



Demonstration of harmonized and cost-effective monitoring - Annex II

Deliverable D.T1.2.2 Methodological approach for the measurements in the pilot regions and final selection of substances

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1. MOTIVATION AND OBJECTIVES OF THE MEASUREMENT CAMPAIGNS

Currently, available data and information on the concentration levels of micropollutants within the Danube River Basin (DRB) is dramatically scarce. It is of insufficient quantity, especially with respect to the identification and quantification of priority emission pathways, and generally of poor quality too, owing to the limitations of the currently employed analytical tools.

The measurement activities within Danube Hazard m³c have thus the primary goal of identifying and quantifying concentration ranges of selected micropollutants in the DRB, not only directly in rivers, but also across different environmental and anthropogenic compartments, which have the potential to contribute to river contamination.

A second fundamental goal is to produce the necessary information that will enable the further development and validation of two models (MoRE and SOLUTIONS), which estimate the contribution of different point and diffuse emission pathways at the catchment scale in addition to expected river loads and river concentrations. Table 1 summarizes the substance-specific input data required by the model MoRE. The substance-specific input required by the SOLUTIONS model (reported in Table 2) does not need data deriving from the monitoring programme, but the validation of its intermediate results does. These are summarized in Table 3. Given the above, a targeted monitoring concept has been designed so to enable the quantification of river concentrations and river loads of selected contaminants across diverse catchments and which considers the data requirements of the MoRE and SOLUTIONS models. Further, the planned campaigns will also be used to contribute to the objectives of capacity building in the project, since they will demonstrate cost-efficient methods to collect information needed for modelling and will strengthen knowledge and capabilities across the DRB with respect to sampling and analytical best practices.

The measurement campaigns will be organized and harmonized within a single pilot action, which involves seven pilot regions, two of which are in Austria, two in Hungary, two in Romania and one in Bulgaria. These in turn are subdivided into sub-catchments, leading to a total of 21 sub-catchments being investigated (detailed description is provided in the Delivery D.T1.2.1 “Final selection and description of pilot regions”). Given the vastness and heterogeneity of the DRB, these pilot regions do not aspire to be representative of the entire basin. Nevertheless, the selection is heterogeneous and covers significant differences and major aspects of micropollutants contamination. In the first place, the selected catchments differ mainly in their geographical, topographic, and especially climatic features. Secondly, given their different land uses, they allow focusing on diverse dominant source and emission pathways of micropollutants, especially mining sites, urban agglomerations, and agriculture. Moreover, since they are distributed over four countries, they enable considering different legacy issues related to diffuse pollution and different state-of-the-art situations concerning wastewater treatment.

In the first part of this document, we present a review of the currently existing approaches for the monitoring of hazardous substances concentrations in rivers and other environmental and anthropogenic compartments. Benefits and disadvantages are presented and discussed. In the second part we present the selection of approaches to be implemented in the Danube Hazard m³c project, as well as the selection of substances to be analyzed.

1.1. Data requirements of MoRE and SOLUTIONS models

Table 1: Requirements of substance-specific data for the MoRE model.

Type of pathway	Pathway	Input data	Spatial scale	Temporal scale
Point	Municipal WWTP effluent	Effluent loads OR water amount and effluent concentration	For each plant or lumped over AU	Annual average
Point	Industrial WWTP effluent or direct industrial discharge	Effluent loads OR water amount and effluent concentration	For each plant or lumped over AU	Annual average
Point	Abandoned mining site	Effluent loads OR water amount and effluent concentration	For each site or lumped over AU	Annual average
Diffuse	Agricultural erosion	Soil content in agricultural land	Lumped over AU	Current conc. level
Diffuse	Erosion from natural soils	Soil content in naturally covered land	Lumped over AU	Current conc. level
Diffuse	Surface runoff from pervious soils	Concentration in surface runoff from pervious land	Lumped over AU	Annual average
Diffuse	Tile drainage	Concentration in tile drainage discharge	Lumped over AU	Annual average
Diffuse	Groundwater	Concentration in groundwater	Lumped over AU	Annual average
Diffuse	Atmospheric deposition	Deposition rate	Lumped over AU	Annual average
Diffuse	Atmospheric deposition	Concentration in rain water	Lumped over AU	Annual average
Diffuse	Discharge through combined sewer overflows	Concentration in combined sewer overflows	Lumped over AU	Annual average
Diffuse	Discharge through storm sewer outlets	Concentration in storm sewer outlets	Lumped over AU	Annual average
Diffuse	Inland navigation	Emissions loads of PAH via steel construction for hydraulic engineering	Lumped over AU	Annual average
Diffuse	Inland navigation	Emissions loads of PAH via motor boat exhaust	Lumped over AU	Annual average

Note: AU = Analytical Unit

In addition, the validation of MoRE requires annual average concentrations or the total annual load of contaminants in rivers at the outlet of each AU employed for the validation.

Table 2: Requirements of substance-specific data for the SOLUTIONS model.

Type of pathway	Pathway	Input data	Spatial scale	Temporal scale
Point & Diffuse	Wastewater	Use volume and use type of chemical, population density map, waste water management maps (connection to sewers, treatment level)	Lumped per SC, use volume optionally per country or even on EU level	Annual average
Point & Diffuse	Stormwater	Use volume and use type of chemical, population density map, paved area map, combined-/separated sewers map	Lumped per SC, use volume optionally per country or even on EU level	Annual average
Point	Abandoned mining site	Effluent loads OR water amount and effluent concentration		Annual average
Diffuse	Agricultural emissions (pesticides)	Amount used	Country level or finer if available	Annual average
Diffuse	Atmospheric deposition	Deposition rate	Lumped per SC	Annual average
Diffuse	Inland navigation	Emissions via steel construction for hydraulic engineering	Lumped per SC	Annual average
Diffuse	Inland navigation	Emissions via motor boats	Lumped per SC	Annual average

Note: SC = sub-catchment, basic spatial unit derived from the underlying hydrology model

Table 3: Intermediate results of the SOLUTIONS model for which validation data are required.

Type of pathway	Pathway	Validation data	Spatial scale	Temporal scale
Point	Municipal WWTP effluent	Effluent loads OR water amount and effluent concentration	For each plant or lumped over AU	Annual average
Point	Industrial WWTP effluent or direct industrial discharge	Effluent loads OR water amount and effluent concentration	For each plant or lumped over AU	Annual average
Diffuse	Agricultural erosion	Soil content in agricultural land	Lumped over AU	Current conc. level
Diffuse	Erosion from natural soils	Soil content in naturally covered land	Lumped over AU	Current conc. level
Diffuse	Surface runoff from pervious soils	Concentration in surface runoff from pervious land	Lumped over AU	Annual average
Diffuse	Tile drainage	Concentration in tile drainage discharge	Lumped over AU	Annual average
Diffuse	Groundwater	Concentration in groundwater	Lumped over AU	Annual average
Diffuse	Discharge through combined sewer overflows	Concentration in combined sewer overflows	Lumped over AU	Annual average
Diffuse	Discharge through storm sewer outlets	Concentration in storm sewer outlets	Lumped over AU	Annual average

2. REVIEW OF EXISTING MONITORING APPROACHES

2.1. Total and dissolved concentrations in rivers

This section describes different measurement approaches and methods used for measuring the dissolved and/or total concentration of hazardous substances in rivers.

Grab (spot) sampling

The most typical sampling method is grab sampling, which consists of the lab personnel travelling to the sampling point, taking a limited amount (usually 1 litre, but for specific substances expected at low concentrations up to 10 litres) of the matrix in some bottle/case, and analysing it in the lab. Efficiency of this method depends – among others – on the frequency, which, however, has its limits. Traditional monitoring programmes rely predominantly on this method (Decker and Simmons, 2016).



Figure 1: Extendable sampling pole with a glass jar. Source: (AU Environmental Protection Policy, 2009)

The data obtained with this approach is representative of the specific place and sampling time only. Spot sampling with a monthly frequency often produces data below detection limits and sometimes accidentally detects elevated concentrations that originate from short-term concentration variation that is representative only for the moment when the sample was collected (Vrana et al., 2014).

Composite samples

Composite sampling is an extension of grab sampling: samples are grabbed with a higher frequency, mixed together, and the so generated mixed sample (composite) is analysed. This is usually done with an automated sampling device. The concentration values of the composite sample are representative of the whole period in which the samples were taken. Samples can be added to the composite at equal time intervals (time proportional, e.g. every hour) or depending on some hydrological property (e.g. flow proportional). In the second case, automated flow measurements are needed at the sampling

location. Linking sampling frequency to turbidity values (measurable online) is also a possibility (Lewis, 1996). In the CrossWater project, Moser et al. used 7-days composite samples to compare river loads with model calculations (Moser et al., 2015).

Flow & turbidity-triggered sampling

Turbidity threshold sampling uses real-time turbidity and river level information to: i) automatically collect targeted water quality samples e.g. during high flow events and ii) to estimate suspended sediment loads during a specific time period. The system uses a programmable data logger in conjunction with a water level measurement device, a turbidity sensor, and a pumping sampler. Specialized software enables the user to control the sampling process by setting threshold values for sample collection. Thresholds are usually chosen so that the square roots of NTU values are evenly spaced to adequately define loads for small storms without oversampling large storms. A programmable data logger, typically recording at 10- or 15-minute intervals, instructs an automatic pumping sampler to collect a sample whenever a threshold is crossed (Lewis and Eads, 2009).

Water passive samplers

The Canton of Thurgau in Switzerland has recently developed a new technique to passively collect water samples. The device, shown in Figure 2, requires a minimum water level of 10-15 cm and is designed for small streams. It is equipped with a valve to sample water proportionally to the water level in the stream. It can collect approximately 2.5 l of water in one week. Although it might be a promising simple and inexpensive approach for monitoring in small streams, evidence of its functioning is still very limited since it has been recently developed.



Figure 2: Water passive samplers developed by the Canton of Thurgau (Switzerland).

Substance passive samplers

Passive samplers for monitoring of aquatic pollutants have been described in the literature for almost three decades, but they are only beginning to gain acceptance. The potential advantages of passive samplers over other sampling and measurement strategies include the ability to integrate pollutant levels over extended sampling periods (up to several weeks), as well as inherent speciation capabilities, allowing for critical in situ speciation of metals. Passive samplers are relatively low-cost and do not

require secure locations or additional infrastructure, making them ideal devices for certain monitoring tasks (Knutsson, 2013).

Passive samplers generally use fewer chemicals and are easier to prepare for analysis, making them a sustainable technology. Thanks to the enrichment principle, they can provide better detection limits. Additionally, they are cheaper than traditional (grab) sampling methods if the same accuracy is needed (Lambert, 2013). Allan et al. (2008), based on the investigation of 5 heavy metals, stated that passive sampling provides information that cannot be obtained by a realistic spot sampling. Due to their novelty, there is still considerable uncertainty over their use, especially in the decision-making process. The uncertainty is understandable since there is no standardized method for their application (Lambert, 2013).

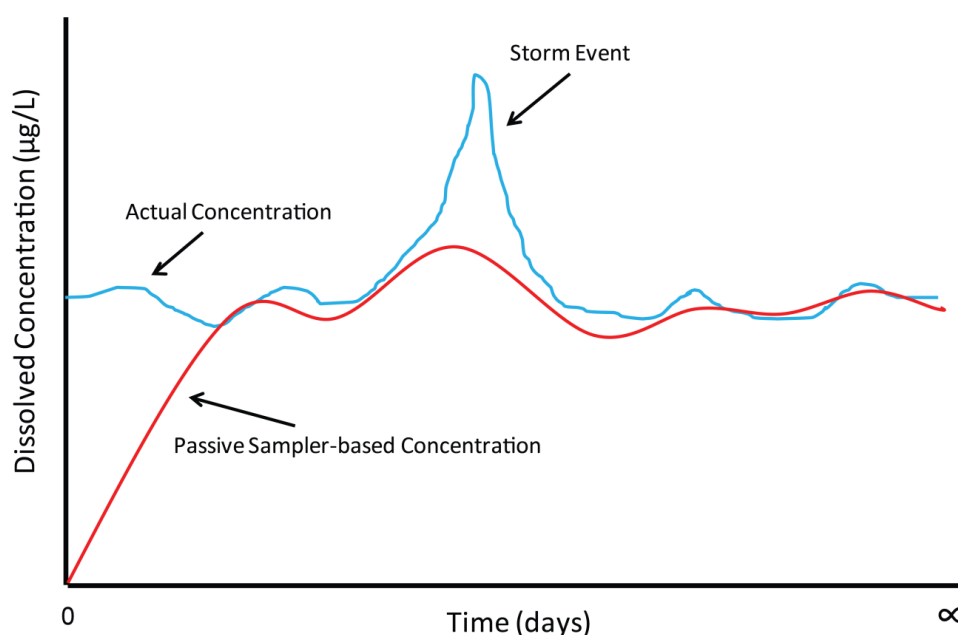


Figure 3 Conceptual diagram of the dissolved water column concentration of a hydrophobic contaminant shown as the actual concentration (blue line) and the passive sampler-based concentration (red line). Source: (US-EPA, 2012).

Allan et al. (2008) deployed Chemcatcher and DGT passive sampling devices in the Meuse River (NL) for 1 – 4 weeks periods and compared their values on 5 heavy metals with frequent spot sampling measurements. They concluded that for Cd, Cu, Ni, Zn, the 1 – 2 weeks deployed samplers yielded concentration values in good agreement with those measured with traditional values. Samplers deployed for periods longer than 2 weeks and Pb concentrations were of weak quality – the former possibly due to biofouling, the latter owing to a small labile fraction. In general, they concluded that passive sampling is a good method when applied together with traditional sampling.

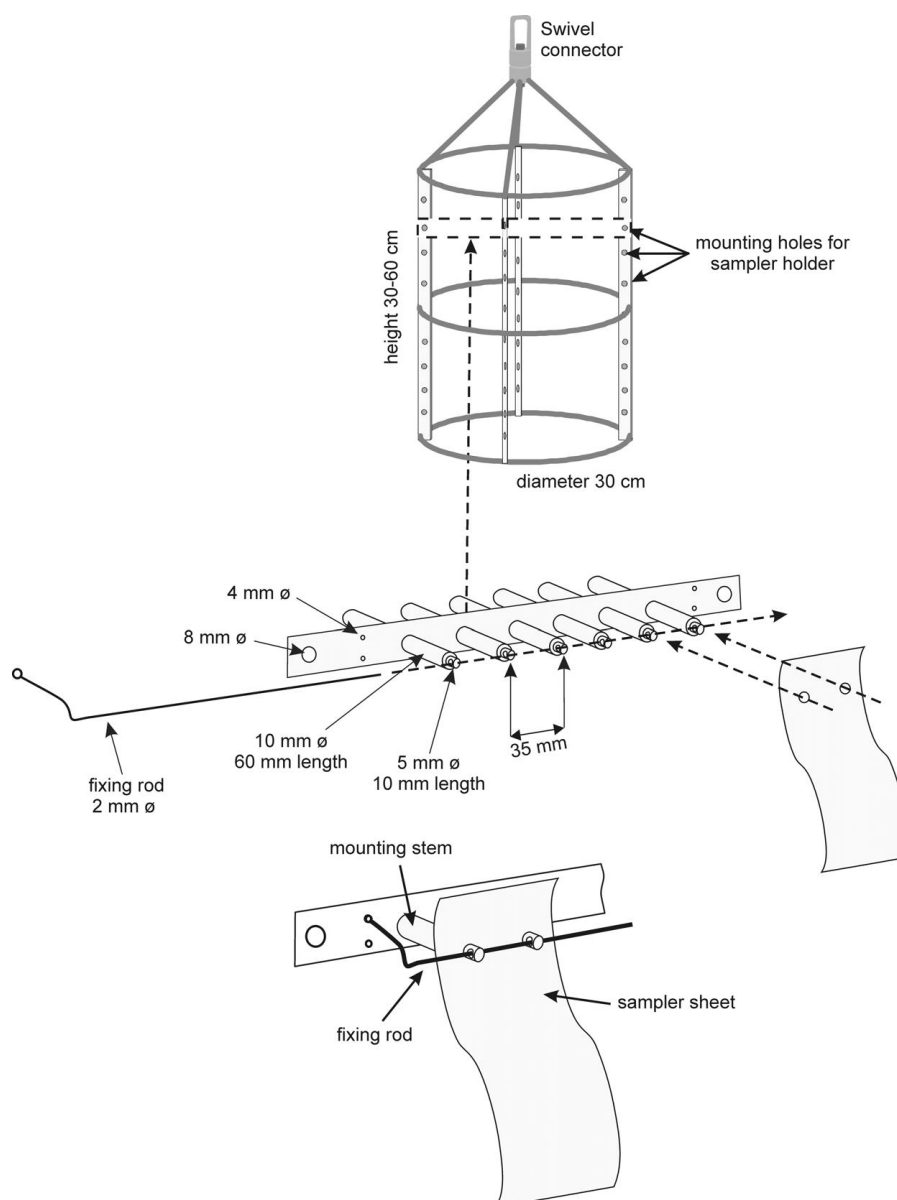


Figure 4 Schematic drawing of deployment frame and sampler holder (silicon rubber passive sampler). Adapted from: Smedes and Booij (2012).

During the years 2010-2011 Vrana et al. (2014) deployed Semi-Permeable Membrane Device (SPMDs) and Diffusive Gradient in Thin Films (DGTs) into the Danube for the quantification of PAHs and heavy metals, respectively. They compared the amounts estimated with the two types of passive samplers with 14-days composite sample concentrations, which yielded them to promising results. They concluded that the ultimate aim of passive sampling is to obtain a measure of the level of pollution that gives a representative measure of the exposure of organisms and compare the contaminant levels in time and space, but not to assess mass balance of compounds in water bodies, since passive samplers only indicate freely available compounds (Vrana et al., 2014). The fact that passive samplers measure the chemical activity of the contaminants (Reichenberg and Mayer, 2006) makes them clearly advantageous in assessing risks of toxicity and bioaccumulation, but of restricted use if the goal is the estimation of total loads in rivers.

2.2. Particle-bound concentrations in rivers

Whereas river sediments are an important source of information for the level of legacy pollution in a water body and for the internal pool of contaminants that could be mobilized or leached into the water column, Suspended Particulate Matter (SPM) reflects better the current contamination level and can better support the validation of emission models, which are based on a balance principle. Moreover, in comparison to sediments, SPM contains a higher percentage of fine-grained fraction, in which particulate-bound contaminants mainly accumulate (e.g. heavy metals (Maniquiz-Redillas and Kim 2016; Sansalone and Buchberger, 1997); or even PFOS (Kunacheva et al., 2011; Ahrens et al., 2009; and Nollet, 2014)).

The analysis of micropollutants in the solid matrix requires a minimum availability of approximately 200-250 g (dry weight) of particulate matter. This amount of sample is needed as some of the trace elements would be below the levels of detection, therefore contaminants need to be extracted and enriched from a larger mass of sediments to increase concentration. The collection of such an amount of SPM is very challenging and cannot be achieved through small volume grab samples.

Devices for the collection of SPM

Different devices have been designed for the collection of relevant amounts of SPM, which range from relatively simple traps located in the river itself to relatively expensive devices located on the river banks and activated electronically.

The main advantage of simple trap or decanting devices is that they are relatively inexpensive and that they mostly rely on a passive principle, i.e. they do not require electricity. They present, however, major disadvantages. Their performance depends on the type of river and on the grain size of the SPM. Clogging problems occur due to very fine sediment or algal growth. Further, they often do not allow collecting the finest fraction (as they do not settle), which is highly relevant for the adsorption of trace pollutants (Phillips et al., 2000). Last, a severe issue affecting their suitability for the project is that they do not allow any back-calculation of real particulate concentrations of contaminants in the water column, because it is not possible to know the corresponding volume of water with exactitude and thus the SPM concentration in it.

A rather expensive alternative, which requires electricity and automatic control, is the use of high-volume samplers. An example of these are the samplers developed and employed within the international INN Project (Kittlaus et al., 2016; Kittlaus and Fuchs, 2015), namely 1 m³ stainless-steel tanks, designed and equipped in a way that optimizes the deposition and the separate collection of SPM (Figure 5). The fact that the total volume of sampled water is known allows the calculation of particulate concentrations of the micropollutants in the water column. The possibility of automatic control allows the targeted sampling at different flow and turbidity conditions.

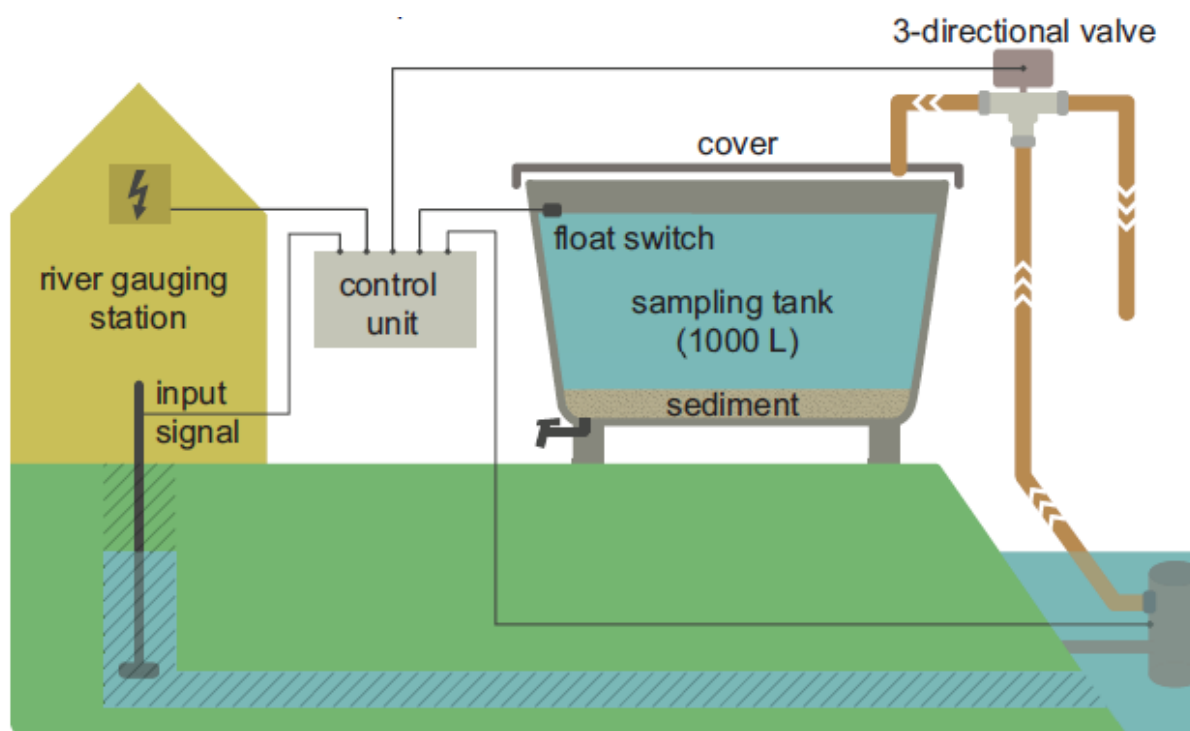


Figure 5 – Large volume sampler arrangement at a river gauge as suggested by (Kittlaus and Fuchs, 2015).

The disadvantage of this method is that depending on the controlling regime the water can stay for some time (days to weeks) in the sampler basin, which poses some risks on the accuracy of the results in case of organic contaminants, as biological decomposition may alter the contaminant concentrations.

Large volume sampling may also be possible using a different approach, based on solid phase extraction principle. The Ohio River Valley Water Sanitation Commission (ORSANCO) (Dinkins and Heath, 1998) developed a method to measure dioxin levels in the river Ohio, which uses a contaminant attracting resin to catch the dioxin inline, while the exact water volume is known using a positive displacement pump. This approach is focused on dissolved contaminants, but suspended sediment is also trapped; therefore it can also be stored and used for analysis. The suspended phase is caught within the 1 μm to 120 μm size interval. The drawback of this approach is that there is a need for regular manual input if large volumes must be sampled, as two sediment filters are connected parallel to switch flows between them, while one of the filters can be changed to a new one. The resin columns also have a limited capacity; therefore, these must be upsized for a large volume sampling.

The Joint Danube Survey in 2013 also used a Large Volume Solid Phase Extraction (LVSPe) device (Figure 6, Figure 7) developed for the survey, which can also successfully enrich contaminants in the solid phase (Schulze et al., 2017) and successfully recovered over 150 compounds. This arrangement allows the extraction of 50 l of water, but also is also designed in a large 1000 l model. It also enables regular sampling for days or weeks. This method is primarily focused on dissolved compounds, but the suspended matter is also available for extraction. The same disadvantage is true for this method as for the previous arrangements, namely that regular manual input is needed to replace sediment traps and also that the equipment is expensive.



Figure 6 - LVSPE during the Joint Danube Survey 2013. Image: André Künzelmann (UFZ, Leipzig, Germany)
(source: <https://freshwaterblog.net/2017/06/09/solutions-simplified-sampling-of-large-water-volumes-for-combined-chemical-and-biological-testing/>)



Figure 7 - Detail view on the large sampling cartridge for up to 1000 liters. Image: André Künzelmann (UFZ, Leipzig, Germany)

(source: <https://freshwaterblog.net/2017/06/09/solutions-simplified-sampling-of-large-water-volumes-for-combined-chemical-and-biological-testing/>)

Sampling locations

Concentration distribution of SPM is uneven through the cross section of rivers, since it has a vertical (Venditti et al., 2016) and a cross horizontal inhomogeneity (Baranya and Józsa, 2013; Holdaway et al., 1999). The concentration of SPM tends to increase near the river-bed and with rising flow velocity. To retrieve a representative sample from smaller rivers an appropriate sampling arrangement is needed. Depth integrated sampling provides a mean to represent one profile of water column instead of one point (Perks, 2014). If the river is shallow and there is a uniform flow across the river, a single point sampling is also feasible at 60% of the stream depth.

Turbidity measurements

A relatively cheap and reliable way to continuously assess SPM in rivers is the use of turbidity measurement devices, which can record turbidity continuously. Turbidity correlates well with SPM (Tananaev and Debolskiy, 2014), but the relationship between these two parameters must be set prior to or parallel to the turbidity measurements (Dalbianco et al., 2017). A good way for this is to use time-integrated samplers for a longer period (2-3 months) to get a representative sample of SPM in the actual river. Then these sediment samples can be used to set up turbidity-SPM relationship curves.



Figure 8 – Time-integrated „Philips“ sampler installation to measure different stage intervals. (Source: <http://outdoordiscovery.org/conservation/macatawa-greenway/research/bacteria-sediment-sampling/>)

The turbidity signal changes with change of the particle size distribution. Organic matter content also has an altering effect on turbidity (Slaets et al., 2014), especially for loam and clay sediments.

Sample preservation and storage

Samples of SPM should be stored in a way that the contaminants to be analysed do not alter during transportation or storage. For some compounds, it might be necessary to add sample preservation agents (Shoemaker et al., 2009). An alternative more general preservation technique is the freezing or the lyophilisation of the SPM samples (Aggio et al., 2016). When several different chemicals shall be measured in the samples, lyophilisation is preferable for preservation.

2.3. Atmospheric deposition

Bulk deposition

The simplest and cheapest method to monitor atmospheric deposition is to measure bulk deposition. In this case, the sampling device is a tray or a bucket. E.g., Esen et al. (2008) and Guo et al. (2014) used stainless steel platter of 60-76 cm diameter, 19 cm deep to measure PAH deposition in Turkey and China, respectively. Both spontaneously settled dust and particles bound to precipitation are collected by this method. The disadvantage of the method is that no information on the partition deposited spontaneously / by rain is gained. Especially from the trays, the deposited material might be removed by higher air turbulences. The bucket must be of inert material (HDPE, glass, or stainless steel; however, stainless steel is not suitable for metals). Buckets are emptied regularly (weekly, monthly, quarterly) or after each rain event. Before and after each usage the bucket must be thoroughly cleaned. 50-100 ml water might be added to the bottom of the bucket + glycol to avoid freezing and reduce the effects of biodegradation (Bergknut et al., 2011).

Wet and wet & dry deposition

Wet deposition measurement happens very similarly to bulk deposition. However, the sampler is equipped with a humidity sensor and a lid, which is closed except during precipitation events (Pekey et al., 2007). With the placement of a second bucket, wet and dry deposition happen alternatively: the lid covers either the wet or the dry bucket (Amodio et al., 2014). In both cases, the vessels must be heated to room temperature during winter time to include snow. For organic materials, the sample must be cooled immediately after the rain event stopping to 2 - 4 °C and kept at this temperature until being analysed. All collectors shall have a cylindrical vertical section of enough height to avoid sampling losses resulting from splashing and the diameter for the opening area, and the volume of the collector needs to be selected to collect all the precipitation for the required sampling duration. Typical sampling periods, in fact, vary from one week to one month, depending on meteorological conditions. The height of the opening area of the collector shall be at least 1.5 m above ground to avoid the sample contamination due to ground during heavy rains. All parts of collectors shall be made of inert materials, such as HDPE or glass. For heavy metals, the sample containers must be cleaned prior to sampling with distilled water and a 1% nitric acid solution to eliminate particles deposited or adsorbed onto container walls during prior collections. After the collection of the deposition, the sample is transferred to the laboratory in the sampling bottle or bucket, filtered, and analysed.

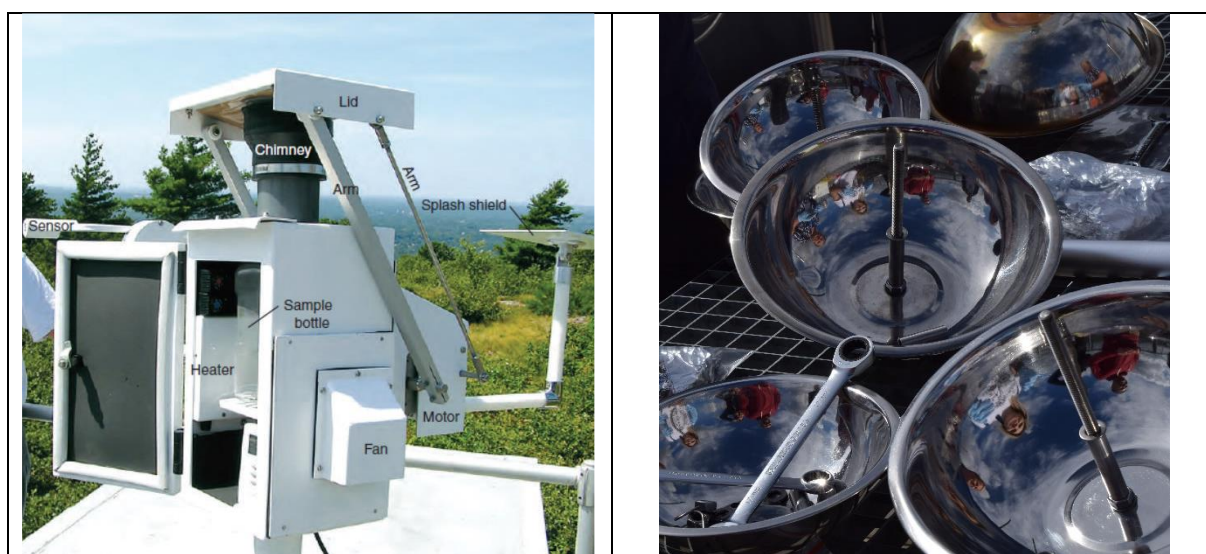


Figure 9 – Air sampling devices. Left: Newly designed wet-deposition sampler, Wet N-con System (Chalmers et al., 2005). Right: Passive air sampler (Chaemfa et al., 2008).

Dry deposition samples can be collected, e.g., in the water surface sampler (WSS) (Muezzinoglu and Cizmecioglu, 2006), having a circular open surface area continuously refreshed with recirculated water that enters from the centre, overflowed from the weirs at the sides, and collected in the WSS holding tank, controlled by an adjustable liquid pump. With this system, at the end of dry deposition sampling, all the water was transferred into a clean plastic bottle with a plastic stopper and carried to the laboratory for its chemical analysis.

Passive air sampling

A simple but widely used air sampler type consists of two stainless steel bowls (30 cm and 24 cm diameter). The bowls are fixed on a joint axis, which holds a polyurethane foam disk. The samplers are deployed in air at the height of 1.5 – 2.0 m, and the PUF disk is removed every 1 to 3 months. The air flows into the sampler housing and freely around the sorbent - PUF disk - fixed in the housing and sheltered against rain and UV light. The sampling occurs through a spontaneous diffusion of the air containing chemicals to the PUF disk. Exposed disks are wrapped in two layers of aluminium foil and kept in the freezer at –18 °C until analysis. Subsequently, target chemicals are analysed in the laboratory, and the levels are recalculated to reconstitute the concentration of the chemicals in the ambient air (Chaemfa et al., 2008).

A passive sampling technique using a funnel-absorber-cartridge device was adopted and validated in the field by Gocht et al. (2007) to monitor the atmospheric deposition of PAHs in rural regions of Southern Germany (Gocht et al., 2007). The sampling system consists of a glass funnel and a large adsorption cartridge packed with a special resin. While bulk deposition percolates through the funnel and cartridge, PAHs from both the water and particle phases are collected from the wet and dry deposition by adsorption and filtration, respectively. In the field, the sampling systems were housed in an aluminium box. After each sampling period, funnels were purged with 200 ml acetone to collect adsorbed and deposited PAHs from the glass surfaces. The cartridges were sequentially solvent extracted in four steps (50 ml for each) with the same acetone used before to clean the funnels (i.e., the purge solution). In the forests, the funnels of the bulk samplers were equipped with a 0.5 mm sieve (stainless steel) to separate the litterfall (spruce needles) from the throughfall.

The collection of bulk deposition of PAHs was achieved by Li et al. (2009) using a stainless-steel funnel attached to a glass filter setup (Li et al., 2009). The funnel was placed horizontally, 1.2 m above the ground level. After about 30 days, the inner surfaces of the stainless-steel funnels were wiped with precleaned cotton. The cotton and filter were combined as particle-bounded deposition fluxes of PAHs.

This technique is not considered appropriate for the purpose of this project, because it is extremely complex to derive deposition rates (required for modelling of emission loads) from air concentrations.

2.4. Soil

Spatial representativeness of soil sampling

The catchments used in the study will be several hundreds of km² in size, and their soils are very heterogeneous. Therefore, it is difficult to get a spatially explicit sampling from the whole watershed. Nevertheless, it is possible to represent the major soil types and the primary land use types by collecting a high number of samples. To increase the representativeness of soil samples, it is a common method to use spatially-integrated composite soil samples instead of point samples. In the LUCAS survey (Tóth et al., 2013), a 4x4 m square area was used with five sub-sampling points in an X shape to create a composite sample. Other studies used larger sample grids of 10 m and 9 sample points within (Rocco et al., 2016) and showed that discrete sample concentrations show much higher local

concentrations than composite samples. In plot scale studies, it is common to use 1 to 5 ha grids with at least 20 sampling points within (Sarkadi et al., 1986). This study suggests that 20 samples should be the minimum number to create a composite sample with an acceptable error of the real mean concentration (Figure 10).

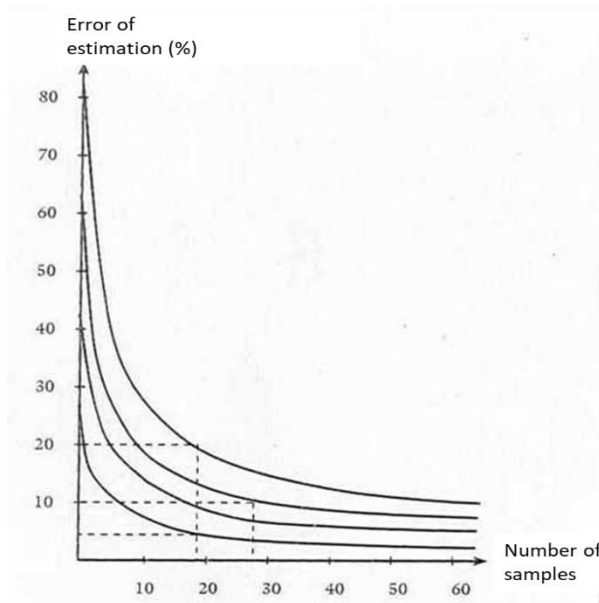


Figure 10 - the relationship between sample number to create a composite sample and the error compared to original soil (Sarkadi et al., 1986)

Tools and methods

In the case of composite soil samples, the weight of each sub-samples shall be around 50 grams, so that depending on the sub-sample numbers, the total weight of one soil sample would be around 1 kg.

Soil samples can be taken using simple auger tools. No specific drill is necessary for this type of soil sample as only chemical analysis will be carried out. There are several well-known soil samplers e.g. Pürckhauer ground augers (Figure 11) specifically suitable for dense, hard soils, Edelman augers for softer soils, but any similar standard locally available stainless steel auger can be suitable to collect soil samples for chemical analysis.



Figure 11 – Pürckhauer auger (left) and Edelman auger (right)

For modelling purposes, the upper layer of the soil profile is the most important as runoff will play a much bigger part than subsurface flow in the emission of the investigated chemicals. For this reason, the upper soil part should be sampled in a way that the plant residues should be excluded from the sampling. For grasslands and forest soils, the upper 10 cm, for agricultural soils the upper 30 cm is relevant due to the tillage mixing of the soil layer. The depth should be similar at each location. Soil samplers should be cleaned between sampling spots (not sub sampling spots).

Storage of the soil samples

Samples would contain many organic contaminants, which may react with plastic materials, while heavy metals should not be stored in metal containers (Batley and Gardner, 1977); therefore glass jars are preferable for storage of soil samples. Glass jars should be sealable.

Soil sampling distribution

Soil sample locations can be determined in a systematic or a randomized manner or by a mixture of these two. As the land use distribution in the catchments is quite random itself, the systematic arrangement is not practical; therefore a randomized sample location selection is favorable.

There are protocols for randomized soil sampling of given agricultural plots (JRC, 2018), but these are hardly applicable at the catchment level. Several methods have been used by soil researchers and soil mapping programmes. For European scale soil mapping within the LUCAS programme (Tóth et al., 2013) the following table was used as a guide for choosing sampling numbers.

Table 4 – Relationships between the goal of the survey, sampling density and scale of derived soil maps

Kind of survey or map and level of intensity	Purpose and use of the of the survey results	Area represented by one sample (ha)	Indicative scale of published maps
precision farming (intensive, level 1)	special; executive purpose – within parcel	< 1	> 1:1000
detailed (field scale, level 2)	special; executive purpose – for parcel	1-50	1:1000 – 1:10.000
semi-detailed (farm to regional scale, level 3)	general and special; planning purpose	50-1000	1:10.000 – 1:100.000
reconnaissance (regional scale, level 4)	general; planning purpose	1000 – 5000	1:100.000 – 1:250.000
reconnaissance (regional to national scale, level 5)	general; orientation purpose on national scale	5000 – 20000	1:250.000 – 1:500.000
exploratory surveys and compilations (national to continental scales, level 5)	general; orientation purpose on continental and global scale	> 20000	< 1:500.000

- Based on the works of: Baranyai et al. (1989), Dent & Young (1981) Legros (1996), Curlik & Surina (1998), Garkusa (1958), Hengl & Husnjak (2006), Rasio & Vianello (1995) Szabolcs (1966) and Western (1978).

According to this table, the catchment scale assessment would be farm to regional scale (level 3), or regional scale (level 4), which would suggest that every soil sample would represent around 1000 ha or 10 km². In the case of a 500 km² catchment, with 50% arable land use, this would mean 25 samples for arable land use. Even if this scaling is suggested for soil property mapping, it can be a guide for soil contamination mapping as well.

Land use

The main land-uses that shall be considered for soil monitoring are agriculture with permanent crops(vinyards, orchards), agriculture with annual crops, woodlands/shrublands, and grasslands.

Soil contaminant levels differ depending on the type of land use since micropollutants are primarily emitted by the anthropogenic activity directly carried out on the soils. Different pollutants, however, are emitted into the soils from different sources and through different pathways; therefore, some of them are not directly connected to a land-use but are directly connected to other land-uses. For example, PAHs are emitted by the combustion of petroleum hydrocarbons directly onto soils when machinery is used for agricultural cultivation, but they are also deposited on soils of diverse land uses via atmospheric deposition (Valentin et al., 2013).

As some of the micropollutants in soils (heavy metals) are of natural (geological) origin, places with intact natural vegetation must also be sampled to define background contaminant levels. In this respect, valuable information is obtained if the selected catchments include areas where anthropogenic impacts are likely to be low (e.g. forests).

Agriculture with annual crops and permanent crops use both pesticides, artificial fertilizers, and animal manure, which act as a source of organic compounds and heavy metals (Edelstein and Ben-Hur, 2018; Zhang et al., 2012). Grassland, shrubland, and woodland are less susceptible to anthropogenic effects. However, grasslands are also fertilized in some instances, therefore, some contamination is expected (Chambers et al., 1999).

2.5. Effluents of wastewater treatment plants

An underlying principle for wastewater effluent sampling is that the greatest possible knowledge concerning household and industry connected to the WWTP is needed. Household effluents are in general quite homogeneous in time, although the population number can fluctuate seasonally or weekly (due to work and vacation patterns). Industrial discharges are widely diverse and can fluctuate extremely. In general, it is beneficial to do the sampling for at least one week and to repeat it seasonally (Moser et al, 2015).

Grab sample

Grab samples consist of either a single discrete sample or individual samples collected over a time not exceeding 15 minutes. The grab sample should be representative of the wastewater conditions at the time of sample collection. The sample volume depends on the type and number of analyses to be performed (Simpson, 2017).

For metals, the sample should be collected into a HDPE, PVC, or Teflon container. For organic compounds, stainless steel is suitable, too. For PFOS, the use of Teflon (also including the clothing of the personnel) should be avoided.

Composite sample

Composite sampling means collecting many samples throughout a longer time into one container and doing the analyses on the mixed liquid. It can be done either time or flow proportionally. A time composite sample consists of equal volume discrete sample aliquots collected at constant time intervals into one container. A time composite sample can be collected either manually or with an automatic sampler. A flow proportional composite sample can be obtained following one of the two following approaches: i) collecting a constant sample volume at varying time intervals proportional to the wastewater flow, ii) collecting the samples by varying the volume of each individual aliquot proportional to the flow, while maintaining a constant time interval between the aliquots (Simpson, 2017).

2.6. Summary of benefits and drawbacks of existing monitoring approaches

Table 5 summarizes the existing monitoring approaches discussed in the previous chapters, as well as their main pros and cons.

Table 5: Pros and cons of different measuring approaches and devices.

Benefits		Drawbacks
Total and dissolved concentrations in rivers		
Traditional (grab) sampling	Most common method Accurate measurement Elaborated protocol Lab analysis can be carried out within a short time	Constrained representativeness in time and place
Composite samples	Representative for longer periods Accidental errors eliminated	Longer awaiting time until lab analysis
Flow & turbidity-triggered sampling	Useful for load estimation	Requirement of continuous monitoring equipment and maintenance Error of flow / turbidity measurement propagates
Water passive samplers	Water-level proportional sampling Relatively cheap	Very recent development Lack of evidence and experience on its operation Currently adequate only for very small streams
Substance passive samplers	Use of fewer chemicals Easier to prepare for analysis Better detection limits Better able to explain toxicity and bioaccumulation results Relatively cheap	Poorly adequate for the estimation of total concentrations and subsequently for the calculation of loads Lack of standardized methods Not well-known/accepted
Particle-bound concentrations in rivers		
Grab samples	No need for expensive automated arrangements Larger flood waves can be selected more easily No failures of automated device With enough samples, yearly load can be assessed directly	Flow proportional sampling is more difficult Time-consuming approach, if a representative number of samples or sampling of events are pursued
Passive time-integrated sampling	Very simple and foolproof design Cheap solution	No concentration can be gained, therefore not appropriate for modelling purposes
Solid-phase extraction (JDS style)	Sediment trapping and dissolved material sampling at the same time	Expensive equipment Higher risk of failure More assistance is needed on site Not possible to run for long periods Not possible to assess yearly loads directly
High volume sampling tank	Lower risk of failure compared to other automated methods	Potential failure in the pump device or pump control device

Benefits		Drawbacks
	Enough amount of sediment is gathered without manual input	
Atmospheric deposition		
Bulk deposition	Simple, cheap, no energy needed (passive)	Settled material might be removed by air turbulence No information on fractions settled by rain Regular maintenance needed
Wet and wet & dry deposition	Information on the fraction deposited by different means	Expensive maintenance needed
Passive air sampling	Simple and inexpensive	Less accurate
Soil		
Composite point samples	Higher spatial representativeness than single point samples Information on spatial distribution can be gained	More measurements are needed, therefore more expensive
Point samples composited by land use	Cheaper solution	Only one concentration per land use will be gained No spatial distribution would be known Risk of over- or underestimation of contamination
Effluents of wastewater treatment plants		
Grab sampling	Most common method Accurate measurement Elaborated protocol Lab analysis can be carried out within a short time	Constrained representativeness in time It does not account for time variations
Composite samples	More representative than grab sample Better for load estimation Time variability can be evaluated	More complicated to carry out Sample conservation problems

3. METHODOLOGICAL APPROACH SELECTED FOR THE MONITORING PROGRAMME WITHIN DANUBE HAZARD M³C

This section describes the design of parallel sampling campaigns, which will be conducted in the pilot regions over one year.

It is planned to start the measurement campaigns at the latest in January 2021 and to end them approximately by December 2021.

3.1. Selected substances

The scope of analysed substances includes substances that are relevant for the DRB, are mobile, and provide information on specific sources and emission pathways: industrial chemicals with wide dispersive use, pharmaceuticals, herbicides, fungicides, and metals. Specifically, the following substances will be analysed:

- Perfluorooctanesulfonic acid (PFOS), Perfluorooctanoic acid (PFOA), and short-chain poly and perfluoroalkyl acids¹ (*industrial chemicals*)
- 16 EPA Polycyclic aromatic hydrocarbons (PAHs, *industrial chemicals, and combustion by-products*)
- Mercury (Hg), cadmium (Cd), copper (Cu), Nickel (Ni), Lead (Pb), Zinc (Zn), and Arsenic (As) (*metals*)
- Diclofenac and Carbamazepine (*pharmaceuticals*)
- 4-tert-Octylphenol (*industrial chemical*)
- Nonylphenol (*industrial chemical*)
- Bisphenol A (*industrial chemical*)
- Metolachlor (*herbicide*) including Metolachlor-ESA and Metolachlor-OA (*metabolites*)
- Tebuconazole (*fungicide*)

To be able to estimate river loads, these substances will be measured in unfiltered water samples. In addition, metals (excluding Hg) and PAHs will be analysed in the dissolved phase to distinguish between particulate and dissolved transport. Further, their total concentration will be measured in soil, bulk atmospheric deposition as well as in raw and treated wastewater within the pilot regions.

3.2. Rivers

Continuous measurements

At each sub-catchment outflow point, continuous measurement of water level, temperature, conductivity, and turbidity will be performed throughout the whole year. Conductivity is an essential water quality indicator, easy to measure, and enables the detection of sudden and unexpected water quality changes. Additionally, conductivity enables the estimation of the share of baseflow or surface flow to total flow. Turbidity is required to estimate the total SPM load over the monitoring year.

To gain accurate turbidity measurements, two aspects are very important:

¹ Short-chain poly and perfluoroalkyl acids are considered as optional. Whether and which specific substances will be analysed depends on the technical capacity of the laboratory, which will obtain the subcontract for part of the analyses of organic micropollutants.

- The placement of the probe in the river needs to be planned and implemented very carefully because the turbidity is not equally distributed over the cross-section (Rode & Suhr, 2006). This also holds true for the sampling spots for establishing the turbidity-SPM-concentration-relationship. The probe should not be placed too close to the channel banks and not too close to the channel bed. Manual turbidity measurements (ideally with the probe to be installed) can help to identify the zone that gives a representative value for SPM. Especially in the case of larger rivers, the cross-section of the sampling spot should be measured in several vertices and several depth/vertices to gain a full picture of the sediment yield distribution. The final location should be in a position that represents the average of the section.
- Drifting of the turbidity-probe caused by the establishment of biofilm on the window of the optical probe has to be avoided by either having an automatic mechanical cleaning or regular manual cleaning. It is preferred to use a probe with an automatic wiper.

Turbidity – SPM connection will be established based on the SPM concentration determined in the weekly spot samples (see below). Where online data from existing gauges or other measuring devices are not available, probes will be installed and calibrated in the preparatory period from September to December 2020.

Weekly spot sampling

At the outlet of each sub-catchment, weekly spot sampling of river water will be carried out throughout one year, approximately from January to December 2021.

The weekly samples will be immediately stored and frozen. An aliquot of each sample will be filtered on the spot after the collection and prior to freezing and will be separately stored for the analysis of PAH and metals in the dissolved phase.

Every two months (if preservation time is shorter than more often) the cumulated frozen samples will be sent to the laboratories responsible for analyzing different compounds. In this way, six composite samples derived from regular weekly spot sampling will be analyzed for each sub-catchment. These samples will provide information on the concentration of the contaminants at baseflow-midflow conditions in the rivers.

Bottles for the storage and the transport to their premises, as well as stabilizing compounds (where applicable) will be provided by each laboratory, together with detailed instructions (Standard Operating Procedures – SOP) on how to perform the sampling, the filtration, the storage and the transport depending on each group of substances. These instructions might also change the preservation period of samples, which in turn also impacts the transportation frequency of the composite samples.

High-flow events sampling

During high-flow events, important processes take place in river catchments, which determine changes in the relevance of emission pathways, such as soil erosion and dilution of point source emissions. Therefore, within the scope of Danube Hazard m³c it is essential to gather information on the concentration of contaminants during such events.

It is planned to sample six high-flow events ideally within the period January-December 2021.

In this context, the aim is to sample rivers when the flow rate is comprised between Q_0 and Q_{10} (0-10% percentage of exceedance), and turbidity rises significantly above its typical baseflow/mid-flow level. Each event should possibly be sampled flow-proportionally during its whole duration, i.e., both in the

rising and descending part of the hydrograph, and the obtained composite samples must be cooled and sent immediately to the laboratories in the provided bottles.

The sampling can either be carried out manually or via autosamplers. In the case of auto sampling, the sampler has to be controlled by the turbidity probe signal in a way that the sample volume is adjusted proportionally to the flow.

Suspended particulate matter

To gain a more in-depth insight into the particle-bound transport of the considered hazardous substances, SPM will be separately collected and analyzed in a selected subset of sub-catchments in Austria and Hungary.

Before deploying any permanent sampling equipment, an analysis of the spatial variability of suspended sediment of the given river section should be carried out. It should be achieved by turbidity measurements and grab samples at several depths of several profiles to understand the distribution of SPM in the cross-section. Pre-project measurements can also be used.

The collection of SPM will be carried out using either the auto-samplers installed for the collection of water samples during high-flow events, or a separate large volume sampler specifically installed for this purpose. If the same sampler is used for both purpose, during specific events, these samplers will be utilized for this purpose instead of water samples. The collectors should be large enough to retain enough water that provide at least 200 g of sediment. This can be estimated from previous SPM records.

High-flow samples should be collected in a flow proportional manner from flood waves. At least **five separate high flow samples** should be gathered throughout the year to get statistically relevant information between flow-particulate matter and contaminant concentrations.

It is preferable to reduce the residence time of sampled water in the auto-sampler to a minimum; therefore, it is desirable to collect *high water samples from one flood wave if possible.* In order to prevent the biological decomposition of the organic contaminant in the auto-sampler (especially in the summertime), the sample collection should not take too long. Water should be collected *in a time-integrated manner within a 3-day window for low flow samples.*

It would be desirable to collect samples of a *large flood when intensive erosion occurs due to intensive rain events* and intensive runoff.

The SPM contained in the auto-sampler will be separated from the water phase by the responsible partner by decanting the water from it slowly to prevent resuspension of settled sediments. Sediment should be collected afterward into a jar of required size and immediately sent to the laboratory in charge of solid sample preparation (i.e. homogenization and lyophilisation). An adequate fraction of the lyophilized SPM will be sent to the other laboratories involved in the project. Samples will be either immediately analyzed or appropriately stored in the laboratories if they need to be mixed to generate composite samples.

3.3. Atmospheric deposition

The input of micropollutants via atmospheric deposition on surfaces (waters, soil, or urban areas) is an essential pathway in many catchments. To quantify this pathway, deposition rates for the substances are necessary. The collection of dry and wet deposition is planned in each sub-catchment of the pilot regions through *bulk deposition samplers*.

The following challenges must be addressed during the sampling:

- Both the amount of precipitation and the concentration of micropollutants in the wet deposition can be highly variable between and during events and years. To cover seasonal effects of pollutant distribution and precipitation amounts, a whole year of sampling is deemed necessary. However, to reduce the associated staff resources, selected months can be sampled to cover to a satisfactory extent the seasonal variations.
- On the one hand, a minimum amount of sample volume is necessary for the analysis and needs to be collected. On the other hand, the bigger the sampling devices get, the more complicated the handling and storage become. Thus, the sampled volume should be a compromise aimed to collect the necessary amount without losing part of samples during intense events.
- Some of the substances are not stable under all conditions, and loss of substances due to evaporation or degradation may occur. The samples need to be taken out of the sampling device immediately after the rain events to avoid evaporation and degradation. They need to be stored in a freezer until analysis. The samples should be protected from direct sunlight at all times by wrapping them in aluminum foil.
- The contamination of samples from soil or vegetation must be avoided. Thus, the samplers should be placed in an open space at least 1.5 m above ground.
- Disturbance of the mean spatial rainfall and dry deposition pattern should be avoided by keeping distance to higher objects (buildings, trees...).
- The location of the samplers should ensure their protection from vandalism.

Device and sampling strategy

The configuration of the bulk deposition samplers will be similar to the one depicted in Figure 12, which shows the device utilized by Foan et al. (2012) to measure PAH deposition.

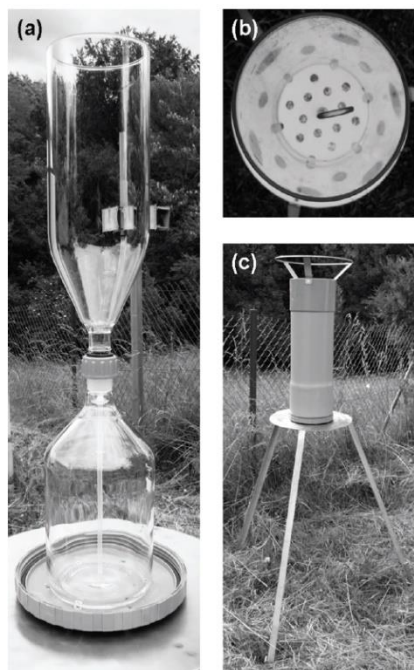


Figure 12: Picture extracted by Foan et al. (2012), where the main elements of the bulk deposition sampler are shown: (a) glass funnel and collection bottle, (b) plate for litter recuperation, (c) collector support and tube for protection against sunlight.

The specific design of the sampler, i.e. the required volume and materials to be utilized, must be defined based on the expected precipitation and on the sampling strategy.

Precipitation characteristics

The selection of pilot regions in the project presents the following precipitation values/ranges:

- Mean annual precipitation: 570-1800 mm/a
- Maximum annual precipitation (estimated): 3600 mm/a
- Minimum annual precipitation (estimated): 285 mm/a
- Maximum event precipitation: design storm for Ybbs headwater catchment (T = 3 years, D = 1 day): 120 mm

Based on these precipitation ranges and on the estimated amount of required volume for the chemical analyse two designs have been conceived for two alternative sampling strategies.

Setup A: sampling during a whole year

For this setup, it is required that the samples are collected from the sampler after every storm event for one year. As there are two sample bottles, they can be exchanged for sampling. The sample must be immediately transferred into a larger storage container in the freezer.

Estimated material requirement:

Organic pollutants and metals (4 l required):

- Funnel (Schlitzsiebnutsche/Büchnertrichter), glass, diameter 73 mm
- Collection bottle, glass, 2 or 5 l, 2 pieces
- Storage bottle, glass, 20 l, 2 pieces
- Plug, aluminum foil

In this option, after four months, after eight months, and at the end of the year, the cumulated bulk deposition collected and frozen in the storage container will be thawed and will be delivered in adequate aliquots to the laboratories for its analysis. In this way, three composite samples of atmospheric deposition (each representing four months period) will be analyzed for two sub-catchments in each pilot region.

Setup B: sampling for 4 months in a year

For this setup, it is required that the samples are collected from the sampler after every storm event during 4 predefined months distributed over one year. As there are two sample bottles, they can be exchanged for sampling. The sample must be immediately transferred into a larger storage container in the freezer.

Estimated material requirement:

Organic pollutants (4 l required):

- Funnel (Schlitzsiebnutsche/Büchnertrichter), glass, diameter 120 mm
- Collection bottle, glass, 5 or 10 l, 2 pieces
- Storage bottle, glass, 20 l, 2 pieces
- Plug, aluminum foil

In this option, each composite sample corresponds to the cumulated deposition collected during each month. The procedure to obtain and to send the samples is the same as indicated for Setup A.

Quality Assurance: Duplicate device is to be installed at each sampling location. The reason behind this is that deposition devices might clog, therefore a replacement sample would be available. This would involve the emptying and cleaning of the secondary devices. The sample of the secondary device would only be transported to the composite if the primary sample is lost or not representative.

3.4. Soil

Sampling strategy

It is planned to collect composite samples for each major land-use type, with a total of 10 composite samples in each pilot region. The minimum threshold for the major land uses is set to 5 % of the total area.

Each composite sample should be composed of at least 20 samples. For one land use type, the sample locations should be distributed along the catchment in a way that all major soil types in the catchment are included.

Land use classes and soil classes should be overlapped by GIS application for each sub-catchment to create land units, which will be the units for composite sampling.

A spatial threshold of minimal area per land unit should be set for each pilot region individually, as the aim is to get a decent cover of the whole area.

The specific sampling points shall be distributed randomly within the land units. The random positioning can be achieved by GIS techniques, and finally, the sample positions should be adjusted manually to position it near to the roads where it can be approached. In the case of forests and grasslands, the total no. of sampling points needed for one composite sample would be divided by the number of soil types, size proportionally. In the case of agricultural land, all land units should be sampled separately.

The proximity of the sampling points should be limited with a distance threshold, meaning the points should not be closer to each other than a certain distance, e.g. 200-500 meters. The coordinates of the sampled spots will be recorded through GPS to enable accurate spatial repetition if necessary.

BUTE will perform the GIS analysis for sampling point preselection for all partners if they submit 3 GIS data set:

- Land use with the four (or less) main land-use classes (woodland and/or shrublands, grasslands, agricultural fields with annual crops, agricultural fields with permanent crops)
- Soil map with the most important 10 different soil types

The partners will receive a point dataset for sampling and should then revise the point positions to make the sampling feasible (taking into account accessibility of the plots etc.).

Given to logistical requirements of the laboratory in charge of the homogenization and lyophilization of the samples, the goal is to conduct the soil sampling campaign at latest at the end of winter 2020/2021, namely by February-March 2021.

Example of selection of sampling points for the Koppány catchment in Hungary

By overlapping land use and soil classes of the catchment, 35 different classes were obtained. These classes were filtered by a 2% threshold of area proportion, which resulted in 3 forest units, 5

agricultural units, and 2 mixed agricultural units (the latter could be merged with agricultural cover type) as shown in Figure 13.

For each agricultural land unit, 25 randomly distributed sampling points were selected. For the forest land units, the 25 sampling points are distributed proportionally to the area of each soil type (Figure 14).

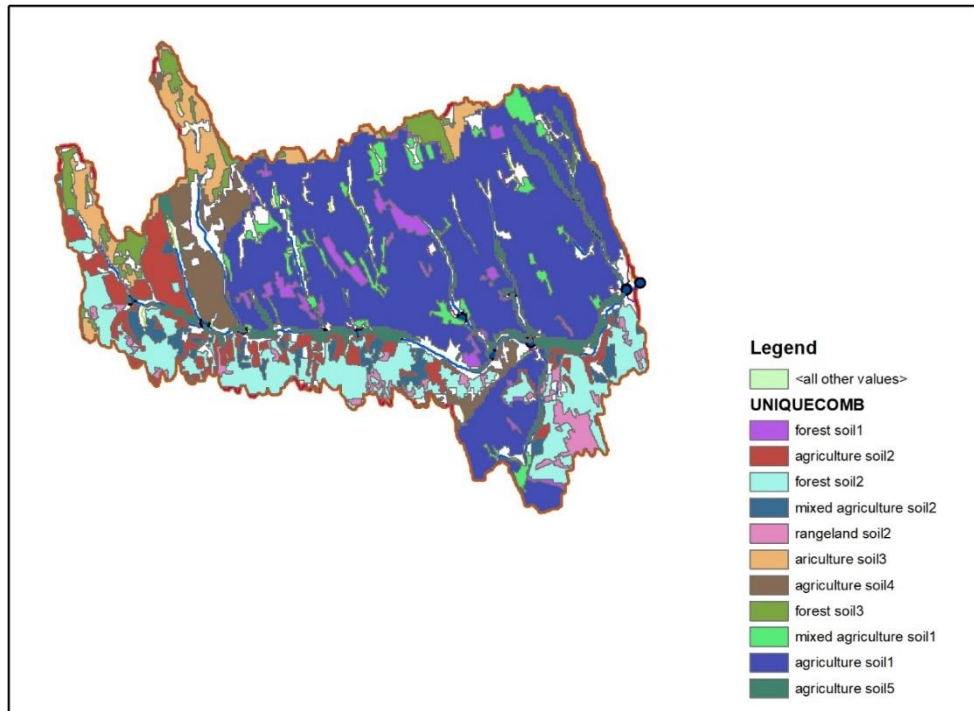


Figure 13: Filtered land-use and soil classes on Koppány catchment.

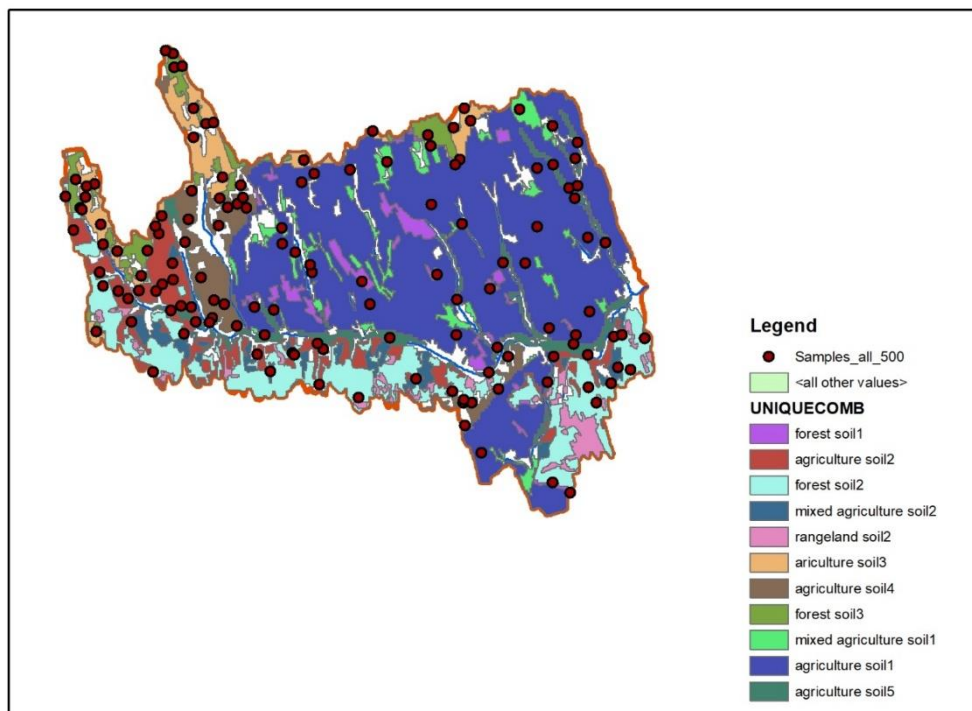


Figure 14: Sampling point locations on the Koppány catchment.

Tools and methods

Soil samples can be taken by simple auger tools; no specific drill is necessary for this type of soil sample as only chemical analysis will be carried out. There are several well-known soil samplers e.g. Pürckhauer ground augers (Figure 11) specifically suitable for dense, hard soils, Edelman augers for softer soils, but any similar standard locally available stainless steel auger can be suitable to collect soil samples for chemical analysis.

For modelling purposes, the upper layers of the soil profile are the most important as runoff will play a much bigger part than subsurface flow in the emissions of such chemicals. For this reason, the upper soil part should be sampled. Litter (plant residues) should be removed from the surface prior to sampling. For grasslands and forest soils, the upper 10 cm shall be sampled, whereas for agricultural soils, the upper 30 cm is relevant due to the tillage mixing of the soil layer. The depth should be similar at each location. Soil samplers should be cleaned between sampling spots.

All soil samples will be collected in clean and sealable glass jars to prevent contaminant reaction with the container's material. Each partner will be in charge of generating the composite samples by merging equal aliquots of the sub-samples straight after sampling on site.

To ensure the same portion per sub-samples, either a Pürckhauer auger should be used, which provides the same volume, or a field scale should be used to provide equal sample portions by weight. The subsamples can be dropped straight into the final clean and sealable glass container, which will be used to send the composite samples to the Environment Agency Austria (PP UBA). Depending on the sub-sample numbers the total weight of one soil sample would be around 1000-1500 g. A glass jar of max 2 l would be sufficient to store the composite samples.

The UBA laboratory will homogenize and lyophilise the composite samples and send aliquots to the other involved laboratories for the analysis of different substances.

Sample number, location, type of sample (land use, composite etc.), depth of sample, name of sample collecting person, date, and time should be written on a separate label, which should be taken to a protective pouch. Sample details should also be written to a record for the samples.

3.5. Influent and effluents of wastewater treatment plants

In addition to effluents of wastewater treatment plants, a subset of untreated influent will also be sampled and analysed. The rationale behind this decision is that in parts of the Danube River Basin wastewater is not treated yet and therefore, this part of the sampling shall deliver relevant information on how to estimate emission loads into water bodies via untreated municipal wastewater.

Sampling method

The influent and effluent of each examined municipal and industrial wastewater treatment plant will be sampled 3 times throughout the year at approximately three months distance. The aim is to obtain each time a flow-proportional weekly composite sample. During every campaign, samples will be collected for seven consecutive days and thereafter merged and homogenized. Depending on the local possibilities, wastewater and wastewater discharge will be sampled either manually or via autosamplers.

Sampled plants

A different number of plants, both municipal and industrial, will be examined in the pilot regions, depending mostly on the contribution of wastewater plant discharges to total river flow and thus on the relative importance of these point sources for the total transported loads of micropollutants in the different catchments.

3.6. Mining sites

The sampling protocol for mining site will be delivered as described in ISO 5667-10 requirements. The sampling frequency will be between 8-12 samples per year for the monitoring period.

3.7. Preliminary numbers of samples per environmental and anthropogenic compartment in each pilot region

Table 6 shows the preliminary estimated number of samples arising for the considered matrices in the pilot regions. Given that a considerable amount of chemical analyses will be carried out by an external laboratory for which a public tender procedure is required, and which is not assigned yet, the final number of samples will be defined as soon as the actual prices for all samples will be known.

Table 6: preliminary number of samples generated within the monitoring campaigns.

Sub-catchments	Atmospheric deposition	Soil	Comments	SPM	River	Wastewater and mining sites	Comments
Wulka main watercourse	4	4	2 arable land 2 forest	0	12	6	(3) Discharge in 1 large municipal WWTPs (3) Wastewater in 1 large municipal WWTP
Nodbach	4	2	2 arable land	6	12	0	
Eisbach	0	4	2 arable land 2 forest	6	12	3	(3) Discharge in 1 municipal WWTP
Headwater Ybbs	4	2	2 forest	6	12	0	
Urlbach	0	4	2 arable land 2 pastures	6	12	0	
Lower Ybbs	4	4	2 arable land 2 pastures	0	12	9	(3+3) Discharge in 1 municipal and one industrial WWTPs (3) Wastewater in 1 municipal WWTP
Cherni Vit	4	2	2 forest	0	12	0	
Beli Vit	0	2	2 forest	0	12	0	
Vit upstr. Disevitsa	4	6	6 arable land	0	12	3	(3) Wastewater discharge
Koppány headwater	4	5	3 arable land 2 forest	0	12	6	(3) Discharge and (3) wastewater in 1 municipal WWTP
Koppány upstr. Tamási	4	5	3 arable land 2 forest	6	12	3	(3) Discharge in 1 industrial WWPT
Herédi Bér-creek	0	4	4 arable land	0	12	6	(3) Discharge in 1 municipal WWTPs (3) Wastewater in 1 municipal WWTP
Tarján-creek	0	3	2 forest 1 pasture	0	12		

Headwater Zagyva	4	3	2 forest 1 pasture	0	12		
Outlet gauge	4			12	12		
Viseu	4	6	4 arable land 2 forest	0	12	6	(3) Discharge (3) wastewater in 1 municipal WWTP
Viseu headwater				0	0	0	
Cisla	4	4	2 arable land 2 forest	0	12	12	((12) Discharge from 6 mining sites?
Someșul Mic headwater	4	4	3 forest 1 pasture	0	12	0	
Nadas	0	2	1 pasture 1 arable land	0	12	0	
Someșul Mic upstr. Apahida	4	4	3 arable land 1 pasture	0	12	18	(12+6) Discharge from 1 municipal and 1 industrial WWPT
Total samples	56	70		42	240	72	

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