20	41	320
Iron (Fe)	143273	116532	32339	34863	44536
Lead (Pb)	7181	1027	1356	23	738
Manganese (Mn)	5589	1862	110789	888	1263
Mercury (Hg)	2.1	1.7	<2	1.6	9.2
Nickel (Ni)	12	11	141	45	21
Zinc (Zn)	8007	1548	77300	186	1809

Table 2: Analytical results for trace metals in samples taken in the vicinity of the Baia Sprie mine tailings pond, close to Tautii de Sul village, Romania. Determinations for liquid in micrograms per litre for whole unfiltered sample, sediments/soils given in milligrams per kilogram dry weight. Arsenic was not analysed as part of the suite of metals determined

Comparison of the analytical values obtained with those in the Tables in the Appendix below show that metal levels in the wastewater samples generally exceed expected "background" levels in freshwaters, in some cases, by a considerable margin. In the case of cadmium, the analysed values of 219 and 241 ug/l compare with a background level of generally less than 1 ug/l found in freshwaters (Table 4a) and are some five times higher than cadmium concentrations found in Restronguet Creek UK, a seawater recipient for mine drainage from non-ferrous metal mining activities. A forty-two fold dilution would be necessary to meet the terms of the EC Water

Framework Directive for cadmium as a dangerous substance (Chave 2001). There is no doubt, therefore, that the cadmium concentrations in the effluents reaching the Sasar River are capable of deleterious impacts upon freshwater ecosystems both in relation to the content of cadmium and the potential for it to bioaccumulate in components of the biota. Similar excursions from "baseline" values are observed for cobalt (200 fold elevation) lead (160 fold elevation), manganese (8000 fold-elevation), nickel (6-12 fold elevation) and zinc (1300 fold-elevation).

The sediments from the boundary stream receiving the tailing pond effluents and leachate through the body of the tailings mass (CEE02038; CEE02042; CEE02043; CEE02042;) generally show a trace element profile resembling the sediment from the tailings pond itself (CEE02040), although in many cases the absolute concentrations are somewhat higher. This is likely to be due to two factors. Firstly, differences in particulate size may be influential and secondly, increased organic matter content may play a role. The boundary stream supports emergent aquatic vegetation. A further potential influence is variability in the composition of the mine output which in turn could influence the quality of the tailings. Considering sample CEE02040 as a reference then the cadmium content at 35 mg/kg represents a 35-fold elevation with respect to "baseline" river sediment and is elevated some 17-3500 times over the concentrations generally present in soil. Cobalt is present at concentrations of up to about 3 times UK freshwater sediments at "background" while copper is elevated by around a factor of 10. Lead is present at approximately 70 times recorded background and mercury at around 5 times this level. Zinc levels were recorded at approximately 700 times reported "background" levels.

In general, these elevated concentrations are consistent with those to be expected from waste minerals derived from mining and beneficiation of non-ferrous metal ores. The impact upon the environment is entirely contingent upon the measures emplaced to contain adequately the wastes, and to contain the leachate. In addition, treatment of the aqueous effluent is an important determinant of overall environmental impact.

Overall, the Baia Sprie tailings management system is acting as a significant source of heavy metals into the wider environment. Constant discharge of metal rich settled effluent via the boundary stream to the Sasar River is accompanied by chronic leachate generation from the body of the site, which can also reach external systems. It is unlikely, given the current process and management technologies in use at the Baia Sprie sites that this mining operation can be put on a sustainable footing either in terms of ongoing operations or in terms of the long term duty of care necessary after abandonment of the operation. Nonetheless, improvements in both of these aspects should be sought.

Management of the operation should be conducted strategically in order that stability of the tailings impoundment is assured in the long term. The object is to avoid the possibility of widespread dispersion of tailings into external river systems either as an ongoing chronic situation or as a result of a catastrophic event. In addition, the effluents generated from acid mine drainage and from operation of the flotation plant should be subjected to rigourous treatment prior to discharge. The treatment regime should also be capable of operating in the long term in order to address problems caused by long term (post-abandonment) generation of mine drainage. This could involve a combination of physical and biologically based treatment aimed at reducing and minimising the quantities of metals discharged from the site, with a view to achieving a zero discharge scenario.

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APPENDIX 1: **"Background" concentrations of trace metals in various environmental media.**

Cadmium (Cd)

Environmental matrix	Concentration	Reference
Freshwater, groundwater, drinking water	<1 ug/l	USPHS 1997, WHO 1992
Seawater (open ocean)	0.02-0.12 ug/l	Sadiq 1992, Bryan and Langston 1992
Seawater (coastal)	0.01-0.17 ug/l	Bryan and Langston 1992
Marine sediment	<1 mg/kg	Sadiq 1992, Salomons and Forstner 1984
Estuarine sediment	0.2 mg/kg	Bryan and Langston 1992
River sediment	1 mg/kg	Salomons and Forstner 1984
1. Soil	0.01-2.0 mg/kg	USPHS 1997, Alloway 1990

Table 1 Background concentrations of cadmium found in water, sediment and soil

Chromium (Cr)

Environmental Matrix	Concentration	Reference
Seawater (open ocean)	0.057-0.234 ug/l	Bryan and Langston 1992
Freshwater	1-30 ug/l	USPHS 1997
Drinking water	0.4-8.0 ug/l	USPHS 1997
Marine sediment	30-200 mg/kg	Bryan and Langston 1992,
Freshwater sediment / suspended particulates	1-500 mg/kg	USPHS 1997
Soil	<1-100 mg/kg 4-80 mg/kg	Alloway 1990 Dudka and Adriano 1997

Table 2 Background concentrations of chromium found in water, sediment and soil

Cobalt (Co)

Environmental Matrix	Concentration	Reference
Freshwater	0.9 ug/l	Bowen 1966
Seawater	0.27 ug/l	Bowen 1966
Soil	1-40 mg/kg	Alloway 1990
Freshwater sediment, UK	6-22 mg/kg	Hamilton 1994
Marine sediment, North Sea	4-5 mg/kg	Hamilton 1994
Marine sediment, Atlantic Ocean	3-6 mg/kg	Hamilton 1994

Table 3 Background concentrations of cobalt found in water, sediments and soil

Copper (Cu)

Environmental Matrix	Concentration	Reference
Seawater (English Channel, Irish Sea, North Sea)	0.35-4.0 ug/l (coastal) 0.14-0.9 ug/l (open ocean)	Law et al. 1994
Seawater (background)	0.1 ug/l	Sadiq 1992, Bryan and Langston 1992
Freshwater, UK	<20 ug/l	Mance et al. 1984
Soil	20 –30mg/kg	Alloway 1990
Marine sediment	10-30 mg/kg	UNEP 1993, Bryan and Langston 1992
Freshwater sediment	45-50 mg/kg	Salomons and Forstner 1984,

Table 4 Background concentrations of copper found in water, sediment and soil

Lead (Pb)

Environmental Matrix	Concentration	Reference
Seawater (estuarine waters around England and Wales)	24-880 ng/l	Law et al. 1994
Seawater (open ocean)	5 ng/l 1-14 ng/l 20-71 ng/l	UPHS 1997 Bryan and Langston 1992 Law et al. 1994
Freshwater (mean value from 39,490 measurements)	3.9 ug/l	USPHS 1997
Drinking water	<5-30 ug/l	USPHS 1997
Soil	10-30 mg/kg	Alloway 1990
Freshwater / marine sediment	20-30 mg/kg	USPHS 1997

Table 5 Background concentrations of lead found in water, sediments and soil

Manganese (Mn)

Environmental Matrix	Concentration	Reference
Seawater (English Channel, Irish Sea, North Sea)		
Seawater (background)		
Freshwater	12 ug/l	Bowen, 1966
Soil, UK	80-7000 mg/kg	Alloway, B.J. 1990, p202
Marine sediment	790 mg/kg	Goldschmidt, 1954
Freshwater sediment		

Table 6 Background concentrations of manganese found in water, sediment and soil

Mercury (Hg)

Environmental Matrix	Concentration	Reference
Seawater (open ocean)	0.001-0.004 ug/l 0.02 ug/l	Bryan and Langston 1992, WHO 1989 USPHS 1997
Freshwater	<0.005 ug/l	USPHS 1997
Marine sediment	0.02-0.1mg/kg	WHO 1989
Freshwater sediment	0.2-0.35 mg/kg	Salomons and Forstner 1984
Soil	0.02-0.625 mg/kg	Alloway 1990, WHO 1989
Fish	<0.2 mg/kg	USPHS 1997

Table 7 Background concentrations of mercury found in water, sediments, soil and fish

Nickel (Ni)

Environmental Matrix	Concentration	Reference
Seawater	0.1-0.5 ug/l	USPHS 1997, Law et al. 1994
Freshwater	<10-20 ug/l	USPHS 1997, Mance and Yates 1984
Freshwater sediment	45-65 mg/kg	Salomons and Forstner 1984
Soil	5-500 mg/kg (average 50 mg/kg) 40 mg/kg	USPHS 1997 Alloway 1990

Table 8 Background concentrations of nickel found in water, sediment and soil

Zinc (Zn)

Environmental Matrix	Concentration	Reference
Seawater	<1 ug/l (open ocean) 0.3-70 ug/l (coastal and estuarine)	Bryan and Langston 1992. UNEP 1993
Freshwater	<50 ug/l	USPHS 1997
Drinking water	0.02-1.2 mg/l	USPHS 1997
Soil	10-300 mg/kg (50 mg/kg average)	Alloway 1990
Freshwater sediment	<100 mg/kg	USPHS 1997, Salomons and Forstner 1984
Marine Sediment	<100 mg/kg	Bryan and Langston 1992, UNEP 1993

Table 9 Background concentrations of zinc found in water, sediments and soil