Demonstration of harmonized and cost-effective monitoring- Annex IV

Analytical lab reports for HS measurements in the Danube Hazard m3c project

1 CONTECTS OF RESPONSIBLE LABS

Parameter	**Contact person**	**Addresses for the sample delivery**	**Email, Telephone**
Hg and other metals	Radmila Milačič	Department of Environmental Sciences Jožef Stefan Institute Jamova 39 1000 Ljubljana SLOVENIA	radmila.milacic@ijs.si Tel:+386 1 4773560
Preparation, lyophilisation and distribution of solid samples	Sandra Kulcsar	Umweltbundesamt GmbH Probeneingang Spittelauer Lände 5 A-1040 Vienna Austria	Sandra.kulcsar@umweltbundesamt.at Tel: +43-(0)1-313 04/5277
16 PAH in solid samples	Sandra Kulcsar	Umweltbundesamt GmbH Probeneingang Spittelauer Lände 5 A-1040 Vienna Austria	Sandra.kulcsar@umweltbundesamt.at Tel: +43-(0)1-313 04/5277
16 PAH in liquid samples	Carmen HAMCHEVICI	**Laboratorul National de Calitatea Apei – A.N. Apele Romane (ANAR)** Street Splaiul Independentei nr. 294, sector 6, 060031 Bucuresti, Romania	carmen.hamchevici@rowater.ro +40 755 063 869
PFAS and other organic substances	Gabor Bordos	WESSLING Hungary Ltd. **Környezetanalitika Mintaátvétel** 6 Anonymus st., Budapest 1045, Hungary	bordos.gabor@wessling.hu +36 20 335 8627

2 PTE MEASUREMENTS AT JOŽEF STEFAN INSTITUTE, SLOVENIA

DETERMINATION OF CONCENTRATIONS OF ELEMENTS BY ICP-MS

Instrumentation

Concentrations of elements were determined by ICP-MS, using instrument Agilent 7700x (Agilent Technologies, Tokyo, Japan) under optimized measurement parameters.

A CEM Corporation (Matthews, NC, USA) MARS 6 Microwave System was used for sample digestion.

Reagents and materials

Ultrapure 18.2 MΩ cm water obtained from a Direct-Q 5 system was used for preparation of samples and reagents. Suprapur nitric acid (67–70% HNO_3) obtained from Carlo Erba was used. Suprapur hydrochloric acid (30% HCl), hydrofluoric acid (40% HF), and hydrogen peroxide (30% H_2O_2) were purchased from Merck. ICP multi-element standard solution XVI (21 elements in diluted nitric acid, 100 mg L^{-1}), for ICP and stock standard solutions of scandium (Sc), germanium (Ge), yttrium (Y), rhodium (Rh) and indium (In) (1000 ± 2 mg L^{-1} in 2-3% HNO_3) obtained from Merck, were used to prepare calibration curves and internal standards for the determination of elements by ICP-MS. Samples were filtered using 0.45 μm Minisart cellulose nitrate membrane filters (Sartorius, Goettingen, Germany). Water samples were collected in low density polyethylene (PE) wide-mouth bottles (volume 0.5 L) obtained from BRAND. The certified standard reference material SPS-SW1 (Reference material for measurements of elements in surface waters) obtained from Spectrapure Standards (Oslo, Norway) and the certified reference materials CRM 320R Trace Elements in Channel Sediment, Community Bureau of Reference were used for the accuracy check.

Analytical procedures

Analytical procedures for the determination of elements in soil, sediment and SPM samples

Approximately 0.2 g of lyophilized soil, sediment or SPM sample was weighed into a Teflon vessel and 2 mL of hydrogen peroxide, 4 mL of nitric acid, 1 mL of hydrochloric and 2 mL of hydrofluoric acid were added. The contents were subjected to microwave assisted digestion (ramp to temperature 20 min, T=140 °C, hold 5 min, ramp to temperature 15 min, T=200 °C, hold 60 min, cool 30 min). After digestion, 12.5 mL of boric acid (4% aqueous solution) was added to dissolve fluorides and complex the excessive boric acid and microwave assisted digestion was applied again (ramp to temperature 15 min, T=140 °C, hold 2 min, ramp to temperature 15 min, T=180 °C, hold 30 min, cool 30 min). After digestion, the contents were transferred into 30 mL graduated PE tubes and concentrations of PTEs (Cr, Ni, As, Cu, Zn Cd and Pb) were determined by ICP-MS in 100-times diluted samples (SIST EN ISO 17294-2:2017).

Analytical procedures for the determination of elements in wastewater samples

For the analysis of wastewater, 2 mL of hydrogen peroxide, 3 mL of nitric acid and 1 mL of hydrochloric acid were added to 10 mL of sample and contents was subjected to microwave assisted digestion (ramp to temperature 30 min, T=90 °C, hold 5 min, ramp to temperature 10 min, T=140 °C, hold 5 min, ramp to temperature 10 min, T=150 °C, hold 15 min, cool 30 min).

After digestion, samples were 10-times diluted and concentrations of PTEs determined by ICP-MS (SIST EN ISO 17294-2:2017).

Analytical procedures for the determination of elements in ATD and soluble concentrations of PTEs river water

Concentrations of PTEs in ATD and soluble concentrations of PTEs in river water samples were determined directly by ICP-MS (SIST EN ISO 17294-2:2017).

Analytical procedures for the determination of total PTEs concentrations in river water

To determine total concentrations of PTEs in river water, 3 mL of nitric acid, 0.1 mL of hydrofluoric acid and 1 mL of hydrochloric acid were added to 10 mL of sample and contents was subjected to microwave assisted digestion (ramp to temperature 30 min, T=90 °C, hold 5 min, ramp to temperature 10 min, T=140 °C, hold 5 min, ramp to temperature 10 min, T=150 °C, hold 15 min, cool 30 min). After digestion, samples were 10-times diluted and concentrations of PTEs determined by ICP-MS (SIST EN ISO 17294-2:2017).

All the analyses were performed in triplicate.

LODs and LOQs

LODs and LOQs for the determination of the total and soluble concentrations of elements in river water samples, total concentrations of elements in wastewater and ATD samples and total concentrations of elements in soils, sediments and SPM. LODs were calculated as the concentration providing a signal equal to 3*s* of the blank sample. To calculate the LODs, 8 blank samples were analysed by ICP-MS.

Element	LODs for total concentrations of elements in river water and wastewater (µg L^{-1})	LOQs for total concentrations of elements in river water and wastewater (µg L^{-1})	LODs for soluble concentrations of elements in river water and ATD (µg L^{-1})	LOQs for soluble concentrations of elements in river water and ATD (µg L^{-1})	LODs for total concentrations of elements in soils, sediments and SPM (mg kg^{-1})	LOQs for total concentrations of elements in soils, sediments and SPM (mg kg^{-1})
Pb	0.15	0.50	0.015	0.050	0.23	0.77
Cd	0.04	0.133	0.004	0.013	0.06	0.20
As	0.10	0.333	0.010	0.033	0.15	0.50
Cr	0.06	0.20	0.006	0.020	0.09	0.30
Ni	0.06	0.20	0.006	0.020	0.09	0.30
Cu	0.13	0.433	0.013	0.043	0.20	0.67
Zn	0.70	2.33	0.070	0.233	1.05	3.50

Attached analythical results table: *DH_SPM_SEDIMENT_SOIL_FINAL.xlsx*

3 PAH DETERMINATION METHODS BY NATIONAL ADMINISTRATION ROMANIAN WATERS (NARW)

Short description of lab procedures used for PAH analyses in water samples received in NARW laboratory

River water samples and atmospheric deposition water samples

1. **Reference Standard method:** SR EN ISO 17993-2004 that transposes EN ISO 17993:2003 (*EN ISO 17993:2003 Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after LLE (ISO 17993:2002*) and internal Laboratory Specific Procedure PSL 10.1, Edition 03, Revision 01;
2. **Sampling:** according to the technical documents established at the beginning of the working Package;
3. **Sampling recipients:** 1 L amber glass, with PTFE cap or PE cap covered inside with aluminum foil
4. **Specific aspects on sampling:** specific details were optimized after the analysis of the first results round (preservation with n-hexane, water samples not filtered);
5. **Preservation and transport:** according to the provisions from the Standard Method and EN ISO 5667-3:2018, cooled at 4 ^{0}C, protected from light;
6. **Sample preparation:**
   a. SPE (solid -phase extraction): STRATA PAH 1.5 g/ 6 mL Tubes
   b. LLE (liquid – liquid extraction): n-hexane
7. **Reference Materials (RM) and Certified Reference Materials (CRM)**:
   a. **RM**: PAH Mix 64 2000 µg/mL in Benzene/Dichloromethane, DRE-YA06100400BD, Lot no 1117660BD, Expiry Date 29.01.2025;
   b. **CRM**: PAH Calibration Mix 10 µg/mL in Acetonitrile, CRM47940, Sigma-Aldrich, Lot no LRAC5365, Expiration Date February 2023;
   c. **CRM**: PAH Mix 2000 µg/mL in Acetonitrile, CRM47543, Sigma-Aldrich, Lot no LRAC 0326, Expiration Date April 2022;
   d. **CRM**: Low Level PAHs WP, QC1223, Sigma-Aldrich, Lot no LRAC9393, Expiration Date March 2024;
8. **Analytical Technique**: High Performance Liquid Chromatography with Fluorescence and Diode Array Detector (HPLC-FLD/DAD)
9. **Analytical Equipment**: Shimadzu Prominence HPLC-FLD, serial number L20154573422 with Fluorescence Detector RF- 10AXL, serial no C20954571793,
   a. **Column:** Nucleosil 100-5 C18 PAH, L= 250 mm, internal diameter = 4.6 mm, stationary phase C18, particle size 5,0 µm;
   b. **Column temp.:** 25 ^{o}C;
   c. **Equilibrium time for column:** 30-60 min;
   d. **Mobile phase:** HPLC water (A) and HPLC Acetonitrile (B), in gradient;
   e. **Flow rate:** 1 mL/min;
   f. **Gradient:** at start time A:B = 35: 65 (vol.) followed by the programme specified in ***Table 1*****;**
   g. **FLD**: working based on the wavelengths from ***Table 1*****;**
   h. **DAD:** set in the range 190-450 nm, used for spectra conformation (98-99%).

Table 1: Method parameters for PAHs analyses by HPLC-FLD

No	Time (min)	Module that changes parameter	Parameter	Parameter value (% comp. A, wavelength, nm)
1	0.10	Controller	Start	
2	5.00	Pumps	B. Conc	65
3	6.50	RF-10 AXL (DET.A)	Emission Wavelength	350
4	6.50	RF-10 AXL (DET.A)	Excitation Wavelength	275
5	9.00	Pumps	B. Conc	65
6	14.00	Pumps	B. Conc	65
7	18.00	RF-10 AXL (DET.A)	Emission Wavelength	425
8	18.00	RF-10 AXL (DET.A)	Excitation Wavelength	375
9	22.00	RF-10 AXL (DET.A)	Emission Wavelength	440
10	22.00	RF-10 AXL (DET.A)	Excitation Wavelength	270
11	24.00	Pumps	B. Conc	85
12	26.00	Pumps	B. Conc	85
13	28.00	RF-10 AXL (DET.A)	Emission Wavelength	405
14	28.00	RF-10 AXL (DET.A)	Excitation Wavelength	315
15	34.00	Pumps	B. Conc	93
16	36.00	Pumps	B. Conc	93
17	36.00	RF-10 AXL (DET.A)	Emission Wavelength	420
18	36.00	RF-10AXL (DET.A)	Excitation Wavelength	330
19	39.50	Pumps	B. Conc	100
20	41.00	RF-10 AXL (DET.A)	Emission Wavelength	460
21	41.00	RF-10 AXL (DET.A)	Excitation Wavelength	375
22	47.50	RF-10 AXL (DET.A)	Emission Wavelength	420
23	47.50	RF-10 AXL (DET.A)	Excitation Wavelength	345
24	49.50	RF-10 AXL (DET.A)	Emission Wavelength	460
25	49.50	RF-10 AXL (DET.A)	Excitation Wavelength	360
26	51.50	RF-10 AXL (DET.A)	Emission Wavelength	500
27	51.50	RF-10 AXL (DET.A)	Excitation Wavelength	300
28	56.00	Pumps	B. Conc	100
29	57.00	RF-10 AXL (DET.A)	Emission Wavelength	350
30	57.00	RF-10 AXL (DET.A)	Excitation Wavelength	275
31	61.00	Pumps	B. Conc	65
32	66.00	Pumps	B. Conc	65
33	67.00	Controller	Stop	

Waste water samples

1. **Reference Standard method: SM 6440C:2012** and **internal Laboratory Specific Procedure PSL 03, Edition 04, Revision 02**

2. **Analytical Technique**: Gas-Chromatography with Mass Detector (GC-MS)
3. **Sampling:** according to the technical documents established at the beginning of the working Package;
4. **Sampling recipients:** 1 L amber glass, with PTFE cap or PE cap covered inside with aluminum foil
5. **Specific aspects on sampling:** specific details were optimized after the analysis of the first results round (preservation with n-hexane);
6. **Preservation and transport:** according to the provisions from the Standard Method and EN ISO 5667-3:2018, cooled at 4 ^{0}C, protected from light;
7. **Sample preparation:**
   a. LLE (liquid – liquid extraction): n-hexane
8. **Reference Materials (RM) and Certified Reference Materials (CRM)**:
   a. **RM**: PAH Mix 64 2000 µg/mL in Benzene/Dichloromethane, DRE-YA06100400BD, Lot no 1117660BD, Expiry Date 29.01.2025;
   b. **CRM**: PAH Calibration Mix 10 µg/mL in Acetonitrile, CRM47940, Sigma-Aldrich, Lot no LRAC5365, Expiration Date February 2023;
   c. **CRM**: PAH Mix 2000 µg/mL in Acetonitrile, CRM47543, Sigma-Aldrich, Lot no LRAC 0326, Expiration Date April 2022;
   d. **CRM**: Low Level PAHs WP, QC1223, Sigma-Aldrich, Lot no LRAC9393, Expiration Date March 2024;
9. **Analytical Equipment**: Shimadzu – QP 2010 Plus, with Selective MS detector QP 2020, serial no: C70504576031
   a. **Column:** capillary column ZB-5MS, L=30 m, IDI = 0,25 mm, stationary phase thickness = 0,25 µm (5% fenil on PDMS)
   b. **Flow gas:** 1 mL/min
   c. **Gas rate:** 36,8 cm/s
   d. **Oven heating gradient:** in ***Table 2***

Table 2: Oven heating programme for PAHs analyses by GC-MS

Isotherm	Isotherm temp. (^{0}C)	Hold time (min)	Oven Program rate (^{0}C/min.)
1	80	3	20
2	210	-	8
3	265	-	3
4	300	6	Post-run

   e. **Detection Mode:** SIM
   f. **Ionisation source temp:** 200 ^{0}C;
   g. **Solvent delay:** 5 min;
   h. **Time sequences and target ions (target and qualification ions) for each PAH:** ***Table 3***

Table 3: Time sequences and target ions (target and qualification ions) for each PAH

Nr. Ctr.	Sequence /Start Time –End time (min)	Group	Compound	Target Ion m/z	Qualification ion m/z
1	6.0-7.5	I	Naphthalene	128	127,102
2	7.5-9.6	II	Acenaphthylene Acenaphthene	152 153	151 154

3	9.6-10.6	III	Fluorene	166	165
4	10.6-12.5	IV	Phenanthrene Anthracene	178	179 152
5	12.5-16.0	V	Fluoranthene Pyrene	202	200
6	16.0-20.0	VI	Benz(a)anthracene, Chrysene	228	226
7	20.0-24.0	VII	Benz(b)fluoranthene, Benz(k)fluoranthene Benz(a)pyrene	252	250
8	24.0-34.0	VIII	Indeno1,2,3(c,d)pyren e Dibenz(a,h)anthracen e Benz(g,h,i)perylene	276	274 138

Attached reports:

NARW_PAH_Data_27.10.2022.xlsx

4 PAH MEASUREMENTS IN SOILS AND SEDIMENTS BY UMWELT BUNDESAMT AUSTRIA

Description of measurements:

Followed by the addition of deuterated surrogate standards, the sample is hot extracted with n-Hexane/Acetone (1:1) as solvents, using a soxhlet apparatus. After cleaning the extract over a silica gel column, the sample is measured via EI GC-MS. Quantification is achieved through an external standard method and the addition of an injection standard. Determination of recovery rate and correction of sample values is conducted by using the surrogate standards.

Attached reports:

- *PB2206_0428-et9_signiert_soil.pdf*

- *PB2210_0689-f1v_signiert_spm.pdf*

5 MEASUREMENT OF ORGANIC COMPOUNDS INCLUDING INDUSTRIAL CHEMICALS AND PESTICIDES AT WESSLING HUNGARY LTD.

Attached reports:

- *Summary report on the lab analysis procedures.pdf*
- *WESSLING_Danube_Hazard_ICPDR_report_RIV_RWW_TWW_ATD_final.xlsx*
- *WESSLING_Danube_Hazard_ICPDR_report_SOILS_final.xlsx*
- *WESSLING_Danube_Hazard_ICPDR_report_SPM_final.xlsx*