Preliminary Analysis of Heavy Metals in Environmental Samples from the Vicinity of the Aurul Goldmine, Romania.

Iryna Labunska, Paul Johnston, David Santillo, Ruth Stringer,
Greenpeace Research Laboratories,
University of Exeter,
Prince of Wales Road,
Exeter, EX4 4PS,
UK

Greenpeace Research Laboratories Technical Note 03/00
20 March 2000

1. Introduction

The Baia Mare Tailings Retreatment Project, described as a "carbon-in-pulp" operation was designed to extract residual gold from mine tailings and other residues produced from historical gold mining operations conducted by the state owned mining company REMIN. The operation was commissioned in early 1999 as a joint project between REMIN and Esmeralda Exploration Ltd of Australia and is located in the Maramures district of north-western Romania. The Romanian registered joint stock company, Aurul S.a. initially conducted tests on materials contained by two old dams and estimated that there were almost 250,000ozs of recoverable gold in these two resources alone. In total the project will process tailings resources of 480,000ozs of gold together with a production 2.2 million ounces of silver at a rate of 50,000ozs of gold and 250,000ozs per annum respectively. The recovery process involves the hydraulic mobilisation of the tailings followed by pumping to the new plant located by an existing flotation facility. The plant has a design capacity of 2.5 million tonnes of tailings/ore per annum. (Esmeralda 1999). Location of the site is shown in Figure 1.

The hydraulically mobilised tailings are piped to the retreatment plant as a slurry and passed through a thickener to achieve constant pulp density and subsequently to a 900kW ball mill. The ball mill is designed to polish the surface of the fine tailings to make processing more effective. A conventional "carbon-in-pulp"plant (CIP) is then used to process the tailings. Such plants (Cohn & Stern, 1999) work on the basis of dissolving gold and silver in a cyanide solution (either sodium cyanide or an equivalent of calcium cyanide with some lime). The Aurul S.a. plant appears to be working currently on between 0.75-2.01 kg cyanide per metric tonne of ore with an added 2.60-5.23 kg/tonne of lime. Poor oxygenation can limit the rate of dissolution and lead to excess cyanide consumption and this appears to have been a problem encountered in early processing at the plant due to poor performance of an on-site gaseous oxygen generator.

The precise details of the process in use at Aurul S.a. do not appear to have been published by the company, and there are references to both CIP and CIL technology in the company literature. In general CIP processes operate as follows: Gold and silver are removed from the processing solution in the CIP process in which the cyanide leached slurry is mixed with activated carbon after thickening to maintain the carbon in suspension . The loaded carbon is removed by screening and the gold and silver stripped using concentrated alcoholic alkaline cyanide and recovered from the solution by electrolysis. This contrasts with the "carbon in leach" (CIL) process in which activated carbon and ore are slurried directly in the cyanide solution in a single unit process operation. Recovery of the gold from the solution is by a similar process.

After gold and silver recovery the residual tailings are pumped to a plastic-lined tailings impoundment which was completed in 1998. No details have apparently been published concerning the treatment of residual effluents and post process water management. Nonetheless, it may reasonably be expected that the process wastes will contain appreciable concentrations of base metals, together with cyanide residues.

On the 30th of January 2000, the tailings dam used for impounding waste material from the Baia Mare Tailings Retreatment Project was breached. It is estimated that the breach of some 25m length along the dam and to a depth of some 1-2m released some 100,000 cubic metres of the impounded materials into the Lapus and Samus tributaries of the River Tisza, one of the largest river in the region and which flows through Hungary.

Accordingly, this report details the results of samples taken in order to attempt to characterise on a preliminary basis the impact of the release upon the receiving environment in relation to a selection of heavy metals of environmental and toxicological significance. Searches of the scientific literature revealed no information on metal inputs, fate and effects for the region concerned.

Figure 1. Location of Baia Mare gold mining and processing operations in Romania Source: Esmeralda (1999)

Sampling and Analysis

Samples were taken at the locations specified in Table 1 and as depicted in Figure 2. All samples were taken in precleaned glass bottles with polypropylene closures. Samples were returned to the analysing laboratory in cooled boxes. The samples were taken in a progressive pattern downstream from the lagoon, with control samples being obtained from points above where the spill entered the river.

SAMPLE NUMBER	SAMPLE TYPE	DESCRIPTION
MI0025	Water	Private Well, Bozinta Mare, near Aurul, House 156
MI0026	Water	Private Well, Bozinta Mare, near Aurul, House 146
MI0027	Water	Stream water, Bozinta Mare, near Aurul, House 186
MI0028	Sediment	Silt and sand from stream upstream of area affected by spill. Bozinta Mare, In front of house 186, nr Aurul mine
MI0029	Water	Private Well, Bozinta Mare, near Aurul, House 186
MI0030	Sediment	Soil/silt from nr. Bozinta Mare, nr. Aurul, field with visible traces of spill, RHS of road
MI0031	Sediment	Soil/silt from nr. Bozinta Mare, ~1km from village. nr. Aurul, field with visible traces of spill, LHS of Road, Tjunction main road/lagoon road
MI0032	Sediment	Creek, main recipient of spill, RHS below water, 20m from confluence with Lapus River nr. Bozinta Mare, nr. Aurul mine, ~700-800m from MI0030/31
MI0033	Sediment	Creek which received main volume of spill. Joins Lapus River ~1km from the village of Bozinta Mare, 10m downstream of MI0032, exposed sediment
MI0034	Sediment	RHS Lapus River, ~5m from MI0033. Confluence of Lapus River and small creek ~1km from Bozinta Mare. Creek received major portion of spill
MI0035	Sediment/ Control 1	RHS of Lapus River above point where spill entered River (1km)
MI0036	Sediment/ Control 2	RHS Lapus River, 5km upstream from spill point [MI0034]
MI0037	Sediment/ Control 3	RHS of Lapus River above point where spill entered River (4km), recreational area
MI0038	Sediment	RHS Samus River 2-3km downstream of confluence with Lapus River, 2.2km from village of Merisor
MI0039	Sediment	RHS Samus River ~1.5 km downstream, MI0038
MI0040	Sediment	RHS Samus River, behind village of Birgau, 1.5 km from MI0039
MI0041	Sediment	Samus River, ~6.4km from turn to village of Birgau, ~7km downstream of MI0040, confluence of small river/stream
MI0042	Sediment	RHS Samus River 800m downstream MI0041
MI0043	Sediment	RHS Samus River, Confluence with small stream, 1km from village of Seini
MI0044	Sediment	Samus River, 20m from bridge on Road 49 between Szamosbecs and Patyod
MI0045	Sediment	Tisza River, 50-75m downstream of bridge on road No 33, 2km west village of Tiszafuered
MI0046	Sediment	sand/silt from new mine basin, 200m from dam breach

Table 1. Sample descriptions and locations Baia Mare, Maramures, Romania.

Analysis was conducted at the South West Region Laboratories of the UK Environment Agency after sample preparation by wet digestion of dried sediment samples using atomic absorbtion spectrophotometry (AAS0 and ultilising appropriate QA/QC procedures. Aqueous samples were analysed directly after acidification. Mercury was determined using hydride generation and AAS.

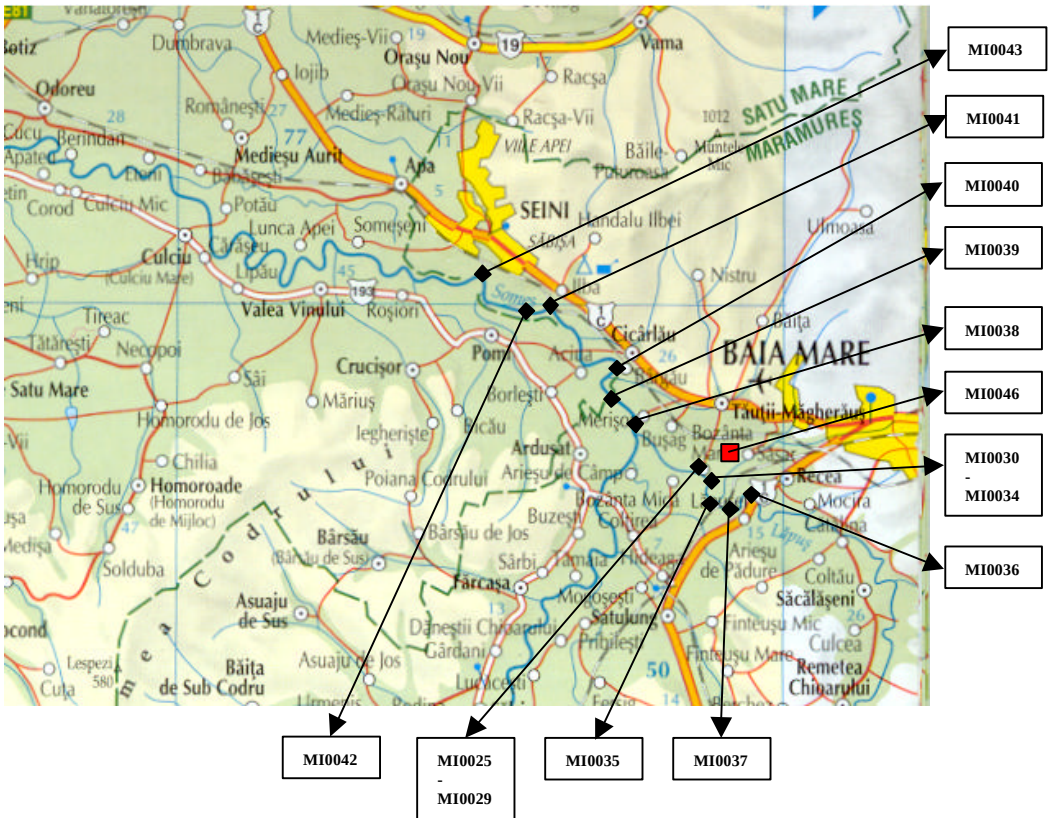

Figure 2: Location of sampling sites around the Aurul S.a mining operation in the vicinity of Baia Mare. Samples were obtained from segments of the Lapus, Samus and Tisza River systems. Location of the tailings lagoon is shown in red. Direction of flow of the major river system is from lower right to upper left quadrant, in the direction of the Hungarian border (see Figure 1)

3.Results

Results are presented in Table 2. Sediments samples are reported in terms of milligrams per kilo dry weight, while water samples are reported as mg/l.

SAMPLE NUMBER	SAMPLE TYPE	Hg	Cd	Cu	Zn	Pb	Cr	Ni
MI0025	Water	0.002	0.00285	0.0081	1.09	0.0022	<0.0005	<0.005
MI0026	Water	0.00002	0.00034	0.0068	0.0825	<0.002	<0.0005	<0.005
MI0027	Water	0.00353	0.0185	0.346	2.13	0.0074	<0.0005	0.0058
MI0028	Sediment	0.04	1.3	29.1	204	37.8	30.9	20.7
MI0029	Water	0.00001	0.00014	0.0032	0.01	<0.002	<0.0005	<0.005
MI0030	Sediment	0.184	3.5	1010	2600	927	81.8	28.8
MI0031	Sediment	0.111	2.6	245	639	227	34.3	15.8
MI0032	Sediment	0.486	3.2	51.9	511	109	18.2	8.4
MI0033	Sediment	0.195	0.7	35.9	135	17.2	29.6	14.1
MI0034	Sediment	1.4	17.2	1890	2700	954	75.8	49.7
MI0035	Sediment/Control 1	1.04	19.4	1700	2610	1100	63	39
MI0036	Sediment/Control 2	0.185	9.1	285	1780	267	76.8	59.3
MI0037	Sediment/Control 3	0.046	5.1	79	1050	150	30.4	24.6
MI0038	Sediment	0.215	3	314	464	85.9	45.5	30
MI0039	Sediment	0.473	13.8	1120	2050	459	72.3	42.1
MI0040	Sediment	0.728	20.2	1690	2910	619	74.5	46.6
MI0041	Sediment	0.196	7	441	1010	95.3	97.4	53.8
MI0042	Sediment	0.158	5.6	327	838	143	46	30.7
MI0043	Sediment	0.105	3.2	298	494	96	34.9	25.6
MI0044	Sediment	0.167	4.9	233	726	94.3	75.6	54.5
MI0045	Sediment	0.12	2	95.5	353	52.4	56.1	40.4
MI0046	Sediment	0.333	19.4	440	2290	798	10.9	4.9
NOTE: All sediment/silt results expressed in mg/kg dry weight, water samples expressed as mg/l								

Table 2: Concentrations of heavy metals determined in environmental samples from the vicinity of Baia Mare, Maramures, Romania.

4. Discussion

a) Drinking water from private wells

Samples MI0025, MI0026 and MI0029 were taken from private wells in Bazinta Mare, close to the Aurul site. Mercury levels were found to range between 0.01 and 2.0 $\mu g\ l^{-1}$. At the upper bound, this is equivalent to the water quality criterion value set for domestic water supplies in the United States (Train 1979). In the European Community under the terms of Directive 75/440/EEC water intended for abstraction for drinking water containing more than 0.5 $\mu g\ l^{-1}$ mercury requires intensive treatment while Directive 80/778/EEC restricts drinking water to 1 $\mu g\ l^{-1}$. The 1$\mu g\ l^{-1}$. standard is also mandated by the World health Organisation. Further details of regulatory criteria are included in the Appendix 1. Hence, water from the well sampled as MI0025 exceeds standard quality criteria for drinking water in the European Community.

In the case of cadmium in the private well waters, this non essential and toxic trace element was detected at concentrations of between 0.14 and 2.85 μg l^{-1}. The upper bound level is somewhat less than the 10 μg l^{-1} currently regarded as a criterion in the US for drinking water and also exceeds the WHO guideline level of 5 μg l^{-1}.. Nonetheless, it exceeds by more than a factor of 2 the current maximum permissible concentration of 1μg l^{-1}. specified for drinking water in the European Community under the terms of Council Directive 80/778/EEC which also coincides with the criterion for treatment of water intended for abstraction. Sample MI0025, therefore, exceeds European Community drinking water quality criteria.

Copper was found to be present in the three samples at concentrations ranging between 3.2 and 8.1 μg l^{-1}. This is substantially lower than the water quality criteria specified for copper under various legislatures as detailed in Appendix 1.

Zinc was found to be present at concentrations between 10 and 1090 μg l^{-1}. Even at the upper bound, these concentrations fall below those specified in the US and by the WHO of 5000μg l^{-1}. In the European Community, a criterion for drinking water is set under Directive 80/778/EEC of 5000μg l^{-1} although a lower guide value of 100μg l^{-1} is specified for outlets of pumping and treatment works into the reticulation system.

Lead was detected only in Sample MI0025 at a concentration of 2.2μg l^{-1}. This is below the 50μg l^{-1} specified as a maximum permissible for drinking water in the European Community and which determines the need for intensive treatment of abstracted water.

Nickel was not detected in any of the samples taken from private wells.

b) Surface water

One surface water sample was taken from a stream located at Bazinta Mare. Mercury was present at a concentration of 3.53 μg l^{-1} and cadmium at a concentration of 18.5μg l^{-1}. These exceed European Community standards which trigger the intensive treatment of water intended for potable use after abstraction. This sample contained 346μg l^{-1} of copper, 2130μg l^{-1} of zinc and 7.4 μg l^{-1} of lead. Nickel was detected at 5.8μg l^{-1}. None of these concentrations exceed maximum permissible concentrations for drinking water although the zinc concentration exceeds the 100μg l^{-1} guideline for waters discharged from treatment and pumping stations.
Significantly, mercury concentrations in Sample MI0027 exceed the 0.05μg l^{-1} criterion for the protection of aquatic life and wildlife specified in the US. Similarly, cadmium exceeds the highest threshold concentration of 12.0μg l^{-1} for less sensitive aquatic life in hard water and exceeds by two orders of magnitude the 0.4μg l^{-1} threshold designed to protect sensitive organisms in soft water (Train 1979). In the case of the other metals present, criteria in the US are set upon a value of 0.01 of the 96-hour LC50 determined using a sensitive resident species but may exceed sensitivity thresholds for salmonid fish (See: Appendix 1).

c) Sediments

Sediments were sampled from a number of locations on the river systems in the vicinity of the Aurul mine. Sample MI0046 of sedimentary material from the tailings basin serves as an indicator of the metal content of the materials discharged after the dam breached into the local watercourses. Difficulties were encountered in the taking of this sample and it is possible that the lower levels of metals recorded were due to inclusion in the sample of materials used in the construction of the lagoon resulting in a relatively high proportion of larger sized particulates. Nonetheless, although designated as a control, Sample MI0035 (Control 1) also serves to indicate baseline levels in the processed rocks since this sample was taken in the vicinity (and erosion zone) of artificially raised mounds of material which are thought to have been composed of minespoil from mining operations. There have been extensive historical mining operations in the region resulting in large quantities of minespoil and tailings. Indeed, reprocessing of these are the basis for current operations of Aurul S.a.

Table 3 shows comparative data taken from published work on the Aznalcollar mine spill in Spain after collapse of a tailings dam there in 1998.

Metal	Mean Concentration	Minimum	Maximum	Normal Range	MI0035	MI0046
Hg	15	7.00	22		1.04	0.333
Cd	33	21	50	0.01-2	19.4	19.4
Cu	1323	880	1800	2-250	1700	440
Zn	8832	6350	16060	1-900	2610	2290
Pb	8091	4330	11710	2-300	1100	798
Cr	30	18	49	5-1500	63	10.9
Ni*	15.9	10.1	23.2	2-750	39	4.9

Table 3: Data for heavy metal content of sludge from the Aznalcollar mine spill in Spain taken from Cabrera *et al.* (1999). * Mercury data from Lopez-Pamo *et al.* (1999). Comparison with samples MI0035 and MI0046 from Baia Mare, Romania. Normal soil ranges are also given, representing the full range of concentrations likely to be encountered (Cabrera *et al.* 1999). [no range given for mercury but see: Appendix 1].

From these data it is apparent that the material released from the Aurul S.a. waste lagoon has a somewhat lower concentration of metals than the material released by the Aznalcollar spill but these were of the same order of magnitude. In the cases of cadmium, copper, zinc and lead, the values recorded at Aurul fall well above the upper end of the ranges considered as normal. The quantities of waste released differed somewhat between the two spills. In the case of the Aznalcollar tailings dam breach some $45x10^5$ cubic metres of waste were released (Simon *et al.* 1999), whereas in the Aurul spill only $1x10^5$ cubic metres was discharged to the receiving watercourse. In addition,

there was one important qualitative difference between the spills in that the Aurul spill involved quantities of cyanide used in the secondary processing of gold containing ores.

While, therefore, it is difficult to draw direct comparisons between the two incidents, there are similarities. The presence of cyanide is likely to affect the speciation of the contaminating metals involved, as well as acting as a potent acute toxicant in its own right. While it appears that the substantial reported fish kills in the impacted river systems were caused by cyanide as a proximate agent, any metals present have the potential to exert longer term impacts due to their potential for bioaccumulation and also through adsorption to sediments which can then act as a long term reservoir for these contaminants (See information in Appendix 1).

Samples MI0030 and MI0031 were of soil/silt taken from a field over which the spill flowed prior to entering the small creek which debouched ultimately to the Lapus River. Both of these samples indicate significant contamination with heavy metals (in particular sample MI0030) suggesting that the discharged waste was highly enriched in metals. Sample MI0031 is less contaminated but values are still much higher than recorded for sample MI0028, a sediment from a stream reportedly unaffected by the spill. Taken together, the concentrations recorded from these samples suggest significant mobilisation of metals as a result of the spill.

The metal content of sediments sampled from the creek which acted as the major recipient of the spill (Samples MI0032, MI0033) must be regarded as surprisingly low given the content of metals in sediment recovered from the lagoon and those recovered as controls (MI0035-37). Observations however, showed the spill had considerably scoured and extended the dimensions of the streambed, removing much of the sediment originally present and exposing the parent geological materials. Hence, concentrations recorded in the creek reflect those of the parent materials rather than the mine wastes. This view is supported by the similarly low levels of metals recorded in a stream sediment (MI 0028) which was unaffected by the spilled waste.

Marked elevations of all sediment metal concentrations were remarked at the confluence of the recipient creek and the Lapus River, 1 km from Bazinta Mare. These concentrations are similar (though lower) to those determined for one of the putative controls (MI0035). Progressively lower concentrations are observed with increasing distance upstream from the confluence (MI0036; MI0037) although the concentrations still suggest an appreciable input from mining activities, possibly as a result of erosion of spoil heaps (see above).

Samples MI0038 through MI0045 show progressive decline of metal content with increasing distance downstream. Samples MI0044 and MI0045 are not shown on the map, having been taken further downstream than the furthest point shown. These results, taken together strongly implicate the Baia Mare, Muramares region in Romania as a significant point source of toxic heavy metals into riverine systems.

5. Conclusions

Results from the analysis of sediments obtained in the vicinity of the Aurul S.a. Tailings Retreatment Project suggest that:

1) Based on analyses of materials from the lagoon and from fields impacted by the spill, significant quantities of toxic heavy metals were mobilised as a result of the breach of the tailings dam.

2) On the basis of sedimentary materials analysed upstream from the area of the spill, there is evidence of significant historical (possibly continuing) mobilisation of toxic heavy metals into riverine systems in the area with impacts extending onsiderable distances downstream.

3) Analysis of samples taken progressively further downstream from Baia Mare strongly suggest that the region is a strong and probably continuing source of toxic heavy metals into local river systems

4) It is not possible to differentiate between metal inputs resultant from the Aurul S.a. accident and historical inputs or current inputs from other sources, including natural mobilisation via erosion.

5) While released cyanide was most likely the cause of the substantial fish mortalities recorded in the recipient waterways after the spill, the role of heavy metals in the system is likely to pose a long term hazard to aquatic communities.

6) In one case, elevated metal concentrations were detected in well water from a well used to supply drinking water such that they exceeeded European regulatory criteria.

6. Recommendations

On the basis of this highly limited study it is nonetheless apparent that an appreciable problem exists in relation to potential inputs of toxic heavy metals from past and current metal mining and related activities in north western Romania. Given the potential hazard to aquatic and terrestrial systems and the ongoing nature of planned mining and processing activities in the region it is necessary to produce a full inventory of such activities taking place in the region, including a retrospective evaluation of historically contaminated sites.

As part of the evaluation process, it will be necessary to conduct a wide ranging and large scale survey of metal concentrations in aquatic and terrestrial environmental media in order to delimit baseline values against which the impact of future activities can be assessed and which provide for the effective regulation of current, continuing operations.

5.References

Cabrera, F., Cloemente, L., Diaz Barrientos, E., Lopez, R., Murillo, J.M., (1999) Heavy metal pollution of soils affected by the Guadiamar toxic flood. Science of the Total Environment 242: 117-129

Cohn, J.g. & Stern, E.W. (1999) Gold and Gold Compounds. In: Kroschwitz, J.I. & Howe-Grant, M; [eds] Kirk- Othmer Ecyclopedia of Chemical Technology (Fourth Edition) publ. John Wiley and Sons, NY. pp738-767

Esmeralda (1998) Esmeralda Exploration Ltd. Company Website. Access through: **www.esmeralda.com.au**

Lopez-Pamo, E., Barrettino, D., Anton-Pacheco, C., Ortiz, G., Arranz, J.C., Gumiel, J.C., Martinez-Pledel, J.C., Aparicio, M., Montouto, O. (1999) The exetent of the Aznalcollar pyritic sludge spill and its effects on soil. Science of the Total Environment 242: 57-88

Simon, M., Ortiz, I., Garcia, I., Fernandez, E., Fernandez, J., Dorronsioro, C., Aguilar, J., Pollution of soils by the toxic spill of a pyrite mine (Aznalcollar, Spain). Science of the Total Environment 242: 105-115.

Train, R.E. (1979) Quality criteria for water. Castle House Publications Ltd. UK