MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) IN SURFACE WATER OF THE HUNGARIAN UPPER SECTION OF THE DANUBE RIVER

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Abstract: The aim of this paper is to investigate the concentrations of polycyclic aromatic hydrocarbons (PAHs) in surface water of the Hungarian upper section of the Danube River in the period of 2007-2010. A total of 77 water samples were collected from the sampling sites located at Rajka, Medve and Komárom (1848, 1806 and 1766 river km) under the authority of the Inspectorate for Environment, Nature and Water of the North Transdanubian Region designated by the Hungarian National Monitoring Programme. Sixteen PAHs identified by the US Environmental Protection Agency (USEPA) as priority pollutants were monitored.

Concentrations of total 16 PAHs (∑PAHs) ranged from 25 to 357 $ng{\cdot}L^{-1}$ with the mean value of 98.27 ± 58.48 $ng{\cdot}L^{-1}$. The low and medium molecular weight PAHs (2-3 and 4 ring) ranged from below method detection limit (<1) to 136 $ng{\cdot}L^{-1}$ while high molecular weight PAHs (5-6 ring) were present at much lower concentrations (<1-25 $ng{\cdot}L^{-1}$). The 2-3-ring PAHs contributed to about 64% while 4-6-ring PAHs accounted for 36% of the ∑PAHs. The dominant species are naphthalene and phenanthrene in the surface water. Concentration ratios of specific PAH compounds including anthracene/(anthracene+phenanthrene) and fluoranthene/(fluoranthene+pyrene) were calculated to evaluate the possible sources of PAH contamination. The levels of ∑PAHs determined in our study were compared with other sections of the Danube and other regions of the world.

Keywords: polycyclic aromatic hydrocarbons, PAH, Danube, monitoring, surface water

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings. The US Environmental Protection Agency (US EPA) has identified 16 unsubstituted PAHs as priority pollutants for measurement in environmental samples, some of which are considered to be possible or probable human carcinogens, and hence their distribution in the environment and potential risks to human health have been the focus of much attention. PAHs originate from both the natural as well as anthropogenic sources that mainly include thermal combustion processes, vehicular emissions, oil contaminations and biomass burning. Combination of their physicochemical properties, such as low aqueous solubility, moderate vapour pressure, high octanol-water partition coefficient and persistence in environment make them capable of long range transport (MANOLI and SAMARA, 1999; MALIK *et al.,* 2011).

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Atmospheric deposition is considered to be an important input of PAHs to surface waters. Low molecular weight PAHs (two- and three-ring) occur in the atmosphere in the vapour phase whereas multi-ringed PAHs (five-ring) are bound to particles. Intermediate molecular weight PAHs (four-ring) are partitioned between the vapour and particulate phases, depending on atmospheric temperature (SROGI, 2007). Beside the atmospheric fallout includes wet and dry deposition of particles the PAHs enter surface waters especially via urban run-off, municipal effluents, industrial effluents and oil spillage or leakage (BAKER and EISENREICH, 1990; MANOLI and SAMARA, 1999). They have a relatively low solubility in water, but are highly lipophilic. Similarly to the process observed in the atmosphere PAHs associate easily with particulate matter and are finally deposited in the sediment. Therefore their concentration in water is low (KO and BAKER, 1995; YUNKER *et al.,* 2002). The concentrations of PAHs in river sediments are generally much higher than in the surrounding water body (MALIK *et al.,* 2011).

The aim of this paper is to investigate the concentrations of PAHs in surface water of the Hungarian upper section of the Danube River in the period of 2007-2010. The water samples were collected from the sampling sites located at Rajka, Medve and Komárom (1848, 1806 and 1766 river km) under the authority of the Inspectorate for Environment, Nature and Water of the North Transdanubian Region designated by the Hungarian National Monitoring Programme. The concentrations of 16 US EPA PAHs were studied. Concentration ratios of specific PAH compounds including anthracene/(anthracene+phenanthrene) and fluoranthene/(fluoranthene+pyrene) were calculated to evaluate the possible sources of PAH contamination. The levels of total 16 PAHs (∑PAHs) determined in our study were compared with other sections of the Danube and other regions of the world. The results of this study add new data to the international database of the Danube River producing comparable and reliable information on water quality.

2. Materials and methods

2.1 Study area and sampling

The length of the Hungarian section of the Danube is 417 km (1433-1850 river km) from which the length along the Hungarian and Slovakian border is 142 km. The Danube has been diverted to the bypass canal of the Gabcikovo Hydroelectric Power Plant and the Slovakian side provides water into the old riverbed from the Hrusov reservoir. Its water quality is characterized at the Rajka sampling site (1848 rkm). Above the Medve sampling site (1806 rkm) the divided water of the river is reunited again. The water quality at the Komárom sampling site (1766 rkm) is significantly influenced by the Moson Danube flowing into the Danube. The sampling sites are shown in Fig. 1.

A total of 77 surface water samples were collected from the three sampling sites mentioned above and analysed for the 16 US EPA PAHs in the period of 2007-2010. The number of sampling was not consistent in the examined years or even at the sampling sites depending on the prevalent National Monitoring Programmes. At one sampling site, a number between 1-12 samples were collected in a year at different months. The sampling location in profile was in the middle of the river (~30 cm below the surface) on the bridge at the sampling sites of Medve and Komárom. The samples were collected on the right side of the Danube River at the sampling site of Rajka. The water samples were directly collected from the river using 2 L brown glass bottles and transferred to the laboratory directly. The samples were stored at 4 °C.

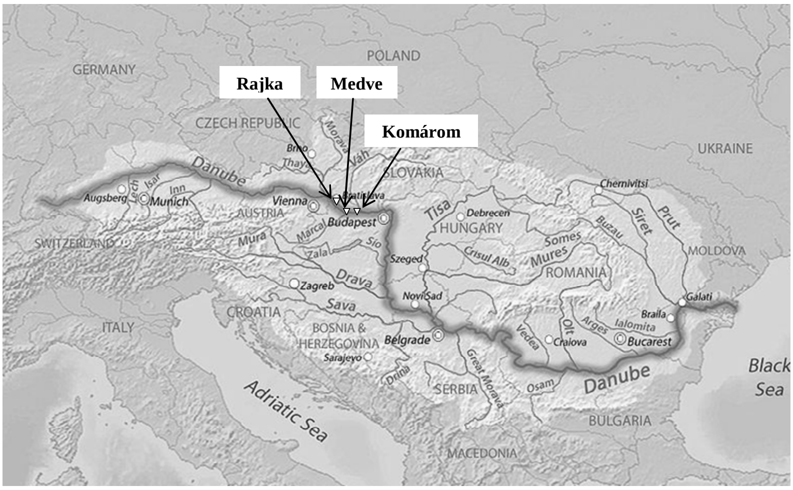

Fig. 1. The sampling locations in the Danube River.

2.2 Analysis

The PAH analysis was conducted in accordance with the Hungarian standard method procedure (MSZ 1484-6:2003). 1 L of the water sample was acidified to pH = 2 with 5 $mol \cdot L^{-1}$ H_2SO_4. 100 ng of a SV Internal Standard Mix (Restek) was added to the sample. Liquid-liquid extraction with 30 mL n-hexane was applied in three times. The extract was dried using anhydrous sodium sulphate and concentrated to 1 mL by a rotary evaporator. PAHs in the concentrated extract were fractionated by a silica gel column (200 mm long, 4 mm internal diameter). The column was first eluted with 30 mL of n-hexane and the eluate was discarded. Further elution was carried out with 30 mL of dichloromethane to obtain PAHs fraction. The PAHs containing fraction was concentrated to 1 mL by using a rotary evaporator, then 100 ng of a WA EPH Aromatic Hydrocarbon Standard (Restek) was added to the sample for further chromatographic analysis.

A gas chromatography-mass spectrometry (GC-MS) system, consisting of a gas chromatograph (Agilent 6890) with a GC column (Rtx-5MS-integra 30 m long, 0.25 mm internal diameter, 0.25 µm coating) and a mass spectrometer (Agilent 5973), was used for the determination. Selected ion monitoring (SIM) mode was employed for the identification and quantification of 16 individual PAH compounds. By this method, the 16 PAH compounds were determined with the limit of detection of about 1 $ng \cdot L^{-1}$.

3. Results and discussion

Figure 2 illustrates the spatial and time distributions of annual average concentration, standard deviation and median of the ∑PAHs in surface water of the Danube River at the different sampling sites in the period of 2007-2010. Table 1 summarises the concentration ranges and the mean values of the individual PAH compounds in all of water samples for the examined period.

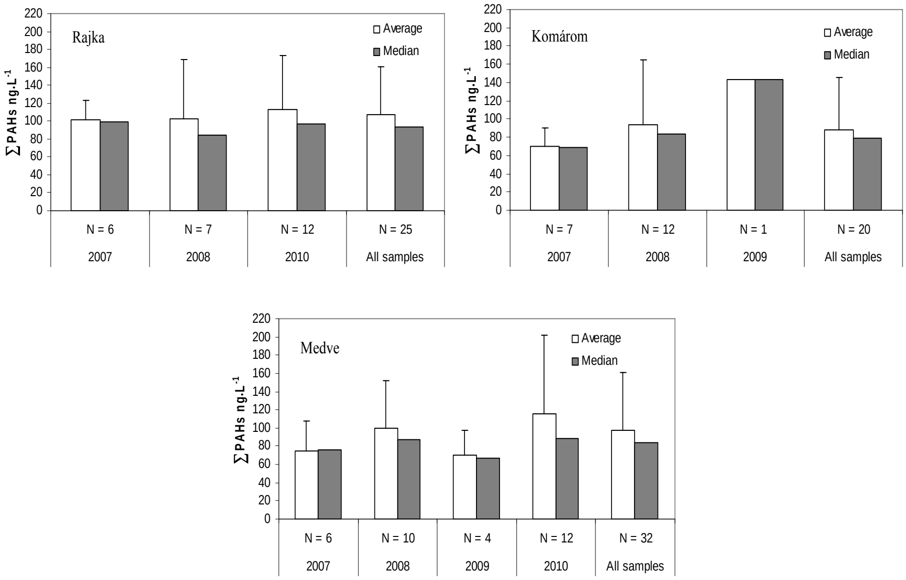

Fig. 2. Mean concentrations, standard deviations and medians of total PAHs in surface water of the Danube River at the sampling sites (N: number of collected samples).

During the study period the concentrations of ∑PAHs in the river water of the Hungarian upper section of the Danube ranged from 25 to 357 ng·L^{-1} with the mean value of 98.27 ± 58.48 ng·L^{-1}. For individual PAHs, two-, three- and four-ring PAHs are the most abundant, the concentrations of them ranged from below method detection limit (<1) to 136 ng·L^{-1}. The concentrations of five- and six-ring PAHs were much lower, ranged from <1 to 25 ng·L^{-1}. Dibenz[*ah*]anthracene was not detected in the water samples. The naphthalene and phenanthrene were the most dominant PAH compounds with the average distribution of 21 and 26% of the total PAHs in the river water, respectively. The 2-3-ring and 4-ring PAHs contributed to about 64 and 28% while 5-6-ring PAHs accounted for 8% of the total PAHs. It is remarkable that fluoranthene and pyrene had also been significantly high average contribution to the ∑PAHs (each about 12%).

A lot of previous studies have been reported about PAHs levels measured for decades in other rivers of the world (MALDONADO *et al.,* 1999; DOONG and LIN, 2004; NAGY *et al.,* 2007; LUO *et al.,* 2008; MALIK *et al.,* 2011, and references therein), although a direct comparison of literature data is difficult due to the difference in the phase analyzed (dissolved, particulate or both), the analytical methods used, and the compounds considered in each study. Comparison of the ∑PAHs concentrations in our study with other data of the Danube River at various sampling sites and some different rivers of the world is presented in Table 2.

Table 1. The concentrations of individual PAHs in all of water samples (N = 77) from Danube River (collected at 1848, 1806 and 1766 river km) in the period of 2007-2010.

PAH compounds	**Total rings**	**Concentration ($ng \cdot L^{-1}$)**	
		Range	**Mean ± SD**
Naphthalene	2	1–120	21.09 ± 19
Acenaphthene	3	<1–15	3.62 ± 3.20
Acenaphthylene	3	<1–20	3.51 ± 3.77
Fluorene	3	<1–18	6.16 ± 3.96
Anthracene	3	<1–15	2.25 ± 2.28
Phenanthrene	3	4–136	25.79 ± 22.55
Fluoranthene	4	<1–130	11.35 ± 17.72
Pyrene	4	1–90	12.49 ± 14.08
Benz[*a*]anthracene	4	<1–13	1.90 ± 1.99
Chrysene	4	<1–9	2.14 ± 1.76
Benzo[*b*]fluoranthene	5	<1–25	2.23 ± 3.86
Benzo[*k*]fluoranthene	5	<1–25	1.95 ± 3.12
Benzo[*a*]pyrene	5	<1–13	1.60 ± 1.90
Dibenz[*ah*]anthracene	5	<1	<1
Indeno[123-*cd*]pyrene	6	<1–4	1.06 ± 0.37
Benzo[*ghi*]perylene	6	<1–5	1.13 ± 0.59
∑PAHs		**25–357**	**98.27 ± 58.48**

For instance, PAH data were collected during the Aquaterra Danube Survey (2004) undertaken in the environmental integrated project of the 6th EU Framework Programme. Numerous samplings were carried out along the longitudinal stretch of the River Danube from the upper section (Germany) to the Black Sea and in major tributaries. The PAH concentrations in water samples at different sampling stations along the whole Danube showed wide variations.

It has to be noted that concentrations of PAHs in our study were lower than in the surface waters of the Ráckevei-Soroksári Danube (the longest side-branch of the Hungarian Danube with its 57 km length is situated south from the capital city Budapest). The ∑PAHs concentrations were in the range of 129-1745 $ng \cdot L^{-1}$ with the mean value of 523 ± 348 $ng \cdot L^{-1}$ in the water samples of the Ráckevei-Soroksári Danube (NAGY, 2007). The higher levels of PAHs can be explained by urban area of Budapest. Furthermore, comparison our results with other sections of the Danube or even different rivers of the world (see Table 2 and the data in the mentioned references above) reveals that the PAH concentrations are relatively low at the Hungarian upper section.

Fig. 3 shows the distributions of monthly average concentration, standard deviation and median of ∑PAHs in surface water of the Hungarian upper section of the Danube.

The average monthly concentration of total PAHs (average of the three sampling sites in the examined four years) was highest in April and lowest in July. The median values were nearly consistent in the range of 65-93 ng·L^{-1} except the value of July with 25 ng·L^{-1}, respectively.

Table 2. Comparative levels of total PAHs in water samples collected from different locations.

Water	Year of sampling	N	n	Concentration (ng·L^{-1})		Reference
				Range	Mean ± SD	
Danube River, Hungarian upper section	2007-2010	77	16	25-357	98.27 ± 58.48	This study
Ráckevei-Soroksári Danube, Hungary	2002-2004	240	15	129-1745	523 ± 348	NAGY, 2007
Danube River, Germany-Black Sea	2004	31	16	28-1163	432 ± 336	NAGY, 2007*
Elbe River, Hamburg, Germany	1992-1993	20	22	60.9-381.6	145.5	GÖTZ *et al.,* 1998
York River, US	1998-1999	23	20	2.09-123	13.1 ± 24.51	COUNTWAY *et al.,* 2003
Mississipi River and Gulf of Mexico, US	1999	6	18	0.06-433.9	50.8 ± 164.6	MITRA and BIANCHI, 2003
Gao-ping River, Taiwan	1999-2000	48	16	10-9400	430	DOONG and LIN, 2004
Tonghui River, Beijing, China	2002	16	16	192.5-2651	762.3 ± 777.4	ZHANG *et al.,* 2004
Pearl River Estuary, China	2002-2003	21	15	12.9-182.4	NA	LUO *et al.,* 2008
Gomti River, India	2004-2006	48	16	60-84210	10330 ± 19940	MALIK *et al.,* 2011

N: number of collected samples, n: number of compounds of ∑PAHs, NA: not applicable

* The data were based on the Aquaterra Danube Survey (2004) Programme

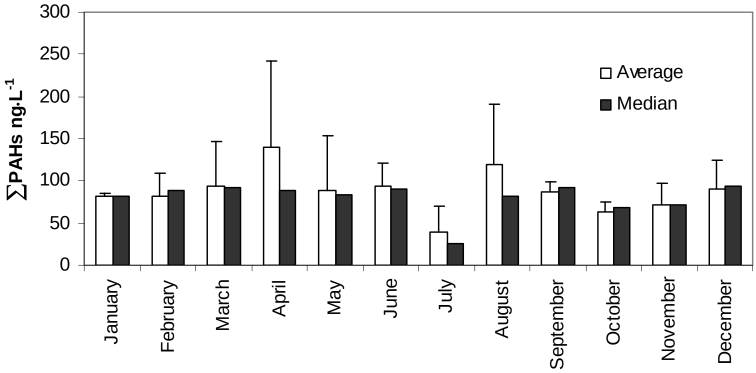

Fig. 3. Temporal variation of monthly average concentration of total PAHs in surface water of the Danube River in the period of 2007-2010.

Significantly higher value of monthly concentrations of ∑PAHs was also found in April at the Ráckevei-Soroksári Danube branch (NAGY, 2007). However, it cannot be explained by the more intense atmospheric fallout whereas the heating season startup can increase the amount of PAHs in autumn. Probably, more fine-grain bound or colloidal PAHs existed in dissolved phase in April. WITT (1995) associated that the lowest concentrations of PAHs also measured in summer is presumably due to the seasonal changes in degradation intensities. Possible explanation could be the increased degree of photodegradation in July due to the high temperature and light intensity in summer (FASNACHT and BLOUGH, 2002).

According to the formation mechanisms, PAHs can be classified as pyrogenic and petrogenic PAHs. Pyrogenic PAHs are formed as a consequence of incomplete combustion whereas petrogenic PAHs are mainly derived from crude oil and its refined products. Several concentration ratios of PAH compositions are used to infer the possible sources (YUNKER *et al.,* 2002; DOONG and LIN, 2004). In this study, the anthracene/(anthracene+phenanthrene) and fluoranthene/(fluoranthene+pyrene) ratios were calculated from the data of the water samples to try identifying the possible PAH origins (see Fig. 4).

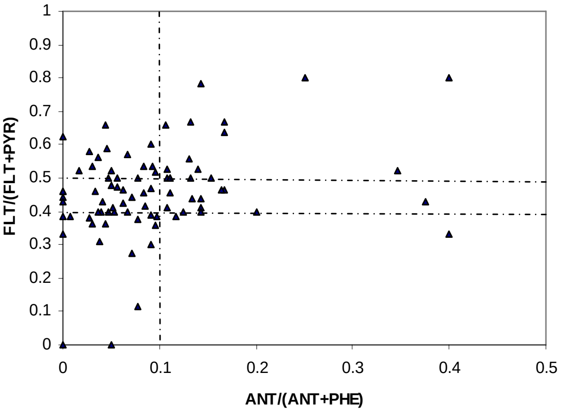

Fig. 4. Cross plot for the concentration ratio of anthracene/(anthracene+phenanthrene) versus fluoranthene/(fluoranthene+pyrene).

The ANT/(ANT+PHE) ratio < 0.1 indicates origin of PAHs from petrogenic sources, whereas the pyrogenic/combustion origin to ratio > 0.1. The concentration ratio of FLT/(FLT+PYR) < 0.4 suggests origin of PAHs from petrogenic sources, whereas value of FLT/(FLT+PYR) ratio 0.4-0.5 indicates PAHs combustion of liquid fuels and ratio > 0.5 infers PAHs combustion of solid fuels. The Fig. 4 illustrates that pyrogenic as well as petrogenic sources are responsible for the PAHs inputs in the surface water of the Danube. A previous study (JANÁK, 2007) reported that major part of the oil pollutions was originated from watercrafts, especially attributed to bilge oil drained into the water by the foreign ships in the Hungarian upper section.

Although concentration ratios of specific PAH compounds are often used for characterizing possible pollution sources, their ratios are influenced by several processes such as photooxidation, chemical oxidation and biodegradation. In addition, seasonal changes can be found in degradation intensities as it is mentioned above.

4. Conclusions

Concentrations of polycyclic aromatic hydrocarbons in surface water of the Hungarian upper section of the Danube River were studied in the period of 2007-2010. The total concentrations of the 16 USEPA PAHs ranged from 25 to 357 ng·L^{-1} with the mean value of 98.27 ± 58.48 ng·L^{-1}. The low and medium molecular weight PAHs (2-3 and 4 ring) ranged from <1 to 136 ng·L^{-1} while high molecular weight PAHs (5-6 ring) were present at much lower concentrations (<1-25 ng·L^{-1}). Of the total PAHs, the 2-3-ring PAHs contributed to about 64% while 4-6-ring PAHs accounted for 36%. Naphthalene and phenanthrene were found as the most dominant compounds with average distribution of 21 and 26% of the total PAHs in the river water. Evaluating the possible sources of PAHs showed that the PAHs were from both the pyrogenic and petrogenic origin in the Danube. Comparison of the ∑PAHs concentrations determined in our study with other section of the Danube and different rivers of the world revealed that the PAH concentrations are relatively low in the Hungarian upper section.

References

BAKER, J.E., EISENREICH, S.J.E.: Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior. Environ. Sci. Technol., 24, 1990, 342-352.

COUNTWAY, R.E., DICKHUT, R.M., CANUEL, E.A.: Polycyclic aromatic hydrocarbon (PAH) distributions and associations with organic matter in surface waters of the York River, VA Estuary. Organic Geochem., 34, 2003, 209-224.

DOONG, R., LIN, Y.: Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River, Taiwan. Water Res., 38, 2004, 1733-1744.

FASNACHT, M.P., BLOUGH, N.V.: Aqueous photodegradation of polycyclic aromatic hydrocarbons. Environ. Sci. Technol., 36, 2002, 4364-4369.

GÖTZ, R., BAUER, O.H., FRISSEL, P., ROCK, K.: Organic trace compounds in water of the river Elbe near Hamburg. Chemosphere, 36, 1998, 2103-2118.

JANÁK, E.: Important water management issues. Report, Inspectorate for Environment, Nature and Water of the North Transdanubian Region, Győr, Hungary, 2007 (in Hungarian)

KO, F.C., BAKER, J.E.: Partitioning of hydrophobic organic contaminants to resuspended sediments and plankton in the mesohaline Chesapeake Bay. Mar. Chem., 49, 1995, 171-188.

LUO, X.J., MAI, B.X., YANG, Q.S., CHEN, S.J., ZENG, E.Y.: Distribution and partition of polycyclic aromatic hydrocarbon in surface water of the Pearl River Estuary, South China. Environ. Monit. Assess., 145, 2008, 427-436.

MALDONADO, C., BAYONA, J.M., BODINEAU, L.: Sources, distribution and water column processes of aliphatic and polycyclic aromatic hydrocarbons in the Northwestern Black Sea water. Environ. Sci. Technol., 33, 1999, 2693-2702.

MALIK, A., VERMA, P., SINGH, A.K., SINGH, K.P.: Distribution of polycyclic aromatic hydrocarbons in water and bed sediments. Environ. Monit. Assess., 172, 2011, 529-545.

MANOLI, E., SAMARA, C.: Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis. Trends Anal. Chem., 18, 1999, 417-428.

MITRA, S., BIANCHI, T.S.: A preliminary assessment of polycyclic aromatic hydrocarbon distributions in the lower Mississippi River and Gulf of Mexico. Mar. Chem., 82, 2003, 273-288.

MSZ 1484-6:2003: Testing of waters. Determination of polycyclic aromatic hydrocarbons content by gas chromatographic-mass spectrometry (in Hungarian)

NAGY, P.G.: Determination of concentration and sources of polycyclic aromatic hydrocarbons and alkylphenols in Danube water and sediment. Ph.D. dissertation, University of Technology and Economics, Budapest, Hungary, 2007 (in Hungarian)

NAGY, P., FEKETE; J., SHARMA, V.K.: Polycyclic aromatic hydrocarbons (PAHs) in surface waters of Ráckevei-Soroksári Danube Branch, Hungary. J. Environ. Sci. Heal A, 42, 2007, 231-240.

SROGI, K.: Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ. Chem. Lett., 5, 2007, 169-195.

WITT G.: Polycyclic aromatic hydrocarbons in water and sediment of the Baltic Sea. Mar. Pollut. Bull., 31, 1995, 237-48.

YUNKER, M.B., MACDONALD, R.W., VINGARZAN, R., MITCHELL, H.R., GOYETTE, D., SYLVESTRE, S.: PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochem., 33, 2002, 489-515.

ZHANG, Z., HUANG, J., YU, G., HONG, H.: Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. Environ. Pollut., 130, 2004, 249-261.

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