Danube Transnational Programme

Danube Hazard m^{3}c

Demonstration of harmonized and cost effective monitoring- Annex V

Description of monitoring activities at 7 pilot catchments in the Danube Hazard m3c project

Content

1 CONTACTS OF RESPONSIBLE PERSONS

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2 Koppány catchment, Hungary

Koppány creek– Törökkoppány (HKH), Tamási (HKT)

2.1 River sampling

Overview

Total number of samples taken:

	Planned	Achieved	Description
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

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes		Discharge based on Q – H function	
Conductivity probes	Yes	Hach 3798-S sc inductive conductivity probe.		Figure 3
Turbidity probe	Yes	Hach Solitax t-line sc submersible probe. FNU range: 0.001-4000. Wiper blade.		Figure 3
Automated sampler	Yes	Own development. Described in Budai et al[1].	The device was installed in the existing water gage house operated by the Water Directorate (ADUVIZIG). The device was developed by our team (ref)	Figure 2, Figure 6
High-flow grabsampling	No			

Lessons learned

- Autosampler: Peristaltic pump operation is fairly safe in terms of clogging, no major problems occurred. Setup was tested for flow velocities and TSS transfer. Minimum required flow rate was established. The drawback of the method is that it can not follow the large variation of river flow in real scale, as the rate of flow with the pump setup can only be tripled (with this applied pump). Silicone tubing has to be lubricated in every two month and replaced after one year.
- Probes:
  - Conductivity probe is reliable, but biofilm growth on the surface of the instrument reduce the measured conductivity. Regular cleaning is necessary (two weeks at least during summer).
  - Turbidity probe wiper stuck in some cases. Otherwise, despite the wiping, some deposition occurs, that need to be removed by cleaning. Deposition causes higher variation and higher mean turbidity values.

[1] Budai, P., Kardos, M.K., Knolmár, M. *et al.* Development of an autonomous flow-proportional water sampler for the estimation of pollutant loads in urban runoff. *Environ Monit Assess* **192**, 572 (2020). https://doi.org/10.1007/s10661-020-08536-3

- Data transfer:
    - Signal transfer 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 record on the instrument is a must for at least a month.

Site photos:

Figure 1 - Törökkoppány station, with antenna, solar panel, later with wind generator

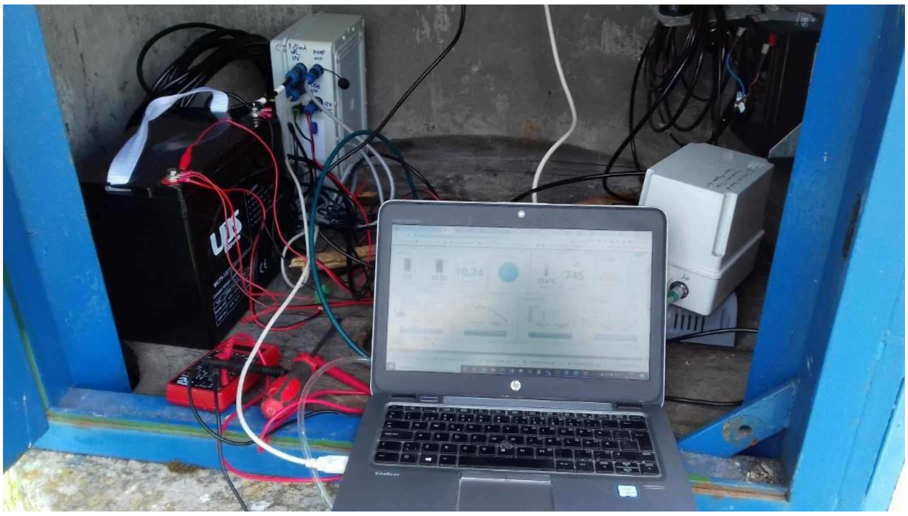

Figure 2 - Water collector arrangement at Törökkoppány station

Figure 3 - Turbidity and conductivity sensor fixing at Törökkoppány station

Figure 4 - Sensor installation at Törökkoppány station

Figure 5 - Water gage house at Tamási station

Figure 6 - River sampler housing at Tamási station

Figure 7 - Turbidity sensor during cleaning at Tamási station, sensor frame at river bank

2.2 Soil sampling

Number of samples taken:

	Planned	Achieved	Description
Soil samples	10+10	10+10	1 composite is made of 20 samples each, and each of the 20 samples is composed in turn of 1-5 subsamples, to be taken close to each other

Tools/method used:

Pürkhauer type sampler, rubber hammer, tools for removal of the soil (metal stick)

Figure 8 - Soil sampler and storage during sampling

Soil sample locations

At Törökkoppány subcatchment (HKH) the samples were divided to three agricultural and one forest composite samples, the lower part of the catchment was divided to three agricultural and two forest samples, and one pasture sample was collected from the whole catchment (Figure 9).

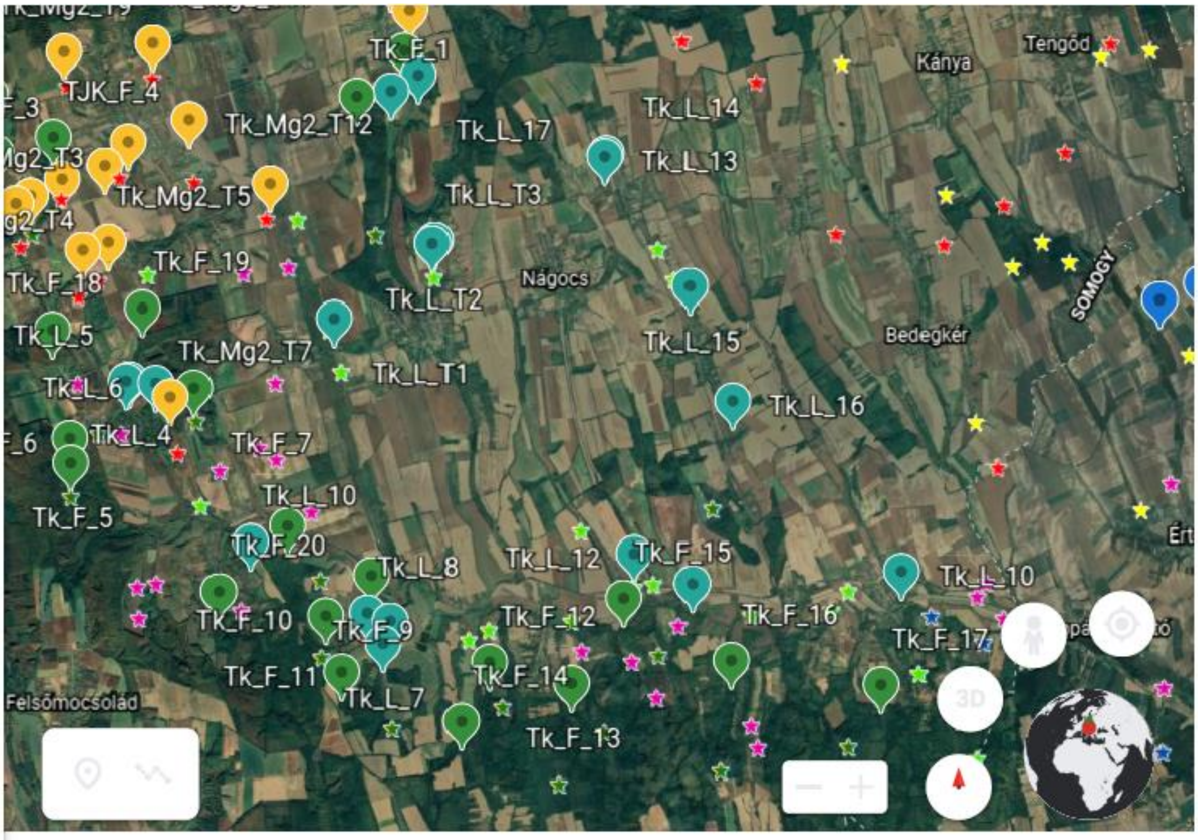

Figure 9 (ONLY EXAMPLE. A full overview of all the locatrions would be required)

Lessons learned

- 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.
- Site access problems (physical, land owners): Owners were helpful in most cases and allowed the sampling.
- Sample processing: 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.

2.3 Atmospheric deposition sampling

Site descriptions

Törökkoppány: The sampler was placed at the garden of a local person (citizen scientist, Figure 10) in Törökkoppány village, who were already collecting rain data. The person emptied the water after each rainfall event to a larger 10l glass bottle, which was kept in a refrigerator.

Tamási: The sampler was placed at the met station of the regional water directorates headquarters, in Tamási town (Figure 11). The arrangement is similar to the above one. A large bottle was also kept in a refrigerator at site, and rainwater was emptied after each rainfall event.

Figure 10 – Atmospheric deposition sampler at Törökkoppány

Figure 11 – Atmospheric deposition sampler at Tamási (orange pipe with funnel)

Instrument used: Simple design (own development) using a 200 mm PVC pipe, in which the 2 l glass sample collector was placed. 300 mm diameter glass funnel was placed on top, without filter. Glass bottle was covered with aluminium foil to reduce direct light entering the bottle.

Number of samples taken (Overview table)

Lessons learned: Many 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. Glass filter should be used if possible to reduce this effect.

2.4 Waste water sampling (including mining)

Site descriptions

Samplers were placed at the inlet and outlet channels of the municipal waste water treatment plant of Balatonlelle town. Electricity supply was provided by the operator, but cooling possibility was not available. Personnel was not involved in the sampling.

Sample overview

	Planned	Achieved	Description
Wastewater samples	3	4	4x2 samples, 1 at outlet, 1 at inlet each time.

Site photos:

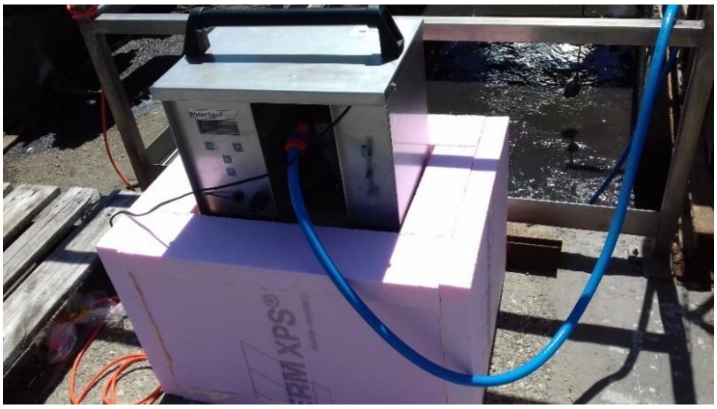

Figure 12 - WaterSam porti sample collector at Balatonlelle inlet chamber

Figure 13 - WaterSam porti sample collector at Balatonlelle inlet chamber

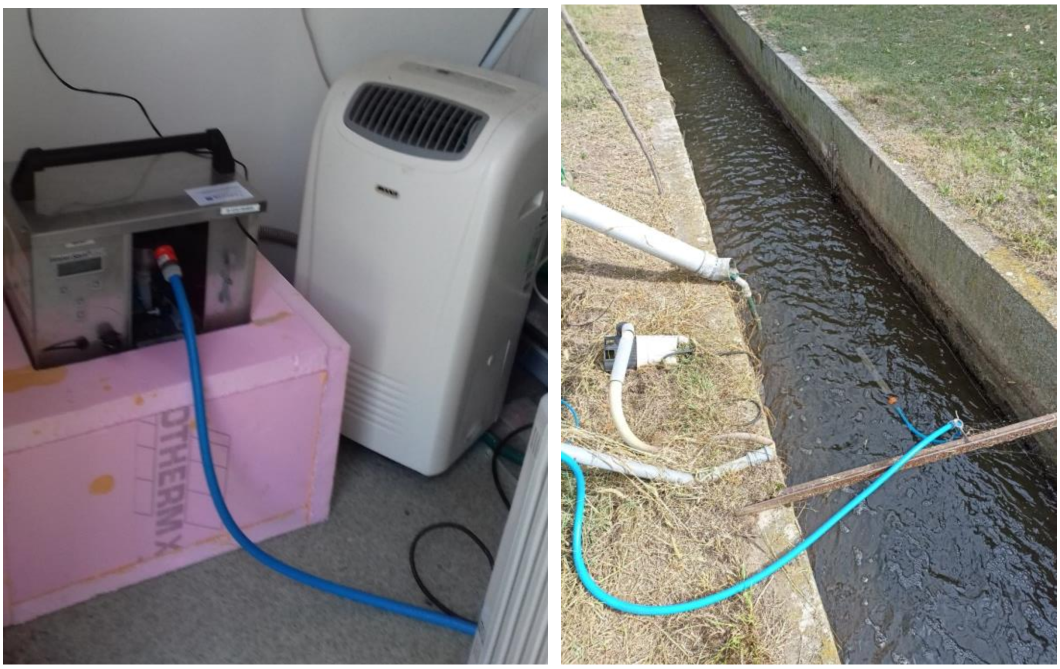

Figure 14- WaterSam porti sample collector at Balatonlelle outlet chamber

Tools used:

WaterSam porti portable sampler. The sampling is operated by vacuum Pump. The sampling can be pre-programmed and up to 24 separate samples can be collected.

Method description: 24 hour composites were collected for one week, by filling one bottle for 24 hours (Figure 15). Each 30 minutes, 20 ml sample was collected. Cooling was done using cooling packs within an isolation box. Cooling packs were changed at each 48 hours.

Figure 15 - sample collector

Lessons learned

Some misfunction 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.

2.5 Suspended sediment sampling

Site descriptions

Philips type sampler was installed at Törökkoppány station at two different height, one for long term collection of baseflow sediment, one for collecting high-flow sediment.

The other method was the large volume (25 l) sampling with the automated sampler.

Figure 16 - Philips type sampler for high-flow condition at Törökkoppány station

Figure 17 - SPM samples from the autosampler (left) and the Philips sampler (right)

Tools used: Philips sample was constructed using standard PVC pipe units. Small diameter hole was drilled at outlet (8mm), larger inlet diameter was used (2 cm).

Large volume sampler was the same described at River Sampling.

Number of samples taken (Overview table)

	Planned	Achieved	Description
SPM samples (HKH+HKT)	0+6	5+2	2 was collected at Tamási, 5 at Törökkoppány. Baseflow sample was collected for 3 month.

Lessons learned

- Sampler device:
  - Philips: Only works well in higher turbidity conditions. At baseflow conditions no sufficient amount of SPM sample was collected for all measurements, but sufficient for ICPMS measurements of metals. High-flow samples were collected well by the sampler.
  - 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.
- Sample handling: Decanting the Philips sampler on site needs two persons, and a large volume sample holder.

2.6 Sample storage and transport

Storage

According to the original SOP, composite samples for PAH measurements had to use glass bottles. Several glass breaks have been experienced during freezing, and handling of the frozen samples, even during transport. For this reason, the method has been changed, and the samples were kept cool (< 4 ^oC) instead of freezing.

Samples stored in PE bottles were frozen for heavy metal analysis. $CaCO_3$ precipitation was observed when the thawing of the first sample was carried out. Using filtering after thawing, there is a high risk of losing particle-bound contaminants from the samples. Therefore the SOP changed: filter the samples onsite right after sampling delivery to the own lab, using specific pure filter, acidifying it and only then freezing.

Transport

A courier DHL Express delivered the samples within 24-hour to Romania (Lab of NARW). To Slovenia (Lab of JSI) and to Austria (Lab of UBA) samples was delivered by car.

3 Viseu and Somes catchments, Romania

3.1 River sampling

Overview

Total number of samples taken:

	Planned	Achieved	Description
Low-flow samples (composites)	6 campaigns in 5 sections (2 on Viseu and 3 on Somesul Mic	30 samples (all planeed)	1 composite is made of 8 spot samples
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

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes	- 3 Pressure level sensors (OTT PLS) - 1 radar sensor (OTT RLS) - 1 shaft encoder sensor (OTT SE200)	Discharge based on Q – H function	
Conductivity probes	Yes	Hach Multi HQ 40d	Manual measurement, after sampling, in the site	
Turbidity probe	Yes	Hach Portable turbimeter 2100QIS	Manual measurement, after sampling, in the site	
Automated sampler	No	–	–	
High-flow grabsampling	No	–	–	



Site photos: Viseu
Manual measurements, in the site, when taking water samples from rivers



Site photos: Somesul Mic
Manual measurements, in the site, when taking water samples from rivers

3.2 Soil sampling

Number of samples taken:

	Planned	Achieved	Description
Soil samples	10 Viseu pilot area	10	1 composite is made of 20 samples each, and each of the 20 samples is composed in turn of 1-5 subsamples, to be taken close to each other
Soil samples	10 Somesul Mic pilot area	10	

Tools/method used:

Manual drilling and coring kit with conical thread, rotary hammer, tools for removal of the soil

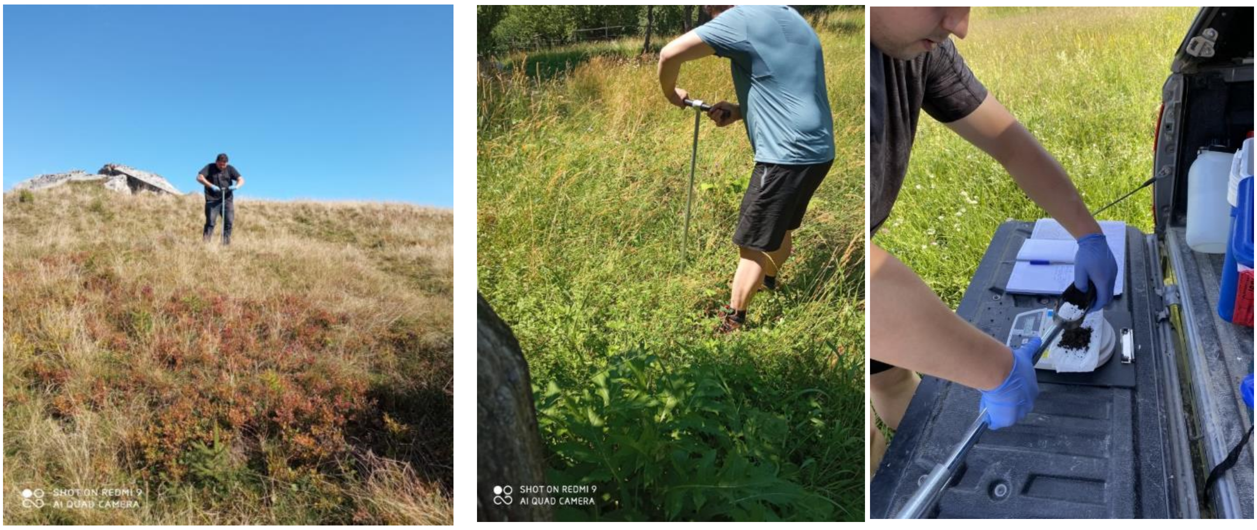

Figure 1 - Soil sampler during sampling campagne

Soil sample locations

Soil samples were taken for two pilot regions of the project: Viseu and Somesul Mic. The determination of the exact soil sampling locations, for each of the two pilot regions, was carried out using GIS methods. The sampling points were thus established to cover the main land use types on the one hand and to be located in easily accessible areas on the other hand.

For the Viseu area the following composite samples were collected:

Watershed	Description	Composit sample	Identifier soil sample site
32001	Moisei area	Agricol	ViseuAgricRV1

		Forest	ViseuForestRV1
		Pasture	ViseuPastureRV1
		Scrub	ViseuScrubRV1
32002	Borsa area	Agricol	ViseuAgricRV2
		Forest	ViseuForestRV2
		Pasture	ViseuPastureRV2
		Scrub	ViseuScrubRV2
32003	Cisla area	Forest	ViseuForestRV3
		Pasture	ViseuPastureRV3

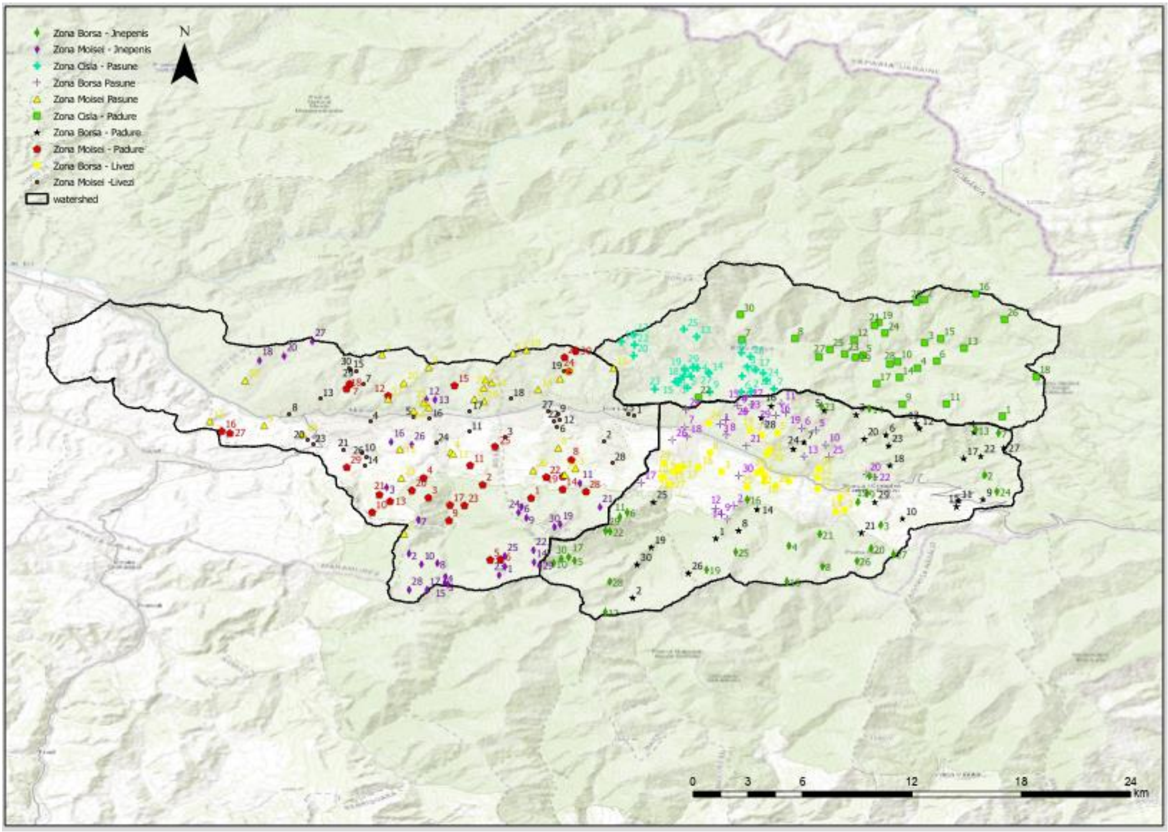

Figure 2 The location of the Viseu Soil Sample

For the Somesul Mic pilot area the following composite samples were collected:

Watershed	Description	Composit sample	Identifier soil sample site
RS1	Mixed use	Agricol1	SOL-RSA-01
		Agricol2	SOL-RSA-02
		Agricol3	SOL-RSA-03
		Pasture	SOL-RSA-21
RS2	Agricultural area	Agricol	SOL-RNN-01
		Pasture	SOL-RNN-21
RS3	Headwater	Forest1	SOL-RSH-11
		Forest2	SOL-RSH-12
		Forest2	SOL-RSH-13
		Pasture	SOL-RSH-21

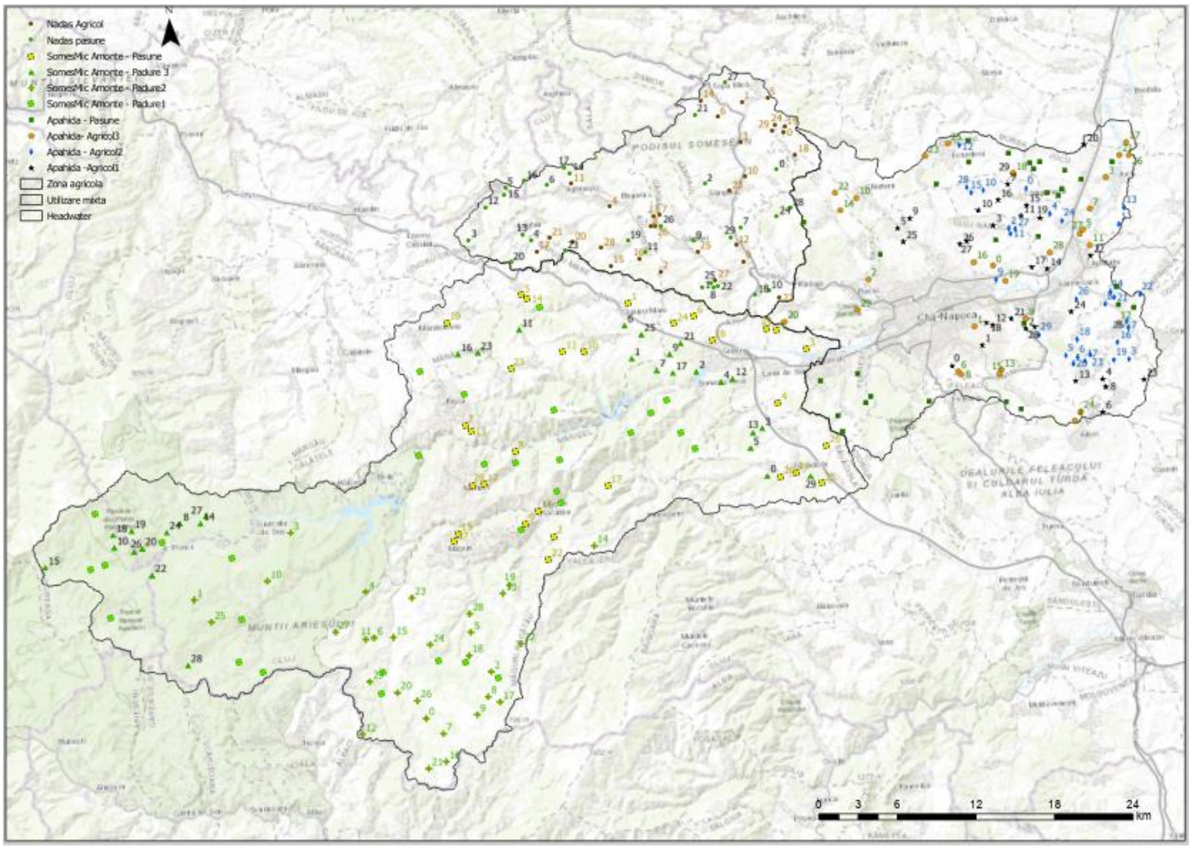

Figure 3 The location of the Somesul Mic Soil Sample

Lessons learned

- 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 take into account 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.
- Before establishing the investigation points, the routes should be digitized, including undeveloped or forest roads, and not just national and county roads.

3.3 Atmospheric deposition sampling

Viseu and Somesul Mic Sites descriptions

Cisla (Baia Borsa): The sampler was placed in the garden ares (Baia Borsa, on the right bank of the Cisla river), NARW experts take care to managed the collecting of rain input .The experts emptied the water after each rainfall event to a larger 10l glass bottle, which was kept in a refrigerator.

Canton Viseu - The sampler was placed at the garden of our NARW point work. The NARW employees emptied the water after each rainfall event to a larger 10l glass bottle, which was kept in a refrigerator.

Somes Water Company - The sampler was placed in the courtyard of our NARW point work. The NARW employees emptied the water after each rainfall event to a larger 10l glass bottle, which was kept in a refrigerator.

Cluj Water County - The sampler was placed at the garden of our NARW point work. The NARW employees emptied the water after each rainfall event to a larger 10l glass bottle, which was kept in a refrigerator.

Figure 4 – Atmospheric deposition sampler at Cisla and Viseu

Instrument used: Simple design: suport metalic in the form of a tripod, made of metal pipes, capable of safely supporting the glass system for rain collection, in which the 10l glass sample collector was placed. A ceramic funnel was placed on top (V= 1000 ml) without filter. Glass bottle was covered with aluminium foil to reduce direct light entering the bottle.

Number of samples taken (Overview table)

	Planned	Achieved	Description
Atmospheric deposition samples	4 campaigns for each site	12	-

3.4 Waste water sampling (including mining)

3.5 Site descriptions

Municipal	Romania	Viseu	Baia Borsa	Baia Borsa UWTP	RVB	Raw	RWW-RVB
Municipal	Romania	Viseu	Baia Borsa	Baia Borsa UWTP	RVB	Treated	TWW-RVB
Municipal	Romania	Somesul Mic	Cluj	Cluj UWTP	RSC	Raw	RWW-RSC
Municipal	Romania	Somesul Mic	Cluj	Cluj UWTP	RSC	Treated	TWW-RSC
Municipal	Romania	Somesul Mic	Apahida	Apahida UWTP	RSA	Raw	RWW-RSA

Municipal	Romania	Somesul Mic	Apahida	Apahida UWTP	RSA	Treated	RWW-RSA
Municipal	Romania	Somesul Mic	Jucu -Tetarom	Jucu Tetarom UWTP	RST	Raw	RWW-RST
Municipal	Romania	Somesul Mic	Jucu -Tetarom	Jucu Tetarom UWTP	RST	Treated	RWW-RST
Mining site	Romania	Viseu	PL Gura Baii	1 Mine	RV1	Raw	RWW-RV1
Mining site	Romania	Viseu	PL Colbu	2 Mine	RV2	Raw	RWW-RV2
Mining site	Romania	Viseu	PL Burloaia	3 Mine	RV3	Raw	RWW-RV3
Mining site	Romania	Viseu	Emerik II (Toroioaga)	4 Mine	RV4	Treated	TWW-RV4
Mining site	Romania	Viseu	PL Borsa	5 Mine	RV5	Raw	RWW-RV5
Mining site	Romania	Viseu	Colbu Mine Gallery	6 Mine	RV6	Raw	RWW-RV6

Sample overview

Wastewater samples	Planned	Achieved	Description
Municipal	3	3	3x2 samples (1 influent and 1 effluent) each time.
Mining site	6	6	-

Site photos (mining area)

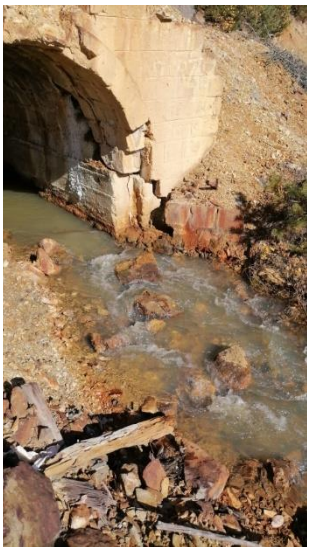

Figure 5 –PL Colbu discharge
Figure 6 –Emerik II (Toroioaga) discharge
Figure 7 –PL Burloaia discharge and sample collector

Tools used:
Sampling was carried out manually with the help of a sampler with a long rod.

3.6 Continuous measurements

Continuous measurements of water level, temperature, pH, conductivity and turbidity were performed at each sub-basin outlet throughout the year. pH and conductivity are basic indicators of water quality that allow the detection of sudden and unexpected changes in water quality.

The locations chosen for automatic continuous measurements were the following:

1. Apahida, Someșul Mic river
2. Baia Borsa, Vișeu river
3. Cluj-Napoca, Someșul Mic river
4. Moisei, Vișeu river
5. Radaia, Someșul Mic river

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes	- 3 Pressure level sensors (OTT PLS) at Cluj-Napoca, Moisei and Radaia - 1 radar sensor (OTT RLS) at Baia Borsa - 1 shaft encoder sensor (OTT SE200) at Apahida	Discharge based on Q – H function	
Turbidity probe	Yes	- 5 turbidity and suspended solids sensors (Hach Solitax ts-line sc. FNU range: 0.001-4000. g/l range: 0.001-50 Wiper blade.)		

Lessons learned -

- Turbidity and suspended solids sensors: It was the first time to work with this sensors on automatic station so it was a very good opportunity to gain experience with the mentainance of this kind of sensors and to have a higher density of measured values for turbidity and suspended solids parameters.
- Despite the fact that these sensors had a self cleaning wiping blade, the sensor lenses have required to be cleaned manualy from time to time, using a special acidic solution. In some of the sections the abundance of tranported suspended solids caused a high frecuency of the deposition on the sensor lenses which influenced the measured values and caused a higher level in processing and corrections of the data sets.

Site photos:

Figure 8 – Cluj Napoca hydrometric station

Figure 9 Installation of radar sensor in Baia Borsa

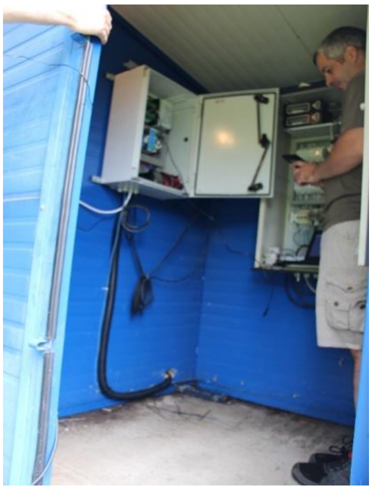

Figure 10 –The tubidity and uspended solids sensor and the automatic station cabin in Baia Borsa

Figure 11 – Installation of the turbidity and suspended solids sensor in Radaia

Figure 12 – Installation of the sensors in Moisei

3.7 Sample storage and transport

Storage

According to the original SOP, composite samples for PAH measurements had to use glass bottles. Several glass breaks have been experienced during freezing, and handling of the frozen samples, even during transport. For this reason, the method has been changed, and the samples were kept cool (< 4 ^{o}C) instead of freezing.

Samples stored in PE bottles were frozen for heavy metal analysis. $CaCO_3$ precipitation was observed when the thawing of the first sample was carried out. Using filtering after thawing, there is a high risk of losing particle-bound contaminants from the samples. Therefore the SOP changed: filter the samples onsite right after sampling delivery to the own lab, using specific pure filter, acidifying it and only then freezing.

Transport

A courier DHL Express delivered the samples within 24-hour to Romania (Lab of NARW). To Slovenia (Lab of JSI) and to Austria (Lab of UBA) samples was delivered by car.

4 Vit catchment, Bulgaria

Sampling locations (Figure 18): Beli Vit (Teteven town, BVB), Cherni Vit (Cherni Vit village, BVC), Vit (Disevitsa village, BVD)

4.1 River sampling

Overview

Total number of samples taken:

	Planned	Achieved	Description
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

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes	VegaPlus 21 radar sensor	Discharge based on Q – H function	Figure 2
Conductivity probes	No			
Temperature probe	Yes	Delta Instruments - Sensotech		Figure 3
Turbidity probe	Yes	Hach - Solitax sc submersible probe. FNU range: 0.001-4000. Wiper blade.		Figure 3
Automated sampler	No			
High-flow grabsampling	Yes	Own development – telescopic pool stick (4m total) with mounted can and/or pipe holder for attachment of glass bottles		Figure 22

Concept and installation of monitoring stations

The Vit pilot region under investigation is divided into five sub-catchments. Monitoring is provided at the outlets of the two upstream catchments (Beli and Cherni Vit) and at the outlet of the pilot region (Disevitsa).

The dominant land use in the upper, mountainous region of the pilot region is forest. In the downstream parts the influence of agriculture increases, with a clear focus on arable land. Rather 30 % of the arable land is situated on fields with a slope of more than 4 %. The area has the lowest population density of all pilot regions and the runoff is moderate.

Pilot region	**Catchment Area [km²]**	**Mean Elevation [m]**	**Population density [Inh/km²]**	**Arable land [%]**	**Arable land > 4% slope [%]**	**Pasture [%]**	**Forest [%]**	**Urban Area [%]**	**Runoff [mm]**
Vit	2206,3	519,8	7	42,8	28,9	5,4	45,4	2,3	197

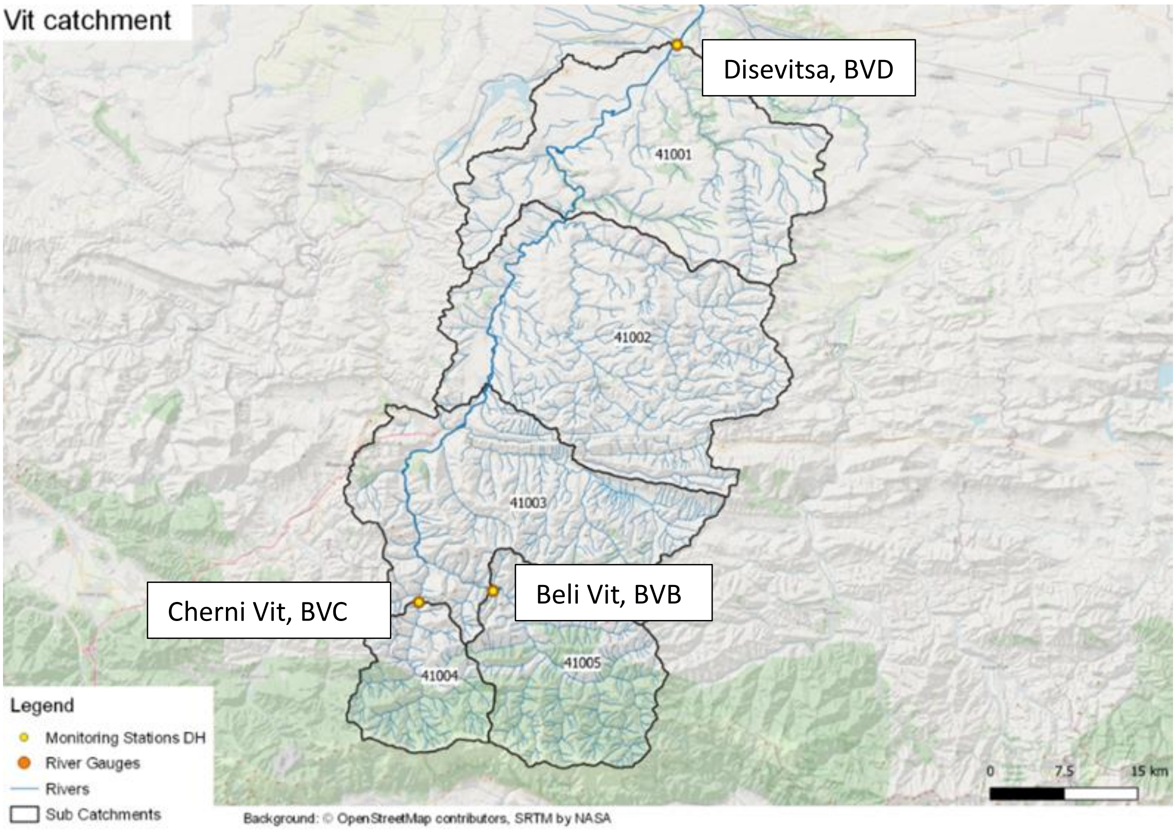

Figure 18 – Monitoring stations across Vit catchment

Lessons learned

- High-flow grabsampling: The wave during a river high–flow event can last a long period (over 24 hours). The duration of the grabsampling should include the peak of the water level and turbidity. To produce flow proportional composite sample, individual samples should be taken at equal time intervals (trough 20 minutes). To keep them cool, bags with ice cubes can be used. Good preparation for the scene is crucial: the bare minimum is to have a dry place to stay (for example tent), warm clothes, towels, a flashlight, food and drinking water. (Figure 23) The on-line data for water level and turbidity should be constantly monitored.
- Probes:
    - Turbidity probe can give increased results due to biofilm growth or in case of obstacles stuck in front (branches or piece of clothing). Regular maintenance and cleaning should be provided (at least once per 2 weeks).
- Battery solar charging:
    - In the autumn and winter the solar panels don't produce enough charge for the batteries because of atmospheric conditions – clouds, fog and reduced sunlight hours. The solution was to use another set of batteries, which has been replaced every week and charged from the power grid when not in use.

Figure 19 – Beli Vit station (left) and Cherni Vit station (right) – overview

Figure 20 – Station unit equipment – data controller; turbidity and temperature probe (mounted on stainless steel pipe); radar sensor; data transferring modem; solar controller; safety switch; VRLA battery

Figure 21 – Probes installation – Beli Vit station

Figure 22 – Grabsampler

Figure 23 – High-flow grabsampling scene during the day and night – Disevitsa station

4.2 Soil sampling

Number of samples taken:

	Planned	Achieved	Description
Soil samples	10	10	1 composite is made of 20 samples each, and each of the 20 samples is composed in turn of 1-5 subsamples, to be taken close to each other

Tools/method used:

Hand auger soil sampler, garden shovel, bucket, portable scale

Figure 24 - Soil sampling equipment on site

Soil sample locations

At Vit catchment, the soil samples were divided into 5 forests, 4 agricultural and 1 pastures groups. In around 50 % of the whole area (the upper part) is no agricultural activities. In the lower part, the land use is mixed. (Figure 24)

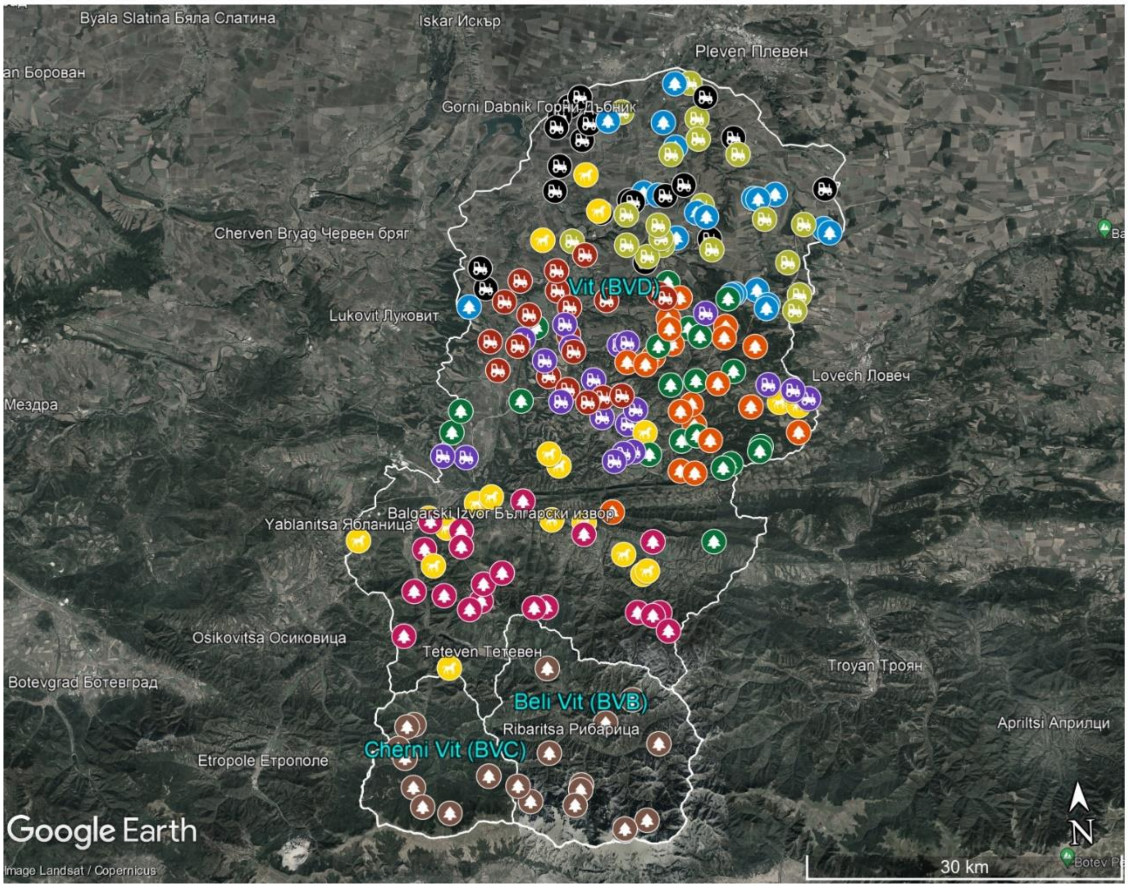

Figure 25 Overview of all the locations for soil sampling

Lessons learned

- 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.
- Site access problems: For the 2 forest samples 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.
- 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.

4.3 Atmospheric deposition sampling

Site descriptions

Dermantsi village and Teteven town: The samplers were placed at the rain data monitoring points of local persons. After each rainfall event, the collected water was transferred into larger 2l glass bottles, which were kept in a refrigerator. Every few weeks the bottles were transported to the lab and mixed in a larger 10 l bottle. Every 3 months samples were sent for analysis.

Instrument used: Simple design (own development) using a ceramic chimney body, in which a 3 l glass jar was placed. 300 mm diameter glass funnel was placed on top, without a filter. The parts were stabilized with extruded polystyrene foam (XPS).

Figure 26 – Atmospheric deposition sampler – overview

Samples overview

	Planned	Achieved	Description
Atmospheric deposition samples	4+4	4+4	1 composite is made from all of the collected samples during 3 months period.

Lessons learned

- Much organic matter and insect deposition were experienced. Glass filter should be used if possible to reduce this effect.

4.4 Wastewater sampling

Site descriptions

In the Vit catchment, there are only a few settlements with centralized mixed sewerage systems. Only 3 of them have small wastewater treatment plants (< 2000 PE). During the sampling period 2 of the WWTP were out of operation and the third was automated, so the access was denied. Five of the samples were taken from sewerage direct discharges of Teteven town (no WWTP), Ugarchin town (no WWTP) and Glozhene village (WWTP bypass) in different weather conditions. The last sample was taken from the effluent of WWTP Lukovit, which is outside of the Vit catchment, however, Lukovit town is close and similar to Teteven town in population and urban planning.

Sample overview

	Planned	Achieved	Description
Wastewater samples	3	6	5 samples from direct wastewater discharge (4 in dry weather and 1 during a rain event) + 1 from wastewater treatment plant.

Site photos:

Figure 27 – Teteven town direct discharge sampling – dry weather (left) and rain event (right)

Figure 28 – Ugarchin town direct discharge sampling – dry weather - grabsampling

Tools used and method description:

Grabsamples were taken and a composite was prepared. In dry conditions, individual samples were in 1 hour intervals during the light part of the day (duration 12 – 14 hours). The rain event was with a duration of around 5 hours and samples were taken in 20 minutes intervals. Where possible, water quantities were estimated by filling a 20 l bucket and measuring the time until overflow.

Lessons learned

During grabsampling a lot of splash of wastewater is created. It is necessary to wear good protective clothing, also to use a long enough stick.

4.5 Sample storage and transport

Storage

The bottles from grabsampling series (river high flow, wastewater) were stored in trays on-site, and bags with ice cubes were used to keep them cool. Labeling of the bottles was done in advance. Each sample was accompanied by a spare one (Figure 29).

According to the original SOP, composite samples for PAH measurements had to use glass bottles. Several glass breaks have been experienced during freezing, and handling of the frozen samples, even during transport. For this reason, the method has been changed, and the samples were kept cool (< 4 ^oC) instead of freezing.

Samples stored in PE bottles were frozen for heavy metal analysis. $CaCO_3$ precipitation was observed when the thawing of the first sample was carried out. Using filtering after thawing, there is a high risk of losing particle-bound contaminants from the samples. Therefore the SOP changed: filter the samples onsite right after sampling delivery to the own lab, using a specific pure filter, acidifying it and only then freezing.

Figure 29 – spare sample storage and collection on site

Transport

A courier DHL Express delivered the samples within 24 hours to Romania (Lab of NARW), Slovenia (Lab of JSI) and Austria (Lab of UBA).

5 WULKA CATCHMENT, AUSTRIA

The Wulka is the main tributary of the Lake Neusiedl. The catchment is split into three parts, the Wulka River itself and the two tributaries Nodbach and Eisbach. While the Nodbach has no input from WWTP, the Eisbach usually mainly consists of WWTP effluent.

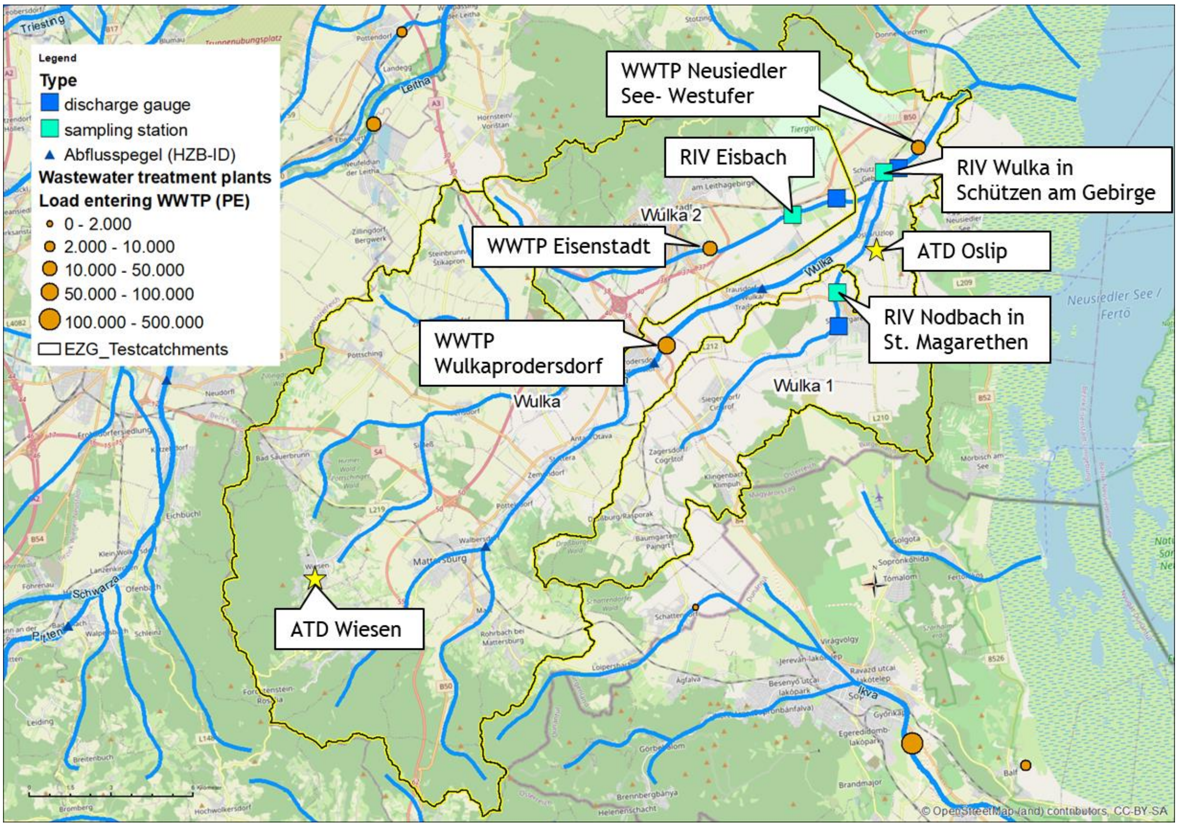

Figure 30: Map of the pilot site with all sampling sites

5.1 River sampling

Overview

Total number of samples taken:

	Planned	Achieved	Description
Low-flow composite samples	18	18	1 composite is made of 7-9 weekly low-flow samples
High-flow composite samples	18	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

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes	Endress+Hauser, Micropilot FMR10	Discharge based on Q – H function derived from official gauge nearby (100m – 2km)	Figure 31
Conductivity probes	Yes	Endress+Hauser, Indumax CLS50D	Inductive conductivity probe, partly influenced by too low water level (Especially Nodbach).	Figure 32
Turbidity probe	Yes	Endress+Hauser, Turbimax CUS51D	Scattered light in 90°/135° and 4 beam crosslight. Cleaning with pressurized air (~5 bar) hourly for 10 sec.	Figure 33
Automated sampler	Yes	Endress+Hauser, LIQUISTATION CSF48	vacuum auto sampler with cooling and heating for sample storage in 24·1 L glass bottles. Application of pipe heating during winter. Remote configuration via web-interface possible.	Figure 31, Figure 35
High-flow grabsampling	No			

Lessons learned

- Autosampler:
  - The remote access via web interface was very useful to check the past sampling and reconfigure the sampling program according the current or predicted hydrological conditions.
  - 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 waste water influence.
  - The installed relays for emergency shutoff of the auto samplers were never used, the ones for the air compressor were used in one case when air pressure was lost caused by some air leakage.
- Probes:
  - Conductivity probe is reliable, but biofilm growth on the surface of the instrument reduce the measured conductivity. Regular cleaning is necessary.
  - Turbidity probe: Precipitation, biofilm and calcium deposits reduce the reliability of the measurements. Regular cleaning with citric acid is necessary to prevent this (Figure 33).
  - Data transfer: Signal transfer 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 record on the instrument is a must for at least a month.
  - Installation in too shallow water leads to measurement disturbance be floating debris or too low immersion depth.

Site photos:

Figure 31: Nodbach station: Autosampler (top) and in situ (bottom)

Figure 32: Conductivity probe

Figure 33: Turbidity sensor a) before cleaning *b) after cleaning*

Figure 34 Sampling site at Wulka (bottom right) and auto sampler inside the hut

Figure 35 Auto sampler and sampling setup at Eisbach station

5.2 Soil sampling

Number of samples taken:

	Planned	Achieved	Description
Soil composite samples	10	10	10 composite samples from 20 sampling locations a 2-3 subsamples.

Instruments/method used:

Pürkhauer sampler with a diameter of 13, 18 and 26 mm (Figure 36) a small shovel and a glass for storage and transport.

Figure 36 - Soil sampling tool (left), sample container with fresh vineyard sub-sample (middle) and sampling process (right)

Soil sample locations

At Wulka pilot region soil samples were taken from 4 different landscape types: forest, arable land, pastures and vineyards. Of the 10 samples taken, 4 are from arable land, 3 from forest, 1 from pasture and 2 from vineyards.

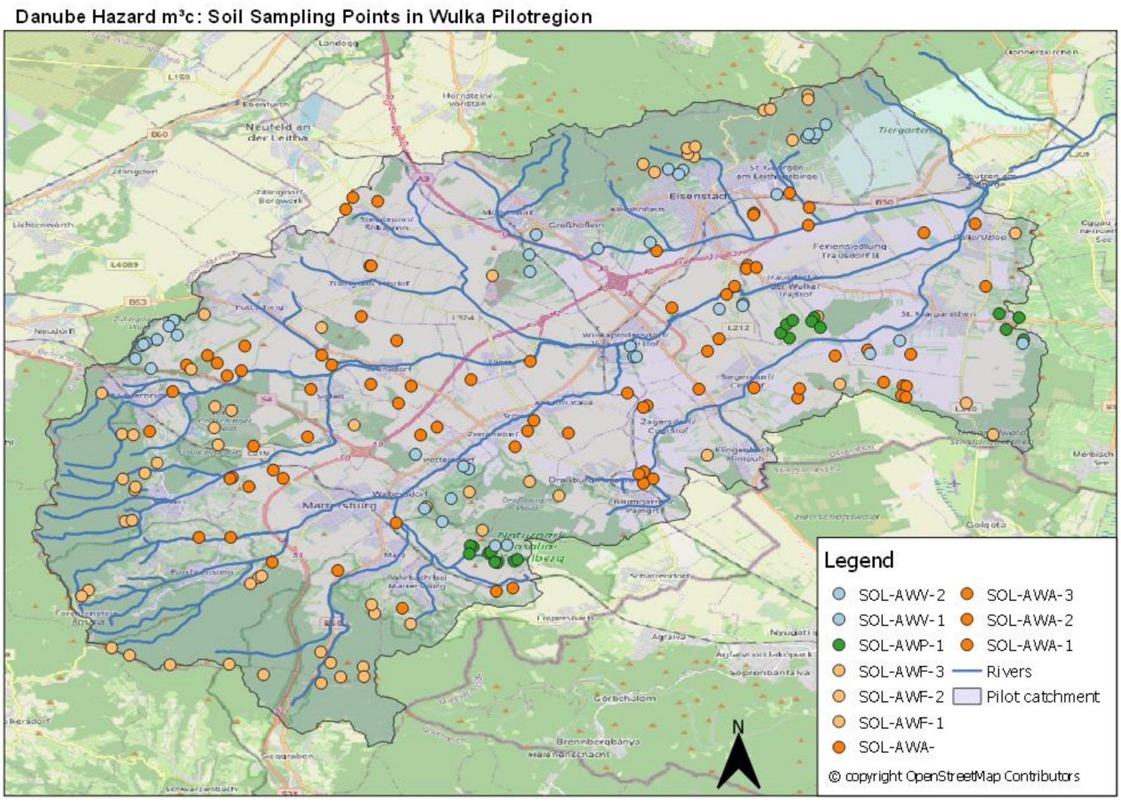

Figure 37: Map of sampling area with soil sampling sites marked with dots

Lessons learned

- 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.
- Site access problems (physical, land owners): Owners were helpful in most cases and allowed the sampling.
- Sample processing: Pürkhauer sampler with relative small diameter was used to reduce sample amount. The benefit was that samples could be used and therefor no cross contamination due to mixing and separation had occurred.

5.3 Atmospheric deposition sampling

Site descriptions

Nodbach: The sampler was based near the riverwater monitoring station at the former wastewater treatment plant St. Margarethen (Now used as stormwater overflow).

Oslip: The sampler was based in the garden of a local person (citizen scientist) in Oslip.

Wiesen: The sampler was based in the garden of a local person (citizen scientist) in Wiesen.

Figure 38 – Atmospheric deposition sampler at Wiesen and the sample freezer

Figure 39 – Atmospheric deposition sampler at Nodbach monitoring station

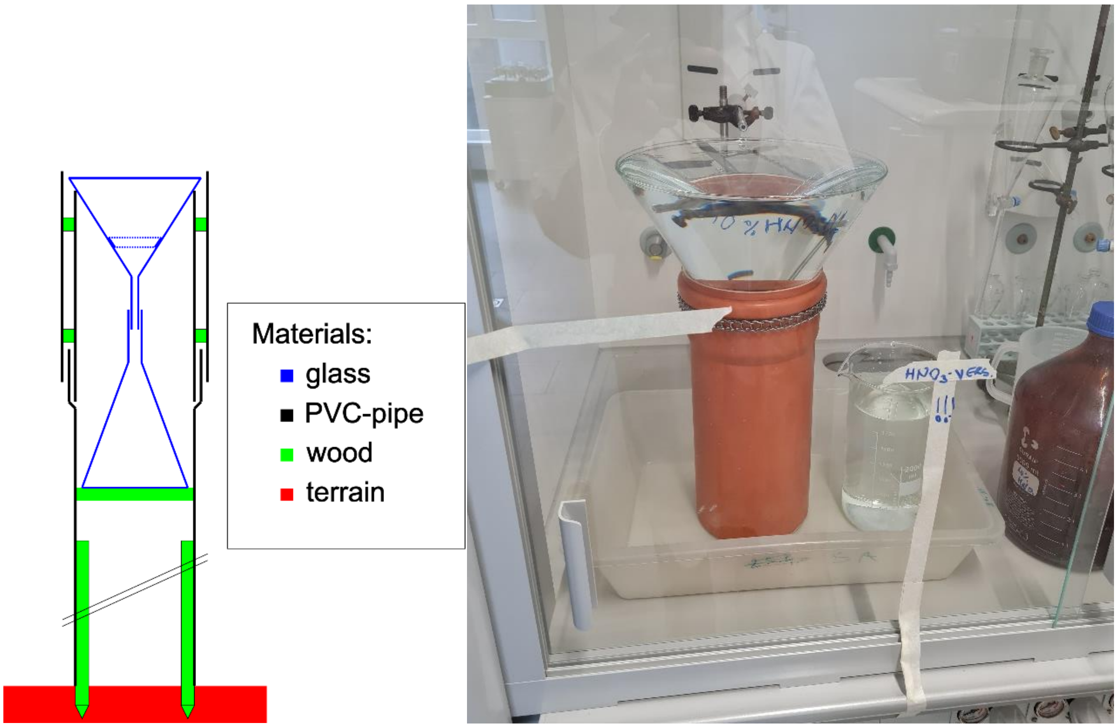

Figure 40 – Atmospheric deposition simple blueprint of design and setup to clean funnel with nitric acid acc. to SOP

Instrument used: Simple design (own development) using a 250 cm PVC pipe, in which the 5 L glass sample collector was placed. 300 mm diameter glass funnel was placed on top, with a sieve-like glass filter, specifically made for this purpose by a glassblower. (Figure 10, Figure 11, Figure 40**Hiba! A hivatkozási forrás nem található.**)

4-5 composite samples over a 1,5 – 6,5 month period were collected.

Sample overview

	Planned	Achieved	Description
Atmospheric deposition samples	8	13	Three sites in rural villages were sampled

Lessons learned:

- Many 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.
- The glass filter can be skipped as it was relatively expensive and things up to 4mm will pass through anyway and larger parts like leaves will be stopped by the funnel stem.
- Working with citizen scientists requires clear communication and tasks, easy to use stations and some flexibility. A protocol for recording the sampling is essential.

5.4 Wastewater sampling

Site descriptions

Two different Waste Waster Treatment Plants (WWTPs) were sampled within the catchment. At WWTP A we sampled influent, effluent, and sewage sludge in three rounds, each for the duration of one week. Sewage sludge sampling was on our own initiative and analysis was financed by other projects. At WWTP B we sampled only the effluent, they also did three rounds of sampling with one week each.

Sample overview

	Planned	Achieved	Description
Wastewater samples	9	12	6 outflow from 2 WWTP , 3 inflow from one WWTP and 3 sewage sludge from one WWTP

Site photos:

Figure 41 – Sampler of effluent at WWTP A (left) and at WWTP B (middle & right)

Tools used:

On site autosampler which the WWTP uses for their daily operational checks.

Method description:

24-hour composites (flow proportional) were collected by WWTP personal for one week. At WWTP A samples were stored in a freezer and at WWTP B in a fridge. The daily samples are mixed flow proportionally to a 1-week composite sample.

Lessons learned

- Providing for each day a separate Bottle and do the Mixing of the composite sample on your own was for us the most practical solution.
- Working with third party requires clear communication and tasks, practical sampling stategies and some flexibility. A protocol for recording the sampling is essential.

5.5 Suspended sediment sampling

Site descriptions

Two SPM samplers with a design adapted from Phillips et at. (2000) were installed at all stations. Starting from November 2021 on they sampled for multiple months at a time and were checked in turn with the regular maintenance. The samples were emptied into a large glass container and decanted in the laboratory. Two other samples were sampled by other methods: One sample was collected by grab samples, due to the luck that an event occurred during site visit. The other sample was collected by auto-sampler during two high-turbidity events.

Figure 42 - Philips sampler and a 20 L glass collection container.

Tools used: Philips sample was constructed using standard PVC pipe units. Small diameter hole (4mm) at in- & outlet which was later enlarged (14 - 20 mm) due too low sample volume.

Number of samples taken (Overview table)

	Planned	Achieved	Description
SPM samples	9	12+2	12 samples with Philipps sampler and 2 with other methods

Lessons learned

- Sampler device: Philips sampler are easy built but installation in riverbed can be tricky. Also the Philips sampler does not sample a representative sample, as very fine particles are not trapped.
- Sample handling: Decanting the Philips 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.

5.6 Sample storage and transport

Storage

According to the original SOP, composite samples for PAH measurements had to use glass bottles. Several glass breaks have been experienced during freezing, and handling of the frozen samples, even during transport. For this reason, the method has been changed for some compartments, and the samples were kept cool (< 4 ^oC) instead of freezing.

Samples stored in PE bottles were frozen for heavy metal analysis. $CaCO_3$ precipitation was observed when the thawing of the first sample was carried out. Using filtering after thawing, there is a high risk of losing co precipitated contaminants from the samples. Therefore, the SOP changed: filtering of the samples onsite right after sampling delivery to the own lab, using specific pure filter, acidifying it and only then freezing.

Transport

The samples were delivered to the different labs within 24 or 48 hours by a courier. In almost all cases the sample temperature at delivery was still below 10°C. If the sample temperature was to high the sample was send again (from backup).

Lessons learned

- A reliable courier is essential for delivery of samples.
- Special precautions on cooling are needed during summer month. Dry ice can help but can also cause glass break during transport.

5.7 Expressions from the laboratory

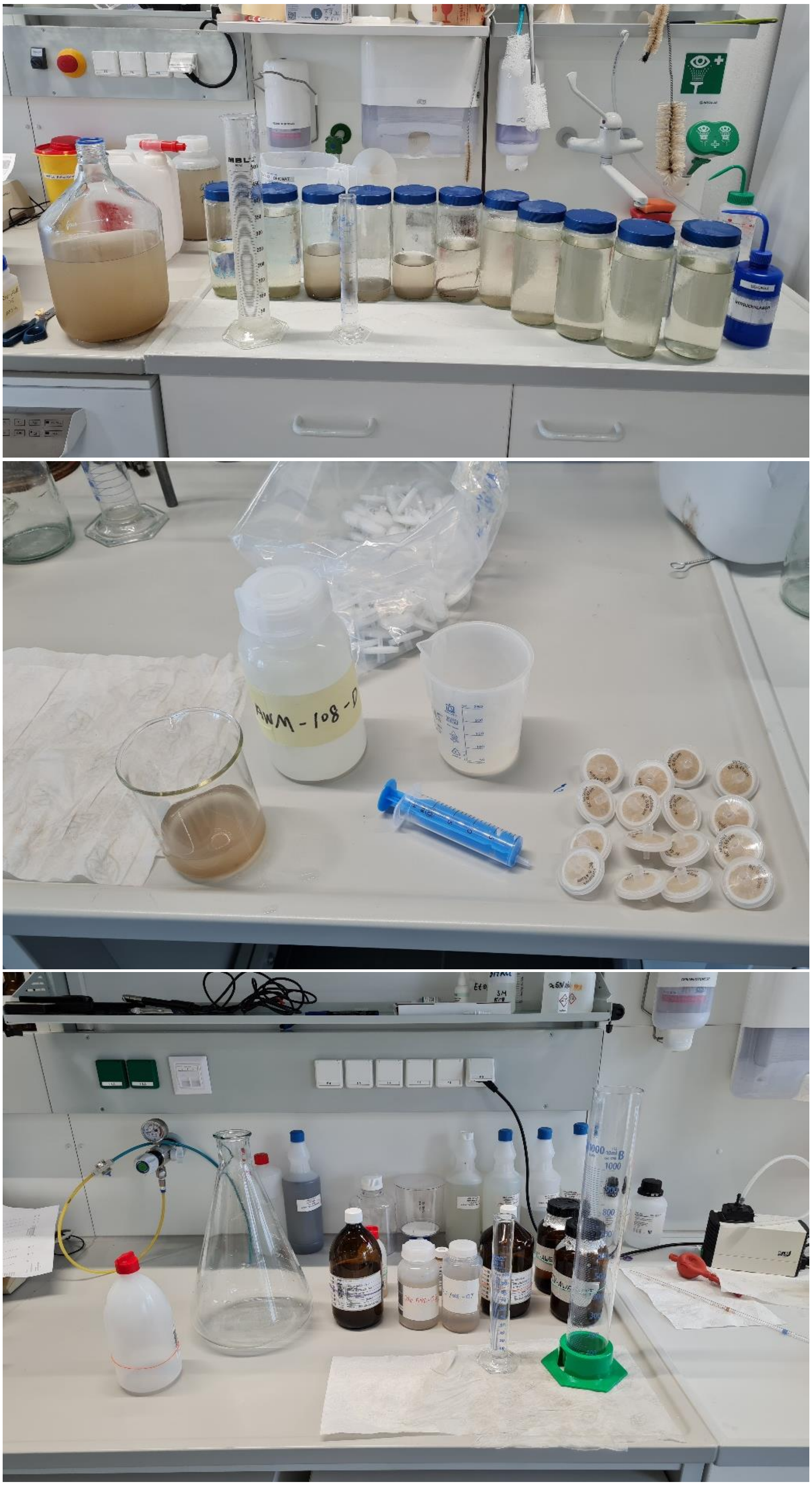

Figure 43 – Mixing of high-flow composite (top), filtration of sample with syringe filters (middle) and distribution to laboratory bottles for analysis (bottom)

6 YBBS CATCHMENT, AUSTRIA

AYH (Headwater, Opponitz), AYU (agrigultural used tributary, Url), AYL ("Outlet" of catchment)

6.1 River sampling

Overview

Total number of samples taken:

	Planned	Achieved	Description
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

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes	SNSR-U-Sonic: ultrasonic water level sensor	Discharge based on Q – H function. Has to be placed above several meters above the water level	-
Conductivity probes	Yes	Hach 3798-S sc inductive conductivity probe.	Installation on custom made foldable probes rail/ rotatable probes pipe	Figure 3
pH probes		1200-S sc digital pH-Sonde	Installation on custom made foldable probes rail/ rotatable probes pipe	Figure 3
Turbidity probe	Yes	Hach Solitax t-line sc submersible probe. FNU range: 0.001-4000. Wiper blade.	Installation on custom made foldable probes rail/ rotatable probes pipe	Figure 3
Automated sampler	Yes	Bühler3011-D, with 12 2-liter glass bottles	Sample volume was set to 30 ml. The sampling was set up to start at Q10, with an interval of 1 sample/hour. Between Q10 and HQ1 the sampling rate increased linearly until 30 samples/ hour at HQ1.	Figure 2, Figure 6
Controller	Yes	sc200 Controller, no network connection	2 controllers were used at each monitoring station.	Figure 4
High-flow grabsampling	No			

Conception and Installation of monitoring stations

The Ybbs catchment, a tributary of the Danube, situated on the northern edge of the Alps is characterized by 60 % of forests and 25% of pastures. It has a mean elevation of 686 m a.s.l. and only 12% of the 1112 km^2 are used for agriculture in the downstream areas. Nevertheless, in the Url, a tributary of the Ybbs, agriculture is the dominant land use. With a population of 68 inhabitants per km^2 the Ybbs catchment related to the other pilot areas shows an average population density. The runoff of the catchment with 811 mm is rather high and the river reach is characterized by several small and large dams.

In the catchment, three continuous monitoring stations were installed, representing different focus:

- Opponitz, Ybbs (434 km^2, headwater with characteristics similar to background conditions)
- Krenstetten, tributary Url (159 km^2, intense agricultural use)
- Greimpersdorf, Ybbs most downstream gauge (1112 km^2, representing the total catchment)

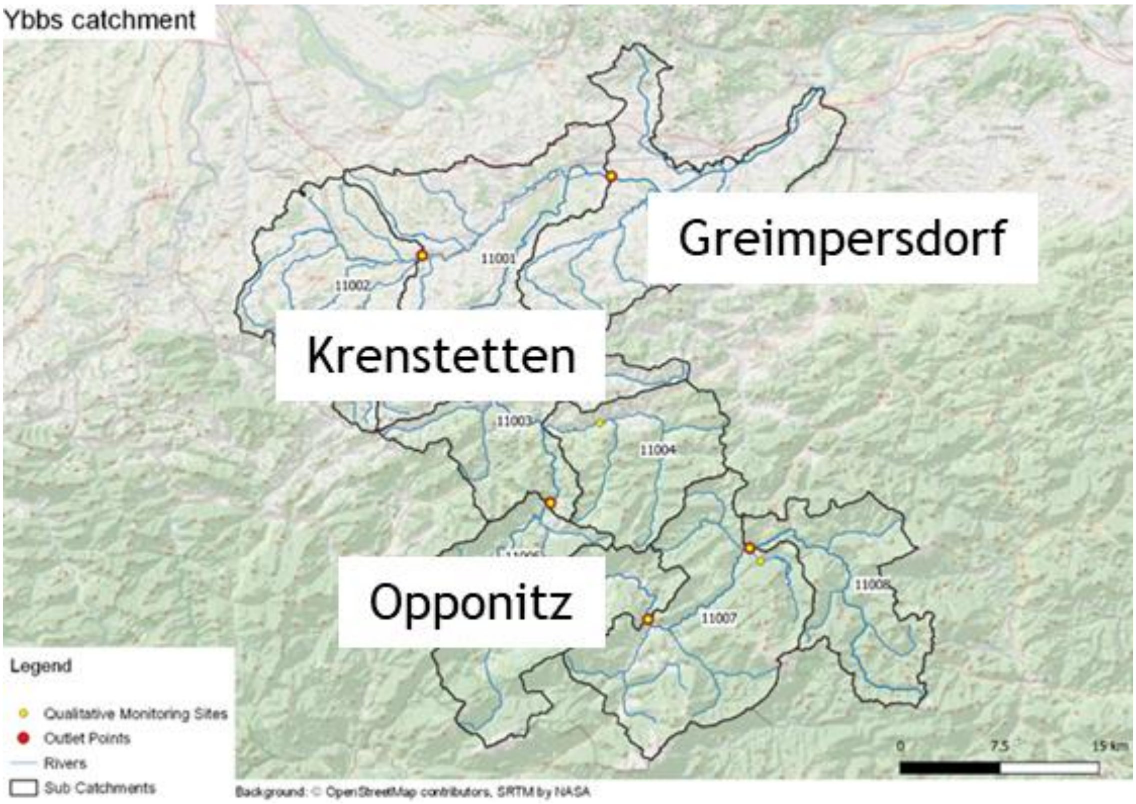

Figure 44 - : The Ybbs catchment (with modelled sub-catchments) and the place of the continuous monitoring stations.

To optimize transformation of the monitoring results and to guarantee a most exact calculation of loads from the monitoring, needed for modelling, all three continuous monitoring stations were associated with already existing gauging stations operated by the province of Lower Austria.

In general, a close cooperation with the responsible administration, the Government of Lower Austria, namely with the Department of Hydrology, was one key aspect for a successful selection and installation of the stations, profiting from their extreme detailed local and technical knowledge.

The close cooperation with well-experienced technicians leads to the installation of a very robust and sustainable system for continuous monitoring, which is essential in a pre-alpine river with possible flood events of 1000 m^3/s an trees, small boulders and large cobbles being transported during such extreme events.

Beneath the detailed and tailor made conception of the monitoring construction, which was realized in the Ybbs catchment with different variants of stainless steel, foldable probes rails, before installation a lot of further aspects must be clarified:

- Who is the owner of the ground?

- Are there further rights of use (e.g. fishing rights)?
- Can the installation influence the flow of the river water or stability of the riverbanks?
- Are all aspects of occupational safety considered?
- Is there a concept for power supply?
- Is there a concept for device safety (especially during extreme events)?
- Is there technical support guaranteed in case of demolition or technical malfunction?
- How can the cleaning of the probes be guaranteed and how often do you have to check its function?
- Is online transmission guaranteed and necessary?
- Is a continuous exploration of the monitoring station by local supporters possible?

In case of the Ybbs catchment (with a tremendous energy of flood in case of an extreme event), the safety aspects were clearly prioritized, which results in a costly, stable construction and less emphasize on data transmission.

Consequently, the automatic sampler were stored in flood save gauge houses if possible (Greimpersdorf and Opponitz). When such an opportunity was not in place, the installation was situated beyond the direct influence of a HQ10 event (Krenstetten).

Greimpersdorf
The monitoring station “Greimpersdorf” could use the existing infrastructure of the hydrological monitoring station at Allersdorf. This station is only few kilometers downstream the gauge of Greimpersdorf. The gauge station at Greimpersdorf is more often flooded and the existing gauge house is much too small to install an automatic sampler.

At Allersdorf optimal conditions were found to install the device with respect to flood safety. Using the cable car, originally installed over the whole river section to record flow velocity profiles, the automatic sampler could be transported into the house (the door was not broad enough). Inside the building we could use electricity. Due to overloads of the power network during the first extreme flood water event and even later, the Government of Lower Austria, installed an independent second network to guarantee a smooth procedure. The vertical difference between waterlevel and automatic sampler was about 5 m and could be handled by the pump. The horizontal distance was more than 30 m in total. Cables and tubes were underground laid (above 0,4m depth) to guarantee safety for all other users and the cables themselves. They were laid in a cable duct to prevent browsing from small rodents and freezing or wetness. A small Dredger realized the installation. Even boulders stabilizing the riverbanks were moved and the cables installed below. A five meters stainless steel, foldable probes rail fabricated after detailed in-situ planning was installed at the embankment, next to the gauge and along the stairs leading to the river. Clamps fastened the cables in the cable tube. The installation of the tubes considers the undisturbed flow dynamic and the depth at average and especially at low flow conditions to avoid drying out and make cleaning and maintenance in most cases possible. Probes installed measured temperature, ph - values, conductivity, suspended solids or turbidity and water level. Furthermore, the tube was installed to pump samples. The installation was done at low flow conditions to guarantee an optimal handling (see Figure 45).

Figure 45 - Pictures from the installation of the continuous monitoring station at Greimpersdorf (setting up the automatic sampler; installation of controllers in gauge house; underground laying of the cables; guide rail with folding mechanism; installation of probes and river at low flow conditions)

The controller, logging all data in a 15-minute interval were installed in the station. Because in the start of the measurements, there was no reliable ratio about water level development at this station compared to the existing gauge station downstream the automatic sampling in the beginning was arranged by suspended solids. Later on it was provided by water level.

Sampling was initialized by a water level above Q10 calculated from long-term level rows. In case of Q10 the sampler pumps 0,03 l into cooled glass bottles in one hour (lowest frequency of pumping) and increases sampling linear with respect to increasing water level up to 30 times and 0,9 l/h (highest frequency of pumping). At HQ1 the increase stops and sampling proceeds with the maximal frequency. The interval between Q10 and HQ1 was choosen to guarantee on the one hand a sufficient number of sampling evens (statistically 10% of the year) and on the other hand the chance to sample enough probe volume at one event. The maximum sampling volume was 24 l without any handling. That means that a 27h HQ1 could be probed automatically, while even much lower events of around 24 h and less could bring sufficient probe volume (around 5 l was needed for the complete analyses)

Opponitz

The monitoring station “Opponitz” provides perfect conditions. The existing infrastructure of the hydrological gauging station at Opponitz could be completely used (Figure 46). An existing new power network exists and provides free sockets. There was enough space for the automatic sampler and the controllers. Tubes and cables could be layed over the floor plate (the house stands on pillars) and along the pillars, thru the cable shaft, which tunnels the sidewalk. The house itself is situated 5 m above mean water level, which guarantees security for the devices. The probes could be installed parallel to the existing pressure probe. They are installed along the parapet on a two meters stainless steel , rotatable probes pipe with an probe rail at the end. While the construction is protected by the current shadow of the parapet (with stairs on it), the probe heads are fully in the current of the river. The rotability of the front construction prevents drying even at low flow conditions. Automatically sampling was exactly arrange like at monitoring station “Greimpersdorf”. The logged data were read out with SD card at each sampling or control interval.

Figure 46 - Pictures from the installation of the continuous monitoring station at Opponitz (gauging station and river at low flow conditions; automatic sampler and controller; cables and tube from above; installation of probes with a foldable guide tube; tubes in the water).

Krenstetten

At the gauge of Krenstetten neither a gauge house nor energy supply was available. Here the original gauging station is arranged by a box and operated via solar energy, both not suitable for the DHm3c monitoring equipment (Figure 47). Fortunately, the WWTP "Oberes Urlbachtal" 200 m downstream has transformed high voltage current for a construction side some years before. Consequently, the transformed high voltage current was used to provide regular energy, renting switch cabinets from a local electrician. While the automatic sampler in general is resistant to rain events and weather stable, we set and fixed him on two wooden pallets to increase stability and to increase its highs. Pallets have the advantage to be on the one hand permeable to water (decreasing water pressure at high flow conditions) and on the other hand easy to be fixed at the ground, e.g. by hammering in edge iron. The automatic sampler was closed with a steel chain and protected from the roughest weather conditions by a tarpaulin. Like in "Greimpersdorf" cables and tubes were installed underground. Here only 10 m of cables and tubes had to be laid and a vertical difference of among 2,5m has to be overcome. The 3 m stainless steel, foldable probes rail was fixed at large rocks used for the stabilization of the riverbanks. To guarantee a perfect fit and because of the profile of the rocks the rail was laterally incised and curved by approximately 20°. The possibility to fold the front part of the rail makes cleaning and maintenance possible.

Figure 47 - Pictures from the installation of the continuous monitoring station at Krenstetten (electric box and meter plus automatic sampler on wooden pallets; automatic sampler and installation of controller; controller in control cabinet; probes after small flood event;

Sampling and maintenance

Sampling of composite sampling was conducted each week over two month, while flood events were probed direct after the event. The cooling to 4 °C in the automatic sampler makes a short delay in sampling due to organizational issues and a several hours trip acceptable even during the summer month.

While conductivity measurements, temperature and water level measurements in general were stable, the suspended solids probe was susceptible to algae and coatings. While in winter, early spring and autumn, wiper function was sufficient to maintain a proper functioning of measurement by the probe for two weeks and even more, in late spring and summer the cleaning was partly necessary every week to avoid measurement drift. Beyond the weekly cleaning, the wiper function should be set to a maximum frequency. Wipers (in our experience and with respect to the situation in our catchment) are valid cleaning the device for rather 6 month and should be than be replaced. In general the cleaning (squeezing out the air and water residues present in the pipes) and the pumping of the vacuum pumps in the automatic samplers were able to pump probes over a vertical distance of 5 m. Due to some physical stress in two cases we face little problems with maintaining the vacuum, which leads to a malfunction of pumping and cleaning. In one case disconnecting the hose for several times led to porosity in another case the upper screw had to be readjusted, but in general the principle is easy to handle and reliable. The cleaning of the tube after each pumping also prevented possible blockage due to ice formation in the winter during low air temperatures.

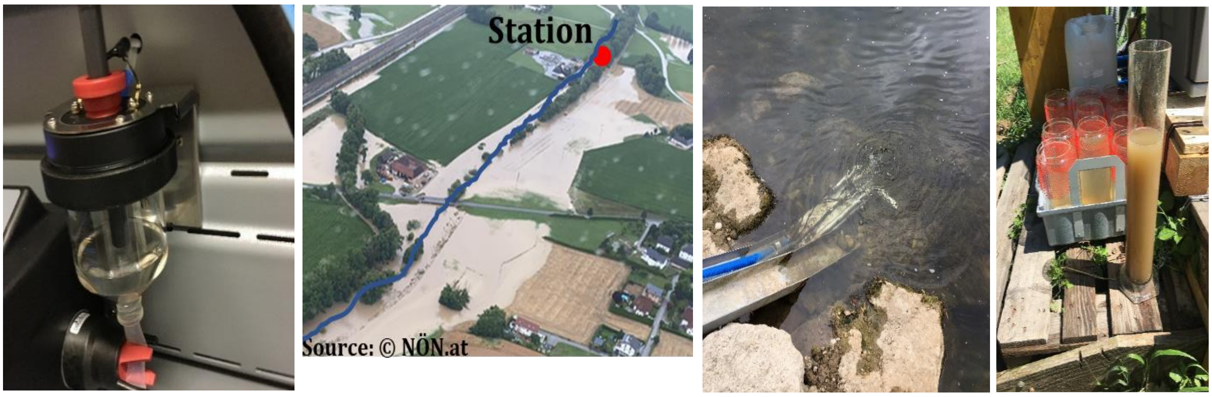

Figure 48 - Vacuum pump and sampling container fixed to 30 ml probe per pumping transported to cooled bottles below; in the middle the importance to plan the sampler location considering aspects of flood-safety; on the right hand sight, the tube is cleaned by squeezing out the air and the sampled suspended solids pumped during a large flood event can be seen.

6.2 Soil sampling

Number of samples taken:

	Planned	Achieved	Description
Soil samples	10+10	10+10	1 composite is made of 20 samples each, and each of the 20 samples is composed in turn of 1-5 subsamples, to be taken close to each other

Tools/method used:

Pürkhauer type sampler, rubber hammer, tools for removal of the soil (metal stick)

Sampling was prepared by a well experienced engineering office (wpa beratende Ingenieure) and was similar to that described by BME.

6.3 Atmospheric deposition sampling

Site descriptions

IN the Ybbs catchment two different stations were established to monitor deposition over one year. Both stations were associated with existing meteorological stations, which guarantees long-term series comparability of the results and online excess to information of daily precipitation at both stations. One station was situated at Opponitz, direct above the continuously monitoring station and gauge in the more mountainous area and could be probed only once a week. Unfortunately, no local controller and supporter could be found here. The second one was situated around 1,5 km away from the monitoring station and gauge of Krenstetten in a rural area. Here the farmer and controller of the meteorological station of the province of Lower Austria, was willing to organize probing of the atmospheric deposition once a day, when necessary. He was equipped with a little freezer and two 5l laminated safety glass bottles suitable for freezing. During wintertime both deposition sampler were equipped with heaters, so that the normal glass bottles could not freeze and burst and that snow trapped in the syphon melts and percolates into the bottles.

Figure 49 - Atmospheric deposition samplers and transformer at Krenstetten and at Opponitz.

Instrument used at each station: Stainless steel deposition samplers designed for the use in alpine areas. In each sampler (two at each place, see Figure 49) a 1 l glass sample collector was placed below a 300 mm diameter glass funnel equipped with a very rough stainless steel filter to hold back only very rough material. Glass bottles were placed inside the stainless steel construction (protected from light or insect infestation). The construction was removed at each sampling. Here also a heater is installed, which has to be connected to the transformation module (see Figure 6) and to the power grid. The heater was essential during the wintertime, with temperatures especially in the mountainous region well below -5°C.

Number of samples taken (Overview table)

	Planned	Achieved	Description
Atmospheric deposition samples	4+4	5+5	1 composite is made of rain events over a period of three month

Lessons learned: Two 5l bottles laminated safety glass bottles have burst (without sample loss) if too much sample (e.g. 2l) was frozen too quickly. A local controller guarantees a daily probing after rainfall events, which extremely reduces travelling efforts and gives daily insight into the operability of the samplers.

6.4 Waste water sampling (including mining)

Site descriptions

Originally, it was planned to monitor one urban WWTP (3 sample campaigns) and one industrial WWTP (two sampling campaigns).

The urban WWTP was equipped by automatic samplers in the influent and the effluent, which are continuously operated in the routine sampling of the treatment plant. The composite samples planned where taken directly by the well trained treatment plant operators. Samples were stored in a freezer, which was provided by Umweltbundesamt.

Sampling of an industrial wastewater treatment plant was not possible. Only one operator in the catchment gave an initial positive feedback. After organizing the sampling and handing over the containers, it turned out that this company was also not prepared to agree to sampling under any circumstances.

Sample overview

	Planned	Achieved	Description
Wastewater samples	5	3	3x2 samples, 1 at outlet, 1 at inlet each time.

Site photos:

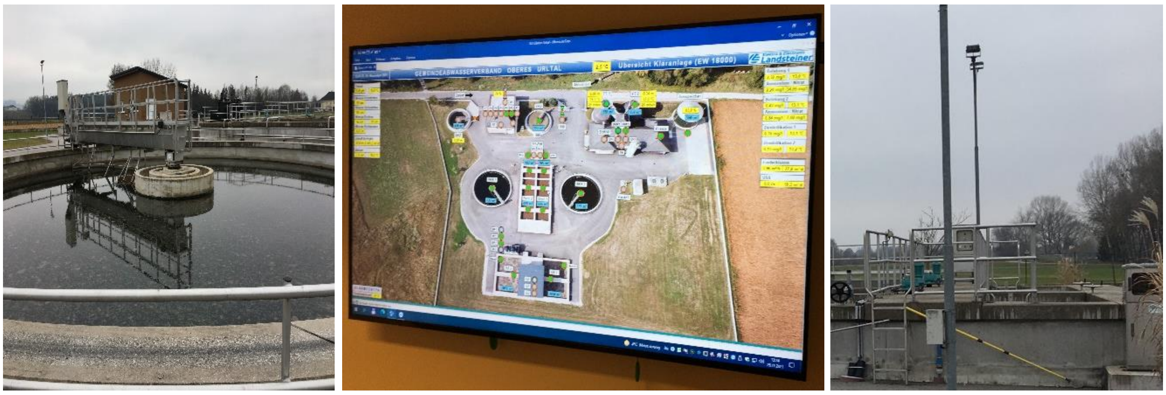

Figure 50 - WWTP monitored in the Ybbs catchment (Secondary sedimentation tank, operating scheme, sampler (right))

Tools used:

The sampling is operated by vacuum Pump. The sampling can be pre-programmed and up to 24 separate samples can be collected.

Method description: 24 hour composites were collected for one week, by filling one bottle for 24 hours with a frequency of one hour.

Lessons learned

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.

Expressions from the laboratory

Figure 51 - Expressions from the laboratory. Different suspended solids concentrations in comparable flood events of the background station AYH and the station Url AYU with agricultural use. Filters used for 0,5l HM (dissolved) from flood event samples. Mixing of WWTP effluent.

7 Zagyva catchment, Hungary

Location codes

HZN: Zagyva-creek @ Nemti;
HZT: Tarján-creek @ Kisterenye;
HZH: Herédi-Bér-creek @ Heréd;
HZ6: Zagyva-creek @ Hatvan.

7.1 River sampling

Overview

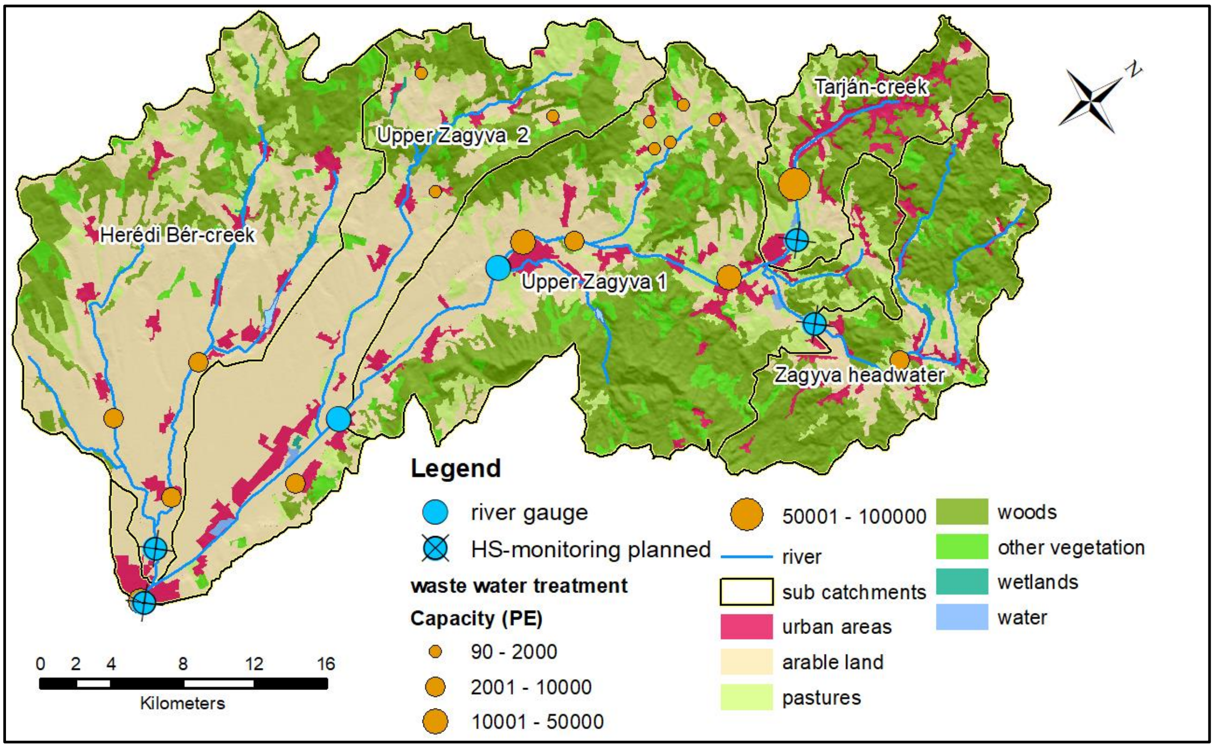

Figure 52 – Zagyva pilot catchment with monitoring stations

Total number of samples taken:

	Planned	Achieved	Description
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 @HZT was sampled with multiple samples

Instrument/method used:

	Yes/No	If yes, type of instrument	Description (installation details)	Photo reference
Water level sensor	Yes	4-20 mA WL sensor Qidian	Discharge based on Q – H function	
Conductivity probes	Yes	Hach 3798-S sc inductive conductivity probe.		
Turbidity probe	Yes	Hach Solitax t-line sc submersible probe. FNU		

		range: 0.001-4000. Wiper blade.		
Automated sampler	Yes	Own development. Described in Budai et al 2020[2].	Devices were installed: - in existing water gage houses operated by the Water Directorate (KDVVizig) @ HZN & HZT. - in backyard of local people @ HZH - on abandoned sluice structure @ Hatvan	
			Instrument 1: Own development (Budai et al., 2020), full time @ all 4 sites. Instrument 2: WaterSam WS Porti 24x1 liter sampler temporarily @ HZN	
High-flow grabsampling	Yes	One high flow sample was taken @ HZH due to malfunctioning of the autosampler		

Lessons learned

- Autosampler: Peristaltic pump operation is fairly safe in terms of clogging, no major problems occurred after setting it outside the HDPE tube, except for site HZT. Setup was tested for flow velocities and TSS transfer. Minimum required flow rate was established. The drawback of the method is that it cannot follow the large variation of river flow in real scale, as the rate of flow with the pump setup can only be tripled (with this applied pump). Silicone tubing has to be lubricated in every two month and replaced after one year.
- Probes:
    - Conductivity probe is reliable, but biofilm growth on the surface of the instrument reduce the measured conductivity. Regular cleaning is necessary (two weeks at least during summer).
    - Turbidity probe wiper stuck in some cases. Otherwise, despite the wiping, some deposition occurs, that need to be removed by cleaning. Deposition causes higher variation and higher mean turbidity values.

[2] Budai, P., Kardos, M.K., Knolmár, M. *et al.* Development of an autonomous flow-proportional water sampler for the estimation of pollutant loads in urban runoff. *Environ Monit Assess* **192**, 572 (2020). https://doi.org/10.1007/s10661-020-08536-3

Site photos

Figure 53 - Solar panel at the off-grid station HZN.

Figure 54 - Mounting the sensors @ HZT. Controller located in the water gauge.

Figure 55 - Sensor controller located on the river bank @ HZH.

Figure 56 – Left: Controller of sensors mounted on top of abandoned sluice structure @ HZ6. right: Taking a grab sample at medium flow conditions @HZ6 station.

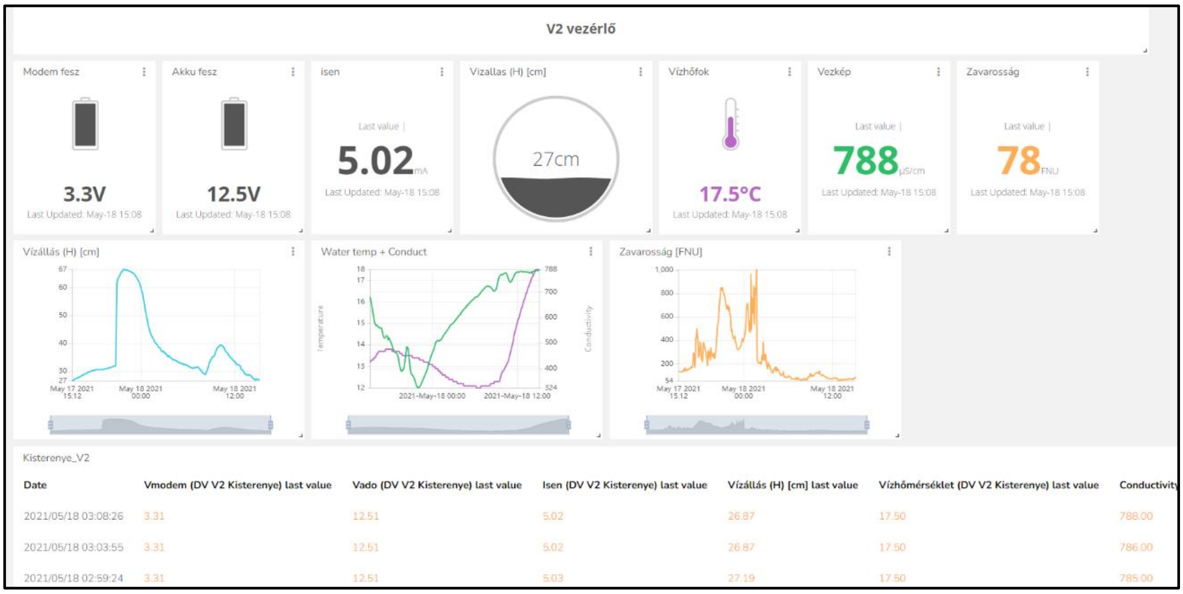

Figure 57 - Website reporting real-time data water level, water temperature electrical conductivity and turbidity values measured @ HZT. Clogging of sensor visible during declining of the flood event.

7.2 Atmospheric deposition sampling

Site descriptions

On both sites (Maconka - HZN) and Kartal - HZ6) a very similar atmospheric deposition sampler was installed (Figure 58).

Instrument used: Simple design (own development based on idea by (Foan et al., 2012)). Parameters: 200 mm PVC pipe, in which the 5 l glass sample collector was placed. 300 mm diameter glass funnel was placed on top, without filter. Glass bottle was covered with aluminium foil to reduce direct light entering the bottle.

Number of samples taken: 4+4, 8 in total (1 sample / location / season).

Lessons learned: Many 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. Glass filter should be used if possible to reduce this effect.

Figure 58 - Atmospheric deposition sampler located on property of the water authority in Maconka.

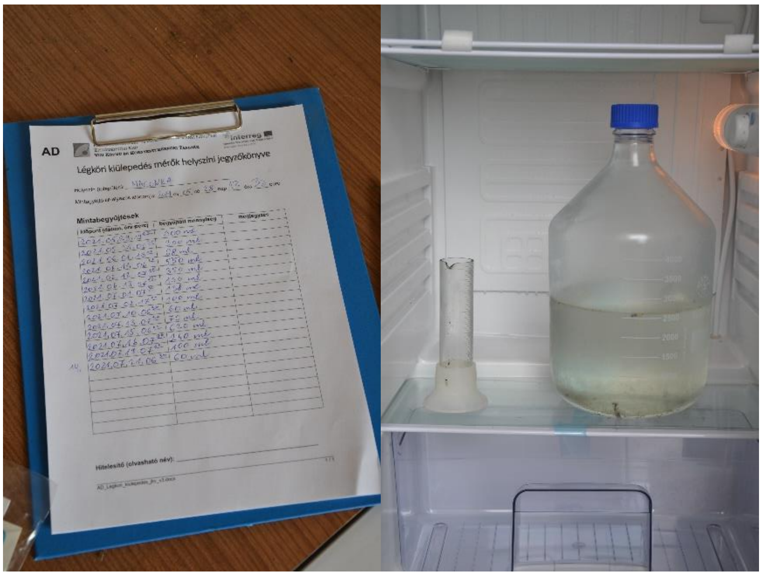

Figure 59 - On-site filled protocol and on-site stored sample @ Maconka.

Figure 60 - Precipitation gauge with online data transmitter (left) and atmospheric deposition sampler (right) located in garden of local resident in Kartal, Hungary. Precipitation gauge developed by Knolmár (see (Knolmár, 2011)*).*

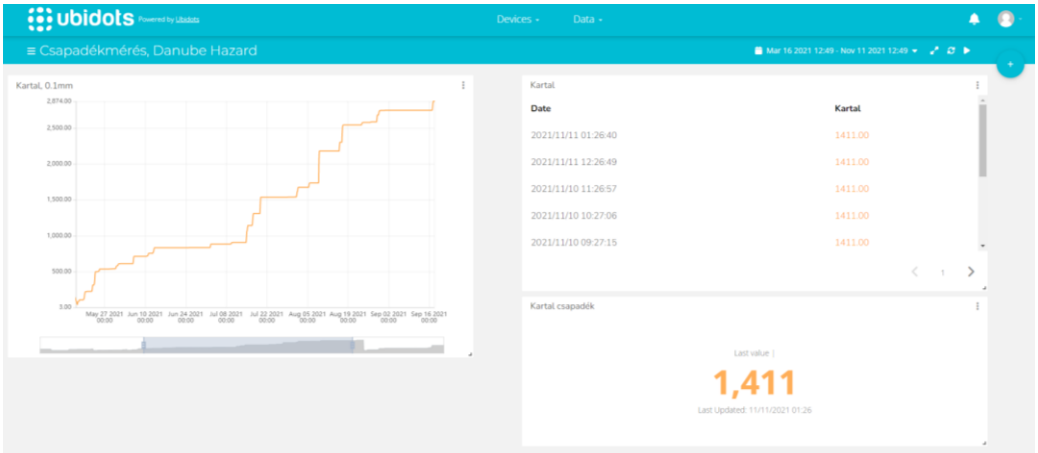

Figure 61 - Website for checking precipitation values measured @ Kartal, Hungary.

7.3 Waste water sampling

Site descriptions

At Salgótarján Municipal WWTP, the automatic sampler (Figure 62, Figure 63) and cooling facilities of the treatment plant laboratory was used. Local personnel assisted in the sampling. Subsamples were collected daily from 24 hours composites. Final composite was homogenized and mixed at University lab proportionally to daily flow rates. At Mátraterenye industrial plant a mobile WTW WaterSam sampler (Figure 64, Figure 65) was used with passive sampling (cooling packs and insulation box).

Sample overview

	Planned	Achieved	Description
Wastewater samples	3	4	4x2 samples, 1 at outlet, 1 at inlet each time.

Site photos:

Figure 62 - Sampling of raw (inflow) wastewater @ HZS.

Figure 63 - Sampling of treated (effluent) wastewater @ HZS.

Fig. 1.: Creating flow proportional composite in the BME VKKT laboratory.

Figure 64 - Sampling the effluent from industrial WWTP HZI.

Figure 65 - Sample collection @ industrial plant HZI.

Figure 66 - Samples stored at municipal plant HZM.

Tools used:

WaterSam porti portable sampler. The sampling is operated by vacuum Pump. The sampling can be pre-programmed and up to 24 separate samples can be collected.

Method description: 24 hour composites were collected for one week, by filling one bottle for 24 hours. Each 30 minutes, 20 ml sample was collected. Cooling was done using cooling packs within an isolation box. Cooling packs were changed at each 48 hours.

Fig. 2.: Sample collector with thermal insulation box.

Lessons learned

Some misfunction 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.

7.4 Suspended sediment sampling

Site descriptions

Philips type sampler was installed at Törökkoppány station at two different height, one for long term collection of baseflow sediment, one for collecting high-flow sediment.

The other method was the large volume (25 l) sampling with the automated sampler.

Tools used: Philips sample was constructed using standard PVC pipe units. Small diameter hole was drilled at outlet (8mm), larger inlet diameter was used (2 cm).

Large volume sampler was the same described at River Sampling.

Number of samples taken (Overview table)

	Planned	Achieved	Description
SPM samples (HKH+HKT)	0+6	5+2	2 was collected at Tamási, 5 at Törökkoppány. Baseflow sample was collected for 3 month.

Site photos

Figure 67 - Philipps sampler installed @ HZN river monitoring station.

Figure 68 - SPM sampling @ river monitoring station HZT. Left: Philips sampler mounted to sample low flow SPM during operation. Middle: Sampler mounted to collect from high flow event. Right: sampler emptied (collected).

Figure 69 - Mounting the Philips sediment trap @ river monitoring station HZ6.

Figure 70 - Demounting the sampler & collecting SPM sample @ river monitoring station HZ6.

Lessons learned

- Sampler device:
    - Philips: Only works well in higher turbidity conditions. At baseflow conditions no sufficient amount of SPM sample was collected for all measurements, but sufficient for ICPMS measurements of metals. High-flow samples were collected well by the sampler.
    - 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.
- Sample handling: Decanting the Philips sampler on site needs two persons, and a large volume sample holder.

7.5 Soil sampling

Number of samples taken:

	Planned	Achieved	Description
Soil samples	10+10	10+10	1 composite is made of 20 samples each, and each of the 20 samples is composed in turn of 1-5 subsamples, to be taken close to each other

Tools/method used:

Pürkhauer type sampler, rubber hammer, tools for removal of the soil (metal stick)

Soil sample locations

At Törökkoppány subcatchment (HKH) the samples were divided to three agricultural and one forest composite samples, the lower part of the catchment was divided to three agricultural and two forest samples, and one pasture sample was collected from the whole catchment (Figure 9).

Photos

Figure 71 - soil sampling on a pasture.

Fig. 3.: Homogenizeing the 3-5 subsamples on field.

Fig. 4.: soil sampling.

Fig. 5.: Accessories for soil sampling: tray & jar.

7.6 Lessons learned

Soil sampling is a real adventure, but driving the pick-up needs experience – created experience ☺.

Fig. 6.: Sampler car stuck in mud 1.

Fig. 7.: Sampler car stuck in mud 2.

Fig. 8.: Sampler car after being freed from mud.

Lessons learned

- 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.
- Site access problems (physical, land owners): Owners were helpful in most cases and allowed the sampling.
- Sample processing: 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.
- Soil sampling is a real adventure, but driving the pick-up needs experience – created experience ☺.

7.7 Sample storage and transport

Storage

According to the original SOP, composite samples for PAH measurements had to use glass bottles. Several glass breaks have been experienced during freezing, and handling of the frozen samples, even during transport. For this reason, the method has been changed, and the samples were kept cool (< 4 ^{o}C) instead of freezing.

Samples stored in PE bottles were frozen for heavy metal analysis. $CaCO_3$ precipitation was observed when the thawing of the first sample was carried out. Using filtering after thawing, there is a high risk of losing particle-bound contaminants from the samples. Therefore the SOP changed: filter the samples onsite right after sampling delivery to the own lab, using specific pure filter, acidifying it and only then freezing.

7.8 Transport

A courier DHL Express delivered the samples within 24-hour to Romania (Lab of NARW). To Slovenia (Lab of JSI) and to Austria (Lab of UBA) samples was delivered by car.

8 References

Budai, P., Kardos, M.K., Knolmár, M., Szemán, G., Turczel, J., Clement, A., 2020. Development of an autonomous flow-proportional water sampler for the estimation of pollutant loads in urban runoff. Environ. Monit. Assess. 192, 572–588. https://doi.org/10.1007/s10661-020-08536-3

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