

ANNEX F

INVESTIGATION OF WATER QUALITY, RIVER SEDIMENTS AND SOIL AT SITES IN THE HRON RIVER BASIN

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F.1 FIELD INVESTIGATION OF WATER QUALITY, RIVER SEDIMENTS AND SOIL AT SITES IN THE LOWER PART OF THE HRON RIVER BASIN.

1. BACKGROUND AND OBJECTIVES OF THE STUDY

Currently, only a surface water quality monitoring programme is carried out in the lower part of the Hron River Basin by SHMU. In this study a three pronged approach was used:

- chemical analysis
- bioassays
- macrozoobenthos analysis

The set of parameters measured in this study were also more comprehensive than that used in the surface water quality monitoring programme carried out by SHMU.

It was recognised that additional surveys were required in the lower part of the Hron River Basin due to the lack of water and soil quality data from monitoring programmes and research studies there. The groundwater boreholes that were used in this study to look at groundwater quality were previously only used to monitor groundwater levels, except for the site at Bina, which was included in the groundwater quality monitoring programme for the first time in 1999 by SHMU.

The lower part of the Hron River Basin was also selected for this field study for the following reasons:

Maps were produced by the JICA team showing patterns of pollution (eg high nitrate levels) and hotspots of pollution by some heavy metals (eg arsenic, copper, lead) in the Hron River basin using data from groundwater sampling carried out by GSSR (Geological Survey of the Slovak Republic) in 1993/94. This highlighted some areas of high pollution in the lower part of the Hron River Basin.

Furthermore, the lower part of the Hron River Basin is of great importance from the point of view of soil and water management. In the lower part of the basin, the vast majority of drinking water and water for irrigation of crops comes from groundwater supplies. There is still a significant percentage of people who are not connected to a public water supply and whose water comes from private wells straight from the groundwater resource (see Interim Report for details, table 5.2-4). The situation for the percentage of the population connected to the public water supply may have improved since the 1997 data used for the interim report, but the REMP team were not able to gain access to this information prior to this annex of the Report being completed.

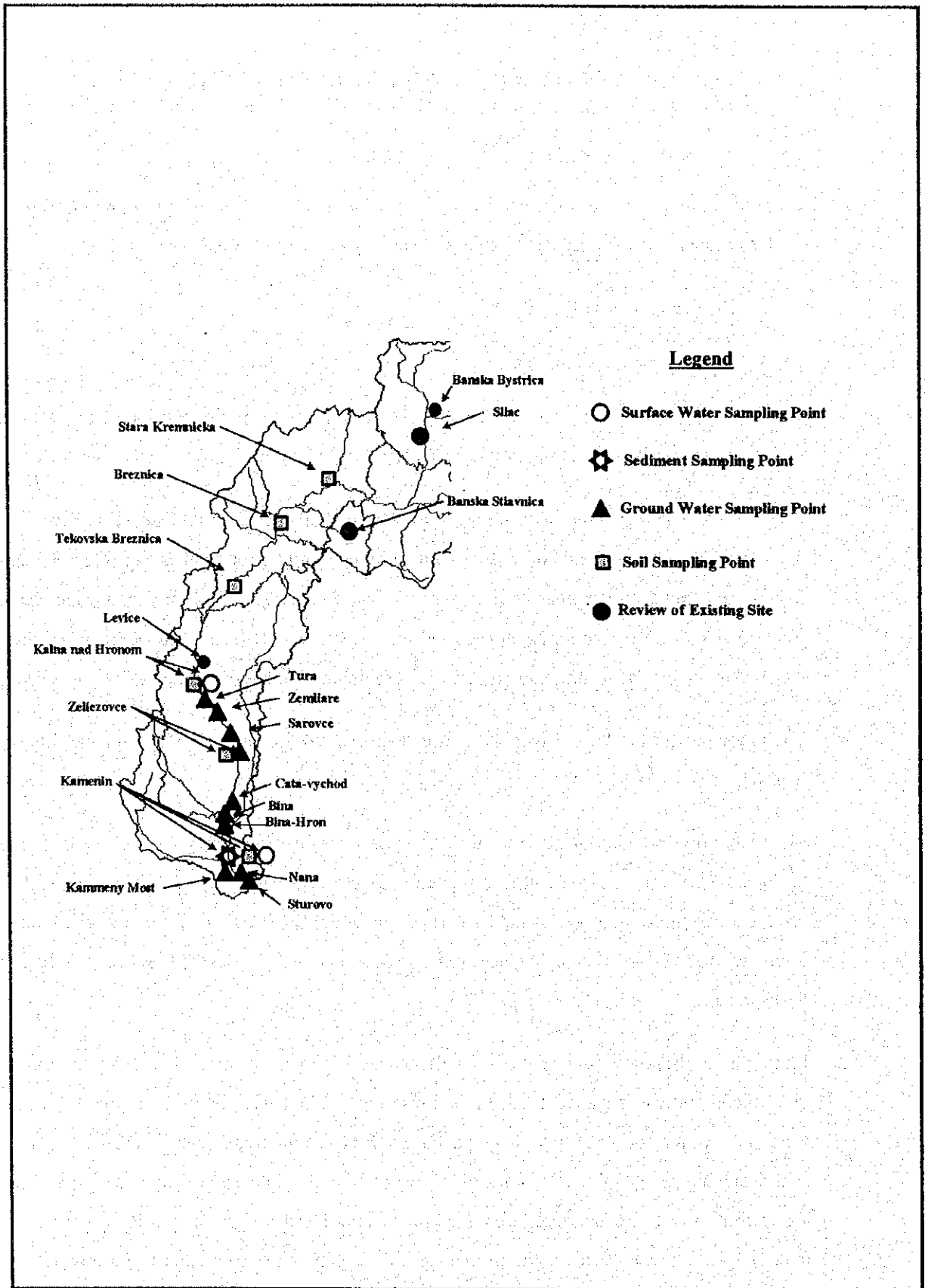


Figure F.1 - 1 Location of Sampling Sites in Lower Hron River Basin Field Study

The combined information from the surface water, sediment, soil and groundwater analyses helps to give a clearer picture of the quality of the lower Hron River Basin and identify patterns of contamination in this area. Information on groundwater and soil quality may be helpful to assess the overall state of groundwater quality and highlight the potential causes of future or present groundwater pollution. The information from this field study will be useful to the REMP team to be fed into their recommendations as part of the final report. It will also be useful for SHMU, and other institutions responsible for water and/or soil quality monitoring, as it could be used to re-organise their monitoring programme in this area; both in terms of the location of sampling sites, and in terms of the parameters monitored. See Figure F.1 - 1 for location of sampling sites for soil, groundwater, surface water and sediments.

2 DESCRIPTION OF PROGRAMME OF FIELD MEASUREMENTS

All sampling and subsequent analyses were carried out in accordance with National or International Standards (STN EN - Slovak Republic National Standard, OECD - Organisation for Economic Co-operation and Development, ISO - International Organisation for Standardisation, ASTM - American Society for Testing and Materials, or USEPA - United States Environmental Protection Act).

2.1 Surface Water

Sampling of river water, including sediments, was carried out in accordance with currently valid international standards ISO 5667-1 and 13. Sampling containers and sample preservatives (where needed) were prepared by the laboratories responsible for the subsequent analysis (both chemical and bioassays). Samples were stored in a refrigerator and cooling boxes immediately after the sampling session during transport to the laboratories. During sampling, current conditions of the immediate sampling area were recorded (see 'sampling report' Appendix F1).

Two surface water samples were taken from two places; Kalna nad Hronom and Kamenin, with a two week gap in between sample taking.

The determinants analysed were basic chemistry: pH, O₂ content, conductivity, redox potential, temperature, nitrates, ammonium and phosphates, and heavy metals: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn.

Temperature, pH, O₂ content, redox potential and conductivity for surface waters were measured in situ. The equipment to measure these parameters was calibrated prior to use.

2.2 Sediments

Sediment sampling was carried out in accordance with ISO/DIS 5667-12 'Guidance on the sampling of bottom sediments'. Sediment samples for chemical analyses and bioassays were taken with a core sampler (a plastic tube with a diameter of 5cm). The core sampling technique was used since this technique minimises the disturbance and subsequent physico-chemical changes to the sediment sample composition. Multiple samples from the first 0-0.1m of the surface sediments around a single point were taken to provide a sufficient volume of sediment for the tests to be carried out. Samples of the Hron River bed sediments were taken twice from Kamenin (with a two week gap in between) using a core sampler and obtaining samples of silty sediment only.

Analyses carried out on these samples were heavy metal analyses: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Specific organics were analysed as well: Polychlorinated Biphenols (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), Bromdichlormethan, 1,1-dichlorethen, Benzene, Xylene, Sterene, Toulene, Ethylbenzene, Benzo(a)pyrene, Fluoranthen, Antracén, Fenantren, Dichlorphenol, Phenol, DDT, Heptachlor, Methoxychlor, Endrin, Aldrin, Dieldrin, Endosulfhan, Chlordane, Hexachlorbenzene, Lindane, Atrazine and Simazine. In addition macrozoobenthos and bioassay analyses were carried out for pore water from these sediments.

Kamenin was chosen as the site for sampling for bioassays and for macrozoobenthos for a few reasons:

Kamenin occurs at a narrow part of the Hron basin that collects water from higher up the catchment area of the Hron REMP study. The Kamenin sampling point also occurs near a SHMU surface water quality monitoring point. Two years background data from this monitoring, in addition to our own chemical analyses of surface water and sediment at Kamenin was available. Although chemical analyses have been carried out for surface water before at Kamenin, sediment, bioassays and macrozoobenthos analyses have not.

(1) Bioassays

It is likely that there will be a complex mixture of chemicals in the Hron since it has a large number of influences. The combination of chemical, biological and bioassay analyses used for this field survey allows us to see whether the conditions, determined by chemical analysis, have an actual effect on the biological system.

Bioassays can be used to identify the true problem for the biological system in an area and can be used to help pinpoint a management strategy, which may help improve the situation. However, in a situation where the pollution is not coming from a single point source (as is the case for the Hron River) there can be some difficulty in pinpointing the exact sources of pollution.

For the bioassays, pore water from the sediment was obtained by centrifuging the sediment sample from Kamenin. This pore water was then used to carry out the bioassays.

All bioassays used were acute tests (i.e. short term). These were used to see whether the pore water was toxic to the organisms. No estimation of the chronic (i.e. long-term) effect of the pore water was carried out.

Daphnia magna immobilisation test OECD 202, ISO 6341.

This test looks at the effect of the pore water on *Daphnia*. The aim of the test is to find the concentration of pore water which, in 24hrs, immobilises 50% of the exposed *Daphnia*. A range-finder test was carried out first - with widely spaced percentages of pore water and a control. This established whether the pore water was toxic to these organisms and also determined a suitable range of concentrations which were used in the definitive toxicity test, where between 3 and 5 concentrations, plus a control, were used.

Lemna minor growth inhibition. Modified ASTM E 1415

This experiment is designed to assess the toxicity of substances to freshwater *Lemna minor*. The objective of the test is to quantify the effects of pore water, from the sediment at Kamenin, on vegetative growth, over the test period, based on frond number. A range of concentrations of pore water plus a control were used.

Vibrio fischeri - MICROTOX (tm) ISO/CD 11 348

This experiment uses the inhibition of the luminescence of the marine bacterium *Vibrio fischeri* to measure the toxicity of a sample of pore water from the sediment. A range of concentrations of pore water from the sediment at Kamenin were used, plus a control.

(2) Macrozoobenthos Analyses

Samples of the bottom sediments for macrozoobenthos analysis were taken using a core sampler for sediments under a water depth greater than 1m. After sampling the macrozoobenthos were kept cool during transport and stored in the laboratory until their identification. Ethanol 80% was used as a preservation medium.

Macrozoobenthos were identified using binoculars and a microscope with keys to various freshwater organisms. Identification of taxa down to species level was carried out if possible. Abundance of species per m² was calculated by extrapolating up from the core sample area and estimating for the 'handnet' sample.

The macrozoobenthos were then analysed using the Saprobe Index. This method gives a certain numerical value to species of different types. According to the composition of the benthic fauna an overall index number can be assigned based on the individual numerical value of each species. This index number can then tell us something about the quality of the sediment in terms of how polluted it is because only certain species can survive in a more polluted environment.

The following formula can be used to calculate the Saprobic Index:

$$SI = \frac{\sum_{i=1}^n (hi * si * Ii)}{\sum_{i=1}^n hi * Ii}$$

hi = abundance of given organisms

Ii = weight of species I in sample

si = saprobic index of individual species i

n = number of individual taxones of organisms

The following formula can be used to express the richness of species in the bottom sediment samples (Shannon Biodiversity Index):

$$H = -\sum_{i=1}^s P_i * \ln P_i$$

S = total species number (species richness)

P_i = contribution of i species to the total biodiversity

2.3 Groundwater

Samples of groundwater were taken from each site (Sarovce, Tura, Zemliare, Bina-Hron, Bina, Cata-vychod, Nana, Kamenny Most, Zelizovce, Sturovo) from existing boreholes (See Map F.1.1-1 for location of sampling sites of ground water).

Each sample was analysed for basic chemistry: pH, O₂ content, conductivity, temperature, sulphates, chlorides, nitrates, ammonium, and heavy metals As, Cd, Cr, Cu, Hg, Ni, Pb and Zn.

Redox potential, pH, water temperature and O₂ content were measured in situ using calibrated equipment. Other measurements were carried out in the laboratory.

2.4 Soil

One objective of the investigation of soils in the lower part of the basin was to look at patterns of heavy metal pollution. It is possible that heavy metals could be transported by the Hron from the mining areas further up in the Hron River Basin.

Soil samples were taken from the A horizon, using a soil borer, from the alluvial plain only, i.e. those areas that are affected by inundation from the Hron river. Soil samples were taken from: Stara Kremnicka, Bzenica, Tekovska Breznica, Kalna nad Hronom, Zelizovce and Kamenin.

At Zelizovce the alluvial plain is very broad and the river terraces are not very distinct (no sharp contours). This soil type consists of a dark, humic A horizon and a gley B horizon - a reducing environment with veins of rust red where oxidation of iron has occurred. The presence of iron indicates that there may be other heavy metals present in the soil as well, but this does not necessarily mean that these metals will be in an available form.

At Kamenin the alluvial plain is much narrower than at Zelizovce because of the mountains either side of the Hron in this area. The alluvial plain undulates in this region and the chemical characteristics of the soil are heterogeneous. Also in Kamenin there is less precipitation and more evaporation from the soil than there is in Zelizovce. Because of this high evaporation rate, salt is deposited in the soil. Salinisation is the biggest problem in this area. Metals may be deposited in the soil in this way also.

The other soil sample sites are taken from further up the Hron basin than Zelizovce or Kamenin, and therefore may be affected more by heavy metals transported by the Hron.

The soil samples were analysed for the following soil characteristics: pH, carbonate status, EC (Electrical Conductivity), texture, TOC (Total Organic Compounds), total and mobile forms of heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn). Mobile forms of heavy metals will be extracted using EDTA (Ethylene Diamine Tetra Acetic acid) and CaCl_2 .

3 RESULTS

3.1 Surface Water

See Table F.1 -1 for results and permissible water pollution levels set by the Slovak Republic Government in 1993 (Regulation 242/1993).

The measured results for the sample sites in Kamenin and Kalna nad Hronom did not differ significantly from those parameters that were measured for surface water in this area as part of the routine monitoring programme for surface water carried out by SHMU, except that the measured oxygen concentration was quite high.

Table F.1 -1. Chemical analysis results for surface water at Kalna nad Hronom and Kamenin sampling sites

	Unit	Permissible concentrations of substance		<i>Kalna nad Hronom</i>		<i>Kamenin</i>	
		For water management river	Other surface water				
Date				29.6. 1999	20.7. 1999	29.6. 1999	20.7. 1999
Time				10 ³⁰	10 ⁰⁰	12 ¹⁵	12 ⁰⁰
Cr	mg/l	-	-	0.004	0.003	0.002	0.003
Hg	mg/l	0.0001	0.0005	0.0004	0.0003	0.0004	0.0003
Zn	mg/l	0.05	0.1	0.065	0.039	0.45	0.42
Cd	mg/l	0.005	0.01	0.0005	0.0004	0.006	0.0003
Cu	mg/l	0.05	0.1	0.008	0.003	0.005	0.0003
Pb	mg/l	0.02	0.05	0.0021	0.0028	0.0026	0.003
As	mg/l	0.02	0.05	0.0041	0.0029	0.0041	0.0031
Ni	mg/l	0.05	0.1	0.009	0.006	0.01	0.007
T _w	°C	-		21.1	18.0	23.3	18.7
pH		-		7.18	7.33	7.69	7.54
O ₂	mg/l	Min.6	Min. 5	7.91	7.4	7.15	7.69
Conductivity	mS/m	-	-	0.17	0.28	0.23	0.31
NH ₄ ⁺	mg/l	0.5	1.5	0.1	0.1	0.1	0.12
NO ₃ ⁻	mg/l	3.4	7.0	5.8	6.3	6.9	7.1
NO ₂ ⁻	mg/l	0.005	0.02	0.14	0.15	0.14	0.15
PO ₄ ³⁻	mg/l	-	-	0.23	0.24	0.27	0.26

This water has a high nutrient content (eutrophic) and has the potential to tend towards eutrophication processes. Due to the high NO₃⁻ and NO₂⁻ the surface water can be classified (according to the Slovak Classification System, STN 75 7221) as class IV for NO₂⁻ and class III-IV for NO₃⁻. Nitrate meets the permissible levels according to those set for surface water for the Slovak Republic (Regulation 242/1993) for 'other surface water' but not for 'water management river'. Nitrite levels do not meet permissible levels for either (see table F.1 - 1). However, Ammonium does not appear to be a problem with its concentrations falling into the class I category for surface water and below the permissible concentrations.

The concentrations of all the heavy metals were measured as being relatively low in the surface waters. Most metals were found to be in category I or II of the Slovak Classification System (STN 75 7221). The highest concentrations of metals were found for Zinc at both Kamenin and

Kalna nad Hronom. Mercury was also found to be higher at both the sites. Mercury can be classified as class III for both sites and Zinc can be classified as class IV for Kamenin (II or III for Kalna nad Hronom) under the Slovak Classification System for water quality.

3.2 Sediments

(1) Chemical Analysis

Slovakia does not have any sediment quality criteria of its own, so Dutch guidelines and their target concentrations (1991) were used to assess the sediment quality. Zinc was found at the highest concentration out of all the metals, but none of the measured heavy metals at the site exceeded the target value for that element.

Table F.1 - 2 Results of the chemical analysis of river bed sediments from Kamenin

<i>Heavy Metals (mg.kg⁻¹ D.W.)</i>				<i>Organic micropollutants (mg.kg⁻¹ D.W.)</i>		
	<i>target value</i>	<i>29.6. 1999</i>	<i>20.7. 1999</i>		<i>29.6. 1999</i>	<i>20.7. 1999</i>
Cr	480	137.2	32.3	PCBs	< 0.1	< 0.1
Hg	0.5	0.24	0.9	PAHs	< 0.1	< 0.1
Zn	480	469.3	249.	Bromdichlormethan	< 0.1	< 0.1
Cd	2	1.3	0.8	1,1 - dichlorethen	< 0.1	< 0.1
Cu	35	54.3	31.0	Benzene	< 0.1	< 0.1
Pb	530	30.0	28.0	Xylene	< 0.1	< 0.1
As	85	3.6	12.	Styrene	< 0.1	< 0.1
Ni	35	15.0	31.0	Toluene	< 0.1	< 0.1
				Ethylbenzene	< 0.1	< 0.1
				Benzo(a)pyrene	< 0.1	< 0.1
				Fluoranthen	< 0.1	< 0.1
				Antracen	< 0.1	1.12
				Fenantren	< 0.1	1.40
				Dichlorphenol	< 0.1	< 0.1
				Phenol	< 0.1	< 0.1
				DDT	< 0.1	< 0.1
				Heptachlor	< 0.1	< 0.1
				Methoxychlor	< 0.1	0.37
				Endrin	< 0.1	< 0.1
				Aldrin	< 0.1	< 0.1
				Dieldrin	< 0.1	< 0.1
				Endosulfhan	< 0.1	< 0.1
				Chlordane	< 0.1	< 0.1
				Hexachlorbenzene	< 0.1	< 0.1
				Lindane	< 0.1	< 0.1
				Atrazine	41.0	6.5
				Simazine	< 0.1	< 0.1

Most of the organic substances were measured at very low concentration levels (less than 0.1mg/kg). Two exceptions were from the second sampling session when the Polycyclic Aromatic Hydrocarbons, Antracen and Fenantren, were detected at higher levels (1.12 mg/kg and 1.4 mg/kg dry weight respectively). See Table F.1 - 2 for results

(2) Bioassays.

None of the organisms showed acute toxic effects from the sediment pore water. For results see Tables F.1 - 3 (for first sediment sample received 29.6.99) and F.1 - 4 (for the second sediment sample received 20.7.99)

Table F.1 - 3 Ecotoxicological test results for sediments collected on 29.6.99 from Kamenin

Test System	Effective concentration (pore water, ml/l)	Effective concentration (recalculated to dry matter content, g/l)
Water plant inhibition test (<i>Lemna minor</i>)	7 day EC50 = 623.96	7 day EC50 = 1747.09
Daphnia immobilization (<i>Daphnia magna</i>)	48 hr EC50 = 1118.46	48 hr EC50 = 3131.69
Light emission inhibition (<i>Vibrio fischeri</i>)	non-toxic	non-toxic

Table F.1 - 4 Ecotoxicological test results for sediments collected on 20.7.99 from Kamenin

Test System	Effective concentration (pore water, ml/l)	Effective concentration (recalculated to dry matter content, g/l)
Water plant inhibition test (<i>Lemna minor</i>)	7 day EC50 = 724.44	7 day EC50 = 1217.06
Daphnia immobilization (<i>Daphnia magna</i>)	non-toxic	non-toxic
Light emission inhibition (<i>Vibrio fischeri</i>)	non-toxic	non-toxic

(3) Macrozoobenthos

Based on the results obtained from analysis of macrozoobenthos from the sediment samples both the saprobic and the Shannon biodiversity indices were calculated. It was calculated that the

Kamenin site could be described as mesaprobian (2.98-3.04) and the Shannon index was calculated as low diversity (1.55-0.58).

See table F.1 - 5 for macrozoobenthos abundance and biological indices

Table F.1 - 5 Macrozoobenthos abundance and biological indices

Class	Taxa	Abundance	Species per m ²
OLIGOCHAETA	Tubifex tubifex	364	25 997
	Limnodrilus hoffmeisterii	909	4 636
	Eiseniella tetraedra	182	273
	Branchiura soveryi	-	91
CHIRONOMIDAE	Chironomus sk. Thummi	728	364
	Polypedium sk. Nubeculosum	273	-
SIMULIDAE	Simulium (Wilhemia) lineatum	91	-
	Total	2547	31361
	Saprobity Index	298	304
	Diversity	1.55	0.548

3.3 Groundwater

Results from the chemical analysis of the groundwater are shown in table F.1. - 6. These results were evaluated in accordance with STN 75 111 'Drinking Water'. This standard defines the maximum allowable concentrations of selected determinands in drinking water. Where the measured value for a chemical exceeds the maximum allowable concentration this is indicated in the results table by highlighting the measured amount in bold.

Nitrates do not comply with the limit value at three sites: Nana, Zemliare and Tura. Nitrite levels are also exceeded at Kamenny Most 2. Ammonium is exceeded at Kamenny Most 1 and Zelizovce.

In Cata, Bina 2, Kamenny Most 1, Nana, Zelizovce and Kamenny Most 2 there were high levels of Sulphates – over the limit values set by the Slovak National Standards. There were also high levels (exceeding the standard) of Chloride at Bina 1, Kamenny Most 1, Nana, and Kamenny Most 2. Kamenny Most (1 and 2), Bina 1 and Nana also show high levels of Na⁺ and K⁺.

Heavy metal content was also analysed. The limits set by Slovak standards were exceeded for Arsenic at Cata, Bina 2 and Kamenny Most. They were exceeded for Nickel at Tura.

Table F.1 - 6 Results of the Chemical analysis of groundwater.

Determinand	Limit value	Unit	000559	000564	056090	000556	000511	000580	002573	000579	000512	127431
Station code			Bina 1	Cata	Banal 2	Kamenny Most 1	Nana	Zemliare	Zeliezovce	Tura	Kamenny Most 2	Sarovec
Sampling site												
Date of sampling			23.7.1999	23.7.1999	29.6.1999	13.7.1999	13.7.1999	12.7.1999	12.7.1999	12.7.1999	22.7.1999	29.6.1999
Na		mg.l ⁻¹	238.00	38.80	32.00	580.00	117.00	16.80	17.60	17.10	117.00	21.60
K		mg.l ⁻¹	10.90	1.21	4.77	13.00	14.90	2.30	2.93	12.60	135.00	3.93
NH ₄ ⁺	0.5	mg.l ⁻¹	0.27	0.20	<0.05	0.62	0.05	0.06	0.75	<0.05	0.13	0.19
Cl ⁻	100	mg.l ⁻¹	116.80	90.30	61.10	867.30	230.10	86.70	76.10	67.30	132.80	92.00
NO ₂ ⁻	0.1	mg.l ⁻¹	0.032	0.024	<0.001	0.016	0.088	<0.001	0.046	0.008	0.146	<0.001
NO ₃ ⁻	50	mg.l ⁻¹	<2.0	<2.0	<2.0	<2.0	57.17	66.74	<2.0	76.30	49.50	35.65
SO ₄ ²⁻	250	mg.l ⁻¹	125.50	283.00	270.20	375.30	416.40	160.60	365.25	103.05	277.50	87.16
KNK ₄₅		mmol.l ⁻¹	13.40	6.60	6.20	10.70	8.20	5.70	4.20	7.30	8.10	7.60
ZNK ₈₃		mmol.l ⁻¹	1.30	0.70	0.50	1.70	1.10	0.50	0.50	0.80	0.60	1.50
O ₂		mg.l ⁻¹	0.50	0.40	0.10	0.10	0.20	7.80	0.00	0.90	2.70	4.40
% O ₂		%	6.00	4.00	2.00	1.00	2.00	71.00	0.00	8.00	27.00	41.00
Conductivity		mS.m ⁻¹	174.00	131.70	111.30	403.00	191.10	115.60	123.60	114.60	197.20	99.10
pH			6.94	6.95	6.71	6.86	7.12	7.15	6.73	6.95	7.04	6.91
T _w		°C	11.40	12.50	11.10	10.00	10.80	10.20	10.20	10.50	12.80	13.00
T _{air}		°C	17.10	17.00	29.00	26.50	26.00	28.00	22.00	25.50	23.90	29.20
As	10	µg.l ⁻¹	1.52	12.10	16.60	1.71	6.16	<1	5.17	1.23	17.30	<1
Cd	3	µg.l ⁻¹	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cu	500	µg.l ⁻¹	4.10	6.10	7.50	9.90	8.70	4.70	5.00	6.80	7.10	17.50
Pb	10	µg.l ⁻¹	<1	1.10	1.98	<1	<1	<1	<1	<1	1.00	1.01
Hg	1	µg.l ⁻¹	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	3000	µg.l ⁻¹	<5	<5	7.00	5.00	10.00	8.00	11.00	6.00	7.00	312.00
Cr	50	µg.l ⁻¹	<1	<1	1.13	<1	<1	<1	<1	<1	<1	<1
Ni	20	µg.l ⁻¹	12.90	16.70	9.45	18.50	17.50	11.20	18.90	28.40	16.80	11.30

3.4 Soil

Tables F.1 - 8 through F.1 - 12 show the results of the chemical, soil texture and soil characteristics analyses of the soil samples. All soils analysed in this study showed a neutral to alkaline pH. For some elements A and B limits are reached (see table F.1 - 7 for limit values set by Ministerstvo Podohospodarstva Slovenskej Republiky - MPSR). All the soils analysed are contaminated by heavy metals to a certain degree. However, the concentrations of heavy metals present in the soil vary depending on where the sample comes from.

The extractable metal content (by EDTA) measures the amount of the metals that are 'available' for uptake eg, by plants. Some of the metals are present in relatively high levels in this available form.

The analysis of the soils also included CaCl_2 extraction. This weak neutral extract shows those metals that would form exchangeable ions in soil colloids. As can be seen in table F.1 - 9 most of the metals are below detection limits under these conditions, Arsenic being the exception, being detected at low levels. The highest amount (0.2 mg/kg) of extractable Arsenic was found in Gleyic fluvisol at Zelizovce.

Table F.1 - 7 Limit Values of Elements in Soils (mg/kg) (MPSR, 1994)

Limit Category	Elements						
	As	Cd	Cr	Cu	Ni	Pb	Zn
A limit	17.4	0.46	90	18.6	15	56	66.5
B limit	30	5	250	100	100	150	500
C limit	50	20	800	500	500	600	3000

A limit: the soil is not contaminated if the concentration of an element is below this limit

B limit: the soil contamination has been analytically proven

C limit: if the concentration of an element reaches this value, it is necessary to carry out immediately definitive analytical mapping of the problem range at the site and to decide on the required corrective measures.

Table F.1 - 8 Total measured metal content in soil samples

Number of sample	Coordinate		Site	FAO Soil unit	Total metal content (mg.kg ⁻¹) - Aqua regia									
	X	Y			As	Cd	Cr	Cu	Ni	Pb	Zn	Hg		
REMP - 1	1302053.73	457831.25	Cadaster Zelizovce	Fluvi-eutric Gleysol	36.125	0.475	30.250	47.250	22.000	36.000	101.250	0.027		
REMP - 2	1319938.38	461589.25	Kamenin	Fluvisol	30.250	1.200	20.500	83.750	15.000	78.500	211.250	0.040		
REMP - 3	1242558.02	437384.41	Stara Kremnicka	Fluvisol	100.525	0.223	16.950	42.400	6.000	68.000	76.250	0.096		
REMP - 4	1249315.33	449833.52	Bzenica	Fluvisol	61.925	2.045	14.775	91.950	13.000	333.500	432.250	0.060		
REMP - 5	1264476.98	460500.77	Tekovska Breznica	Fluvisol	39.225	1.928	21.375	107.050	10.250	133.750	343.500	0.090		
REMP - 6	1282357.30	468206.87	Kalna nad Hronom	Fluvisol	48.525	1.160	26.700	194.225	18.000	120.750	213.000	0.140		

Table F.1 - 9 Measured extractable metal content in soil samples- CaCl₂

Number of sample	Coordinate		Site	FAO Soil unit	Extractable metal content (mg.kg ⁻¹) - 0.01 M CaCl ₂									
	X	Y			As	Cd	Cr	Cu	Ni	Pb	Zn	Hg		
REMP - 1	1302053.73	457831.25	Cadaster Zelizovce	Fluvi-eutric Gleysol	0.210	< 0.050	< 0.100	< 0.500	< 0.500	< 0.500	< 0.300	< 0.005		
REMP - 2	1319938.38	461589.25	Kamenin	Fluvisol	0.130	< 0.050	< 0.100	< 0.500	< 0.500	< 0.500	< 0.300	< 0.005		
REMP - 3	1242558.02	437384.41	Stara Kremnicka	Fluvisol	0.030	< 0.050	< 0.100	< 0.500	< 0.500	< 0.500	< 0.300	< 0.005		
REMP - 4	1249315.33	449833.52	Bzenica	Fluvisol	0.050	< 0.050	< 0.100	< 0.500	< 0.500	< 0.500	< 0.300	< 0.005		
REMP - 5	1264476.98	460500.77	Tekovska Breznica	Fluvisol	0.100	< 0.050	< 0.100	< 0.500	< 0.500	< 0.500	< 0.300	< 0.005		
REMP - 6	1282357.30	468206.87	Kalna nad Hronom	Fluvisol	0.023	< 0.050	< 0.100	< 0.500	< 0.500	< 0.500	< 0.300	< 0.005		

Table F.1 - 10 Measured extractable metal content in soil samples-EDTA

Number of sample	Coordinate		Site		FAO Soil unit	Extractable metal content (mg.kg ⁻¹) - 0.05 MEDIA									
	X	Y	Cadaster	Zeliezovce		As	Cd	Cr	Cu	Ni	Pb	Zn	Hg		
REMP - 1	1302053.73	457831.25	Cadaster	Zeliezovce	Fluvi-eutric Gleysol	0.632	0.110	<0.100	13.000	5.000	12.500	25.000	0.009		
REMP - 2	1319938.38	461589.25	Kamenin		Fluvisol	0.538	0.130	<0.100	27.000	3.000	21.600	40.000	0.025		
REMP - 3	1242558.02	437384.41	Stara Kremnicka		Fluvisol	1.033	0.118	<0.100	14.000	<1.000	17.250	9.000	0.095		
REMP - 4	1249315.33	449833.52	Bzenica		Fluvisol	0.873	1.250	<0.100	40.000	2.000	139.250	86.250	0.059		
REMP - 5	1264476.98	460500.77	Tekovska Breznica		Fluvisol	1.435	1.233	<0.100	46.000	1.000	61.750	67.250	0.051		
REMP - 6	1282357.30	468206.87	Kalna nad Hronom		Fluvisol	0.713	0.923	<0.100	110.000	4.000	59.000	41.000	0.102		

Table F.1 - 11 Soil texture of the samples

Number of sample	Coordinate		Site		FAO Soil unit	Soil texture				
	X	Y	Cadaster	Zeliezovce		2,0 - 0,25 mm	0,25 - 0,05 mm	0,05 - 0,01 mm	< 0,001 mm	
1	1302053.73	457831.25	Cadaster	Zeliezovce	Fluvi-eutric Gleysol	3.030	15.570	13.710	29.800	37.880
2	1319938.38	461589.25	Kamenin		Fluvisol	0.930	27.740	25.570	24.990	20.760
3	1242558.02	437384.41	Stara Kremnicka		Fluvisol	9.369	37.837	28.338	14.792	9.664
4	1249315.33	449833.52	Bzenica		Fluvisol	14.791	29.494	27.723	16.119	11.783
5	1264476.98	460500.77	Tekovska Breznica		Fluvisol	26.113	40.829	17.182	8.448	7.428
6	1282357.30	468206.87	Kalna nad Hronom		Fluvisol	1.207	13.138	37.927	28.107	19.621

F.1 - 12 Soil characteristics of the samples

Number of sample	Coordinate		Site		FAO Soil unit	Depth (cm)	Soil reaction		Electrical conductivity (µS/cm)	Carbonate content (%)	Humus content (%)
	X	Y	Cadaster	Zeliezovce			pH/H ₂ O	pH/KCl			
1	1302053.73	457831.25	Cadaster	Zeliezovce	Fluvi-eutric Gleysol	0 - 20	8.04	6.49	98	0.00	2.03
2	1319938.38	461589.25	Kamenin		Fluvisol	0 - 20	8.39	7.18	193	1.15	1.39
3	1242558.02	437384.41	Stara Kremnicka		Fluvisol	5 - 10	7.64	6.58	98	0.00	2.12
4	1249315.33	449833.52	Bzenica		Fluvisol	5 - 10	7.28	6.31	115	0.00	3.61
5	1264476.98	460500.77	Tekovska Breznica		Fluvisol	5 - 10	7.75	6.91	117	0.00	2.37
6	1282357.30	468206.87	Kalna nad Hronom		Fluvisol	5 - 10	7.23	6.13	191	0.00	2.80

3.5 Conclusions

(1) Surface Water

The high measured oxygen concentration may be due to the recent heavy rain and flood conditions resulting in greater movement in the water. It is also possible that due to the high nutrient levels present in the water, coupled with the sunny conditions, there may be large amounts of phytoplankton photosynthesising and producing oxygen.

Surface water can be classified as eutrophic. It has particularly high nitrite levels – probably from the nitrification of nitrate. However, ammonia levels are not high; this suggests that the possible source of the nitrite is from inorganic rather than from organic sources. This suggests that maybe the problem of eutrophication is due to excess nitrate from a source outside the natural system, possibly fertilisers.

Heavy metals were generally not found in concentrations that are considered problematic. However zinc was found to fall into class IV of the Slovak classification at Kamenin and mercury was found at class III levels in Kamenin and Kalna nad Hronom.

(2) Sediments

The low concentrations of metals and organic compounds measured at Kamenin may be explained by the dilution effects of two previous floods. However, the sediment taken for testing was the grey-black colour indicative of older sediments, therefore the low amount of heavy metals and organic pollutants measured may be a true reflection of the situation, at least for the Kamenin river bed sediments.

Zinc metal was found in the highest amounts in the sediment, but none of the heavy metal's concentrations measured exceeded the target values (based on Dutch guidelines) for sediment quality. Most organic substances were measured at low levels, except for on the second sampling day when two different Polycyclic Aromatic Hydrocarbons were detected at higher levels. The low levels of heavy metals and organic substances measured in the chemical analyses correlates well with the fact that no acute toxic effects were seen in the bioassays.

Sediment was found to be mesosaprobic with a low diversity index value which indicates high nutrient levels present.

(3) Groundwater

Several sites are above the limit values for nitrate. This is probably from agricultural fertiliser input, the map 'agricultural land use of the Study Area by cadasters' shows that in the lower part of the Hron River Basin between 60-100% of the land use is agricultural. If we compare these results with the map produced from GSSR's survey carried out in 1993/4 it can be seen, however, that the nitrate level has reduced from the very high levels seen then. This is probably due to a reduction in agricultural fertiliser use, following changes in the Slovak economy.

High sulphate levels are also seen in several places. A possible source of sulphate may be from fertiliser inputs into the soil in the form of ammonium sulphate. The ammonium is converted to nitrate, which can then be used by the crop plants, this then leaves the sulphate. The sulphate is then leached out of the soil (due to natural rainfall and due to irrigation) into the groundwater. Another possible explanation is that the sulphur may come from water draining down from old mines. It is most likely that several different sources will contribute to sulphate contamination of groundwater.

(4) Soil

The concentrations of heavy metals present in the soil vary depending on where the sample comes from. This points to a variety of activities affecting the heavy metal concentrations in the soils in this area. It is most likely that a combination of mining, industrial and agricultural activities in the basin are reflected in the patterns of heavy metal contamination seen in the soil. For example, copper concentration increases further downstream, this may be due to increased copper fungicide application in the farmland and vineyards of the lower basin.

Kremnica's mining areas may be a source of As to the Hron Basin, Stianicke vrchy mountains (Bzenica) may be the source of Pb, Zn and Cd, relating to the types of ores being mined in these areas (polymetallic Pb, Zn, Ag and Sb ores).

The extractable metal content (by EDTA) measured the amount of the metals that are mobile and 'available' for uptake, for instance by plants. Some of the metals were present in relatively high levels in this available form. The mobile forms of these heavy metal contaminants could enter the food chain and cause problems for human health.

The transport of these metal ions to groundwater through the soil profile is unlikely to happen due to soil depth, soil properties, humus content and the sorption capacity of the soils. The redistribution of these elements is more likely to be due to the erosion of suspended particles and run-off since dissolved species in surface water can supply groundwater.

Colloidal particles could be a source of simple and hydrated ions, which migrate in surface and groundwater. Depending on the hydrothermal regime and geochemical barriers these can be redistributed in the water basin and result in heterogenic dispersal of soil heavy metal contamination in alluvial soils.

The highest amount (0.2 mg/kg) of extractable Arsenic (detected by CaCl_2 extraction) was found in Gleyic fluvisol at Zelizovce. Gley's typically have a higher Fe^{2+} oxide content (due to oxidation-reduction phenomena). Arsenic has a higher affinity to secondary oxides and therefore the registered amount of Arsenic seen in this analysis could be due to the adsorption of Arsenic onto amorphous Fe and Mn sesquioxides. Groundwater fluctuation in the unsaturated zone of the soil profile may cause rapid changes in sorption/desorption processes, resulting in dissolution and exchange reactions making the heavy metals more or less available. These dynamic processes have not as yet been studied, however.

3.6 Recommendations

The above section highlighted some conclusions. This section outlines further recommendations and gives suggestions on who might be responsible for these actions in Slovakia.

(1) General

Institutions with responsibilities for monitoring should not simply collect data without checking its value/significance. There should be consideration of the potential problems highlighted by the monitoring data, the causes of these problems and actions that could potentially solve these problems. There should also be consideration of who should be responsible for ensuring that these actions are carried out and that monitoring continues, to see whether the actions are effective in solving the problem. Institutions that may be involved for ground and surface water and soil quality issues include: ZsVak (Western Slovak Water Supply and Sewerage Company), VUVH (Slovak Water Research Institute), VUPOP (Soil Science and Conservation Research Institute), SAZP (Slovak Environmental Agency), State Health Institute, MZP (Ministry of

Environment), MP (Ministry of Agriculture), StVak (Central Slovak Water Supply and Sewerage Company) and PH (Povodie Hrona).

(2) Surface Water and Sediments

Surface water quality monitoring is currently undertaken by SHMU; in areas where potential problems are identified, sediment chemical analyses and bioassays could be used as follow up tests. SHMU does not have the capability to do these tests but there are companies in Slovakia (eg ETC – Ekotoxikologicke Centrum, Bratislava) who could be subcontracted by SHMU to carry out this work. SHMU could then take responsibility for the analyses of these results ie, looking at whether the potential problem highlighted by the surface water quality monitoring is a real problem for the biological system. If it is found to cause a real problem, some action plans to try and improve the situation could be introduced. This may involve consultation with other organisations such as those outlined above in the 'General' section.

For surface water in the Lower Hron River Basin, it would be a good idea to continue to monitor these places for heavy metal concentrations, particularly Zinc and Mercury, to check that levels of these metals do not become unacceptable. It may be a good idea also to investigate potential sources of these metals in the areas around Kamenin and Kalna nad Hronom and see if anything can be done to limit further the inputs of these metals into the river system.

(3) Groundwater

It would be good to extend the current groundwater monitoring into the lower part of the Hron Basin, particularly looking at nitrate levels which have been identified as above the limit value for Slovakia in this area. If the levels of nitrate measured do not decrease, consideration could be given to potential solutions. For example, by reducing the amount of nitrate input by limiting the amount of fertiliser input to be used by farmers in certain areas where there is a particular problem with high nitrate levels. This would have to be done with SHMU working with the Ministry of Agriculture and the Slovak Water Research Institute and possibly the Soil Science and Conservation Research Institute.

It would be useful to continue monitoring the nitrate levels in areas where it is above the limit value at the moment, to check that levels continue to decrease to below the limit value.

Measures could also be put in place by ZsVak and StVak, working with the State Health Institute, to ensure that water containing nitrate over the limit value is not used to supply drinking water. High nitrate levels can cause health problems, particularly for young children. In the lower part of the basin, much of the drinking water comes from groundwater sources and some people are supplied with drinking water from wells (Based on data from the Interim Report see F.1.1.2).

(4) Soil

Further studies investigating potential pollution problems from heavy metals in the lower part of the Hron River Basin should concentrate on assessing the concentrations of available metal ions. It is these available forms of metals that can enter the food chain and cause problems for plant growth and/or human health. It is suggested that the Soil Science and Conservation Research Institute should be responsible for such a study, in collaboration with the Ministry of Agriculture and State Health Institute.

Groundwater fluctuation in the unsaturated zone of the soil profile may cause rapid changes in the sorption/desorption processes, resulting in dissolution and exchange reactions. These dynamic processes have not as yet been studied, however. This may therefore be a priority for research, particularly focussing on what the results mean for availability of metal ions and the implications for crop and human health. It is suggested that the Soil Science and Conservation Research Institute should be responsible for such a study, in collaboration with the Ministry of Agriculture and State Health Institute.

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5 APPENDIX - SAMPLING REPORT

Sampling Report

Name of sampling site: Hron - Kalná nad Hronom r. k. 63.7
 Location of sampling point: Right bank side – water
 Sample code: Hron – Kalná nad Hronom
 Date/time of sampling: 29.6.1999
 20.7.1999
 Sample type: Water
 Sample characteristics: (grain size estimates, colour, odour, visible layers...)
 Water - Slightly brown colour caused by suspended solids

Hydrometeorological conditions:
 Sunshine weather

Depth of water column: 20 cm
 Depth of sample sediments: -
 Type of sampler: Manual by glass and plastics bottles - water

Sampling personnel:
 Mr. Zdeno Miláček – water
 Mr. Peter Roncák - sediment
 Mr. Martin Murin - sediment

In situ measurements:	water	
	29.6.1999	20.7.1999
pH	7.18	7.33
T _{water} [°C]	21.10	18.0
Redox [mV]	-	-
O ₂ content [mg.l ⁻¹]	7.91	7.40
Conductivity [mS.cm ⁻¹]	0.17	0.28

Sampling Report

Name of sampling site: Hron – Kamenin, r. k.10.9
Location of sampling point: Left bank side – water and sediment
Sample code: Hron – Kamenin
Date/time of sampling: 29.6.1999
 20.7.1999
Sample type: Water and sediment
Sample characteristics: (grain size estimates, colour, odour, visible layers...)

Water - Slightly brown colour caused by suspended solids
 Sediment – upper part fine sediment, followed by sand layer,
 Grey colour

Hydrometeorological conditions: Sunshine weather

Depth of water column: 20 cm

Depth of sample sediments: 10 cm

Type of sampler: Plastics core sampler – sediment, biology (deep water)
 Manual by glass and plastics bottles - water

Sampling personnel: Mr. Zdeno Miláček – water
 Mr. Peter Roncák - sediment
 Mr. Martin Murin - sediment

In situ measurements:	Water		sediment
	29.6.1999	20.7.1999	
pH	7.69	7.54	
T _{water} [°C]	32.30	18.70	
Redox [mV]	-	-	
O ₂ content [mg.l ⁻¹]	7.15	7.69	
Conductivity [mS.cm ⁻¹]	0.23	0.31	

F.2 DESK STUDY: CONTAMINATION IN SLIAC - VLKANOVÁ

(1) Introduction

It is generally true that if oil products are used without any protection, eg measures to prevent spillage, this can result in the pollution of both groundwater aquifers and the soil. This was the case for an area around Sliac - Vlkanová that was used by the Soviet army. During the last years of the presence of the Soviet army in this locality, some decontamination activities were carried out. However, only after the Soviet army had departed could complete restoration of the groundwaters and soils begin. Both in-situ and ex-situ techniques were proposed and used for the treatment of heavily contaminated areas. Complete remediation of the area also included removal of ground and underground constructions, pipe and tube systems and illegal waste dumps. In this brief report some results and findings from the investigations and remediation activities within the contaminated area are summarised. This report is based only on the results and information available to the general public and was prepared after discussion with a representative of the Ministry of Defence of the Slovak Republic.

(2) Locality Description

The Sliac-Vlkanová study area is situated on the right bank of the Hron River in the Zvolenská valley. This area is a part of the 2nd protection zone of the Sliac and Kováčova spa spring (which has curative and rehabilitation facilities). Part of the area around Sliac is also used as both a public and Slovak air force airport. The Vlkanová area was used as a depot for oil products and organic solvents. Due to a lack of protective and preventative measures, stored substances were spilled and penetrated the soil and groundwater systems. Both systems were found to be heavily contaminated. For example, in 1996 it was calculated by Galisova (1998) that the amount of soils in the Sliac area contaminated with concentration levels of oil substances greater than 500 mg/kg, was approximately 61 416 m³. In the Vlkanová area it was estimated that the volume of soil with contamination greater than 220 mg/kg was 119 950 m³. In the period between 1980 and 1990, 380 000 litres of oil substances were pumped from the groundwater (Ondrejčáková *et al.* 1998). At Sliac, on the Hron River, concentrations of oil substances expressed as Non-polar Extractable Substances (NES) were measured in the range 0.03-0.3 mg/l. These values classify the surface waters as class IV according to the Slovak standard for NES (Adamková *et al.* 1999).

(3) Survey and Investigation Activities

Survey and remediation activities began in 1980 during the withdrawal of the Soviet army. Until 1992 the destruction of the contaminated soils focussed mainly on ex-situ techniques. This was followed by the destruction of the buildings and underground pipelines and tube systems which had contained or piped oil substances in the Sliac and Vlkanová areas. Surveys of the contaminated sites were completed in 1993-4 and mapped, particularly focussing on the soil contamination. During this period, drainage systems, along with two waste water treatment plants, were constructed. Based on the results and findings from the surveys it was decided to complete remediation using in-situ techniques. These in-situ techniques are still running today. Remediation actions relating to groundwaters continue today using drainage systems, waste water treatment plants (mentioned above) and remediation wells.

(4) Remediation of the Contaminated Soils Ex-situ

Some of the contaminated soils were remediated using ex-situ techniques at decontamination sites with a capacity of 10 000 m³. Ex-situ techniques were based on the microbiological degradation of the soil substances.

(5) Remediation of the Contaminated Soils In-situ

Contaminated soils in the Sliac locality were also cleaned up using in situ techniques. One technique is based on the bioventing method. In Vlkanová the situation was difficult due to the wide spectrum of the chemical contaminants present in the area. For this reason, the contaminated area in Vlkanová was subdivided into several zones, where different specific techniques were used. These techniques are based on the saturation of the system with oxygen and nutrients for autochthonous flora (Cop, 1998). This flora is separated from the natural system, enriched with nutrient in bioreactors and then replaced back into the soil systems. In other zones, bioventing techniques were used in addition to biodegradation techniques H - 10 (Cop, 1998). Table F.2 - 1 shows estimated volumes of contaminated soils treated using in-situ and ex-situ techniques in Vlkanová.

Table F.2 - 1 Contaminated soil volume treated with in-situ and ex-situ techniques at Vlkánová. Limit concentration of hydrocarbons in soil: >200 mg/Kg d.w.

	In situ (m ³)		Ex situ (m ³)	
	to 31. 12. 1994	To 31. 12. 1996	to 31. 12. 1994	to 31. 12. 1996
Vlkanová	108 853	108 853	43 814	11 097

(6) **Clean - up of the Groundwater**

Groundwater in parts of Sliac and much of Vlkánová are contaminated with a wide spectrum of both aliphatic and aromatic hydrocarbons. Therefore a waste water treatment plant (WWTP) was built to clean - up contaminated groundwaters. Five drainage systems were constructed in Sliac and two were constructed in Vlkánová. The length of these drainage systems is approximately 3 km. The WWTP is fully automatic and a continuous analytical programme controls the remediation process.

During the remediation process (between 1992 and 1997) 75 093.23 litres of free oil substances were pumped through this system (Galisová, 1998). In Table F.2 - 2 the amount of hydrocarbons eliminated from groundwater in Sliac and Vlkánová are shown

Table F.2 - 2 Amount of hydrocarbons eliminated from groundwater at Sliac and Vlkánová.

	NES-IR	NES-IR	Aromatic hydrocarbons	Aliphatic chlorinated hydrocarbons	Aromatic Chlorinated hydrocarbons
	(kg/year)				
1992 - 1994	698.868	1 083.154	824.960	149.610	0.514
1995 - 1997	1 744.500	1 213.923	400.329	124.586	22.704
Total:	2 443.368	2 297.077	1 225.259	274.220	23.218

(7) **Other Remediation Activities**

Into the battery of the remediation activities to complete the cleaning process in Sliac and Vlkánová, techniques were introduced to remove pipelines, tubes, buildings materials and the rest of pumping stations and illegal dumping sites (for example Tri duby - Majer site).

(8) Conclusion

Both in-situ and ex-situ techniques have been used to clean up contaminated land and groundwater in the Sliac and Vlkanova areas. The successfulness of these techniques should be monitored (e.g. by measuring contamination at periodic intervals and determining from these analyses whether or not the techniques are effective in remediating the contamination). This information could then be used as a basis for determining which clean-up technologies will be most effective for use in other areas contaminated with hydrocarbons. It is suggested that the Ministry of Environment could be responsible for this information, in collaboration with the Ministry of Defence.

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F.3 DESK STUDY: CONTAMINATION IN BANSKA STIAVNICA

For the following description, information was taken from: Curlik, J. and Forgac, J., "Acid Sulphate weathering and its impact on soil acidification and pollution in area of Banska Stiavnica," Proceedings no.21 Vedecké pracé ch.21.

(1) Introduction

Concern over the processes of acidification and their adverse effect on soils and freshwater systems has grown in recent decades. Soil acidification is caused mostly by acid deposition. However, in some areas, the weathering of hydrothermally altered and pyritized rocks, mined wastes and settling pits, and material containing pyrite may contribute, on a local scale, to soil acidification (and consequently to the leaching and mobilisation of chemical elements, including heavy metals) due to acid sulphate weathering. In this resume of a paper by Curlik and Forgac these soil acidification processes are discussed using the mining town of Banska Stiavnica as an example, which is within the Hron River Basin study area, and the adjacent alluvial plain.

Acid sulphate soils are described as soils having one or more of the following characteristics:

- 1) A pH below 4 within the top 50cm depth, due to oxidation of pyrite (Fe_2S) and the subsequent formation of sulphuric acid (Van Breemen, 1982)
- 2) A flooded soil that contains minerals or organic materials with more than 0.75% sulphur, and less than three times as much carbonate expressed as CaCO_3 , as sulphide sulphur

The formation of acid sulphate soils requires a physiography or favourable environment that provides oxidation of pyrite upon drainage as a result of natural processes or human activities

Soil acidification and the resulting drop on pH can be defined as a decrease in acid neutralisation capacity (ANC) of soil. Potential causes of soil acidification are shown in Table F.3.1-1
The sulphur cycle is relevant to understanding acid sulphate weathering and its contribution to soil acidification: The sulphur cycle generally does not contribute to the H^+ production in soil. Generally, the cycle is closed and the hydrogen released by sulphate through mineralisation and oxidation (H^+ sources) is balanced by sulphate uptake (H^+ sinks) by plants. The processes induced by acid deposition and/or pyrite weathering lead to disruption in the balance of the Sulphur cycle, which leads to soil acidification by the leaching of SO_4^{2-} with accompanying cations.

Table F.3 - 1 Soil Acidification Reasons and Consequences

Reasons		Consequences
Natural Factors	Human activities	
<ul style="list-style-type: none"> - Acid (non calcareous) parent material - Root respiration - Decomposition of plant residues (CO₂), acidic substances - Leaching as a result of permanent or dominant downward flow (high precipitation and low water retention) - Natural acidic depositions 	<ul style="list-style-type: none"> - change in land use practice - change in agricultural technology - improper fertiliser application (form, dosage) - amelioration (acidic amendments, drainage) - industrial and urban wastes and sewage waters - wet and dry acidic deposition (air pollution due to industrial and urban development) 	<ul style="list-style-type: none"> - reduction in pH - reduction in carbonate content - reduction in buffer capacity - more intensive weathering - leaching and/or immobilisation of plant nutrients - unbalanced fertility status of the soils - limited nutrient uptake by plants - lower fertiliser use efficiency - mobilisation of toxic elements
Pyrite weathering		

(2) Study Site, Description of Investigations and Discussion of Results

The study was focussed on three areas in the Banska Stiavnica locality:

- 1) The soils on the slope influenced by percolating acid water below the pyritised quartzite refuse heap and downhill at Sobov;
- 2) The soils on the same slope not influenced by acid water, but influenced by acid sulphate weathering;
- 3) Alluvial soils of the Stiavnicky potok river, influenced by dissolved species of metals and by weathering of particulates containing pyrite (sulphides).

In each of these areas the soil pH was measured and total content of some metals was analysed. See Table F.3 - 2 for results of these analyses.

Table F.3 - 2 Amount of Trace Elements (mg/kg) Contained in the Soils of the Study Area.

Trace element content (mg/kg) in the alluvial soils of the Stianicky potok river										
Number		Depth (cm)	As	Cd	Hg	Pb	Se	Zn	pH /H ₂ O	PH /KCl
1	1a	3-20	67.0	3.4	0.42	1700	0.3	602	3.65	3.30
	1b	80	60.8	5.1	0.26	1665	0.3	739	3.39	3.20
2	2a	3-15	87.2	3.7	0.61	2665	0.3	740	4.21	3.52
	2b	50	56.1	7.5	0.69	4300	0.1	1390	4.02	3.40
3	3a	3-30	46.1	7.0	0.40	1700	0.4	1034	3.90	3.70
	3b	70-80	49.1	20.8	0.29	1337	0.3	1766	4.45	3.50
	3c	100-120	135.7	222.1	0.61	35.2	0.2	12875	5.80	5.25
4	4a	10	82.0	1.9	0.42	1570	0.3	468	5.20	4.30
	4b	70-80	41.2	19.3	0.26	1625	0.3	2212	4.75	3.75
5	5a	3-10	23.3	18.4	0.50	2445	0.1	2894	4.77	3.76
	5b	70-80	41.4	114.9	0.74	6165	0.2	4500	4.41	3.40

Localities

1: South of Antol, close to the river

2: South of Antol, west of the river

3: North of Prencov, South west of Kalvaria 409m

4: South of the crossroads to Krnisov

5: North of Hontianske Nemce south south west of Kalvaria Dianis

Southern (SW) slope below the quartzite refuse heap										
Number		Depth (cm)	As	Cd	Hg	Pb	Se	Zn	pH/H ₂ O	pH/ KCl
6	6a	3-15	28.7	1.3	0.07	186	1.5	87	2.62	2.22
	6b	60-65	28.3	1.4	0.06	119	1.0	73	2.40	2.00
7	7a	3-20	16.0	2.0	0.16	230	2.8	124	2.62	2.22
	7b	50-60	16.0	1.9	0.13	232	4.7	124	2.40	2.00
8	8a	3-15	20.7	0.2	0.26	162	0.7	112	2.77	2.38
	8b	50-60	22.9	0.1	0.13	109	2.1	77	4.10	3.50
9	9a	3-10	26.9	0.1	0.25	245	3.2	143	4.34	3.68
	9b	50-60	12.9	0.2	0.15	46	0.8	120	5.60	5.03
10	10a	3-10	34.8	1.9	0.26	950	0.9	319	3.00	2.58
	10b	55-60	9.9	0.3	0.05	126	0.6	97	4.00	3.42

The slope not influenced by percolating water from Sobov										
Number		Depth (cm)	As	Cd	Hg	Pb	Se	Zn	PH /H ₂ O	PH /KCl
1	11a	3-10	6.0	1.9	0.07	300		143	4.72	3.54
	11b	40-50	1.4	2.1	0.03	178		109	5.14	3.74
1	12a	3-15	10.8	2.3	0.20	377		172	4.54	3.40
	12b	60-65	8.7	2.2	0.08	277		188	4.74	3.56
1	13a	3-15	45.3	1.4	0.02	42		105	5.00	3.74
	13b	40-50	31.6	2.1	0.03	38		106	4.71	2.42

Localities:

6: 10m south from the Sobov quartzite refuse heap

7: 50m south from the Sobov quartzite refuse heap

8: 200m south from the Sobov quartzite spoil heap

9: 700m south from the Sobov quartzite spoil heap

10: South East 200mS from the Sobov quartzite spoil heap ~300m from the crossroad to Sklene Teplice

11: East of Banska Stiavnica 300m North of Kalvaria

12: South of Beliansky rybnik (on the slope from Kalvaria

13: 50m above the road between Banska Stiavnica and Tepla

From the results it is obvious that all the soils are acidic and polluted. There is a tendency for the metal content to decrease down the soil profile. In the soils influenced by percolating acid water, the high soil acidity is a result of the acidic water percolating down the slope. The high acidity of this water is a result of acid sulphate weathering of the pyrite in the quartzite found in the outcrops and spoil heaps in this area.

Soils not influenced by percolating water are polluted and acidic too. Their acid character is due to the acid sulphate weathering of the pyrite content of the parent rocks (pyritized andesite).

The soils in the alluvial plain of the Stiavnicky Potok river are heavily polluted until ~ 40km downstream from the Banska Stiavnica mining district. A feature of these alluvial soils (fluvisols) is that they generally have an acidic character, with the pH increasing in the subsoils.

The very high content of Lead and Zinc in this alluvial area is caused by the polymetallic character of the mining ores (galenite-sphalerite) at Banska Stiavnica. These ores were reworked very close to the Stiavnicky potok river. The wastes with pyrite and other sulphitic ores were drained straight into the river for an extended period of time. During high water levels and flooding the particulate matter containing these metals and ores were irregularly distributed in the inundation zone of the river. The material weathered and produced some additional acidity to the soil through acid sulphate weathering. Due to weathering and pedogenesis, parasulphatic soils (soils that are influenced by pyrite oxidation but are not sufficiently acidic to be classified as acidic sulphate soils) developed. The pyrite content of the soil is low, but enough to free some metals to the soil.

The content of pyrite in the rocks, refuse heaps and slope deposits vary. The same is true of the soils. Pyrite levels can also be lowered as pedogenesis proceeds. That is why typical acid sulphate soils are rare. Para- or pseudo- acid sulphate soils or horizons are most common, this is also true for the Banska Stiavnica study area. The soils that have the greatest potential to be true acid sulphate soils are those that have developed on the settling pits and refuse heaps.

In other areas of Europe it is evident that soil acidification is a result of acid deposition from the air via precipitation. However, mining activities date back hundreds of years in the Banska Stiavnica area. The acid mine water percolating through the sulphitic material of the spoil heaps brings the dissolved metal species to the soils on the slope below the spoil heaps and the river

plain. The potential acid load contained in old spoil heaps containing pyrite may play a key role in soil acidification and consequently in soil pollution in the Banska Stiavnica area for some time to come.

(3) Conclusion

In the Banska Stiavnica ore district and in the catchment area of the Stiavnicky potok river, strongly acidic and polluted soils are present due to acid sulphate weathering.

The redistribution of sulphurous material to the alluvial plain of the river (Stiavnicky potok) together with multi-sourced dissolved species of chemical elements freed by acid sulphate weathering contributes to alluvial soils pollution. The high metal pollution in these soils (eg Pb, Zn, Cd, As and Se) is related to the polymetallic character of the mined ores (Pb-Zn) in this district.

The importance of acid sulphate weathering may only be regional, but the effects can be long-lasting and can result in a time delayed response as more pyrite weathers, this creates greater acidity and therefore an increased availability of toxic elements.

Acid sulphate weathering may also be an important factor contributing to the acidification and availability of metal pollutants in other areas of the Hron River Basin which have either pyritized bedrock or mining areas where spoil heaps containing pyrite occur.