



Output O.T1.2
Demonstration of a harmonized and cost-effective measurement concept for the monitoring of HS river pollution and of HS emission pathways in 7 pilot regions
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ABBREVIATIONS

Chemical substance abbreviations

Abbreviation	Name	CAS number
Metals		
Cr	Chromium and its compounds	7440-47-3
Ni	Nickel and its compounds	7440-02-0
Cu	Copper and its compounds	7440-50-8
Zn	Zinc and its compounds	7440-66-6
As	Arsenic and its compounds	7440-38-2
Cd	Cadmium and its compounds	7440-43-9
Pb	Lead and its compounds	7439-92-1
Hg	Mercury and its compounds	7439-97-6
Al	Aluminium and its compounds	7429-90-5
Fe	Iron and its compounds	7439-89-6
La	Lanthanum	7439-91-0
Ce	Cerium	7440-45-1
PAHs		
Naph	Naphthalene	91-20-3
Ace	Acenaphthene	83-32-9
Acy	Acenaphthylene	208-96-8
Fluo	Fluorene	86-73-7
Ant	Anthracene	120-12-7
Phen	Phenanthrene	85-01-08
Fla	Fluoranthene	206-44-0
Pyr	Pyrene	129-00-0
BaA	Benzo(a)anthracene	56-55-3
Chry	Chrysene	218-01-9
BbF	Benzo(b)fluoranthene	205-99-2
BkF	Benzo(k)fluoranthene	207-08-9
BaP	Benzo(a)pyrene	50-32-8
DahA	Dibenzo(a,h)anthracene	53-70-3
BghiP	Benzo(g,h,i)perylene	191-24-2
Ind123cdP	Indeno(1,2,3-cd)pyrene	193-39-5
16-PAH_EPA	Sum of the 16 US-EPA PAHs	
PFAS		
PFPeA	Perfluoropentanoic acid	2706-90-3
PFHxA	Perfluorohexanoic acid	307-24-4
PFHpA	Perfluoroheptanoic acid	375-85-9
PFOA	Perfluorooctanoic acid	335-67-1
PFNA	Perfluorononanoic acid	375-95-1

Abbreviation	Name	CAS number
PFDA	Perfluorodecanoic acid	335-76-2
PFUnDA	Perfluoroundecanoic acid	2058-94-8
PFDoDA	Perfluorododecanoic acid	307-55-1
PFTTrDA	Perfluorotridecanoic acid	72629-94-8
PFTeDA	Perfluorotetradecanoic acid	376-06-7
PFBS	Perfluorobutane sulfonic acid	375-73-5
PFHxS	Perfluorohexane sulfonic acid	355-46-4
PFOS	Perfluorooctane sulfonic acid and its derivatives	1763-23-1
Phenols		
BpA	Bisphenol A	80-05-07
OP	Octylphenol (4-(1,1',3,3'-tetramethylbutyl)- phenol)	140-66-9
4-NP	4-nonylphenol	104-40-5
Pesticides		
Met	Metolachlor	51218-45-2
Met-ESA	Metolachlor ESA	171118-09-5
Met-OA	Metolachlor OA	152019-73-3
Met_SUM	Sum of the above three	
TCZ	Tebuconazole	107534-96-3
Pharmaceuticals		
CBZ	Carbamazepin	298-46-4
DCF	Diclofenac	15307-86-5

Further abbreviations

AD – atmospheric deposition

Dis – dissolved (filtered) concentrations (in river)

EC – electric conductivity

FNU - formazin nephelometric unit, a measure for turbidity

HM – heavy metals, including As

HS – hazardous substances

IWW – industrial wastewater

MWW – municipal wastewater

NTU - nephelometric turbidity unit – another measure for turbidity

PAH – polycyclic aromatic hydrocarbons

PFAS – per- and polyfluoroalkyl substances

PTE – potentially toxic elements

RIV – concentration measured in river water

SPM – suspended particulate matter

Tot – total concentrations (in river)

TSS – total suspended solids

WW – wastewater

WWTP – wastewater treatment plant

1. INTRODUCTION TO THE CONCEPT

1.1. General concept

The innovative measuring concept is based on time and/or space integrated composite sampling as well as stratified sampling focusing on flow, climatological or land use patterns and considering specific pressures in order to derive maximum information out of minimum number of samples. The measurements campaign primarily entailed HS concentrations in surface waters, but focused also on other environmental and anthropogenic compartments relevant for point and diffuse emissions of HS into water bodies.

1.2. Used methods for monitoring in different matrixes

1.2.1. Scope of the monitoring

The scope of the monitoring within the project Danube Hazard m³c covers a wide range of micropollutants, which have been determined in samples from different environmental and anthropogenic matrices by four laboratories. The analysed substances were selected following the most important contaminants set by the Water Framework and its daughter Directives (Directive 2000/60/EC, 2000; Directive 2008/105/EC, 2008; Commission Directive 2009/90/EC, 2009; Directive 2013/39/EU, 2013; Commission Directive 2014/101/EU, 2014) and selected specific contaminants, which are expected to be emitted via different pathways. The substances as well as the responsible laboratories for the analysis are summarized in Table 1-1. The monitoring campaign covered a one-year long period and started in February 2021.

Table 1-1. Substances analysed within the project Danube Hazard m³c, sampled matrices and responsible laboratories

Compound class	Analytes	Analytical laboratory performing the analysis	Sampled matrix
heavy metals and metalloids	Hg, Cd, Cu, Ni, Pb, Cr, Zn, As	Jožef Stefan Institute (JSI)	river water SPM atmospheric deposition wastewater soil
Polycyclic aromatic hydrocarbons (PAH)	16 single PAH (US-EPA-list)	National Administration "Romanian Waters" (NARW)	river water atmospheric deposition wastewater
	16 single PAH (US-EPA-list)	Environment Agency Austria (UBA)	SPM soil
Per- and polyfluoroalkyl substances (PFAS)	PFOS, PFOA ¹	Wessling Hungary Ltd	river water SPM atmospheric deposition wastewater soil
Phenols	4-tert Octylphenol		
	Nonylphenol		
	Bisphenol A		
Pharmaceutical compounds	Diclofenac		
	Carbamazepine		
Biocides	Tebuconazole		
	Metolachlor (incl. Metabolites)		

In addition, all partners responsible for monitoring in pilot regions performed regular sampling and analysis at their own premises to determine the total suspended solids (TSS) content in river samples at the location where turbidity probes were operated. Such sampling has been carried out at low flow but even more importantly at high flow conditions (grab samples or autosampler) to calibrate turbidity against suspended solids. This is essential to be able to estimate reliable suspended particulate matter (SPM) river loads and thus builds a very important basis for the subsequent modelling.

1.2.2. Pilot regions

Seven pilot regions have been involved in the monitoring campaign (Fig. 1-1). They represent a wide variety of conditions both in terms of natural and anthropogenic conditions. River monitoring took place at 20 locations (Table 1-2). There were several stations with very limited anthropogenic influence. For detailed description of the pilot regions see Annex A1: "Deliverable D.T1.2.1 Pilot region descriptions – internal document.

¹ Several other PFAS were analysed as well, but with lower analytical precision resulting in higher level of quantitation (LOQ) and therefore only few measurement results above the LOQ



Fig. 1-1. Location and size of the pilot regions across the Danube River basin.

1.2.3. River sampling

The general concept for river sampling was to collect information on pollutant levels separately for base flow conditions and high flow conditions (see below) as for some pollutants the concentrations (and therefore the loads also) under these conditions are significantly different due to the following effects: sediment bound transport from the catchment, mobilisation of urban sources or diluting dilution of point source emission loads. *Base flow* concentrations were determined by six bi-monthly composite samples created from weekly collected grab samples during base flow to mid flow conditions.

High flow samples were generated as flow proportional event composite samples. Three different approaches were applied depending on the available sampling equipment:

- Automated samplers with multiple bottles were available in the Ybbs and Wulka pilot region. Here the sampling was started by a water level or discharge threshold and then continued in a time proportional manner. At each sampling time step one bottle was completely filled. This resulted in up to 24 l samples per event. In the laboratory the samples were mixed depending on the in proportion to the discharge of the river at the sampling time.
- Automated samplers with a variable frequency peristaltic pump and only one big collection container (home-made setup) were used in the Zagyva and Koppány pilot region. The flow proportional sampling was achieved by an automated adjustment of the peristaltic pump rotation rate based on the actual discharge (measured by water level). No further mixing of samples in the lab was necessary.
- Grab sampling during flood events was performed in the Viseu, Somes and Vit pilot regions. The flow proportional composite sample was generated by mixing of collected samples in the lab in proportion to the discharge of the river at the sampling time.

The triggering of the high flow samples was delivered by flow thresholds. As a general rule, the 10% exceedance level (Q₁₀) flows (and water levels) were set as the threshold based on long term statistics (10 years). Seasonally however, the thresholds were dynamically changed as during dry seasons sometimes meaningful erosive runoff events occurred with lower flood levels, while during the wet season events with higher flows do not mobilise significant amounts of SPM.

To support the interpretation of the results from sampling and allow extrapolation of results from sampled periods into periods without sampling, inline monitoring was implemented at several monitoring sites. The ultimate aim was to derive continuous time series for the parameters total suspended solids (TSS) and discharge (Q) by measuring turbidity and water level. Furthermore, the parameters water temperature, electrical conductivity and pH were measured at some stations.

The overview of the pilot regions and measured parameters and sampling methods is shown in Table 1-2.

Table 1-2 Monitoring stations, measured parameters and sampling methods.

WL – water level; Turb. – turbidity; EC – electric conductivity; Temp – Temperature; SPM – suspended particulate matter; BF – base flow; HF – high flow; grab: grab sampling; auto: autosampler; Phil: Phillips sediment trap.

Pilot region	Subcatchment	Station name	Inline monitored parameters	Sampling	Method
Koppány	Lower	Tamási	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab; HF:– auto; SPM: Phil/auto
	Upper	Törökkoppány	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab; HF: auto; SPM: Phil/auto
Somes	Lower Somesul	Apahida	WL	Base flow, high flow	Grab;sampling for both strata
	Nadas river	Radaia	WL	Base flow, high flow	Grab;sampling for both strata
	Upper Somesul	Upstream Cluj-Napoca	WL	Base flow, high flow	Grab;sampling for both strata
Viseu	Viseu total	Moisei	WL	Base flow, high flow	Grab;sampling for both strata
	Cisla	Baia Borsa	WL	Base flow, high flow	Grab;sampling for both strata
Vit	Vit total	Disevitsa	WL,?	Base flow, high flow	Grab;sampling for both strata
	Beli Vit	Teteven	WL, Turb, Temp.	Base flow, high flow	Grab;sampling for both strata
	Cerni Vit	Cherni Vit	-	Base flow, high flow	Grab;sampling for both strata
Wulka	Wulka main riv.	Schützen am Gebirge	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab; HF: auto; SPM: Phil/auto/grab;
	Eisbach	Osli	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab; HF: auto; SPM: Phil/auto/grab;
	Nodbach	St. Margarethen	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab; HF: auto; SPM: Phil/auto/grab;
Ybbs	Lower Ybbs	Greimpersdorf	WL, Turb, EC, Temp., pH	Base flow, high flow,	BF: grab;HF: auto;
	Urlbach	Krenstetten	WL, Turb, EC, Temp., pH	Base flow, high flow,	BF: grab;HF: auto;
	Upper Ybbs	Opponitz	WL, Turb, EC, Temp., pH	Base flow, high flow,	BF: grab;HF: auto;
Zagyva	Lower/mid Zagyva	Hatvan	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab;HF: auto; SPM: Phil/autos
	Heréd	Heréd	WL, Turb, EC, Temp.,	Base flow, high flow	BF: grab;HF: auto
	Tarján	Kisterenye	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab;HF: auto; SPM: Phil/autos
	Upper Zagyva	Nemti	WL, Turb, EC, Temp.,	Base flow, high flow, SPM	BF: grab;HF: auto; SPM: Phil/autos

1.2.4. Wastewater sampling

Wastewater samples were collected at 15 stations (including mining sites) across the seven pilot regions. Where automated samples were available (Fig. 1-2) samples were collected during one week, each day producing a 24-hour composite sample. Subsamples were mixed proportionate to daily average flow rates retrospectively. Samples were cooled during collection either by built-in cooling (Ybbs, Wulka, Vit) or by passive cooling, using insulated boxes and cooling-packs (Koppany, Zagya, Fig. 1-3). Grab samples were collected at Somes and Viseu pilot regions. A series of grab samples, mixed to composite was delivered at Vit catchments from direct wastewater discharges and WWTP outlets (Fig. 1-4).



Fig. 1-2. Sampler of effluent at WWTP A (left) and at WWTP B (middle & right) at Wulka pilot region



Fig. 1-3. Passive cooling of portable sampler at Balatonlelle WWTP (Koppány)



Fig. 1-4. Mining discharge locations at PL Colbu, Emerik II (Toroioaga) and PL Burloaia in the Viseu pilot regions

1.2.5. Atmospheric deposition sampling

Simple bulk deposition collection was delivered at all locations using large diameter glass or ceramic funnels (Fig. 1-5, Fig. 1-6) to collect enough water during the sampling periods, which were covering a minimum of one month and was collected at least three times in different seasons. Samples collected during precipitation events were immediately collected after the event and poured into a larger container on site. Following the initial negative experiences with breaking of the samples, the consortium decided to change the method of preservation from freezing to cooling. Samples at Wulka and Ybbs pilot region were frozen using specific safety glass containers.



Fig. 1-5. Two examples of the applied simple deposition samplers at Viseu (left) and Zagzyva (right) pilot regions



Fig. 1-6. Atmospheric deposition samplers and transformer at Krenstetten and at Opponitz.

1.2.6. Soil sampling

The primary objective of the sampling was to get representative concentration levels of the soil matrix with relatively cost-efficient harmonised approach. As the sampling was planned to also support emission modelling, the samples were stratified by land use and partially soil type so that a more precise emission inventory could be set up.

The soil sampling therefore targeted all the major land uses on the pilot regions with special focus on agriculture, but forests and pastures were also sampled in a quantity relevant to their share of the total catchment area. Beside land use, soil information was also considered, using soil texture maps and organic matter content maps of the area, where available. Based on land use and soil information, an overlap was created by GIS software (ArcGIS 10.1), resulting a larger number of homogenous spatial units, from which the most dominant ones have been kept for analysis, so that 10 spatial units were formed at the end (Fig. 1-7).

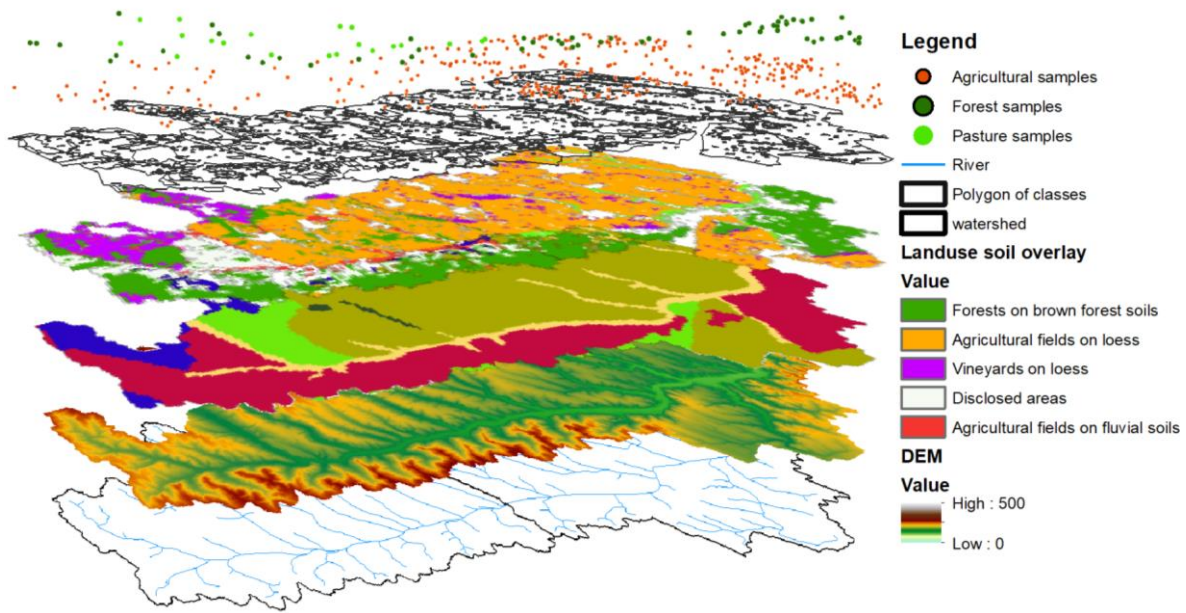


Fig. 1-7. Geospatial information used at Koppány pilot region to provide sampling locations

On each unit, 20 samples have been located with random sampling. All together ca. 200 samples were taken in each pilot region (Fig. 1-8), producing 10 composite samples per pilot region.

The soil sampling has been carried out using hand held auger probes. The samples were collected from the upper 30 cm in case of arable land, and the upper 10 cm in case of pastures and forests. At each spots the samples were taken from further 3-5 subsamples, which were mixed on site. At each spot 50 g of sample were collected into a glass jar, which was held in cool place until delivery to the preparation lab, where the samples were homogenized, sieved with 2 mm sieve and lyophilized.

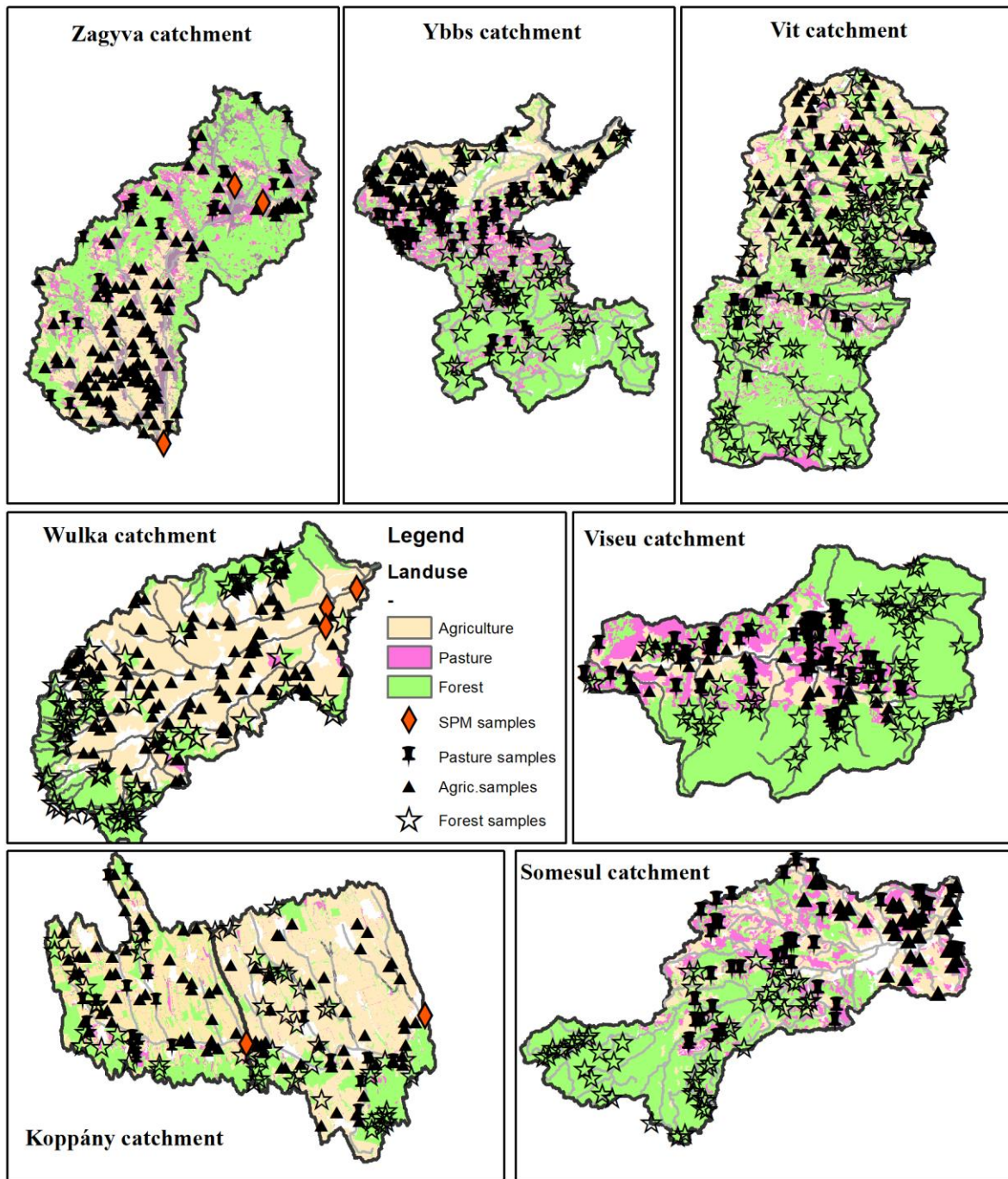


Fig. 1-8. Soil and SPM sampling locations on the pilot regions.

1.2.7. SPM sampling

Suspended particulate matter has been sampled in three pilot regions: the Wulka, Zagyva and Koppány (Fig. 1-8). The sample collection was done at the three river sampling locations at the Wulka, one station was positioned at the Nodbach creek, one at the Eisbach creek and one at the Wulka pilot region outlet. On the Zagyva pilot region samples were collected at three

locations also, at the river sampling points of the Tarján creek, upper Zagyva creek at Nemti, and at the outlet station of the whole pilot region in Hatvan town. Sampling have been done using two approaches: (1) a simple time integrated Phillips sampler (Phillips et al., 2000) and (2) flow-proportional automatic sampler (Hungarian pilot regions: (Budai et al., 2020); Wulka: Endress+Hauser LIQUISTATION CSF48).

Phillips type sampler is a simple design time integrated sampler, constructed from a larger diameter collector pipe and small diameter inlet and outlet nozzles. As the flow velocity drops in the collector pipe, settling takes place. The very finest diameter material is however lost due to the continuous throughflow in the pipe.

The samplers have been placed at two positions: (1) base flow position, when the pipe is continuously collecting the samples (for months) and (2) high flow position, with which floods above selected thresholds are sampled (short events with higher SPM concentration (Fig. 1-9).



Fig. 1-9. Phillips type sampler for high flow condition at Törökkoppány station

The collection methods are different in many ways. The Phillips samplers can be used to collect samples over a long period of time, therefore there is a bigger chance to collect sufficient amounts of sediment especially during low flow periods. Phillips samplers, however cannot be related to concentrations of a certain flood event, as they are not designed to collect all the SPM in the water phase (part of the fine sediments are released through the outlet hole). In other words, samples from a Phillips sampler are suitable to provide representative

concentration of a given substance carried by the suspended matter over longer periods of low flow, but not applicable to provide SPM concentration from a certain flood event. The automatic samplers are suitable to provide exact SPM concentrations of a flood event and therefore link contaminant levels to it. The downside of this collection method is the limited sample volume and therefore the limited sample amount. The latter was used to create sufficient amounts for PTE analysis only, and from some extremely erosive runoff events at Koppány station, sufficient solid matter (> 1 kg) was collected to measure all the investigated substances.

For more information on the sampling methodology, see Annex A2: “Deliverable D.T1.2.2 Methodological approach for the measurements in the pilot regions and final selection of substances – internal document”

2. DESCRIPTION OF ACTIVITIES

2.1. Activities in the pilot regions

2.1.1. River sampling (base flow, high flow)

River sampling have been successfully delivered according to the plans in most pilot regions (Table 2-1). Initially 126 base flow/mid flow composite samples were planned in the seven pilot regions and 12 grab sample in the Reni station of the Danube. In the sampling campaign all planned base flow samples were collected. With regard to the high flow samples the planned sample number was 126, out of which 126 have been collected. There has been a shift of the collected sample numbers, in some pilot regions (Zagyva, Vit) there were not enough high flow events but in other pilot regions there were more samples collected (Wulka, Koppány). All together the sampling was fully delivered according to the plans.

Table 2-1. Summary table for river sampling at the 7 pilot regions.

		Planned (per station)	Achieved	Description
Koppány	Low flow samples (composites)	6+6	6+6	1 composite is made of 8 low flow spot samples
	High flow samples	6+7	12+8	Event composites collected by autosampler Some high flow events were sampled with multiple samples
Zagyva	Low flow samples (composites)	6+6+6+6	6+6+6+6	1 composite is made of 7-8 low flow spot samples
	High flow samples	6+6+6+6	6+8+1+4	Event composites collected by autosampler One high flow event @H2T was sampled with multiple samples
Viseu and Somesul Mic	Low flow samples (composites)	6 campaigns in 5 sections (2 on Viseu and 3 on Somesul Mic)	30 samples (all planned)	1 composite is made of 8 spot samples

		Planned (per station)	Achieved	Description
	High flow samples	6 campaigns in 5 sections (2 on Viseu and 3 on Somesul Mic	6+6+4+3+3	Event composites collected manually
Vit	Low flow samples (composites)	6+6+6	6+6+6	1 composite is made of 8 low flow spot samples
	High flow samples	6+6+6	4+4+3	Event composites collected by grab sampling
Ybbs	Low flow samples (composites)	6+6+6	6+6+6	1 composite is made of 8 low flow spot samples
	High flow samples	6+6+6	8+5+3	Event composites collected by autosampler One high flow event was sampled as grab sample
Wulka	Low flow composite samples	6+6+6	6+6+6	1 composite is made of 7-9 weekly low flow samples
	High flow composite samples	6+6+6	24 (Eisbach 7 + Wulka 10 + Nodbach 7)	High flow events sampled by autosampler. High flow samples are flow-proportional composite sample out of 5-24 samples

2.1.1.1. Lessons learned

High flow grab sampling: The wave during a river high-flow event can last a long period (over 24 hours) depending on the river size and precipitation event characteristics. The duration of the grab sampling should include the peak of the water level and turbidity. To keep them cool, bags with ice cubes can be used. Good preparation for the scene is crucial to stay for the necessary duration: the bare minimum is to have a dry place to stay (for example tent), warm clothes, towels, a flashlight, food and drinking water. The on-line data for water level and turbidity should be constantly monitored. This sampling approach requires a very high personal motivation and availability of the sampling stuff, otherwise only parts of flood events can be sampled.

High flow sampling with peristaltic pump: The sampling speed of the peristaltic pumps can only be varied in a rather narrow range, as the flow velocity needs to be kept high enough to carry the suspended solids but to high pump rates will fill up the sampling container too fast to

sample the whole event. The unpredictability of flood wave size and duration and the narrow range of pump frequency makes it difficult to find a configuration which samples flow proportional a whole event. In the project no bigger flood event could be successfully sampled over the whole duration of the flood wave.

High flow sampling with auto-sampler and time-proportional sampling scheme: The advantage of using a time-proportional sampling scheme is the predictability of the total possible sampling duration. As the event duration is usually easier to predict than the cumulated discharge of an event, the full coverage of events can be more easily achieved. Nevertheless, the choice of the right sampling frequency needs a good knowledge about the typical event characteristics at the river, to find the right compromise between having enough samples to generate a flow proportional composite sample with enough volume for analysis of all compounds (several litres may be needed) from short events and being able to sample long events until the end of the flood wave. In DHm³c, several flood events were successfully sampled with this setup at several stations.

Considering autosamplers and in particular vacuum pumps, physical stress caused the vacuum to drop, causing sampling volume problems. Frequent cleaning was necessary. Ice formation during winter is also an issue. Regarding peristaltic pumps: Clogging occurred in some rare cases. Using filters may cause further problems as they are prone to be completely jammed with algae. Minimum sample velocity to be set in order to avoid sediment deposition in pipes. In Hungarian pilot regions 1.5 l/min discharge proved to be adequate with 6 mm pipe diameter. The remote access to the sampler via web interface was very useful to check the past sampling and reconfigure the sampling program according the current or predicted hydrological conditions. This is a very much advised feature. We experienced some problems concerning insect infestation in the sampler housing were mostly solved by installing traps. Pipe heating was necessary at the Nodbach station to avoid ice in the suction hose, which leads to damage of the vacuum system. This was not the case at the two other stations, where the suction hose was shorter and the river temperature higher due to higher wastewater influence.

The installed relays for emergency shutoff of the autosamplers (Endress+Hauser) in the Wulka pilot region were never needed, the ones for the air compressor were used in one case when air pressure was lost caused by some air leakage.

2.1.2. Suspended sediment sampling in rivers

River suspended particulate matter (SPM) was collected at only three pilot regions as this was not the main focus of the project, however fine suspended particles carry a lot of interesting information with regard to catchment transport processes. In the Wulka pilot region, the sample collection was carried out at three river monitoring locations namely in the Wulka river at the catchment outlet and in its two tributaries Nodbach and Eisbach. In the Zagyva pilot region, samples were collected at three locations also, at the river sampling points of the Tarján creek, upper Zagyva creek at Nemti, and at the outlet station of the whole catchment in Hatvan town. SPM samples within the Koppány pilot region were collected at two locations,

both being in the Koppány river, one at the outlet point and one at Törökkoppány, a station at the outlet of the more hilly and natural upper part of the watershed (Fig. 2-1, Fig. 2-2).



Fig. 2-1. SPM samples from the autosampler (left) and the Phillips sampler (right)



Fig. 2-2. Phillips sampler at Wulka station and a 20 L glass collection container.

2.1.2.1. *Lessons learned*

- Phillips sampler device: Phillips sampler are easy built but installation in riverbed can be tricky.
- Sample handling: Decanting the Phillips sampler on site needs two persons, and a large volume sample holder. It is important to dissolve the SPM by swirling to obtain the whole sample.
- Autosampler: at high flow events also sufficient amount of sample was collected for all analysis (1-2 kg). This is site specific. Recommended for locations with erosive runoff events.

2.1.3. Atmospheric deposition collection

Atmospheric deposition samples were collected at 15 stations within the 7 pilot regions. 56 samples were planned and all planned samples were collected at all locations. In some stations further samples were collected (e.g. Nodbach sub catchment), resulting in a total number of 64 samples (Table 2-2).

Sampling method: simple design bulk deposition samplers were used, consisting of glass or ceramic funnels and glass collector bottles. Bottles were covered with aluminium foils to cover the sample from direct sunlight. Samples were collected after each rain events and stored in dark, cold conditions. In some locations the samples were frozen, using precautionary methods to lose samples if glass containers break.

Table 2-2 Planned and achieved sample numbers for bulk deposition sampling

Pilot region	Station	Code	Planned	Achieved
Wulka	Oslip	AWO	4	4
	Wiesen	AWW	4	4
	St. Margarethen	AWN	0	5
Ybbs	Headwater	AYH	4	5
	Lower Ybbs	AYL	4	5
Vit	Cherni		4	4
	Disevitsa upstream		4	4
Koppány	Headwater		4	5
	Tamási		4	4
Zagyva	Hatvan		4	4
	Nemti, Maconka		4	4
Viseu	Viseu canton		4	4
	HS Csla		4	4
Somesul Mic	Somes Water C.		4	4
	Cluj SGA		4	4
		SUM	56	64

2.1.3.1. *Lessons learned*

During the atmospheric deposition sampling campaigns, partners reported the following lessons.

- Two 5 l bottles laminated safety glass bottles have burst (without sample loss) if too much sample (e.g. 2 l) was frozen too quickly. A local person executing daily probing after rainfall events extremely reduces travelling efforts and gives daily insight into the operability of the samplers.
- Much organic matter and insect deposition were experienced, which in some case caused the elevation of electrical conductivity (i.e. the total ion content) of the collected sample.
- Freezing water in glass bottles is not practical due to several glass breaks during the campaign.
- A glass filter covering the funnel outlet to hold back coarse material like leaves can be skipped as it is relatively expensive and things up to 4 mm will pass through anyway and larger parts like leaves will be stopped by the funnel stem anyhow.
- Working with citizen scientists requires clear communication and tasks, easy to use stations and some flexibility. A protocol for recording the sampling is essential.

2.1.4. Wastewater sampling

All together 72 wastewater samples have been foreseen, out of which 34 raw wastewater and 38 treated wastewater samples were planned (Table 2-3, Table 2-4). The planned numbers have been slightly exceeded as 44 raw waste/mining water samples and 34 treated waste/mining water samples were collected. The number of industrial samples were somewhat lower as some of the operators were not responsive upon approach. All six planned mining site samples were collected, while municipal wastewater samples have been exceeded in several locations. The extra sample numbers were covered by foreseen spare samples, that were initially included in the budget.

Table 2-3. Planned and collected raw waste/mining water samples

Pilot region	Station	Type	Code	Planned	Achieved
Wulka	Wulka - A WWTP	Municipal	AWA	3	6
Ybbs	Lower Ybbs	Municipal	AYA	3	3
Vit	Disevitsa upstream	Municipal	BVT	0	5
Koppány	Balatonlelle WWTP	Municipal	HKL	3	4
Zagyva	Salgotarjan WWTP	Municipal	HZS	3	3
	Matraterenye	Municipal	HZM	0	1
Viseu	Baia Borsa	Municipal	RVB	3	3

Pilot region	Station	Type	Code	Planned	Achieved
	PL Gura Baii	Mining site	RV1	2	2
	PL Colbu	Mining site	RV2	2	2
	PL Burloaia	Mining site	RV3	2	2
	PL Borsa	Mining site	RV5	2	2
	Colbu Mine Gallery	Mining site	RV6	2	2
Somesul Mic	Cluj	Municipal		3	3
	Apahida	Municipal		3	3
	Jucu	Industrial		3	3
			SUM	34	44

Table 2-4. Planned and collected treated waste/mining water effluents

Pilot region	Station	Type	Code	Planned	Achieved
Wulka	Wulka - A WWTP	Municipal	AWA	3	3
	Wulka - B WWTP	Municipal	AWB	3	3
Ybbs	Lower Ybbs	Municipal	AYA	3	3
	Lower Ybbs	Industrial	AYB	3	0
Vit	Disevitsa upstream	Municipal	BVT	3	1
Koppány	Balatonlelle WWTP	Municipal	HKL	3	3
	Tamasi	Industrial	HKT	0	0
Zagyva	Apc WWTP	Industrial	HZA	3	3
	Salgotarjan WWTP	Municipal	HZS	3	3
	Matraterenye	Municipal	HZM	0	1
Viseu	Baia Borsa	Municipal	RVB	3	3
	Emerik II (Toroioaga)	Mining site	RV4	2	2
Somesul Mic	Cluj	Municipal		3	3
	Apahida	Municipal		3	3
	Jucu	Industrial		3	3
			SUM	38	34

2.1.4.1. *Lessons learned*

During the wastewater sampling campaigns, following lessons were reported by project partners to be learnt.

- The instrument used in Hungary (WaterSam Porti mobile device) caused some concerns, as in some case, malfunction of the device was experienced, causing inadequate amount of samples. Daily check by local personnel is strongly advised. Instrument with built in cooling is much recommended.
- Vit pilot region: during grab sampling a lot of splash of wastewater is created. It is necessary to wear good protective clothing, also to use a long enough stick.
- Ybbs: Uncertainties caused by rain events can cause problems, if dry weather sampling is preferred. Daily check by local personnel is strongly advised. Organization of sampling industrial wastewater must be prepared over a longer period. Involving state officials with appropriate jurisdiction could increase the chances of obtaining a sampling permit.
- Wulka: Providing for each day a separate bottle and let the project partner do the mixing of the composite sample was preferred by WWTP operators. Working with third party requires clear communication and tasks, practical sampling strategies and some flexibility. A protocol for recording the sampling is essential.

2.1.5. Soil sampling

Soil sampling campaigns were planned at all the seven pilot regions. The sampling campaign was delivered during the spring and summer 2021. Sampling took place in one-two weeks and took a significant effort from all partners. In most cases partners delivered the sampling themselves, in some cases subcontractors were hired to collect samples (NARW, UBA). At all sites all the 10 planned composite soil samples have been collected (Table 2-5).

Table 2-5. Soil samples in the pilot regions. AGR: agricultural; FOR: forest; PAS: pasture; VIN: vineyard; SCR: scrubland. All planned samples were achieved.

Country	Pilot region	AGR	FOR	PAS	other
Austria	Wulka	4	3	1	VIN: 2
	Ybbs	4	5	1	
Hungary	Koppány	6	3	1	
	Zagyva	6	3	1	
Romania	Somesul Mic	5	3	2	
	Viseu	2	3	3	SCR: 2
Bulgaria	Vit	4	2	4	
SUM		31	22	13	4

Sampling locations have been selected by random sampling as described above. The presented locations were based on land use data, that is not too accurate, especially at the

boarders, sometimes outdated, sometimes biased during the processing of the original remote sensing data. Careful review of each location was necessary using up to date satellite images. Even with careful design, the locations were sometimes inaccessible, therefore some of the points were necessary to be replaced within the spatial unit (Fig. 2-3).



Fig. 2-3. Pürckhauer auger type soil sampler used in most pilot regions.

2.1.5.1. Lessons learned

Regarding the soil sampler instrument: in compacted dry soil, the sampling was almost impossible. Rubber hammer was used. In forest and tilled agricultural soils the sampling was easy. Main problems occurred on grasslands and in places where the plantation was already high. In these places the soil was heavily compacted in some cases. Auger type soil sampler instrument: Due to the rotation motion for extracting the soil sample, the auger soil sampler met no difficulties even over stiff and compacted land.

We faced occasional site access problems (physical, land owners). Owners were helpful in most cases and allowed the sampling. 2 forest samples in the Vit pilot region a group of hunters was met. It is a good idea to check the hunting season duration and speak with local hunting parties in advance. If a vehicle is left on a side road for a long period of time, a note with a phone number on the front panel should be left – in one case our car was reported as „abandoned in the wild” to the police authorities from passing by a tractor driver. Access to soil sampling points is extremely important. Often geospatial analysis using GIS methods can determine the most accessible locations of these points. However, this analysis does not consider whether the land is fenced or not. Another aspect to be mentioned here is the spatial resolution of the maps used (digital terrain model, road maps, and land use map), a low resolution of the input data can wrongly determine a point with a different land use than the real one. That is why in the maps made for the location of the sampling points the type of land use was also mentioned.

Regarding sample processing, soil sub-samples were collected in a bucket and homogenized by physical defragmentation. Immediately afterward 100 grams were measured and placed in a glass jar on site. In order for the scale to work properly, a flat and hard surface is needed – the measurements can be done in the trunk of a car. Soil samples were collected in a ceramic tray and homogenized by physical defragmentation of the samples. Soil was mixed with spoon several times, then adequate amount was measured to the collector glass jar. Very dry samples were hard to defragment. Prückhauer sampler with relatively small diameter (13 mm) was used to reduce sample amount. The benefit was that samples could be used in their fully amount and no homogenisation, mixing or separation was necessary in the field, therefore the risk of bias due to incomplete mixing or inhomogeneous splitting of sample and cross contamination due to mixing and separation was excluded.

2.1.6. Inline river monitoring

One cornerstone of the monitoring program was to complement the sampling with inline monitoring at the key points of the pilot regions to get continuous information about important parameters for load calculation. Load calculation were serving the goal to validate catchment emission models that were applied on all pilot regions within the work package T2 of the project. The measured parameters were *water level and/or velocity, temperature, electrical conductivity and turbidity*. Sensors (and automated samplers) were installed at the following locations:

Pilot	Subcatchment	Water level sensors	Conductivity probe	Temperature probe	Turbidity probe	Automated sampler
Koppány	Headwater	✓	✓	✓	✓	✓
	Outlet	✓	✓	✓	✓	✓
Somesul Mic	Apahida, Outlet	✓	✓	✓	✓	X
	Cluj-Napoca, Somesul Mic	✓	✓	✓	✓	X
	Radaia, Headwater	✓	✓	✓	✓	X
Viseu	Moisei	✓	✓	✓	✓	X
	Borsa	✓	✓	✓	✓	X
	Cisla	X	X	X	X	X
Vit	Disevitsa, Vit	✓	X	✓	✓	X
	Beli Vit	✓	X	✓	✓	X
	Cherni Vit	✓	X	✓	✓	X
Wulka	Nodbach	✓	✓	✓	✓	✓
	Eisbach	✓	✓	✓	✓	✓
	Wulka	✓	✓	✓	✓	✓

Pilot	Subcatchment	Water level sensors	Conductivity probe	Temperature probe	Turbidity probe	Automated sampler
Ybbs	Greimpersdorf, Outlet	✓	✓	✓	✓	✓
	Kernstetten, Url	✓	✓	✓	✓	✓
	Opponitz, headwater	✓	✓	✓	✓	✓
Zagyva	Upper Zagyva	✓	✓	✓	✓	✓
	Tarjan-cr.	✓	✓	✓	✓	✓
	Hered-cr.	Velocity meter	✓	✓	✓	✓
	Zagyva outlet	✓	✓	✓	✓	✓

The continuous operation of the inline monitoring took a lot of effort from the partners, including sensor cleaning, data collection, solving data transfer problems, maintenance etc. Installation of the instruments also proved to be challenging in most cases, typical problems were to provide sensor positioning and fixing that is representative and flood resistant in the same time. Each location provided different possibilities, construction teams had to adapt to local conditions. Examples from three stations can be seen in Fig. 2-4, Fig. 2-5, Fig. 2-6. Another typical issue was to lay cables in a safe way, which was either solved by digging the cables underground or to install the cables in protection pipes.

The other major part of the inline monitoring was the data collection and data processing. Large amount of data has been collected (almost 2 years of continuous data, with 1-10 min interval).



Fig. 2-4. Autosampler and sampling setup at Eisbach station



Fig. 2-5. Autosampler and probe arrangement at Opponitz station (Upper Ybbs)



Fig. 2-6. Solar panels and wind turbine installed in Hungarian stations to provide electricity supply for sensors and autosamplers (left: Nemti, Zagyva, right: Törökkoppány, Koppány)

2.1.6.1. Lessons learned

Regarding inline measurements, during conductivity measurements, temperature and water level measurements in general were stable, the turbidity probes were susceptible to algae growth and precipitation of mineral coatings. Regular cleaning with citric acid is necessary to prevent this. In winter, early spring and autumn, wiper function or pressurized air cleaning was sufficient to maintain a proper functioning of measurement by the turbidity-probes for two weeks and even more, in late spring and summer the cleaning was partly necessary every week to avoid measurement drift. Inductive conductivity probes are generally easy to maintain and work reliably, but biofilm growth on the surface of the instrument reduce the measured conductivity. Regular cleaning is necessary if precise measurements are needed. Installation in too shallow water leads to measurement disturbance by floating debris or too low immersion depth of probes during low flow periods.

Regarding power supply and data transfer, direct data transfer to the maintaining institutions is advantageous, as problems can be notified earlier and status of sampling and probes can be checked without the need to travel to the station. Data transfer via GSM and LORA-Wan were used. GSM connections have a higher energy demand than LORA-Wan and are therefore suitable where connection to the power grid is available. Signal transfer via GSM have been lost several times, due to weak signal strength. Antenna have been installed to improve data

transmission, but it did not solve the problem entirely. Data logging at side is a must for at least a month to provide backup for the data not transmitted. Power supply: If a connection to the power grid is available it should be used, as it makes the measurement setup much more reliable and easier to design. Solar panels and wind turbines: The charging of the batteries during reduced sunlight condition can be insufficient to keep the batteries fully loaded. Added wind turbine (especially at windy locations) produces extra support for the batteries but during winter regular check on battery levels is necessary and they needed to be replaced every now and then. From this point of view the good sizing of the electrical system is crucial, just as the online data transfer of battery voltage.

Further details regarding sampling can be found in Annex A3: "Description of monitoring activities at 7 pilot regions."

2.2. Laboratory work

2.2.1. Preservation of samples

Sample preservation was initially determined by the consortium for all sampled matrix and for all samples. The methods were described in the Standard Operations Procedures (SOP) document that was revised a few times during the project when alterations of the methods were needed (See final version of the document in Annex A4: "Standard Operating Procedure – Protocol for sampling, storage and transport during monitoring in the pilot regions – Internal document"). Table 2-6 summarizes the applied preservation applied for the different substance groups and matrices.

Preservation of samples during collection:

River samples were kept in cold condition during transport using cooling packs and insulation boxes. Filtration and acidification were carried out in lab right after sample transportation (within 4 hours after collection).

Wastewater samples were collected in cooled instruments. Cooling was either made by active or passive cooling (insulation boxes and cooling packs). Wastewater samples were collected daily or bi-daily. Samples were stored in cold (< 4°C) and dark conditions until the total weekly samples were collected. Samples were mixed proportionally to the measured discharge right after the final amount of sample was collected. Preservation was applied as described in Annex A4: "Standard Operating Procedure – Protocol for sampling, storage and transport during monitoring in the pilot regions – Internal document".

Atmospheric deposition samples were collected throughout a month or for several months. To preserve the samples, it was decided in the consortium that freezing would be the best procedure, but also it is required to use large volume (10 l) glass bottles to avoid substance loss by ad-/absorption in/to plastic. The initial negative experiences of glass breaks forced out to change the preservation from freezing to cooling in dark conditions (< 4°C).

Soils and suspended sediments: Following sampling, the samples were kept in dark, cold conditions until delivery to the UBA lab, where samples were homogenized and lyophilized to preserve contaminants.

Table 2-6. Sampling, preservation and storage information for the liquid phase samples

Parameter	River base flow and high flow	Wastewater (raw and treated)	Atmospheric deposition
Metals and Hg	Glass bottle for collection, 0.16 l of whole water, 0.5 l Teflon bottle, 0.16 ml of HCl s.p. (30%) or 0.16 ml of HNO ₃ s.p. (65%) (add proportional aliquot after weekly addition of fresh sample) <i>Frozen samples</i>	Glass bottle for collection, 1 l of whole water in 1 l PE bottle, mL ml of HCl s.p. (30%) or 1.0 ml of HNO ₃ s.p. (65%) <i>Frozen samples</i>	Glass bottle for collection, 0.5 l of whole water in 0.5 l Teflon bottle, 0.5 ml of HCl s.p. (30%) or 0.5 ml of HNO ₃ s.p. (65%) <i>Frozen samples</i>
Metals (for analysis in filtered samples)	0.16 l of filtered water in 0.5 l Teflon or PE bottle, 0.16 ml of HCl s.p. (30%) or 0.16 ml of HNO ₃ s.p. (65%) (add proportional aliquot after weekly addition of fresh sample) <i>Frozen samples</i>	No dissolved sample	No dissolved sample
16 PAH	1 l of whole water in amber glass bottle. The inner surface of plastic cups must be covered with aluminium foil to avoid contamination from plastic material.	1 l of whole water in amber glass bottle. The inner surface of plastic cups must be covered with aluminium foil to avoid contamination from plastic material. <i>Samples to be kept in cold condition and</i>	1 l of whole water in amber glass bottle. The inner surface of plastic cups must be covered with aluminium foil to avoid contamination from plastic material.

Parameter	River base flow and high flow	Wastewater (raw and treated)	Atmospheric deposition
	<i>Samples to be kept in cold condition and transported within 48 hours</i>	<i>transported within 48 hours</i>	<i>Samples to be kept in cold condition and transported within 48 hours</i>
PFOS, PFOA	Collected in glass bottle, stored in 250 ml PE bottle, <i>frozen</i> .	Collected in glass bottle, stored in 250 ml PE bottle, <i>frozen</i> .	Collected in glass bottle, stored in 250 ml PE bottle, <i>frozen</i> .
Diclofenac, Carbamazepine, Bisphenol A	Collected in glass bottle, stored in 1 l dark glass, cooling (2-4 °C)	Collected in glass bottle, stored in 1 l dark glass, cooling (2-4 °C)	Collected in glass bottle, stored in 1 l dark glass, cooling (2-4 °C)
4-tert-Octylphenol, Nonylphenol	Collected in glass bottle, stored in 1 l dark glass, cooling (2-4°C)	Collected in glass bottle, stored in 1 l dark glass, cooling (2-4°C)	Collected in glass bottle, stored in 1 l dark glass, cooling (2-4°C)
Metolachlor (incl. Metabolites), Tebuconazole	Collected in glass bottle, stored in 2x40 ml EPA vial., cooling (2-4°C)	Collected in glass bottle, stored in 2x40 ml EPA vial., cooling (2-4°C)	Collected in glass bottle, stored in 2x40 ml EPA vial., cooling (2-4°C)

2.2.2. Description of analytical methods

2.2.2.1. Analytical procedures of potentially toxic elements

Analysis were carried out by the Jožef Stefan Institute in Ljubljana. All the analyses were performed in triplicate.

Table 2-7. Laboratory methods, LOD and LOQ values applied for determination of HM in aqueous matrices. Unit of LOQ and LOD values is ng/l for Hg and µg/l for the rest of the compounds. LOD and LOQ values refer to RIV Tot, WW samples. For AD and RIV Dis, values 10-times lower apply. All methods are accredited.

Abbreviation	Name of determinand	CAS number	Method of analysis	Norm applied	LOQ	LOD
Cr	Chromium	7440-47-3	ICP-MS	ISO 17294-2:2016	0.2*	0.06*
Ni	Nickel	7440-02-0	ICP-MS	ISO 17294-2:2016	0.2*	0.06*
Cu	Copper	7440-50-8	ICP-MS	ISO 17294-2:2016	0.433*	0.13*
Zn	Zinc	7440-66-6	ICP-MS	ISO 17294-2:2016	2.33*	0.7*
As	Arsenic	7440-38-2	ICP-MS	ISO 17294-2:2016	0.333*	0.1*

Abbreviation	Name of determinand	CAS number	Method of analysis	Norm applied	LOQ	LOD
Cd	Cadmium	7440-43-9	ICP-MS	ISO 17294-2:2016	0.133*	0.04*
Pb	Lead	7439-92-1	ICP-MS	ISO 17294-2:2016	0.5*	0.15*
Hg	Mercury	7439-97-6	CVAAS	ISO 17294-2:2016	2.7*	0.8*

2.2.2.1.1. River water

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

LODs were calculated as the concentration providing a signal equal to 3s of the blank sample. To calculate the LODs, 8 blank samples were analysed by ICP-MS.

2.2.2.1.2. Atmospheric deposition

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

2.2.2.1.3. Wastewater samples

For the analysis of wastewater, 2 ml of hydrogen peroxide, 3 ml of nitric acid and 1 ml of hydrochloric acid were added to 10 ml of sample and contents was subjected to microwave assisted digestion (ramp to temperature 30 min, T=90 °C, hold 5 min, ramp to temperature 10 min, T=140 °C, hold 5 min, ramp to temperature 10 min, T=150 °C, hold 15 min, cool 30 min). After digestion, samples were 10-times diluted and concentrations of PTEs determined by ICP-MS (SIST EN ISO 17294-2:2017).

2.2.2.1.4. Soil and SPM

Approximately 0.2 g of lyophilized soil, sediment or SPM sample was weighed into a Teflon vessel and 2 mL of hydrogen peroxide, 4 mL of nitric acid, 1 mL of hydrochloric and 2 mL of hydrofluoric acid were added. The contents were subjected to microwave assisted digestion (ramp to temperature 20 min, T=140 °C, hold 5 min, ramp to temperature 15 min, T=200 °C, hold 60 min, cool 30 min). After digestion, 12.5 ml of boric acid (4% aqueous solution) was added to dissolve fluorides and complex the excessive boric acid and microwave assisted digestion was applied again (ramp to temperature 15 min, T=140 °C, hold 2 min, ramp to temperature 15 min, T=180 °C, hold 30 min, cool 30 min).

After digestion, the contents were transferred into 30 ml graduated PE tubes and concentrations of PTEs (Cr, Ni, As, Cu, Zn Cd and Pb) were determined by ICP-MS in 100-times diluted samples (SIST EN ISO 17294-2:2017).

2.2.2.2. Polycyclic aromatic hydrocarbons (PAH)

2.2.2.2.1. Soil and sediment

Analysis of PAH substances from soil and sediment have been carried out by laboratory of the Environment Agency Austria (UBA, Umweltbundesamt GmbH).

Preparation: Homogenisation and sieving on a 2mm sieve to remove larger fractions.

Preservation: After sieving the samples were dried using lyophilisation method at UBA lab.

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

2.2.2.2.2. River water and atmospheric deposition

Analytical methods for water phase have been carried out by the laboratory of the NARW.

Table 2-8. Laboratory methods, LOD and LOQ values for determination of PAH in aqueous samples.

Unit of LOQ and LOD values is ng/l. All methods are accredited. The 16 US-EPA PAH determined were CAS_91-20-3_Naphthalene, CAS_83-32-9_Acenaphthene, CAS_208-96-8_Acenaphthylene, CAS_86-73-7_Fluorene, CAS_120-12-7_Anthracene, CAS_85-01-8_Phenanthrene, CAS_206-44-0_Fluoranthene, CAS_129-00-0_Pyrene, CAS_56-55-3_Benzo(a)anthracene, CAS_218-01-9_Chrysene, CAS_205-99-2_Benzo(b)fluoranthene, CAS_207-08-9_Benzo(k)fluoranthene, CAS_50-32-8_Benzo(a)pyrene, CAS_53-70-3_Dibenzo(a,h)anthracene, CAS_191-24-2_Benzo(g,h,i)perylene, CAS_193-39-5_Indeno(1,2,3-cd)pyrene.

Sampled matrix	Abbrev.	Name of determinand	CAS number	Method of analysis	Norm applied	LOQ	LOD
AD, RIV	PAH	16 PAH		HPLC-FLD	ISO 17993:2004	1.6	0.5
WW	PAH	16 PAH		GC-MS	SM 6440C:2012	10	5

The following reference **Standard method** was used in the analysis: SR EN ISO 17993:2004 that transposes EN ISO 17993:2003 (EN ISO 17993:2003 Water Quality – Determination of 15 polycyclic aromatic hydrocarbons (PAH) in water by HPLC with fluorescence detection after LLE (ISO 17993:2002) and internal Laboratory Specific Procedure PSL 10.1, Edition 03, Revision 01;

Samples have been prepared by two methods:

- a. SPE (solid -phase extraction): STRATA PAH 1.5 g/ 6 ml Tubes
- b. LLE (liquid – liquid extraction): n-hexane

High Performance Liquid Chromatography with Fluorescence and Diode Array Detector (HPLC-FLD/DAD) was used by Shimadzu Prominence HPLC-FLD with Fluorescence Detector RF-10AXL. Nucleosil 100-5 C18 PAH columns have been used (L= 250 mm, internal diameter = 4.6 mm, stationary phase C18, particle size 5,0 µm).

2.2.2.2.3. Wastewater

Analytical methods for wastewater have been carried out by the laboratory of the NARW.

For wastewater samples the following reference standard methods have been used: SM 6440C:2012 and internal Laboratory Specific Procedure PSL 03, Edition 04, Revision 02. The analysis has been carried out using Gas-Chromatography with Mass Detector (GC-MS) (Shimadzu – QP 2010 Plus, with Selective MS detector QP 2020).

Samples have been prepared with LLE (liquid – liquid extraction) method using n-hexane solvent.

2.2.2.3. Organic substances

Analysis were carried out by Wessling Hungary Ltd.

Table 2-9. Laboratory methods, LOD and LOQ values applied for the determination of PFAS, phenols, pesticides and pharmaceuticals.

Unit of LOQ and LOD values ng/l. LOD and LOQ values refer to AD and RIV samples. For WW, values 10 times higher apply except for OP and 4-NP where the values in the table hold for AD, RIV and WW samples. All methods are accredited except for PFPeA.

**The determined PFAS are CAS_2706-90-3_Perfluoropentanoic acid, CAS_307-24-4_Perfluorohexanoic acid, CAS_375-85-9_Perfluoroheptanoic acid, CAS_375-95-1_Perfluorononanoic acid, CAS_335-76-2_Perfluorodecanoic acid, CAS_2058-94-8_Perfluoroundecanoic acid, CAS_307-55-1_Perfluorododecanoic acid, CAS_72629-94-8_Perfluorotridecanoic acid, CAS_376-06-7_Perfluorotetradecanoic acid, CAS_375-73-5_Perfluorobutane sulfonic acid, CAS_355-46-4_Perfluorohexane sulfonic acid.*

***The determined compounds are CAS_51218-45-2_Metolachlor, CAS_171118-09-5_Metolachlor ESA, CAS_152019-73-3_Metolachlor OA.*

**The first norm refers to AD and RIV, the second to WW.*

Abbrev.	Name of determinand	CAS number	Method of analysis	Norm applied	LOQ	LOD
PFOS	Perfluorooctane sulfonic acid	1763-23-1	HPLC-MS/MS	WBSE-121:2019	0.15	0.04
PFOA	Perfluorooctanoic acid	335-67-1	HPLC-MS/MS	WBSE-121:2019	0.15	0.04
PFXA, PFXS	PerfluoroX acid*		HPLC-MS/MS	WBSE-121:2019	2	0.6
Met	Metolachlor**		HPLC-MS/MS	WBSE-93:2020, WBSE-123:2016 ⁺	10	3
TCZ	Tebuconazole	107534-96-3	HPLC-MS/MS	WBSE-93:2020, WBSE-123:2016 ⁺	10	3
CBZ	Carbamazepin	298-46-4	HPLC-MS/MS	WBSE-124:2019	1	0.3
DCF	Diclofenac	15307-86-5	HPLC-MS/MS	WBSE-124:2019	1	0.3
BpA	Bisphenol A	80-05-7	HPLC-MS/MS	WBSE-124:2019	10	3
OP	Octylphenol	140-66-9	GC-MS	ISO 18857-1:2007	10	5
4-NP	4-nonylphenol	104-40-5	GC-MS	ISO 18857-1:2007	10	3

There were four substance groups analysed, therefore a short description is given here.

2.2.2.3.1. Preparation of water samples

500 cm³ water sample were weighted into an extraction funnel, the pH was set to 2 using 98% sulphuric acid or with 37% hydrochloric acid, then 50 µl surrogate standard solution was added and extracted 3 times using 10-10-10 cm³ dichloromethane on a shaker (duration: 10 minutes, at 300 rpm). After phase separation extracts were collected into an Erlenmeyer-flask and if needed it was covered with a watch glass or aluminium-foil and stored in a dark place (max. 24 hours).

The extracts were dried on anhydrous sodium sulphate and then the drying agent was washed multiple times into a 20 cm³ head-space vial. Then the sample were concentrated to 1 cm³ at 35 °C. The extract was transferred to an amber coloured autosampler vial using automatic pipettes and 20 µl internal standard solution was added.

2.2.2.3.2. Preparation of soil-, sediment- and sludge samples

10 g of sample were measured into a 40 cm³ EPA vial. For the soil samples approx. 2 g of anhydrous sodium-sulphate, (more if necessary) 10 cm³ acetone, 100 µl 98% sulphuric acid (or 100 µl 37% hydrochloric-acid) and 50 µl surrogate standard solution were added, then the samples were shaken on a shaker for 10 minutes (300 rpm). Samples were extracted 3 times using 10-10-10 cm³ dichloromethane on a shaker (duration: 10 minutes, at 300 rpm). The extracts were collected into Erlenmeyer-flasks and, if needed, covered with watch glass or aluminium foil and stored in a dark place (for max. 24 hours).

The extracts were dried on anhydrous sodium sulphate and then the drying agent was washed multiple times into a 20 cm³ head-space vial. Then the sample were concentrated to 1 cm³ at 35°C. The extract was transferred to an amber coloured autosampler vial using automatic pipettes and 20 µl internal standard solution was added.

Selective ion monitoring (SIM) was used for MS analysis. The target ions and qualifier ions from the table are detected the specified times from the table (these values can differ from the ones seen here depending on the length and type of the column). Rxi-5SilMS (30 m × 0.25 mm × 0.25 µm) columns or others suitable columns were used, with Helium gas 5.0 with 1.1 cm³/min constant flow. Transfer line temperature was minimum 315°C.

For detailed description, see Annex A5: "Laboratories' analytical reports".



Fig. 2-7. The used GC-MS equipment

For detailed description on the analytical procedures, see Annex A5: “Laboratories’ analytical reports”.

2.2.2.3.3. Determination of PFAS

Surface water and wastewater samples were prepared by solid phase extraction. Wastewater samples were diluted by a factor of 10 using deionized water. Mixed mode SPE (Solid Phase Extraction) cartridges were used. Large volume of sample was loaded. The eluate was evaporated and the residue was dissolved in methanol/water mixture. An aliquot of the re-dissolved residue was transferred to an autosampler vial and was analysed.

Soil samples were spiked with internal standards and extracted with water. The mixture was centrifugated and the supernatant was concentrated by SPE method as was done for the water sample.

The PFAS compounds were measured in negative ionization mode by HPLC coupled triple-quadrupole mass spectrometer (Fig. 2-8).

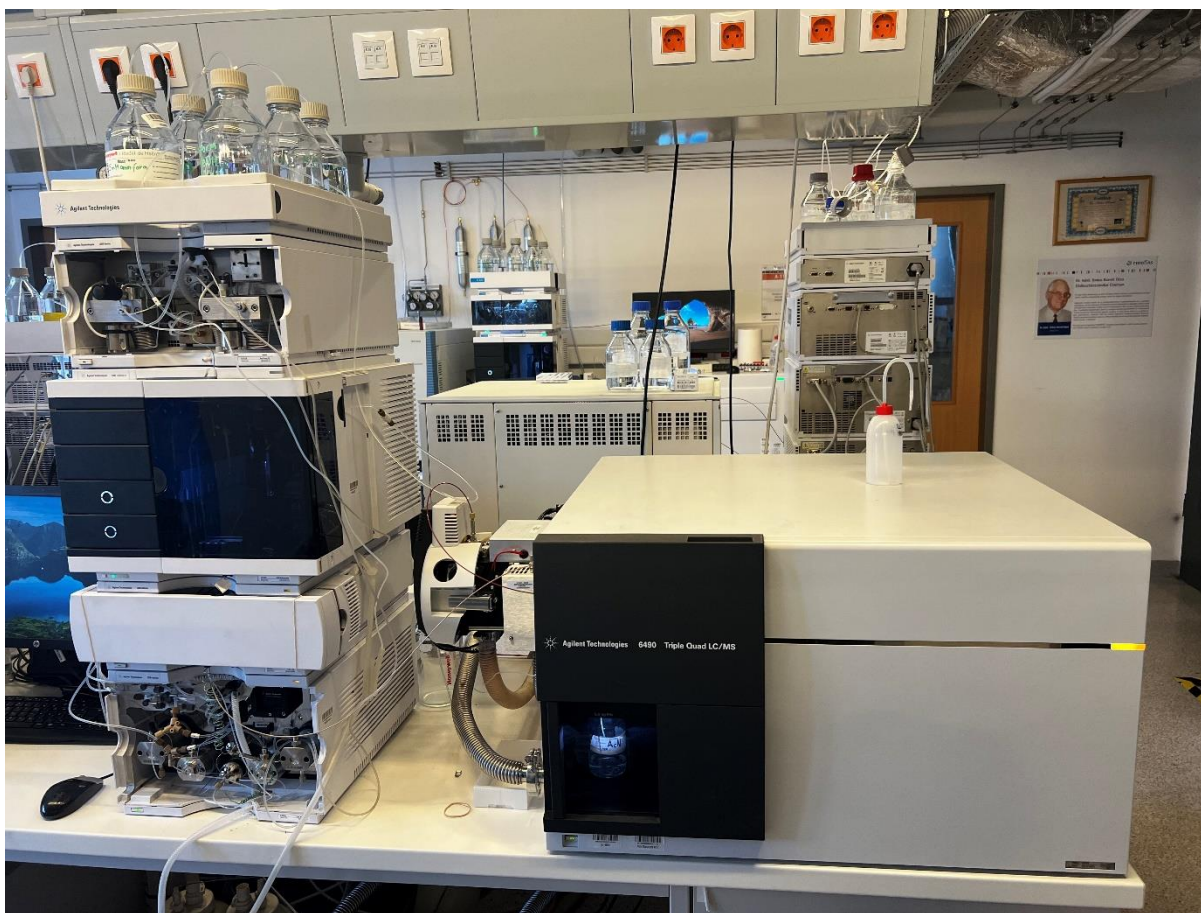


Fig. 2-8. HPLC-MS for the analysis of PFAS, pesticides and pharmaceutical residues (Wessling laboratory)

2.2.2.3.4. Determination of octyl- and nonylphenols

Application area: The method can be applied to determine octyl- and nonylphenol content of surface water, groundwater, wastewater, drinking water, sewage sludge, soil, sludge, liquid and solid waste using liquid-liquid extraction or solid-liquid extraction followed by gas chromatography-mass spectrometry.

References:

- MSZ EN ISO 18857-1:2007, Determination of selected alkylphenols - Part 1: Method for non-filtered samples using liquid-liquid extraction and gas chromatography with mass selective detection
- EPA Method 8270E:2017, Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)

2.2.2.3.5. Determination of metolachlor, tebuconazole, metolachlor-ESA and metolachlor-OA

Surface water samples were transferred into autosampler vials and internal standards were added and homogenized. Wastewater samples were diluted by a factor of 10 using deionized water. An aliquot of wastewater sample was transferred into autosampler vials and internal

standards were added and homogenized. The samples were analysed with large volume injection method.

Soil samples were spiked with the internal standards and were extracted by shaking with water and acetonitrile. The mixture was centrifugated. The supernatant was transferred to another tube and salt was added. The obtained solution was thoroughly shaken and centrifuged. The acetonitrile layer was transferred in an autosampler vial and was analysed.

Metolachlor and tebuconazole were measured in positive ionization mode, Metolachlor-ESA and Metolachlor-OA were measured in negative ionization mode by HPLC coupled triple-quadrupole mass spectrometer.

2.2.2.3.6. Determination of carbamazepine, diclofenac and bisphenol-A

Surface water and wastewater samples were prepared with solid phase extraction method to concentrate the analytes. Wastewater samples were diluted by a factor of 10 using deionized water. A mixed mode SPE (Solid Phase Extraction) cartridge was used loading large volume of samples. The eluate was evaporated and the residue was dissolved in HPLC mobile phase. An aliquot of the re-dissolved residue was transferred to an autosampler vial and was analysed.

Soil samples were spiked with the internal standards and were extracted by shaking with acetonitrile/water. The mixture was centrifuged and the solution was transferred into autosampler vial and was analysed.

Carbamazepine was measured in positive ionization mode; diclofenac was measured both positive and negative ionization mode and bisphenol-A was measured in negative ionization mode by HPLC coupled triple-quadrupole mass spectrometer.

2.3. Monitoring in the Danube River

Due to budget constraints, the original plan of doing sampling in the main Danube itself had to be skipped already in the project application phase. However, with the involvement of member state administrations, regular TNMN monthly sampling could be extended almost to totally cover project substances for one year at 6 locations. In particular, following stations were involved, the measurement results of which were processed in frames of the project. Number of samples analysed for the various substances is summarized in Table 2-10.

- DE2 Jochenstein (~2204 river km)
- SK1 Bratislava (~1869 river km)
- HU5 Hercegszanto (~1435 river km)
- HR1 Batina (~1429 river km)
- HR11 Ilok (~1302 river km)
- RO5 Reni (~132 river km)

Table 2-10. Number of samples taken at the Danube stations.

	HM	PFAS	PAH	Other organics
Jochenstein	60	12	11	12
Bratislava	12	-	18	12
Hercegszántó	11	12	12	12
Batina & Ilok	12	12	12	12
Reni	-	12	-	12

Samples were analysed in local labs: Bavarian Environmental Agency, UBA Austria, Water Research Institute Slovakia, Wessling Hungary.

3. MONITORING RESULTS

3.1. Concentration of all substances across pathways in the pilot regions

Overview graphs of concentrations (each matrix separately, then comparison) + Short analysis of the results, highlighting the value of the approach (Máté)

3.1.1. Metals

Except for Cd, all analyzed metals were **detected** in practically all RIV Tot, AD, MWW, samples; all analyzed metals were detected in almost all (>95%) IWW, Mining and soil samples. Some metals were not detected in a smaller part of RIV Dis samples: Zn, Cd and Pb was missing from 18, 71 and 46% of the samples, respectively. Cd was missing from 48, 11 and 48% of the RIV Tot, AD and MWW samples, respectively.

By far the highest **concentrations** of HM were found in mining drainages: For Zn and Cu in the range of mg/l, but for As, Cd, Ni and Pb also in the range of 100 µg/L.

The second most contaminated matrix is usually head to head river water & WW effluents. River water samples cover the widest range of concentrations for all PTEs; however, some extremely high values as outliers outreach concentrations measured in wastewaters (in case of As, Cr, Cu, Ni, Pb, Zn). Dissolved concentrations in river water are usually significantly lower (for all compounds) or even one order of magnitude lower than total concentrations (Cr, Ni, Cu, Pb, Hg). The lowest concentrations can be found in atmospheric deposition samples and filtered river samples. For AD, orders of magnitude are 10 µg/l for Zn, 1 µg/l for Cu and As, 0.1 µg/l for Cr, Ni, Pb; 0.01 for Cd and 0.001 µg/L for Hg (see Fig. 3-1 top).

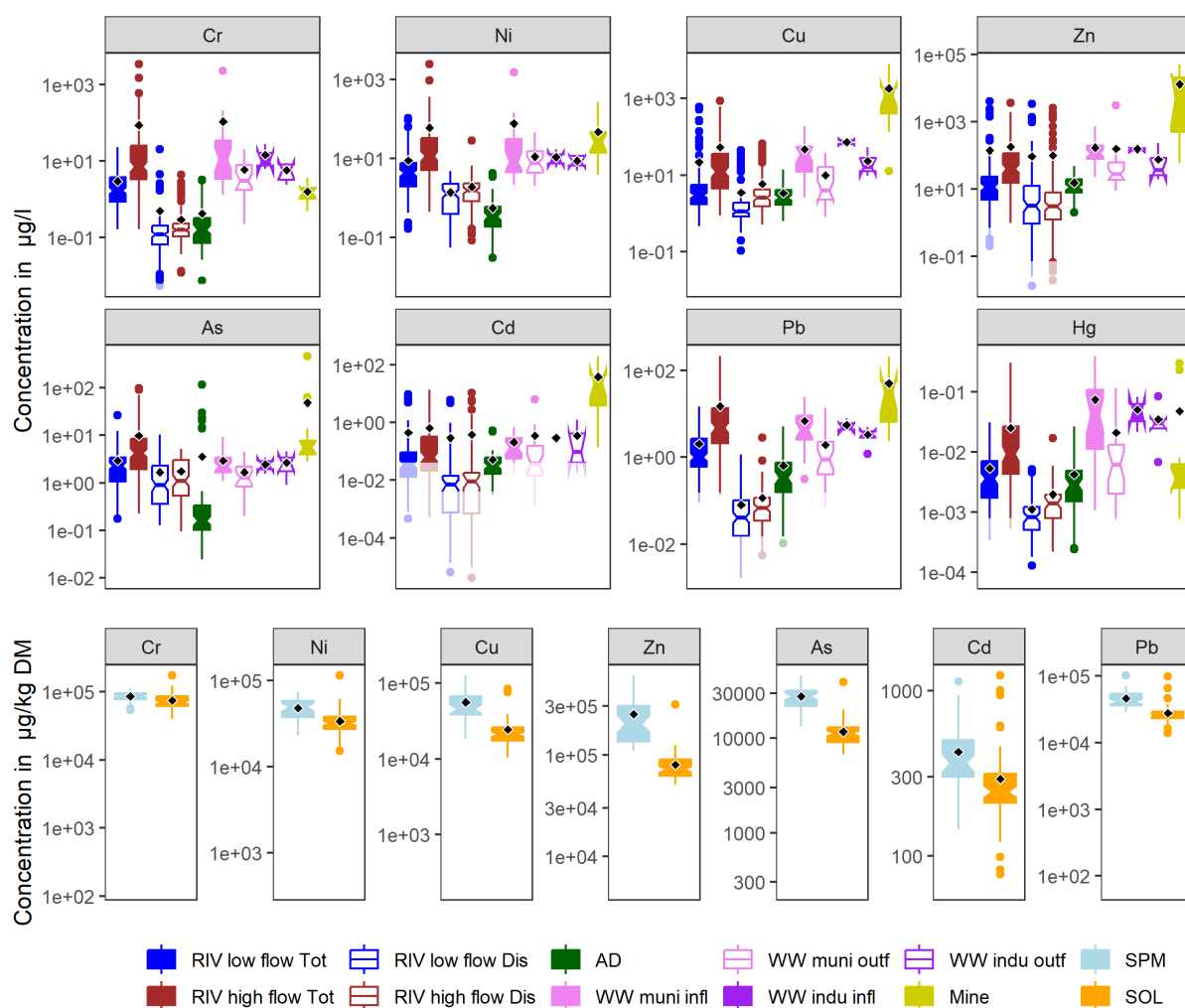


Fig. 3-1. Concentration of HMs across aqueous (top) and solid (bottom) pathways.

Notches in the boxplot show $1.58 \cdot IQR / \sqrt{n}$ which is roughly the 95% CI of the median. Lighter colours at the bottom of a bar indicates ROS-modelled values. Black diamonds represent calculated mean values.

In soil samples, Zn and Cr exhibited the highest concentrations (51.3 – 313 and 39.3 - 174 mg/kg DM, respectively). Concentration of Ni, Pb, Cu and As was an order of magnitude lower: between 15.2 – 115, 13.9 – 98, 10.4 - 84.2 and 6.78 - 39.5 mg/kg DM, respectively. The lowest concentration range was exhibited by Cd (0.077 - 1.24 mg/kg DM) (see Fig. 3-1 bottom).

3.1.2. PAHs

Only Naph, Phen and Fla **occurred** in more than 50% of the RIV samples whereas the 8 PAHs with 18 or more C atoms (BaA, Chry, BbF, BkF, BaP, BghiP, Ind123cdP and DahA) occurred in <10% of the RIV samples. A similar but less contrast picture is shown by AD samples: Naph, Phen, Fla, Pyr occurred in >50% of the samples whereas the larger compounds in only 20-40% of the samples. Only Naph and Phen was found in substantial share (75-90%) of the MWW samples, and Ace and Fluo in a few (19%) of them. Only Naph and Phen was found in IWW samples. Naph, Ace, Fluo, Phen and Fla taugt up in Mining effluent samples with a wide range

of occurrence ratio ranged from 100% for the 2-ring Naph to 30% for the 4-ring Fla. Here again hydrophobicity might be an explanation, but – in case of IWW – the particular activity also determines the composition of the WW. For soil, the situation is reverse: higher molecular weight (>200) and higher ring number (>= 4) compounds like Fla, Pyr, BaA, Chry, BaP, BbF, BkF, BghiP, Ind123cdP and DahA are almost ubiquitous (usually >90%) whereas compounds with 2-3 rings were rare to occur (in 3-46% of the samples).

Highest mean **concentrations** of Σ PAH16 were measured in MWW and AD (0.0636 +/- 0.079 $\mu\text{g/l}$ and 0.0606 +/- 0.0583 $\mu\text{g/l}$, respectively), followed by Mining, RIV and IWW samples (0.15 +/- 0.176, 0.0254 +/- 0.0306 and 0.0182 \pm 0.0124 $\mu\text{g/l}$, respectively) which underlines the fact that these substances are really ubiquitous, reaching surface waters through many pathways.

Concerning soil samples, mean concentration of Σ PAH16 in forest soils exceeded those in agricultural and pasture soils (84.2 vs 63 and 49.8 $\mu\text{g/kg}$, respectively). In agricultural soils, the upper 25 cm of the soil is frequently mixed during tilling operations (where applied) therefore the concentrations in the tilled layer is evened out. It is however contradictory that in pasture soils, where the sampling was carried out in the same horizon as for the forest soils, the PAH concentration are significantly lower (Fig. 3-2).

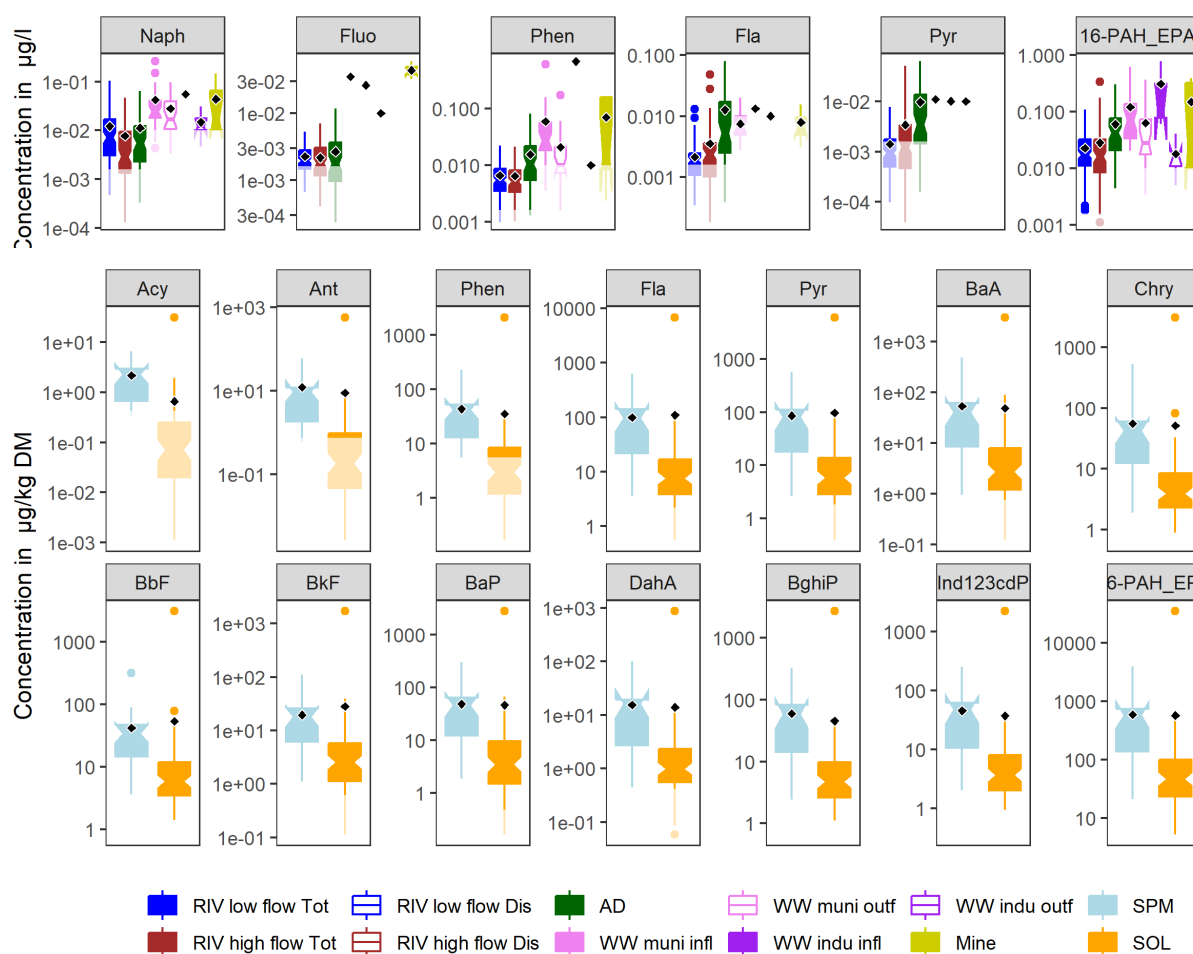


Fig. 3-2. Concentration of PAHs across aqueous (top) and solid (bottom) pathways.

Notches in the boxplot show $1.58 * IQR / \sqrt{n}$ which is roughly the 95% CI of the median. Lighter colors at the bottom of a bar indicates ROS-modelled values. Black diamonds represent calculated mean values.

3.1.3. PFAS

When investigating the detection rates of the PFAS attention has to be given to the fact that LOQ for PFOS and PFOA in aqueous matrices was one order of magnitude lower than for other PFAS. The two PFAS produced traditionally in the greatest volumes (PFOA and PFOS) were found in 80 and 60% of the river samples, respectively. From the other PFAAs, shorter (5-7) chain acids and sulfonates were **detected** in 7-35% of the river samples whereas longer chain acids were completely missing from all aqueous samples. Regarding atmospheric deposition, PFOA was detected in 92% of the samples whereas PFOS in 19% of the samples; PFHpA in 8% of the samples. Similar holds for both municipal and industrial wastewaters: PFOA could be quantified in 63-33%, whereas PFOS in 41-17% of the samples, respectively, but no other compounds occurred in substantial share of the samples. No PFAAs were found at all in mining effluent waters.

Soil is somewhat different: except for the very long chain ($n > 13$) compounds, each substance was detected in soils. The detection rate decreases with the increase of the chain length (from

100% for pentanoic ... nonanoic acid to 39% for dodecanoic acid). Seemingly, soil is an accumulator of these substances, and shorter chain substances occur more often. (Gao et al., 2019) also observed that shorter chain PFAAs have higher detection frequencies.

River concentrations were between <0.00015 - 0.0187 and <0.00015 - 0.0162 µg/L for PFOA and PFOS, respectively. Regarding metabolites and precursors, the concentration of shorter chain acids and shorter chain sulfonates was <0.002 – 0.02 and <0.02 – 0.018 µg/l, respectively. Atmospheric deposition had concentrations of <0.00015 - 0.00113 and <0.00015 - 0.00733 for PFOA and PFOS. WW concentrations ranged between <0.0015 – 0.0049 and <0.0015 – 0.0219 µg/l for PFOA and PFOS, respectively. Soil concentrations were between 0.005 - 1.21 and 0.01 - 0.383 µg/kg DM for PFOA and PFOS, respectively. Regarding metabolites and precursors (n = 5-7, 9-10), the concentration was between 0.006 – 0.68 µg/kg. PFAA concentrations in soils show heterogeneity across land uses. The total concentrations of the 13 analyzed variants for all soils were in the range of 0.093-4.231 mg/kg with means of 0.371, 1.101 and 0.699 mg/kg for agricultural lands, forests and pastures, respectively. The highest average concentrations were found for perfluorooctanesulfonic acid (PFOA) with 0.087, 0.246 and 0.147 mg/kg for agricultural, forest and pasture soils respectively. PFOA was followed by PFPeA and PFOS and the distribution between the land uses was similar, with highest values for forest followed by pasture and agricultural lands (Fig. 3-3).

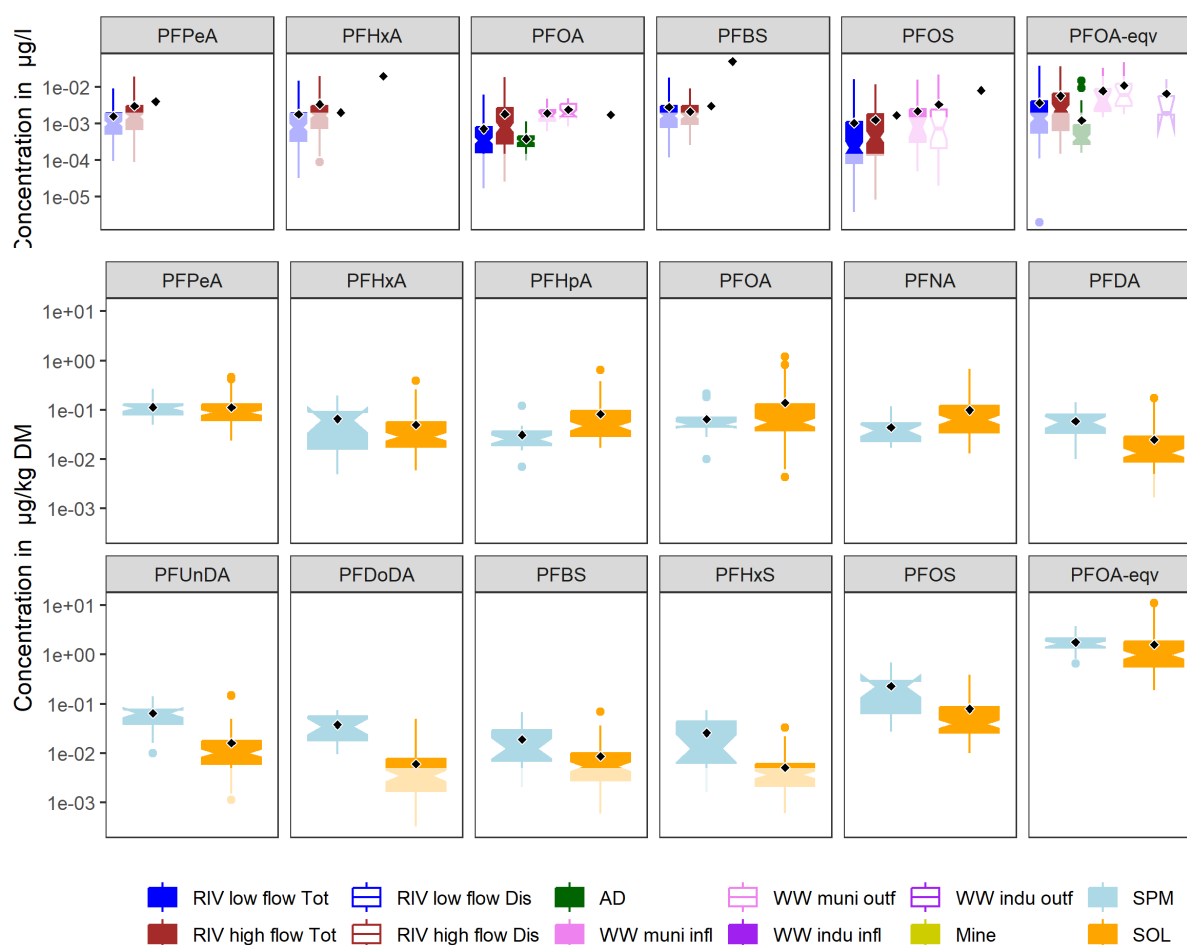


Fig. 3-3. Concentration of PFAS across aqueous (top) and solid (bottom) pathways.

Notches in the boxplot show $1.58 \cdot IQR / \sqrt{n}$ which is roughly the 95% CI of the median. Lighter colors at the bottom of a bar indicates ROS-modelled values. Black diamonds represent calculated mean values.

3.1.4. Phenols, Pesticides & Pharmaceuticals

Out of the three phenols, Nonylphenol was not **detected** in any of the samples. No soil sample exhibited measurable concentration of any phenols. BpA occurred in ~65% of the AD and IWW samples and in smaller share (26-35%) of the MWW and RIV samples but was missing from Mining effluents. OP occurred in 50% of the Mining effluent samples(!) and in smaller share (5-15%) of the AD, RIV and MWW samples but was missing from IWW samples.

Detection frequency of both the original pesticides was higher in high flow than in low flow (35% vs 10% and 36% vs 12% for Met and TCZ, respectively). In contrary, the two metabolites could be detected in less or equal low flow samples than high flow samples (49% vs 49% and 41% vs 44% for Met-ESA and Met-OA, respectively). This underlines the process of degradation with time: low flow samples reached the monitoring locations with substantially longer travel times which allowed them to transform. Detection in AD and soil is in line with that in high flow: 33 - 36% and 10-13% for Met – TCZ in AD and soil, respectively. While no pesticide was detected

in Mining effluents, there were a few detects of metabolites in municipal and industrial WW effluents (4 and 2 detects, respectively). Met and TCZ could be detected in 10 and 13% of the soil samples, respectively whereas detects of metabolites was neglectable.

Both CBZ and DCF were **detected** in all MWW samples and 82-84% of IWW and RIV samples. Surprisingly, they were also found in part of the AD samples (8 and 38% for CBZ and DCF, respectively). As expected, pharmaceuticals were not detected in Mining effluents and soil.

Concentrations of BpA ranged from 28.9 / 5.07 (maximum / mean conc., respectively) in IWW to 0.29 / 0.018 µg/l (maximum / mean conc., respectively) in RIV. Mean / maximum concentration of OP in the mining effluents of the Viseu pilot region was 0.09 / 0.034 µg/l.

Maximum Met **concentration** was 80, 0.8 and 0.21 in high flow, low flow and AD, respectively; maximum TCZ concentration was 2, 0.06 and 0.11 in high flow, low flow and AD, respectively. Max / mean concentration was 4.02 / 0.176 and 0.28 / 0.049 for Met-ESA whereas 6.74 / 0.214 and 0.21 / 0.021 for Met-OA in river high flow and low flow, respectively, indicating that concentrations of both pesticides as well as their metabolites are about one order of magnitude lower in high flow samples than in low flow samples. Concerning pesticides concentrations, there is a substantial difference however within pilot regions. There are only 3 pilot regions, where the detection frequency of any pesticide in river water fell above 20%: Wulka, Koppány and Zagyva. In addition, detection frequencies for metabolites were above 20% on the Ybbs, Somes and Vit pilot regions, too, with the above-mentioned regularity that these substances have in most of the cases lower detection frequencies in high flow than in low flow.

The highest **concentrations** were measured in MWW and IWW samples followed by RIV and AD. Maximum / median RIV concentrations were 1.33 / 0.0425 and 1.99 / 0.0555 µg/L for CBZ and DCF, respectively. AD samples containing CBZ originate from the Zagyva, Somes and Viseu pilot regions, whereas samples containing DCF cover all pilot regions. Maximum / mean concentration of CBZ and DCF in AD samples was 0.02 / 0.0064 and 0.313 / 0.0082 µg/L respectively (Fig. 3-4).

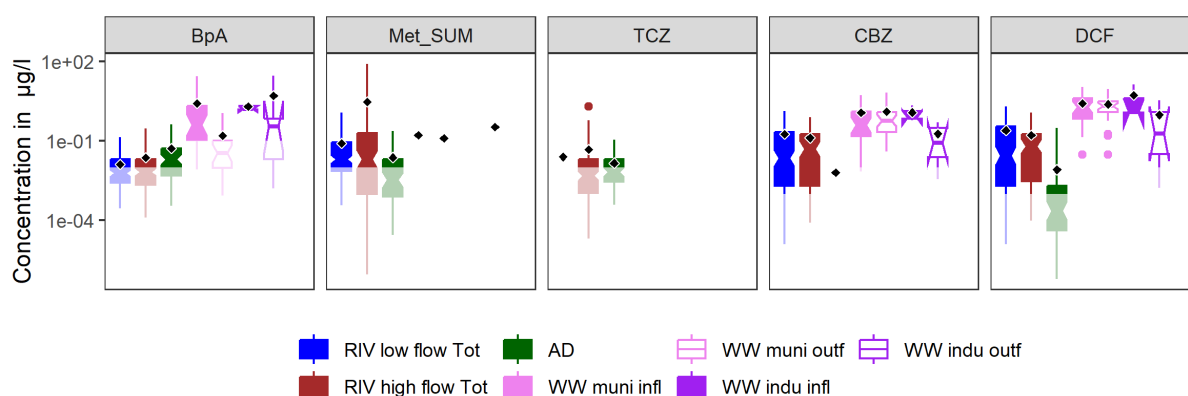


Fig. 3-4. Concentration of BpA, pesticides and pharmaceuticals across aqueous pathways. Notches in the boxplot show $1.58 \cdot IQR / \sqrt{n}$ which is roughly the 95% CI of the median. Lighter colors at the bottom of a bar indicates ROS-modelled values. Black diamonds represent calculated mean values.

3.2. Concentrations across pilot regions / countries

3.2.1. River water

3.2.1.1. *Metals*

As already stated, mining activities exhibit the highest concentration of metals. This is also reflected in the river concentrations of the Viseu pilot region (both low and high flow, both total and dissolved concentrations) in particular for Cu, Zn and Cd. Metals are known for their affinity to adsorb on small particles, which explains the elevated concentration of total metals during high flow events. The reason for this phenomenon being less pronounced on the last three pilot regions (Somes, Viseu and Vit) is that in these three pilot regions, the difference between actual river flow during collection of high flow vs low flow samples was small (i.e. we did not manage to catch really good high flow events). The elevated As concentration of groundwaters in the Pannonian region (Giménez-Forcada et al., 2022) are reflected by the dissolved As concentrations in river water. The most pristine water of the alpine pilot region Ybbs are reflected by the lowest dissolved Pb concentrations in low flow samples (Fig. 3-5.).

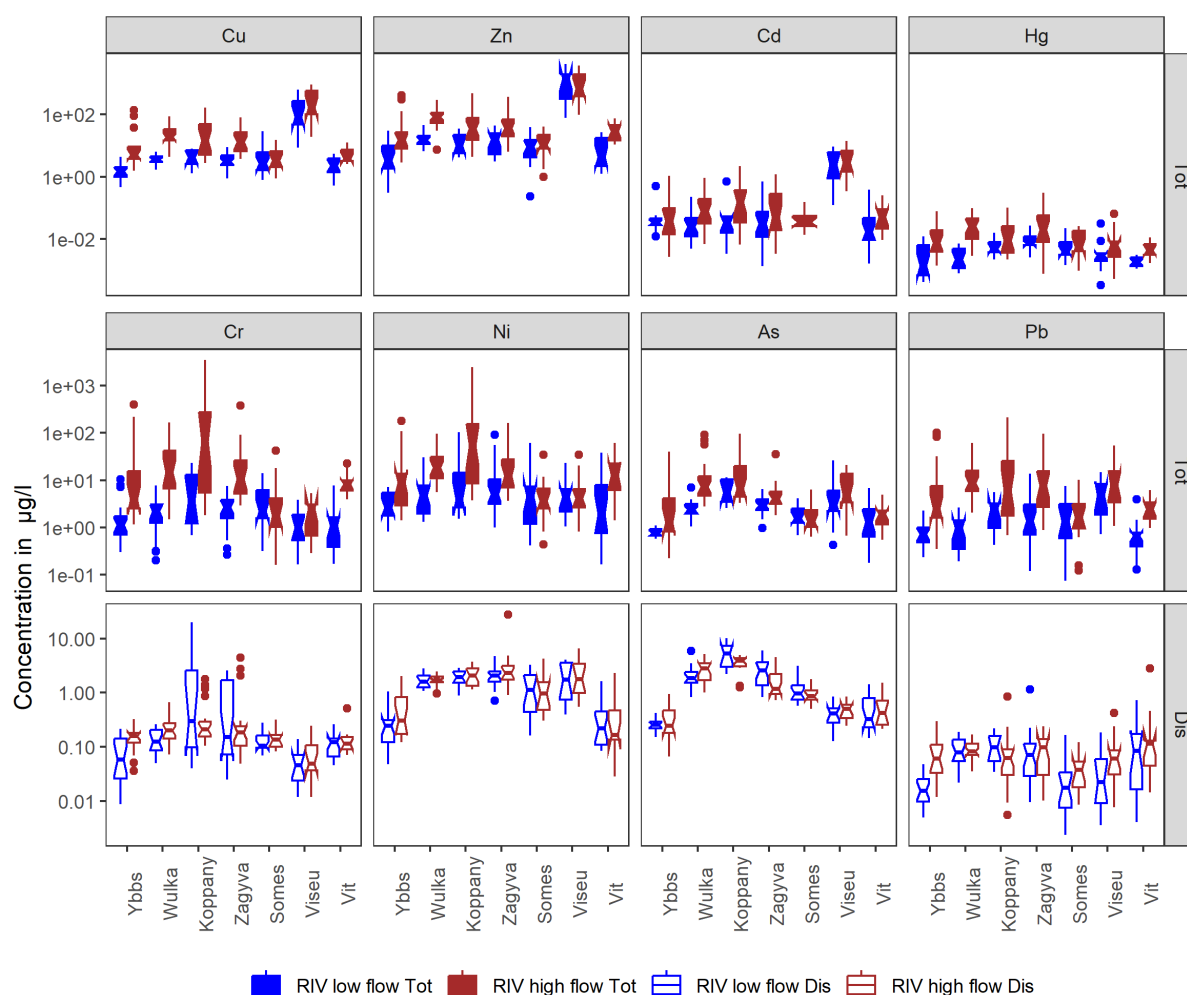


Fig. 3-5. Concentration of HMs across pilot regions. Notches in the boxplot show $1.58 \cdot IQR / \sqrt{n}$ which is roughly the 95% CI of the median.

3.2.1.2. PAHs

Behavior of **PAHs** is fuzzy for the first glimpse and thus worth for investigation. Regarding the bunch of the PAs, there is no real difference between low flow and high flow concentrations of the 6 main PAHs that were detected in surface waters, although Naph is somewhat diluted (has lower concentrations in high flow) while Pyr is somewhat concentrated during high flow events. In particular, ratio of high flow to low flow median and mean values are between 41 - 64% for Naph and Ace, between 92 – 98 % for Fluo and Phen while between 124 – 241% for Fla and Pyr. This clearly indicates, that the higher molecular weight, ring number and hydrophobicity compounds tend to associate more to particles and thus enrich during high flow events. The bunch investigation, however, masks some spatial patterns which is most visible when comparing the Wulka and the Koppány pilot regions. On the Wulka, concentration of Σ PAH and especially Phen is higher in high flow samples than in low flow samples while it is the other way round on the Koppány (ratio of high flow mean to low flow mean Phen values is 1.42 and 0.73 on the Wulka and Koppány, respectively). The reason

behind is in the source of the PAHs: on the Wulka, it is more the AD while on the Koppány, it is more the WW (mean Phen concentration in AD / WW is 20.7 / 9.8 and 12.8 / 25.9 ng/l in the Wulka and Koppány pilot regions, respectively.) From this aspect, the Zagyva and Somes pilot regions are similar to the Koppány, while the Ybbs, Viseu and Vit pilot regions show no pattern (Fig. 3-6.)

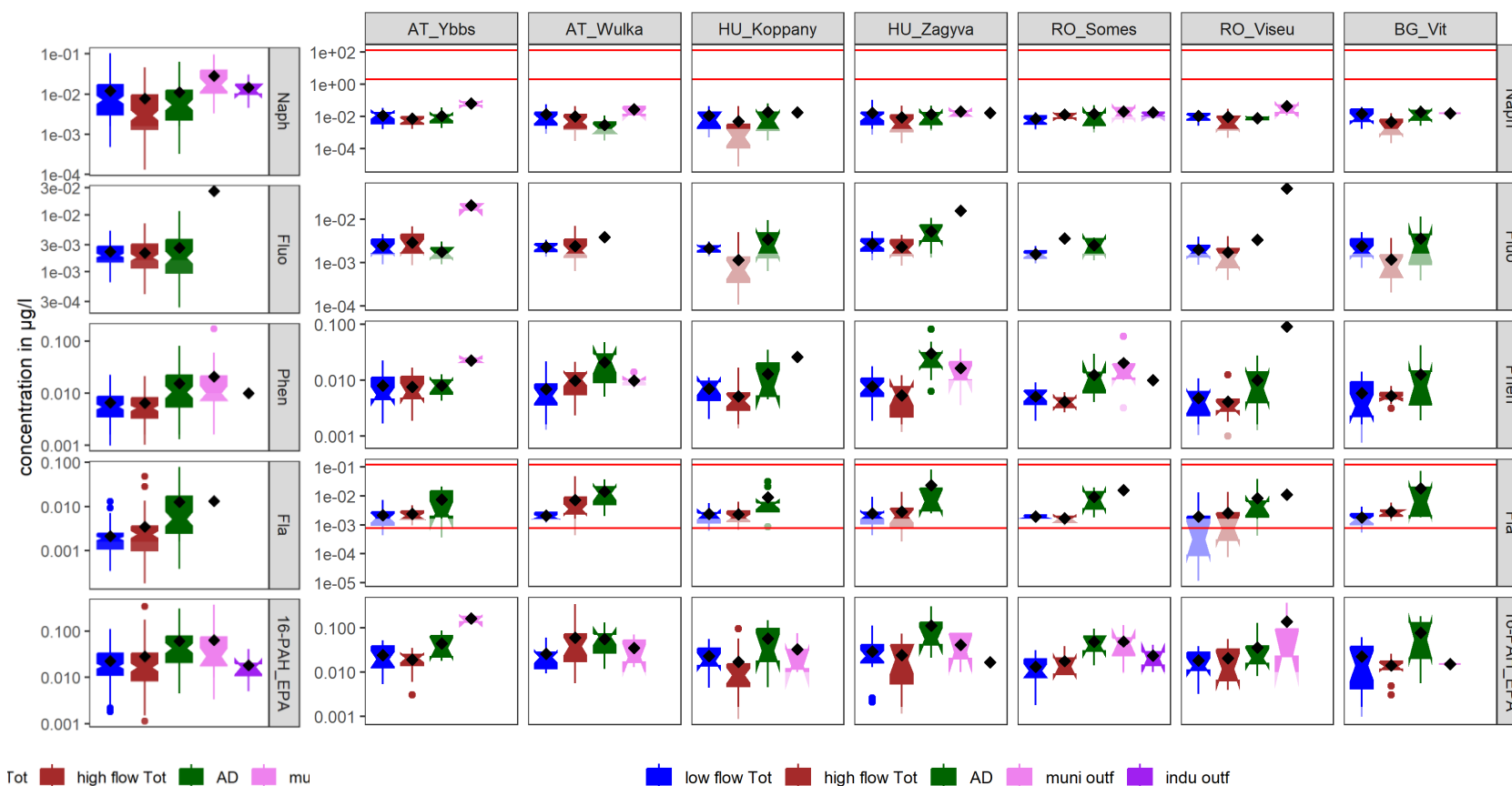


Fig. 3-6. Concentration of most frequent PAH across pathways in all pilot regions (left) and by pilot regions (right).
Black diamonds: mean values; Red horizontal lines: proposed new EQS values (EC, 2022). Light colors indicate ROS-modelled values.

3.2.1.3. Further organic compounds

Regarding PFAS, there is a tendentious difference between carbocyclic acids and sulfonates. While the former tend to have larger concentrations during high flow events than during low flow periods, the latter have slightly lower or same range of concentrations during high and low flow events. Another tendency to be observed is the decrease in riverine concentrations for almost many substances when listing the pilot regions from Wulka to Vit, northwest to southeast. The Ybbs is here however an exception, it shows ranges of concentrations characteristic for the Hungarian pilot regions or even lower. A possible explanation lies in the difference in economic development of the pilot regions.

BpA tends to show somewhat higher concentrations during high flow events. This does not hold for the Koppány and the Somes pilot regions, but the latter are mostly ROS-modelled values and thus uncertain. On the other hand, there is no clear tendency in BpA concentrations across pilot regions. Pesticides were mainly detected on the Austrian and Hungarian pilot regions, - as expected – mainly during high flow events. Pharmaceuticals are expected to be diluted by high flow events, which is partly proven (especially on the Koppány pilot region, for both pharmaceuticals). The three Central-European pilot regions (Wulka, Koppány and Zagyva) show somewhat elevated riverine concentrations of the pharmaceuticals compared to the rest of the pilot regions (Fig. 3-7).

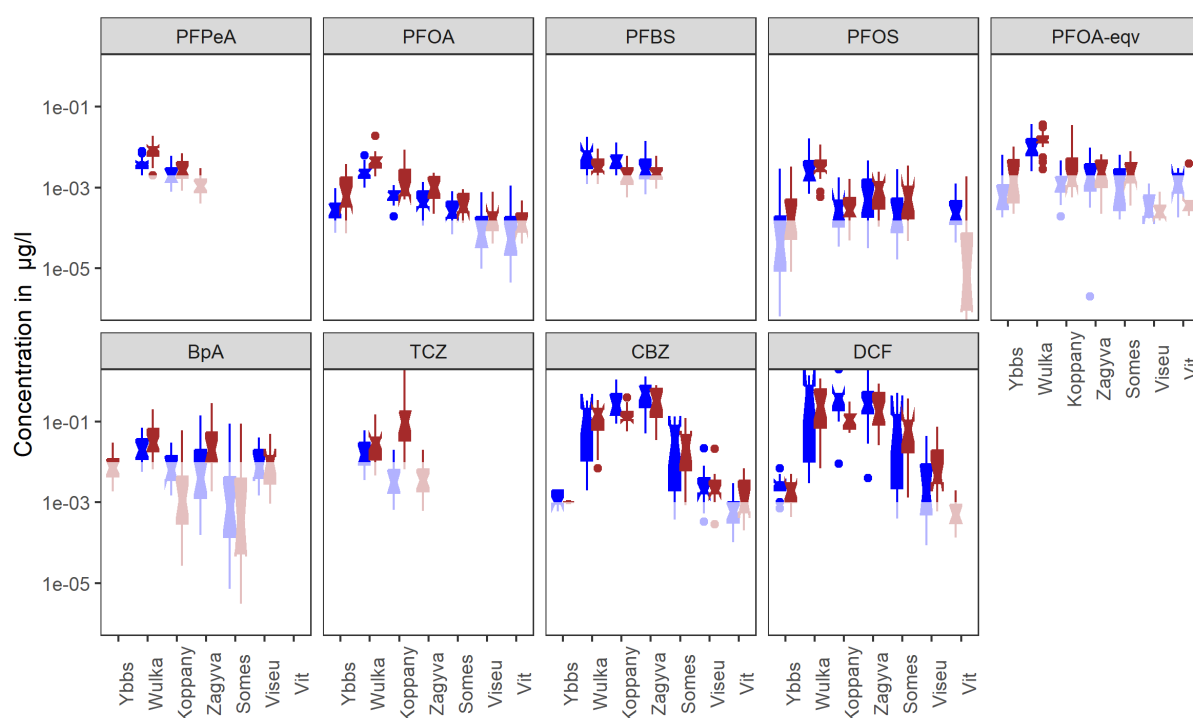


Fig. 3-7. Concentration of PFAS and other organic substances in low- and high flow samples across pilot regions. Blue: low flow; brown: high flow samples. Light colors indicate ROS-modelled values.

3.2.2. Wastewater

Number of WW samples is much smaller than those of RIV samples. In addition, regulations for WW vary by country, which has the consequence that it is has more sense to compare WW values by country. Influent concentration of HM are usually larger in Hungary, whereas the tendency in effluent values varies by compound.

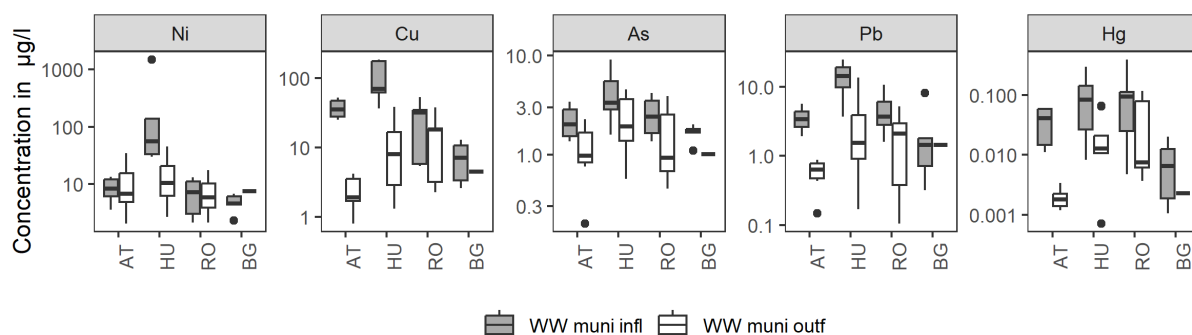


Fig. 3-8. Concentration of HM in raw & treated municipal WW samples.

Regarding organic compounds, both in- and effluent concentrations are relatively constant throughout the countries. PAHs are partly removed, especially longer molecular weight ones, most probably because they tend to adsorb to particles. On the contrary, PFOA varies both within and across countries and is not removed at all but it might exhibit slightly higher concentrations in the outflow as in raw WW (see the case of Austria on Fig. 3-9). Pharmaceutical concentrations are somewhere in between, they show some variance across countries.

There are some outliers in the results. Hungary, for example, exhibits higher concentration of both pharmaceuticals. The fact that the plant HZS treats wastewaters from a county-scale hospital, only partly explains this anomaly – the underlying process might be the higher consumption of these substances throughout the country but further investigation is needed to underline this statement. Plant HKB showed one order of magnitude higher concentrations of BpA, and somewhat higher concentrations of PFAS than other plants, indicating industrial activity on the drained area.

Regarding removal efficiencies, the concentration of some PAH forms and BpA was slightly reduced during treatment (median removal efficiency was 37%, 57% and 89%, for Naph, Phen and Bpa, respectively). Other industrial chemicals as well as pharmaceuticals trespass wastewater treatment practically unaffected (median removal efficiency was -47%, -13%, 13%, -12%, and 25% for PFOS, PFOA, OP, CBZ and DCF, respectively). Negative removal efficiencies for pharmaceuticals might be surprising, but were documented previously, too and are associated with high uncertainties in lab determination of the compounds due to the very low concentrations (Yang et al., 2017) (Fig. 3-9.).

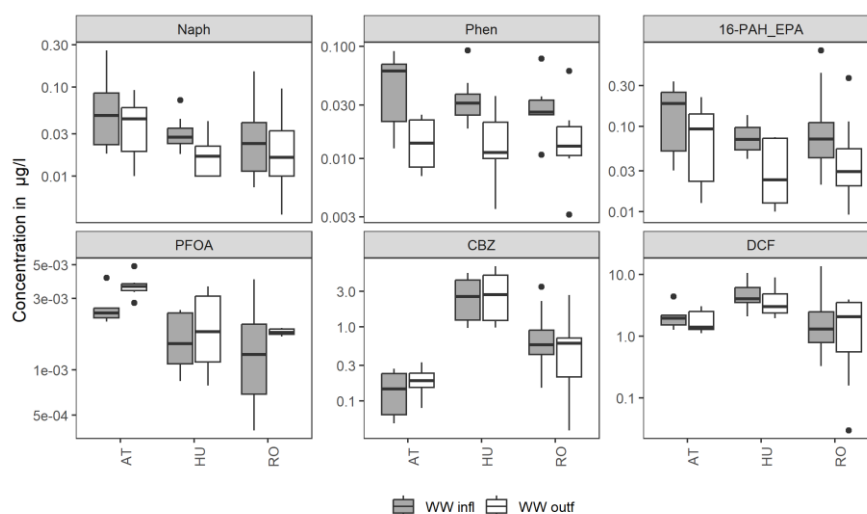


Fig. 3-9. Concentration of selected organic pollutants in raw & treated WW samples. Only plants with both in- and outflow samples included (whether municipal or industrial).

3.2.3. Atmospheric deposition

Lowest Σ PAH16 values were shown in the Viseu pilot region (25 ng/l at the Viseu de Sus station) while highest ones on the Zaggyva pilot region (125 ng/l at station Nemti). This can be regarded as a rather narrow range considering the large distances between the stations. There is a difference in the composition of the Σ PAH, however: the biggest contrast can be observed between the Nodbach and the Cluj stations. In the former, low C-number PAHs (Naph, Ace, Fluo, Ant) are missing while in the latter, high C number ($C > 17$) PAHs are missing. Since both stations are more or less situated in developed areas, further investigation is needed to reveal the reason for this difference (Fig. 3-10.).

Measured concentrations can be compared according to the environment in which the stations were located. However, there is no substance for which there would be a significant difference between rural and urban-industrial sites. For most substances, the concentrations range within a rather narrow interval across all sites, but there are a few exemptions. Amount of BpA in atmospheric deposition samples in the Koppány pilot region was 1-2 orders of magnitude higher than in other pilot regions (Fig. 3-11.).

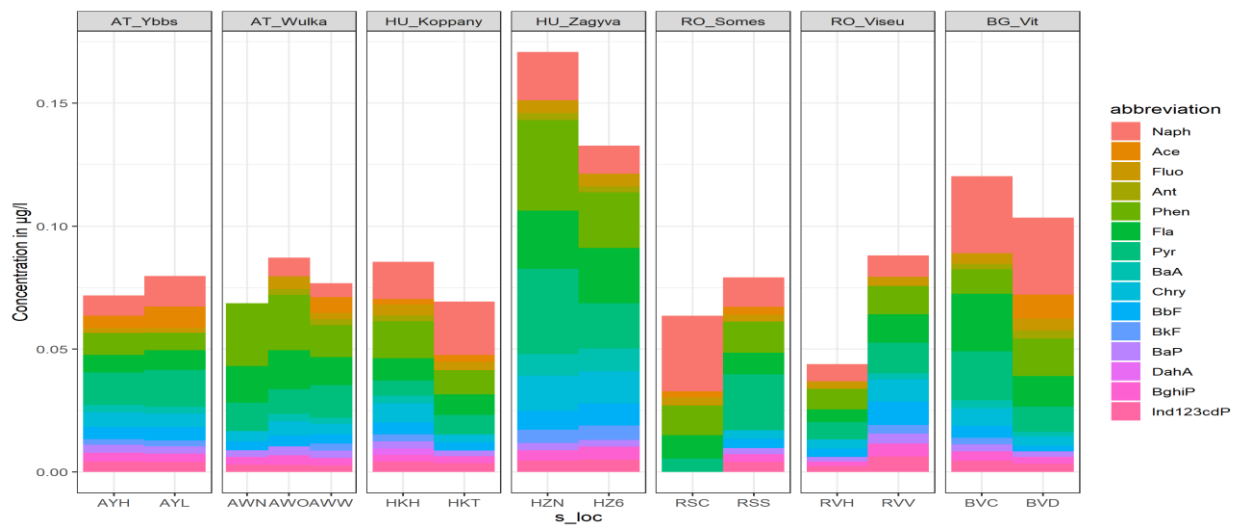


Fig. 3-10. Concentration of PAH forms in atmospheric deposition across sampling locations.

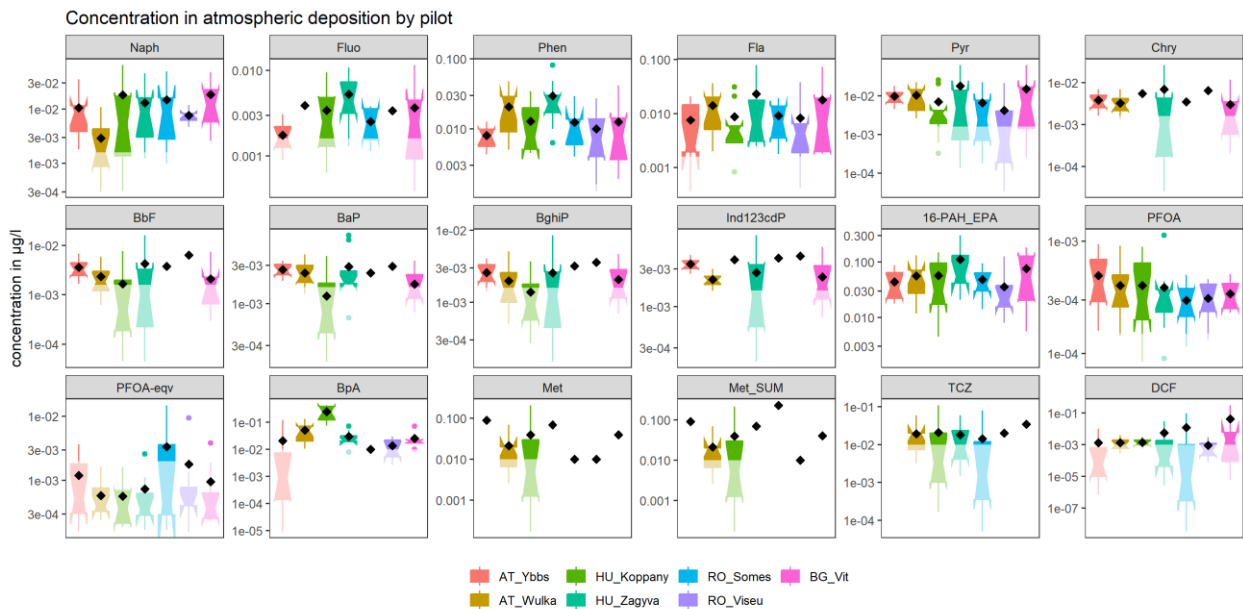


Fig. 3-11. Concentration of selected pollutants in atmospheric deposition across pilot regions.
Light bottom part of a box denotes ROS-modelled values.

3.2.4. Soil & SPM samples

Soil concentrations are in general much less variable within the pilot regions than river concentrations. This might be due to the fact that they are composite samples composed from samples originating from 20 locations and thus differences might be levelled out. Cd exhibits the lowest while Cr & Zn the highest concentrations for all pilot regions, the latter especially for SPM (Fig. 3-12).

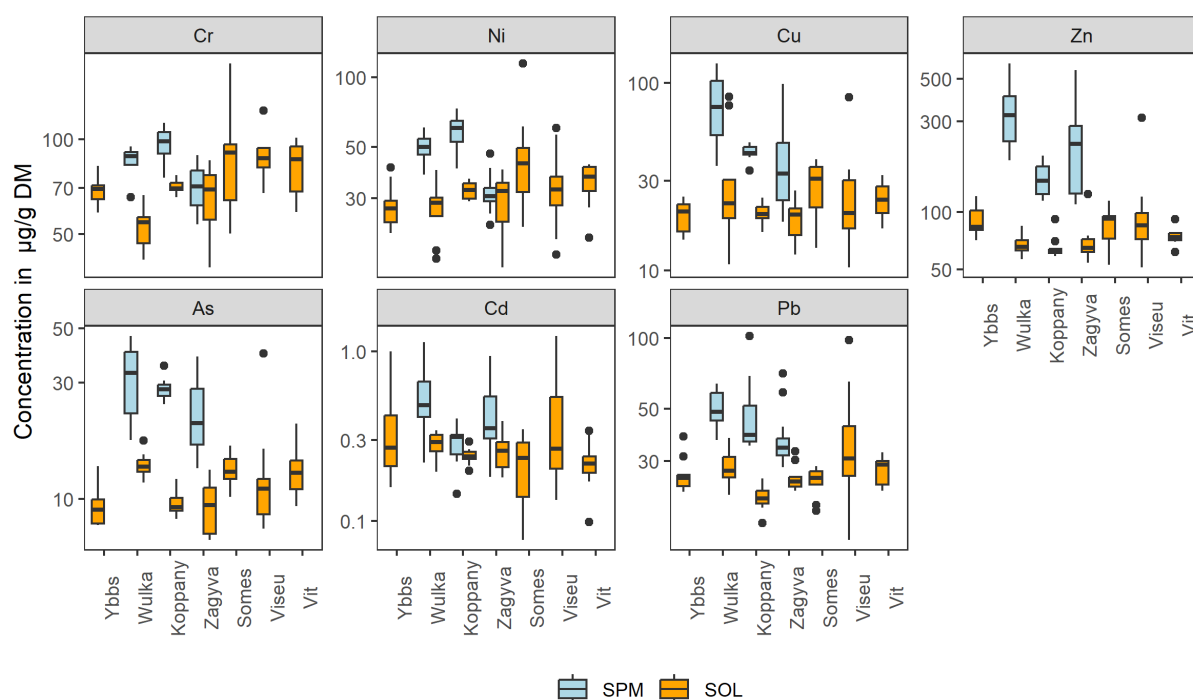


Fig. 3-12. HM concentrations in SOIL and SPM samples.

Concentration of Cr, Ni, Cu and Zn is higher in agricultural soils than in forest soils for almost all pilot regions. For As and Cd, it varies; but for Pb, agricultural soils exhibit lower concentrations than forest soils. All PAHs exhibit lower concentrations in agricultural soils than in forest soils in all countries / pilot regions – except for the Somes. We suspect that these tendencies reflect legacy pollution: high atmospheric concentrations of Pb and PAHs were adsorbed on leaves (forests have leaf area indices much higher than agricultural crops), after falling they became soil. Further investigations could confirm or deny this statement. Both PAH and PFAS, both in forest and agricultural soils decrease in the direction of northwestern to southeastern countries (AT – HU – RO – BG) i.e. their concentration increases with economic development. The only exception is PFPeA, which has higher concentrations in BG agricultural soils, too, probably due to one or more outliers in agricultural soils. The reason for Somes soils as outliers might be the industrial activity in a relatively closed valley (Fig. 3-13).

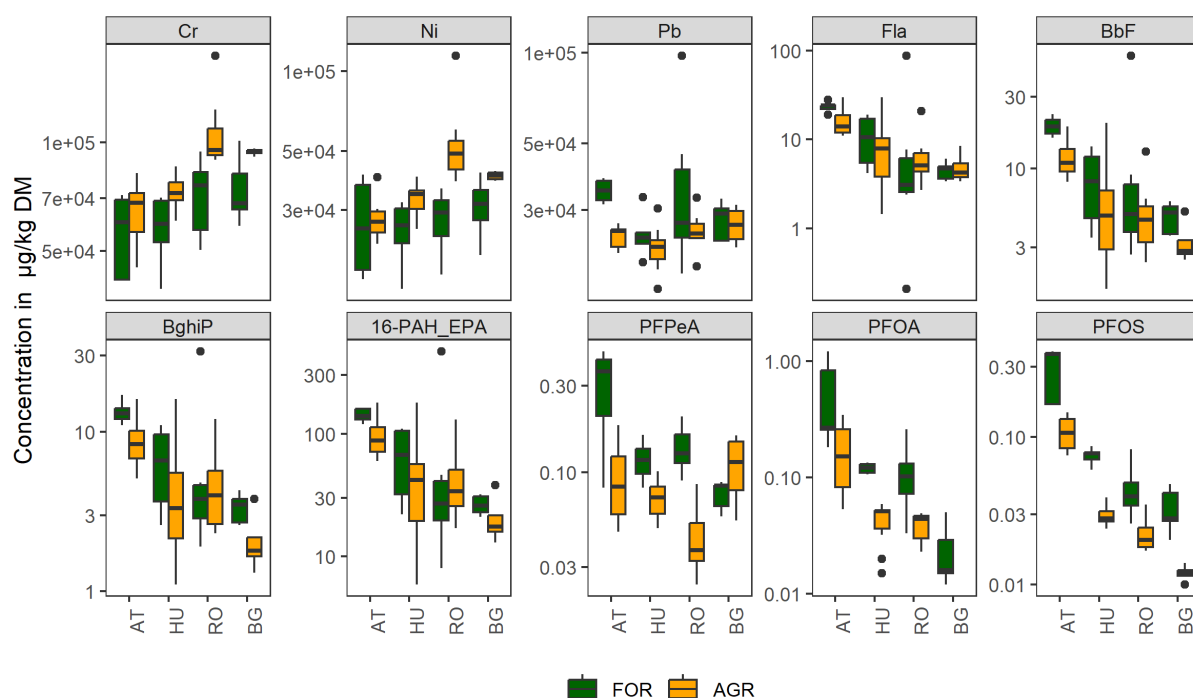


Fig. 3-13. Concentration of HM, PAH and PFAS in forest and agricultural soils across the pilot countries.

The spatial pattern across the pilot regions are similar in case of most PAH compounds. Slightly different behavior and pattern can be identified for DahA, which is in higher concentrations in the Koppány pilot region in relative terms to the other substances. There are obviously very high values of PAH concentrations at some pasture and forest samples from the Somes and Viseu pilot regions; agricultural samples from these two pilot regions however show concentration ranges comparable to the other pilot regions.

Besides PAH and PFAS, only pesticides were found in detectable amounts in agricultural soils of three pilot regions. Metolachlor was found in 5 out of 6 agricultural soil samples of the Koppány pilot region with an average concentration of 0.1 mg/kg. Tebuconazole, however, was found in all the agricultural soil samples of the Zagyva pilot region with an average concentration of 0.055 mg/kg. These occurrences of specific pesticides might be explained by area specific agricultural practices, including the selection of chemicals for application and the timing of the pesticide application due to climatic reasons.

3.3. Concentrations in the Danube River

Interpretation of concentrations measured in the Danube samples is hindered by the diversity of substances measured at the stations and by varying – and in many cases too high – limits of quantification. Still, some trends are to be seen. Most heavy metals have balanced concentrations except for some outliers at specific stations – they might be associated to higher water flow periods, further investigation is needed to confirm this. Higher geogenic arsenic in the Pannonian region is again reflected in somewhat elevated concentrations of As

in the Hercegszántó station data (the southern border of Hungary). Higher Pb concentrations at the Bratislava station might reflect legacy contamination of the industrialized upper-middle regions of the watershed. There is a slight decrease in the concentration of PAHs along the longitudinal section of the river. Highest PFOA levels were measured at both Croatian stations (Batina, Ilok). A possible explanation is that countries located in the middle part of the watershed are in the economic situation to purchase PF-containing clothing and accessories but not aware enough of the risks to try to avoid them. Lower PFAS-levels close to the mouth might either be related again to the economic situation or to the removal of these substances with SPM settling above the Iron Gate. Concentration of both pesticides is lower on the upper sections compared to the lower sections suggesting that these chemicals are still in use in the southern and eastern part of the watershed. Both pharmaceuticals could be detected and quantified in each section and show rather homogeneous concentrations. Further investigations, and – first and foremost – a strict interlaboratory comparison and evaluation is needed to confirm and reject the above speculations (Fig. 3-14).

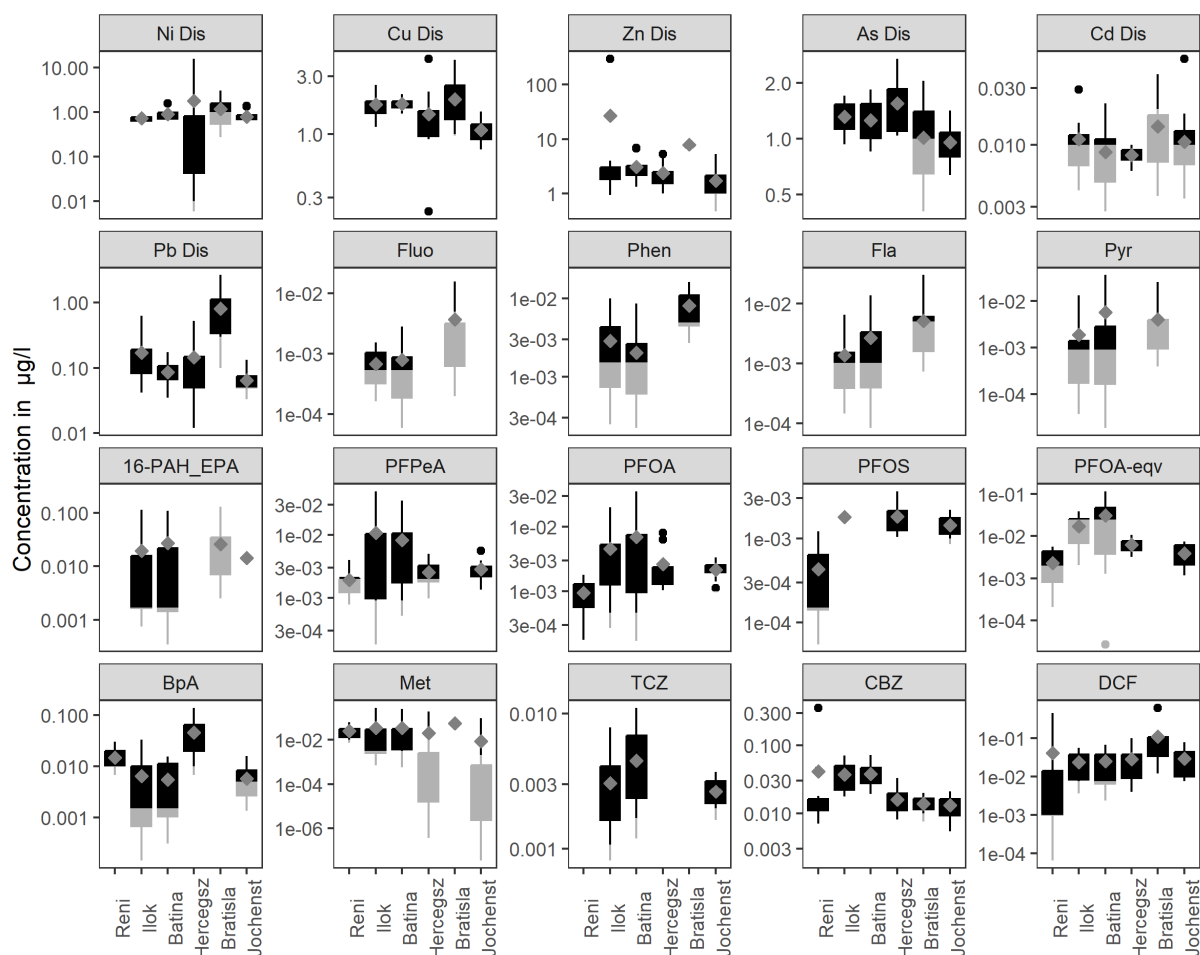


Fig. 3-14. Concentration of various substances along the Danube River. Dis = dissolved (filtered) portion. Grey diamonds show mean values. Grey part of the boxes and whiskers show ROS-modelled values.

3.4. Load calculation

3.4.1. Introduction to the aims and concept

The necessity of load estimations is rooted in the approach to how catchment scale estimation of hazardous substances are dealt with. Proper estimation of sources and the identification of pathways related to individual chemicals can be best delivered with emission models. These models however can be only calibrated and validated by mass fluxes of the substances in other words loads. The estimation of annual loads have several ways, in most cases loads are calculated based on frequent discharge data and temporally scarce water quality data (e.g. 12 measurements per year). Using such data leads to large estimation errors, especially due to the largely nonlinear characteristics of river flows and therefore, also of river loads. To overcome this problem a stratified sampling approach have been initiated in the DHm3c project, where loads associated with base flow conditions and high flow conditions are separately addressed in the monitoring. In this chapter the applied data processing and load calculation methods are described, followed by the introduction of the load calculation results, leading to conclusions about the viability of the approach.

Throughout the chapter on load calculation, following terms are used.

Load	Mass flux of the given HS at a river section [M/T]
River flow	Water flux through a river cross section
Flow condition	River river flow is classified into base flow and event flow.
Base flow	River flow which occurs most of the time throughout the year (Low- to mid-flow(MQ))
Event flow	River flow which exceeds base flow (caused by rainfall or snowmelt)

All calculations were done using the statistical software R (Version 4.2.2) (Everitt & Hothorn, 2003; R Core Team, 2019)

We used a time window of 1 year which corresponded with the sampling dates of the low flow samples. An example can be seen on Fig. 3-15 and Fig. 3-16.

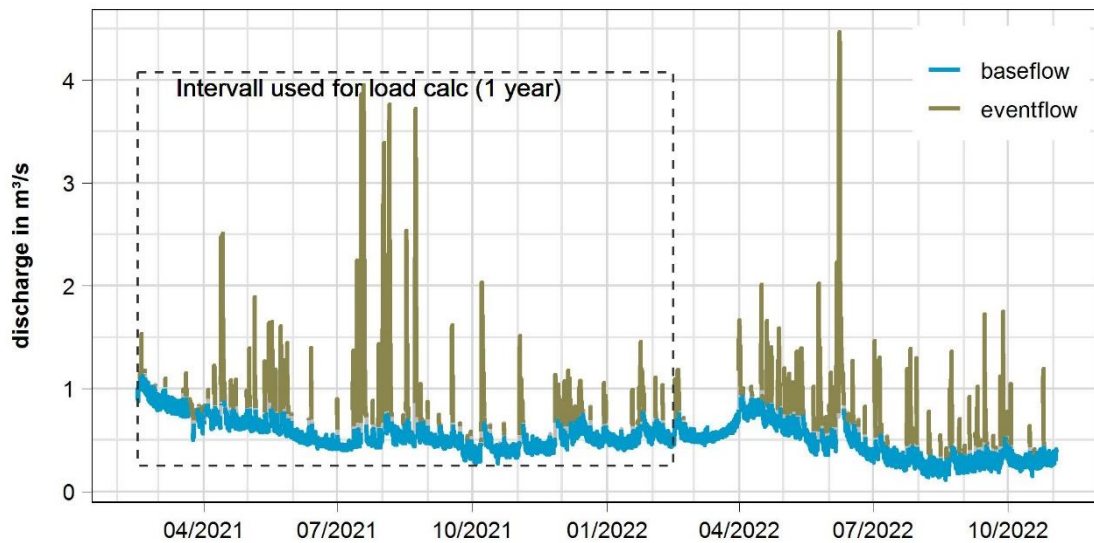


Fig. 3-15. - River flow timeline of Wulka river with colour according to flow condition. Dashed box show the interval used for the load calculation (1 year).

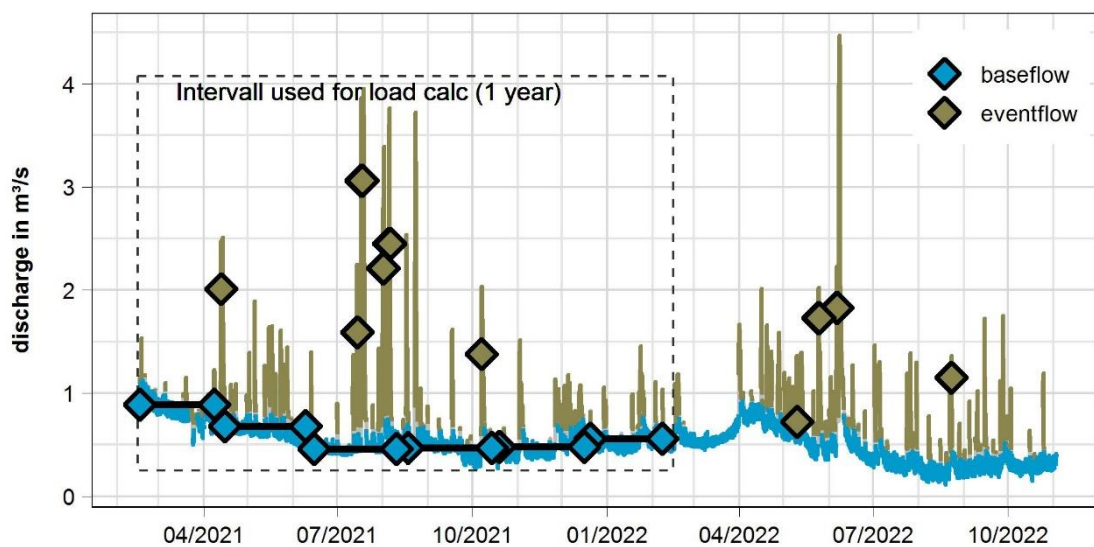


Fig. 3-16. River flow timeline of Wulka river with colour according to flow condition. Dashed box show the interval used for the load calculation (1 year). Diamonds show the composite samples used for concentrations data. Fill colour indicate flow condition, distance between diamonds show time between first and last sample and height on y-axis show mean river flow during sampling.

The load was calculated for each station, each substance, each matrix type (total or filtered).

3.4.2. Flow data processing, base flow separation

River flow data is available for each of the 20 monitoring stations out of the 7 DH m³c pilot regions. How this data was collected can be found in Annex A1: “Deliverable D.T1.2.1 Pilot region descriptions – internal document”

Timesteps of continuous measurement data collected at the online stations vary between 30 secs. and 1 h.

The river flow data was aggregated into 1 h timesteps (mean) and gaps in the timeline (max. 2 timesteps) were filled by linear interpolation. For this calculation step the R package “DTSg” was used (Hepp, 2022). The data series is reduced to a length of 1 year in order to calculate representative annual loads. The collection of the water samples is mostly within this period.

To separate the river flow into the two flow conditions, the Lynne-Hollick (LH) base flow filter from the R package “hydrostats” (Version 0.2.4) is used (Bond, 2022; Ladson et al., 2013). The package’s „base flow“ function with all their default values is used.

Because the base flow value (BF), calculated by the filter, is only the lower threshold of river river flow, it must be increased by a (constant or variable) value to include the observed variability of the rivers base flow. As each river behaves differently, a factor (threshold_factor) was introduced to fit the method to each river dataset. The individual threshold factor for each monitoring station can be found in Table 3-1. One of the following two formulas is used to calculate the separation threshold in m³/s:

- Constant threshold: $\text{separation_threshold} = \text{BF} + \text{mean}(\text{BF} * \text{threshold_factor})$
- Variable threshold: $\text{separation_threshold} = \text{BF} + \text{BF} * \text{threshold_factor}$ (for stations: “DH-RIV-HKH” & “DH-RIV-HZ6”)

Table 3-1. Threshold factor for each station used for the flow separation method

COUNTRY	PILOT REGION	STATION NAME	TF
AT	AT Wulka	DH-RIV-AWM	0.4
AT	AT Wulka	DH-RIV-AWE	1
AT	AT Wulka	DH-RIV-AWN	0.9
AT	AT Ybbs	DH-RIV-AYU	1.4
AT	AT Ybbs	DH-RIV-AYL	1
AT	AT Ybbs	DH-RIV-AYH	0.7
HU	HU Koppany	DH-RIV-HKH	0.7
HU	HU Koppany	DH-RIV-HKT	0.1
HU	HU Zagyva	DH-RIV-HZH	0.7
HU	HU Zagyva	DH-RIV-HZ6	0.3

COUNTRY	PILOT REGION	STATION NAME	TF
HU	HU Zagyva	DH-RIV-HZT	1
HU	HU Zagyva	DH-RIV-HZN	0.8
BG	BG Vit	DH-RIV-BVB	0.4
BG	BG Vit	DH-RIV-BVC	0.1
BG	BG Vit	DH-RIV-BVD	0.3
RO	RO Viseu	DH-RIV-RVV	0.4
RO	RO Viseu	DH-RIV-RVC	0.4
RO	RO SomMic	DH-RIV-RSU	0.3
RO	RO SomMic	DH-RIV-RSD	0.3
RO	RO SomMic	DH-RIV-RNR	0.3

The final separation of river flow into flow condition was done by the following condition:

River flow \leq separation_threshold -> base flow

River flow $>$ separation_threshold -> event flow

A visual representation of how the event separation works, can be seen in Fig. 3-17.

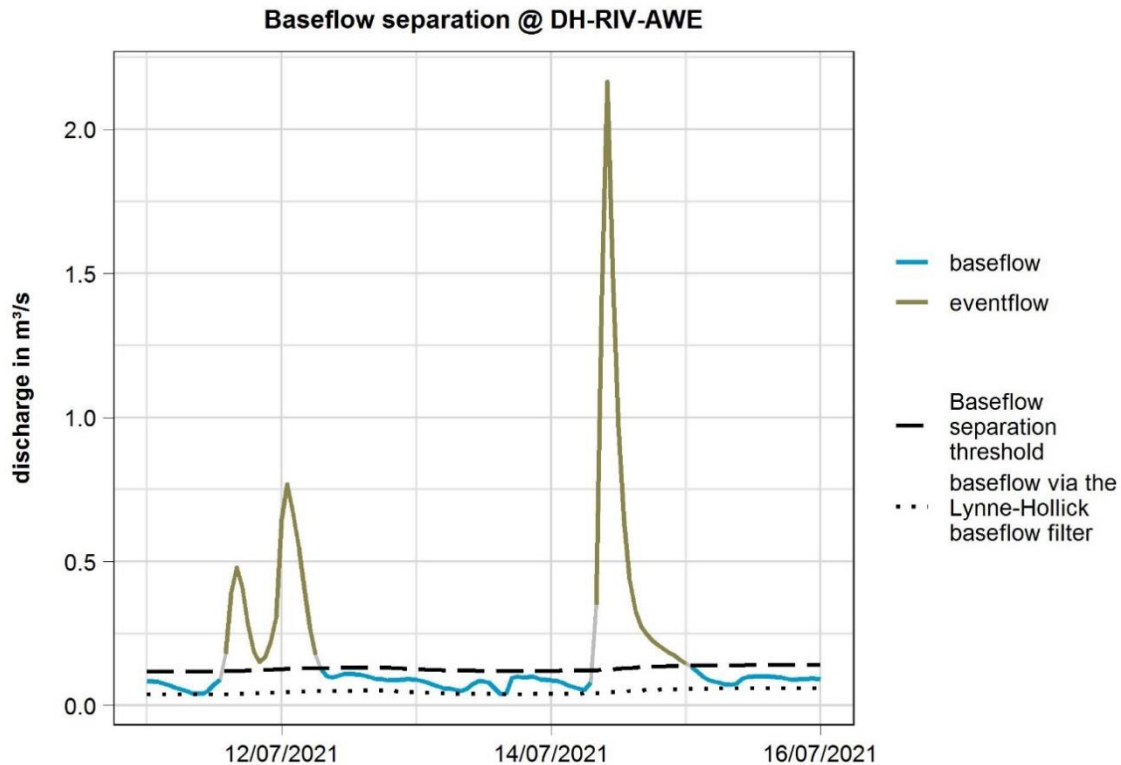


Fig. 3-17. River flow of Eisbach station (Wulka pilot region) with the final separation of flow condition. Khaki: event flow; blue: base flow; dotted line: Lynne-Hollick filter separation line; dashed line: the base flow separation threshold

3.4.2.1. Base flow separation results

River flow conditions have very strong consequences on both the measured concentrations and the loads calculated from it. It is important therefore to see, whether the sampled period represents average conditions or a dryer or wetter year. On Fig. 3-18, a comparison of actual measured versus calculated long term average river loads for all stations included in our monitoring campaign. For most stations (16 out of 20) the actual year produced a slightly dryer than average condition, while at 2 stations (two stations at Vit catchment) somewhat wetter condition was sampled. The more significant deviation was experienced at Nodbach (Wulka), Upper Koppány, Upper Zagya and also Zagya outlet and at the middle station of River Somes (Fig. 3-19). In terms of the share base flow index (BFI = ratio of annual base flow to total river flow), the distribution among the catchments is inhomogeneous (Fig. 3-20). The highest BFI was experienced at stations with the highest share of wastewater discharge (Upper Koppány, two stations at Wulka and the Tarján creek at Zagya). At sites with larger upland catchments and more natural conditions (Somes, Vit and Ybbs) the share of event flows are much higher, resulting a lower BFI (0.2-0.5). This fact puts emphasis on the pathways that are related to rainfall-runoff processes. These are the runoff driven erosion, combined sewer and storm

water system overflows. One smaller sidestream of the Zagyva (HZH) shows extremely high BFI, due to very small dry weather flows and relatively large runoff volumes.

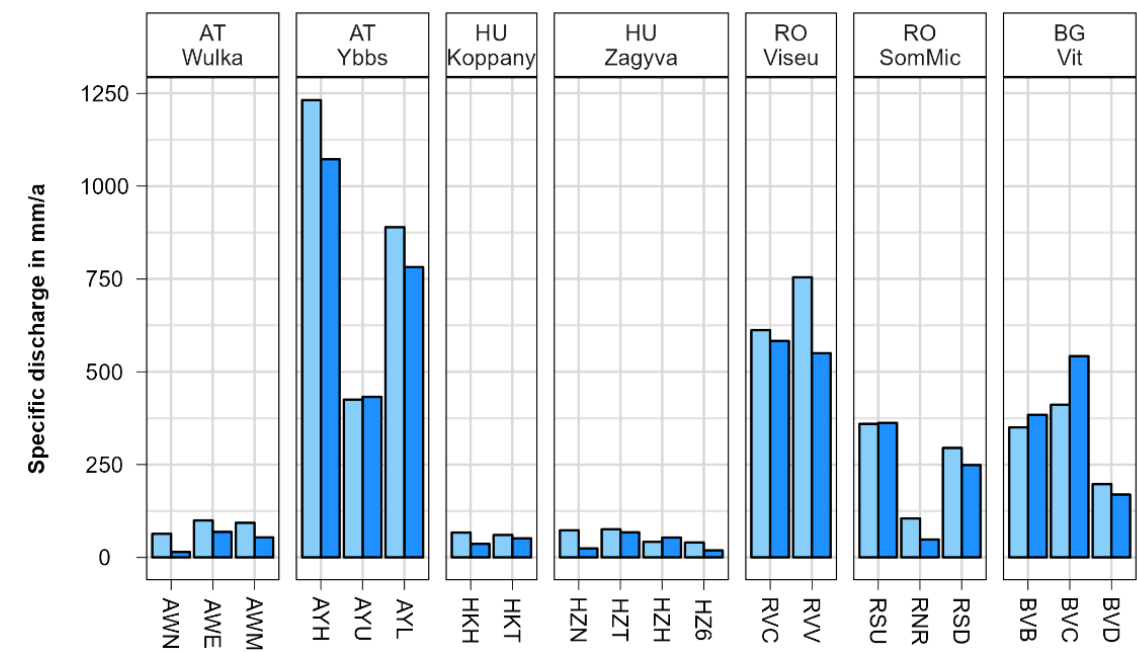


Fig. 3-18. Specific annual river flow long vs short term over the 20 DHm³c river monitoring stations.
Light blue: long term. Dark blue: short term.

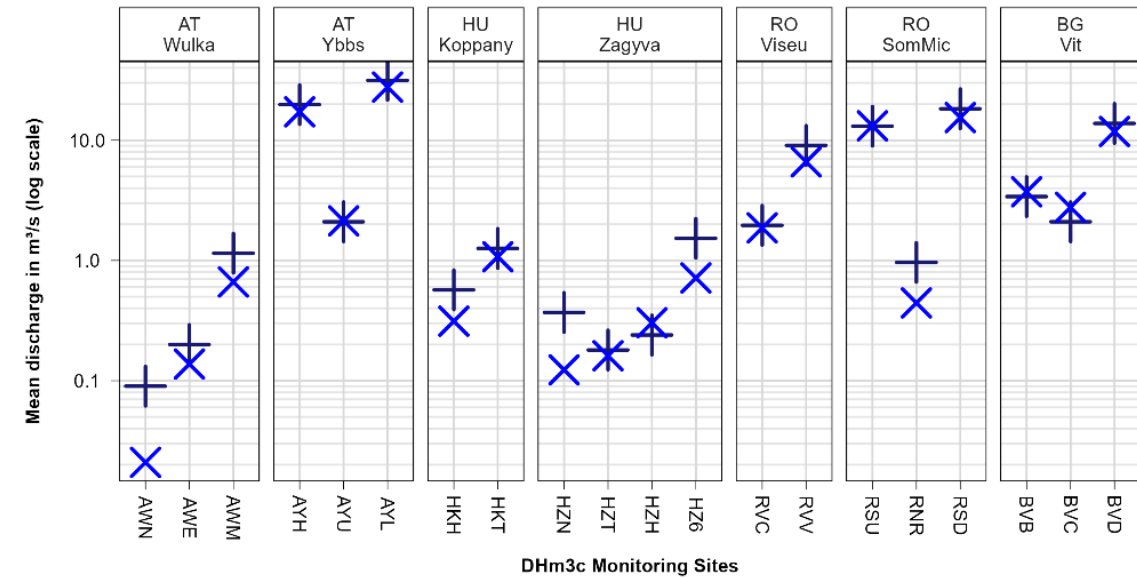


Fig. 3-19. Mean annual river flow (long vs. short term) over the 20 DHm³c river monitoring stations.
+: long term; x: short term.

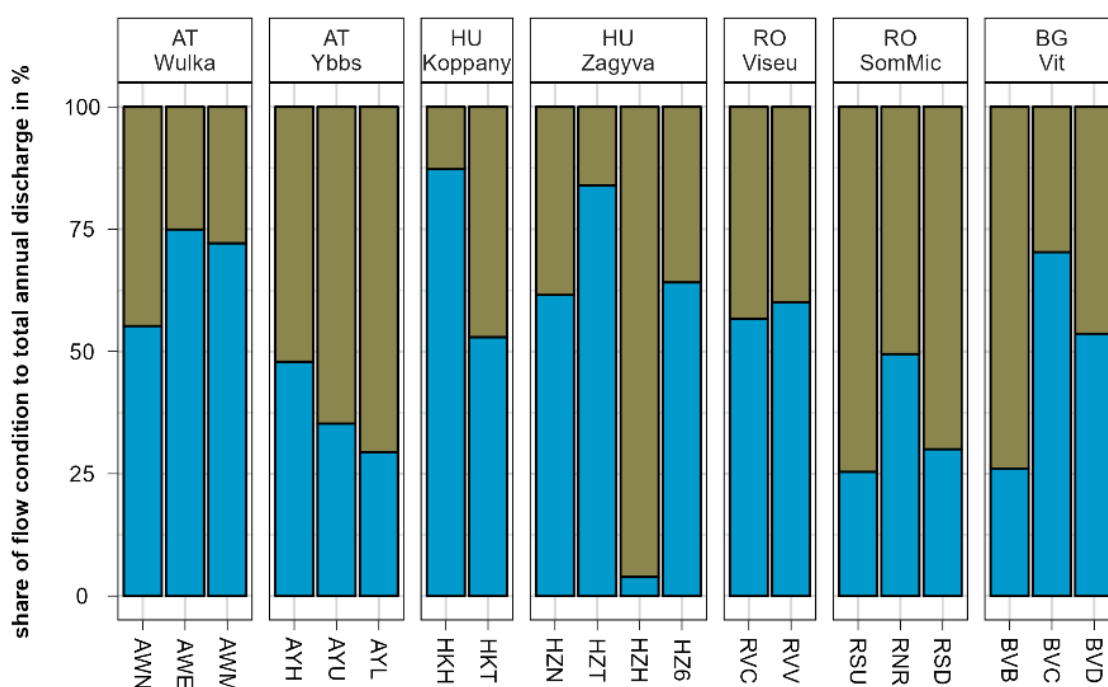


Fig. 3-20. Role (share) of the two flow conditions in yearly delivered water amount over the 20 DHm³c river monitoring stations.

Brown: event flow; blue: base flow.

3.4.3. Processing of concentration measurement data

The concentration data collected during the DH m³c monitoring campaign have been analysed. The composite samples have been taken under various flow condition which can be classified into two flow conditions: base flow (low-flow to mid-flow(MQ)) and event flow (high-flow). The event flow is characterized by increased transport of suspended particulate matter. For detailed information about how the flow conditions during sampling were defined. All samples were analyzed for total substance concentration of 47 micropollutants. Additionally, for heavy metals, dissolved concentration was analyzed by filtering the samples with 0.45 µm filters.

To avoid a bias in the calculated loads caused by outliers, average concentrations per substance, station, and matrix type (total or filtered) and flow condition was calculated. To be robust against single outliers with the rather small sample numbers, the median was chosen to calculate the average concentrations. As we are dealing with micropollutants, where environmental concentrations often occur around the lower limit of the analytical range of the available lab methods, for many substances a significant share of measurements are below the analytical LOQ (limit of quantification/quantitation), hence the data is partly censored.

To calculate statistical descriptor from censored data, we used the “ros” function from the R package “NADA” (Version 1.6-1.1). “ROS” stands for “Regression on Order Statistics” and is the “state-of-the-art”-method to deal with censored data (Helsel, 2012). The limiting factor is that the method only performs a reasonable calculation under these two conditions:

- There are at least 3 uncensored values (above LOQ)
- At least 20% of data is above LOQ.

The median concentration was based on one of the below methods, depending on the available data (first to last):

- 1) Value per flow condition (ROS)
- 2) Value for all samples (ROS)
- 3) Highest LOQ (equal to maximum evaluation)

Wherever possible, the median was calculated using ROS, but for those cases where this was not possible, a worst-case evaluation was chosen. To be consistent, the method is the same within each combination of substance, station, and matrix type (total or filtered).

In the case where there are, for each flow condition, enough measurements above the LOQ, the average concentration is calculated with ROS based on the flow condition, this reflects case 1 and is shown in Fig. 3-21. Fig. 3-22 shows the other two cases. For total matrix base flow, only 1 value is above LOQ, so ROS can't calculate a median value by the flow condition. Therefore, all samples are used, and because there are now 4 values above LOQ, ROS can calculate the median.

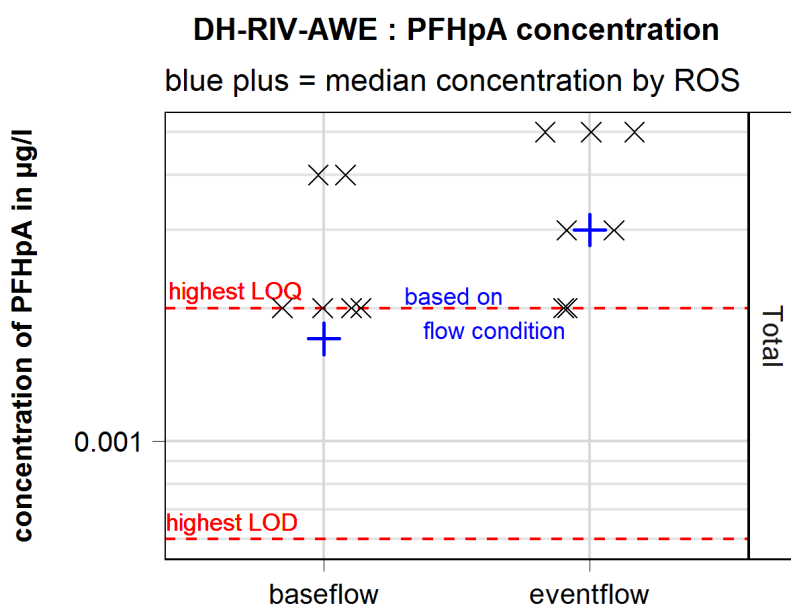


Fig. 3-21. Example 1: Concentration of PFHpA per flow condition for sample matrix total. All measurements are plotted as X-points. Plus-points show the median concentration and the text shows the source, which indicates that the median concentration is calculated by ROS for each flow condition.

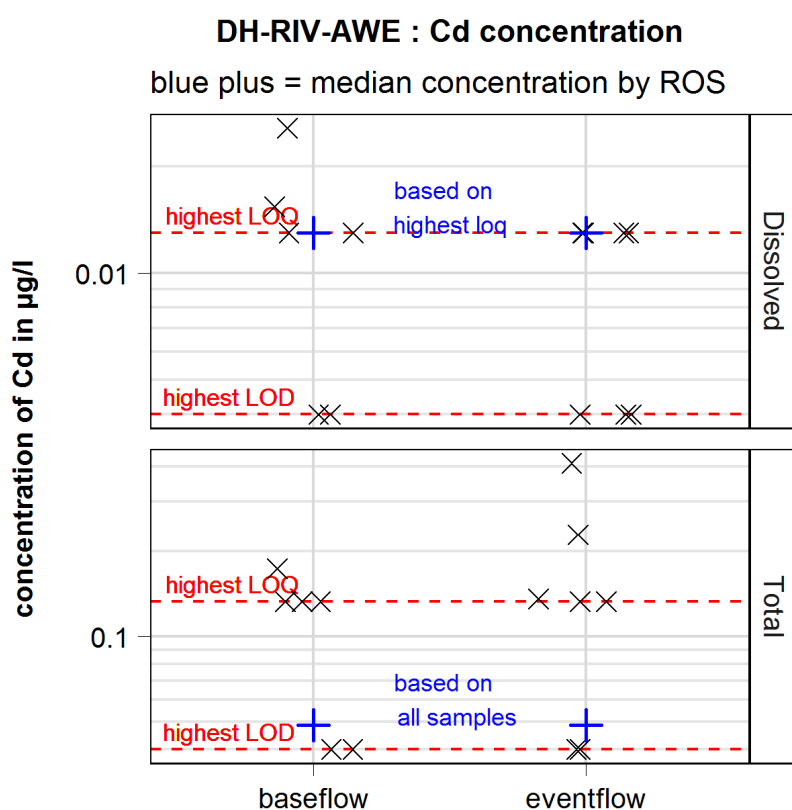


Fig. 3-22. Example 2: concentration of Cadmium (Cd) per flow condition and sample matrix. All measurements are plotted as X-points. Plus-points show the median concentration and the text shows the source.

The annual loads were also used to validate the results of the MoRE model. As the results come with an uncertainty, a different approach is used. The conditions on how to calculate the concentration is shown in Table 3-2.

Table 3-2. Different conditions on how to calculate the concentration for MoRE Model Validation

Source	Concentration by ROS	Concentration from LOQ
Lower threshold	25 th percentile	0
Median threshold	50th percentile	Highest LOQ/2
Upper threshold	75th percentile	Highest LOQ

3.4.4. Load calculation methodology

3.4.4.1. Load calc. method 1: "simulated grab sampling"

National hazardous substances monitoring is often done by taking 6-12 grab samples per year in equidistant time steps without consideration of the flow situation. Due to the more frequent occurrence of low- to mid-flow conditions, the chance that the low frequency grab samples are received during such situations is very high. To compare the resulting loads from

the flow stratified sampling to loads from traditional sampling a second approach was applied. To calculate the loads, only the median concentration of the base flow samples is used. The load per timestep is converted into load per year and then averaged. With this method we avoid dealing with data gaps in the river flow dataset (gaps can be up to a few weeks).

$$L_{BFonly} = \frac{1}{n} * \sum_{i=1}^n (\hat{C}_{BF} \times Q_{i,timestep} \times CU)$$

Form. 3.2-1.

CU	conversion factor to convert the calculated values into a specific unit (annual loads)
L	annual river load
n	number of all timesteps
\hat{C}	contaminant concentration (M/L ³)
Q_j	mean hourly river river flow (L ³ /T) at the i^{th} timestep
L	length
M	mass
T	time

3.4.4.2. Load calc. method 2: using the advantage of stratified sampling

The load calculation method was developed to fit to the flow-stratified DHm³c monitoring campaign strategy (Output O.T1.2).

The pre-processed concentration data was merged into the pre-processed flow data according to the flow condition, matrix type, substance and station name. Then a load per timestep is calculated by multiplying the river flow with concentration and a conversion factor, as shown in Form. 3.2-2.

The load per timestep was converted into load per year and then averaged. With this method, we can overcome the problem of data gaps in the flow dataset (gaps can be up to a few weeks). The annual load for each flow condition was then reduced to the actual share of the flow condition to reflect the actual distribution throughout the year. Both loads were then summed up to get the annual load. This can be written in a mathematical formula:

$$L_{BF+EF} = \frac{s}{n} * \sum_{i=1}^n (\hat{C}_{BF} \times Q_{i,BF} \times CU) + \frac{(1-s)}{m} * \sum_{j=1}^m (\hat{C}_{EF} \times Q_{j,EF} \times CU)$$

Form. 3.2-2.

where

CU	conversion factor to convert the calculated values into a specific unit (M/T)
s	share of base flow river flow to total river flow [0,1]
n	number of base flow timesteps
m	number of event flow timesteps

L	annual river load
\hat{C}	median contaminant concentration (M/L ³) (subscript indicates flow condition)
Q_i	mean hourly river river flow (L ³ /T) at the i^{th} timestep
BF	base flow
EF	event flow
L	length
M	mass
T	time

3.4.5. Results of load calculation

3.4.5.1. *Heavy metals*

Nickel and Zinc are shown here as examples for the behaviour of heavy metals.

The observed nickel median concentrations for the dissolved fraction are below the current EQS, but with the new proposed EQS some rivers would exceed this threshold as seen in Fig. 3-23. For the total fraction, the event flow concentrations are about 0.5 to 1 order of magnitude higher than for base flow throughout the pilot regions. This is supported by the literature.

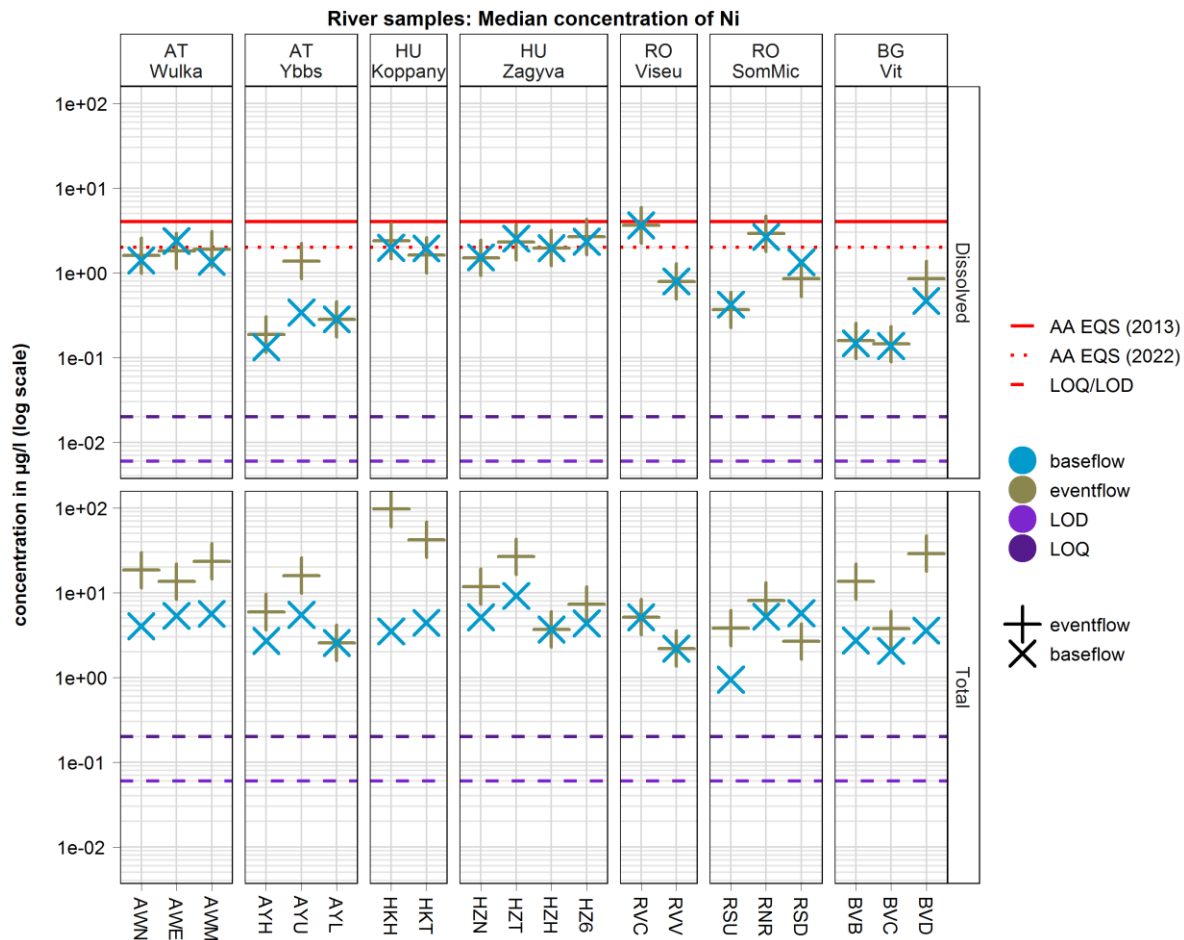


Fig. 3-23. Median concentration of Nickel used for the load calculation.
Concentrations for both flow conditions and sample matrixes with LOQ/LOD and the AA EQS

The specific loads in Fig. 3-24 reveal a heterogeneous distribution of loads throughout the pilot regions. For the dissolved fraction, the Romanian mining catchment stands out, clearly indicating the elevated background concentrations from the mining sites. In case of total fraction the Austrian Ybbs and Bulgarian Vit catchments show the highest specific loads. This is due to geogenic sources and high specific river flows. The specific loads of zinc are extremely high for the mining areas in Romania, see Fig. 3-25. This is the same case for As, Cd, Cu, Pb.

Conventional monitoring approaches for an EQS-based assessment with e.g. monthly grab samples miss situations with high concentrations of total suspended solids (TSS) and associated chemicals. This is a clear shortcoming, especially in the context of load observations. Fig. 3-24 emphasises this by showing the importance of event flow sampling for the heavy metal nickel. Loads are underestimated by half when event flow is not taken into account.

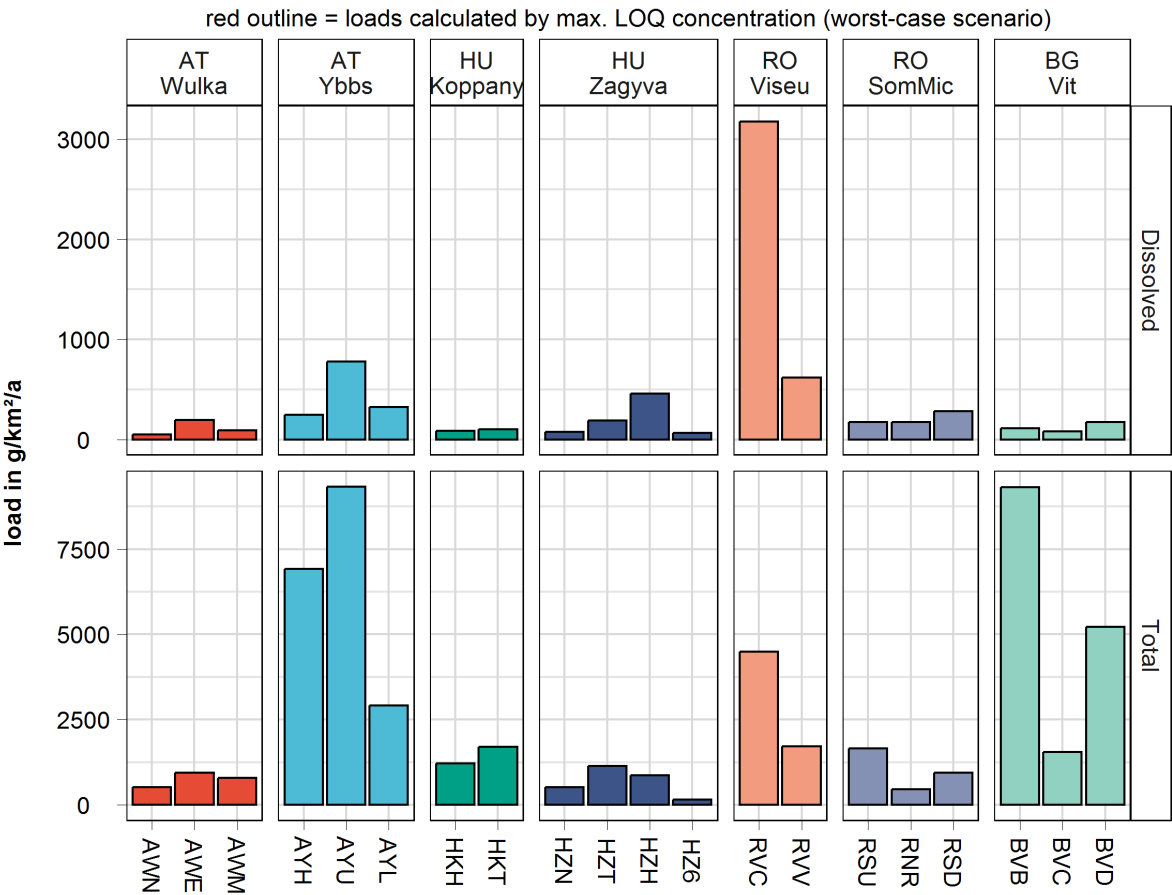


Fig. 3-24. Specific annual river loads of nickel for both sample matrixes.
Columns with red outline are loads calculated by max. LOQ (worst-case scenario).

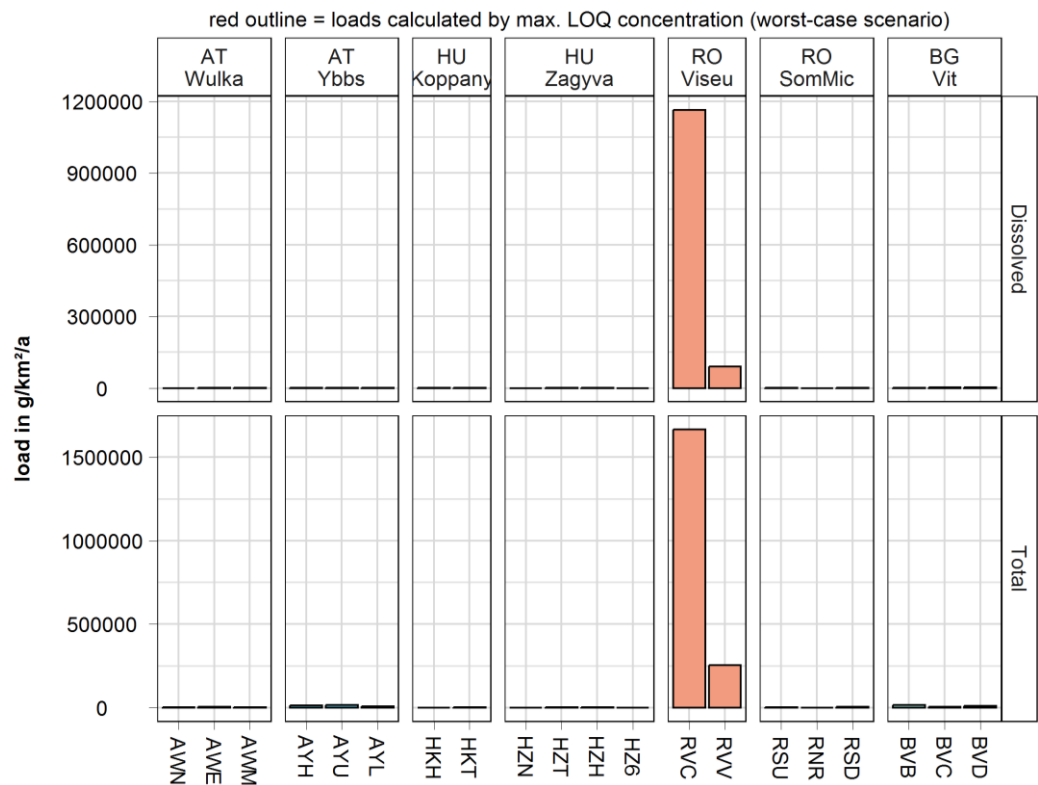


Fig. 3-25. Specific annual river loads of zinc for both sample matrixes. Columns with red outline are loads calculated by max. LOQ (worst-case scenario).

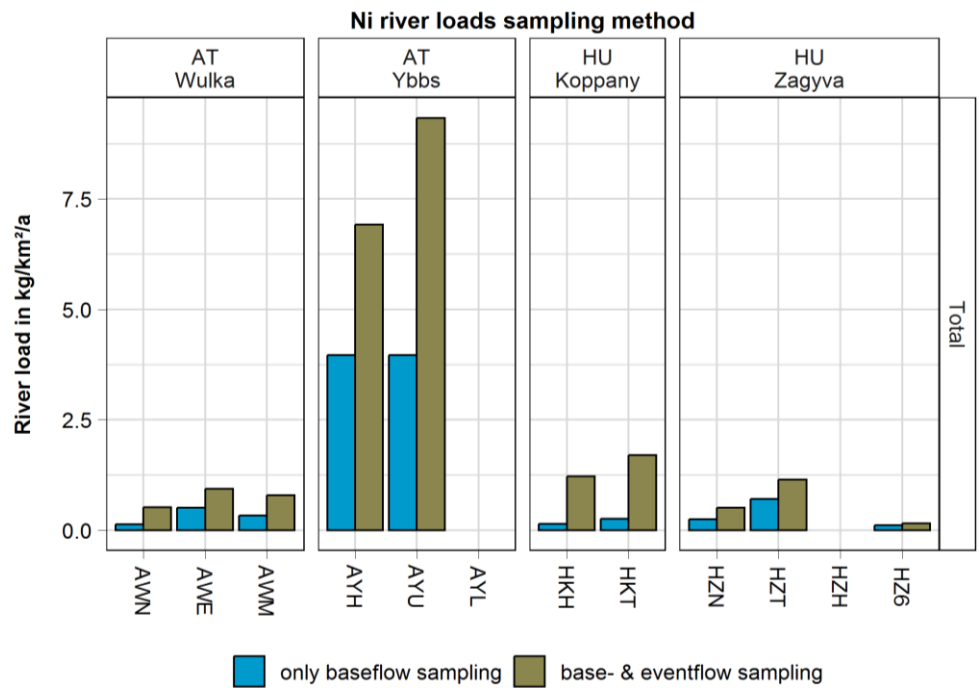


Fig. 3-26. Comparison of load calculation methods. Blue bars show specific loads calculated only with base flow samples and brown bars the specific loads calculated with both base flow and event flow samples.

3.4.5.2. Industrial chemicals

PFOS is shown here as example for industrial chemicals, , as it was detected in most of the pilot regions (Fig. 3-27). Especially the areas with high population densities (Wulka in Austria, Upper Zagyva below Salgótarján WWTP effluent and Somes below the effluents of Cluj Napoca WWTP) and low dilution factors show elevated values above the EQS (Environmental quality standard).

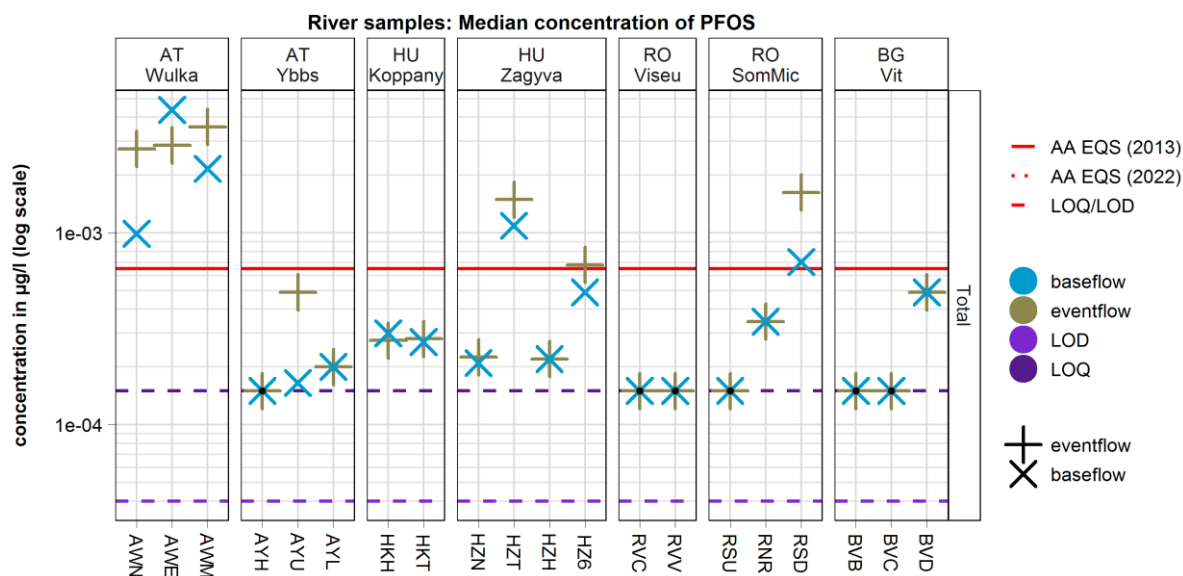


Fig. 3-27. Median concentration of PFOS used for the load calculation.
Concentrations for both flow conditions with LOQ/LOD and the AA EQS

The Austrian catchments and one Romanian station have the highest specific loads. Catchments with very low population densities (Viseu: RVV, RVC, Vit: BVB, BVC, Ybbs: AYH) show very high uncertainties because those loads could only be calculated using LOQ-concentration, hence it can be considered as worst-case scenario (Fig. 3-28).

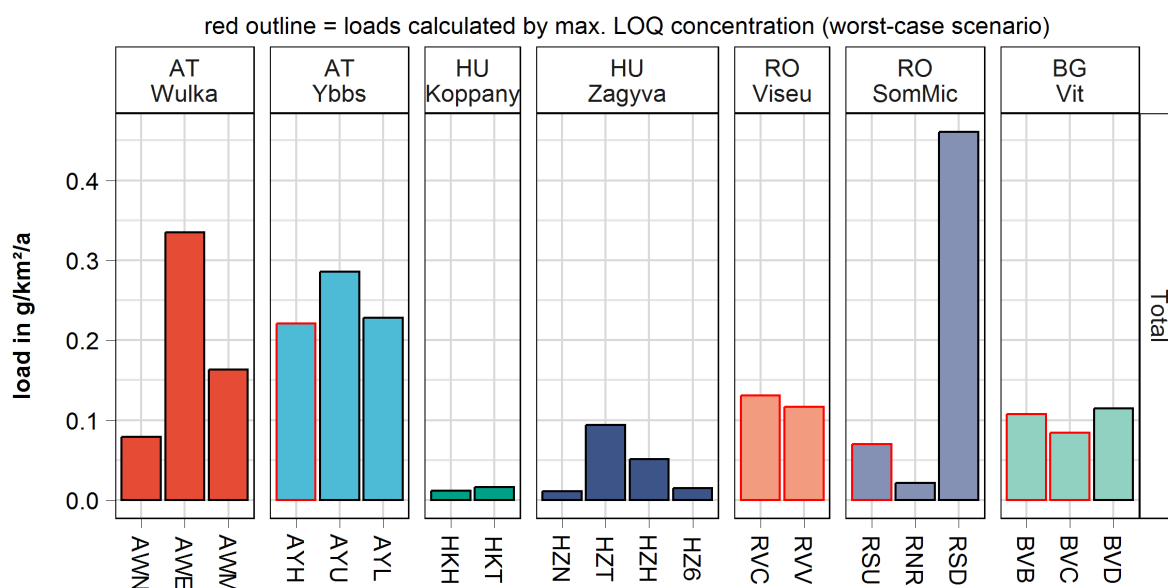


Fig. 3-28. Specific annual river loads of PFOS.

Columns with red outline are loads calculated by max. LOQ (worst-case scenario).

3.4.5.3. Pesticides

Metolachlor ethanesulfonic acid (Metolachlor ESA) is a metabolite of the herbicide Metolachlor. It is found in the river waters throughout the pilot regions in various concentrations, see Fig. 3-29, which is likely due to the strongly varying application rates across the regions. With regard to specific loads (Fig. 3-30), the catchment “AYU”, which is dominated by agricultural land use, stand out due to relative high concentrations and specific river flows compared to the other regions. Load estimation comparison (Fig. 3-31) show differences for the Ybbs and Koppány catchments, the two most polluted rivers at least based on concentrations. While for the Ybbs the differences in annual loads are marginal by the comparison, for Koppány catchment, the there is a twofold underestimation if high flow loads are neglected. This is coming from the fact that in the Ybbs the high flow and low flow concentrations are in the same range (quite unexpected result), while at the Koppány, there is a large difference in the concentrations when sampling the two strata (high-turbidity samples might explain this large deviation). This highlights the unique circumstances found in catchments.

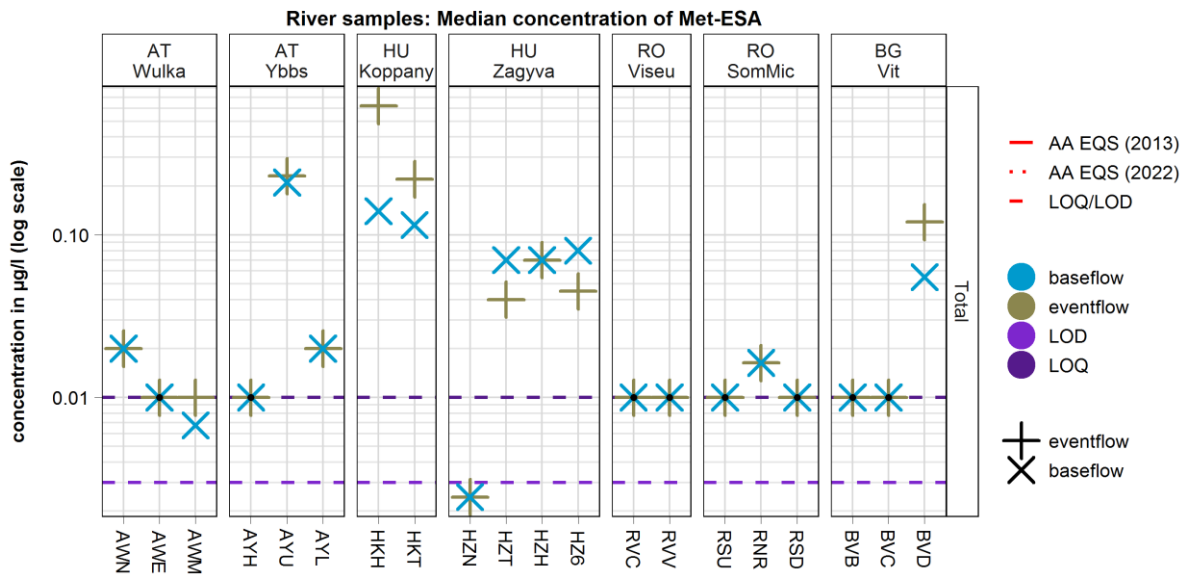


Fig. 3-29. Median concentration of Metolachlor ESA used for the load calculation.
Concentrations for both flow conditions and sample matrixes with LOQ/LOD and the AA EQS

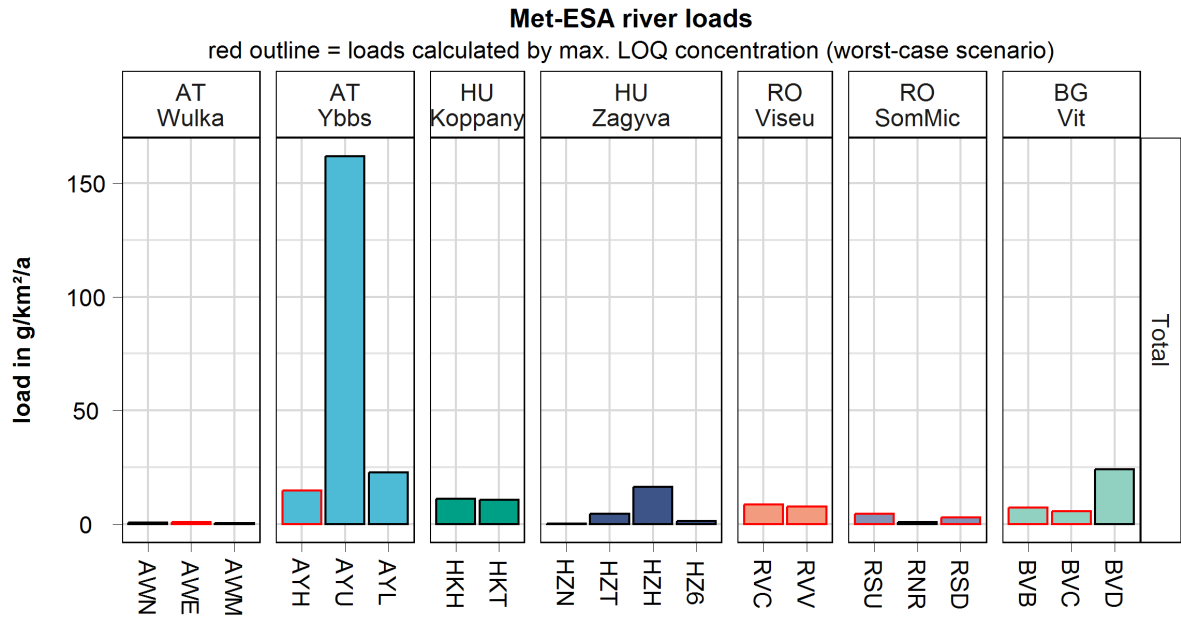


Fig. 3-30. Specific annual river loads of Metolachlor ESA.
Columns with red outline are loads calculated by max. LOQ (worst-case scenario).

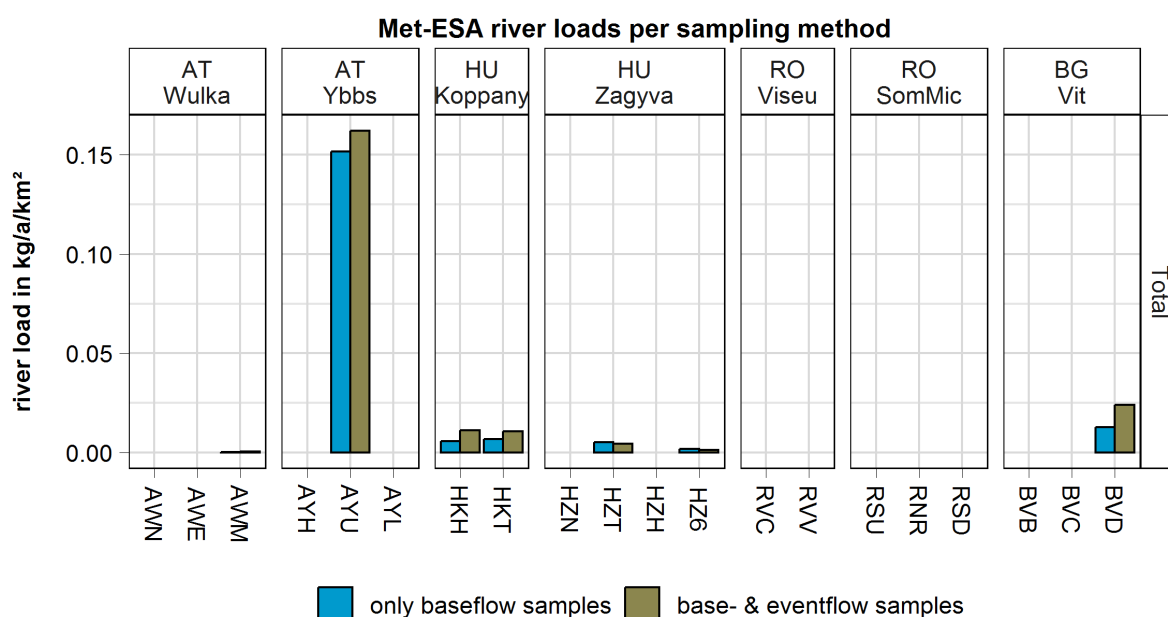


Fig. 3-31. Comparison of load calculation methods.

Blue bars show specific loads calculated only with base flow samples and brown bars the specific loads calculated with both base flow and event flow samples.

3.4.5.4. Pharmaceuticals

Diclofenac, as an example for pharmaceuticals, is an indicator for anthropogenic pollution, related mostly to WWTP effluents and combined sewer overflows. The measured concentrations of Diclofenac (Fig. 3-32) are up to 2 order of magnitudes above the newly proposed EQS threshold in the higher populated pilot regions.

The influence of WWTP effluent for diclofenac is, as expected, clearly visible in (Fig. 3-33). For example the Stations “AWE” and “AWN” have approx. the same size upstream catchment but “AWE” is downstream of a big town with WWTP, and “AWN” has no WWTP inflow. The loads are by an order of magnitude higher for the WWTP influenced station “AWE”. This confirms that sewage treatment plants are a major source of this pharmaceutical. However, diclophenac was also detected at “AWN”, albeit in low concentrations. This means that there are also other diffuse sources of diclofenac. By comparing the specific loads over the disposing inhabitants, increasing loads with increasing disposing inhabitants’ density can be observed (Fig. 3-34.).

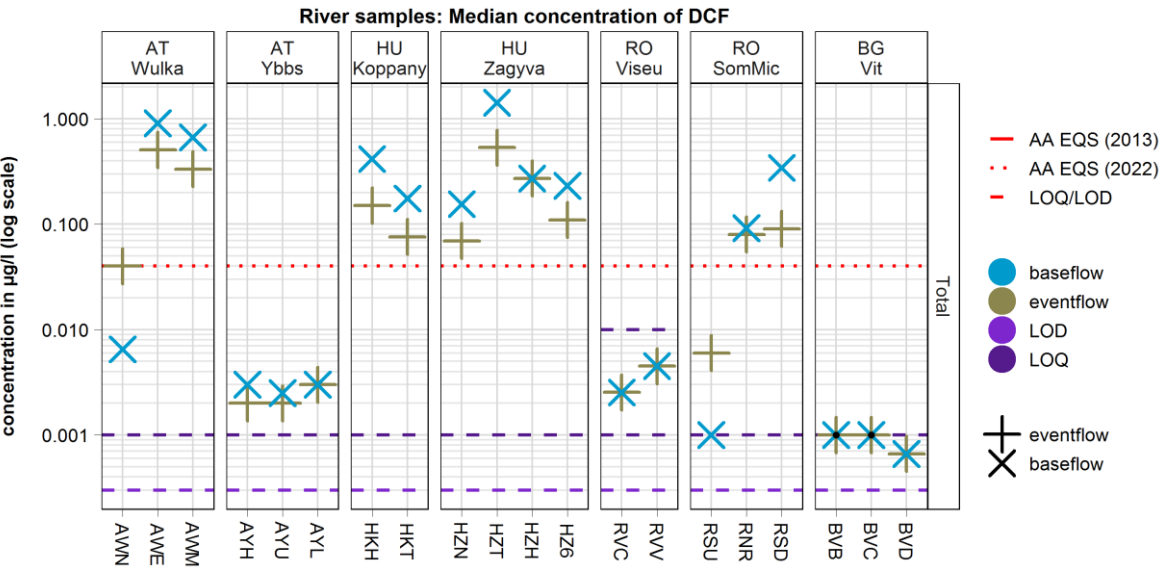


Fig. 3-32. Median concentration of Diclofenac used for the load calculation.
Concentrations for both flow conditions with LOQ/LOD and the AA EQS

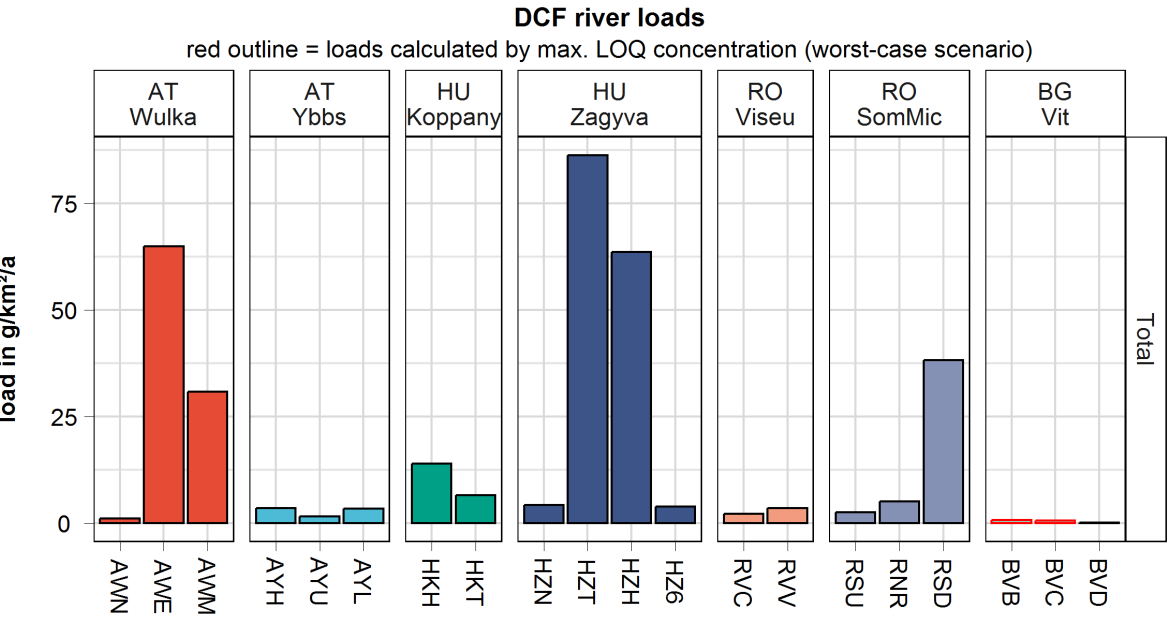


Fig. 3-33. Specific annual river loads of Diclofenac.
Columns with red outline are loads calculated by max. LOQ (worst-case scenario).

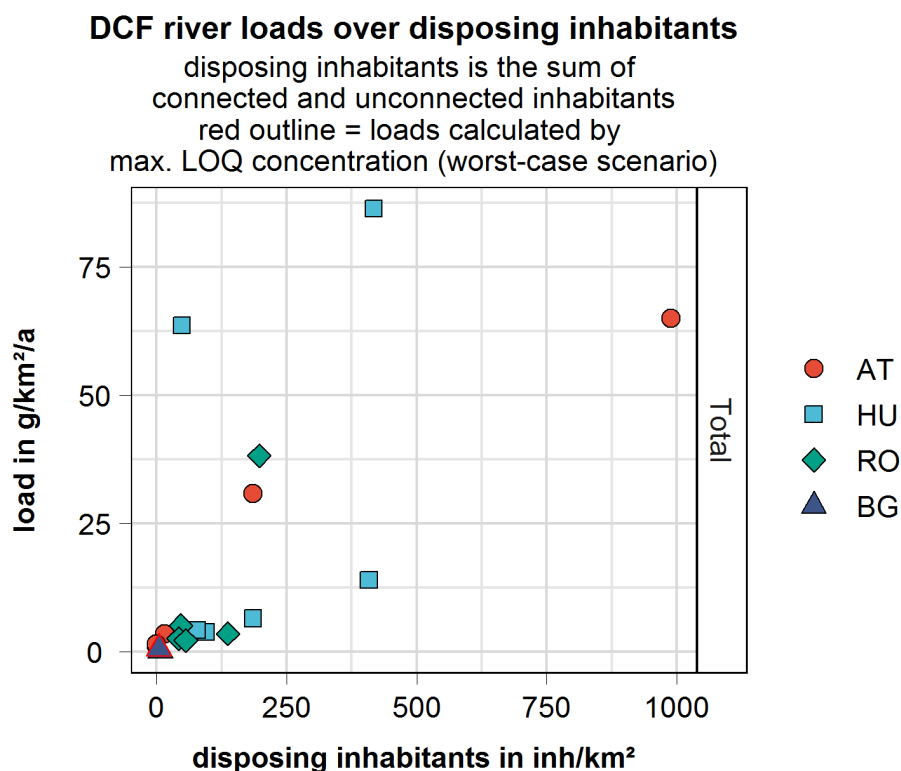


Fig. 3-34. Specific load over disposing inhabitants density for the substance diclofenac. Colour indicate the country of the station.

3.5. Conclusions – the added value of the developed sampling approach

3.5.1. Heavy metals in rivers

Some extremely high HM values were detected in river high flows, even outreaching concentrations measured in wastewaters (in case of As, Cr, Cu, Ni, Pb, Zn), which clearly indicates that these originate (at least partly) from diffuse sources and are washed off / resuspended during surface runoff/higher river flow conditions (high flow events).

3.5.2. PAH

One possible explanation for lower molecular weight PAH forms occurring more often in aqueous samples and less often in soil samples is that they show lower hydrophobicity, the threshold seems to be around $\log K_{ow} = 5.5$.

3.5.3. Conclusions of load calculation

Discharges during sampling were lower than average, except for the two headwaters in the Bulgarian basin, and the sidereach of the Ybbs River and the Somes above Cluj Napoca. A large variation of area-specific loads was observed for most substances across the catchments. This variability is likely to be related to the large differences in catchment characteristics and

emissions. The large influence of wastewater discharges and the high share of high-flow loads should be emphasized in this respect. Pharmaceuticals are good indicators of anthropogenic point sources in the catchment but it was found that they may also enter the waterways by diffuse pathways, which is a new finding of this project. The inclusion of high-flow events in the monitoring has a significant effect on annual load estimates in case of certain substances and catchments and should therefore play an important part of any sampling program. Mining sites effluents showed extremely high specific load values with respect to heavy metals (Cd, Cu, Pb and Zn) and arsenic. The varying occurrence of pesticides in the rivers indicate that their application rate varies strongly across the regions.

4. SUMMARY

4.1. River sampling

4.1.1. Base flow composites sampling

As base flow monitoring, bi-monthly composites were collected from 8 weekly grab samples in 20 river sections of 7 pilot regions for a 1 year long period. The traditional grab sampling approach is very stable and reliable however demanding in terms of human resources. Costs of lab analysis however were reduced substantially by the composite approach. By the bi-monthly approach six samples were collected, that also provided a chance to see seasonal variations in concentration levels and to produce statistics. The only downside of the approach is the limitations in the sample preservation. Some substances (e.g. PAHs) needs to be stored in glass bottles and for long term storage they also need to be frozen. This problem in this monitoring have been solved by keeping the glass bottles and changing the storage from freezing to only cooling in low temperatures (<4 °C) and dark conditions. This solution obviously brings some risk to loose samples during storage. According to our observations (including a small experiment delivered for PAH loss during storage and transport) the levels in total samples were more relevant than dissolved phase samples, therefore during the campaign, dissolved samples were stopped to be measured. Total concentrations were measured to be lost up to 30-40% within two weeks. This leads to the conclusion that the base flow river concentration sampling for PAH is not appropriate by the long term composite method. In case of the other substances, the approach is feasible and efficient, while in case of PAHs the option to freeze the sample in a glass bottle still remains an option. Another experience spotted by BME laboratory was the occurrence of calcium carbonate precipitation as the result of freezing and thawing of the samples for metal (PTE) analysis. This could be prevented by the initial acidification of the sample prior to freezing. The findings of this approach have been supported by a series of experiment, written down in a paper and is to be submitted soon to a scientific journal.

Measured river concentrations of the analysed elements gave a detailed insight into sources, spatial variability in the occurrence or actually spatial homogeneity in the behaviour of certain substance groups. A good example of clear pattern in the occurrence of Arsenic in higher concentrations in the lower part of the Basin and lower in the mountainous catchments.

4.1.2. High flow composite sampling

Flow proportional sampling of high flow events have been delivered in the monitoring campaign at 20 locations in seven pilot regions. The sampling have been carried out with either automated sampler devices or with grab sampling. The samples were therefore representing the flood wave mean concentrations, which provided an opportunity to estimate yearly loads from high flow events and base flow events separately. While high flow event grab sampling was very demanding in physical and mental means, automated sampling required also large efforts, that is to operate and maintain the devices. The latter also required

immediate removal of the sample following the flood wave and prepare it for sample preservation and transport immediately (optimally within 24 hours). This required strict logistical order.

High flow concentrations of selected chemicals showed significant increase compared to low flow samples: Phenols, BpA and PFOA and pesticides showed such behaviour, indicating that diffuse sources are more relevant than point sources. On the other hand, chemicals with dominant point source related pathways showed lower concentrations in high flow composites (pharmaceuticals). The value of high flow sampling is undoubtedly high if more accurate yearly load calculations are to be done.

4.1.3. Lessons learned

A wide range of experiences have been collected during this extensive campaign, which are written in detail in the pilot activity descriptions and in Annex A3: "Description of monitoring activities at 7 pilot regions". The most important lessons are related to the operations of high flow sampling with advanced devices and sensitive sensors (turbidity), which require high frequency maintenance.

4.2. Wastewater sampling

Raw wastewater samples were collected at 9 municipal, 5 mining and one industrial site, while treated wastewater were collected at 10 municipal, 1 industrial and 1 mining sites. Three samples were planned at most locations within a one year period to also highlight seasonal differences in effluent concentrations. Sampling were in most sites carried out by continuous autosampling for 1 week, producing seven daily composites, which were flow proportionally mixed retrospectively. In some of the treatment plants and raw sewage effluents (Vit) daily composite grab samples (hours) were collected. Samples were homogenised with mixers then subsampled by the required amount.

Observed concentrations show interesting pictures with regard to the spatial distribution and temporal variance of the micropollutants in the wastewater discharge. As an example, pharmaceutical concentrations were found to be higher in Hungarian wastewater streams than in other locations. Bisphenol A and perfluorinated compounds were found in higher concentration at the Balatonlelle station compared to the rest of the plants. Samples from mining activities also show some interesting results, phenols were found in unexpected quantities, while zinc and copper concentrations were found in extremely high concentrations.

4.2.1. Lessons learned

The preferred method of cooling is built in active cooling systems as passive cooling requires frequent site visits to keep the temperatures below the required levels. Automated samplers also require regular checking as sometimes reduced sample amounts were collected due to unknown reasons (probably temporary clogging). The involvement of onsite personnel is not

advised (mixed experiences), it is preferred to control the sampling on our own with regular site visits and sample collection.

4.3. Atmospheric deposition sampling

Bulk atmospheric deposition samples were collected at 15 stations within the 7 pilot regions. Sample collection was delivered with various simple design collectors (and also professional heated devices at Ybbs pilot region), using large diameter (~30 cm) glass or ceramic funnels and glass sample collectors. Samples were collected after rain events and stored in dark, cold/frozen conditions in a larger composite glass collector. Despite initial glass brake issues, in two locations freezing was maintained by using high quality safety bottles (which also broke in some instances but no sample was lost). Sampling was delivered throughout a year, in most places 4 samples were collected from a 1-3 months long period. By design the samples were aiming to be collected from one month, but dryer months required the sampling to be extended by several weeks or months.

Deposition concentrations showed lot of interesting patterns. In some instances very surprising substances (BpA and DCF) were found in the collected samples. PAH substances did not show very high variation across the catchments, but clearly higher concentrations were measured at Zagyva station, which might be owed to the relatively close vicinity of a coal power plant (a major emitter in the catchment). Pesticides have been found in 6 out of 7 catchments in low concentrations. Perfluorinated alkyl substances (mostly only PFOA) were also detected in all catchments in very low concentrations (<1 ng/l). DCF (25/64 samples) and BpA (40/64 samples) were also detected in several samples, showing that atmospheric emissions (or the recirculation of deposited pollutants from historic emissions) of these chemicals are also present.

4.3.1. Lessons learned

The collection method requires a devoted onsite person to handle event samples. Discrepancies have occurred in the basic water quality parameters in some sites due to handling or storage problems. Frozen samples in glass containers need very cautious design. High quality safety glass containers with plastic protection layer is needed to avoid sample loss upon glass break. Organic matter and insect deposition were experienced in the samples, which in some case caused the elevation of electrical conductivity (i.e. the total ion content) of the collected sample.

4.4. Soil sampling and observed concentrations

At each pilot region, 10 composite soil samples (each one consisting of 20 subsamples) were collected with an intensive soil sampling campaign during the spring and summer of 2021. Samples were collected from all major land uses present in the catchment, predominantly tilled agricultural land (rowcrops), pasture and forests, but at some catchments, vineyards and

scrublands were separately collected. Beside the land use, soil information was also used to create homogeneous spatial units that might show differences compared to each other.

The stratified composite soil sampling approach proved to be successful in terms of value and spatial representativity of the contamination levels. This was indirectly proven by the comparison of measured concentrations with that of the SPM samples at three out of the seven pilot regions (Wulka, Koppány, Zagyva). Concentration levels of two substance groups (metals and PAHs) show very strong correlation within the pilot regions, proving that the substances in the suspended sediments come predominantly from soils. Clear distinction was found of the soil concentration levels across land use types in all monitored pilot regions. The highest concentration levels of the pollutants that are primarily transported via atmospheric processes were found in forests, which is fully in alignment with the findings of several research studies. The applied monitoring approach to gain concentration levels for the aim of inventorying of hazardous substances can be advised for a wider practise. Even though it is a resource intensive approach, the high value of the outputs for national/regional emission inventories may pay off. The high number of samples to create one composite sample ensures the wider spatial representativity, while the number of spatial units can reflect on the spatial variability of the concentration levels within the pilot regions and across the land uses and soil types. Observed concentration ranges across the Danube Region highlighted large spatial variability in the occurrence of the examined substances. Metal concentrations in soils showed much elevated levels in the two Romanian catchments compared to the other five watersheds, which is clearly indicating the higher geogenic sources in the area. However anthropogenic sources are also proved for most examined elements in most pilot regions. The presence of PAH compounds in soils (13 out of 16 were found in quantifiable levels everywhere) were demonstrated in all catchments, with a large spatial variability. For most compounds the Austrian Wulka pilot regions showed the highest level of contamination, followed by the Ybbs, Zagyva and Viseu pilot regions, while in Somes, Koppány and Vit catchments significantly lower level (factor of 3 to 5 compared to Wulka) of contamination were present. Presence of PAH in forests were significantly higher than for pastures and agricultural soils.

The presence of PFAS compounds were also evident in most catchments (8 substance out of 13 mostly above LOQ), while their spatial variability were larger and clear pattern were not repeated for the substances, indicating different sources and pathways for them. Highest levels of contamination were observed at the Wulka and Ybbs pilot regions. Observed levels for landuses differ significantly, with highest mean concentration in forests (Value), while similar levels found for pasture and agricultural lands.

The occurrence of the examined pesticides were not generic, only two catchment showed detectable concentration for Metolachlor (Koppány) and Tebuconazole (Zagyva). Presumably the differences in the application practise and in the timing of the application may have resulted in these differences.

4.4.1. Lessons learned

Sample locations has to be carefully selected using all type of GIS and remote sensing data. Final selection of appropriate locations can be achieved on site (In some cases fenced property was restricting access). Heavily compacted soils cannot be sampled with pürckhauer type sampler, auger head sampler is more appropriate at those locations. Processing of heavily compacted soil on site is also challenging, ceramic mortar can be a useful tool to breaking up fragments. Site access to a large number of samples can be an issue as it is very uneconomic to get permission to so many properties. In the current campaign, permissions were asked on site where owners were present. Permissions were granted in most cases, however denial was also experienced.

4.5. SPM sampling

Sampling has been carried out in three catchments (8 sites all together). Two sampling approach was applied, one passive and one automated method. The first being very cost efficient and proved to be extremely useful to collect information on base flow (or mixed base flow/high flow) contaminant concentration levels of the suspended sediments of river water. In high flow conditions the method has limitations with regard to the quantity of the collected sediments. In locations with very intense erosive events it is suitable to collect several kg of samples from one flood wave, however in positions where lower turbidity flood waves are expected, the sampler would collect only smaller amount of sediments. Automated samplers with larger collection tanks are also very useful tools, however their operation and maintenance are more resource demanding, and higher skills are needed. The great advantage of such devices is that concentration levels in the SPM can be directly linked to flood conditions, SPM concentrations, therefore loads can be calculated from it. Their suitability is also depending on SPM levels in runoff, as sufficient amount of solid can be difficult to collect unless very large tanks are used (several 100 l). Their final advantage is that this method collects the total sediment phase including the finest (and most valuable in terms of carrying surface) sediment phase. According to our experiences, both approach has their value and can be advised to use for the right purpose: Phillips type samplers are more advised to be used for the monitoring of SPM in base flow/midflow conditions and with the aim to get an overview of concentration levels during these conditions. The use of large volume autosampler is more advised for more detailed investigative monitoring for research purposes especially during high flow conditions. The use of such device is more feasible when a larger spectrum of elements/contaminant substances can be measured from one sample to gain the most information from the invested energy and resources.

Concentrations found in SPM samples were generally higher compared to concentrations in soils, while a very strong correlation was found with them in case of PAHs and metals, indicating that the primary source of these contaminants in the suspended sediments is the soil in the catchments. The rate of increase compared to soil concentrations is different for the substance groups, PAHs being the highest (7-8 on average), metals the second (2-3 on average) and very mixed for PFAS. The comparison of the two matrices also highlighted some

other sources (e.g. Zn, PFOS) in SPM appearing in different levels in different catchments, therefore it proved to be an interesting tool to help source investigation.

4.5.1. Lessons learned

Preliminary information about SPM concentrations during low flow and high flow conditions is necessary to prove the suitability of the sampler for the collection of suspended sediment in larger quantities. Outflow pipe clogging was not experienced, however biofilm growth can cause problems in warmer water temperatures. The emptying of the collector pipe requires a large sample collector bottle and two men in order to not loose sample.

5. CONCLUSIONS

The proposed and developed monitoring approach seemed to be efficient with respect to all resources and also regarding outcomes.

As discussed in chapter 3.2, while being similar in many aspects (e.g. AD concentration of most substances), there are important differences between pilot regions from other aspects (e.g. soil concentrations of PAH and PFAS). The list of substances – as expected – really covered and reflected both the natural diversity (e.g. low flow concentrations of dissolved As) as well as the wide range of anthropogenic influences (e.g. pesticides present in some pilot regions while missing in others). At the same time, new and unexpected findings were brought by the concept (e.g. uniform monitoring of pesticides in all pathways and locations lead to the finding that pharmaceuticals might be present also in catchments with no WW influence).

The low flow composite samples seem to cover well the low flow concentrations. Event-oriented sampling of high flows – although required lots of efforts – seemed to supply substantial amount of additional information. Another resource-intensive activity was the installation and operation of in-line sensors – which, similarly to the autosamplers delivered information essential for load calculation and for understanding of the catchment and riverine processes. We could make use of this additional information during the load calculation.

The stratified random sampling protocol applied in soil sampling reached the target it was applied for: while no tendency can be observed when comparing pilot-wise concentrations, clear trends will draw when comparing land-use wise concentrations against countries (see chapter 3.2.4). SPM sampling helps establishing and understanding the relationship between soil and river high flow events.

Covering the range of pathways – while confirming already existing or trivial information as the wide range of chemicals that reach surface waters through WW discharges – enabled their quantification, but lead to new findings, too. On the other hand, some pathways were missing from the monitoring program, in particular groundwater, which turned to be a drawback when facing modelling needs / uncertainties.

Further processing of the monitoring data might lead to new results, may deliver new observations. E.g. it would be interesting to relate high flow concentrations / loads to catchment characteristics like the share of different land use classes or indicators of economical development. Low flow concentrations might be related to wastewater or inhabitant-related characteristics (e.g. share of WW in the river or dilution capacity).

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ANNEXES

Annex A1: “Deliverable D.T1.2.1 Pilot region descriptions – internal document”

Annex A2: “Deliverable D.T1.2.2 Methodological approach for the measurements in the pilot regions and final selection of substances – internal document”

Annex A3: “Description of monitoring activities at 7 pilot regions”

Annex A4: “Standard Operating Procedure – Protocol for sampling, storage and transport during monitoring in the pilot regions – Internal document”

Annex A5: “Laboratories’ analytical reports”