Mining waste spill from the Baia Borsa processing complex in Romania

Assessment Mission to Hungary and Romania

UNDAC MISSION REPORT

United Nations Environment Programme, UNEP /
Office for the Co-ordination of Humanitarian Affairs, OCHA

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INTRODUCTION

On 10 March 2000 torrential rains (37 litres per square metre according to a local weather station) and melting snow from the slopes surrounding the Novat artificial reservoir at a mine in Baia Borsa, Romania, led to an unmanageable rise in the reservoir's water level. At about 11 a.m. on 10 March, approximately 20,000 tons of mineral waste was flushed into the Viseu River from the decantation reservoir of the Baia Borsa Preparation Enterprise mine. The waste been stored following the processing of complex ores of lead, copper and zinc. The Enterprise is the local branch of the state-coordinated company Remin S.A. – Baia Mare. The accident led to pollution of the River Vaser with minerals and possibly heavy metals. This river is a tributary of the River Tisza that flows through the Ukraine and enters Hungarian territory at the town of Tiszabecs.

On 11 March 2000 the Hungarian authorities appealed to the Joint United Nations Environmental Programme (UNEP)/Office for the Coordination of Humanitarian Affairs (OCHA) Unit to provide urgent assistance in the form of independent sampling and analysis. The incident was the second spill in the region within a month, the first being the pollution caused by contaminated water from the Aurel gold plant in late January 2000.

BACKGROUND – THE DISASTER

Baia Borsa is situated in the county of Maramures, in the Carpathian Mountains of northern Romania. The reservoir lies about 250 km east of the Hungarian border close to the Ukraine, in areas where the population subsists mainly on the proceeds from agriculture and mining. The three remaining mining companies in Baia Borsa produce copper, lead and zinc. Formerly there were many other mining companies in the region but privatization and other changes led to a number of enterprises being shut down. The impact of the closures on the local population has been significant. Many families have remained but are unemployed while others have left Romania to seek work abroad.

The Baia Borsa Preparation Enterprise mining company produces copper, lead and zinc. The ore in which the metals are embedded is milled and then separated from the metal. The residue of this process is pumped through a pipeline to the small valley of Novat, 830 metres above sea level where it is deposited. The depot consists of a series of three connected ponds where the residue is separated from the water. Under normal conditions, water from the lowest pond is pumped back into the first depot. The uppermost pond, where the accident occurred, is about 100 metres wide at the dam and approximately 400 metres long. The heavy rainfall of 10 March, combined with melted snow descending from the slopes above, smashed a section of the dam built with sediment from the mine. The residue from the separation process washed through the breach into the River Novat and subsequently into the Viseu. From there it flowed through the Ukraine into Hungary and into the waters of the River Tisza. The V-shaped breach in the dam is about 30 metres long and 25 metres high. About 150 metres downstream from the first pond a provisional dam is being constructed with stones and earth for containment of the mineral waste. At present, the new dam is not strong enough to withstand another spill from the first depot. Consequently, in the event of another such spill, the River Viseu and the Tisza would be susceptible to further pollution.

Polluted waters reached Ukrainian territory during the night of 10 March 2000. Ukraine's Ministry of Ecology and Natural Resources brought the accident to the attention of the relevant monitoring institutions and alerted local authorities and, in cooperation with the Zakarpatsk Region Epidemiological Service, close monitoring of the quality of surface waters began.

On 13 March yet another spill of mineral waste was released from the same source in Romania. On the evening of 14 March Ukrainian authorities reported through the local media that a black slick about 40 km long was steadily moving towards the Hungarian border.

IMPACT OF THE DISASTER IN HUNGARY

The "cyanide" spill, which had taken place 5 weeks prior to the second mineral waste spill, had already had a negative impact on the River Tisza and the population living in the area. The middle section of Lake Tisza is Hungary's largest fishing ground. It contains some fifty species of fish, twelve of which are protected. According to reports released by Hungarian authorities, more than 1,200 tons of fish were killed in the cyanide spill; the total damage is estimated at HUF 874 million.

In addition, the fauna and flora of Hortobagy National Park were reportedly placed at risk by the "cyanide" spill. The 55,000 hectares of alkaline, grassy lowland is home to some of the most unique curiosities and treasures in Europe. The parkland surrounding the Lake abounds in water lilies and fern, water chestnuts and willows. Birds in the sanctuary on the northern shores of the lake feed on the fish and insects attracted by the water, as do countless migrant species.

The impact on the local economy has been remarkable. Fish consumption has decreased drastically not only in the disaster region, but also throughout Hungary. A significant reduction in tourism, a major economical factor in the area, is also feared.

The visual effects of the second spill were apparently not as drastic as those caused by the first cyanide spill five weeks earlier. People all over Hungary, and in particular those living along the River Tisza, reacted very emotionally. The tourism industry in the area has been growing rapidly over the past years and many people depend on it for a living. Some local authorities reported that more than 60 per cent of tourists in this area come to fish on the River Tisza.

According to measurements presented by the Hungarian authorities, the first wave of mineral waste reached Hungary on 12 March at midnight. At that time, the water contained a total per litre concentration of 2900 microgrammes of zinc, 2900 microgrammes of lead and 860 microgrammes of copper. The per litre concentration of dissolved zinc, diluted lead and copper was 92 microgrammes, 100 microgrammes and less than 20 microgrammes respectively. On 12 March at 02:00 a.m. the per litre zinc concentration peaked at 230 microgrammes, and lead traces were measured at 130 microgrammes per litre. On 16 March at 06:00 a.m. the wave reached Szolnok (river km 340). Due to the various tributaries entering the River Tisza, the Hungarian authorities were only able to detect a total per liter concentration of only 210 microgrammes of copper, 440 microgrammes of zinc and 230 microgrammes of lead in the water at Szolnok.

THE UNITED NATIONS DISASTER ASSESSMENT AND COORDINATION (UNDAC) MISSION

In response to the request made by the Government of Hungary, a four-member UNDAC mission was dispatched to Budapest on 13 March 2000. The team was composed of three experts provided by the Government of Switzerland, two chemists and one logistician, along with a staff member of OCHA who acted as team leader. The team set out to take water and sediment samples and to make a rough analysis of dissolved copper and zinc. They were also equipped to test for cyanide, though this task was not specifically mentioned in their terms of reference. It was understood that these were preliminary measures, as conclusive evidence of heavy metals and other pollutants in the water and the sediment could only be revealed through more detailed laboratory analysis, in this case on the premises of the Spiez laboratory in Switzerland.

The UNDAC team was tasked to conduct independent sampling and analysis of the River Tisza water and sediments. The team members agreed that sampling and analyses should be carried out at selected spots over a considerable period of time in order to obtain a representative overview of water quality. The agreed to sampling sites were the same as those tested after the earlier "cyanide" spill. In addition, it was agreed that samples should be taken at the source of the spill, pending the agreement of Romanian authorities.

Early on 14 March a first briefing took place with the Government Commissioner of Tisza-Szamos, whose post had been established after the "cyanide" spill. The Hungarian authorities gave their full consent to the work plan presented by the UNDAC team.

Sampling and Analysis:

At 12:00 p.m. on 14 March the first sample was taken near **Tiszafüred** (river km 426). Sampling and analysis continued at this spot for 24 hours.

Field Laboratory in Tiszafüred

Sampling Point Tiszafüred

At the Tiszafüred measuring point, initial and provisional analysis of samples showed no increase of copper or zinc while cyanide levels were slightly higher than normal

Due to the second spill of 13 March, the team split up on the evening of 14 March. Two members left for **Tivadar,** where they took a first sample at 00:45 on 15 March (river km 705). Sampling continued at Tivadar until 16 March 04:00. Sedimentary samples were taken from the riverbed and others were taken upstream with the use of a boat.

The whole of 16 March was devoted to visiting the site of the accident in **Romania**. Water and sediment samples were taken at the mineral waste depot near **Baia Borsa**. This mission was conducted jointly with a delegation from the European Commission (EU). The UNDAC team took this opportunity to share information and discuss views on the impact of the emergency on the ecosystem of the affected rivers with the experts deployed by the European Commission.

On 17 March the UNDAC team departed for Budapest where a debriefing took place with the Government Commissioner. On 18 and 19 March the UNDAC team left Hungary.

EUROPEAN COMMISSION ASSESSMENT TEAM

The EC General Directorate for the Environment in Brussels dispatched a team to investigate the damage caused to the ecosystems of the rivers Novat, Viseu and Tisza. The team also evaluated measures taken by the Romanian authorities to avoid further spills, as well as to advise and lend technical support to Romanian and Hungarian authorities in monitoring the extent of the physical, chemical and biological damage caused by the spill.

The EC team was composed of three experts from Austria, one from Germany and one from France, three of whom were biologists and two chemists. The EC experts were to draft a report on the basis of the data collected, summarizing the overall impact of the incident and recommending changes for avoiding future spills, and to identify projects aimed at recovery of the ecosystem. During the mission the UNDAC team had the opportunity to discuss a number of issues with the EU team and to clarify a number of key items.

SAMPLING

Summary of Sampling Results

The effects of the dam breach at the Novat Baja Borsa mine in Romania on March 10 and 13, 2000 resulted in higher levels heavy metals in the river Tisza. Samples were taken at various points along the river and were analyzed at NC-Laboratory in Spiez (Switzerland).

The highest levels of lead from the March 10 incident reached Tiszafüred (river km 426) on March 15, 2000 between 04.00 and 06.00 a.m. The total concentration was 337 µg lead/L, 731 µg zinc/L and 209 µg copper/L, more than 97% of the metals were directly bound to the inorganic slick in the river water. With a river flow of 1353 m^3/s, the total load of heavy metals (per hour) in Tiszafüred on March 15, 2000 at 06.00 a.m. were to 1,64 t lead/h, 3.56 t zinc/h and 1.02 t copper/h.

Prior to the accident heavy metal concentrations in the river in Tiszafüred already carried 0.50 t lead/h, 2.51 t zinc/h and 0.54 t copper/h (March 14, 5.00 p.m.). These values indicate earlier events of contamination with heavy metals; these values present the base load.

The highest level of lead, from the accident dated March 13th reached Trivadar (river km 705) on March 15, 2000 at about 12.00 p.m. and March 16 at 02.00 a.m. The total concentration was 419 µg lead/L, 588 µg zinc/L and 212 µg copper/L, about 90% were directly bounded to the inorganic slick in the river water. With a river flow of 459 m^3/s, the total load of heavy metals (per hour) in Trivadar on March 16, 2000 at 02.00 a.m. were 0.69 t lead/h, 0.97 t zinc/h and 0.35 t copper/h. The heavy metal concentrations the river in Trivadar prior to the accident were 0.11 t lead/h, 0.23 t zinc/h and 0.06 t copper/h (March 15th 2000, 08.00 p.m.).

It is interesting to note that the maximum concentration of the dissolved heavy metals were detected at both locations approximately two hours before the highest concentrations of heavy metals bound to the slick could be analysed. This effect shows the higher mobility of the dissolved impurities. Beside the above-mentioned contamination in the samples, the following heavy metals were also detected: nickel, arsenic, cadmium, thallium, molybdenum, manganese and mercury.

With the bursting of the dam Novat on March 10, approximately 20,000 tons of heavy metal-containing waste were lost to the underlying river system, according to information obtained from Hungarian and Romanian authorities. The amount of heavy metals bound to the slick particles were found to be in the order of magnitude of 70 t lead, 150 t zinc and 40 t copper.

The heavy metals (in insoluble form) were incorporated in the fine-grained particles of slick. These can be found in the sediments of the rivers Novat, Vaser, Viseu and Tisza. Due to slow dissolution, a long-lasting period of a constant load of heavy metals is expected for both the river sediments and water.

The total heavy metal content and the amount of dissolved heavy metals do not allow any interpretation on the acute fish toxicity. The main problem remains the long-term toxicity of the heavy metals due to bioaccumulation in the food chain. As this aspect very much depends on the variable bioavailability, it is recommended that an extensive bio-monitoring program be established.

Sampling Procedures

Water Samples

Samples taken in Hungary

From the River Tisza, near the town of Tiszafüred (river-km 426; Hungary), water samples were taken from a swimming port platform named ¨Sabics¨. In Trivadar (river-km 705;

Hungary), water samples were taken at the bridge (9th strutting of the bridge; from left river side). At river km 715, 718 and 720 the samples were taken from a boat. A heavy, open-topped 200 mL vessel made of steel was used for sampling. The vessel, fixed on a line, was lowered into the river water to a depth of approximately 1 metre. Each flask was rinsed at least once with river water. No filtration of the sample was performed. All samples were brought to the NC-Laboratory in Spiez (Switzerland) for a full analysis.

Figure 1- Sampling Platform at ¨Szabics¨ Harbour, Tiszafüred, Hungary

Sampling location
River km : 426
N 047° 36‘ 17.2“
E 020° 42‘ 41.1“

Samples from the river
Begin: March 14, 2000, 00:10 p.m.
End : March 15, 2000, 12:00 a.m.
Rate: 1 sample per hour

Sample codes:
ZA/R-2000-026-001 - ZA/R-2000-026-020

Sediment Samples (see 3.1.2)
March 14, 2000, 02:00 p.m.
March 15, 2000, 11:00 a.m.

Sample codes:
ZA/R-2000-026-101 - ZA/R-2000-026-102

Tisza - Flow rate

- Mean value (observed over a period of several years): 600 m^3/s
- March 14th, 2000 : 1353 m^3/s (Reference: B. Turcsany, Hungarian authorities)

The water samples were taken from the swimming platform (a place with strong / good river flow).

Figure 2 -Sampling from the Bridge at Trivadar, Hungary

Tisza - Flow rate

- Mean value (observed over a period of several years): 230 m^3/s
- March 15th, 2000 01:45 p.m: 459 m^3/s (Reference: B. Turcsany, Hungarian authorities)

Sampling location
River km : 705
N 048° 03‘ 35.6“
E 022° 30‘ 56.4“

<u>Water samples from the bridge</u>
Begin: March 15, 2000, 00:45 a.m.
End: March 16, 2000, 06:00 a.m.

Rate: 1 sample per hour (from 15 March,19:00)

Sample codes:
ZA/R-2000-026-021 - ZA/R-2000-026-043

<u>Water samples from the boat</u>
March 15, 2000, 04:50 p.m. River km 715
March 15, 2000, 05:10 p.m. River km 718
March 15, 2000, 05:25 p.m. River km 720

Sample codes:
ZA/R-2000-026-044 - ZA/R-2000-026-046

<u>Sediment samples</u> <u>(see 3.1.2)</u>
March 15, 2000, 04:30 p.m.

Samples codes:
ZA/R-2000-026-103 - ZA/R-2000-026-104

Sediment Samples

<u>Hungary</u> – Tiszafüred (river km 426) – With the aid of equipment from local authorities, the sampling took place at the right side of the river (about 10 m from the right riverbank at a depth of approximately 1.5 m). Depending on the condition of the subsoil, sediment samples were up to 10 cm thick. The samples were transferred without any stabilization into PE-bags. All analyses were made in the NC-Laboratory in Spiez.

<u>Hungary</u> -Trivadar (river km 705) – These samples were taken manually from a riverbank (previously flooded on March 10th). One sample was a homogeneous light sludge. The second sample showed dark grey inclusions in the light sludge. Depending of the condition of the

subsoil, sediment samples were up to 5 cm thick. The samples were transferred into PE-bags. The analyses were made in the NC-Laboratory in Spiez.

Romania – Novat dam

These samples were taken manually. Depending of the condition of the soil, sediment samples were up to 5 cm thick. The samples were transferred into PE-bags. The analyses were made in the NC-Laboratory in Spiez.

Figure 3 - Part of the pond (settling area) near the end of the pipeline Novat Dam – Baja Borsa, Romania

Pond with pipeline
N 047° 43‘ 43“
E 024° 38‘ 52.7“

Water samples (dark “Slurry”)
March 16th, 2000, 05:45 p.m.

Sample codes:
ZA/R-2000-026-047 - ZA/R-2000-026-048

Sediment samples
March 16th, 2000, 05:50 p.m.

Sample codes:
ZA/R-2000-026-105 - ZA/R-2000-026-106
(about 200 g)

Figure 4 - View from the top of the dam near the breach

Sampling location
N 047° 43‘ 40.1“
E 024° 38‘ 37“

Sediment sample
March 16th, 2000, 06:00 p.m.
Sample code:
ZA/R-2000-026-107 (about 200 g)

Novat - Dam at its bottom near the breach
N 047° 43‘ 38.1“
E 024° 38‘ 35.7“

Sediment sample
March 16, 2000, 06:15 p.m.

Sample code
ZA/R-2000-026-108 (about 200 g)

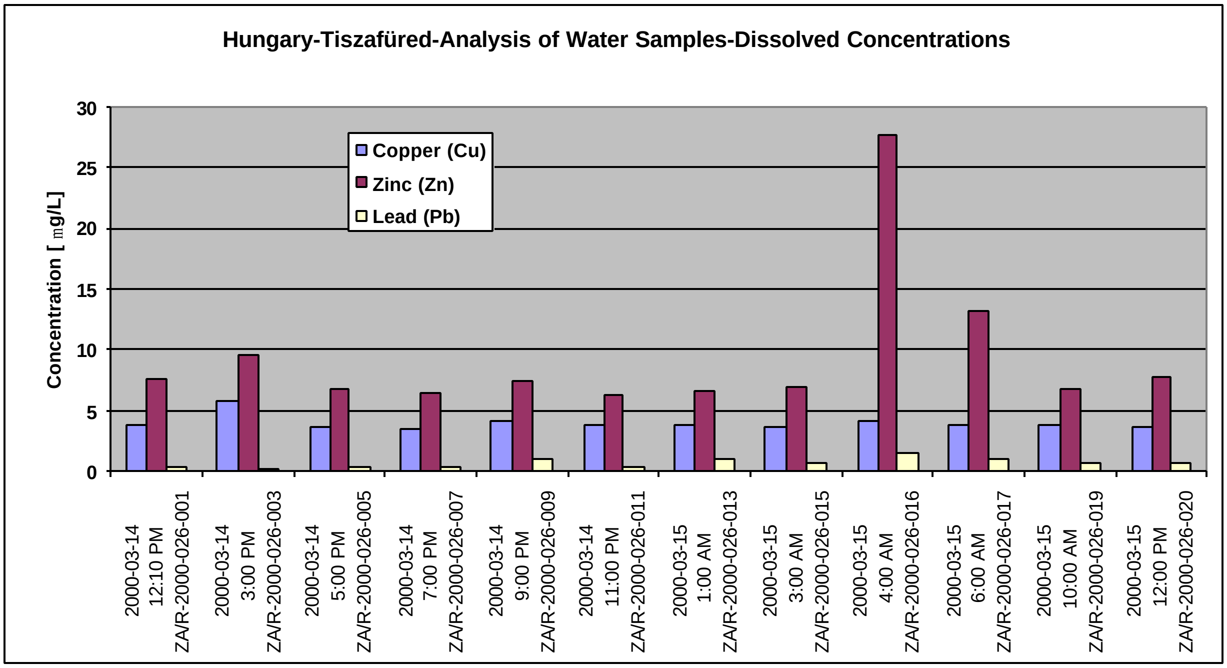
Chemical Analyses

Chapter 4 contains the detailed description of the sample preparation and analytical methods.

Hungary / Tiszafüred / Harbour “Szabics” (River km 426)

Figure 5 shows the soluble concentrations of zinc, copper and lead (after filtration; 0.45 µm filter) in the river water between March 14, 00:10 p.m. and March 15, 12:00 a.m.

Figure 5 - Hungary-Tiszafüred-Analysis of Water Samples-Dissolved Concentrations



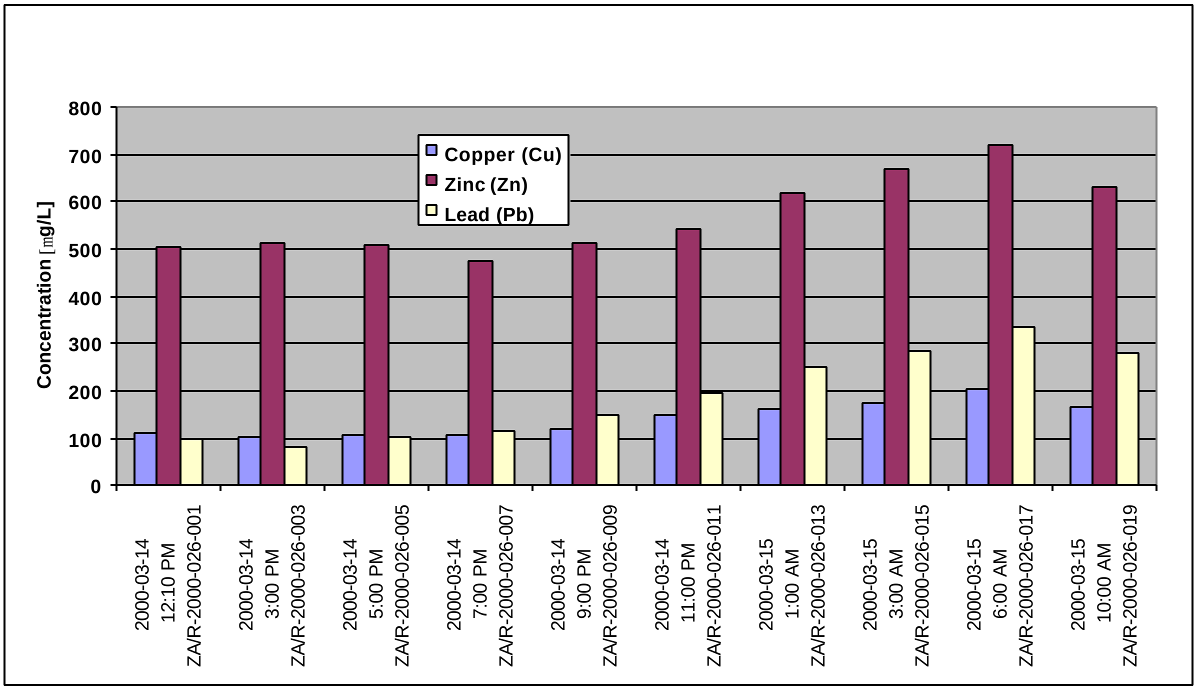
The highest concentration of soluble zinc was detected on March 15, 2000 at 04:00 a.m.

Table 1

Heavy Metal	Concentration [μg/L]
Lead (Pb)	**1.49**
Zinc (Zn)	**27.7**
Copper (Cu)	**4.1**

Figure 6 shows the insoluble concentration of zinc, copper and lead in the water between March 14, 00:10 p.m. and March 15, 10:00 a.m.

Figure 6 - Hungary-Tiszafüred-Analysis of Water Samples-Undissolved Concentrations



The highest concentrations of insoluble zinc, copper and lead were detected on March 15, 2000 at 06:00 a.m.

Table 2

Heavy Metal	Concentration [µg/L]
Lead (Pb)	**336**
Zinc (Zn)	**718**
Copper (Cu)	**205**

The maximum heavy metal load in the river water, observed on March 15, 2000, 06.00 a.m.:

Table 3

Heavy Metal	Concentration insoluble [µg/L]	**Content insoluble [%]**	**Concentration soluble** [µg/L]	**Content soluble [%]**	**Total Concentration [mg/L]**
Lead (Pb)	336	99.7	0.94	**0.3**	**336.94**
Zinc (Zn)	718	98.2	13.2	**1.8**	**731.2**
Copper (Cu)	205	98.2	3.86	**1.8**	**208.86**

The heavy metals are mostly in an insoluble chemical modification.

Hungary – Tiszafüred – Assessment of the Heavy Metal Load

The highest level of lead, from the accident of March 10 reached Tiszafüred (river km 426) on March 15, 2000 between 04.00 and 06.00 a.m. The total concentration was 337 µg lead/L, 731 µg zinc/L and 209 µg copper/L, more than 97% of these directly bound to the inorganic slick in the river water. With a river flow of 1353 m^3/s, the total load of heavy metal (per hour) in Tiszafüred on March 15, 2000 at 06.00 a.m. can be added up to 1,64 t lead/h, 3.56 t zinc/h and 1.02 t copper/h.

Before the accident, heavy metal concentrations in the river in Tiszafüred already carried 0.50 t lead/h, 2.51 t zinc/h and 0.54 t copper/h (March 14, 5.00 p.m.). These values indicate earlier heavy metal contamination of the river with the present values identifying the base load.

Table 4 shows an integration of the histograms of Figures 1 and 2 for the period between March 14, 2000 08:00 p.m. and March 15, 12:00 a.m. The base load of the river water, based on the sample from March 14, 2000, 07:00 p.m., was subtracted in this calculation.

Table 4

Element	Load [t]
Lead	11.6
Zinc	12.2
Copper	4.7

These calculated values must be interpreted with a large uncertainty as they are based on a very small sample volume (0.2 L) and added up to the total water flow of the river with 1353 m^3/s.

Hungary – Tiszafüred – Analyses of River Sediments

Sediment samples from the river were taken before and after the spill (pollution flow).

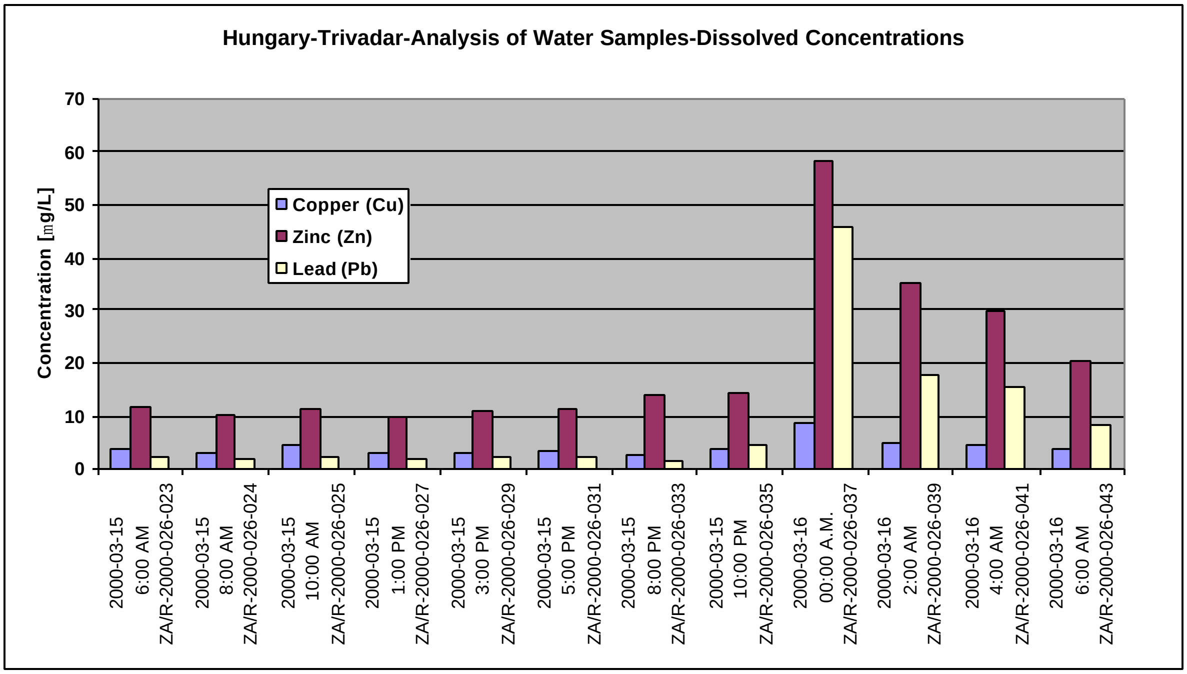
Table 5 - Heavy metal concentrations from sediment samples

Parameters	Microwave digestion of the wet sediments	Unit refers to dried sample at 105°C	Method of Measurement	ZA/R-2000-026-101	ZA/R-2000-026-102
Time of Sampling				02:00 PM	11:00 AM
Date of Sampling				2000-03-14	2000-03-15
Chromium (Cr)	X	mg/kg	6	66.2	64.0
Manganese (Mn)	X	mg/kg	6	1096	1056
Cobalt (Co)	X	mg/kg	6	14.4	13.5
Nickel (Ni)	X	mg/kg	6	25.4	25.2
Copper (Cu)	X	mg/kg	6	131	153
Zinc (Zn)	X	mg/kg	6	421	437
Arsenic (As)	X	mg/kg	6	28.0	30.8
Molybdenum (Mo)	X	mg/kg	6	1.34	1.30
Cadmium (Cd)	X	mg/kg	6	2.07	2.42
Thallium (Tl)	X	mg/kg	6	0.476	0.378
Lead (Pb)	X	mg/kg	6	63.0	59.0
Mercury (Hg)	X	mg/kg	5	0.38	0.26

No significant changes in the heavy metal concentrations were observed in the river sediments taken before and after the pollution flow passed Tiszafüred.

Hungary – Trivadar (River km 705)

Figure 7 - soluble concentrations of zinc, copper and lead in the river water between March 15, 00:45 a.m. and March 16, 06:00 a.m.



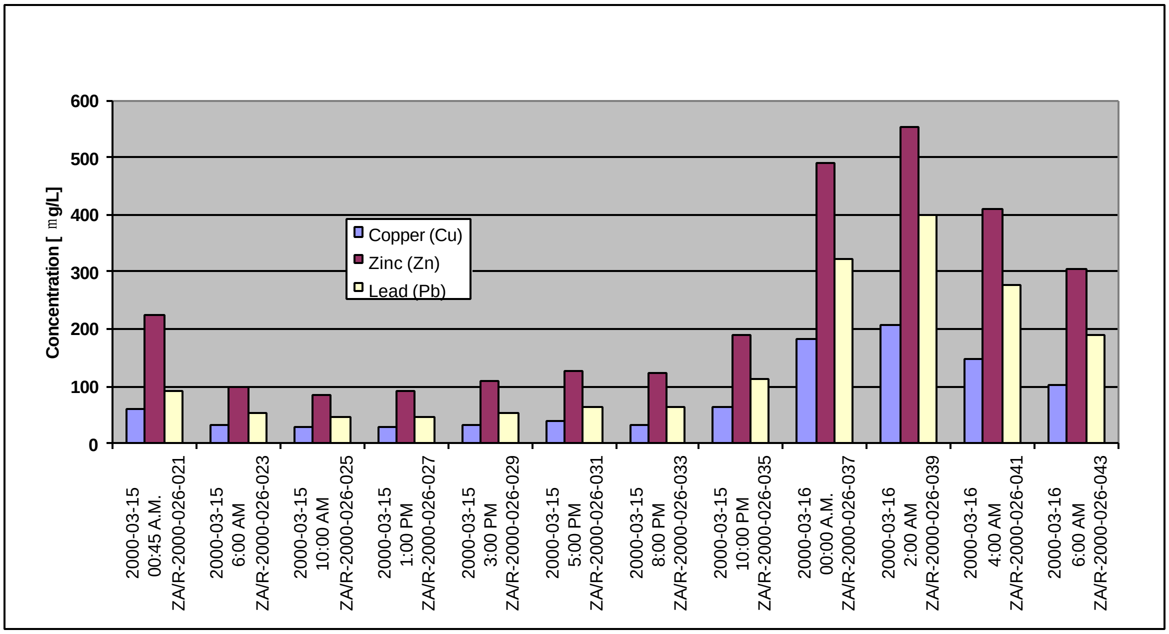
The highest concentrations of soluble zinc, copper and lead was detected on March 16th, 2000 at 00:00 a.m.

Table 6

Heavy Metal	Concentration [µg/L]
Lead (Pb)	**45.9**
Zinc (Zn)	**58.3**
Copper (Cu)	**8.7**

Figure 4 shows the insoluble concentration of zinc, copper and lead in the water between March 15th 00:45 a.m. and March 16th 06:00 a.m.

Figure 8 - Hungary-Trivadar-Analysis of Water Samples-Undissolved Concentrations



The highest concentrations of insoluble zinc, copper and lead were detected on March 16th, 2000 at 02:00 a.m.

Table 7 -

Heavy Metal	Concentration [µg/L]
Lead (Pb)	**401**
Zinc (Zn)	**553**
Copper (Cu)	**207**

Table 8 - Heavy metal concentrations in the river water, March 16, 02:00 a.m

Heavy Metal	Concentration insoluble [µg/L]	**Content insoluble [%]**	**Concentration soluble** [µg/L]	**Content soluble [%]**	**Total Concentration [mg/L]**
Lead (Pb)	401	**95.7**	18.0	**4.3**	**419**
Zinc (Zn)	553	**94.0**	35.3	**6.0**	**588.3**
Copper (Cu)	207	**97.6**	5.15	**2.4**	**212.15**

It is interesting to know that the maximum concentrations of the dissolved heavy metals were found at both places about two hours before the highest concentrations of heavy metals bound on slick could be analysed. This effect shows the higher mobility of the dissolved impurities. The majority of the heavy metal content (in insoluble form) is incorporated in the fine-grained particles of the slick.

Hungary - Trivadar – Analyses of River Water (Sampling from the Boat

Table 9 - Soluble concentrations of heavy metals at river km 715, 718 and 720.

Parameters	Acified with Nitric acid (pH < 2) after	Filtration: Membrane filter 0.45	Unit	Method of Measurement	ZA/R-2000-026-044 River-km 715	ZA/R-2000-026-045 River-km 718	ZA/R-2000-026-046 River-km 720
Time of Sampling					04:50 PM	05:10 PM	05:25 PM
Date of Sampling					2000-03-15	2000-03-15	2000-03-15
undissolved Part. (> 0.45 mm)		X	mg/L	1	129.5	68.2	81.9
pH		X	[-]	2	8.0	7.9	7.9
Conductivity		X	mS/cm	3	236	241	241
Chromium (Cr)	X	X	mg/L	4	0.314	0.330	0.186
Manganese (Mn)	X	X	mg/L	4	6.88	7.35	13.2
Cobalt (Co)	X	X	mg/L	4	0.140	0.173	0.164
Nickel (Ni)	X	X	mg/L	4	< 1	< 1	< 1
Copper (Cu)	X	X	mg/L	4	2.23	4.63	4.94
Zinc (Zn)	X	X	mg/L	4	15.1	28.0	29.9
Arsenic (As)	X	X	mg/L	4	0.326	0.506	0.560
Selenium (Se)	X	X	mg/L	4	0.327	0.485	0.670
Molybdenum (Mo)	X	X	mg/L	4	0.222	0.225	0.205
Cadmium (Cd)	X	X	mg/L	4	0.047	0.079	0.104
Thallium (Tl)	X	X	mg/L	4	0.029	0.026	0.026
Lead (Pb)	X	X	mg/L	4	3.15	10.7	16.1
Mercury (Hg)	X	X	mg/L	5	n.a.	< 0.1	n.a.

n.a. : not analysed

Table 10 - Concentration of insoluble heavy metals in water samples

Parameters	Filtration: Membrane filter 0.45	microwave digestion of filter residue	Unit	Method of Measurement	ZA/R-2000-026-044 River-km 715	ZA/R-2000-026-045 River-km 718	ZA/R-2000-026-046 River-km 720
Time of Sampling					04:50 PM	05:10 PM	05:25 PM
Date of Sampling					2000-03-15	2000-03-15	2000-03-15
Chromium (Cr)	X	X	mg/L	4	32	< 0.2	< 0.2
Manganese (Mn)	X	X	mg/L	4	103	103	115
Cobalt (Co)	X	X	mg/L	4	1.73	1.97	2.39
Nickel (Ni)	X	X	mg/L	4	11.1	< 5	< 5
Copper (Cu)	X	X	mg/L	4	31.2	47.1	79.9
Zinc (Zn)	X	X	mg/L	4	111	154	217
Arsenic (As)	X	X	mg/L	4	< 0.05	< 0.05	< 0.05
Molybdenum (Mo)	X	X	mg/L	4	< 0.05	< 0.05	< 0.05
Cadmium (Cd)	X	X	mg/L	4	0.136	0.372	0.570
Thallium (Tl)	X	X	mg/L	4	0.747	0.985	0.979
Lead (Pb)	X	X	mg/L	4	62.8	82.4	150
Mercury (Hg)	X	X	mg/L	5	n.a.	0.16	n.a.

n.a. : not analysed

Comment:

Tables 9 and 10 both show increasing heavy metal concentrations. This fact may indicate that sampling was not carried out at the maximum concentration of the pollution.

<u>Hungary - Trivadar – Analyses of River Sediments</u>

In Trivadar, two sediment samples were taken from a previously flooded sandbank – polluted by the spill (pollution flow) of March 10, 2000.

Table 11 - Results from two sediment samples from a contaminated sandbank, March 10

Parameters	Extraction with boiling Nitric acid	Filtration: Folded Filter	Unit refers to dried sample at 105°C	ZA/R-2000-026-103 light sludge	ZA/R-2000-026-104 light sludge with dark inclusions
Time of Sampling				04:30 PM	04:30 PM
Date of Sampling				2000-03-15	2000-03-15
Chromium (Cr)	X	X	mg/kg	16.3	28.9
Cobalt (Co)	X	X	mg/kg	8.92	22.4
Nickel (Ni)	X	X	mg/kg	27.4	47.4
Molybdenum (Mo)	X	X	mg/kg	0.29	1.07
Copper (Co)	X	X	mg/kg	32.1	513
Zinc (Zn)	X	X	mg/kg	92.9	1463
Cadmium (Cd)	X	X	mg/kg	0.40	6.14
Lead (Pb)	X	X	mg/kg	27.8	877
Mercury (Hg)	X	X	mg/kg	0.11	n.a.

n.a. : not analysed

Comparing the light sludge (before spill) and the sample with dark inclusions (after event from March 10th), a strong increase of lead, zinc, copper and cadmium concentrations were determined. This effect may indicate the spilled material from the Novat dam (Baja Borsa).

Romania - Novat – Analyses of the Slurry Samples – Water Samples fromthe Pipeline

Sedimentation pond near the pipeline at location N 047° 43‘ 43“; E 024° 38‘ 52.7“

Table 12 - Concentrations of soluble heavy metals and anions in the two equal water samples

Parameters	Acified with Nitric acid (pH < 2) after	Filtration: Membrane filter	Unit	ZA/R-2000-026-047	ZA/R-2000-026-048
Undissolved Particles (> 0.45 mm)		X	mg/L	13995	18448
pH		X	[-]	7.7	7.7
Conductivity		X	mS/cm	301	331
Chromium (Cr)	X	X	mg/L	0.488	0.277
Manganese (Mn)	X	X	mg/L	985	1209
Cobalt (Co)	X	X	mg/L	1.48	1.74
Nickel (Ni)	X	X	mg/L	< 1	< 1
Copper (Cu)	X	X	mg/L	17.4	9.86
Zinc (Zn)	X	X	mg/L	316	312
Arsenic (As)	X	X	mg/L	2.87	2.53
Selenium (Se)	X	X	mg/L	1.45	1.46
Molybdenum (Mo)	X	X	mg/L	3.02	3.18
Cadmium (Cd)	X	X	mg/L	2.44	2.61
Thallium (Tl)	X	X	mg/L	0.492	0.550
Lead (Pb)	X	X	mg/L	240	191
Mercury (Hg)	X	X	mg/L	<0.1	<0.1
Fluoride (F)		X	mg/L	260	290
Chloride (Cl)		X	mg/L	2210	2150
Nitrate (NO3)		X	mg/L	860	610
Sulphate (SO4)		X	mg/L	97400	109000

Table 12 shows the solubility of the heavy metals in the water samples near the pipeline. The analyses show high zinc, lead and sulphate concentrations.

Table 13 - Concentration of insoluble heavy metals and anions in the two equal water samples from the sedimentation pond

Parameters	Filtration: Membrane filter 0.45	microwave digestion of filter residue	Unit	Method of Measurement	ZA/R-2000-026-047	ZA/R-2000-026-048
Time of Sampling					05:35 PM	05:40 PM
Date of Sampling					2000-03-16	2000-03-16
Chromium (Cr)	X	X	mg/L	4	269	326
Manganese (Mn)	X	X	mg/L	4	12546	14718
Cobalt (Co)	X	X	mg/L	4	928	1138
Nickel (Ni)	X	X	mg/L	4	< 5	< 5
Copper (Cu)	X	X	mg/L	4	51048	59423
Zinc (Zn)	X	X	mg/L	4	161387	188613
Arsenic (As)	X	X	mg/L	4	4506	5810
Molybdenum (Mo)	X	X	mg/L	4	49	59
Cadmium (Cd)	X	X	mg/L	4	743	884
Thallium (Tl)	X	X	mg/L	4	246	297
Lead (Pb)	X	X	mg/L	4	22689	22719
Mercury (Hg)	X	X	mg/L	5	24	8

Table 14 - insoluble content in the water samples ZA/R-2000-026-047 and -048:

Heavy Metal	Insoluble Content [%]
Lead (Pb)	**99.1**
Zinc (Zn)	**99.8**
Copper (Cu)	**99.9**

Romania - Novat Dam – Analyses of dam material

Table 15 - Heavy metal concentrations from a sediment sample and two samples of dam material

Parameters	Microwave digestion of the wet sediments	Unit refers to dried sample at 105°C	ZA/R-2000-026-105 sedimentation pond	ZA/R-2000-026-107 Dam - at the top	ZA/R-2000-026-108 Dam - at the bottom
Chromium (Cr)	**X**	**mg/kg**	**22.1**	**4.76**	**11.3**
Manganese (Mn)	**X**	**mg/kg**	**1112**	**522**	**691**
Cobalt (Co)	**X**	**mg/kg**	**72.8**	**137**	**65.9**
Nickel (Ni)	**X**	**mg/kg**	**6.09**	**< 5**	**< 5**
Copper (Cu)	**X**	**mg/kg**	**4718**	**2115**	**1593**
Zinc (Zn)	**X**	**mg/kg**	**15525**	**9235**	**6026**
Arsenic (As)	**X**	**mg/kg**	**328**	**454**	**357**
Molybdenum (Mo)	**X**	**mg/kg**	**4.22**	**4.04**	**2.48**
Cadmium (Cd)	**X**	**mg/kg**	**65.3**	**38.6**	**25.3**
Antimony (Sb)	**X**	**mg/kg**	**104**	**40.4**	**42.4**
Thallium (Tl)	**X**	**mg/kg**	**17.2**	**8.35**	**13.4**
Lead (Pb)	**X**	**mg/kg**	**8225**	**3882**	**3086**
Mercury (Hg)	**X**	**mg/kg**	**1.9**	**1.5**	**0.7**

The dam is built up with dark sandy material. In dry condition the material is stable and non-slippery. In wet condition the material changes into an unstable sludge. Sample **ZA/R-2000-026-106** was not completely analysed and is therefore not mentioned in Table 15.

Romania - Novat Dam – Assessment of the Heavy Metal Spill on March 10th, 2000

Based on official data from Romania, about 20,000 tons of sludge and dam material were Released during the incident. With the small number of samples an accurate calculation of the spills of heavy metals is not possible. Based on the analyses of the samples from the dam material (ZA/R-2000-026-107 and ZA/R-2000-026-108) an assessment was performed, mentioned in Table 16.

Table 16

Element	Mean value ± 1s (ZA/R-2000-026-107 and ZA/R-2000-026-108) [%]	Spilled amount of heavy metals [t]
Lead	**0.35 ± 0.06**	***~ 70***
Zinc	**0.76 ± 0.23**	***~ 150***
Copper	**0.19 ± 0.04**	***~ 40***

ANALYTICAL METHODS

Sample Preparation

- **Water samples**: The samples were filtered (0.45 micrometer, nitrated cellulose filter). The flasks were rinsed with diluted nitric acid 2%. For the ICP-mass spectrometry 400 Mikroliter of nitric acid 35% was added to 20 mL of each water sample (filtrate).
- **Filtration residues and sediments – Total digestion:** The filter residues from the above mentioned water samples were dried in a vacuum at 50 ^{o}C. The filters were completely digested with the microwave digestion technique in a mixture of nitric and hydrofluoric acid. The evaporation of the silicon was performed after addition of perchloric acid. An aliquot of 0.5 g of the wet sediment samples was digested in the same way. In addition to this, the solid ratio was determined by the moisture analyzer HR 73 (Mettler) at 105 ± 5 ^{o}C.
- **VBBo extraction of the sediments (Swiss Standard Procedure)**: The sediments were extracted (wet) with boiling nitric acid (c= 2 mol/L) in the ratio 1+10 (weight/volume) for 2 hours (temperature about 95 ^{o}C). After the extraction, the samples were passed through a folded filter 602 ½ ; Schleicher & Schüll at about 60 ^{o}C directly into PE-bottles. In addition, the solid ratio was determined by the moisture analyzer HR 73 (Mettler) at 105 ± 5 ^{o}C.

Measurement Method

- ICP-MS-technology (ELAN 6000) was used for the determination of the metals in the water and the total digestion of the sediment samples. The analysis program "Totalquant®" of Perkin-Elmer was applied; it allows a rapid, semiquantitative determination within a measurement precision of about ± 10%.
- All Mercury concentrations were measured with the Flow-Injection Mercury System (FIMS), after stabilizing the samples with $KMnO_4$. The measurements are based on atomic absorption spectrometry and are considered selective.
- The metal content of the sediments was detected quantitatively by ICP-MS-Technology (after extraction and suitable dilution). The results refer to the dry weights (105 ± 5 °C).

STATISTICAL AND MEASUREMENT UNCERTAINTY

Water samples

For the screening analyses of the heavy metals, the ICP-MS-technology was applied in combination with Totalquant®-program. This technology is a semiquantitative method with a uncertainty of measurement of about ± 10% (1-sigma). For checking the certainty, the Initial-Verification Standard (Perkin-Elmer), the Standard Reference Material NIST Nº 1640 “Trace Elements in Natural Water” and the Standard Reference Material LGC 6010 “Hard Drinking Water (UK) – metals” were measured too. Based on these control measurements a uncertainty of ± 10% (1-sigma) issued in the results.

Ionchromatography

The presented results have an uncertainty of ± 2% (1-sigma).

Filtration residue and sediment samples – Total digestion

For the screening analyses of the heavy metals, the ICP-MS-technology was applied in combination with Totalquant®-program. This technology is a semiquantitative method with an uncertainty of measurement of about ± 10% (1-sigma). For checking the certainty the Initial-Verification Standard (Perkin-Elmer), the Standard Reference Material IAEA SL-1 “Sea Lake Sediment” and the Standard Reference Material IAEA SD-M-2/TM “Marine Sediment” were also measured. Based on these control measurements, with exception of the Manganese - and Nickel concentration, an uncertainty of ± 10% (1-sigma) issued in the results. The recovery for the Manganese- and Nickel concentration was 80%.

VBBo extraction of the sediments (Swiss Standard Procedure)

The analyses of the sediments with the ICP-MS-technology are based on the CLP (Contract Laboratory Protocol). The accuracy was checked by analyzing of the Standard Reference Sample ISE 925 (International Soil Exchange). Typically recovery rates of 100 ± 5% were found. The recovery for mercury in the Standard Reference sample ISE 925 (International Soil Exchange) was about 130 %.

RECOMMENDATIONS

- Continued measurement of pollutants along the affected rivers in order to monitor pollution levels and assess the long-term effects on the river ecosystem (water, sediments, flora and fauna).
- Establishment of a register listing all depots and other potential threats posed by industrial sites in the area.
- Specialized assessment of the geological and ecological situation;
- Specialized assessment of waste disposal or storage conditions;
- On the basis of the register a list of actions deemed necessary to reduce hazards should be drawn up.
- Implementation of short-, mid-and long-term action plans

    Short-term measures:

    - Stabilization of depots to prevent further spills. This can be achieved by constructing dams and redirecting water flow from mountain springs, melting snow and heavy rains, into the existing depots.

    Mid- and long-term measures:

    - Identification of other possible devices for mineral waste disposal
    - Establish durable solutions for the provision of safe drinking water (as a precautionary measure)
    - Avoid all future accumulation of mineral waste
    - Gradually change mining techniques and find alternative solutions for boosting the local economy
- Additional recommendations, identified in an April 2000 UNDP report on the Region, identified:
    - An urgent need to cover and stabilize a number of mining waste deposits throughout the Maramures region, seven in all, from wind and water erosion to protect against the release of heavy metals which have a high potential for polluting surface and groundwater.
    - An emergency overflow for floodwaters should be built to prevent a new dam failure at the Novat Dam.
    - Urgent upgrading of the Colbu I Dam (near the Novat Dam).

- A need for environmental monitoring of the Tisza catchment area. UNDP forwarded a comprehensive proposal for this purpose.
- Training aimed at improved management and prevention of releases resulting in accidental water pollution.

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