UNEP

UNEP Balkans Technical Report

Analytical Results of UNEP Field Samples from Industrial Hot Spots and Refugee Sites in the Former Yugoslav Republic of Macedonia

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1.0 Introduction

During the week of 10-17 September 2000, a UNEP mission visited the Former Yugoslav Republic of Macedonia (FYR of Macedonia) to assess environmental conditions in the aftermath of the Kosovo conflict. The mission divided into three subgroups that investigated the impacts of the refugee influxes into FYR of Macedonia; industrial 'hot spots' posing urgent threats to public health and the environment; and FYR of Macedonia's institutional capacities for environmental protection.

During the mission, UNEP's team of international experts worked closely with national experts from FYR of Macedonia. The 'hot spot' subgroup visited ten environmental sites throughout the country. At the sites, UNEP experts met with company and local officials, inspected facilities and environmental conditions, and took samples, as appropriate. The following report summarizes UNEP's sample results and contains expert observations on site conditions. To read the complete UNEP assessment, *Post-Conflict Environmental Assessment—FYR of Macedonia*, please refer to the UNEP Blakans website at: http://balkans.unep.ch. To order a hard copy of the report, please call 41 22 917 8616, send an e-mail to ljerka.gosovic@unep.ch, or write to UNEP – Balkans, International Environment House, Chemin des Anémones 15, 1219 Châtelaine, Geneva, Switzerland.

2.0. Analytic Methods

The following is a discussion of laboratory results based on soil, water and air samples taken in the field by UNEP experts.

Soils and sediments were analyzed in fractions smaller than 2 millimeters. Heavy metals in sediments were analyzed in fractions smaller than 20 µm. Organic compounds were analyzed with gas chromatography/mass spectrometry (GC/MS), High Performance Liquid Chromatography (HPLC) and Gas Chromatography/Electron Capture Detection (GC/ECD).

Samples were investigated for polynuclear aromatic hydrocarbons (PAHs), phthalates, tensides (ionic and non-ionic) and semi-volatile chlororganic pollutants. For polychlorobiphenyls (PCBs), the German standard methods DIN 38414-20 and DIN EN ISO 6468 were used. PAHs were analysed according to U.S. Environmental Protection Agency (USEPA) method 610, volatile and semi-volatile chlorinated compounds following USEPA method 624.2 by GC/MS. Analysis of volatile and semi-volatile compounds were realized using the Stir Bar Sorptive Extraction (SBSE) technique in the water phase with the help of 'Twisters' that were donated by Gerstel GmbH, Mülheim, Germany.

Solid samples were analysed by GC/MS after Soxhlet extraction with n-hexane/acteone. The analysis of air samples was performed in a GC/MS system (full-scan measurements) after thermodesorption of tenax tubes.

Mercury was analyzed with Atom Absorption Spectroscopy (AAS) after digestion with hydrochloric and nitric acid. All other elements (Cr, Cu, Mn, Ni, Cu, Zn, As, Cd, Pb, Sb, Hg) were analysed with Total X-ray Fluorescence Spectroscopy (TXRF) and Inductively Coupled Plasma Atom Emission Spectroscopy (ICP/AES) after total digestion with nitric and hydroflouric acid.

All soil and sediment concentrations are related to dry weight.

Organic samples were analyzed by Dr. Bernard Wronski and Dr. Volker Wehner, and Dr. Ralph Donau of the Brandenburg State Office for Environment in Potsdam, Federal Republic of Germany. Metals were analysed at GALAB, Geesthacht, Germany (Mr. Maximilian Hempel, Mr. Eckard Jantzen, and Mr. Jürgen Kuballa).

3.0 Sites Visited and Sample Results

3.1 Ferro-alloy plant at Jegunovce, ('HEK Jugochrom')

The HEK Jugochrom plant at Jegunovce produces nearly 60,000 tons of ferro-alloys (e.g., ferrochrome, ferrosilicon) per year. The raw materials used are chromium ore, quartz, coal and ferrous iron. In 1982, the plant began monitoring soil and groundwater and confirmed that surface water and the upper secondary aquifer were contaminated by chromium. The production of chromium and chromium compounds nevertheless continued until 1993, and the chromium shed has not yet been cleared and secured. A UNEP sample taken from the **floor of the shed** contains **103,368 mg/kg of chromium (Cr)**.

Plant management informed UNEP that, in order to minimize soil and groundwater pollution, it converts the contaminated groundwater from Cr(VI) into Cr(III) and pumps it directly into the Bistrica River. Cr(III) compounds normally convert gradually to insoluble salts, such as Cr(III)-hydroxide and Cr(III)-oxidhydrate. In running water, Cr(III) accumulates sediments and develops low mobility. To estimate pollution from heavy metals, UNEP took water samples downstream of the wastewater outflow, and sediment samples both before and after the wastewater outflow pipe. **Water** sample results found: **Cu: 0.04 mg/l, Zn: 0.089 mg/l, Mn: 0.025 mg/l**. Chromium, nickel, lead and cadmium were not found in significant quantities in the wastewater outflow. Higher concentrations of heavy metals were found in the **sediment** below the wastewater outflow: **Cr: 88 mg/kg, Cu: 177 mg/kg, Zn: 1,290 mg/kg, Ni: 265 mg/kg, Mn: 265 mg/kg, and Pb: 122 mg/kg**.

The factory's production process is currently emitting a large amount of dust and fly ash. Fly ash concentrations have been measured as averaging 3–6 g/m³, with annual dust emissions averaging 9,000–17,000 tons per year. UNEP took samples from soil and vegetable material located 500 meters from the factory. The samples were analyzed for heavy metals. The **soil** samples showed: **Cr: 129 mg/kg; Cu: 344 mg/kg; Zn: 453 mg/kg; Ni: 109 mg/kg; Mn: 1,242 mg/kg; and Pb: 86 mg/kg**. In the **vegetable material** the following concentrations were found: **Cu: 11 mg/kg; Zn: 31 mg/kg; Ni: 15 mg/kg; and Mn: 57 mg/kg**. Chromium and lead levels were not significant in these samples.

The assumption that used mineral oils were polluted with PCBs could not be confirmed. An oil sample was taken from the transformer station, but no traces of technical PCB mixture were detected.

Sample results from ferro-alloy factory in Jegunovce; HEK Jugochrom – 14 September 2000

UNJES01: Soil sample from dust on way to factory

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/kg	121	344	453	109	1,242	86	<10

UNJEP01: Plant sample from dust on way to factory

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/kg	<10	11	31	15	57	<10	<10

UNJES02: Soil sample from chromium salt in former production shed

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/kg	103,368	73	169	163	156	34	<10

UNJEW02: Water sample from channel after pipe

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	<0.005	0.04	0.089	<0.005	0.025	<0.02	<0.005

UNJEW03: Water sample from sedimentation basin near water treatment station.

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	12.24	<0.005	0.014	0.017	<0.005	<0.02	<0.005

UNJESD01: Sediment sample from channel from factory to river

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/kg	88	177	1,290	265	265	122	<10

UNJEO01: Oil from basin for collecting transformer oil.

No PCBs found.

3.2 Organic chemicals plant, Skopje, ('OHIS A.D')

The industrial chemical plant OHIS A.D. is located in Skopje near the Vardar River. The plant produces a variety of chemical products, and for some time produced technical HCH mixture and lindane. Plant management informed UNEP that the production was stopped on account of difficulties in the separation of γ-HCH from the other isomers.

Approximately 10,000 tons of technical mixture of HCH have been stored in an uncovered concrete basin for 20 years. Management assumes the mixture was put into barrels and covered with soil. The condition of the barrels is unknown today. The geology of the storage area can be characterized as sand and gravel with a thin layer of clay.

Technical HCH mixture is produced by the photochlorination of benzene. It contains 65-70% α-HCH; 7-10% β-HCH; 14-15% γ-HCH (lindane); 7% δ-HCH; 1-2% ε-HCH; and 1-2% of other chlororganic compounds – e.g., heptachlor- and octachlorcyclohexanes. Lindane is separated by extraction with methanol. The mixture of other HCH-isomers can be converted by thermal treatment to useful by-products like trichlorbenzene and hydrogen chloride.

The average concentration of HCH isomers in agricultural soils is 0.01 mg/kg. The water solubility of α- and γ- HCH is much higher than that of β- and δ-HCH. (The water solubility

of lindane is 6 mg/l at 20°C.) In several European countries the use of lindane has been prohibited since 1974-1978.

A second substantial problem at OHIS A.D. is that the factory's wastewater treatment facility does not work (the basins of the biofilters are dry). The factory's wastewater is, therefore, being discharged directly into the river without any treatment. A now-closed chlorine alkali electrolysis plant used mercury, and its wastewater drained to the Vardar River. The plant also is storing tens of thousands of square meters of industrial and hazardous waste in poorly constructed storage facilities.

Mercury was found in soil (500 mg/kg) and water (65 mg/l) samples. Water samples taken from a small wastewater canal near the plant's chlorine alkali electrolysis facility, however, did not contain significant pollutants. Mono- and dicarbonoic acids in the range of C_3 to C_{20} were detected. The level of the monocarbonoic acids was low, and the dicarbonoic acids were found to contain approximately 10 mg/l in the range of $C_2 – C_5$. Phthalatic compounds such as di(methylpropyl)phthalate (DMPP), dibutylphthalate (DBP), di(isohexyl)phthalate (DIHP), dihexylphthalate (DHP), dicylohexylphthalate (DCHP), di(ethylhexyl)phthalate (DEHP), dioctylphthalate (DOP) and dinonylphthalate (DNP) were found, with concentration levels of about 0.5 mg/l in some. The dominant compounds are DMPP and DBP.

Sample results from organic chemicals plant, Skopje, OHIS A.D. – 12 September 2000

UNSKW01: Water sample from salt electrolysis channel:

Organic contamination: low level of monocarbonoic acids; 10 mg/l of dicarbonoic acids C_3-C_{20}; phthalates: dominant compounds are DMPP and DBP.

UNSKW02: Water sample from salt electrolysis channel

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	0.016	<0.005	0.026	<0.005	<0.005	<0.02	<0.005

UNSKW03: Water sample from salt electrolysis channel

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Hg	Cd
mg/l	0.023	0.006	0.126	<0.005	0.01	<0.02	0.65	<0.005

UNSKA01: Air sample from near fertilizer plant.

No relevant compounds detected.

UNSKB01: Soil sample from near the chlorine gas plant. In addition to the metals listed below, the sample contained an insignificant level of mineral oil).

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Hg	Cd
mg/kg	51	55	189	36	224	503	500	<10

3.3 Lead and zinc smelter, Veles ('MHK Zletovo')

No samples taken.

3.4 Zinc and lead mine, Probistip (Rudnici Zletovo)

The Rudnici Zletovo mine produces 1,000 tons of zinc concentrate and 800 tons of lead concentrate per day. The mine's flotation process uses xanthates, cyanides, metal sulfates, pine

oil and lime. Solid waste from the process contains zinc, lead, cadmium and cyanide. This waste is deposited in two hydro-tailing areas in Probistip.

UNEP **water** samples found heavy metals in drainage wastewater from Rudnici Zletovo's hydro-tailings: **Cu: 0.023 mg/l, Zn: 0.3621 mg/l, Ni: 0.005 mg/l, Cd: 0.005 mg/l**. These levels compare, for example, with German water quality objectives for heavy metals in surface waters of 0.0014 for zinc and 0.004 for copper, 0.014 for zinc, 0.0044 for nickel, and 0.00072 for cadmium. The concentrations of heavy metals measured in the sediment are generally not significant for industrial sites.

Sample results from zinc and lead mine, Probistip, Rudnici Zletovo – 15 September 2000

UNSLW01: Water sample from brook with water from tailing dam

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
Mg/l	<0.005	0.023	0.36	<0.005	10.37	<0.02	<0.005

UNSLSD01: Sediment sample from brook with water from tailing dam

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/kg	16	21	62	31	643	21	<10

3.5 Thermal power plant, Bitola ('REK Bitola')

No samples taken.

3.6. Landfill site, Drisla

The Drisla landfill has the capacity to hold over 26 million m³ of urban waste. Today, although the landfill is only 4% full, the site poses significant environmental challenges due to the soil's geological structure and the lack of an impermeable lining and gas drainage system. At present, untreated water drains directly to the Markova River.

UNEP water samples were taken directly from the surface of the landfill and from the river 2.5 kilometers downstream of the landfill. The samples were analyzed for organic and inorganic pollutants.

The **water** sample from the landfill surface was strongly contaminated with approximately **10 mg/l of dicarbonoic acids from $C_2 – C_5$**. The analysis contained a high concentration of alkylphenols, with longer carbon chains, as well as carbonoic acids with terpenic structure up to C_{20} and also di- and tri-hydroxybenzenes. The landfill's urban wastes caused this pollution. The long-chain compounds are fragments of substances with tensidic structure (ionic and non-ionic). They appeared in the chromatogram in the retention time range from 26–32 minutes as a typical fingerprint. The concentration of heavy metals in this sample slightly exceeded the German quality objective for surface waters.
The analyses of **water sample from Markovo River** 2.5 kilometers downstream of the landfill showed a similar composition. The concentration of dicarbonoic acids was not so different from the sample taken directly from the dumpsite. The contamination with **tensidic compounds**, however, was **5-6 times higher** in this sample.

Containers with clinical wastes were found at the landfill. Although logistics made it impossible to take samples of this waste, it can be assumed that this material is untreated and contains pathogenic germs.

Samples results from landfill site, Drisla – 11 September 2000

UNDRW01: Wastewater sample from a pool on the landfill

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	0.068	0.019	0.031	0.015	0.248	<0.02	<0.005

[Organic contamination: dicarbonoic acids C2 - C5 10mg/l; di- and tri-hydroxybenzenes; alkylic phenols with longer chains; tensides.]

UNDRW02: Water sample from Markovo River, 2.5 km downstream from landfill

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	<0.005	<0.005	0.045	<0.005	<0.005	<0.02	<0.005

[Organic contamination: dicarbonoic acids C2- C5 10mg/l; di- and tri-hydroxybenzenes; alkylic phenols with longer chains; 5-6 times higher concentration of tensides then in UNDRW01.]

3.7 Fertilizer factory, Veles ('MHK Zletovo')

No samples taken.

3.8 Copper mine, Radovis ('Buchim, S.C.')

The copper mine in Radovis produces approximately 4 million tons of ore per year and a similar quantity of tailings. The mine uses a flotation process to enrich the copper ore. Crude ore is crushed and separated from other mineral components in a flotation basin with a tensidic water solution (alkansulphonates, alkylsulfates, esters of phosphoric acids). Waters from the hydro-tailing dam and wastewater from the flotation process are contaminated with heavy metals. Both reached the Topolnica River untreated.

A UNEP **surface water** sample taken at a distance of 2.5 kilometers from the Bucim factory contained **200.4 mg/l of copper**. This compares with the 0.004 mg/l German quality objective for copper in surface water. The water comes from the mine's hydro-tailing dam. The concentrations of other heavy metals like Cr, Ni, Zn, Pb, Mn were not significant. A **sediment** sample taken at the same location found **2,145 mg/kg** of copper, far higher then the 60 mg/kg German quality objective for river sediments. The concentration of **copper in the mine's wastewater** was found to be **50.5 mg/l**.

Sample results from copper mine in Radovis, Bucim S.P. – 15 September 2000

UNBUW01: Water sample from brook containing wastewater 2.5 km from factory

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	<0.005	200.4	1.6	0.77	56.0	0.055	<0.005

UNBUW02: Water sample from brook containing wastewater 2.5 km from factory

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	<0.005	50.5	0.462	0.231	16.15	<0.02	<0.005

UNBUW03: Water sample from brook containing wastewater 2.5 km from factory

Organic contamination: carbonoic acids especially from C16- C18 with 10mg/l; 0.5mg/l phthalates (DBP; DMPP; DEHP); ionic and non-ionic tensides from flotation.

UNBUSD01: Sediment sample from brook containing wastewater 2.5 km from factory

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/kg	14	2,145	21	15	731	15	<10

3.9 Metal resurfacing factory, Kicevo ('Tane Caleski')

Tane Caleski resurfaces metals, screws and wires. Surface treatment is achieved using solutions with salts of chromium and zinc, mineral acids, cyanides and other hazardous chemicals. Wastewater from the process is discharged untreated into a small, uncovered canal that leads to the Vardar River. Neutralization occurs by mixing acidic and basic parts. A planned sewage treatment facility has not been constructed due to lack of finances. The results of water samples showed no contents of mineral oil parts. It appears that the leakage of oil from 1.5 tons per month is going over the soil pathway.

Metal resurfacing factory, Kicevo, Tane Caleski – 14 September 2000

UNKIW01/UNKIW02: Water samples from sedimentation basin

Organic contamination: 10 mg/l carbonoic acids, especially C16-C18; 0.5mg/l phthalates (DBP; DMPP; DEHP); low levels of tensides; no mineral oil in process water.

UNKIW03: Water sample from water channel near factory.

Organic contamination: 10 mg/l carbonoic acids, especially from C16-C18; 0.5mg/l phthalates (DBP; DMPP; DEHP); low levels of tensides; no mineral oil in process water.

UNKIW04/UNKIW05: Water samples from water channel near factory

Organic contamination: 10 mg/l carbonoic acids, especially from C16-C18; 0.5mg/l phthalates (DBP; DMPP; DEHP); tensides.

3.10 Lojane mine

The Lojane mine, north of Kumanovo, was a source of chromium and antimony at different times during the period between 1923 and 1979. It was also the site of an antimony smelter. UNEP visited an open dumpsite for the mine and smelter's process wastes.

A **dust** sample taken by UNEP found heavy metal concentrations measuring: **As: 8,093 mg/kg and TL: 140 mg/kg**. Analyses of water near the dumpsite showed concentrations of **Cr: 3.93 mg/l; QO: 0.01 mg/l; and As: 0.25 mg/l**. A sediment sample, however, showed much higher levels of heavy metals: **Cu: 161 mg/kg; Zn: 2,438 mg/kg; Ni: 19 mg/kg; As: 459 mg/kg; Cd: 12 mg/kg; and Pb: 1,655 mg/kg**. These analyses indicate that this dumpsite poses potential risks to soil, groundwater and human health in the region.

Sample results from Lojane mine – 15 September 2000

UNLOW01: Water sample from the base of the dumpsite; possible drainage water

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd	As	Sb
mg/kg	3.93	<0.005	<0.005	<0.005	<0.005	<0.02	<0.005	0.25	0.04

UNLOS01: Soil sample from perimeter of dumpsite

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd	As	Sb
mg/kg	99	26	48	1.68	1,102	131	<10	8.093	457

UNLOSD01: Sediment sample from pool of drainage water

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd	As	Sb
mg/kg	<10	161	2,438	19	28,777	1,655	12	459	<10

3.11 Refugee camps (Radusa, Bojane and Cegrane)

The three refugee camps were situated near villages. The sites have been mostly vacated and cleared. The sites in Radusa and Bojane are not being actively used, although the inhabitants of the village Bojane are using the camp area as a dumpsite. The Cegrane camp is used for a 'permaculture' (permanent agriculture) project. Water for the villages of Radusa and Bojane, and consequently for the camps, was supplied from wells or via pipelines from springs in the mountains of Kosovo.

UNEP took water samples from the areas surrounding the camps of Radusa and Bojane. The samples did not contain significant pollutants, but showed similar levels of organic pollution. Mono- and dicarbonoic acids were found in the range from C_3 to C_{20}. The level of the monocarbonoic acids was very low. Dicarbonoic acids in range of $C_2 – C_5$ were found at levels of approximately 10 mg/l. Phthalatic compounds, such as DMPP, DBP, DIHP, DHP, DCHP, DEHP, DOP and DNP, were detected in the water in total concentration levels of approximately 0.5 mg/l. The dominant compounds were DMPP and DBP.

Soil samples from latrines showed insignificant levels of chemical contamination. Heavy metal concentrations in a groundwater sample were below applicable thresholds for drinking water. In sum, environmental pollution was not traced back to the campsites.

Radusa, Refugee camp and village, Radusa – 13 September 2000

UNRAW01/UNRAW02/UNRAW03: Water samples from garden directly behind camp and ambulance.

Organic contamination: low level of monocarbonoic acids; dicarbonic acids $C_2 – C_5$ with 10mg/l; and 0.5 mg/l phthalates (dimethylpropylphthalate (DMPP), dibutylphthalate (DBP), diisohexylphthalate (DIHP), dihexylphthalate (DHP), dicyclohexylphthalate (DCHP), diethylhexylphthalate (DEHP), dioctylphthalate (DOP) and dinonylphthalate (DNP).

UNRAS01: Soil sample from near latrines

No noticeable organic contamination.

Rasce, Refugee camp and village – 13 September 2000

UNRCW01: Water sample from well in village of Bojane

Organic contamination: low level of monocarbonoic acids; dicarbonoic acids C2- C5 with 10mg/l; 0.5 mg/l phthalates (dimethylpropylphthalate (DMPP), dibutylphthalate (DBP), diisohexylphthalate (DIHP), dihexylphthalate (DHP), dicyclohexylphthalate (DCHP), diethylhexylphthalate (DEHP), dioctylphthalate (DOP) and dinonylphthalate (DNP).

UNRCW02: Water sample from well in village of Bojane

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	<0.005	<0.005	0.058	<0.005	<0.005	<0.02	<0.005

UNRCW03: Water sample from village of Bojane

Heavy metals	Cr	Cu	Zn	Ni	Mn	Pb	Cd
mg/l	<0.005	<0.005	0.106	<0.005	<0.05	<0.025	<0.005