



# **SITE-SPECIFIC SEDIMENT QUALITY EVALUATION GUIDELINES**

**OUTPUT T6.1**



**Project title**

Sediment-quality Information, Monitoring and Assessment System to support transnational cooperation for joint Danube Basin water management

**Acronym**

SIMONA

**Project duration**

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### **Appendix 1. English narrated videos**

<https://drive.google.com/drive/folders/1Ql3SbJP6FxnKVRVaCrUe9Qc2P-Sq2cMp?usp=sharing>

### **Appendix 2. Sampling manuals**

<https://drive.google.com/drive/folders/1bzi8IXq7Vhvmlyt654JJNBZJoc5myuax?usp=sharing>

## 1. INTRODUCTION

The main objective of the SIMONA project is to achieve an improved, harmonized and coordinated sediment quality monitoring practice in the Danube River Basin. For this purpose, a harmonized Sediment Sampling Protocol and a Laboratory Analysis Protocol have been established within the project, and sampling and laboratory analysis has also been extended with a passive sampling system. On the basis of the preliminary results of the SIMONA project it had become clear that 1. HS contamination is strongly influenced by site-specific conditions of the monitoring site such as total organic carbon (TOC) content or the grain size distribution of the sediments, and 2. point sampling is inappropriate for the monitoring of the changes of the dynamic fluvial system which is also site-specific. For these reasons, a passive sampling system has been developed and tested in the Drava Test Area at the Barcs Experimental Station on the Drava River, Hungary, representing lowland fluvial conditions, in the Upper Tisa Test Area on the Lapus River, Romania, representing mountainous fluvial conditions, and in the South Danube Test Area, Danube River, Bulgaria. Each of the three Test Areas have tested the passive membrane absorbent sampling methods for pesticides and PAHs, the Upper Tisa Test Area tested the Joint Danube Survey (JDS) sediment trap box in addition, while the Drava Test Area was the central location of method development.

PILOT TEST AREA	JDS BOX <i>Unique</i>	PASSIVE SAMPLER	ONLINE SENSORS
<b>DRAVA RIVER</b> (installed-11.2020)	X	X	Flow rate, Turbidity pH, Dissolved oxygen Conductivity
<b>UPPER TISA- LAPUS RIVER</b> (installed-05.2021)	X	X	Flow rate Turbidity
<b>SOUTH DANUBE- SILISTRA</b> (installed-04.2021)	-	X	-

**Figure 1.** The main components of the continuous passive sediment quality monitoring system installed at the different Test Areas.

The River Drava was selected for testing because it is one of the largest and most significant rivers in Central Europe:

- The whole length of the river is approximately 749 km, it is running 140 km long, along the border between Hungary and Croatia.
- These countries are downstream regions of the river with meandering character, different biogeographical properties and sedimentation.
- There is a regional historical pollution, originating mainly from mining and smelting industry in the Alps can be found in the sediments and in the soils in the floodplain.
- Moreover, industrial areas, water power plants, water reservoirs, agricultural areas, forests and numerous settlements can be found all along the river.

## **2. PASSIVE MONITORING SYSTEM FOR LONG-TERM MONITORING AND SITE-SPECIFIC EVALUATION**

The Barcs Experimental Station was developed at the out-of-use municipal port due to its accessibility, the lack of ship traffic that does not handle ship traffic as the location for installation of passive monitoring system. Also, trained personnel of the nearby Regional Water Authority help in the operation of the station.



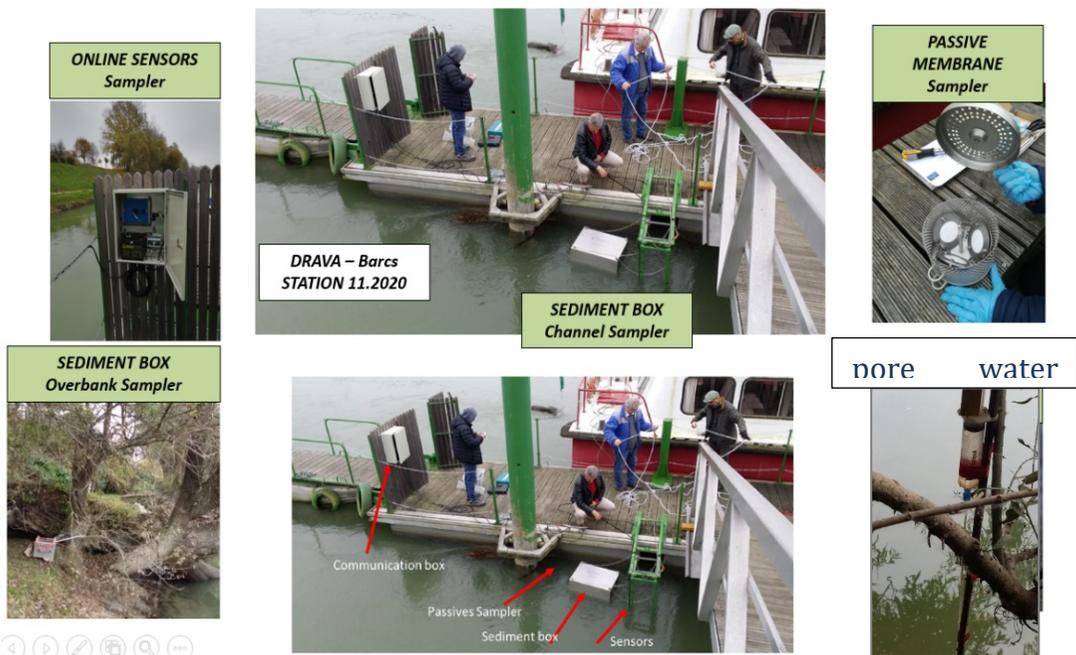
**DRAVA RIVER  
BASIN**



**Figure 2.** The Experimental Station located in the Drava River Basin at Barcs at the Croatian-Hungarian border. Picture shows the municipal port and its pontoon used for the monitoring system development.

The continuous passive sediment quality monitoring system had the following components:

- the standard Join Danube Survey sediment trap box used in the Join Danube Survey 4 Programme on the Danube River, submerged in the river water to capture suspended sediment in the river,
- another standard sediment trap box put on the floodplain to capture flood event sediment,
- Passive Membrane Sampler having a pesticide, PAH and metal absorbent membrane,
- In addition, turbidity and flow sensors were installed,
- a communication box that sent the measurement results to the receiving website every 15 minutes,
- pH, EC, DO and T probes were also installed which delivered the measured data to the receiving web site online at every 15 minutes,



too, a vacuum pore water sampler was also placed in the bottom sediment.

**Figure 3.** *The components of the continuous passive sediment quality monitoring system.*

The suspended sediment samples were collected every month from the sediment boxes and the passive membranes were replaced also every month.



**Figure 4.** *The passive membrane sampler ('artificial fish'). Note the 3 different types of selective sampling membranes: Pesticides, PAHs and Metals.*

The monitoring system was designed and tested to be used by 2 personnel for regular sampling.

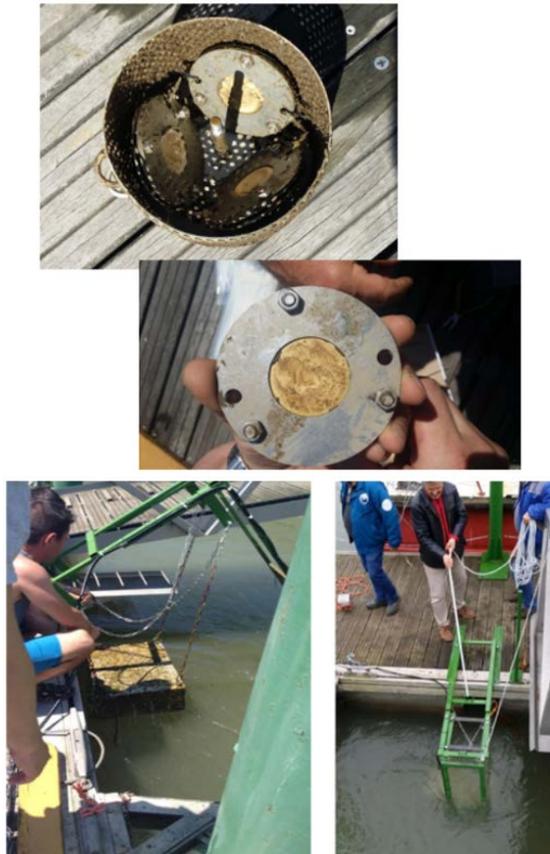


**Figure 5.** The installation of the JDS sediment trap box into the river requires a manually operated fix crane. The Velocity and turbidity sensors data is used to estimate the sediment and water quantity that reached the sediment trap during the collection period.

Based on the operational experience, the sediment sampling system, most notably the JDS sediment box, have been improved and further developed from both a technical and a scientific point of view:

- JDS box handling has been significantly improved,
- we have also applied powder-free membranes.

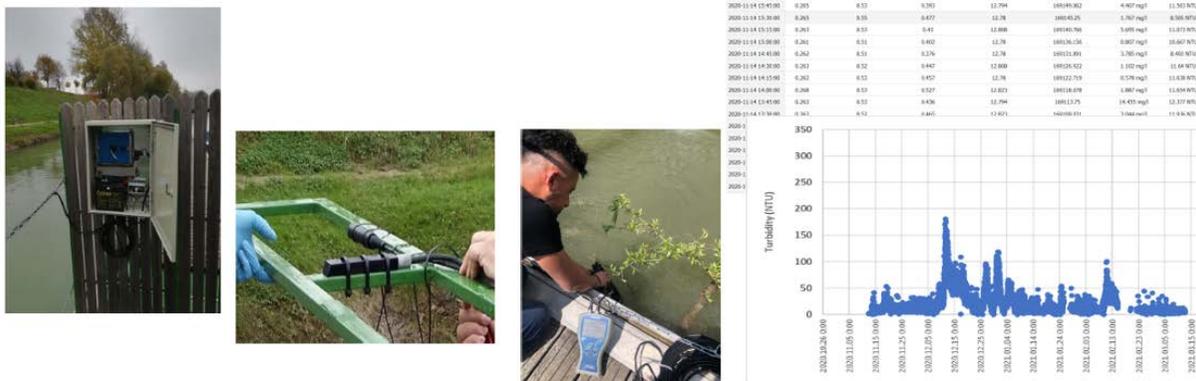
For this reason, we used new membrane holders specific for the Metals, PAH and Pesticides specific membranes.



**Figure 6.** *The installation of the JDS sediment trap box into the river requires a manually operated fix crane. The Velocity and turbidity sensors data is used to estimate the sediment and water quantity that reached the sediment trap during the collection*



**Figure 7.** *The standard JDS has been converted to the tool applicable for regular monitoring sample collection. The holes-and-plugs innovative development has reduced the sample removal from 1 hour (see picture on the right) to 20 minutes (see the picture on the left).*



**Figure 8.** Left: the online information transmitter unit. Middle: calibration of the probes by taking measurements on site with different probes. Right: 15 minutes Turbidity data series.

Calibration of the passive JDS sediment trap box has considered three independent data sources:

- suspended sediment sampling with the barrel sediment sampling method (30 L barrel) at each sampling event,
- field parameters were measured for turbidity and flow velocity; with these parameters it is relatively simple to estimate the water and suspended sediment entering the sediment box under water,
- the water authority takes a monthly sample of suspended sediment in the cross-section of River Drava.



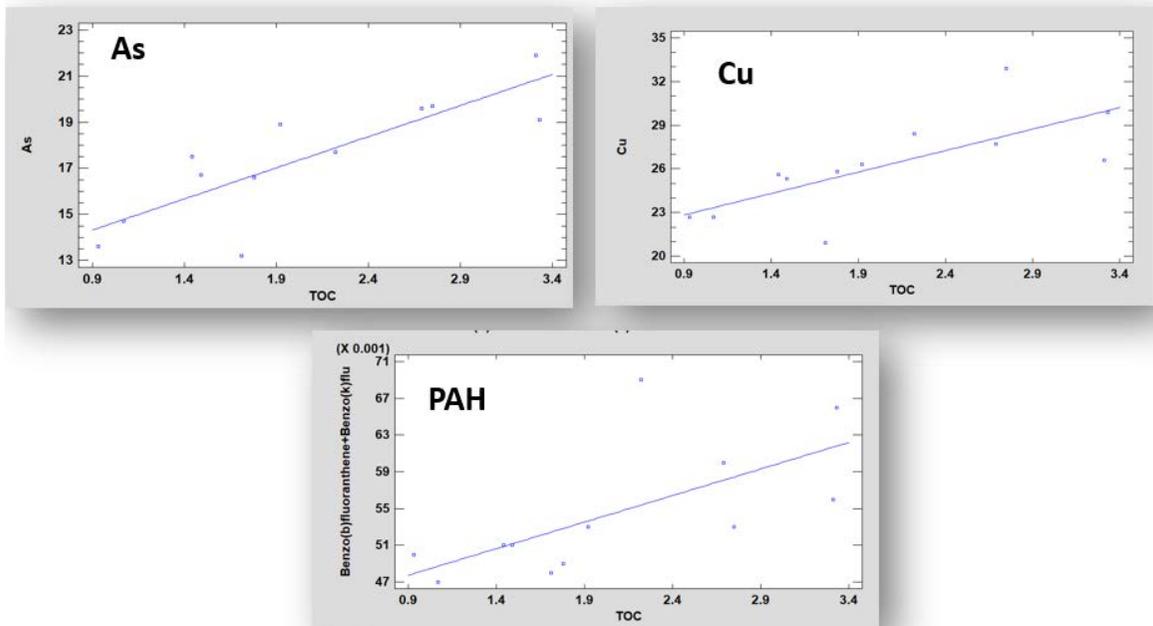
**Figure 9.** Left: standard sediment trap box emplaced on the floodplain. Right: suspended sediment trapped by the box during the last flooding event.



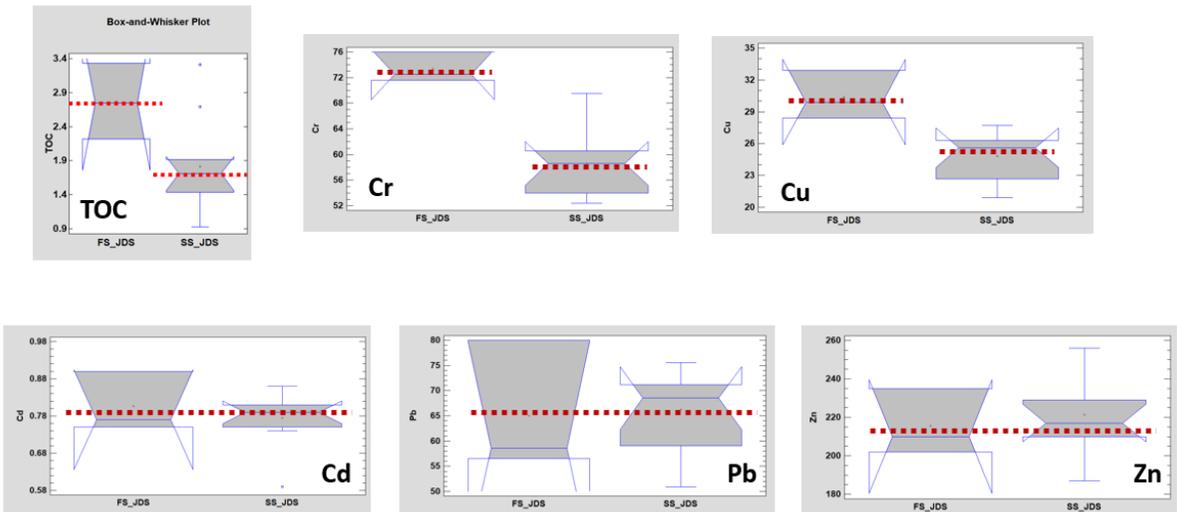
**Figure 10.** Standard JDS sediment trap box and passive membrane installed in the Upper Tisa Test Area, Romania. The JDS box originally developed for large rivers has been adapted to suspended sediment sampling in shallow river by the SIMONA project.



**Figure 11.** The passive membrane installed in the South Danube Tisa Test Area in River Danube, Bulgaria. Note the same sampling station on a pontoon in a port like in the Drava Test Area.

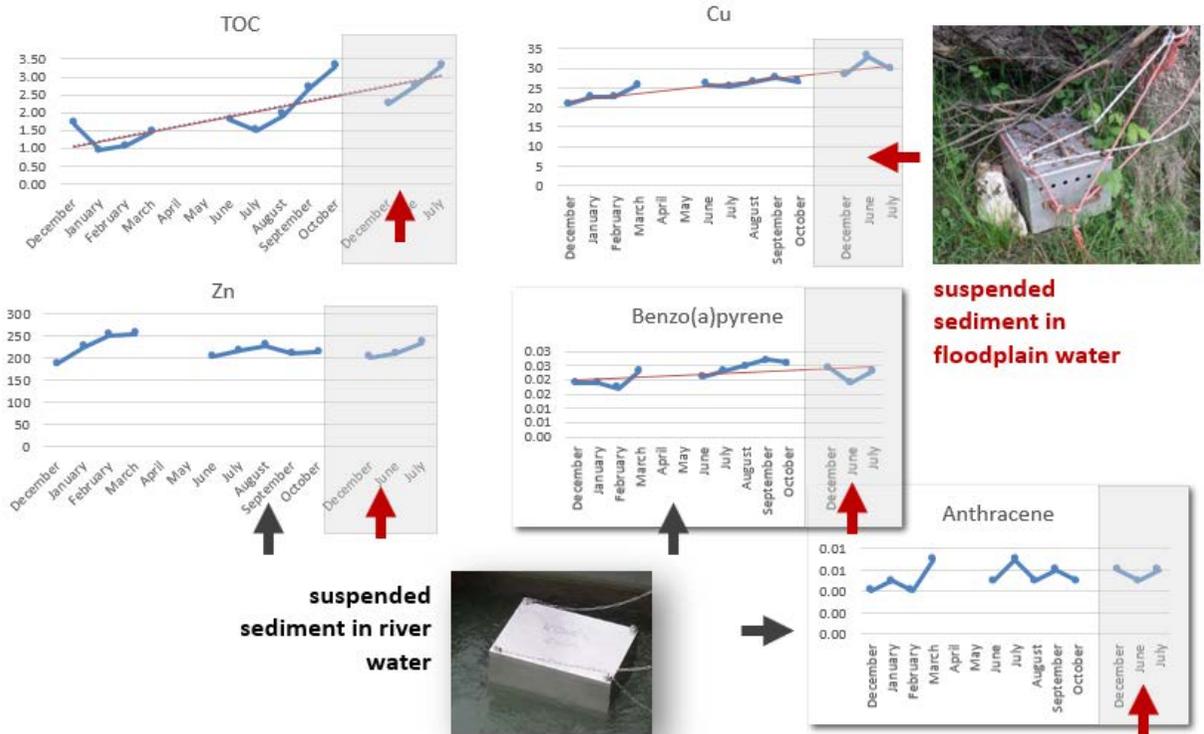


**Figure 12. Site-specific evaluation and modelling of the suspended sediment quality in the Drava Test Area. Note the dependence of toxic metals and PAHs on the local concentration of total organic carbon (TOC) content.**



**Figure 13. Site-specific evaluation** of the suspended sediment quality in the Drava Test Area. **Left** box plots: concentrations in the suspended sediment samples taken from the floodplain sediment trap box. **Right** box plots: concentrations in the suspended sediment samples taken from the river sediment trap box. Note that TOC, Cr and Cu tend to have higher concentrations in the suspended sediment during flooding.

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**Figure 14. Site-specific evaluation** of the suspended sediment quality in the Drava Test Area. **Grey** arrow indicates suspended sediment captured by the sediment box in the river water. **Red** arrow and transparent grey shading indicate suspended sediment captured by the sediment box in the flood water during flood events. Note the temporal (seasonal) character of TOC and Cu, and its lack for Zn. Compare to Figure 13.

### 3. PASSIVE MEMBRANE ABSORBENT SAMPLING METHODS FOR PESTICIDES AND PAHS

#### INTRODUCTION

Passive membrane sampling of dissolved hazardous substances in river water was tested in the River Drava test area for one year, and in the Upper Tisa and the South Danube test areas for half a year. in the 2020-2021 period.

The main components of the passive sampling system were (a) sediment trap box for the systematic collection of suspended particles, (b) sensors for recording different physicochemical parameter such as water temperature, turbidity, dissolved oxygen, and pH, and (c) passive adsorbent samplers for the uptake of different contaminants. There are numerous commercially available or home-made passive sampler devices (e.g., silicon rubber, SPE disks, POCIS) providing the time weighted average (TWA) concentration of dissolved pollutants, and their sorbent phases are selective for different groups of target components. First, we have tested the Polar Organic Chemical Integrative Sampler (POCIS) designed for hydrophilic organic chemicals (pesticide residues). Next, we have applied the POCIS selective for glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) and several SPE disks for sampling of metals, polycyclicaromatic hydrocarbons (PAHs) and pesticide residues.

We have used the Affinisep passive samplers for the monitoring of different classes of pollutants. The disk-based passive samplers (Chelating, HLB, C18) included in the SIMONA sampling protocol were used to collect metals, pesticides, and PAHs. For glyphosate and AMPA metabolite a selective POCIS phase was applied (see Figure 1).



**Figure 15.** *Passive samplers before and after one month use in the Drava River.*

Based on the results of preliminary experiments, regular passive sampling was carried out in the the Upper Tisa (Baia Mare, Romania) and the South Danube (Silistra, Bulgaria) test areas using the same devices and methodology tested in Drava River (Barcs, Hungary).

Instrumental analysis was performed at the Bálint Analitika Ltd. using liquid chromatography coupled with mass spectroscopy (LC-MS) or gas chromatography coupled with tandem mass spectroscopy (GC-MS/MS) for determination of 85 target pesticides, in addition to a GC-MS selective ion monitoring (SIM) method for 19 PAH compounds. The results of the measurements refer to the amount of contaminants collected by the entire disk at the current stage of evaluation, and are currently being calibrated

to absolute concentrations for the liquid phase. However, based on the scientific literature, data related to the sampling rates ( $R_s$ ) and time weighted average (TWA) levels of dissolved pollutants were also calculated in some cases.

Suspended sediment samples were collected monthly either in a 30-liter water sample (point sample), or in a standardized sediment trap box used for long-term sample collection. Contamination levels were quantitatively determined in both sample types. During the monitoring phase, water temperature, turbidity, dissolved oxygen levels and pH were measured on a continuous basis by electrochemical and photoelectric sensors.

## RESULTS

The point samples collected in the barrel contained little sediment, which significantly limited the reliability of the analytical measurement. In contrast, the sediment trap box collected the suspended sediment by the baffles of the box, allowing the analysis of a significant amount of sample.

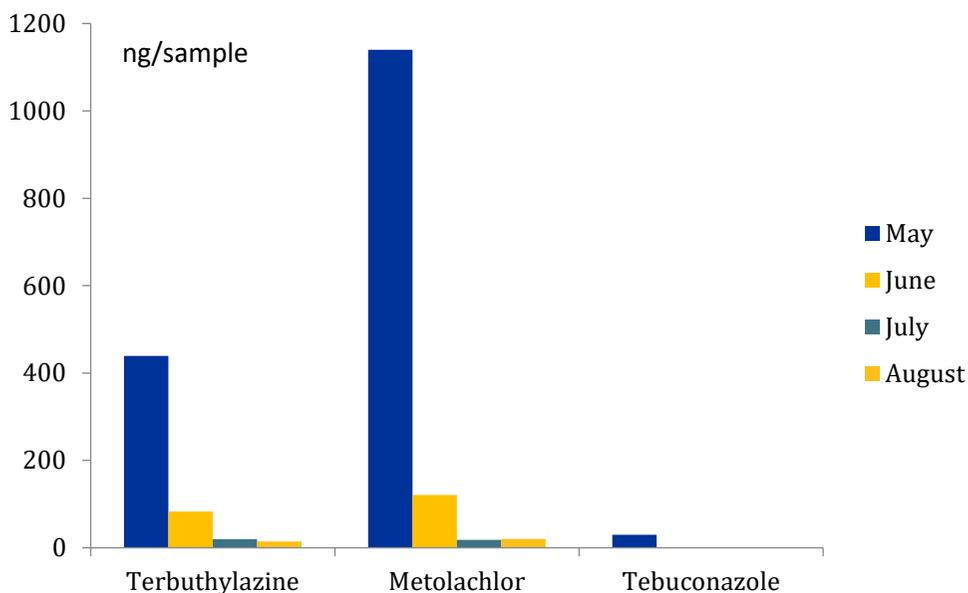
We have compared the passive sampling procedures using the binding phase (adsorbent) in the form of a disk and powder (POCIS) during the development of the monitoring procedure in the Drava River. According to the results of our preliminary investigations in 2020, the amounts of pesticide residues adsorbed by the two types of binding phases were similar. In some cases, the membrane holding the adsorbent was torn, so the powder was lost, thus, we decided to use a disk. Some literature data indicated that these membranes also retain some components, therefore, we have also tested the purity of the membrane used in the POCIS device before and after the sampling in the Drava River. Although we have not found any pollution interacting with the pesticide residues, we used the disks without these membranes in order to avoid the loss of analytes. Detailed test with PAHs selective disks (C18) in parallel sampling showed that membranes indeed retain these non-polar compounds and significantly lower amounts were measured with the disks covered with membrane compared to the disk without membrane.

Instruction sheets provided by the manufacturer proposed in some cases different solvents and more possibilities for the elution of target

components (pesticides, PAHs). We have tested our own elution procedures which fit better to the analytical protocol applied. Thus, acetone and then dichloromethane with ultrasound agitation was used for extraction of disks prior to gas chromatographic measurements and methanol was applied prior to liquid chromatographic determination of certain pesticides. Efficiency of these procedures were checked and they were suitable for preparation of passive sampler disks during the whole monitoring period.

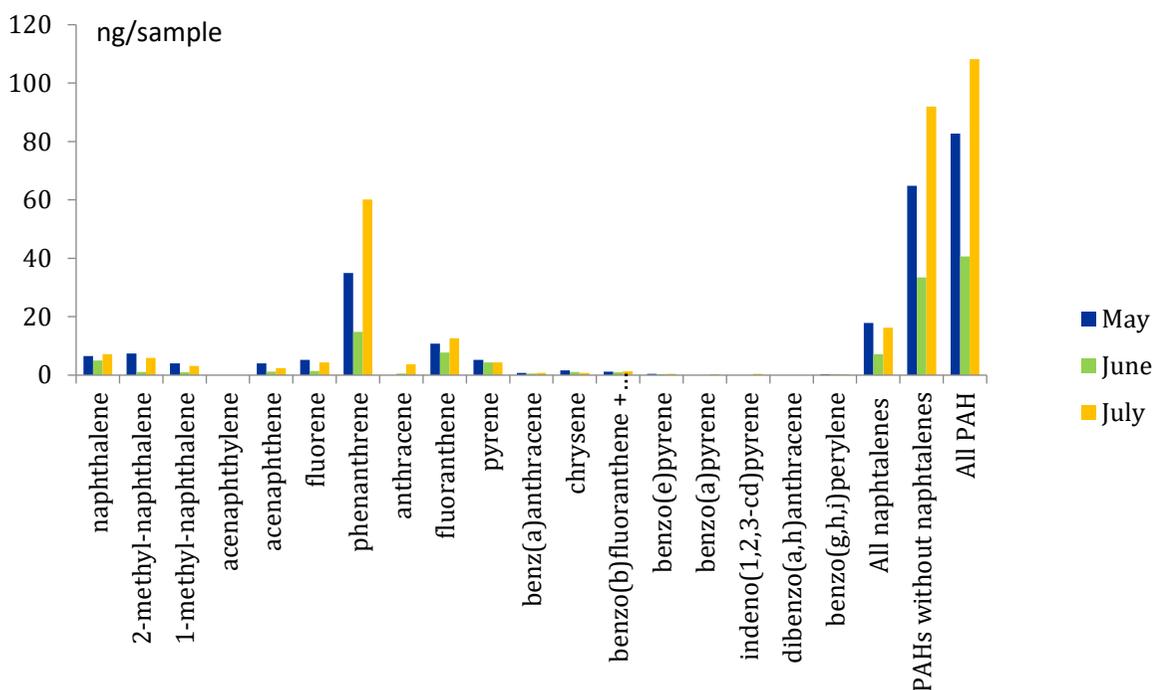
Regarding the pesticide residues, pollution pattern and trends were in accordance with our expectations. Results prior to the agricultural season indicated that isoproturon and persistent diuron are the main background pollutants. These active ingredients are no longer authorized in the EU except for the Netherlands and Bulgaria, respectively. Bentazone was present in all samples with a peak level of 6.6 in June. DEET insect repellent appeared at level of 22.2 and 30.6 ng/sample in June and July, respectively. The concentrations of terbuthylazine, S-metolachlor and tebuconazole increased significantly during the spring, and then decreased gradually during the summer except of tebuconazole, which was detected only in May. The highest concentrations (1140 ng/sample) were measured for the chloroacetamide type herbicide, S-metolachlor in May, while terbuthylazine from the triazines was present at 439, 83, 19.7 and 14.3 ng/disk sampled in May, June July and August, respectively (see Figure 2). Chlorophenoxy acids appeared later at lower levels. 2,4-D and mecoprop-P concentrations measured in June, were 18.2 and 8.8 ng/sample respectively, whereas only about 1 ng/sample of mecoprop-P and MCPA were detected in July.

Point water samples were collected when the passive samplers were changed every month. Levels of the pesticide active ingredients measured in these samples were in the range of 1 to 20 ng/L. These values are in the same order of magnitude and similar to TWA concentrations calculated from the sampling rates ( $R_s$ ) taken from the literature [3,4]. On the basis of these values the calculated highest TWA concentration for terbuthylazine was 23.5 ng/L in May, and the concentration of metolachlor remained under 10 ng/L in the winter.



**Figure 16.** Amount of pesticide active ingredients having the highest concentrations among the studied hazardous substances.

Two of the 19 PAH target compounds, acenaphthylene and dibenzo(a,h)anthracene were below the detection limit in all samples collected. In addition, anthracene was not detected in May, whereas neither benzo(a)pyrene, nor indeno(1,2,3-cd)pyrene were detectable in the sample collected in June. The other compounds were measurable at levels between 0.312 and 35.0 ng/sample. The total PAH concentration measured in the May sample was about twice as high as in June, and the level in July was higher than in May (83 ng/sample). Among the 19 PAHs phenanthrene had the highest concentration, but fluoranthene, pyrene and naphthalenes contributed significantly to the total PAH concentration, too (see Figure 3).



**Figure 17.** Amount of PAH compounds measured in the C18 disk

In the case of the POCIS sampler selective for glyphosate and AMPA, the levels of AMPA metabolite exceeded significantly that of the parent herbicide compound: 5.5 ng/sample of glyphosate and 126.5 ng/sample of AMPA were collected in March, while 21.8 and 353.5 ng/sample were measured in June.

Similar results were obtained in the Danube River test area at Silistra (Bulgaria), where the pollution pattern for the pesticide residues and trends were in accordance with those observed in the Drava River at Barcs (Hungary). Unfortunately, the pesticide selective HLB disk have been lost in August, so we could sample only five months for pesticide residues. Isoproturon and persistent diuron were the main background pollutants with the levels below 1 ng/sample except for the May sample. Bentazone was present in all samples except for September with a peak level of 10.4

ng/sample in October. DEET insect repellent appeared at level of 68.8 ng/sample in June and its level decreased gradually. The concentration of S-metolachlor was the highest (195 ng/sample) in May followed by terbuthylazine (94.9 ng/sample). Tebuconazole peak level appeared in June (65.8 ng/sample). Then the amounts determined for these ingredients decreased during the summer and autumn.

All the 19 PAHs were detected in June and October in the Danube River at Silistra, whereas 3 or 6 compounds were below the detection limit in the other months. Similar to the Drava River results, phenanthrene had the highest concentration, followed by the priority compound fluoranthene and pyrene, but naphthalenes also significantly contributed to the total PAH concentrations. The highest total PAH concentration was found in August (128 ng/sample), the levels in other periods were between 60.3 and 77.1 ng/sample, although different pattern was observed for the individual components.

Regarding the pesticide residues in the Somes River in the Upper Tisa test area, Romania, somewhat different results were obtained. Only four months were monitored from June to September. The background pollutants were the same, DEET appeared at higher levels (between 21.4 and 57.7 ng/sample) and priority compounds isoproturon and diuron were present in all samples at low levels (below 2 ng/sample). Bentazone appeared only in June and July at low levels up to 0.32 ng/sample. Pesticide active ingredients, which had the highest levels at the other test areas, were detected rarely. Metolachlor and terbuthylazine were measured as 58.2 and 27.6 ng/sample in June, respectively, and 10.1 ng/sample was determined for metolachlor in August. Some other ingredients (e.g. 2,4-D) appeared in June, but later they were not detected.

Among the PAH compounds, the same were the most significant pollutants. Phenanthrene had the highest concentration level, followed by the priority compound fluoranthene and pyrene, but naphthalenes also contributed to the total PAH concentrations. However, the levels for the individual compounds as well as the total amounts were significantly lower in the hilly Upper Tisa test area as compared to other two sampling sites.

## SUMMARY

The use of the disk was proven to be more convenient compared to the POCIS containing sorbent powder between two membranes. Use of the membrane for the disks decreases the background noise in the chromatogram, but further experiments are required for a more precise assessment of the effect. We have also observed that the elution procedures provided by the manufacturer are not defined with sufficient accuracy, thus, these processes need to be optimized and fit into the analytical procedure. Therefore, different hydrophilic/lipophilic balanced (HLB) disks were prepared for the LC and GC determinations of pesticide residues. We have developed our own elution procedures as well.

Among the priority compounds belonging to the pesticides, only isoproturon and diuron appeared in the passive sampling at low levels. Altogether 85 pesticides including glyphosate and aminomethylphosphonic acid (AMPA) were monitored in the Drava River. Among pesticides, the time weighted average concentrations of terbuthylazine, S-metolachlor and tebuconazole were the highest. Some chlorophenoxy acids (2,4-D, mecoprop-P and MCPA) also appeared at lower levels. Bentazone was detected in all samples at low levels and presence of DEET was also often observed. Among the 19 PAHs phenanthrene occurred at the highest concentrations but priority compounds fluoranthene and naphthalene also contributed significantly to the total PAH concentrations. Levels of anthracene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene were occasionally below limit of detection but the other five priority compounds were measured in all samples.

As for the ubiquitous pollutants glyphosate and AMPA, they occurred also in all samples but the concentrations measured for AMPA metabolite were higher than for glyphosate.

Similar results were obtained for the point samples and from estimations using the sampling rates ( $R_s$ ) from the scientific literature. Determination of sampling rates for further pesticide active ingredients have to be performed with the same sampling device to facilitate determination of

time weighted average concentrations. The current European list of priority compounds contains the persistent and most toxic components but for the regular monitoring further compounds should be involved. Among the pesticide active ingredients thiabendazole, azoxystrobin, boscalid, propiconazole, terbuthylazine-desethyl, clomazone, pendimethalin, dimethenamid, pyrimethanil, metrafenone, PBO, thiacloprid and tetraconazole were also detected with the SIMONA passive sampling systems. Results obtained for the Danube Basin at Silistra, Bulgaria were similar to those for Drava River at Barcs, Hungary but slightly different pollution pattern was observed for the Somes River in the Upper Tisa area at Baia Mare, Romania.

## **REFERENCES**

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- [2] B. Becker et al., *Environ Sci Pollut Res* 28, (2021) 11697