

PASSIVE SAMPLING FOR PESTICIDES AND PAHs IN THE SIMONA PROJECT

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Abstract

Passive samplers (solid phase extraction, SPE disks and Polar Organic Chemical Integrative Sampler, POCIS) were tested to monitor 85 pesticides (including glyphosate and aminomethylphosphonic acid, AMPA), 19 polycyclic aromatic hydrocarbons (PAH) components, metals 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, DEET and diuron were detected in all samples at low levels. Among the 19 PAHs phenanthrene occurred at the highest concentrations, but fluoranthene, pyrene and naphthalenes also contributed to the total PAH concentration. 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.

Introduction

In the frame of project SIMONA (DTP2-093-2.1) entitled “Sediment-quality Information, Monitoring and Assessment System to support transnational cooperation for joint Danube Basin water management” [1], development and test of a monitoring system was carried out in one of the test areas of the Drava River Basin (at Barcs) in 2020-2021. The project, proceeding with the participation of 17 full partners and 13 associated partners from 14 countries, aims to respond to the current demand for effective and comparable measurements and assessments of sediment quality in surface waters in the Danube river basin by delivering a ready-to-deploy sediment-quality information, monitoring and assessment system to support transnational cooperation for water management in the region. Thus, the main objective of project SIMONA 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 [2] within the project, and laboratory analysis has also been extended by a passive sampling regime.

The main components of the passive sampling system were (a) sediment box for the systematic collection of suspended particles, (b) sensors for recording different physicochemical parameter (e.g., temperature, turbidity, dissolved oxygen, pH) and (c) passive samplers for 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 to of 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, polycyclic aromatic hydrocarbons (PAHs) and pesticide residues.

Experimental

We have used 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.

Instrumental analysis was performed at Bálint Analitika Ltd. using liquid chromatography coupled with mass spectroscopy (LC-MS) or gas chromatography chromatography coupled with tandem mass spectroscopy (GC-MS/MS) for determination of 85 target pesticides and 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 solved 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 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 and discussion

The point samples collected in the barrel contained little sediment, which significantly limited the reliability of the analytical measurement. In contrast, the sediment box collected and partially separated 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 surface water (Drava). According to the results of our preliminary investigations in 2020, the amounts of bound pesticide residues were similar, but in some cases the membrane holding the adsorbent was torn, so the powder was lost, thus we decided to use a disk.

Regarding the pesticide residues, pollution pattern and trends were in accordance of our expectations. Preliminary results prior to the agricultural season indicated that bentazone, DEET and persistent diuron are the main background pollutants. The latter active ingredient is no longer authorized in the EU. 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 1). 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 in 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.

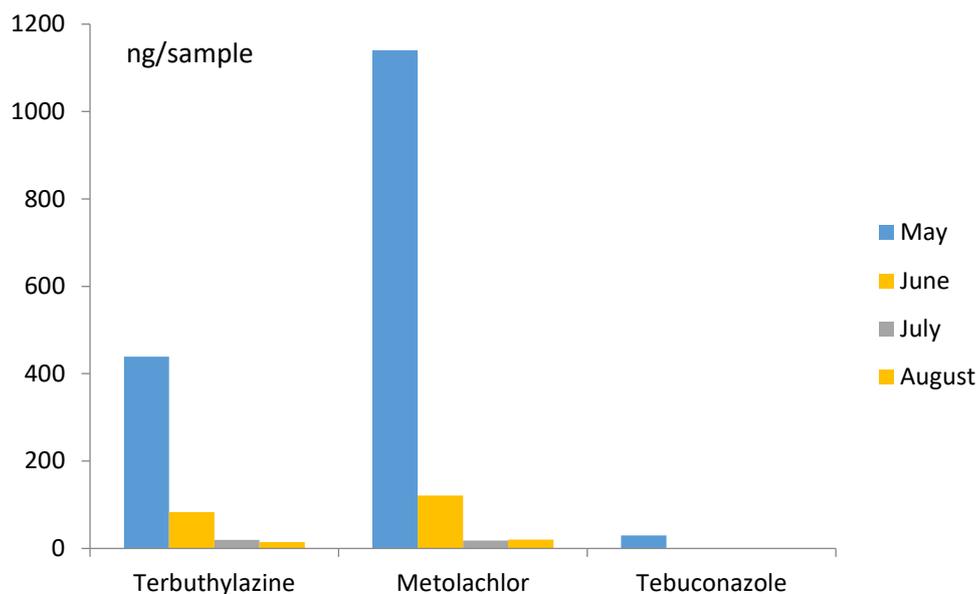


Figure 1 Amounts of pesticide active ingredients having the highest concentrations

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 also significantly contributed to the total PAH concentration (see Figure 2).

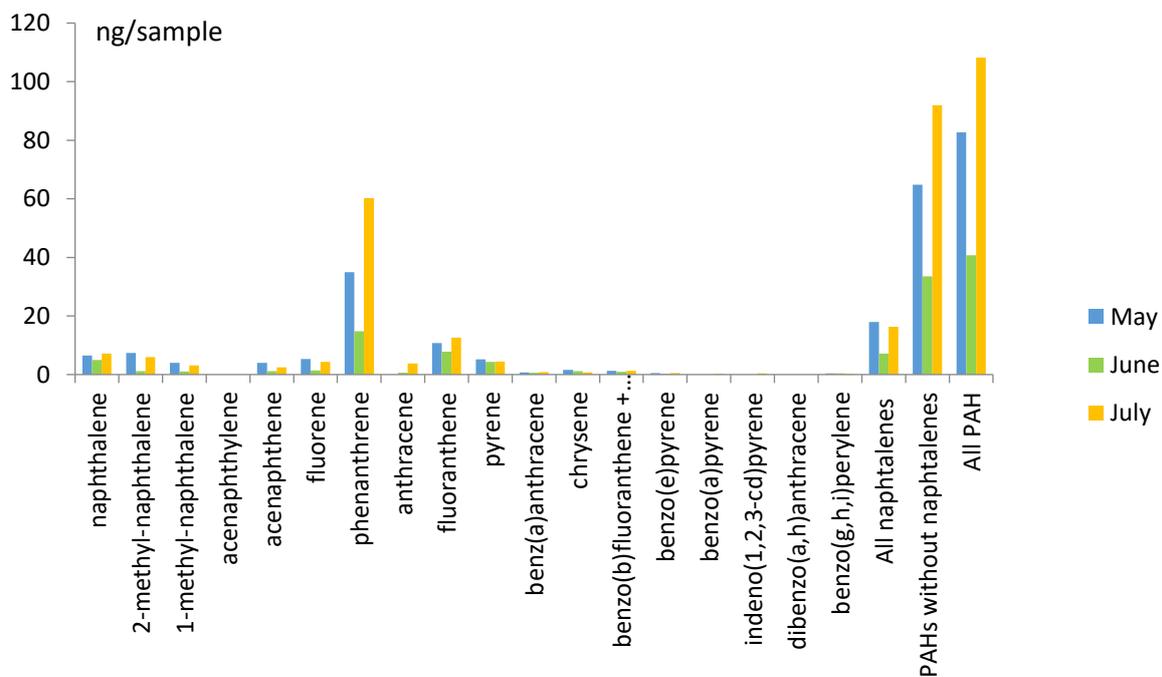


Figure 2 Amounts of PAH compounds measured on the C18 disk

In the case of the POCIS sampler selective for glyphosate, the higher concentration of the AMPA metabolite compared to glyphosate was noticeable: 5.5 ng of glyphosate and 126.5 ng of AMPA were collected in March, while 21.8 and 353.5 ng/sample were measured in June.

Conclusion

The use of the disk was proven to be more convenient compared to the POCIS containing sorbent powder between the 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. The test is now in progress regarding the application of the membranes together with the C18 disks as they are present in all samples. We have also observed that the elution procedures provided by the manufacturer are not defined at an expectable 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.

Similar results were obtained for grab samples (point sample) and from estimations using the sampling rates (R_s) from the scientific literature. The current list of priority compounds contains 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.

Acknowledgements

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References

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