

LEVELS AND ORIGIN OF POLYCYCLIC AROMATIC HYDROCARBONS IN FLUVIAL SEDIMENT OF DRAVA RIVER

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Abstract

Within the scope of an international monitoring program to assess water and sediment quality in the Danube basin, sediment samples (river bottom/bank, suspended and active floodplain/overbank) were collected in the summer of 2020 at a sampling site in the Drava river to monitor 19 polycyclic aromatic hydrocarbons (PAHs) as apparent water contaminants. Among these, 8 PAHs were specified as priority pollutants in the corresponding EU Directive on environmental quality standards (2008/105/EC). The highest levels were measured for fluoranthene (1.73 µg/g), benzo(b)fluoranthene+benzo(k)fluoranthene (0.765 µg/g) and anthracene (0.528 µg/g) sampled from the upper 5 cm layer of the bottom sediment on 5th August 2020.

Introduction

In the frame of the SIMONA project (DTP2-093-2.1) titled “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 test area at Drava River (Barcs, Hungary) in August 2020. Different sampling methods were compared in order to develop the harmonized sampling protocol [2] and the different sediment types were separately analyzed for different classes of pollutants (potentially toxic elements/metals, pesticides, and PAHs). The main parts of the system included a) a sediment box for collection of suspended particles, b) sensors for recording different physicochemical parameter (e.g., temperature, turbidity, dissolved oxygen level, pH), and c) passive samplers for uptake of different contaminants. Here we report the results of PAH analyses for samples taken by vacuum core-sampler (bottom sediment), spade or cake sampler (floodplain sediment) and by using a barrel for collection of water (suspended sediment). In the cases of vacuum corer and spade, sediments from two different depths were collected. Upon sample preparation and instrumental analysis, isomer ratios were calculated based on the analytical results to determine the possible origin of PAH contamination (pyrogenic or petrogenic).

Experimental

For the monitoring program, the sampling site was set up on the Drava river (Barcs, Hungary). Coordinates of the site were: WGS Lat (N) 45.95088, Long (E) 17.44650. Sampling was carried out from 5th to 8th of August in 2020.

Different sampler devices were used to collect sediment samples. Bottom sediment samples were collected by a vacuum core-sampler, and the PAH content of upper 5 cm and that of the subsequent 5 to 10 cm layer were determined. Suspended sediment samples were collected together with 30-liter batches of water into a barrel using a pump. The fine material that settled from the water collected was filtered in the laboratory. Active floodplain/overbank sediments were sampled using a spade or a cake sampler, at depths level of 0–5 cm in the topsoil (or top

layer). Another type of sample was also collected from the 40–50 cm bottom layer. The same harmonized methodology was used for the sediment sampling, performed in other test areas of the Danube river basin in the frame of SIMONA project [4-6]

Instrumental analysis was performed at the premises of Bálint Analitika Ltd. using a GC-MS method with an ion trap mass detector operating in the selective ion monitoring mode for determination of the 19 target PAH compounds. The list of these priority pollutants issued by the U.S. Environmental Protection Agency (EPA) in 1976 [3] contains 16 PAHs, which are routinely analyzed in environmental samples. Among these compounds 8 are on the list of priority compounds in the field of water policy in the European Union [7,8] as well, and 6 of them are identified as priority hazardous substances (Table 1). In addition, 3 PAH compounds (2-methyl-naphthalene, 1-methyl-naphthalene, benzo(e)pyrene) were also determined in the different sediment phases collected. Total PAH concentrations included the levels of acenaphthene, acenaphthylene, benz(a)anthracene, chrysene, dibenzo(ah)anthracene, fluorene, phenanthrene and pyrene as well.

Table 1. Priority pollutant and other contaminant polyaromatic hydrocarbon (PAH) substances analysed in the present sediment monitoring study

Category	Substance	Rings	logK _{ow} *
Priority substances	naphthalene	2	3.28
	fluoranthene	4	4.90
Priority hazardous substances	anthracene	3	4.45
	benzo(a)pyrene	5	6.06
	benzo(b)fluoranthene	5	6.04
	benzo(k)fluoranthene	5	6.06
	benzo(g,h,i)perylene	6	6.50
	indeno(1,2,3-cd)pyrene	6	6.58
Additional measured compounds	1-methyl-naphthalene	2	3.87
	2-methyl-naphthalene	2	3.86
	benzo(e)pyrene	5	6.44

* The octanol-water partition coefficient: a measure of lipophilicity.

Results and discussion

Regarding the PAH residues, the pollution pattern and trends were in accordance with our expectations. Bottom sediment samples collected by the vacuum core-sampler had the highest PAH content, but differences between the upper 5 cm and the 5–10 cm layer were not straightforward. Typical levels were between the limit of detection (LOD=0.001 µg/g) and 0.006 µg/g. The highest levels were measured for fluoranthene (1.73 µg/g), benzo(b)fluoranthene + benzo(k)fluoranthene (0.765 µg/g) and anthracene (0.528 µg/g) sampled from the upper 5 cm on 5th August 2020 at the the Drava river. The second highest values were determined for the sample taken at the same site from the 5–10 cm layer, but containing the highest amounts of phenanthrene (1.05 µg/g), naphthalene (0.949 µg/g) and 2-methyl-naphthalene (0.719 µg/g) with significant amounts of fluorene (0.449 µg/g) and pyrene (0.355 µg/g).

The point samples collected into the barrel contained little amounts of suspended sediment. Although all target PAHs were detected, but amounts remained mostly close to the LOD. Levels in the suspended sediment phase exceeded the limit of quantitation (LOQ) for anthracene, benzo(a)pyrene, benzo(b)fluoranthene + benzo(k)fluoranthene, benzo(g,h,i)perylene, fluoranthene and indeno(1,2,3-cd)pyrene. The highest levels were determined for fluoranthene

(0.281 $\mu\text{g/g}$) and anthracene (0.292 $\mu\text{g/g}$) sampled on 5th August 2020 in Drava River. To improve the reliability of the analytical measurement, amounts of the sample could be increased by using a centrifuge additionally to remove floating material for the water phase, or applying a standardized sediment box for long-term collection, which partially separates the suspended sediment by the baffles of the box.

Sampling of floodplain sediment at two depths had the objective to identify in the analyzed samples recent contamination transported by the flood events and the pre-industrial natural background. Samples taken from the bottom layer (40–50 cm) contained only very low levels of PAHs near to the LOD. The top layer contained also low levels, and the highest concentration was measured for benzo(b)fluoranthene + benzo(k)fluoranthene (0.078 $\mu\text{g/g}$). That sample was taken by cake sampler and the corresponding value for the sample collected by spade contained only 0.060 $\mu\text{g/g}$. Some amounts of fluoranthene (0.052 $\mu\text{g/g}$) and benzo(a)pyrene (0.041 $\mu\text{g/g}$) also appeared in the same sample.

Fresh loads enter the water phase either from atmospheric depositions or from urban run-off, and different other sources appear first in the suspended sediment, as due to their hydrophobic characters their water solubility being very low. Elder contamination bound to the particulate matter are finally deposited in the bottom sediment, where slow microbial metabolism leads to the degradation of PAHs. The higher the molecular weight and the higher the octanol-water partition coefficient ($\log K_{ow}$), the slower the degradation rate. Resuspension during flood events can mobilize PAH substance, which may increase their levels in the active floodplain sediment. On the other hand, consumption and metalibolization of PAHs by aquatic species may eliminate some of the accumulated contamination from the bottom sediment.

The octanol-water partition coefficient ($\log K_{ow}$) values for the target components ranged between 3.28 and 6.58, thus, PAHs with five or more rings are proposed to be monitored in the sediment phase ($\log K_{ow} > 5$), whereas PAHs with two to four rings appear in both (water and sediment) phases ($\log K_{ow} = 3-5$). However, based on the experimental data [9], high molecular weight PAH compounds (5 or 6 rings) contributed up to 11% to the total PAH content in the non-filtered Danube river water sample. Due to the strong affinity of the target compounds to the particulate matter, filtration during sample preparation of water removes most of the hydrophobic pollutants together with the suspended sediment, which substantially influences the results of the chemical analysis. In the bottom sediment samples in our survey the four-ring PAHs dominated, whereas in suspended sediment the four- and five-ring species were equally dominant, and in flood plain sediment the most abundant group belonged to the five-ring isomers (Fig. 1.).

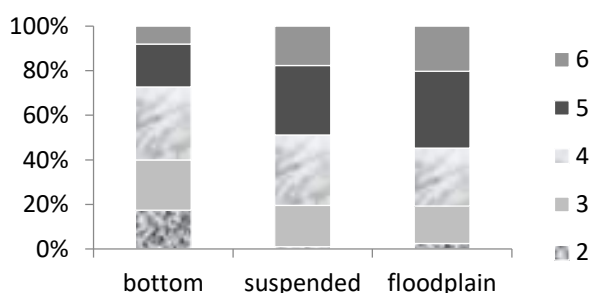


Figure 1. Composition pattern of PAH compounds measured in bottom, suspended and floodplain sediments.

The origin of the PAH contamination was determined by using the isomer ratios of different pairs. There are several molecular indices, calculated from the corresponding concentrations, that can be used for identification of the pollution source. We have used ratios for 4 isomer

pairs to identify the possible sources (see Fig. 2). Worthy of note, that zero values indicated that anthracene, fluoranthene, benz(a)anthracene or indeno(1,2,3-cd)pyrene were not detected in the corresponding sample and numerous 0.5 values for the Drava samples originate from the fact that the level of target compounds were near to limit of detection and therefore the ratio from LODs was 1:2. Nevertheless, the other values may vary as they are presented in Fig. 2.

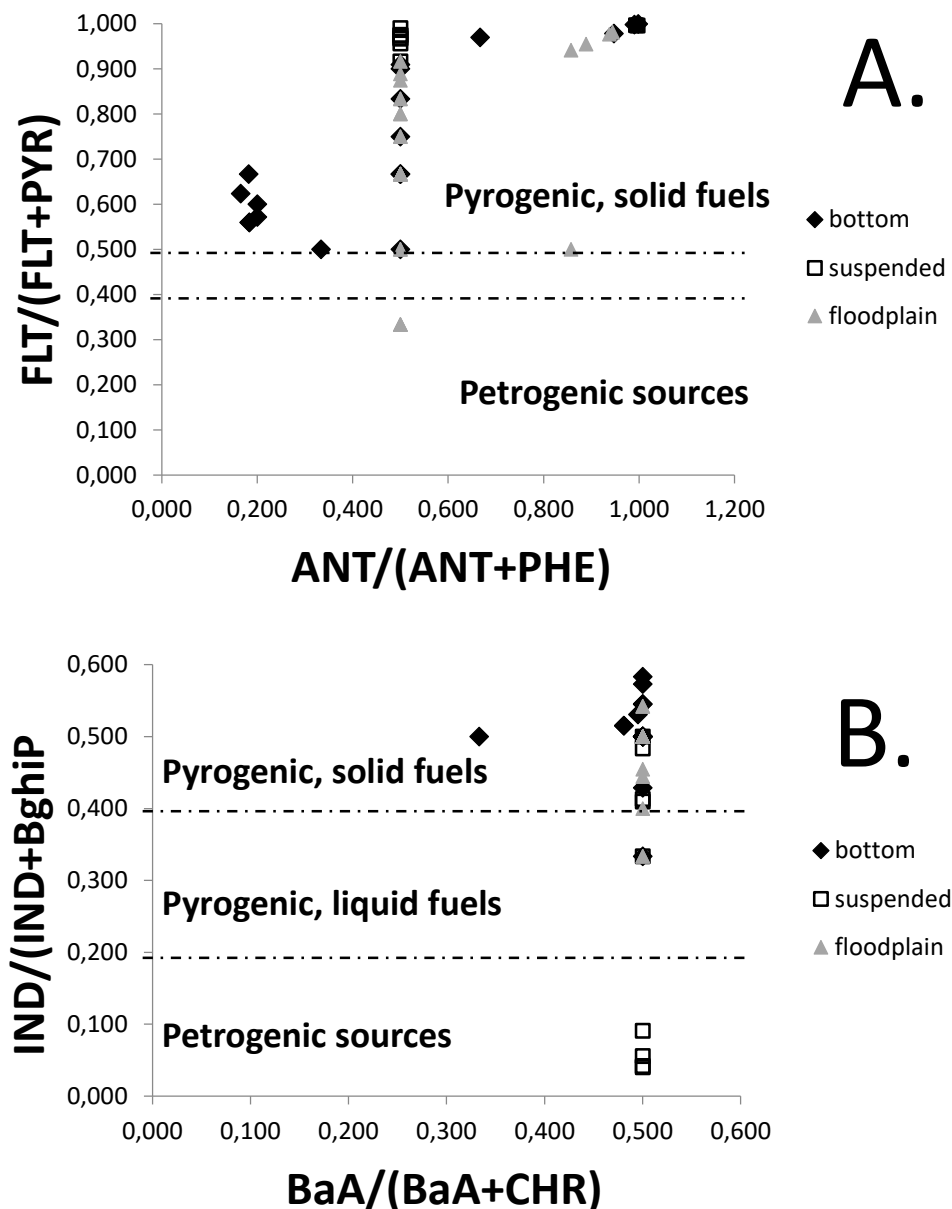


Figure 2. Cross-plot for the concentration ratios **A.** of anthracene/(anthracene + phenanthrene) ($ANT/(ANT+PHE)$) versus fluoranthene/(fluoranthene + pyrene) ($FLT/(FLT+PYR)$) and **B.** benz(a)anthracene/(benz(a)anthracene + chrysene) ($BaA/(BaA+CHR)$) versus indeno(1,2,3-cd)pyrene/(indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene) ($IND/(IND+BghiP)$) in sediments.

Typical levels were low for all types of the sediment samples taken at Drava sampling site. Ratios of anthracene/(anthracene + phenanthrene) were above 0.1 in every samples, indicating the pyrogenic origin of PAH contamination. Combustion of solid fuels as a source was confirmed by all values calculated for fluoranthene/(fluoranthene + pyrene) except three floodplain samples. Worthy of note that in these cases the concentrations of fluoranthene and pyrene were very low (LOD). Both benz(a)anthracene and chrysene levels were near to LODs,

but indeno(1,2,3-cd)pyrene/(indeno(1,2,3-cd)pyrene + benzo(g,h,i)perylene) values below 0.2 for 4 suspended sediment samples suggested petrogenic origin of PAH compounds, however indeno(1,2,3-cd)pyrene levels were around the LOD. The ratios for the remaining suspended sediment samples (0.2–0.5) indicated that combustion of liquid fuels is the main source, and also about the half of the floodplain samples belonged to this category. The calculated values for the rest of the flood plain samples were 0.5, although they contained indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene, but only near the LODs. Combustion of solid fuels was the dominant source in bottom sediment samples, except for a single case, where the ratio, calculated from the LOD for indeno(1,2,3-cd)pyrene, correlated presumably to the combustion of liquid fuels.

Conclusion

PAH contamination levels in the sediment of the Drava river are low, although all the 19 PAH components monitored in this study could be detected. The highest concentrations appeared in the bottom sediment followed by the suspended sediment, and the lowest amounts were determined in the floodplain sediment. Among the PAH compounds, the groups containing 4 or 5 rings dominated, and the larger molecules are more abundant in the floodplain sediment. Possible sources of PAH contamination are mostly related to the combustion of solid fuels.

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