

*25th International Symposium on Analytical and Environmental Problems***INVESTIGATION OF PRIORITY POLLUTANTS IN THE SEDIMENT PHASE –
PROJECT SIMONA****Mária Mörzl¹, Zsófia Kovács², Győző Jordán³, András Székács¹**

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Abstract

The Framework Directive (WFD) of the European Union (EU) aims to achieve good status for water bodies in EU, but there occurs a delay in its implementation related to priority pollutant substances. A key issue in water protection and management is that priority pollutants should be monitored not only in the water bodies, but also in sediments and the biota. Distribution between the water and sediment phases is strongly affected by numerous factors, including the polarity of the analytes, as well as amorphous organic matter and suspended matter content in the water body, and are often affected by methodological parameters. As a result, certain pollutants will be detected in the water phase, others in the sediment, again others in both, as indicated by reported cases in the scientific literature. This challenge is illustrated in the case of project “Sediment-quality Information, Monitoring and Assessment System” (SIMONA) (2018-2021) within the Danube Transnational Program.

Introduction

Water protection is one of the priorities of the European Commission. The European Water Policy aims to protect clean water in the European Union (EU) by preventing water pollution and to restore clean water from polluted sites. Thus, the EU Water Framework Directive (WFD), as one of the key EU policy measures, aims to reach a good status both chemical and ecological, for water bodies in Europe [1]. Water pollutants that jeopardize such good status represent a threat to the aquatic environment, and the WFD specified the most hazardous substances of these to be phased out. For this purpose, priority substances (PSs) presenting a significant risk to or via the aquatic environment were listed in 2008 [2]. The first watch list for European Union-wide monitoring of water bodies was published in 2015 [3] containing ten substances or groups of components, that was further extended in 2018 [4].

Nonetheless, the original goals of the EU water protection policy have not yet been achieved, and there appears a delay in the implementation of the objectives set in the WFD [5]. Previously monitoring at the point of discharge was typical to control the emission of specific pollutants (end-of-pipe). In turn, regulation has shifted lately towards systematic (integrated) thinking that focuses on sustainability, flexible water governance, determination of indicators, complex understanding of drivers, pressures, state impacts and responses in catchments. In addition to the determination of emissions and maximum limits, environmental quality standards (EQSs) have been set for certain substances, and management actions must account for the effects of multiple stressors. Monitoring and assessment need to better reflect improvement in the ecological status and long-term tendencies [6].

Affecting factors that influence distribution of pollutants

The current list of 20 PSs, 13 priority hazardous substances (PHSs) [2], 11 substances subject to review for possible identification as PSs or PHSs, and 8 substances on watch list [3] includes, among other groups of toxic compounds, pesticide active ingredients and their metabolites or contaminants. In addition, chemical intermediates, by-product polyaromatic hydrocarbons (PAHs), polybrominated biphenylethers (PBDEs), biocides, metals, as well as hormones and antibiotics are also found on the lists.

These compounds are regularly measured in water bodies, their EQSs are intended also for sediment and biota, yet far less information is available about their substantive concentration in the sediment. Partition of the components depends on their polarity characterized by their octanol/water partition coefficient (K_{ow}). On the other hand, higher organic matter content in the sediment bind more non-polar components compared to those with lower organic content. Therefore, the equilibrium constant is often given to organic matter content of soils (K_{oc}). Distribution between the two phases results in different mobilities, which is strongly influenced by other factors e.g., suspended matter content. Worthy of note, that there is no equilibrium in the rivers between water body and the sediment. Based on the K_{ow} , compounds having $K_{ow} < 3$ are water pollutants, while components characterized by $K_{ow} > 5$ are sediment pollutants. Other components ($3 \leq K_{ow} \leq 5$) are present in both phases. Partition influences the analytical results and contamination levels determined in water. Analysis of the entire water body often fails as the water sample is filtered prior to sample preparation (solid phase extraction) or instrumental analysis (liquid chromatography) in numerous analytical protocols. Certain pollutants, however, are partially or completely removed by filtration. Faludi et al. [8] determined substituted phenols in both the Danube river and its suspended matter. Yet e.g., priority substance pentachlorophenol was detected only in the suspended phase, which is rarely analyzed.

Temporal variation of the analytes is high in the water phase, but less variable in the sediment. If a spot sample is taken, only the concentration currently present in water can be measured. Nowadays, pollutant levels on a longer time-scale can be determined in surface water by the use of passive samplers. These keep collecting pollutants for one or two weeks, but the derived information differ from the results obtained for spot samples. Both information are important as not only the maximum, but also the average concentrations are often regulated for certain pollutants. Grab sampling and collection by polar organic chemical integrative sampler (POCIS) for organic compounds with a $0 \leq \log K_{ow} \leq 5$ were simultaneously applied, and the results were compared [9]. Pollution patterns reflect the land use and loads, but also the presence of persistent components. For example, herbicide active ingredient atrazine is still detected, despite of its ban in the EU in 2004. A partial cause of this water polluting characteristics is accumulation and practically no decomposition of the compound in the anaerobic soil zones, and subsequent leaching to surface water. Unfortunately, illegal use of this prohibited pesticide active ingredient also occurs: fresh loads of atrazine were confirmed by its high concentration together with its low metabolite levels (desethyl atrazine). Atrazine was detected by us in Hungarian water and soil samples as well at around 2010, after its ban in 2007, but it did not appear any further during monitoring of the Danube river in 2015, indicating that its level decreased below the detection limit of our method [10].

Comparison of pollution patterns and contamination levels of sediment and water samples [11] showed significant spatial variations in water and sediment. Seasonality in concentration was observed in water, but not in sediment, although sediment concentrations varied substantially among different years. Average measured non-equilibrium distribution coefficients exceeded equilibrium hydrophobic partitioning-based predictions for 5 of the 7 detected contaminants by at least an order of magnitude. Agreement increased with

hydrophobicity and persistence. These observations indicate non-equilibrium conditions between water and sediment phases and slow rate of adsorption. Among detected compounds, the distribution of more polar and degradable components showed greater variability, probably due to their degradation. On the other hand, non-sorptive components (based on their $\log K_{ow}$ values) were found also in the sediment indicating the importance of other processes (e.g. complex formation).

Inorganic components of the sediment may occasionally be equally important, as it was observed for example in the case of glyphosate and iron-oxide. Gama et al. [12] studied the distribution of different herbicides. Non-polar compounds with high $\log K_{ow}$ and K_{oc} values were more likely to be found in the inorganic fraction of the sediment, whereas more polar herbicides with high solubility and low K_{oc} values were dispersed between both the organic and inorganic fractions. The interaction between chemicals and amorphous organic matter (e.g., humic and fulvic acids, proteins, lignin, polysaccharides) might also modify the partition process.

Partition among the water-dissolved phase (DP), suspended particulate matter (SPM) and sediment may also become characteristic. Montuori et al. [13] measured pollution by organophosphate pesticides (OPP) in the Sarno river (Italy), and detected these compounds in DP, SPM and sediment samples simultaneously. Total OPP concentrations ranged from 5.58 to 39.25 ng L⁻¹ in the water phase as the sum of the DP and SPM, and from 0.19 to 3.98 ng g⁻¹ in the sediment samples. Their conclusion has been that chlorpyrifos is a pseudo-persistent pollutant, and that higher levels of chlorpyrifos found in DP than in SPM samples and sediment samples indicate fresh inputs.

The SIMONA project

Sediment quality is an existing problem in the Danube River Basin (DRB), and countries in the region lack sufficient institutional capacity, including information, guidelines and methods, to build a transnational sediment monitoring network for trend assessment of hazardous substances. The international project SIMONA (Sediment-quality Information, Monitoring and Assessment System) was launched in 2018, as a part of the Danube Transnational Program (DTP), to support transnational cooperation for joint DRB water management by harmonized sediment monitoring [14]. The main objective of project SIMONA, carried out by the participation of 17 full consortium partners and 12 strategic associated partners from 12 DRB countries, is to respond to the current demand for effective and comparable measurements and assessments of sediment quality in surface waters in the DRB by delivering a ready-to-deploy sediment quality information, monitoring and assessment system to support transnational cooperation for joint DRB water management. For this purpose, project SIMONA aims to develop an improved, harmonized and coordinated sediment quality monitoring system of the water body status in the DRB. Together with experts trained in sediment quality management by SIMONA, the project will also generate international cooperation between stakeholders concerning the monitoring of PHS concentrations in water, in sediments and in biota. The immediate and middle term benefit of the project will be a transparent method supported by an online platform information technology tool (SIMONA-tool) for sediment quality monitoring that will encourage the cooperation in transnational water management, as well as the sediment quality assessment.

Working groups in the project collect currently existing protocols and develop transnationally harmonized guidance in the field of sediment sampling, laboratory measurement of PSs and data evaluation, including quality assessment and quality control procedures. Outputs of the project will be integrated into the SIMONA-tool developed, containing a sediment quality evaluation protocol for PHSs, three harmonized protocols (sampling, laboratory and

evaluation), as well as earlier monitoring data for sediment. Evaluation of data will be based on predefined formula and display of the information (e.g. for decision-making authorities).

Conclusion

As demonstrated by the scientific results reported, equilibrium between the water and sediment phases is a complex issue, and actual distribution of pollutants depends on numerous factors. More accurate assessments of exposure and risk to surface water ecosystems can be performed by improving the prediction of fate and transport processes. This requires a dual solution. On the one hand, there is a knowledge gap in exploring the affecting factors related to the partition of PHSs in the sediment that requires further investigations. On the other hand, a harmonized protocol is necessary to compare the monitoring results and to determine the background levels in the DRB.

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