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Output 1.1

Testing and demonstration of harmonized and cost-efficient monitoring strategies in non-EU countries and in new critical compartments as a basis for HS emissions and pollution inventories

Activity leader

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Table of content

Abstract

Pollution of surface waters by trace organic and inorganic contaminants remains insufficiently understood due to major knowledge and data gaps. To support effective mitigation, emission and water quality models are essential for quantifying pollution pathways and spatial patterns at catchment and national scales. However, these tools require a robust data basis on the occurrence and concentration levels of the contaminants in surface waters and in other environmental and engineered compartments. Building on previous initiatives such as the Danube Hazard m^{3}c project, the Tethys project addresses remaining gaps by targeting largely unmonitored compartments and emission pathways, particularly in non-EU countries. A pilot action was conducted to demonstrate cost-efficient, fit-for-purpose monitoring strategies for developing hazardous substance emission inventories.

The pilot action succeeded in demonstrating the feasibility and added value of the joint conceptualisation, planning and execution of a harmonised 1-year sampling campaign in 11 EU and non-EU countries within the Danube River Basin and across multiple environmental compartments. It showed that good organization, communication, and collaboration are crucial for the implementation of successful monitoring, especially at transboundary scale. Clear instructions in the Standard Operating Procedure are crucial to prevent contamination, ensure representative sampling and yield reliable and comparable results. The presented approach, based on cost-efficient monitoring strategies, demonstrates strong potential for enabling improved assessment of trace contaminant emissions and pollution in both established and newly identified critical compartments, for enabling the implementation and validation of pathway-oriented emission models and for establishing solid emission inventories at national and transnational level.

This report summarises the conceptual framework and joint design of the monitoring strategy aiming to optimize the allocation of available resources to best support the implementation of the transnational pathway-oriented emission model more. It also describes in detail the selected sampling sites and sampling frequency in each country as well as the applied methodologies. Last, a short summary of the results of the analyses of metals, PFAS and pharmaceuticals is provided.

1 Motivation and objectives of the pilot action

Pollution of the aquatic environment by trace organic and inorganic contaminants is a well-recognised issue. However, its effective control and reduction is still hindered by severe gaps of knowledge and detailed system understanding. To better assess the extent of surface water pollution beyond the limited number of locations included in national monitoring programmes, and to identify effective mitigation measures, it is necessary to understand and quantify the contribution of different emission pathways at catchment and national scales. In this context, emission and water quality models can support the identification of the most relevant emission pathways for different types of contaminants, the description of how pollution is distributed across large river basins, and the targeted allocation of resources for more in-depth investigations. Multiple models have been developed to address these questions, each of them with specific strengths and weaknesses as well as a different level of complexity and data requirements. The Tethys project focuses on the implementation of the MoRE model at transnational and national levels. This tool is designed to apply the pathway-oriented approach set out in the third tier of the modelling framework for establishing emission inventories of priority substances, as detailed in the WFD CIS Guidance Document No. 28 (EU, 2012). This model has been shown to outperform simpler modelling approaches in estimating concentrations and loads of trace contaminants in unmonitored surface waters (Kittlaus et al, 2022). However, it is largely a data-driven modelling approach that requires extensive and robust input data on the occurrence and concentration levels of trace contaminants in multiple environmental and engineered compartments.

The Interreg Danube Transnational Programme project, Danube Hazard m^{3}c, which was completed in March 2023, demonstrated innovative monitoring approaches and enhanced institutional capacity via a series of national training sessions in multiple Danube countries. Nevertheless, new solutions and capacity building are required that go beyond the scope of the Danube Hazard m^{3}c project. For example, there is a need to focus on largely unmonitored compartments and emission pathways, such as stormwater overflows, to identify unknown hotspots of per- and polyfluoroalkyl substances and of other legacy pollutants, and to address the serious deficiencies and gaps in data availability identified especially in non-EU countries.

In such context, within the Tethys project we carried out a pilot action to test and demonstrate how to design and carry out a fit-for-purpose and cost-efficient monitoring as a basis for hazardous substances (HS) emissions and pollution inventories. This pilot action was mostly dedicated to non-EU countries, but it also included a focus on emission pathways from environmental and urban compartments which are still largely unmonitored and yet are recognized as emerging critical emissions loads of HS in both EU and non-EU countries. This document provides a compact report of the conceptual framework, of the activities carried out, of the main results achieved and of the main lessons learned, with a focus on the methodologies applied. A more extensive presentation and discussion of the results of the monitoring campaign are provided in the Output 1.7 of the Tethys project.

2 Process of joint conceptualisation of the monitoring campaign and joint elaboration of the Standard Operating Procedure

Intensive efforts for the joint conceptualisation of the monitoring campaign and the joint elaboration of the Standard Operating Procedure (SOP) were undertaken to plan and organize all aspects and technical details of the pilot action. To support the first essential step in designing a monitoring campaign for the development of an emission inventory, we conducted a critical analysis of key data gaps relevant to the emission models, namely main lack of information regarding the occurrence and concentration of specific contaminants and specific compartments either required to quantify the emission loads from specific emission pathways or to validate the modelling results. The basis for such analysis was the concentration database generated in the Interreg DTP Danube Hazard m^{3}c project (Kittlaus et al., 2024). Based on this analysis, a core team of the partnership elaborated a first draft proposal of specific sampling locations and sampling frequency in the different countries and across compartments.

In February 2024, during an online meeting, JSI presented the draft concept to all partners involved and launched an iterative process of joint definition of the monitoring campaign. This enabled on the one hand all involved partners to strengthen their institutional capacity to design fit-for-purpose monitoring programmes for generating inventories of HS emissions and surface-water pollution to support modelling, and on the other hand it ensured the integration of the best national and local knowledge and the selection of the most adequate locations. After several iterations of written feedback and revisions, a final draft of the detailed monitoring campaign and of the SOP were elaborated.

In May 2024, JSI organized and hosted a two-day workshop in Ljubljana with participation from all involved project partners. During the workshop, the draft SOP, the proposed sampling sites, the HS to be analysed, as well as the sampling frequency in each country were discussed and lastly approved. Based on the agreed decisions of the workshop, JSI and TU Wien finalized the SOP described in document *D1.1.1, Protocol for Sampling, Storage, and Transport of Samples* (D1.1.1, 2024). Meanwhile, the other project partners initiated the communication with local authorities, wastewater treatment plant operators, and industrial stakeholders to obtain the necessary sampling permits.

2.1 Workshop in Slovenia and finalization of the detailed plan

The workshop on sampling strategies and sample preparation procedures, organized by JSI, was held on 27 and 28 May 2024 in Ljubljana, Slovenia.

Objective of the workshop: To discuss and jointly prepare all the steps and actions needed to ensure the successful launch of the monitoring campaigns.

Project partners from ten countries attended the workshop in person, and UHMI followed it online. BME presented the objectives of monitoring HS in support of the MoRE emission model validation. Based on these objectives, sampling strategies and sample preparation procedures were developed and presented by JSI for metals (note: The term “metals” also includes arsenic, which is classified as a metalloid), and by TU Wien for PFAS and pharmaceuticals. Technical aspects of sample transport, sample labelling, sampling frequency in EU and non-EU countries, and sample delivery were also provided. Special attention was given to explaining the measures required to prevent sample contamination. To this end, it was agreed that JSI would provide all necessary containers and sampling equipment (suprapur acids, syringes, and filters for sample filtration), while TU Wien would supply the appropriate containers for PFAS and pharmaceutical sampling.

All eleven project partners then presented proposed sampling sites in their respective countries for the collection of river water, wastewater, groundwater, and urban stormwater runoff samples. A fruitful discussion with the team members from BME in charge of developing the transnational MoRE model in the Tethys project led to further improvements of the sampling sites in support of the monitoring activities.

It was highlighted that, for river water, sampling sites for model validation should be consistent with the Transnational Monitoring Network (TNMN) locations and be near river gauging stations that have discharge and water level (Q-H) rating curves or continuous flow measurements. Sampling sites should cover the major Danube tributaries as well as the Danube River at country borders, and their selection should be coordinated with other countries to avoid redundancy. Hotspots (such as mining, industrial, or municipally related pollution sites) and background locations should also be situated near river gauging stations. In general, it was agreed that samples would be collected under base flow conditions.

For wastewater, it was proposed that, at wastewater treatment plants (WWTPs), seven daily composite samples (24-hour mixed samples taken each day) be combined into a flow-proportional weekly composite sample, or that seven grab samples taken at the same time each day be combined into a time-proportional weekly composite sample. If no WWTP is available, untreated wastewater should be collected at the site of its discharge into the river.

It was agreed that groundwater and urban stormwater runoff samples would be collected in countries with established sampling infrastructure and the necessary equipment.

During the one-year monitoring period, 25 samples were planned for collection in EU countries and 100 samples in non-EU countries.

Based on the agreements from the workshop, the document D1.1.1 “Sampling Strategy and Standard Operating Procedure was completed by the end of June 2024 (D1.1.1, 2024).

The workshop was of great importance for the successful start of the one-year monitoring campaign in September 2024 (see photos in Figure 1).

The event took place in a very warm and collaborative atmosphere. In the afternoon of the first day, the project partners visited the JSI laboratories for metal analysis, took a short trip to Ljubljana Castle, and attended a dinner where further informal discussions continued.

Figure 1: Photos from the workshop in Ljubljana.

3 Planned logistics and organisation of the monitoring campaign

The project partners received the SOP by the end of June 2024, which provided all the details required for the monitoring campaigns.

JSI, TU Wien and BME jointly prepared templates for labelling sampling sites for metal analysis, as well as a separate template for PFAS and pharmaceutical analysis. In addition, a template for recording on-site parameters necessary to support the monitoring activities was provided.

The project partners received detailed instructions on the sampling procedures for each group of HS, including how to prevent contamination at the sampling site, as well as guidelines for sample storage and transport.

The project partners shared the addresses and contact persons (including email addresses and telephone numbers) for receiving the sampling bottles and sampling accessories.

JSI and TU Wien supplied the project partners with pre-cleaned sampling bottles and all necessary sampling accessories by 15 August 2024, along with the addresses and contact persons (including email addresses and telephone numbers) to whom the partners should send the samples collected during the monitoring campaigns.

TU Wien provided project partners from non-EU countries with the required customs documentation to ensure that samples are not held at the border and can be delivered to TU Wien and JSI as quickly as possible.

By the end of August 2024, everything was ready for the start of the one-year monitoring campaigns in September 2024.

Each project partner notified the laboratory in advance of sample delivery. Analyses of HS were performed immediately upon receipt of the samples.

The project partners followed the sampling protocols outlined in the SOPs in full detail, ensuring that all planned samples were collected and analysed on time.

4 Laboratory methods applied in determination of HS

4.1 Laboratory methods applied at JSI for the determination of metal concentrations

4.1.1 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.

4.1.2 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), for ICP and stock standard solutions of scandium (Sc), germanium (Ge), yttrium (Y), rhodium (Rh) and indium (In) (1000 ± 2 mg/L 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 1 L for wastewater, and 0.25 L for total element content in river water and 0.05 L for the dissolved metal content in river water) obtained from BRAND. The accuracy of metal determination by ICP-MS was checked for each set of samples by analysing the standard reference material SPS-SW1 (Surface Water – Trace Metals Reference Material, LGC Standards, UK).

4.1.3 Analytical procedures

Sampling, storage and transport procedures are described in detail in *Deliverable 1.1.1 Protocol for sampling, storage and transport of samples.*

Table 1: CAS IDs for metals for the analysed metals

Element	CAS number
Cr	7440-47-3
Ni	7440-02-0
Cu	7440-50-8
Zn	7440-66-6
As	7440-38-2
Cd	7440-43-9
Pb	7439-92-1

4.1.3.1 Analytical procedures for the determination of total metal concentrations in river water, urban stormwater runoff and wastewater samples

Frozen samples were thawed and thoroughly mixed prior to analysis.

To determine the total concentrations of metals in river waters and urban stormwater runoff samples, 3 mL of HNO_3, 1 mL of HCl, and 0.1 mL of HF were added to 10 mL of sample. The mixture was subjected to microwave-assisted digestion under the following conditions:

Ramp to 90 °C in 30 min, hold for 5 min
Ramp to 140 °C in 10 min, hold for 5 min
Ramp to 190 °C in 10 min, hold for 15 min
Cool for 30 min

After digestion, the samples were transferred to 50 mL PE-marked tubes and diluted 2-times, resulting in a final 10-times dilution. Metal concentrations were then determined using ICP-MS in accordance with SIST EN ISO 17294-2:2017.

For the analysis of wastewaters, 2 mL of H_2O_2, 3 mL of HNO_3, and 1 mL of HCl were added to 10 mL of sample, and the same analytical procedure was applied as described for river and storm runoff water samples.

4.1.3.2 Analytical procedures for the determination of dissolved metal concentrations in river water and groundwater samples

Frozen samples were thawed and thoroughly mixed prior to analysis.

The concentrations of dissolved metals in river water and groundwater samples were determined directly using ICP-MS, in accordance with SIST EN ISO 17294-2:2017.

4.1.3.3 Limits of detection and limits of quantification

Limits of detection (LODs) and limits of quantification (LOQs) for the determination of the total metal concentrations in river water samples, urban stormwater runoff and wastewater samples, and dissolved metal concentrations in river water and groundwater samples, are presented in Table 2 and in Table 3, respectively. The LODs and LOQs were calculated as the concentration providing a signal equal to 3*s* and 10*s* of the blank sample (MilliQ water acidified as samples analysed), respectively. To calculate the LODs and LOQs, 8 blank samples were analysed by ICP-MS.

Table 2: LODs and LOQs for the determination of the total metal concentrations in river water, urban stormwater runoff and wastewater samples at the JSI laboratory.

Parameter	Analytical method	LOD (µg/L)	LOQ (µg/L)
Cr	ICP-MS	0.06	0.20
Ni	ICP-MS	0.10	0.33
Cu	ICP-MS	0.13	0.43
Zn	ICP-MS	0.70	2.33
As	ICP-MS	0.10	0.33
Cd	ICP-MS	0.04	0.13
Pb	ICP-MS	0.15	0.50

Table 3: LODs and LOQs for the determination of the dissolved metal concentrations in river water, urban stormwater runoff and wastewater samples at the JSI laboratory.

Parameter	Analytical method	LOD (µg/L)	LOQ (µg/L)
Cr	ICP-MS	0.006	0.02
Ni	ICP-MS	0.01	0.03
Cu	ICP-MS	0.013	0.04
Zn	ICP-MS	0.07	0.23
As	ICP-MS	0.01	0.03
Cd	ICP-MS	0.004	0.01
Pb	ICP-MS	0.015	0.05

4.2 Laboratory methods applied at CETI for the determination of metal concentrations

4.2.1 Instrumentation

Concentrations of elements were determined by ICP-MS, using instrument Agilent 7700x (Agilent Technologies, Tokyo, Japan) under optimized measurement parameters.
A Berghof (Germany) SpeedWave XPERT was used for sample digestion.

4.2.2 Reagents and materials

Ultrapure water (18.2 MΩ·cm) obtained from a Barnstead GenPure Pro UV/UF system (Thermo Scientific) was used for the preparation of all samples and reagents. Supra-grade nitric acid (69%) and hydrochloric acid (35%) were obtained from Carl Roth. An ICP multi-element standard solution (CPA Chem, Ref. No. E5B8.K1.5N.L1) containing 21 elements (Al, Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Sb, Se, Tl, V, Zn, and Sn; each at 100 µg/mL in 5% HNO_3) and stock standard solutions of scandium (Sc), rhodium (Rh), lutetium (Lu), and indium (In) (1000 ± 2 mg/L in 2% HNO_3), also obtained from CPA Chem, were used to prepare calibration curves and internal standards for ICP-MS analysis. Samples were filtered through 0.45 µm Minisart cellulose nitrate membrane filters (Sartorius, Goettingen, Germany). Water samples were collected in low-density polyethylene (PE) wide-mouth bottles (1 L for wastewater, 0.25 L for total element content in river water, and 0.05 L for dissolved metal content in river water), obtained from BRAND. The accuracy of potentially toxic element (PTE) determination by ICP-MS was verified for each sample set using the standard reference material NW-TMDA-54.6. This trace element matrix reference material consists of filtered and diluted Lake Ontario water preserved with 0.2% nitric acid (Environment and Climate Change Canada).

4.2.3 Analytical procedures

4.2.3.1 Sampling, storage, and transport of samples

Sampling, storage and transport procedures are described in detail in *Deliverable 1.1.1 Protocol for sampling, storage and transport of samples.*

4.2.3.2 Analytical procedures for the determination of total metal concentrations in river water and wastewater samples

River water samples were thoroughly mixed prior to analysis. To determine the total concentrations of metals in river waters and urban stormwater runoff samples, 0.5 mL of HNO_3 and 1.5 mL of HCl were added to 20 mL of sample. The mixture was subjected to microwave-assisted digestion under the following conditions:

Ramp to 145 °C in 5 min, hold for 5 min
Ramp to 180 °C in 3 min, hold for 10 min
Cool for 10 min

After digestion, the samples were transferred to 30 mL PE-marked tubes and diluted to 25 mL, resulting in a final 1.25-times dilution. Metal concentrations were then determined using ICP-MS in accordance with MEST EN ISO 17294-2:2017.

For the analysis of wastewater samples, the same digestion procedure was applied as for river water samples.

4.2.3.3 Analytical procedures for the determination of dissolved metal concentrations in river water

The water samples were thoroughly mixed prior to analysis. The concentrations of dissolved metal in river water samples were determined directly using ICP-MS, in accordance with MEST EN ISO 17294-2:2017.

4.2.3.4 Limits of detection and limits of quantification

Limits of detection (LODs) and limits of quantification (LOQs) for the determination of total and dissolved metal concentrations in river water and wastewater are presented in Table 4. The LODs and LOQs were determined from the analysis of low-concentration standard solutions. The LOD was calculated as the mean concentration of the standard plus three standard deviations, and the LOQ as the mean concentration plus ten standard deviations. Since dissolved metal concentrations were analyzed directly and total metal concentrations were determined after microwave-assisted digestion and slight dilution of the samples (from 20 mL to a final volume of 25 mL), the dilution factor (1.25×) was considered negligible. Therefore, the same LODs and LOQs were applied for both total and dissolved metal concentrations.

Table 4: LODs and LOQs for the determination of the total metal concentrations in river water, urban stormwater runoff and wastewater samples at the CETI laboratory.

Parameter	Analytical method	LOD (µg/L)	LOQ (µg/L)
Cr	ICP-MS	0.03	0.10
Ni	ICP-MS	0.10	0.33
Cu	ICP-MS	0.10	0.30
Zn	ICP-MS	1.00	3.00
As	ICP-MS	0.03	0.10
Cd	ICP-MS	0.01	0.03
Pb	ICP-MS	0.06	0.20

4.3 Laboratory methods applied at TU Wien for the determination of PFAS and pharmaceutical concentrations

4.3.1 Instrumentation

Concentrations of elements were determined via LC-MS/MS, using the instruments Agilent 1290 Infinity II (Agilent Technologies, Tokyo, Japan) under optimized measurement parameters, PAL RTC (PAL, CTC Analytics AG, Switzerland), Sciex QTRAP 6500+ (Sciex, AB Sciex LLC, Marlborough, USA), as well as Phenomenex Luna Omega PS column C18 as analytical column and Phenomenex Luna C18 as delayed column.

4.3.2 Reagents and materials

Ultrapure water obtained from a MiliQ Veolia Water Solution & Technologies system was used for preparation of samples and reagents. Methanol & Ammoniumhydroxyde were purchased from Merck. HPLC grade organic solvents: Ethanol (CAS 64-17-5), Acetonitrile (CAS 75-05-8) and Acetic acid (CAS 64-19-17) as well as mobile phase for online solid phase extraction and column chromatography were purchased from Sigma Aldrich. Mix and Single Substances Internal Standards (PFAC30PAR 1 mg/L and MXI 1mg/L, MPFAC-HIF-IS 1 mg/L, Wellington Laboratories, Canada) were used to prepare calibration curves. Wastewater samples were filtered using 1.0 µm VWR glass fiber filters (Avantor, Inc.). Water samples were collected in polypropylene (PP) or high-density polyethylene (HDPE) wide-mouth bottles (volume 1 L) obtained from Azlon. The accuracy of PFAS determination by LCMS was checked for each set of samples by analysing the mixed PFAS- standards (MPFAC-HIF-ES 1 mg/L Wellington Laboratories, Canada).

4.3.3 Analytical procedures

Sampling, storage and transport procedures are described in detail in Deliverable 1.1.1 “Protocol for sampling, storage and transport of samples”.

4.3.3.1 Analytical procedures for the determination of pharmaceuticals concentrations in river water, urban storm runoff water and wastewater samples

Pharmaceutical analysis employed online solid phase extraction (SPE) coupled to LC-MS/MS following internal method IWR-12:2023. The system comprised an Agilent HPLC (binary pumps, degasser, PAL autosampler) and an Applied Biosystems QTRAP 6500 MS/MS. Online SPE utilized a Phenomenex Strata X cartridge while separation occurred on a Phenomenex Luna C18 column with guard cartridge. Water samples were filtered (1 µm glass fibre). Analytical standards were prepared in ethanol (1 mg/mL). The injection volume of 10 mL for online SPE and a gradient elution (0.1% acetic acid in water and acetonitrile) for LC separation was used. Quantification was performed via MRM ESI (450°C, N_2 collision gas). LOD and LOQ were determined at 3σ and 10σ (S/N) from standard chromatograms (Kromidas, 2011).

4.3.3.2 Analytical procedures for the determination of PFAS concentrations in river water, urban storm runoff water and wastewater samples

PFAS in samples were quantified via liquid chromatography with tandem mass spectrometry (LC-MS/MS) (EPA, 2024). External calibration standards (≥ 5 levels, 50–1000 ng l^{-1} in methanol) were spiked with 50 µL of internal standard for recovery assessment and calibration establishment. Sample injection was performed using a PAL RTC autosampler. Chromatographic separation was achieved by HPLC using an Agilent 1290 Infinity II (Agilent Technologies Inc., Tokyo, Japan) with a Phenomenex Luna Omega PS column C18 (C18 100 x 3.0 mm 100 Å) and a Phenomenex Luna C18 (50 x 3 mm 110 Å) delay column. The separation is achieved by using a binary gradient mobile phase consisting of ultra-pure water with 20 mM Ammonium acetate buffer (A) and HPLC-MS grade methanol (B) at a constant flow of 0.6 mL/min.

4.3.3.3 Limits of detection and limits of quantification

Limits of detection (LODs) and limits of quantification (LOQs) for the determination of the pharmaceuticals and PFAS concentrations in river water samples, ground water, urban storm runoff water and wastewater samples, are presented with their CAS-ID in Table 5 and Table 6, respectively. The LODs and LOQs were calculated as the concentration providing a signal equal to 3s and 10s of the blank sample (MilliQ water), respectively. Two methods were applied to calculate the LODs and LOQs: one according to DIN 32645, using five standard samples with 25 repetitions, and the other by calculating the S/N ratio from the chromatograph (Kromidas, 2011).

Table 5: CAS-IDs, LODs and LOQs for the determination of the pharmaceutical concentrations in river water, ground water, urban storm runoff water and wastewater samples at the TU Wien laboratory.

Substance	CAS number	LOQ [ng/L]	LOD [ng/L]
Sulfamethoxazol	723-46-6	2.2	0.73
Carbamazepine	298-46-4	0.7	0.23
Metoprolol	51384-51-1	22.2	7.40
Trimethoprim	738-70-5	10.1	3.37
Diclofenac	15307-86-5	5.1	1.70
Amisulprid	71675-85-9	0.5	0.17
Citalopram	59729-33-8	14.5	4.83
Venlafaxine	93413-69-5	2.5	0.83
Irbesartan	138402-11-6	6.6	2.20
Bezafibrat	41859-67-0	0.88	0.29
Ibuprofen	15687-27-1	9.5	3.17
Hydrochlorothiazide	58-93-5	1.66	0.55

Table 6: CAS-IDs, LODs and LOQs for the determination of the PFAS concentrations in river water (RW), ground water (GW), urban storm runoff water (SW) and wastewater (WW) samples at the TU Wien laboratory.

Group	Substance	CAS number	LOQ RW [ng/L]	LOD RW	LOQ GW [ng/L]	LOD GW [ng/L]	LOQ WW/SW [ng/L]	LOD WW/SW [ng/L]
PFCA	PFBA	375-22-4	1.40	0.47	0.27	0.09	4.31	1.44
PFCA	PFPeA	2706-90-3	0.91	0.30	0.90	0.30	4.55	1.52
PFCA	PFHxA	307-24-4	0.28	0.09	0.31	0.10	1.60	0.53
PFCA	PFHpA	375-85-9	0.31	0.10	0.53	0.18	2.69	0.90
PFCA	PFOA	335-67-1	0.33	0.11	0.70	0.23	0.73	0.24
PFCA	PFNA	375-95-1	0.33	0.11	0.39	0.13	0.60	0.20
PFCA	PFDA	335-76-2	0.11	0.04	0.24	0.08	0.40	0.13
PFCA	PFUnDA	2058-94-8	0.21	0.07	0.50	0.17	0.20	0.07
PFCA	PFDoDA	307-55-1	0.12	0.04	0.49	0.16	0.30	0.10
PFCA	PFTrDA	72629-94-8	0.28	0.09	0.87	0.29	0.31	0.10
PFCA	PFTeDA	376-06-7	0.41	0.14	0.81	0.27	0.43	0.14
PFSA	PFBS	375-73-5	0.38	0.13	0.32	0.11	0.35	0.12
PFSA	PFPeS	2706-91-4	0.32	0.11	0.45	0.15	0.24	0.08
PFSA	PFHxS	355-46-4	0.17	0.06	0.81	0.27	0.75	0.25
PFSA	PFHpS	375-92-8	0.09	0.03	0.38	0.13	0.05	0.02
PFSA	PFOS	1763-23-1	0.15	0.05	0.45	0.15	0.81	0.27
PFSA	PFNS	68259-12-1	0.07	0.02	0.15	0.05	0.53	0.18
PFSA	PFDS	335-77-3	0.06	0.02	0.19	0.06	0.34	0.11
AFFF-related	4:2 FTS	757124-72-4	0.05	0.02	0.14	0.05	0.10	0.03

Group	Substance	CAS number	LOQ RW [ng/L]	LOD RW	LOQ GW [ng/L]	LOD GW [ng/L]	LOQ WW/SW [ng/L]	LOD WW/SW [ng/L]
AFFF-related	6:2 FTS	27619-97-2	0.06	0.02	0.53	0.18	0.08	0.03
AFFF-related	8:2 FTS	39108-34-4	0.18	0.06	0.55	0.18	0.40	0.13
FASA	PFOSA	754-91-6	0.10	0.03	0.11	0.04	0.10	0.03
FASAA	N-MeFOSAA	2355-31-9	0.10	0.03	0.13	0.04	0.10	0.03
FASAA	N-EtFOSAA	2991-50-6	0.10	0.03	0.15	0.05	0.10	0.03
PFECA	GenX	13252-13-6	0.20	0.07	0.26	0.09	0.81	0.27
PFECA	ADONA	919005-14-4	0.09	0.03	0.12	0.04	0.06	0.02
PFESA	9Cl-PF3ONS	73606-19-6	0.10	0.03	0.13	0.04	0.08	0.03
PFESA	11Cl-PF3OUdS	763051-92-9	0.10	0.03	0.13	0.04	0.06	0.02
PFCA	PFHxDA	67905-19-5	0.44	0.15	0.44	0.15	0.98	0.33
PFCA	PFODA	16517-11-6	0.59	0.20	1.44	0.48	1.13	0.38
FASA	N-MeFOSA	31506-32-8	0.11	0.04	0.37	0.12	0.19	0.06
FASA	N-EtFOSA	4151-50-2	0.08	0.03	0.43	0.14	0.25	0.08
FASE	N-MeFOSE	24448-09-7	0.09	0.03	0.10	0.03	0.16	0.05
FASE	N-EtFOSE	1691-99-2	0.10	0.03	0.10	0.03	0.13	0.04
PFSA	PFUnDS	749786-16-1	0.10	0.03	0.15	0.05	0.27	0.09
PFSA	PFDoDS	79780-39-5	0.07	0.02	0.17	0.06	0.55	0.18
PFSA	PFTrDS	791563-89-8	0.09	0.03	0.12	0.04	0.23	0.08
AFFF-related	FBSA	30334-69-1	0.07	0.02	0.10	0.03	0.16	0.05
AFFF-related	FHxSA	41997-13-1	0.10	0.03	0.10	0.03	0.06	0.02
AFFF-related	Capstone A	80475-32-7	0.79	0.26	1.69	0.56	0.69	0.23
AFFF-related	Capstone B	34455-29-3	2.63	0.88	13.50	4.50	1.36	0.45

4.4 Laboratory methods applied at CETI for the determination of PFAS and pharmaceutical concentrations

4.4.1 Instrumentation

The determination of per- and polyfluoroalkyl substances (PFASs) and pharmaceutical compounds in the analysed water samples was performed using a UHPLC-MS/MS system. The separation of target analytes was achieved using an Agilent 1290 Infinity II UHPLC coupled to an Agilent 6475 LC/TQ mass spectrometer. Chromatographic resolution was ensured through the use of a Zorbax Eclipse Plus C18 analytical column (100 × 2.1 mm, 1.8 µm), while potential contamination arising from perfluorinated components within the system was effectively mitigated by incorporating an InfinityLab PFC Delay Column (4.6 x 30 mm)

Sample preparation for PFAS and pharmaceutical compounds analysis in river water and wastewater was carried out using an automated solid-phase disk extraction procedure. The extraction was performed with the Biotage Horizon 5000 automated water extractor and HLB SPE disk.

4.4.2 Reagents and materials

Material

a. Polypropylen Vials, 1.5 mL, screw cap
b. Pipettes

Chemicals

a. Acetonitrile - LCMS grade
b. Acetonitrile - HPLC grade
c. Deionized Water
d. Methanol – LCMS grade
e. Methanol – HPLC grade
f. Ammonium Acetate
g. Formic acid

Analytical Standards

Table 7: Native Perfluorinated Compound Solution Mixture, PFAC-MXC, Wellington Laboratories.

No.	Component	Acronym	C (ng/mL)
1.	Perfluoro-n-butanoic acid	PFBA	2000
2.	Perfluoro-n-pentanoic acid	PFPeA	2000
3.	Perfluoro-n-hexanoic acid	PFHxA	2000
4.	Perfluoro-n-heptanoic acid	PFHpA	2000
5.	Perfluoro-n-octanoic acid	PFOA	2000
6.	Perfluoro-n-nonanoic acid	PFNA	2000
7.	Perfluoro-n-decanoic acid	PFDA	2000
8.	Perfluoro-n-undecanoic acid	PFUnA	2000
9.	Perfluoro-n-dodecanoic acid	PFDoA	2000
10.	Perfluoro-n-tridecanoic acid	PFTrDA	2000
11.	Perfluoro-n-tetradecanoic acid	PFTeDA	2000
12.	Perfluoro-n-hexadecanoic acid	PFHxDA	2000
13.	Perfluoro-n-octadecanoic acid	PFODA	2000
14.	Potassium perfluoro-1-butanesulfonate	PFBS	2000
15.	Sodium perfluoro-1-pentanesulfonate	PFPeS	2000
16.	Sodium perfluoro-1-hexanesulfonate	PFHxS	2000
17.	Sodium perfluoro-1-heptanesulfonate	PFHpS	2000
18.	Sodium perfluoro-1-octanesulfonate	PFOS	2000
19.	Sodium perfluoro-1-nonanesulfonate	PFNS	2000
20.	Sodium perfluoro-1-decanesulfonate	PFDS	2000
21.	Sodium perfluoro-1-dodecanesulfonate	PFDoS	2000

Table 8: Mass-labelled PFAS extraction standards solution, MPFAC-C-ES, Wellington Laboratories.

No.	Component	Acronym	C (ng/mL)
1.	Perfluoro-n-(13C4)butanoic acid	MPFBA	2000
2.	Perfluoro-n-(13C5)pentanoic acid	M5PFPeA	2000
3.	Perfluoro-n-(1,2,3,4,6-13C5)hexanoic acid	M5PFHxA	2000
4.	Perfluoro-n-(1,2,3,4-13C4)heptanoic acid	M4PFHpA	2000

5.	Perfluoro-n-(13C8)octanoic acid	M8PFOA	2000
6.	Perfluoro-n-(13C9)nonanoic acid	M9PFNA	2000
7.	Perfluoro-n-(1,2,3,4,5,6-13C6)decanoic acid	M6PFDA	2000
8.	Perfluoro-n-(1,2,3,4,5,6,7-13C7)undecanoic acid	M7PFUdA	2000
9.	Perfluoro-n-(1,2-13C2)dodecanoic acid	MPFDoA	2000
10.	Perfluoro-n-(1,2-13C2)tetradecanoic acid	M2PFTeDA	2000
11.	Sodium perfluoro-1-(2,3,4-13C3)butanesulfonate	M3PFBS	2000
12.	Sodium perfluoro-1-(1,2,3-13C3)hexanesulfonate	M3PFHxS	2000
13.	Sodium perfluoro-1-(13C8)octanesulfonate	M8PFOS	2000

4.4.3 Analytical procedures

Sampling, storage and transport procedures are described in detail in Deliverable 1.1.1 “Protocol for sampling, storage and transport of samples”.

4.4.3.1 Analytical procedures for the determination of PFAS and pharmaceuticals concentrations in river water and wastewater samples

The preparation of water samples for PFAS and pharmaceutical compounds analysis was performed using the Horizon Biotage 5000 automated extraction system. The entire procedure is carried out through a sequence of controlled steps. The system first conditions the solid-phase extraction disk to establish optimal retention conditions for the target compounds. After conditioning, the water sample is automatically introduced and passed through the disk, allowing the analytes to be retained while the matrix is removed. The instrument then conducts the extraction process, followed by the elution step in which the retained PFAS and pharmaceutical compounds are released from the disk using suitable solvents. The eluate containing the concentrated analytes is collected and prepared for subsequent LC-MS/MS analysis.

Table 9: Procedure of sample preparation at the CETI laboratory using Horizon Biotage 5000.

Phase	Solvent	Purge (sec)	Pump flow rate	Saturate (sec)	Soak (sec)	Drain (sec)
Disk conditioning	Ethy Acetate,15mL	60	2	1	120	30
		60	2	1	120	30
	Methanol,15mL	60	2	1	120	30
		60	2	1	120	30
	Water, 15 mL	60	2	1	120	30
Sample loading	Vacuum pump rate: 1		Done Loading Delay: 0			
Air dry disk	Dry: 500 sec		Pump rate: 6			
Elution of analytes	Ethy Acetate,10mL	60	1	1	150	60
		60	1	1	150	60
		60	1	1	150	60
	Methanol,15mL	60	1	1	150	60
		60	1	1	150	60
		60	1	1	150	60

After elution of the analyte, the extract is evaporated to a volume of 1 mL.

4.4.3.2 Limits of detection and limits of quantification

Limits of detection (LODs) and limits of quantification (LOQs) for the determination of the pharmaceuticals and PFAS concentrations in river water samples, ground water, urban storm runoff water and wastewater samples, are presented with their CAS-ID in Table 10 and Table 11, respectively. The LODs and LOQs were calculated as the concentration providing a signal equal to 3s and 10s of the blank sample (MilliQ water), respectively. Two methods were applied to calculate the LODs and LOQs: one according to DIN 32645, using five standard samples with 25 repetitions, and the other by calculating the S/N ratio from the chromatograph (Kromidas, 2011).

Table 10: CAS-IDs, LODs and LOQs for the determination of the pharmaceutical concentrations in river water and wastewater samples at the CETI laboratory.

Substance	CAS number	LOQ (ng/L)	LOD (ng/L)
Carbamazepine	298-46-4	0.20	0.07
10,11-dihydro-10,11-DiOH-Carbamazepine	35079-97-1	0.30	0.10
10,11-dihydro-10-OH-Carbamazepine	29331-92-8	0.30	0.10
2-OH-Carbamazepine	68011-66-5	0.20	0.07
Diclofenac	15307-86-5	0.40	0.13
4-OH-Diclofenac	64118-84-9	1.00	0.33
Codeine	76-57-3	1.00	0.33
Morphine	57-27-2	1.00	0.33
Heroin	561-27-3	2.50	0.83
6-Monoacetyl Morphine	2784-73-8	1.00	0.33
Amphetamine	300-62-9	0.90	0.30
Methamphetamine	537-46-2	0.90	0.30
MDA	4764-17-4	0.90	0.30
MDMA	42542-10-9	0.90	0.30
MDEA	82801-81-8	0.90	0.30
o-Desmethyl-Tramadol	144830-15-9	0.50	0.17
Tramadol	36282-47-0	0.50	0.17
Benzoylecgonine	519-09-5	0.20	0.07
Cocaine	50-36-2	0.20	0.07
Methadone	76-99-3	1.00	0.33
Midazolam	59467-70-8	0.50	0.17
Flurazepam	17617-23-1	0.60	0.20
Bromazepam	1812-30-2	4.00	1.33
Nitrazepam	146-22-5	0.80	0.27
Clonazepam	1622-61-3	0.90	0.30
Triazolam	28911-01-5	0.80	0.27
Alprozolam	28981-97-7	0.40	0.13
Lorazepam	846-49-1	0.40	0.13
Oxazepam	604-75-1	0.30	0.10
Nordiazepam	1088-11-5	0.30	0.10
Diazepam	439-14-5	0.50	0.17
Naproxen	22204-53-1	2.50	0.83
11-OH-THC	36557-05-8	3.00	1.00
THC-COOH	56354-6-4	3.00	1.00
delta 9-THC	1972-08-3	3.00	1.00

Table 11: CAS-IDs, LODs and LOQs for the determination of the PFAS concentrations in river water (RW) and wastewater (WW) samples at the CETI laboratory.

Group	**Substance**	**CAS number**	**LOQ RW (ng/L)**	**LOD RW (ng/L)**	**LOQ WW (ng/L)**	**LOD WW (ng/L)**
PFCA	PFBA	375-22-4	0.95	0.32	2.85	0.95
PFCA	PFPeA	2706-90-3	0.14	0.05	0.42	0.14
PFCA	PFHxA	307-24-4	0.09	0.03	0.22	0.07
PFCA	PFHpA	375-85-9	0.06	0.02	0.18	0.06
PFCA	PFOA	335-67-1	0.05	0.02	0.13	0.04
PFCA	PFNA	375-95-1	0.05	0.02	0.16	0.05
PFCA	PFDA	335-76-2	0.04	0.01	0.19	0.06
PFCA	PFUnDA	2058-94-8	0.06	0.02	0.19	0.06
PFCA	PFDoDA	307-55-1	0.11	0.04	0.29	0.10
PFCA	PFTrDA	72629-94-8	0.30	0.10	0.53	0.18
PFCA	PFTeDA	376-06-7	0.30	0.10	0.59	0.20
PFSA	PFBS	375-73-5	0.05	0.02	0.17	0.06
PFSA	PFPeS	2706-91-4	0.04	0.01	0.17	0.06
PFSA	PFHxS	355-46-4	0.04	0.01	0.15	0.05
PFSA	PFHpS	375-92-8	0.04	0.01	0.21	0.07
PFSA	PFOS	1763-23-1	0.04	0.01	0.15	0.05
PFSA	PFNS	68259-12-1	0.04	0.01	0.21	0.07
PFSA	PFDS	335-77-3	0.07	0.02	0.24	0.08
PFCA	PFHxDA	67905-19-5	1.51	0.50	2.68	0.89
PFCA	PFODA	16517-11-6	1.62	0.54	2.61	0.87
PFSA	PFDoS	79780-39-5	1.43	0.48	2.43	0.81

5 Sampling campaigns

5.1 Austria

In Austria, urban stormwater runoff samples were collected at five sampling sites in Vienna over the course of one year. Vienna predominantly employs a combined sewer system. To prevent contamination from sewage, samples were collected from separate stormwater sewers located in three districts of the city. The specific sampling sites were selected using Vienna's Sewer Information System (Wien Kanal - KANIS 2023).

Urban stormwater runoff sampling sites

1 – Urban stormwater runoff (URW-ATSW1) (16.292394, 48.140118). The sampling site has a catchment area of 0.15 km^2 and is influenced by a parking lot, commercial and residential area, and light industry. The site exhibits a persistent flow, even during dry periods. Frequency of sampling: five times over one year.
HS measured: PFAS, pharmaceuticals.

2 – Urban stormwater runoff (URW-ATSW2) (16.287812, 48.136471). The sampling site has a catchment area of 0.08 km^2 and is impacted by heavy industry, commercial and residential areas, a park, and a firefighting station. The site exhibits a persistent flow, even during dry periods. Frequency of sampling: five times over one year.
HS measured: PFAS, pharmaceuticals.

3 – Urban stormwater runoff (URW-ATSW3) (16.287798, 48.136564). The sampling site has a catchment area of 0.50 km^2 and is mainly influenced by residential and commercial areas, shopping mall, and several schools. The site exhibits a persistent flow, even during dry periods. Frequency of sampling: five times over one year.
HS measured: PFAS, pharmaceuticals.

4 – Urban stormwater runoff (URW-ATSW4) (16.292680, 48.140441). The sampling site has a catchment area of 0.017 km^2 and is impacted by a parking lot, an adjacent landfill, and heavy industry. Frequency of sampling: once in one year.
HS measured: PFAS, pharmaceuticals.

5 – Urban stormwater runoff (URW-ATSW5) (16.339258, 48.155061). The sampling site has a catchment area of 0.24 km^2 and is the least impacted among the locations. It is mostly surrounded by forest and park areas, with some commercial and light industrial influence. Frequency of sampling: four times over one year.
HS measured: PFAS, pharmaceuticals.

6 – Urban stormwater runoff (URW-ATSW6) (16.316991, 48.154079). The sampling site has a catchment area of 2.23 km^2 and is therefore the largest. It is impacted by industry, commercial areas, residential areas and a park. Frequency of sampling: three times over one year.
HS measured: PFAS, pharmaceuticals.

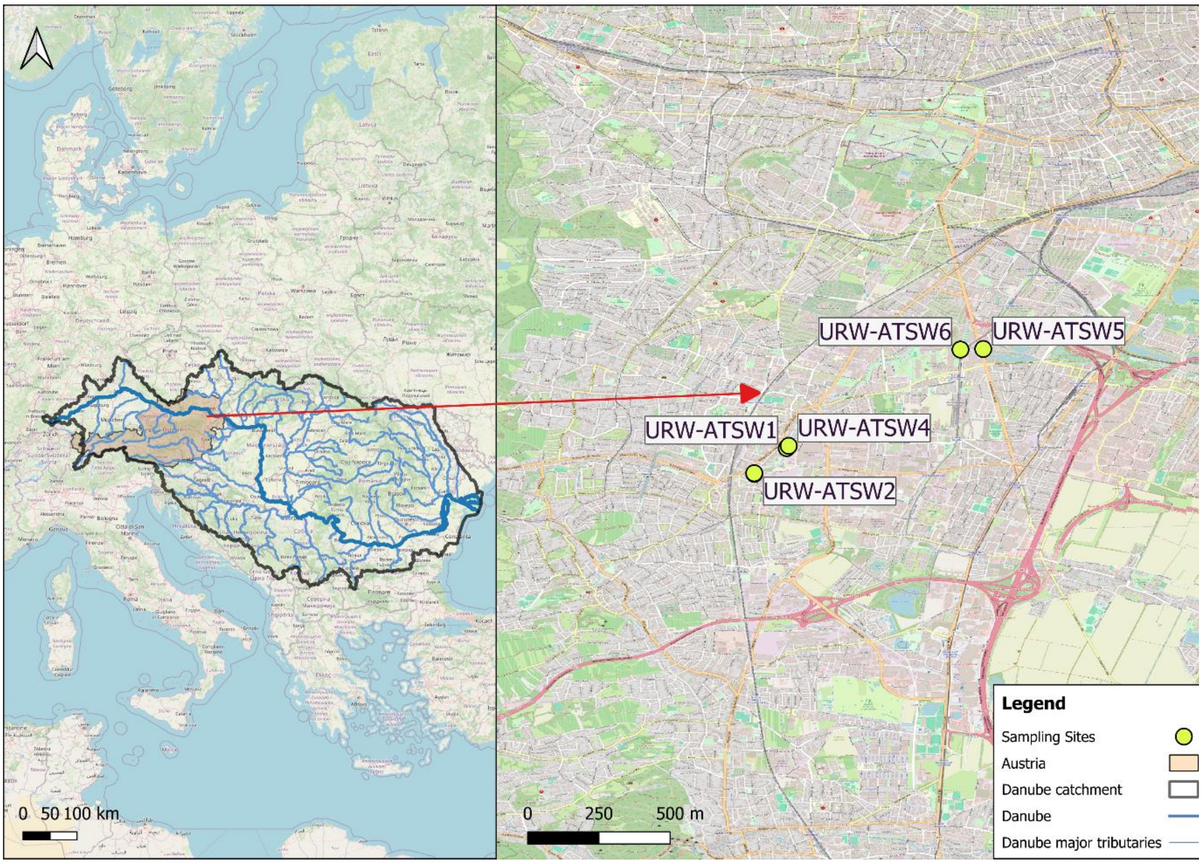

Figure 2: Map of the sampling campaign in Austria.

1 – Sampling site URW-ATSW1

2 – Sampling site URW-ATSW2

Figure 3: Photos of sampling sites in Austria. Left: URW-ATSW1. Right: URW-ATSW2.

5.2 Slovakia

Slovakia aimed to generate data supporting the validation of the MoRE model, taking into account the geographical context and focusing on transboundary monitoring sites near the closing profiles of the rivers Váh, Hron, Ipeľ, Hornád, Bodrog, and Morava. There are existing long term data series for these sites, but no data are yet available concerning pharmaceuticals and PFAS in water. Metals were also included in order to provide at least estimation of their concentrations that could be below the LOD, using conventional analytical techniques for monitoring and chemical status assessment. All of these rivers are influenced by all sorts of industry, agriculture, infrastructural constructions, emissions of municipal and industrial WWTPS and sewer systems without wastewater treatment, as well as atmospheric deposition. River sampling was conducted twice over the course of one year. Wastewater sampling was conducted three times during the same year. Samples were collected with an automatic sampler to obtain a time-proportional composite sample over a 24-hour period for seven consecutive days.

River water sampling sites

1 – Devín (RIV-SKMO), Morava River (16.69601, 48.21104). Morava is the only river which does not originate in Slovakia. Its catchment area is 26 579,7 km^2 and in Slovakia its catchment area is 2282 km^2. The closing profile used for monitoring in this study is the water body (WB) SKM0002 in Devínska Nová Ves, which is currently failing to reach good chemical status due to benzo(a)pyrene in water and Mercury, PBDE and PFOS in fish. The selected sampling site is a background location in a pristine area, with no known sources of pollution.
HS measured: metals, PFAS, pharmaceuticals

2 – Komárno (RIV-SKVA), Váh River (18.14193, 47.76160) with the total catchment area of 18 769 km^2. The sampling point is in the WB SKV0027. River Váh is the biggest solely Slovak tributary of the Danube and is influenced by all kinds of industry and effluents of industrial and municipal WWTP, sewer systems without wastewater treatment, agriculture and atmospheric deposition. This water body is failing to reach good chemical status due to benzo(a)pyrene, 4-tert-octylphenol in water as well as mercury and PBDE in fish. The ecological potential is categorised as bad.
HS measured: metals, PFAS, pharmaceuticals.

3 – Kamenica nad Hronom (RIV-SKHR), Hron River (18.72568, 47.82516) is the closing profile of Hron with the total catchment area of 5465 km^2. The sampling point is in the WB SKR0005, which is failing to reach good chemical status caused by benzo(a)pyrene and fluoranthene in water and by mercury and PBDE in fish. The ecological status is categorised as average.
HS measured: metals, PFAS, pharmaceuticals.

4 – Salka (RIV-SKIP), Ipeľ River (17,76258, 47.88596) is the closing profile of Ipeľ with the toal catchment area of 3649 km^2. The sampling point is in the WB SKI0004, which is failing to reach good chemical status due to mercury and PBDE in fish. However, the chemical status without ubiquitous compounds is good.
HS measured: metals, PFAS, pharmaceuticals.

5 – Ždaňa (RIV-SKHO), Hornád River (21.34443, 48.60426) is the closing profile of Hornád with the total catchment area of 4414 km^2. The sampling point is in the WB SKH0004, which is failing to reach the good chemical status due to benzo(a)pyrene in water and to mercury and PBDE in fish.
HS measured: metals, PFAS, pharmaceuticals.

6 – Streda nad Bodrogom (RIV-SKBO), Bodrog River (21.74987, 48.39580) is the closing profile of Bodrog with the total catchment area of 7272 km^2. The sampling point is in the WB SKB000, which is failing to reach the good chemical status due to benzo(a)pyrene in water and to mercury, PBDE and PFOS in fish.
HS measured: metals, PFAS, pharmaceuticals.

7 – Military airport Sliač, Banská Bystrica (RIV-SKSL), Hron River (19.13920, 48.63098). It was selected as a potential hotspot site, expected to be polluted mainly by PFAS, with outlet of surface runoff directly to river Hron. The catchment includes a military area with training site also for firefighters.
HS measured: metals, PFAS, pharmaceuticals.

8 – Dačov lom mLyn, Lešť military and firefighter training site (RIV-SKPP), Plachtinský potok (19.26661, 48.30583). Several streams are merging into Plachtinský potok.
HS measured: metals, PFAS, pharmaceuticals.

9 – Bačkov (RIV-SKBP), Bačkovský potok (21.60658, 48.74282). This is a reference site, being a stream without known anthropogenic pressures and pollution. It belongs to the sub-basin of Bodrog.
HS measured: metals, PFAS, pharmaceuticals.

10 – Vernár ŽST (RIV-SKHN), Hnilec River (20.23365, 48.88543). This is a reference site, being a stream without known anthropogenic pressures and pollution. It belongs to the sub-basin of Hornád.
HS measured: metals, PFAS, pharmaceuticals.

11 – Osada Čierny Váh (RIV-SKIL), Ipoltica River (19.96879, 48.98948). This is a reference site, being a stream without known anthropogenic pressures and pollution. It belongs to the sub-basin of Váh.
HS measured: metals, PFAS, pharmaceuticals.

12 – Moštenica (RIV-SKMP), Moštenický potok (19.28042, 48.30583). This is a reference site, being a stream without known anthropogenic pressures and pollution. It belongs to the sub-basin of Hron.
HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

13 – WWTP Hlohovec (WW-SKHl) (17.77654, 48.41230). This plant treats municipal wastewater (combined sewers) from the city of Hlohovec, with a population of approximately 20 000. It also receives wastewater from a pharma industry. Its projected capacity is 27 500 PE and in 2024 it treated 1.783.971 m^3. The receiving water body for the effluent is the Váh River.
HS measured: PFAS, pharmaceuticals.

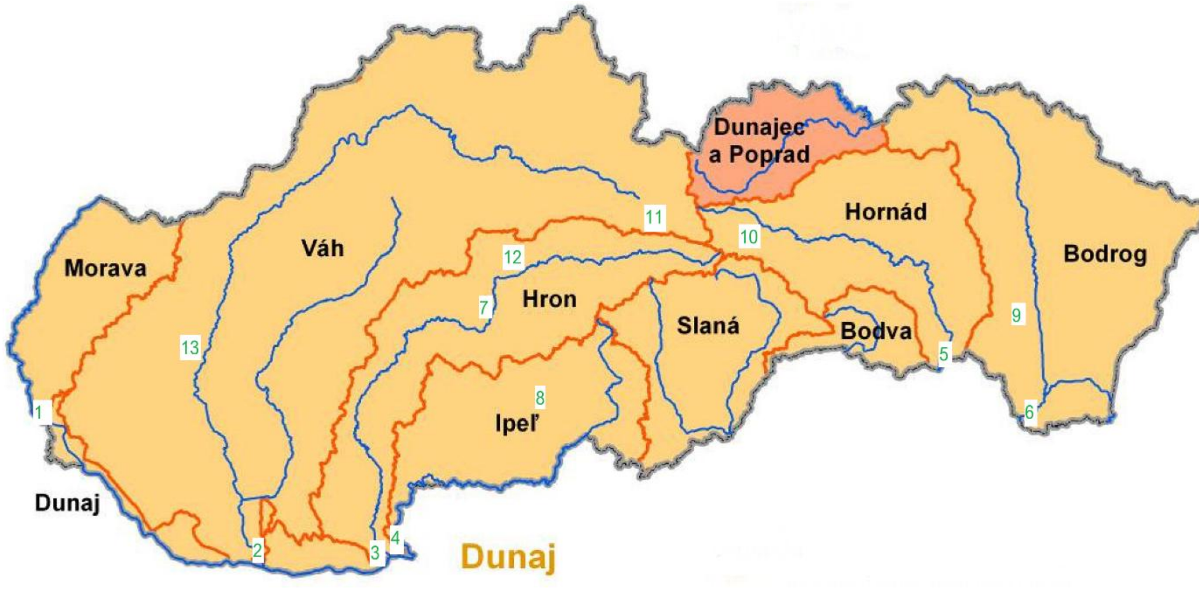

Figure 4: Map of the sampling campaign in Slovakia.

Figure 5: Photos of sampling sites in Slovakia. Left: Osada Čierny Váh, Ipoltica River, background location (No. 11 on the map). Middle: Salka, Ipeľ River (No. 4 on the map). Right: Outlet of surface runoff from the Military Airport Sliač (No. 7 on the map).

5.3 Hungary

In Hungary, the main objective of the monitoring campaign was to address the most critical gaps in order to apply the MoRE model. Due to the limited availability of samples, priority was given to increasing the number of data points in main rivers and tributaries for model validation, as well as increasing the availability of data regarding specific emission pathways. In line with these aims, PP-BME took samples at three types of site between September 2024 and June 2025 for the following purposes: (i) river sampling (watercourse) at medium and large rivers to characterise pollution at the catchment scale and validate national and transnational emission models, (ii) sampling of 'hotspot' watercourses to reveal local, airport-specific pollution and (iii) a targeted campaign to characterise concentrations in urban runoff from stormwater sewers and combined sewer overflows. River sampling was conducted four times over the course of one year, once in each season. Stormwater sampling was adjusted to precipitation events, with sampling taking place 4–7 times per location.

River water sampling sites

1 – Maros (RIV-HUMA), River Maros at station Makó (20.455539, 46.202679), the fourth largest river in Hungary, a tributary of the Tisza River. The Maros (Mureș) originates in Transylvania, its catchment area is 30 149 km^2, most of which is in Romania. Its length is 725 km, of which only 48 km falls on the territory of Hungary. The mean annual flow is 170 m^3/s. Frequency of sampling: four times (each season).
HS measured: metals, PFAS, pharmaceuticals.

2 – Lónyai Main-Canal (RIV-HULB) at station Buj (21.639977, 48.092662). The monitoring station is located on a medium-sized river of national importance which is heavily impacted by human activity and characterised by low runoff, which is typical of the flatlands of Hungary. The artificial canal is 91 km long and collects water from seven smaller canals before flowing into the Tisza. The total catchment area is 2040 km^2, dominated by agricultural land, but the emission of municipal wastewater of 270 000 PE is also significant. The annual mean outflow at the catchment outlet is 1.30 m^3/s. Frequency of sampling: four times (each season).
HS measured: metals, PFAS, pharmaceuticals.

3 – Zala (RIV-HUZA) at station Zalaapáti (17.121597, 46.727365). River Zala is a medium-sized river of national importance, which is characterised by mixed land use and moderate anthropogenic (urban and agricultural) impacts. Its catchment belongs to the watershed of Lake Balaton (the largest shallow lake in Eastern Europe). Its total length is 126 km and flows into Lake Balaton through the Kis-Balaton Water Protection System. The entire catchment area lies in the Zala hills. The catchment area upstream to the Kis-Balaton is 1514 km^2, and its land use is dominated by agricultural and forest areas (around 57% and 37%), the soils of the watershed are highly erodible. The largest town in the catchment around 90 000 PE. Frequency of sampling: four times (each season).
HS measured: metals, PFAS, pharmaceuticals.

4 – Pápa Military Aerodrome (RIV-HUPB), aerodrome dich (17.491628, 47.385557). The hotspot sampling site is a small ditch that comes from the airport and drains the surface and subsurface runoff from the airport. Frequency of sampling: ones.
HS measured: PFAS.

4 – Darza (RIV-HUDA), Darza-creek at site Pápa (47.3631, 17.4588). The sampling site was selected for measuring hotspot pollution originating from the Pápa Military Aeroport via the dich flows to the creek. Frequency of sampling: ones.
HS measured: PFAS, pharmaceuticals.

Urban stormwater runoff sampling sites

5 – Ipacsfa storm sewer monitoring station (SW-HUIF), Budapest, Ipacsfa street - Közdűlő street corner, storm sewer manhole of the Budapest Sewer Works (19.173748, 47.426192). The

sampling took place in the separated system precipitation channel. The rainwater flows from the road network primarily through gullies into the stormwater channel network. The channel section size is 220 cm circular section. The watershed area of the sampling point extends to a main road (the road leading to Ferihegy Airport) in the north. Watershed area (surface of total roads): 0.86 km^2, representing municipality with 15 000 inhabitants with developed industry and tourism activities. Frequency of sampling: adjusted to precipitation events (4 samples in total).

HS measured: metals, PFAS, pharmaceuticals.

7 – Ferencváros Combined Sewer Overflow (CSO) (SW-HUFV), Ferencváros pumping station of the Budapest Water Works (19.071549, 47.467942). Sampling is carried out at two pumping stations in the Budapest combined sewer system. During rainfall, if the discharge exceeds the three-time dilution threshold, the CSOs start to operate. Under normal operating conditions, the excess water is discharged into the Danube via gravity flow. The catchment area is 87.35 km². Sampling frequency is adjusted to precipitation events and samples are taken from the outflow drain when it operates in gravity mode (6 samples in total).

HS measured: metals, PFAS, pharmaceuticals.

8 – Angyalföld CSO (SW-HUAF), Angyalföld pumping station of the Budapest Water Works (19.066954, 47.540882). Catchment area is 56.93km^2. Sampling frequency is adjusted to precipitation events and samples are taken from the outflow drain when it operates in gravity mode (7 samples in total).

HS measured: metals, PFAS, pharmaceuticals.

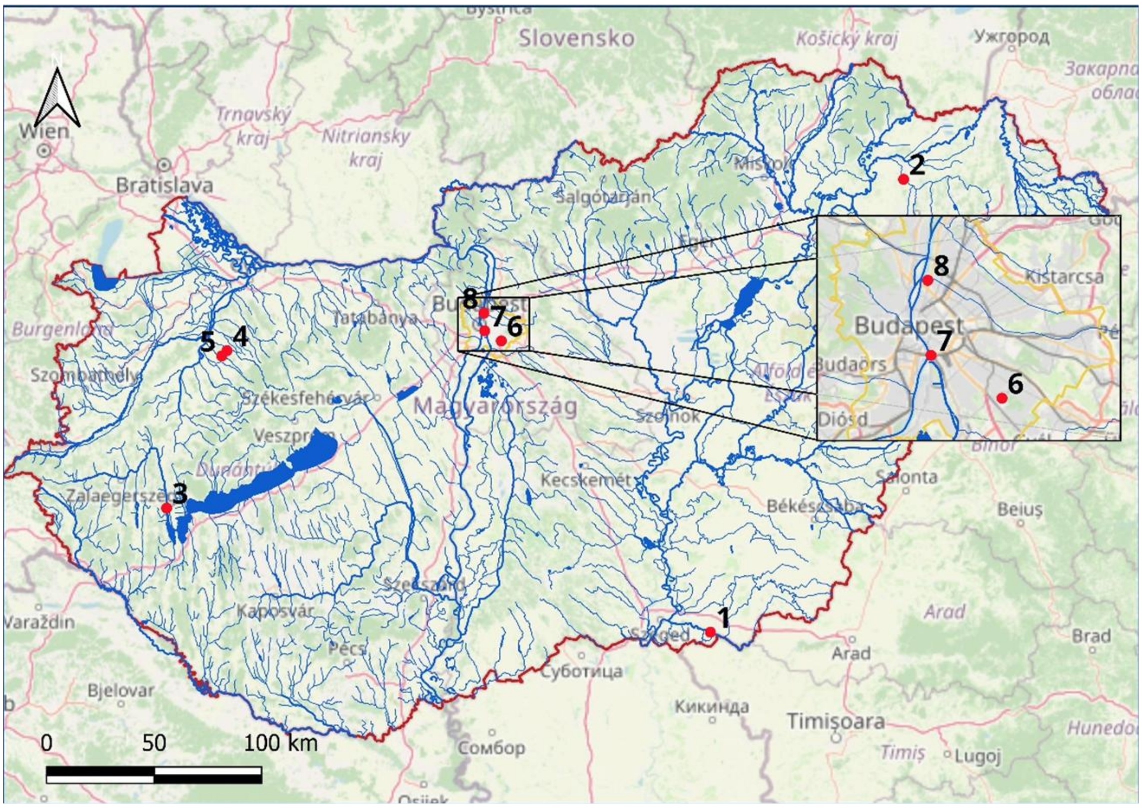

Figure 6: Map of the sampling campaign in Hungary.

Figure 7: Photos of sampling sites in Hungary. Left: Makó, Maros River (No. 1 on the map). Middle: Zalaapáti, Zala River (No. 3 on the map). Right: Ipacsfa stormwater sewer (No. 6 on the map).

5.4 Romania

In Romania, water sampling was performed in the Danube River Basin, namely in the main tributaries before their confluences with the Danube River (Argeș River, Jiu River, Siret River and Prut River) and also from selected wastewater treatment plants.

Sampling campaigns were conducted quarterly, once every 3 months, throughout the entire monitoring year. River sampling was conducted four times over the course of one year, once in each season. Wastewater sampling was conducted three times during the same year.

Sampling sites were strategically selected, downstream of urban or industrial areas, and at the outlet of the treatment plants, to assess the impact of anthropogenic sources on water quality. Moreover, for the rivers, a reference location was selected, which does not have any known anthropogenic impact and pollution.

River water sampling sites

1 – Jiu downstream confluence, Garbov River (RIV-ROGR) (22.95858, 45.27364). Background site located in the Jiu River near the source of the river from the Carpathian Mountains, with natural vegetation without any anthropogenic influence. Frequency of sampling: four times (each season).
HS measured: metals, PFAS, pharmaceuticals.

2 – Zăval (RIV-ROZV), Jiu River (23.84548, 43.84190, RO19 TNMN site). Sampling site located in the Jiu River that is a left tributary of the Danube River, upstream of the confluence with the Danube. The sampling site is impacted by the dense population of Craiova, a large city with around 300,000 inhabitants (WWTP Făcăi Craiova). Other pressures that could affect the site water quality are diffuse emissions from agriculture.
HS measured: metals, PFAS, pharmaceuticals.

3 – Clătești (RIV-ROCL), Argeș River (26.594255, 44.146848, RO9 TNMN site). The monitoring site is located upstream of the confluence between the Argeș River and the Danube. The water quality at this site is influenced by human agglomerations and diffuse pollution from agricultural activities. A significant pressure also comes from the main tributary, the Dâmbovița River, which flows through Bucharest and receives treated wastewater from the Glina Wastewater Treatment Plant, serving nearly two million inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

4 – Șendreni (RIV-ROSE), Siret River (27.928735, 45.405385, RO10 TNMN site). The sampling site is located upstream of the confluence between the Siret River and the Danube, north of Galați City (250.000 inhabitants). The water quality in this area is affected by multiple anthropogenic pressures, including the large urban agglomeration of Galați, diffuse pollution from agricultural activities, and intensive industrial development, particularly in the manufacture of non-metallic mineral products and the metallurgical sector.
HS measured: metals, PFAS, pharmaceuticals.

5 – Giurgiulești (RIV-ROGI), Prut River (28.201863, 45.470571, RO11 TNMN). The sampling site is located upstream of the confluence between the Prut River and the Danube. The area is influenced by significant anthropogenic pressures, including dense population of human agglomerations and industrial activities, in particular food industry and farms. Near the Giurgiulești monitoring station, the Prut River forms the natural border between Romania and the Republic of Moldova.
HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

6 – WWTP Glina Bucharest (WW-RO-BUC), (14.610632; 46.117488) with a capacity of 1.880.000 PE, treats both municipal and industrial wastewater from the capital city of Romania, which has a population exceeding two million inhabitants. The effluents from the WWTP are discharged into the Dâmbovița River, significantly impacting the water quality downstream of the discharge point.

HS measured: metals, PFAS, pharmaceuticals.

7 – WWTP Făcăi-Craiova (WW-RO-CR) (23.820537, 44.26001). The receiving river of the WWTP effluents is Jiu River. The WWTP Craiova with a capacity of 385.000 PE treats the waste waters from households and industry (mainly vehicle and food industry).

HS measured: metals, PFAS, pharmaceuticals.

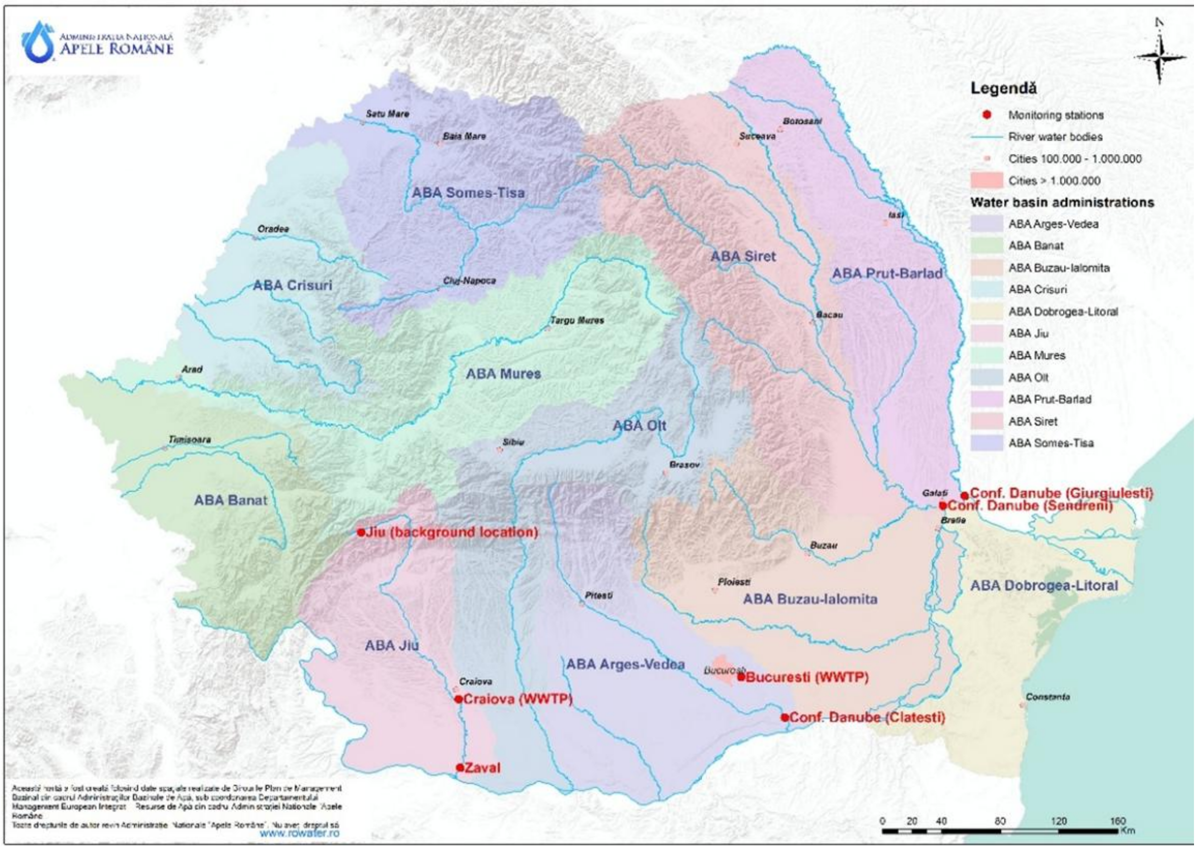

Figure 8: Map of the sampling campaign in Romania.

Figure 9: Photos of sampling sites in Romania. Left: Jiu downstream confluence, Garbov River, background location (No. 1 from description). Right: Șendreni site, Siret River (No. 4 from description).

5.5 Bulgaria

In total 4 river sampling sites and 3 effluents from WWTP were included in the monitoring campaign performed in Bulgaria. The river sites are located on the downstream of 4 big rivers in the northern part of Bulgaria, i.e. in The Danube basin. The points were chosen to be the same as the last gauging station for water quantities monitoring on the main body of the rivers, before they flow into the Danube. The selection of the WWTPs was based on their capacity and served population. River sampling was conducted four times over the course of one year, once in each season. Wastewater sampling was conducted three times during the same year.

One additional extraordinary river water sampling was performed at City of Ruse, after the flood events in Central Europe in September 2024.

River water sampling sites

1 – Butan village, (RIV-BGOG), Ogosta river (43.6405, 23.7343), catchment area of the site: 2 969 km^2 – the total population in the catchment area is around 147 189 inhabitants (year 2023), with two large agglomerations – Vratsa and Montana. The area is mostly rural, however there are few facilities for car batteries and metal processing.
HS measured: metals, PFAS, pharmaceuticals.

2 – Orehovitsa village, (RIV-BGIS), Iskar River (43.5878, 24.3589), catchment area of the site: 8 363 km^2 – the total population in the catchment area is around 1 531 326 inhabitants (year 2023). It includes the city of Sofia, which is the capital of Bulgaria, as well as various industries.
HS measured: metals, PFAS, pharmaceuticals.

3 – Karantsi village, (RIV-BGYA), Yantra river (43.3803, 25.6672), catchment area of the site: 6 860 km^2 – the total population in the catchment area is around 283 161 inhabitants (year 2023), and the biggest agglomerations are Veliko Tarnovo and Gabrovo. Several facilities are located in the area, one of them being a big plastic packaging producer.
HS measured: metals, PFAS, pharmaceuticals.

4 – Bozichen village, (RIV-BGRL), Rusenski Lom River (43.7197, 25.9469), catchment area of the site: 2 895 km^2 – the total population in the catchment area is around 118 510 inhabitants (year 2023), with the largest agglomeration, Razgrad, having less than 30 000 inhabitants. The catchment is not industrialized, but there is one relatively small facility of pharmaceuticals production.
HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

5 – WWTP Kubratovo (Sofia), (WW-BGKU) (42.7593, 23.3759). This is the biggest WWTP in Bulgaria, serving the sewer system of the capital of the country, with capacity of 1 833 333 PE. The plant treats mixed waters and the receiving water body is the Iskar River. The load for year 2023 was 1 032 938 PE.
HS measured: metals, PFAS, pharmaceuticals.

6 – WWTP Veliko Tarnovo, (WW-BGVT) (43.1018, 25.6207). The WWTP has a capacity of 165 625 PE, however the load for the year 2023 was only 50 620 PE. The plant treats mixed waters, with one of the main emitters in the sewer system being a facility for wood processing. The receiving water body is the Yantra river.
HS measured: metals, PFAS, pharmaceuticals.

7 – WWTP Montana, (WW-BGMO) (43.4309, 23.2543). With the capacity of 98 618 PE, the WWTP treats mixed waters. The load for year 2023 was about 33 761 PE. The receiving water body is the Ogosta river.
HS measured: metals, PFAS, pharmaceuticals.

Extraordinary river water sampling during Danube flood event

8 – City of Ruse, (RIV-BGDA), Danube River (43.8605, 25.9545), sample from this site was taken only once - after the flood events in Central Europe in September 2024 and during the highest peak of water flow in Danube near the city of Ruse on 7.10.2024.
HS measured: metals, PFAS, pharmaceuticals.

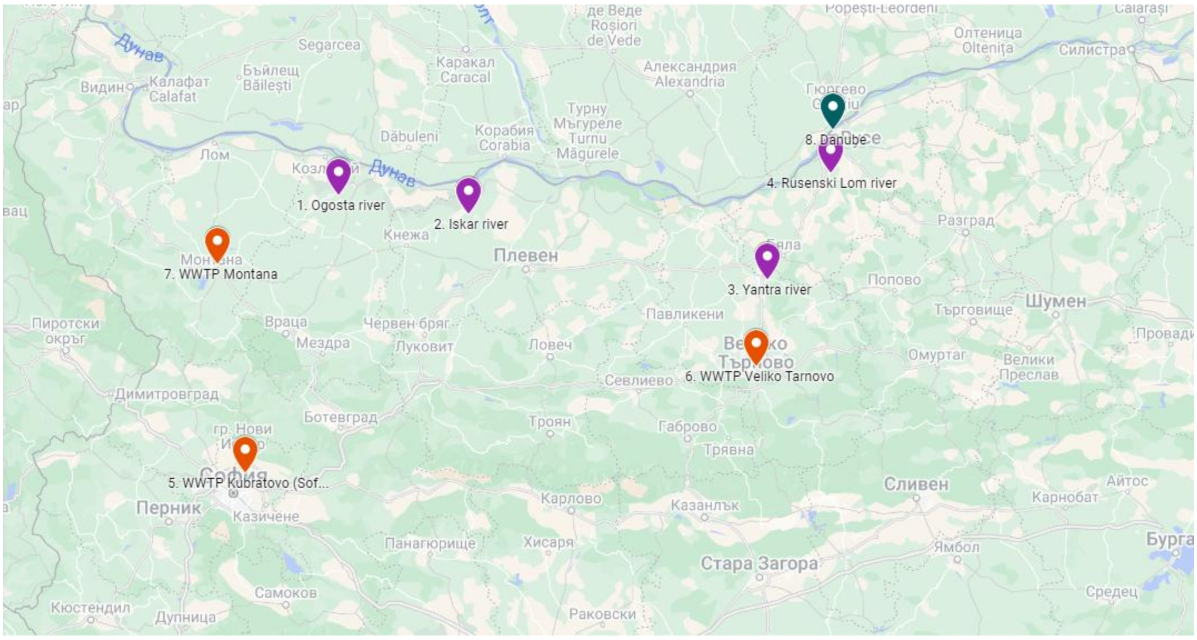

Figure 10: Map of the sampling campaign in Bulgaria.

Figure 11: Photos of sampling sites in Bulgaria. Left: Orehovitsa village, Iskar River (No. 2 on the map). Right: WWTP Kubratovo, Kubratovo effluent channel (No. 5 on the map).

5.6 Croatia

Sampling sites for wastewater and river water in Croatia were selected both in the sub-basin of Sava River and in sub-basin of Drava and Danube River.

Sampling points for river water were determined in order to examine the possible presence of contamination by selected hazardous substances in the surface waters. The selected four river stations are situated downstream of larger cities (stations 2, 3 and 4) or downstream of the confluence of the Mura River (station no. 1), taking into account nearby locations of hydrological stations.

Over the course of one year, at regular intervals, four sampling campaigns at river monitoring stations were carried out as planned. Each sampling period was chosen with special attention, to ensure that sampling would be conducted during stable weather conditions, completely without precipitation or bad weather.

For wastewater sampling sites an emphasis was on treated urban wastewaters at the outlet of wastewater treatment plants in four agglomerations with different total generated load. Although total load is mostly generated by resident population, in large cities the discharges from industrial sites are also connected to the public collecting system, significantly contributing to possible pollution with hazardous substances such as metals or different organic compounds.

Over the course of one year, three sampling campaigns were successfully carried out at regular intervals at all four selected wastewater treatment plants. Samples were taken with automatic sampler, as 7-day 24-hour composite time proportional sample, preserved and stored according to SOP document on monitoring.

River water sampling sites

1 – Botovo (RIV-HRBO), Drava River (16.938270, 46.241300). The monitoring station is located a few kilometres downstream of the confluence of the Mura River with the Drava River.
HS measured: metals, PFAS, pharmaceuticals.

2 – Downstream from Osijek City (RIV-HRPD), Drava River (18.864250, 45.553050). The monitoring station is located upstream of the confluence with the Danube River. The sampling site is impacted by the population of the Osijek agglomeration with approx. 120,000 inhabitants and well-developed industry – food industry (milk and dairy, brewery, bakery, confectionary), production and recovery of plastic materials, chemical industry – detergents and cleaning products, personal care products; clinical hospital; WWTP Osijek with capacity 170,000 PE.
HS measured: metals, PFAS, pharmaceuticals.

3 – Donje Mekušje (RIV-HRDM), Kupa River (15.597710, 45.487190), a right tributary of the Sava River. The monitoring station is located in the middle part of river’s course. It is impacted by the population of the Karlovac-Duga Resa agglomeration with approx. 50,000 inhabitants. Industrial impact is derived by food industry (brewery, milk and dairy, meat and products), textile industry, general hospital, etc. and WWTP Karlovac with capacity 98,000 PE.
HS measured: metals, PFAS, pharmaceuticals.

4 – Oborovo (RIV-HROB), Sava River (16,248200; 45,686980). The monitoring station is situated in the upper part of the river’s course. It is impacted by the population of several agglomerations: Zagreb with 770,000 inhabitants, Velika Gorica with 59,000 inhabitants and Rugvica with 23,000 inhabitants. Industrial load is coming from chemical-pharmaceutical industry, food industry (milk and dairy, ice-cream and pastry, bakery, oil and products, meat and products, confectionary, beverages), clinical hospitals, waste disposal site, WWTP Zagreb with capacity 1.2 mil. PE, WWTP Velika Gorica with capacity 35,000 PE and WWTP Rugvica with 25,000 PE.
HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

5 – WWTP Zagreb (WW-HRZG), (16.086990, 45.790490). The receiving water body for the WWTP effluent is the Sava River. The plant with capacity 1.2 million PE treats municipal, industrial, and stormwater discharges, with more than 130 million cubic meters of wastewater annually. It

serves a population of approximately 770,000 inhabitants and, together with industry, the urban agglomeration generates a total load of 850,000 PE. The treatment plant is equipped with secondary treatment.

HS measured: metals, PFAS, pharmaceuticals.

6 – WWTP Osijek (WW-HROS), (18.780750, 45.542150). The receiving water body for the WWTP effluent is the Drava River. The plant with capacity 170,000 PE treats municipal, industrial, and stormwater discharges, with more than 13 million cubic meters of wastewater annually. It serves a population of approximately 120.000 inhabitants and, together with industry, the urban agglomeration generates a total load of 141,500 PE. The treatment plant is equipped with tertiary treatment.

HS measured: metals, PFAS, pharmaceuticals.

7 – WWTP Slavonski Brod (WW-HRSB), (18.041240, 45.141270). The receiving water body for the WWTP effluent is the Sava River. The plant with capacity 80,000 PE treats municipal, industrial, and stormwater discharges, with more than 6 million cubic meters of wastewater annually. It serves a population of approximately 62.000 inhabitants and, together with industry, the urban agglomeration generates a total load of 76.000 PE. The treatment plant is equipped with tertiary treatment.

HS measured: metals, PFAS, pharmaceuticals.

8 – WWTP Sisak (WW-HRSK), (16.415060, 45.446950). The receiving water body for the WWTP effluent is the Sava River. The plant with capacity 60.000 p.e. treats municipal, industrial, and stormwater discharges, with more than 4 million cubic meters of wastewater annually. It serves a population of approximately 37.000 inhabitants and, together with industry, the urban agglomeration generates a total load of close to 39.700 PE. Treatment plant is equipped with tertiary treatment.

HS measured: metals, PFAS, pharmaceuticals.

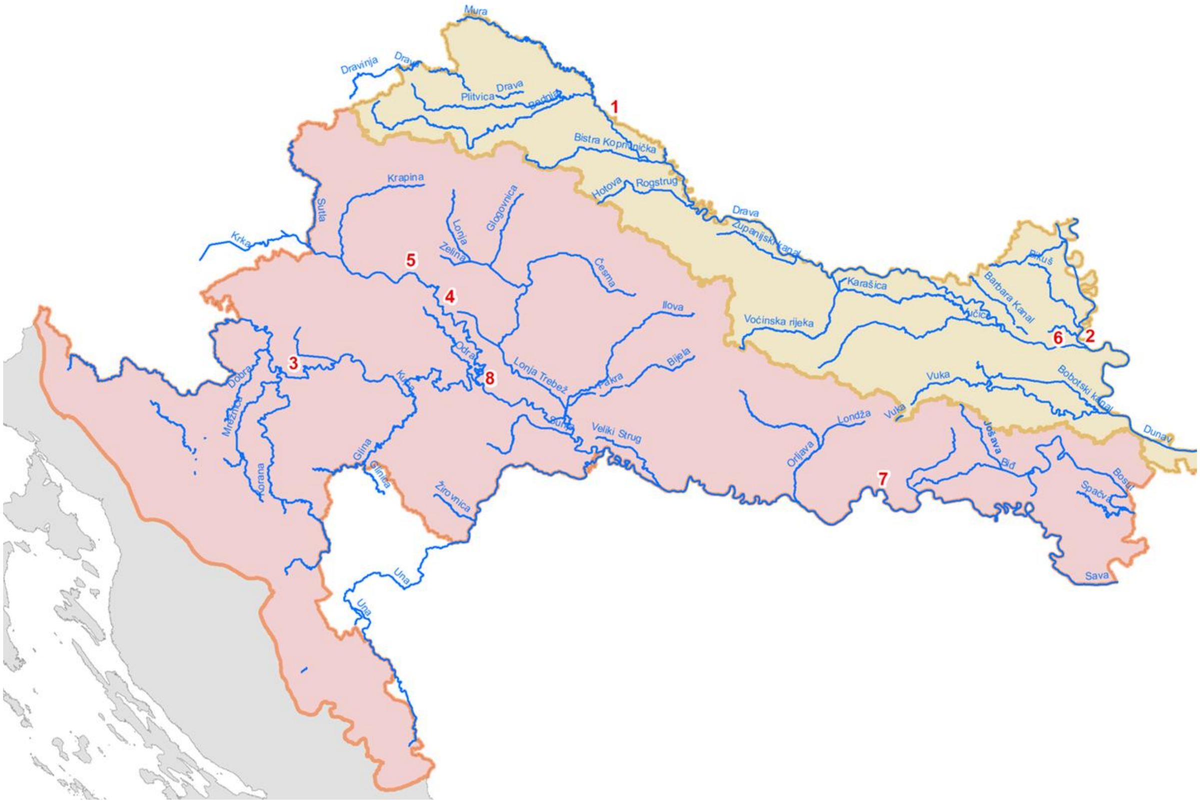

Figure 12: Map of the sampling campaign in Croatia.

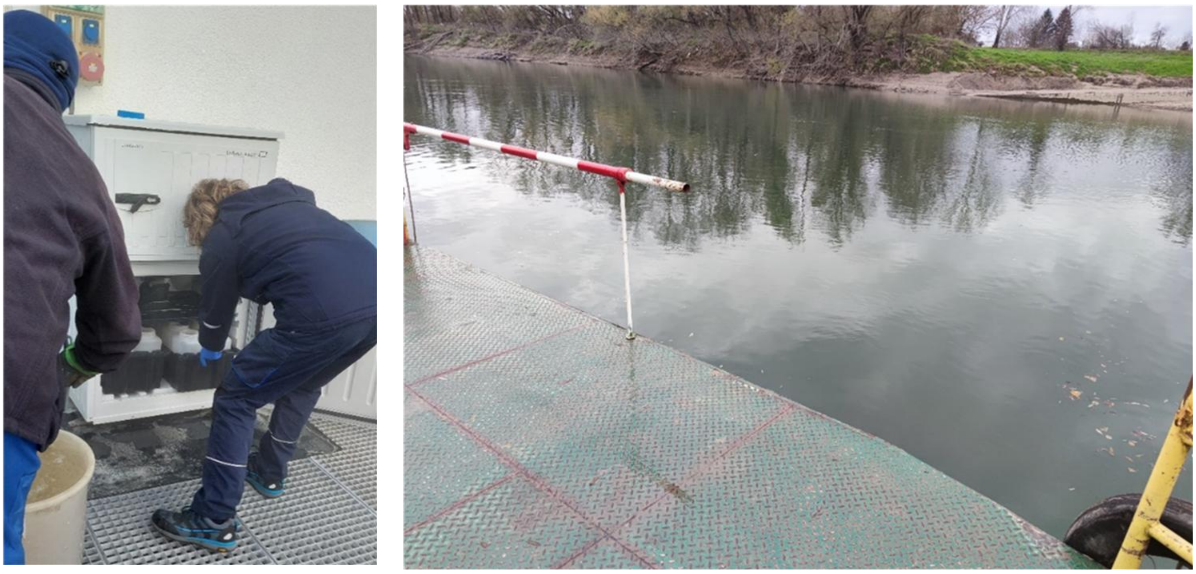

Figure 13: Photos of sampling sites in Croatia. Left: WWTP Zagreb (No. 5 on the map). Right: Oborovo, Sava (No. 4 on the map).

5.7 Slovenia

In Slovenia, sampling was performed in the Sava River and its main tributaries before their confluences with the Sava at six sampling sites, as well as at the Domžale-Kamnik wastewater treatment plant. The sampling sites were selected to represent various sources of pollution associated with different industrial and human activities. River sampling was conducted four times over the course of one year, once in each season. Wastewater sampling was conducted three times during the same year. Samples were collected with an automatic sampler to obtain a time-proportional composite sample over a 24-hour period for seven consecutive days.

River water sampling sites

1 – Mojstrana (RIV-SIMO), Sava Dolinka River (13.96135, 46.46107). Background location in a pristine area, with no known sources of pollution.
HS measured: metals, PFAS, pharmaceuticals.

2 – Beričevo (RIV-SIBE), Kamniška Bistrica River (14.626013, 46.088265), a left tributary of the Sava River, upstream of the confluence. The sampling site is impacted by the dense population of the Domžale municipality with 40,000 inhabitants and well-developed industry: (Tosama Domžale – sanitary material) Induplati (textile industry), local electroplating workshops, Novartis Mengeš (pharmaceutical industry), Pig farm Ihan (50,000 animals), WWTP Domžale-Kamnik (Municipal-industrial WWTP with 149,000 PU).
HS measured: metals, PFAS, pharmaceuticals.

3 – Zalog (RIV-SIZA), Ljubljanica River (14.621801, 46.062122), a right tributary of the Sava River, near the confluence. The sampling site is impacted by the dense population of the Ljubljana municipality with 300,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

4 – Zidani Most (RIV-SIZM), Savinja River (15.173129, 46.085046) a left tributary of the Sava River, near the confluence. The sampling site is impacted by the dense population of the Celje municipality with 70,000 inhabitants and well-developed industry (Cinkarna – chemical industry, Štore – metalworks, Libela Elsi – weighing scales, EMO – enamelware, Aero – paint factory, Zlatarna Celje – goldsmith's, Laško municipality with 15,000 inhabitants with developed industry and tourism activities: Laško brewery, Thermal Spa Laško, Thermal Spa Rimske Terme).
HS measured: metals, PFAS, pharmaceuticals.

5 – Krška vas (RIV-SIKV), Krka River (15.591477, 45.894161), a right tributary of the Sava River, near the confluence. The sampling site is impacted by the Military airport Cerklje and by the dense population of the Novo mesto municipality with 37,000 inhabitants and well-developed industry (Krka, Pharmaceutical industry, Revoz, Car industry – Renault group).
HS measured: metals, PFAS, pharmaceuticals.

6 – Brežice (RIV-SIBR), Sava River (15.59199, 45.89790). The sampling site on the Sava River before the Croatian border is impacted by 5 up-stream hydroelectric power plants with dams and nuclear power plant Krško.
HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

7 – WWTP Domžale-Kamnik (WW-DK) (14.610632, 46.117488). The receiving water body for the WWTP effluent is the Kamniška Bistrica River, a left tributary of the Sava River. The plant (149,000 PE) treats municipal, industrial, and stormwater discharges, with a capacity of up to 9 million cubic meters of wastewater annually. It serves a population of approximately 40,000 inhabitants and is influenced by local industrial activities, including Tosama Domžale (sanitary products), Induplati (textile industry), and several electroplating workshops.
HS measured: metals, PFAS, pharmaceuticals.

Figure 14: Map of the sampling campaign in Slovenia.

Figure 15: Photos of sampling sites in Slovenia. Left: Mojstrana, Sava Dolinka River, background location (No. 1 on the map). Right: Zalog, Ljubljanica River, right tributary to the Sava River (No. 3 on the map).

5.8 Ukraine

The Danube Basin within Ukraine is hydrologically divided into four sub-basins: the Tisza Sub-basin, the Prut Sub-basin, the Siret Sub-basin, and the Lower Danube Sub-basin.

Orographically, the first three are located within the Carpathian Mountains or their foothills, while the Lower Danube Sub-basin represents the lowland area that includes the Danube Delta.

The Tisza Sub-basin lies entirely within the Transcarpathian Oblast. Its main rivers include the Tisza River with its tributaries — the Latorytsia, Teresva, Rika, and Borzhava Rivers. These are mountain rivers characterized by rapid flow and frequent floods. The Prut Sub-basin is located within the Chernivtsi Oblast. The hydrographic network of this sub-basin is formed by the Prut River, the upper areas of its tributary, the Siret River, and numerous small mountain streams. The Siret sub-basin extends across the Chernivtsi, Ivano-Frankivsk, and Ternopil Oblasts. Its river network is shaped by the Siret River and its tributaries. The Lower Danube Sub-basin is situated in the southern part of Ukraine in Odesa Oblast.

The monitoring program was based on the previously elaborated sampling strategy, covering all four Danube sub-basins. At 11 river sampling sites, water samples were collected four times, once in each season. Wastewater samples were collected three times annually at 10 wastewater treatment plants representing the largest urban agglomerations. Samples were collected manually to obtain a time-proportional composite sample over a 24-hour period for seven consecutive days.

River water sampling sites

Tisza Sub-basin

1 – Chop (RIV-UACH), Tisza River (22.206944, 48.425647). Border with Hungary, large railway junction.
HS measured: metals, PFAS, pharmaceuticals.

2 – Dilove (RIV-UADI), Tisza River (24.147558, 47.915606). Border with Romania. The sampling site is impacted by the dense population of the Rakhiv municipality with 15,500 inhabitants. The main activities include the forestry and woodworking industry (about 40 enterprises), food processing, and small livestock farms producing meat and dairy products.
HS measured: metals, PFAS, pharmaceuticals.

3 – Nove Davydkove (RIV-UAN.D), Latoritsia River (22.543264, 48.441294). The sampling site is impacted by the dense population of the Mukachevo municipality with 86,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

4 – Storozhnytsya (RIV-UAST-UZH), Uzh River (22.213489, 48.605814) The sampling site is impacted by the dense population of the Uzhhorod municipality with 155,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

5 – Chorna Tisza (RIV-UAC.T), Chorna Tisza River (24.321600, 48.315597). Background location in a pristine area, with no known sources of pollution.
HS measured: metals, PFAS, pharmaceuticals.

6 – Teresva (RIV-UATE), Teresva River (23.676425, 48.000361). Background location in a pristine area, with no known sources of pollution.
HS measured: metals, PFAS, pharmaceuticals.

7 – Khust (RIV-UAKH), Rica River (23.270097, 48.180739). The sampling site is impacted by the dense population of the municipality Khust with 28,000 inhabitants. The presence of enterprises in the woodworking and textile industries.
HS measured: metals, PFAS, pharmaceuticals.

8 – Nelipyno (RIV-UANE), Vicha River (23.029270, 48.560603). Close location to railway lines.
HS measured: metals, PFAS, pharmaceuticals.

Prut sub-basin

9 – Kostychany (RIV-UAKO), Prut River (26.498200, 48.217731), border with Romania. The sampling site is impacted by the dense population of the Novoselytsia municipality with 8,000

inhabitants. Presence of small food industry enterprises, agricultural activities. Influence of a large enterprise, Tarasovetska Poultry Farm LLC, which is engaged in broiler chicken breeding, pig farming, feed production, dairy farm, own slaughterhouse and shops for the production of sausages and delicatessen.

HS measured: metals, PFAS, pharmaceuticals.

Siret sub-basin

10 – Storozhynets (RIV-UAST-SIR), Siret River (25.714619, 48.150539), border with Romania. The sampling site is impacted by the dense population of the municipality Storozhynets with 14,500 inhabitants. The city has small enterprises in the food, pulp and paper, and construction materials industries.

HS measured: metals, PFAS, pharmaceuticals.

Lower Danube sub-basin

11 – Reni (RIV-UARE), Danube River (28.275028, 45.452611), the mouth of the Danube River. This point is particularly significant, as it is located downstream of the confluence of the last tributary of the Prut River and upstream of the beginning of the delta formation, where the Danube starts to divide into numerous branches.

HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

12 – WWTP Uzhhorod (WW-UAUZ), (22.2539167, 48.9433333). The receiving water body for the WWTP effluent is the Uzh River. The plant (156,000 PE) treats municipal wastewater, with a capacity of up to 55 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

13 – WWTP Mukachevo (WW-UAMU), (22.6518333, 48.8516667). The receiving water body for the WWTP effluent is the Latoritsia River. The plant (86,000 PE) treats municipal wastewater, with a capacity of up to 43 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

14 – WTP Khust (WW-UAKH), (22.4569722, 48.2750000). The receiving water body for the WWTP effluent is the Khustets River, a right tributary of the Tisza River. The plant (28,000 PE) treats municipal wastewater, with a capacity of up to 5 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

15 – WWTP Vynohradiv (WW-UAVY), (23.04861111, 48.96666667). The receiving water body for the WWTP effluent is the Tisza River. The plant (27,000 PE) treats municipal wastewater, with a capacity of up to 2 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

16 – WWTP Berehove (WW-UABE), (22.63055556, 48.96666667). The receiving water body for the WWTP effluent is the Verke River, a left tributary of the Serne River. The plant (25,000 PE) treats municipal wastewater, with a capacity of up to 2 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

17 – WWTP Svaliava (WW-UASV), (22.96866667, 48.17166667). The receiving water body for the WWTP effluent is the Latoritsya River. The plant (19,000 PE) treats municipal wastewater, with a capacity of up to 1,6 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

18 – WWTP Rakhiv (WW-UARA), (24.17952778, 48.55833333). The receiving water body for the WWTP effluent is the Tisza River. The plant (16,000 PE) treats municipal wastewater, with a capacity of up to 1,4 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

19 – WWTP Izmail (WW-UAIZ), (28.5532000, 45.1727000). The receiving water body for the WWTP effluent is the Danube River. The plant (70,000 PE) treats municipal and industrial wastewater with a capacity of up to 15,3 million cubic meters of wastewater annually.

HS measured: metals, PFAS, pharmaceuticals.

20 – WWTP Kolomiya (WW-UAKO), (25.09833333, 48.63833333). The receiving water body for the WWTP effluent is the Prut River. The plant (63,000 PE) treats municipal wastewater, with a capacity of up to 6,9 million cubic meters of wastewater annually.
HS measured: metals, PFAS, pharmaceuticals.

21 – WWTP Chernivtsi (WW-UACH), (26.2650000, 48.5666667). The receiving water body for the WWTP effluent is the Prut River. The plant (264,000 PE) treats municipal wastewater, with a capacity of up to 55 million cubic meters of wastewater annually.
HS measured: metals, PFAS, pharmaceuticals.

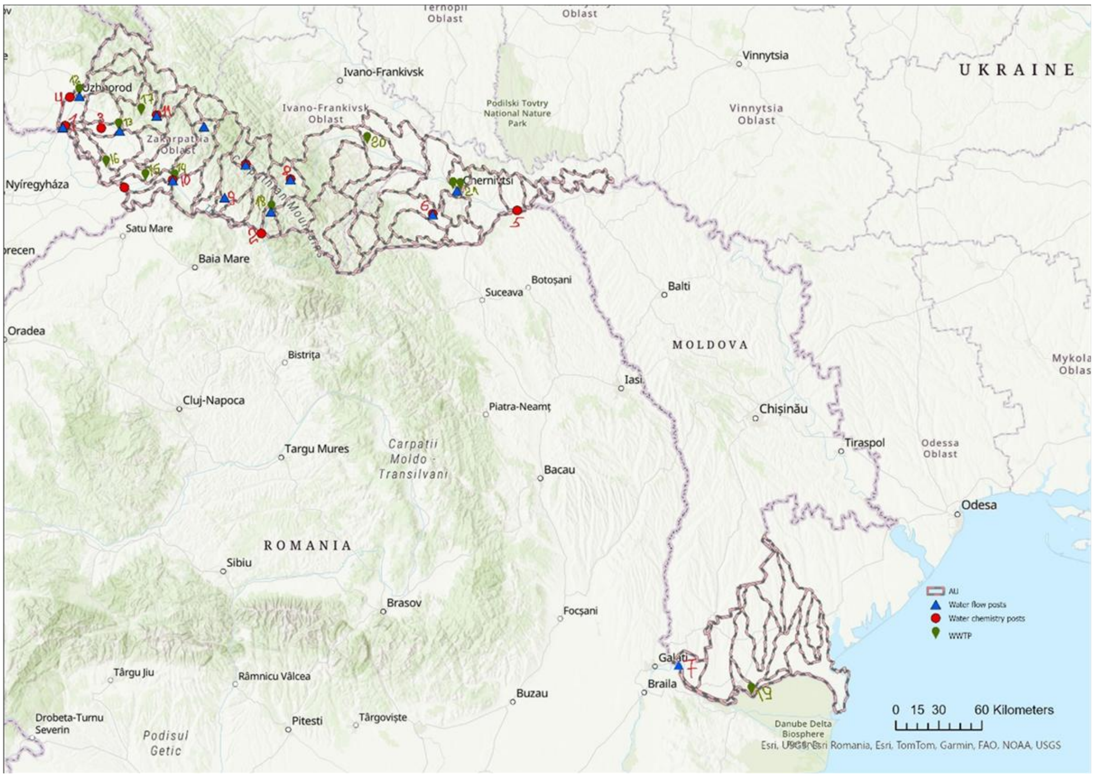

Figure 16: Map of the sampling campaign in Ukraine.

Figure 17: Photo of a sampling site in Ukraine: Nelipyno, Vicha River (No. 8 on the map).

5.9 Serbia

The surface water sampling campaigns in Serbia encompassed four extensive periods of data collection, covering a broad temporal span and multiple river basins. The campaigns were conducted across 19 consistent sites located on key rivers such as the Danube, Tisza, Kolubara, Sava, Velika Morava, Pek, Timok, Borska river, Drina, Južna Morava, Ibar, Zapadna Morava and Canal Galovica. The first sampling campaign took place from September 2 to September 24, 2024, focusing on early autumn conditions. The second campaign extended from November 1st to November 15th, 2024, capturing late autumn hydrological states. The third campaign covered an early spring period from March 24th, 2025, to April 9, 2025. Finally, the fourth campaign occurred between June 1st and July 8th, 2025. One additional surface water sample was collected from the RIV-RSZE sampling site during peak high flow conditions on the 30.09.2024. The numerous selected surface water sampling sites cover a variety of landscapes with different intensities of anthropogenic activities within the catchments themselves. These include mining activities, urban activities, industrial activities, agriculture, etc.

The wastewater discharge monitoring campaigns in Serbia, spanned from September 2024 to August 2025 and involved multiple locations. The campaigns focused on key wastewater treatment plants and raw sewerage discharges in cities like Kruševac, Šabac, Subotica, and Belgrade, and included a wastewater discharge from a cardboard factory. Three wastewater sampling campaigns were conducted. The first sampling campaign was carried out in the period September-October 2024. The second campaign took place from late March to early July 2025. The third campaign extended from June to August 2025, capturing summer data on major discharge sites and treatment plants. Overall, these campaigns provided essential insights into the spatial and temporal variability of wastewater discharges across Serbia, supporting the project efforts.

Groundwater was also sampled at 4 locations in the vicinity of Belgrade with two sampling campaigns being conducted, one during September 2024 and one during April 2025. It is noted that during the second sampling campaign it was not possible to collect a groundwater sample from one of the piezometers (GW-RSPD) as it had been removed due to construction work.

River water sampling sites

1 – Bezdan site (RIV-RSBZ), Danube River (18.849, 45.864). The surface water sampling at the Bezdan site covers a catchment area of 210,250 km² with an average long-term river flow of 2750 m³/s and a suspended solid concentration of 37.6 mg/L. This validation site lies on the border with Hungary and is influenced by industrial activities upstream in Hungary.
HS measured: Metals, PFAS, and pharmaceuticals.

2 – Zemun (RIV-RSZE), Danube River (20.411, 44.850), segment between the Sava and Tisa confluences, covers the catchment of 412,762 km² with a mean flow of 3686 m³/s and suspended solids averaging 18.85 mg/L. It is a validation site impacted by around 250,000 inhabitants and numerous industries including metal, chemical, pharmaceutical, wood, textile, construction, food, and agriculture.
HS measured: Metals, PFAS, and pharmaceuticals.

3 – Ritopek (RIV-RSRI), Danube reservoir from the Velika Morava to the Sava (20.959, 44.694), covers a catchment of 525,820 km², with river flow averaging 5200 m³/s and solids at 23.23 mg/L. Located 4 km downstream of the Vinča landfill, this validation site is impacted by Belgrade's 2 million inhabitants, the landfill, and agricultural activities in the village of Ritopek near it.
HS measured: Metals, PFAS, and pharmaceuticals.

4 – Banatska Palanka (RIV-RSBP), (21.340, 44.826) on the Danube reservoir from the Nera to Velika Morava, has a catchment of 568,648 km², river flow of 5440 m³/s, and solids of 7.6 mg/L. This

validation site is a border profile on the Romania border with the Danube forming a natural boundary.
HS measured: Metals, PFAS, and pharmaceuticals.

5 – Radujevac (RIV-RSRA) (22.680, 44.263) downstream of the Iron Gate II dam on the Danube, has a catchment of 577,085 km^2, flow of 5556 m^3/s, and solids of 1.7 mg/L. This validation site is impacted by the IHP Prahovo Chemical complex located 8 km upstream, producing 300,000 tons of NPK fertilizer annually.
HS measured: Metals, PFAS, and pharmaceuticals.

6 – Titel (RIV-RSTI), Tisa River (20.313, 45.198) near the confluence with the Danube, covers 157,174 km^2 with a river flow of 810 m^3/s and solids of 30.67 mg/L. This validation site is impacted by 13,000 inhabitants engaged in agriculture, livestock farming, and wood packaging manufacture.
HS measured: Metals, PFAS, and pharmaceuticals.

7 – Jamena (RIV-RSJA), Sava River (19.084, 44.878) from the Drina confluence to the border with Croatia, covers 64,073 km^2 with river flow 1131 m^3/s and solids 24.39 mg/L. It is a validation site on the Croatian border.
HS measured: Metals, PFAS, and pharmaceuticals.

8 – Novi Beograd (RIV-RSNB), Sava River (20.410, 44.796) from the Danube confluence to the Kolubara confluence, covers catchment area 95,719 km^2, flow 1561 m^3/s, solids 16.36 mg/L. It is downstream of Belgrade's 2 million inhabitants and multiple industries including thermal power, dairy, hygiene, wood, textile, construction, food, and beverage industries.
HS measured: Metals, PFAS, and pharmaceuticals.

9 – Badovinci (RIV-RSBD), Drina River (19.343, 44.777) on the Drina from the Sava to the Lešnica confluence, covers 19,350 km^2 with flow 395 m^3/s and solids 12.9 mg/L. It is a validation border site with Bosnia and Herzegovina.
HS measured: Metals, PFAS, and pharmaceuticals.

10 – Ljubičevski most (RIV-RSLJ), Velika Morava River (21.132, 44.586) covering catchment of 37,320 km^2, flow 233 m^3/s, solids 59.2 mg/L. It is a validation site southwest of Požarevac, influenced primarily by agriculture.
HS measured: Metals, PFAS, and pharmaceuticals.

11 – Maskare (RIV-RSMA), Zapadna Morava River (21.396, 43.672) cover catchment of 14,721 km^2, river flow 113 m^3/s, solids 32.68 mg/L. This validation site is mainly impacted by agricultural activities and the city of Kruševac with 58,000 inhabitants, with industries including chemical and metal works.
HS measured: Metals, PFAS, and pharmaceuticals.

12 – Mojsinje (RIV-RSMO), Južna Morava River (21.485, 43.631) covers a catchment of 15,390 km^2, with an average long-term flow of 99 m^3/s, and total suspended solids concentration of 36.15 mg/L. It is located on the Južna Morava River near the settlement of Stalać, Serbia. It is a validation site influenced by metal works, home appliance production, tool manufacturing, and chemical industry. Upstream of the Mojsinje monitoring location within the Morava River Basin lie the cities of Niš (popultaion of roughly 180,000), Leskovac, and Vranje. The area is impacted by a large furniture manufacturing facility in Vranje, Niš International Airport, and the regional Center for Emergency Management as well as past metal processing in Niš.
HS measured: Metals, PFAS, and pharmaceuticals.

13 – Batrage (RIV-RSBA), Ibar River (20.615, 43.297) upstream of Gazivode reservoir covers catchment of 810 km^2, flow 9.8 m^3/s, solids 30.41 mg/L: It is a validation site before inflow into Kosovo.
HS measured: Metals, PFAS, and pharmaceuticals.

14 – Kraljevo (RIV-RSKR), Ibar River (20.689, 43.718) near Kraljevo, covers catchment of 7,925 km^2, flow 56.4 m^3/s, solids 25.25 mg/L. This validation site is impacted by various industries including food production, textiles, leather, wood, rubber, metal works, and furniture production.
HS measured: Metals, PFAS, and pharmaceuticals.

15 – Rajac (RIV-RSTM), Timok River (22.571, 44.104), covers catchment of 4,180 km², flow 27.6 m³/s, solids 18.81 mg/L. It is a validation border site with Bulgaria.
HS measured: Metals, PFAS, and pharmaceuticals.

16 – Rgotina (RIV-RSBR), Borska River (22.275, 44.009), covers catchment of 320 km², flow 2.82 m³/s, solids very high at 258.93 mg/L due to intensive gold and copper mining activities and city of Bor population (48,000). This is a hotspot site.
HS measured: Metals, PFAS, and pharmaceuticals.

17 – Beograd (RIV-RSGA), Galovica kanal (20.342, 44.770) covers catchment of 750 km², low flow 0.77 m³/s, no data on solids. This is a hotspot near Belgrade airport and E-75 motorway with metals, PFAS, and pharmaceuticals.
HS measured: Metals, PFAS, and pharmaceuticals.

18 – Draževac (RIV-RSKO), Kolubara River (20.208, 44.580) covers catchment of 3,588 km², flow 21.4 m³/s, solids 41.82 mg/L. It is a validation site.
HS measured: Metals, PFAS, and pharmaceuticals.

19 – Braničevo (RIV-RSPK), Pek River (21.535, 44.718) covers catchment of 1,180 km², flow 8.36 m³/s, solids 33.56 mg/L. It is a hotspot affected by intense mining activities from the Majdanpek mining complex.
HS measured: Metals, PFAS, and pharmaceuticals.

Wastewater sampling sites

20 – WWTP Šabac (WW-RSSA), (19.7269516, 44.7453971). The WWTP receives discharges from households and industry (Municipal-industrial WWTP with 126 000 PU. It is impacted by the population of approximately 55,000 inhabitants and industrial activities such as: Ceramic tile production, Chemical production, Food industry (Milk and milk product production), Vehicle part production.
HS measured: Metals, PFAS, and pharmaceuticals.

21 – WWTP Subotica (WW-RSSU), (19.697755, 46.082323). The WWTP receives discharges from households and industry (Municipal-industrial WWTP with 150 000 PU. It is impacted by the population of approximately 120 000 inhabitants and industrial activities such as: Electrical wiring and machine production, Printing industry, Rubber and Tyre production. Coordinates:
HS measured: Metals, PFAS, and pharmaceuticals.

22 – WWTP Kruševac (WW-RSKR) , (21.3323596, 43.6114155). The WWTP receives discharges from households and industry (Municipal-industrial WWTP with 90 000 PU. It is impacted by the population of approximately 55,000 inhabitants and industrial activities such as: Metal industry, Chemical production, Rubber industry, Food industry.
HS measured: Metals, PFAS, and pharmaceuticals.

23 – WW discharge Belgrade Ušće (WW-RSUS), (20.4423014, 44.8228393). Untreated wastewater discharge into the Sava River. Municipal sewage.
HS measured: Metals, PFAS, and pharmaceuticals.

24 – WW discharge Belgrade Sajam (WW-RSSM), (20.4335505, 44.7970577). Untreated wastewater discharge into the Sava river. Municipal sewage.
HS measured: Metals, PFAS, and pharmaceuticals.

25 – WWTP Cardboard factory (WW-RSUM), (20.3078143, 44.6912528). Outlet of wastewaters from the cardboard factory in Umka. Cardboard factory technological process.
HS measured: Metals, PFAS, and pharmaceuticals.

Groundwater sampling sites

26 – Groundwater sampled at Piezometer PA (GW-RSPA), (20.2635551, 44.7836957), features a well installed at a depth of less than 20 meters below the terrain surface. The long-term mean water depth in this well is regulated by the water level of the Sava River, indicating strong hydraulic connectivity with nearby surface waters. This site belongs to the East Srem Upper

most aquifer groundwater body. The predominant land use around the well is non-irrigated arable land. The sampling location’s water quality is impacted by its proximity to the Belgrade International Airport as well as active agricultural practices in the surrounding area. Expected sources of pollution include the airport operations and the adjacent E-75 motorway, both of which may contribute contaminants to groundwater through runoff and infiltration.
HS measured: Metals, PFAS, and pharmaceuticals.

27 – Groundwater sampled at Piezometer PB (GW-RSPB), (20.3259538, 44.785926) features a well installed at a depth of less than 20 meters below the terrain surface. The long-term mean water depth in this well is regulated by the water level of the Sava River, indicating strong hydraulic connectivity with nearby surface waters. This site belongs to the East Srem Upper most aquifer groundwater body. The predominant land use around the well is non-irrigated arable land. The sampling location’s water quality is impacted by its proximity to the Belgrade International Airport as well as active agricultural practices in the surrounding area. Expected sources of pollution include the airport operations and the adjacent E-75 motorway, both of which may contribute contaminants to groundwater through runoff and infiltration.
HS measured: Metals, PFAS, and pharmaceuticals.

28 – Groundwater sampled at Piezometer PC (GW-RSPC), (20.3144564, 44.7739871) features a well installed at a depth of less than 20 meters below the terrain surface. The long-term mean water depth in this well is regulated by the water level of the Sava River, indicating strong hydraulic connectivity with nearby surface waters. This site belongs to the East Srem Upper most aquifer groundwater body. The predominant land use around the well is non-irrigated arable land. The sampling location’s water quality is impacted by its proximity to the Belgrade International Airport as well as active agricultural practices in the surrounding area. Expected sources of pollution include the airport operations and the adjacent E-75 motorway, both of which may contribute contaminants to groundwater through runoff and infiltration.
HS measured: Metals, PFAS, and pharmaceuticals.

29 – Groundwater sampled at Piezometer PD (GW-RSPD), (20.3059127, 44.7932035) features a well installed at a depth of less than 20 meters below the terrain surface. The long-term mean water depth in this well is regulated by the water level of the Sava River, indicating strong hydraulic connectivity with nearby surface waters. This site belongs to the East Srem Upper most aquifer groundwater body. The predominant land use around the well is non-irrigated arable land. The sampling location’s water quality is impacted by its proximity to the Belgrade International Airport as well as active agricultural practices in the surrounding area. Expected sources of pollution include the airport operations and the adjacent E-75 motorway, both of which may contribute contaminants to groundwater through runoff and infiltration.
HS measured: Metals, PFAS, and pharmaceuticals.

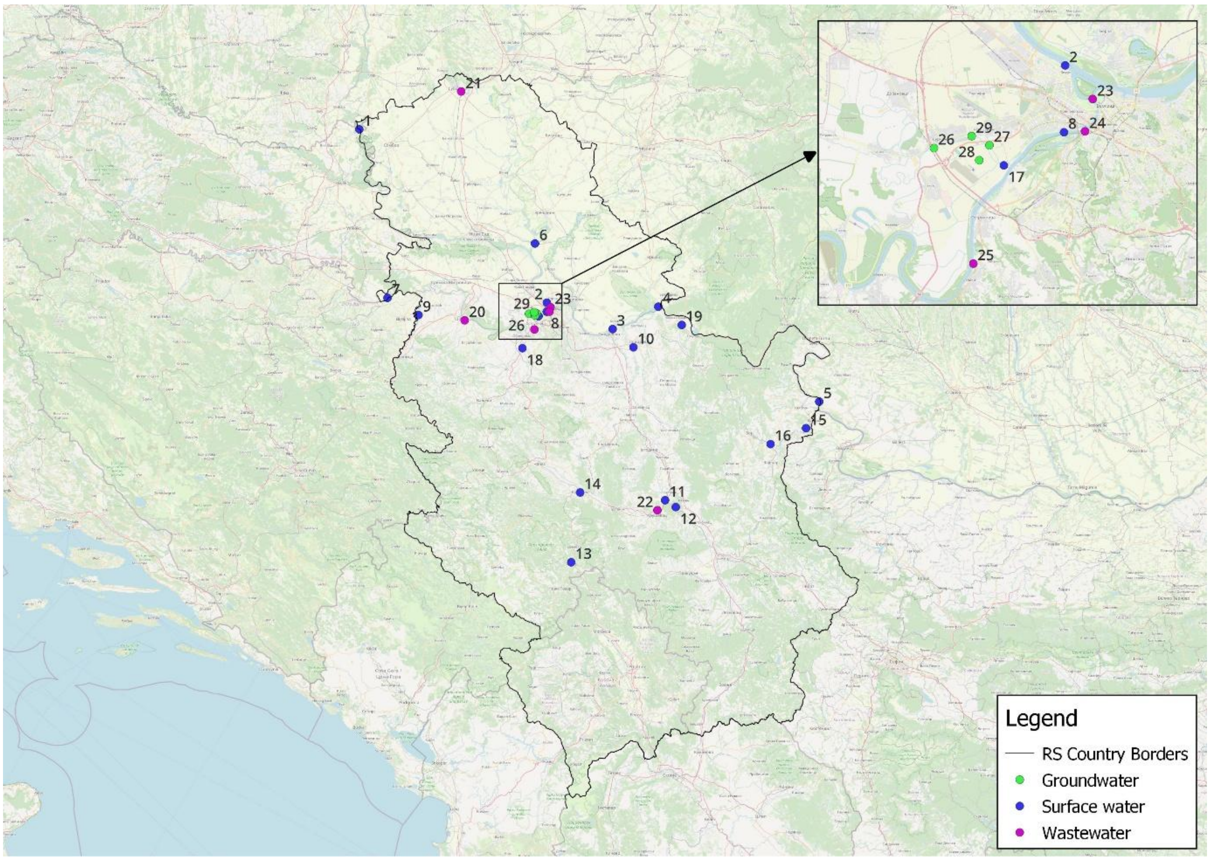

Figure 18: Map of the sampling campaign in Serbia.

Figure 19: Photo of a sampling site in Serbia. Left: Maskare, Zapadna Morava River (No. 11 on the map). Right: Novi Beograd, Sava River (No. 8 on the map).

5.10 Montenegro

In Montenegro, sampling was carried out at seventeen river monitoring sites, river Tara, river Lim, river Ibar and river Ćehotina and two of their tributaries. These locations represent a combination of background locations, hotspot areas and TNMN sites positioned near international borders. The monitoring network was designed to capture a wide range of environmental conditions, from pristine high-mountain headwaters to river sections affected by urbanization, industrial activities and geological features. Background sites were selected in ecologically preserved and undisturbed areas to represent natural conditions, while hotspot locations were chosen in zones exposed to anthropogenic pressures such as municipal wastewater, landfills, industry and intensive settlement influence. TNMN sites were positioned at hydrologically significant border profiles in line with international monitoring obligations for transboundary waters. River water sampling was performed four times during one year, once per season. Wastewater sampling was conducted three times within the same year. Samples were collected with an automatic sampler to obtain a time-proportional composite sample over a 24-hour period for seven consecutive days.

River water sampling sites

1 – Gusinje (RIV-MEGU), Vruja River (19.828072, 42.549023). This background site is located in a remote and pristine mountainous area with no detectable anthropogenic influence. Due to its isolation from human activity, this site is important for understanding natural occurrence of contaminants and baseline ecological status. It serves as a comparative point for assessing pressures detected downstream.

HS measured: metals, PFAS, pharmaceuticals.

2 – Plav (RIV-MEPL), Lim River (19.927583, 42.609150). This hotspot location lies within the urban area of the Plav municipality (9050 inhabitants) and reflects direct human influence on the Lim River. Municipal wastewater and surface runoff may introduce nutrients, organic matter and micropollutants into the aquatic system. The site is important for assessing how settlement-related activities affect a sensitive mountain river ecosystem.

HS measured: metals, PFAS, pharmaceuticals.

3 – Andrijevica (RIV-MEAN), Lim River (19.792533, 42.744333). This site represents a hotspot influenced by the Andrijevica municipality (3910 inhabitants). Urban runoff and untreated wastewater can affect water quality. The location is relevant for evaluating the cumulative influence of smaller settlements on middle-course river stretches. Monitoring results from this site support comparisons with more heavily urbanized areas downstream.

HS measured: metals, PFAS, pharmaceuticals.

4 – Berane (RIV-MEBE), Lim River (19.872986, 42.868732). This hot spot site is under the influence of the Berane municipality (24645 inhabitants) and its wastewater treatment plant. Although treatment infrastructure exists, effluents and urban runoff still represent a pressure on the river system. The site is important for assessing the effectiveness of wastewater treatment and its role in reducing pollutant loads.

HS measured: metals, PFAS, pharmaceuticals.

5 – Bijelo Polje (RIV-MEBP), Lim River (19.777242, 43.050792). This hotspot location is exposed to multiple pressures, including discharges from the Bijelo Polje municipality (38,660 inhabitants) and industrial activities such as food processing (meat, milk), pellet production and wood-drying facilities.

HS measured: metals, PFAS, pharmaceuticals.

6 – Dobrakovo (RIV-MEDO), Lim River (19.774528, 43.122531). This TNMN site is located near the border with Serbia and represents an internationally relevant profile. Its position allows for tracking pollutant transport across national boundaries. Monitoring at this location supports regional cooperation and long-term evaluation of transboundary water quality.

HS measured: metals, PFAS, pharmaceuticals.

7 – Opasanica (RIV-MEKO), Tara River (19.522148, 42.693944). This background site is situated in an ecologically preserved river section with no registered anthropogenic pressures. The Tara River is known for its high-quality waters and natural landscapes, and this profile reflects those characteristics. Data from this site serve as a natural benchmark for comparison with impacted stretches downstream.
HS measured: metals, PFAS, pharmaceuticals.

8 – Mojkovac (RIV-MEMO), Tara River-downstream of municipal landfill (19.572936, 42.932759). This hotspot site lies upstream of Mojkovac and is influenced by the municipal landfill. Landfill leachate and surface runoff may introduce contaminants into the river, potentially affecting ecological conditions. In the first half of 2025, the landfill was closed and repaired.
HS measured: metals, PFAS, pharmaceuticals.

9 – Mojkovac (RIV-MERU), Rudnica River (19.578943, 42.955724). This hotspot is situated before the confluence with the Tara River in an area naturally rich in lead and zinc ore. Geological conditions may contribute to elevated background concentrations of metals in water and sediment.
HS measured: metals.

10 – Mojkovac (RIV-MEMOI), Tara River-downstream of WWTP (19.565424, 42.96393). This hotspot site is directly affected by effluent discharged from the municipal wastewater treatment plant in Mojkovac. Although treatment infrastructure is in place, the released effluent and associated urban runoff continue to exert pressure on the river system. The location is therefore important for evaluating the performance of the wastewater treatment process.
HS measured: metals, PFAS, pharmaceuticals.

11 – Šćepan Polje (RIV-MESP), Tara River (18.840450, 43.348330). This TNMN site is positioned upstream of the confluence of the Tara and Piva rivers, near the origin of the Drina River and close to the border with Bosnia and Herzegovina. The site is hydrologically significant and relevant for monitoring transboundary water transport.
HS measured: metals, PFAS, pharmaceuticals.

12 – Hajla (RIV-MEHA), Ibar River (20.102572, 42.798929). This background site is located in a pristine high-mountain environment without anthropogenic pressures. The area represents natural conditions in the upper part of the Ibar catchment. Results from this site provide a reference for assessing impacts further downstream.
HS measured: metals, PFAS, pharmaceuticals.

13 – Rožaje city center (RIV-MERO), Ibar River (20.167014, 42.844235). This hotspot site is under pressure from the Rožaje municipality (23,184 inhabitants). Urban wastewater and runoff may influence water quality and ecological conditions in this river section.
HS measured: metals, PFAS, pharmaceuticals.

14 – Rožaje, exit from the city (RIV-MEROI), Ibar River (20.174712, 42.84614). This hot spot site is influenced by municipal discharges originating from the urban area of Rožaje (23,184 inhabitants). Untreated or partially treated wastewater, along with stormwater runoff, can alter the chemical and ecological status of the river at this section. The location is relevant for evaluating the impact of settlement-related pressures on the upper Ibar River and for tracking potential changes in water quality over time.
HS measured: metals, PFAS, pharmaceuticals.

15 – Bać (RIV-MEBA), Ibar River (20.307817, 42.893783). This TNMN border site enables the tracking of pollution transport towards Serbia. Its transboundary relevance makes it important for joint water management and collaborative monitoring. Data from this site complement upstream and downstream observations.
HS measured: metals, PFAS, pharmaceuticals.

16 – Tješanj (RIV-MEPLJ), Ćehotina River (19.535706, 43.173153). This background site is located in a clean and undisturbed environment. It represents natural conditions in the Ćehotina catchment and provides a baseline for comparison with impacted stretches.
HS measured: metals, PFAS, pharmaceuticals.

17 – Pljevlja (RIV-MEVE), Vezišnica River (19.323022, 43.347920). This hot spot site is located upstream of the confluence with the Ćehotina River and is influenced by the nearby Thermal Power Plant. Industrial activities and associated runoff can introduce pollutants to the aquatic system. The site is monitored to evaluate industrial impacts and their spatial extent.
HS measured: metals, PFAS, pharmaceuticals.

18 – Mjedenički Stream (RIV-MEMP) (19.052405, 43.400379), before its confluence with the Ćehotina River, flows through an area naturally enriched with sulphide minerals such as galena, pyrite, sphalerite, and chalcopyrite. Due to the mineralogical composition of the surrounding terrain and the occurrence of complex physicochemical weathering and oxidation processes, the pH value is significantly decreased (pH < 4). The presence of *Thiobacillus* bacteria additionally enhances and accelerates these oxidation reactions, intensifying the release of metals from the mineral matrix. Consequently, inflows from both surface runoff and mine workings contribute to elevated concentrations of dissolved metals in the stream water.
HS measured: metals.

19 – Jelice (RIV-MEJE), Ćehotina River (19.054761, 43.434512). This TNMN site is situated near the border with Bosnia and Herzegovina and represents an important transboundary monitoring point. The site allows for the evaluation of pollutant transport between countries and supports international cooperation.
HS measured: metals, PFAS, pharmaceuticals.

Wastewater sampling sites

20 – WWTP Mojkovac (WW-MEMO) (42.962316, 19.572550). The receiving water body for the treated effluent is the Tara River, an ecologically valuable and sensitive watercourse. The plant treats municipal wastewater and stormwater discharges and has a constructed capacity of approximately 5250 population equivalent (PE).
HS measured: metals, PFAS, pharmaceuticals.

21 – WWTP Berane (WW-MEBA) (19.870665, 42.862104). The treated effluent from the Berane wastewater treatment plant is discharged into the Lim River. The facility processes municipal wastewater and stormwater inflow and is designed for a total capacity of approximately 20000 population equivalent (PE). HS measured: metals, PFAS, pharmaceuticals.

22 – WWTP Pljevlja (WW-MEPV) (19.301977, 43.361683). The treated effluent from the Pljevlja wastewater treatment plant is released into the Ćehotina River. The facility handles municipal wastewater as well as stormwater inflow and is designed for a total capacity of approximately 28,000 population equivalent (PE). Monitoring at this location provides insight into the plant's effectiveness and its potential contribution to downstream pollutant loads.
HS measured: metals, PFAS, pharmaceuticals.

23 – Bijelo Polje – untreated wastewater discharge (WW-MEBP) (19.748960), 43.031873). At this location, untreated municipal wastewater from the Bijelo Polje area (≈38,600 inhabitants) is discharged directly into the Lim River, without prior treatment.
HS measured: metals, PFAS, pharmaceuticals.

24 – Bijelo Polje – untreated wastewater discharge (WW-MEBPI) (19.771464, 43.048558). At this location, untreated municipal and industrial wastewater (raw sewage) from the Bijelo Polje area is discharged directly into the Lim River, without any prior treatment.
HS measured: metals, PFAS, pharmaceuticals.

25 – Rožaje – untreated wastewater discharge (WW-MERO) (20.174075, 42.845887). Raw municipal wastewater from the Rožaje (≈13,600 inhabitants) enters the Ibar River without treatment. Such direct discharges may affect local water quality and contribute to downstream pollutant loads.
HS measured: metals, PFAS, pharmaceuticals.

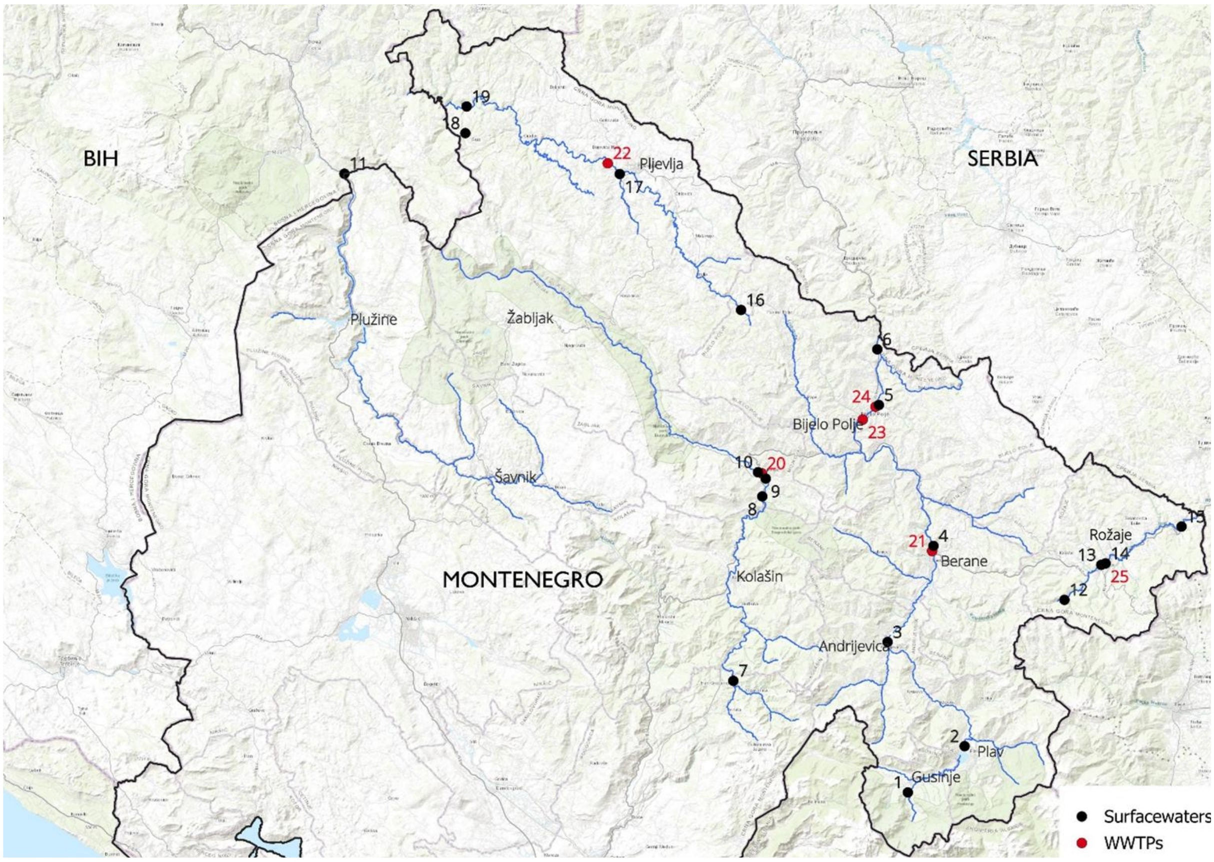

Figure 20: Map of the sampling campaign in Montenegro.

Figure 21: Photo of a sampling site in Montenegro. Left: Hajla, Ibar River, background location (No. 12 on the map). Right: Jelice, Ćehotina River (No. 19 on the map).

5.11 Bosnia and Herzegovina

In Bosnia and Herzegovina, sampling was performed at 13 river sampling sites in the Sava River Basin (District) of Republika Srpska, at four outlets of treated and untreated urban wastewater, at five outlets of industrial wastewater, as well as groundwater sampling at two locations - piezometers. The sampling sites were selected to represent various sources of pollution associated with different industrial and human activities, except for two river locations that have been chosen as reference of background conditions.

River sampling was conducted four times over the course of one year, once in each season. Wastewater sampling was conducted three times during the same year, and groundwater sampling was carried out by collecting the current sample two times with an interval of six months.

River water sampling sites

1 – Gradiška (RIV-BA-RSGR), River Sava (17.251912; 45.148882). This sampling site is impacted by the population of the Gradiska municipality with approximately 25,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

2 – Rača (RIV-BA-RSRC), River Sava (19.346280; 44.887999). This sampling site is impacted by the population of the Bijeljina city with approximately 42,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

3 – Novi Grad (RIV-BA-RSNG), Una River (16.370902; 45.042276), a right tributary of the Sava River. This sampling site is impacted by the population of the Novi Grad municipality with approximately 10,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

4 – Kozarska Dubica (RIV-BA-RSKD), Una River (16.836886; 45.188696), a right tributary of the Sava River. This sampling site is impacted by the population of the Kozarska Dubica municipality with approximately 17,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

5 – Razboj (RIV-BA-RSRZ), River Vrbas (17.456010; 45.060957), a right tributary of the Sava River. This sampling site is impacted by the population of the Banja Luka city, Trn and Laktasi municipalities with approximately 170,000 inhabitants, in total.
HS measured: metals, PFAS, pharmaceuticals.

6 – Doboj (RIV-BA-RSUS), River Bosna (18.073780; 44.663767), a right tributary of the Sava River. This sampling site is impacted by the population of the Sevarlije municipality with approximately 5,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

7 – Modriča (RIV-BA-RSMO), River Bosna (18.294698; 44.969901), a right tributary of the Sava River. This sampling site is impacted by the steel and iron production, as well as the population of the Doboj city, Modrica, Vukosavlje and Garevac municipalities with approximately 63,000 inhabitants, in total.
HS measured: metals, PFAS, pharmaceuticals.

8 – Pavlovića most (RIV-BA-RSPM), River Drina (19.336141; 44.772874), a right tributary of the Sava River. This sampling site is impacted by the population of the Zvornik city, Janja, Karakaj, Branjevo and Kozluk municipalities with approximately 42,000 inhabitants, in total.
HS measured: metals, PFAS, pharmaceuticals.

9 – Foča (RIV-BA-RSFO), River Drina (18.744645; 43.485506), a right tributary of the Sava River. This sampling site is impacted by the population of the Foca municipality with approximately 12,000 inhabitants.
HS measured: metals, PFAS, pharmaceuticals.

10 – Stanić Rijeka (RIV-BA-RSSR), River Spreča (18.107537; 44.732344), a right tributary of the Bosna River. This sampling site is impacted by the dense population of the Tuzla municipality with 100,000 inhabitants and industry production of soda, cement, thermal power plants.
HS measured: metals, PFAS, pharmaceuticals.

11 – Lužani (RIV-BA-RSLU), River Ukrina (17.957894; 45.073957), a right tributary of the Sava River. This sampling site is impacted by the population of the Derventa municipality with approximately 18,000 inhabitants.
HS measured metals, PFAS, pharmaceuticals.

12 – Rudice (RIV-BA-RSRU), River Vojskova (16.349590; 44.996120), a right tributary of the Una River. Background location in a pristine area, with no known sources of pollution.
HS measured metals, PFAS, pharmaceuticals.

13 – Tjentište (RIV-BA-RSTJ), River Sutjeska (18.68993; 43.353668), a left tributary of the Drina River. Background location in a pristine area, with no known sources of pollution.
HS measured metals, PFAS, pharmaceuticals.

Wastewater sampling sites

14 – Gradiška (WW-BA-RSKEJ), CS Kej – Gradiška (17.259380; 45.159137). The sewage system of the city is partially mixed, without pre-treatment before discharge into the Sava River. It collects wastewater from about 17,000 inhabitants and 900 economic facilities (city hospital, furniture production, etc).
HS measured metals, PFAS, pharmaceuticals.

15 – Banja Luka (WW-BA-RSKAM), Kampus (17.223487; 44.804162). One of the discharges from households of Banja Luka city. The sewage system of the city Banja Luka consists of a several outlets into the Vrbas River without WWTP. This system is among the largest in the city. It collects residential and commercial wastewater.
HS measured metals, PFAS, pharmaceuticals.

16 – Doboj (WW-BA-RSGI), GL ispust (18.095916; 44.743858). Discharges from households of Doboj city.
HS measured metals, PFAS, pharmaceuticals.

17 – Bijeljina (WW-BA-RSVO), Velika Obarska (19.139243; 44.803706). Municipal WWTP with a capacity of 40,000 PE, receiving the urban wastewater of Bijeljina.
HS measured metals, PFAS, pharmaceuticals.

18 – Banja Luka (WW-BA-RSHF), Hemofarm (17.199118; 44.826685). Discharge of previously treated wastewater from the pharmaceutical industry into the sewage system.
HS measured metals, PFAS, pharmaceuticals.

19 – Banja Luka (WW-BA-RSCX), SHP Celex (17.222898; 44.775173). Discharge of previously treated wastewater from the paper industry into the sewage system.
HS measured metals, PFAS.

20 – Teslić (WW-BA-RSDT), Devic tekstil (17.854877; 44.628186). Discharge of previously treated wastewater from the textile industry into the surface water.
HS measured metals, PFAS.

21 – Zvornik (WW-BA-RSAL), Alumina (19.113129; 44.419198). Discharge of previously treated wastewater from the bauxite ore processing industry into the surface water.
HS measured metals, PFAS.

22 – Bijeljina (WW-BA-RSED), EKO DEP (19.170968; 44.751618). Discharge of WWTP efluent from the regional waste landfill into the surface water.
HS measured metals, PFAS, pharmaceuticals.

Groundwater sampling sites

23 – Banja Luka (GRW-BA-RSBL), DEPOT (17.173029; 44.840330) groundwater. This sampling site is impacted by the regional waste landfill in Banja Luka.
HS measured metals, PFAS, pharmaceuticals.

24 – Bijeljina (GRW-BA-RSBN), EKO DEP (19.172177; 44.751726) groundwater. This sampling site is impacted by the regional waste landfill in Bijeljina.
HS measured metals, PFAS.

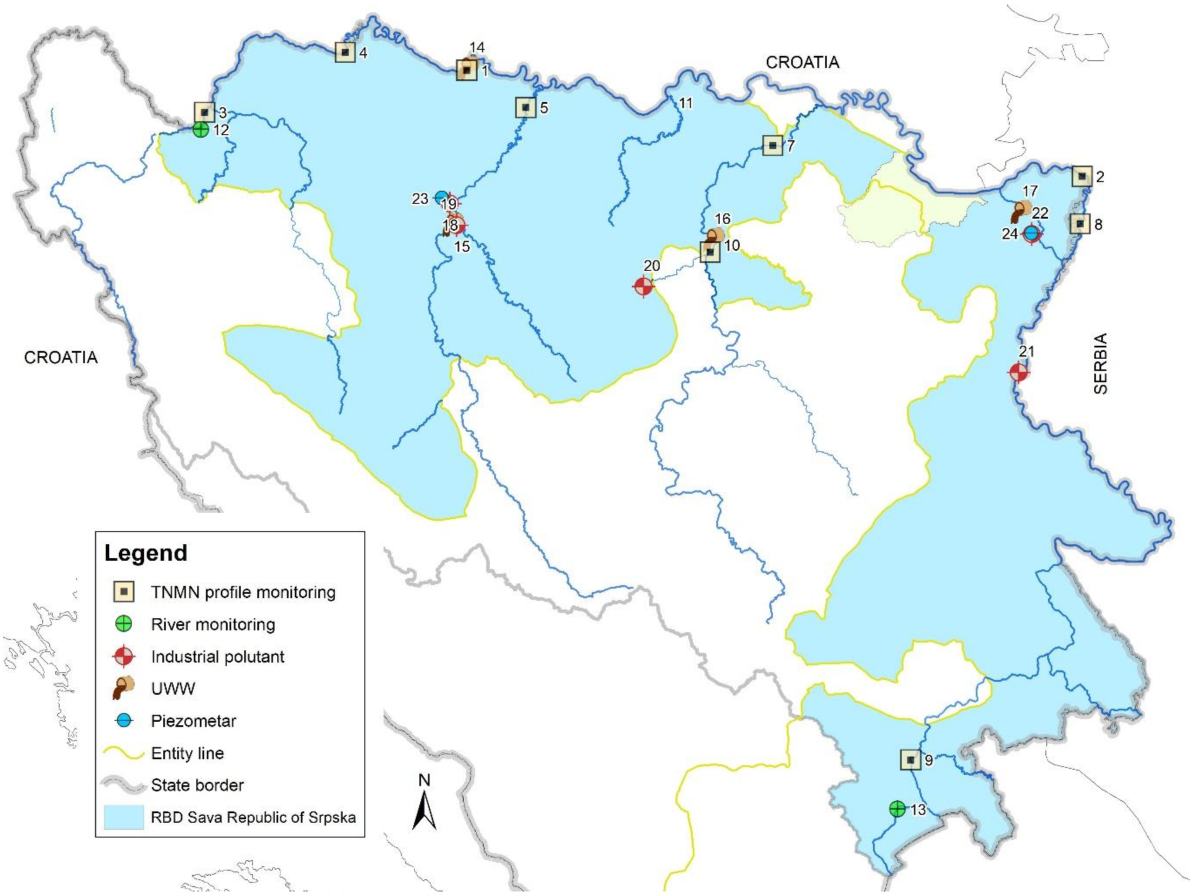

Figure 22: Map of the sampling campaign in Bosnia and Herzegovina, Republika Srpska.

Figure 23: Photo of a sampling site in Bosnia and Herzegovina, Republika Srpska. Left: Tjentište, River Sutjeska-Background location (No. 1 on the map). Right: Una, Kozarska Dubica-TNMN location (No. 2 on the map).

6 Overview of the results

6.1 Results of metal analyses

Metal concentrations (Zn, Cu, Ni, Cr, As, Cd, and Pb) were quantified in four types of water samples: river water, wastewater, groundwater, and urban stormwater runoff samples. In river water, both total and dissolved metal concentrations were measured. In wastewater and urban stormwater runoff samples, total metal concentrations were determined, whereas in groundwater, only dissolved metal concentrations were analysed.

6.1.1 Metal concentrations in river water samples

Data from a one-year monitoring campaign conducted in six EU and four non-EU countries showed that total and dissolved concentrations of Zn, Cu, Ni, Cr, As, Cd, and Pb in river water are generally comparable to previously reported values from the Danube River Basin (Kardos et al., 2024; Milačič et al., 2023, 2017; Liška et al., 2015), except at known hotspots.

For these metals, the Water Framework Directive (WFD) (Directive 2000/60/EC) and its Daughter Directives (Environmental Quality Standards 272/2009; Directive 2013/39/EU) establish environmental quality standards (EQS) for dissolved metal concentrations in surface waters (Table 12). With regard to Ni and Pb, Directive 2013/39/EU (which amends Directives 2000/60/EC and 2008/105/EC concerning Priority Substances in Water Policy) reduced the EQS values compared to Directive 2000/60/EC: the EQS for dissolved Ni content was lowered from 20 ng/mL to 4 ng/mL, and for Pb from 7.2 ng/mL to 1.2 ng/mL, with the EQS now referring to bioavailable concentrations of Ni and Pb.

Table 12: EQS for dissolved metal concentrations.

Metal	EQS	
	Directive 2013/39/EU – Priority Hazardous Substances	Environmental Objectives 272/2009 – Specific Pollutants
Cd	<40 mg/L $CaCO_3$……………………….≤0.08 ng/mL 40–50 mg/L $CaCO_3$ …………………..0.08 ng/mL 50–100 mg/L $CaCO_3$ …………………0.09 ng/mL 100–200 mg/L $CaCO_3$………………..0.15 ng/mL ≥100 mg/L $CaCO_3$ ……………………..0.25 ng/mL	
Pb[*]	1.2 ng/mL	
Ni[*]	4 ng/mL	
Cr		Cr(III) 4.7 ng/mL, Cr(VI) 3.4 ng/mL
Zn		≤10 mg/L $CaCO_3$…………………………..8 ng/mL 10–100 mg/L $CaCO_3$ …………………..50 ng/mL >100 mg/L $CaCO_3$ ……………………100 ng/mL
Cu		≤100 mg/L $CaCO_3$)……………………….5 ng/mL >100 mg/L $CaCO_3$ ……………….………30 ng/mL
As		25 ng/mL

[*] These EQS refer to bioavailable concentrations of Ni and Pb

The EQS values for dissolved metal concentrations, as defined by Directive 2013/39/EU and the EC Environmental Objectives (272/2009 – Specific Pollutants), were in general exceeded at monitoring stations located in known hotspots.

Extremely high metal concentrations (both total and dissolved) were determined in the Mjedenički Stream in Montenegro (up to 500,000 ng/mL Zn; 500 ng/mL Cu; 15 ng/mL Cr; 660 ng/mL Ni; 500 ng/mL Cd; and 750 ng/mL Pb) in the area of zinc and lead mine, where complex physicochemical and microbiological processes lead to the release of heavy metals from mineral matrices. The EQS values for dissolved metals were exceeded by up to 10,000 times for Zn, about 20 times for Cu, 2 times for Cr, 150 times for Ni, 3,300 times for Cd, and 440 times for Pb.

At the other sampling sites, the metal concentrations in river water were as follows:

High Zn concentrations (up to 1,000 ng/mL dissolved Zn) were measured at Mojkovac (Rudnica River) in Montenegro, an area affected by former lead and zinc mining activities. At the remaining sampling locations, Zn slightly exceeded the EQS value of 50 ng/mL at Foča (Drina River) in Bosnia and Herzegovina, influenced by the population of the Foča municipality, including rafting camps located nearby, and at Mojsinje (Južna Morava River) in Serbia, affected by metal-processing industries.

Dissolved Cu concentrations occasionally slightly exceeded the EQS value of 30 ng/mL at Rogotina (Borska River) in Serbia, where intensive gold and copper mining operations are carried out. At this site, total Cu concentrations were up to 100 times higher than dissolved concentrations, indicating that Cu is primarily bound to suspended solids.

Total and dissolved Ni concentrations of approximately 30 ng/mL (with dissolved Ni exceeding the EQS of 4 ng/mL) were observed in the River Spreča, a tributary of the Bosna River in Bosnia and Herzegovina. This site is influenced by emissions from the cement industry and thermal power plant activities in the Tuzla municipality. At the Batrage site (Ibar River) in Serbia, high total Ni concentrations (80 ng/mL) reflect the geogenic Ni content of serpentine rocks, while dissolved Ni (around 1 ng/mL) remained below the EQS of 4 ng/mL. At other sampling sites in Bosnia and Herzegovina, Serbia and Montenegro, dissolved Ni concentrations occasionally slightly exceeded the EQS. It should be noted that only dissolved Ni concentrations were determined, and bioavailable Ni was not calculated. A comparison to the EQS was made based on dissolved Ni concentrations, which are higher than the bioavailable Ni content.

Despite high total As concentrations in the Borska River in Serbia (up to 150 ng/mL), associated with gold and copper mining, dissolved As concentrations remained well below the EQS of 25 ng/mL. Conversely, in the Ogosta River in Bulgaria, both total and dissolved As concentrations (around 40 ng/mL) indicated the release of As from geogenic sources to the environment due to the extraction procedures used in processing lead and zinc ore.

In the Rudnica River in Montenegro, total and dissolved Cd concentrations were similar, with dissolved Cd exceeding the EQS of 0.25 ng/mL by approximately 10 times. In the Borska River in Serbia, dissolved Cd concentrations exceeded the EQS by about two times, while total Cd concentrations were roughly five times higher than dissolved levels.

Dissolved Pb concentrations at the other sampling sites across the investigated river catchments were in general below the EQS value of 1.2 ng/mL, and were occasionally slightly exceeded at sampling sites in Bosnia and Herzegovina. It should be noted that only dissolved Pb concentrations were determined and that bioavailable Pb was not calculated. A comparison to the EQS was made based on dissolved Pb concentrations, which are higher than the bioavailable Pb content.

6.1.2 Metal concentrations in wastewater samples

The new Urban Waste Water Treatment Directive (EU) 2024/3019 does not specify permissible concentrations for Cd, Pb, Cu, Zn, Cr, Ni, or As in wastewater effluent. Instead, it focuses on the collection, treatment, and discharge of urban wastewater to protect the environment and human health. The directive emphasizes the need for effective treatment to prevent adverse effects on receiving waters and to meet the objectives of EU water legislation. The European countries apply the National Guidelines to ensure that treated water released into the surface waters meet the objectives of EU water legislation. A comparison of the monitoring results with Slovenian national legislation, specifically the Regulation on the Emission of Substances and Heat in the Discharge of Wastewater into Waters and Public Sewerage (Official Gazette 64/2012, 2012), shows that discharges from all wastewater treatment plants examined in the project complied with the EQS standards for metals.

6.1.3 Metal concentrations in groundwater samples

The new EU Groundwater Directive (Proposal Directive, 2024) provides guidelines for Member States to establish threshold values for pollutants in groundwater. However, it does not specify exact threshold values for Cd, Pb, Cr, Ni, Zn, Cu and As.

Elevated Cr and Zn concentrations (up to 80 and 180 ng/mL, respectively) were determined in groundwater samples in Serbia. The new EU Groundwater Directive (Proposal Directive, 2024) provides guidelines for Member States to establish threshold values for pollutants in groundwater. However, it does not specify exact threshold values for Cd, Pb, Cr, Ni, Zn, Cu, or As.

Elevated Cr and Zn concentrations (up to 80 and 180 ng/mL, respectively) were detected in groundwater in Serbia. These values are associated with direct interactions with discharges from the Galovica Canal, nearby highway emissions, wastewater from the settlements of Surčin and Ledine, and agricultural activities. In Bosnia and Herzegovina, elevated Zn concentrations (up to 100 ng/mL) were observed and are linked to the impact of the Bijeljina waste landfill.

6.1.4 Metal concentrations in urban stormwater runoff samples

In urban stormwater runoff samples collected in Hungary, Zn concentrations reached up to 250 ng/mL, primarily attributed to ZnO additives used in car tires. Cu concentrations of up to 80 ng/mL are linked to Cu released from automotive brake components. Additionally, Cr and Ni concentrations of up to 60 ng/mL and 20 ng/mL, respectively, are associated with brake wear and industrial emissions.

6.2 Results of PFAS and pharmaceutical analyses

This section presents a short overview of the results of the analyses for per- and polyfluoroalkyl substances (PFAS) and pharmaceuticals in four distinct water compartments: river water, wastewater, groundwater, and urban stormwater runoff. Total concentrations were measured in all samples.

6.2.1 Sampling and analytical scope

As described in detail in the previous sections on the design and purpose of the pilot action, the number of measurements conducted for PFAS and pharmaceuticals varied significantly by country and water compartment.

The highest number of measurements were conducted in river water samples in non-EU countries, whereas the lowest number of measurements was conducted in all countries for groundwater, wastewater and stormwater (Figure 24). The number of compounds analysed in samples from ME was lower than in the other countries, as these were analysed in the CETI laboratory, whereas all other samples were processed in the laboratory of TU Wien (Figure 25).

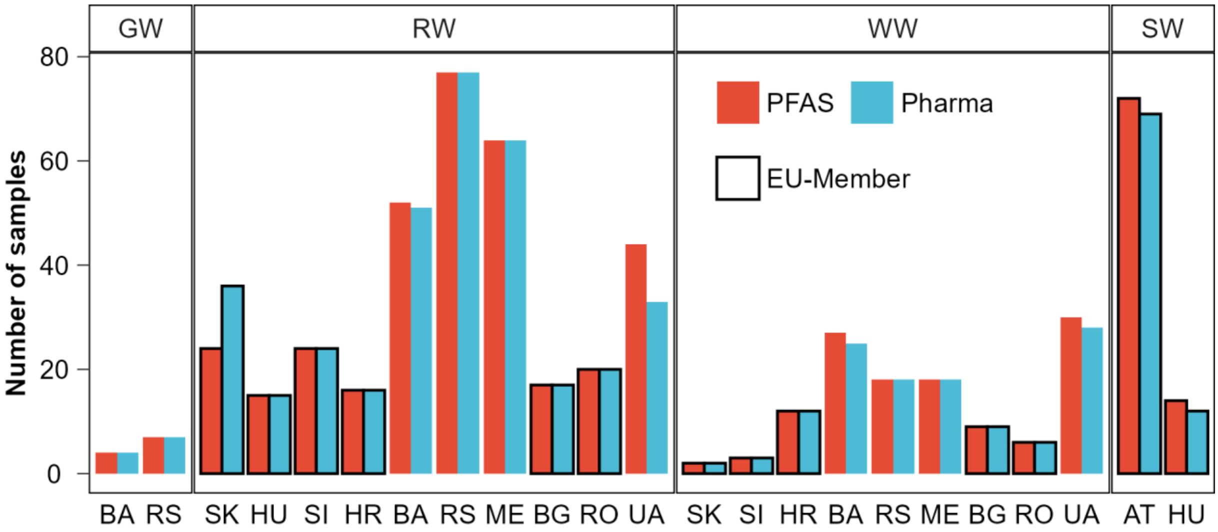

Figure 24: The number of samples analysed for PFAS compounds and pharmaceuticals is shown across different compartments and countries. EU countries are highlighted with black outline.

6.2.2 Detection frequencies

Figure 25 provides a compact overview of the detection rate, namely the proportion of samples with measured values above LOQ, in the investigated compartments and in the different countries for PFAS. A significant portion of the targeted PFAS, particularly long-chain compounds, were not detected in most samples. Detection rates were generally uniform across countries, with the notable exception of Montenegro (ME), which exhibited a lower overall detection rate, probably attributable to its different analytical methodology. For the PFCA group, detection rates decreased with increasing chain length. In the PFSA group, only PFBS, PFHxS, and PFOS were frequently detected, while others were rarely or never detected. The other PFAS substances showed consistently low to zero detection rates. Only two substances (6:2 FTS and FBSA) were frequently detected, with higher occurrences in upstream Danube countries (SK, HU, SI, HR, RS) compared to downstream countries (UA, RO, BG, BA).

Comparing water compartments, groundwater samples had the lowest overall detection rates, whereas stormwater samples showed the highest detection rates, including for compounds that were infrequently detected in other compartments.

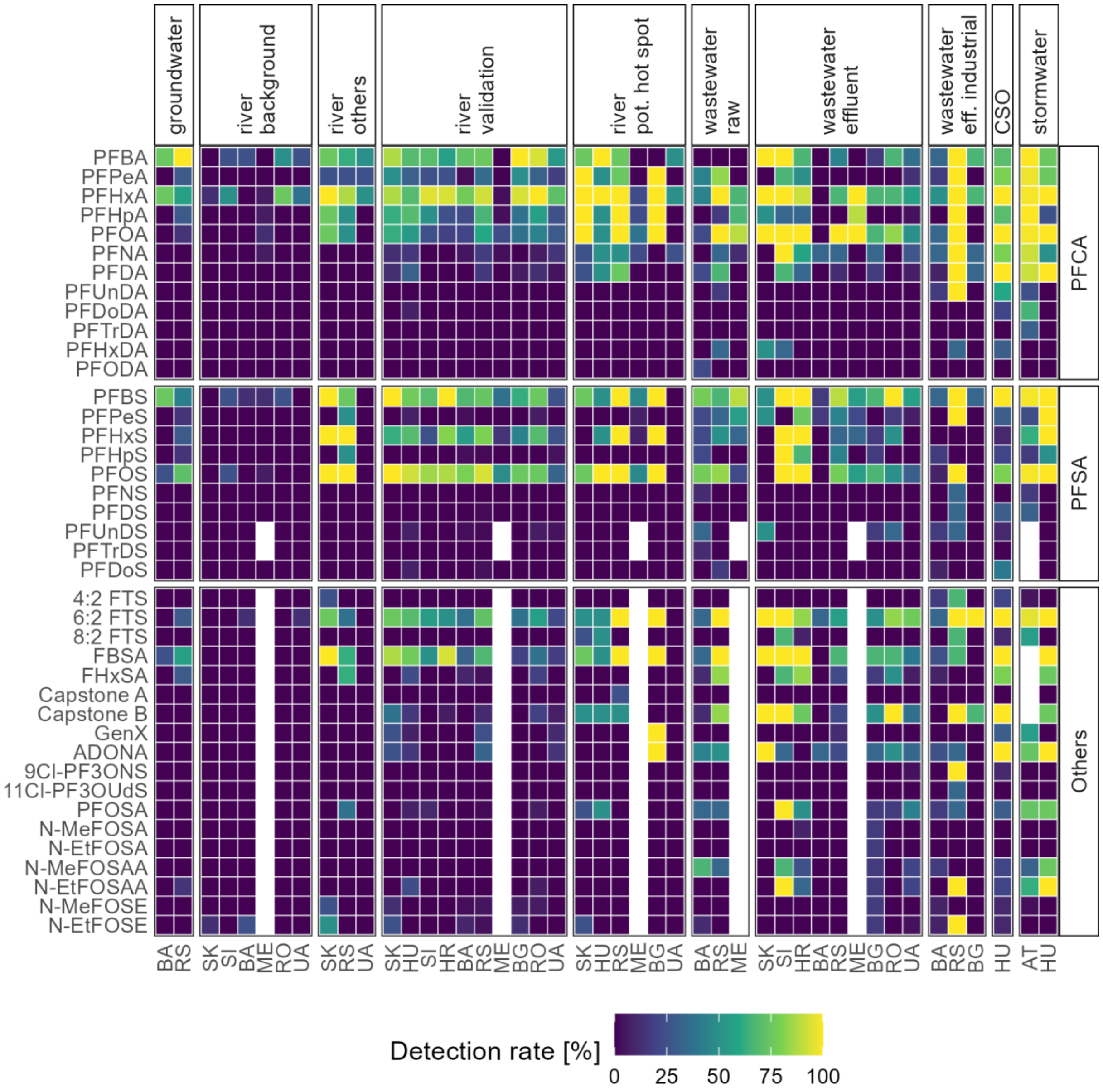

Figure 25: Detection rate of PFAS compounds across compartments and countries. Detection is defined here as measurement above LOQ.

Figure 26 provides a compact overview of the detection rate for pharmaceuticals, namely the proportion of samples with measured values above LOQ, in the investigated compartments and countries. The pattern of detection for pharmaceuticals is distinct from that of PFAS. In surface waters, bezafibrate, citalopram, and Ibuprofen had low detection rates, while others were frequently detected. Montenegro (ME) and Slovakia (SK) generally showed lower detection rates in rivers than other countries. In wastewater effluent, nearly all substances had very high detection rates, except for bezafibrate in Slovenia (SI). Another notable exception included ibuprofen in SK samples and all parameters in BA samples. The river locations initially identified as potential hotspots for pharmaceuticals show low to medium detection rates; therefore, it can be concluded that either these are wrongly identified as hotspots for pharmaceutical contamination or the pharmaceuticals being emitted into these rivers might substances not included in this target analysis. CSO and stormwater samples exhibited very high detection rates across most compounds. In contrast, groundwater samples had very low detection rates, apart from metoprolol and trimethoprim, which were consistently detected in samples from RS and BA.

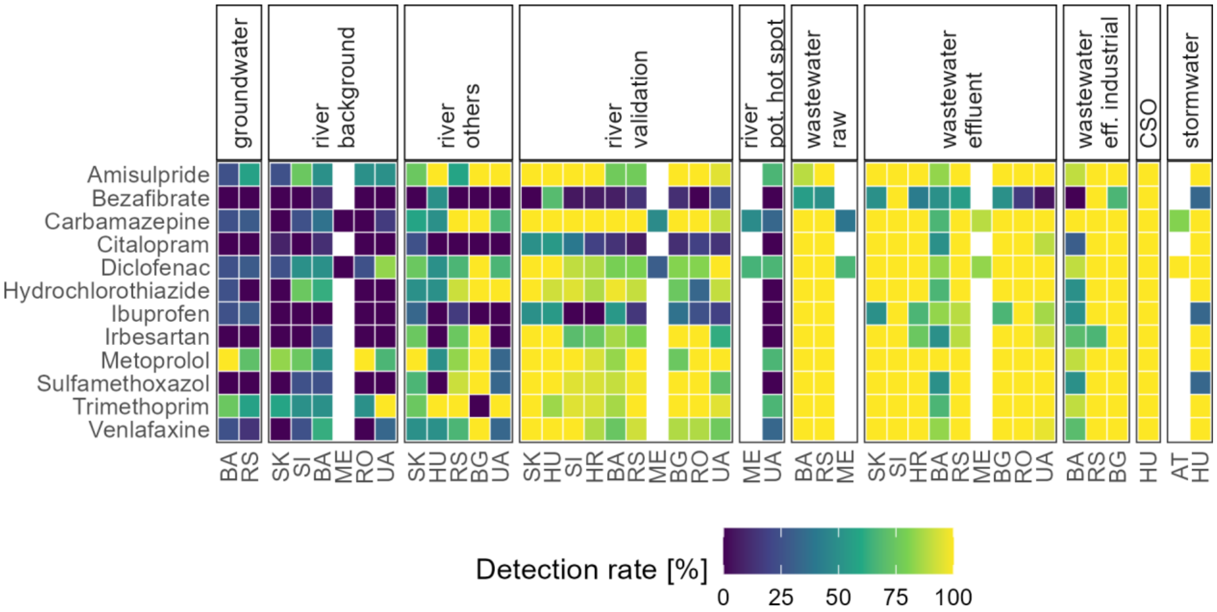

Figure 26: Detection rate of pharmaceuticals across compartments and countries. Detection is defined here as measurement above LOQ.

6.2.3 PFAS and pharmaceutical concentrations across compartments

The distribution of PFAS concentrations vary considerably among chemical groups and water compartments. For the PFCA group, stormwater runoff exhibits the highest median concentrations, followed by wastewater, which contain some outlier samples with levels as high as or higher than stormwater. River water and groundwater show the lowest medians, though both present outliers with elevated concentrations. The PFSA group presents a more complex picture. For PFBS and PFOS, highest levels were found in stormwater runoff samples, while river water show the lowest levels. In contrast, PFHxS was most prevalent in groundwater based on median values, although stormwater and wastewater show higher maximum concentrations in a few outlier samples.

For other PFAS groups, including AFFF-related compounds, PFECA, PFESA, FASA, FASAA and FASE, robust comparisons were often precluded by most data being below the LOQ. Nevertheless, where compounds like Capstone B, FBSA, 6:2 FTS, FHxSA, ADONA, N-EtFOSAA, and PFOSA were quantifiable, stormwater runoff consistently shows higher median concentrations. It is critical to note that outlier samples from wastewater and river water could still reach comparable or even higher concentrations.

The highest concentrations of the analysed pharmaceuticals were detected in CSO, stormwater runoff and wastewater, while river water and groundwater show progressively lower levels. The investigated groundwater is largely uncontaminated, with most measurements below the LOQ. Key differences can be observed in substance profiles. Stormwater, CSO and wastewater had similar levels for some compounds (e.g., metoprolol, hydrochlorothiazide), but wastewater had higher levels for persistent substances like venlafaxine, trimethoprim, carbamazepine and diclofenac. In contrast, stormwater shows higher levels of bezafibrate, irbesartan and ibuprofen, indicating removal by wastewater treatment. Although river water was typically less contaminated, its outlier concentrations and elevated carbamazepine levels indicate significant influence from wastewater sources.

7 Conclusions and outlook

The pilot action succeeded in demonstrating the feasibility and added value of the joint conceptualisation, planning and execution of a harmonised 1-year sampling campaign in 11 EU and non-EU countries within the Danube River Basin and across multiple environmental compartments. It showed that good organization, communication, and collaboration are crucial for the implementation of successful monitoring, especially at transboundary scale. Clear instructions in the SOP are crucial to prevent contamination and ensure representative sampling, which thereby yields reliable HS analysis results. The presented approach, based on cost-efficient monitoring strategies, demonstrates strong potential for enabling improved assessment of HS emissions and pollution in both established and newly identified critical compartments, for enabling the implementation and validation of pathway-oriented emission models and for establishing solid emission inventories at national and transnational level.

The results from the monitoring campaigns show that metal concentrations in river waters generally comply with the EQS criteria established by the WFD, except at known hotspots linked to industrial, mining, or other urban municipal activities. Wastewater treatment in both EU and non-EU countries is largely effective with respect to metals, as discharges from treatment plants do not exceed levels that would endanger the environment or human health. They also meet the objectives of EU water legislation, which requires effective treatment of urban wastewater to prevent adverse impacts on receiving waters. In areas where wastewater is discharged directly into streams and rivers without prior treatment, the chemical status of water bodies is noticeably poorer due to elevated metal concentrations. Insufficient wastewater treatment also directly contributes to elevated metal concentrations and reduced groundwater quality at the locations studied. Urban stormwater runoff is strongly influenced by traffic, with metals from tire additives and brake components being washed from road surfaces into waterways during heavy rainfall.

The results from the monitoring campaigns for PFAS and pharmaceuticals revealed significant variations across four water compartments—river water, wastewater, groundwater, and urban stormwater runoff—in multiple countries. PFAS and pharmaceutical measurements varied by country and compartment, with stormwater and wastewater exhibiting the highest detection rates and concentrations, while groundwater had the lowest ones. PFAS contamination patterns were complex and compound-specific: long-chain PFAS compounds were rarely detected, whereas short-chain PFAS (e.g. PFBS, PFHxA, PFOS) and AFFF-related PFAS were more frequently found, particularly in wastewater and stormwater. Country-specific differences were observed, with some countries (e.g. Serbia and Slovenia for wastewater, and Hungary for river water) showing higher contamination levels. However, data from Montenegro were not directly comparable probably due to differences in the applied analytical methods. The findings, despite the relatively low number of samples, indicate CSO and stormwater runoff as a potentially highly relevant compartment for PFAS and pharmaceutical contamination, while wastewater is confirmed to play a significant role—particularly for persistent compounds. The groundwater samples investigated in the project were largely uncontaminated, though occasional outliers indicated local pollution. Additionally, significant site-specific variations were observed, with "hotspot" and "validation" sites typically more contaminated than "background" locations. These results underscore the need for targeted monitoring and mitigation strategies to address these emerging pollutants in different water environments and locations.

8 References

D1.1.1: Protocol for Sampling, Storage, and Transport of Samples. June 2024. Deliverable of the Tethys project.

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy. Official Journal of the European Union, L 348, 84-97. https://eur-lex.europa.eu/eli/dir/2008/105/oj. Accessed December 27, 2025.

Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy. Official Journal of the European Union, 12 Aug. 2013, L 226/1-17. EUR-Lex, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32013L0039. Accessed December 27, 2025.

Directive (EU) 2024/3019 of the European Parliament and of the Council of 27 November 2024 Concerning Urban Wastewater Treatment. Official Journal of the European Union, 27 Nov. 2024. EUR-Lex, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32024L3019. Accessed December 27, 2025.

European Communities Environmental Objectives (Surface Waters), 2009. Regulations S.I. No. 272/2009. https://www.irishstatutebook.ie/eli/2009/si/272/made/en/pdf.

EU (2012). Technical guidance on the preparation of an inventory of emissions, discharges and losses of priority and priority hazardous substances. Guidance document No. 28. https://legacy.emissieregistratie.nl/erpubliek/documenten/06%20Water/02%20Achtergrondrapporten/WFD%20guidance%20on%20emission%20inventories.pdf. Accessed December 27, 2025.

Kardos, M.K., Clement, A., Jolánkai, Z., Zessner, M., Kittlaus, S., Weber, N., Gabriel, O., Bertine Broer, M., Soare, F., Hamchevici, C., Sidau, M., Tonev, R., Milačič, R., Ščančar, J., Horvat, M., Marković, K., Kulcsar, S., Schuhmann, A., Bordós, G., Pataj, E., Zoboli, O., 2024. Development and testing of an efficient micropollutant monitoring strategy across a large watershed. Sci. Total Environ. 948, 174760. https://doi.org/10.1016/j.scitotenv.2024.174760.

Kittlaus, S., Kardos, M. K., Dudás, K. M., Weber, N., Clement, A., Petkova, S., ... & Zoboli, O. (2024). A harmonized Danube basin-wide multi-compartment concentration database to support inventories of micropollutant emissions to surface waters. Environmental Sciences Europe, 36(1), 1-21. https://doi.org/10.1186/s12302-024-00862-4.

Kittlaus, S., Clara, M., van Gils, J., Gabriel, O., Broer, M. B., Hochedlinger, G., ... & Zoboli, O. (2022). Coupling a pathway-oriented approach with tailor-made monitoring as key to well-performing regionalized modelling of PFAS emissions and river concentrations. *Science of The Total Environment*, *849*, 157764. https://doi.org/10.1016/j.scitotenv.2022.157764.

Liška, I., Wagner, F., Sengl, M., Deutsch, K., Slobodník, J., 2015. ICPDR (International Commission for the Protection of the Danube River) Joint Danube Survey 3. A Comprehensive Analysis of Danube Water Quality, Final Scientific report of the International Commission for the protection of the Danube River. Vienna, Austria. p. 231–239. https://www.icpdr.org/sites/default/files/nodes/documents/jds3_final_scientific_report.pdf. Accessed December 27, 2025.

Milačič, R., Zuliani, T., Vidmar, J., Oprčkal, P., Ščančar, J., 2017. Potentially toxic elements in water and sediments of the Sava River under extreme flow events. Sci. Total Environ. 605–606, 894–905. http://dx.doi.org/10.1016/j.scitotenv.2017.06.260.

Milačič, R., Marković, K., Marković, S., Ščančar, J., Jolánkai, Z., Clement, A., Musa, I., Krisztián Kardos, M., Zoboli, O., Zessner, M., 2023. Changes in concentrations of potentially toxic elements during storage of hard river water samples at low temperatures using different sample preservation procedures. J. Soils Sediments 23, 4173–4186. https://doi.org/10.1007/s11368-023-03625-5.

Official Gazette of the Republic of Slovenia (2012). Regulation on the emission of substances and heat from the discharge of wastewater into water and public sewers. Official Gazette of the Republic of Slovenia, 64/2012, p. 6392. (In Slovenian language). https://www.uradni-list.si/_pdf/2012/Ur/u2012064.pdf. Accessed December 27, 2025.

Official Journal of the European Communities, 2000. Directive 2000/60/EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy L 327/1. https://eur-lex.europa.eu/eli/dir/2000/60/2014-11-20. Accessed December 27, 2025.

Proposal for a Directive of the European Parliament and of the Council amending Directive 2000/60/EC establishing a framework for Community action in the field of water policy, Directive 2006/118/EC on the protection of groundwater against pollution and deterioration and Directive 2008/105/EC on environmental quality standards in the field of water policy Mandate for negotiations with the European Parliament (2024). https://eur-lex.europa.eu/procedure/EN/2022_344. Accessed December 27, 2025.