World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:12, No:3, 2018

An Assessment of Water and Sediment Quality of the Danube River: Polycyclic Aromatic Hydrocarbons and Trace Metals

A. Szabó Nagy, J. Szabó, I. Vass

***Abstract*—**Water and sediment samples from the Danube River and Moson Danube Arm (Hungary) have been collected and analyzed for contamination by 18 polycyclic aromatic hydrocarbons (PAHs) and eight trace metal(loid)s (As, Cu, Pb, Ni, Cr, Cd, Hg and Zn) in the period of 2014-2015. Moreover, the trace metal(loid) concentrations were measured in the Rába and Marcal rivers (parts of the tributary system feeding the Danube). Total PAH contents in water were found to vary from 0.016 to 0.133 µg/L and concentrations in sediments varied in the range of 0.118 mg/kg and 0.283 mg/kg. Source analysis of PAHs using diagnostic concentration ratios indicated that PAHs found in sediments were of pyrolytic origins. The dissolved trace metal and arsenic concentrations were relatively low in the surface waters. However, higher concentrations were detected in the water samples of Rába (Zn, Cu, Ni, Pb) and Marcal (As, Cu, Ni, Pb) compared to the Danube and Moson Danube. The concentrations of trace metals in sediments were higher than those found in water samples.

***Keywords*—**Surface water, sediment, PAH, trace metal.

I. Introduction

TRACE metals and PAHs are two of the serious pollutants in the aquatic environment due to their toxicity, persistence and bioaccumulation. They can be derived from both natural and anthropogenic sources [1]-[6]. The highest concentration data are generally found around industrial areas and urban centers [3]-[6]. Trace metals and PAHs generally exist in low concentration levels in the water column [1], [2]. However, in most aquatic systems, concentrations of these pollutants in suspended sediment and the top few centimeters of bottom sediment are far greater than concentrations in the water column [1], [4], [5]. In addition, trace metals and PAHs are accumulated in aquatic plants, fish and many other animals (e.g. invertebrates) [7]-[9]. For example, a study on biomonitoring of heavy metals in fish from the Croatian part of the Danube River has indicated a hazard for consumers of fish based on the mercury accumulation [8].

In this paper, concentrations of trace metals, PAHs and the metalloid arsenic determined in surface water and sediment samples of the Hungarian upper section of the Danube River and Moson Danube Arm in the period of 2014–2015 are assessed with regards to quality guidelines. The measured concentration data are compared with the results of Rába and Marcal rivers which are parts of the tributary system feeding the Danube. The monitoring of surface waters and sediments was carried out within the framework of national water quality monitoring program.

A. Szabó Nagy and J. Szabó are with the Physics and Chemistry Department, Széchenyi István University, Győr, H 9026 Hungary (phone: 36-96-503-168; fax: 36-96-613-558; e-mail: nszaboa@sze.hu; jszabo@sze.hu).

I. Vass is with the Government Office for Győr-Moson-Sopron County, Environmental Protection Laboratory, Győr, H 9028 Hungary (e-mail: vass.istvan@gyor.gov.hu).

II. Materials and Methods

A. Study Area

The length of the Hungarian Danube section is 417 km (1850–1433 rkm) from which the length along the Hungarian and Slovakian border is 142 km [10], [11]. The sampling site (S) locations in the Hungarian upper section of the Danube (between 1848–1717 rkm, S1-S5), Moson Danube (2.4 and 45 rkm, S6-S7), Rába (1.9 rkm, S8) and Marcal rivers (18.4 rkm, S9) are shown in Fig. 1. A more detailed description of the study area can be found in our previous works [10], [11].

B. Data and Measurements

Dissolved trace metal(loid)s (As, Zn, Hg, Cd, Cr, Ni, Pb, and Cu) and PAHs (the 16 US EPA (Environmental Protection Agency) priority PAHs, 2-methylnaphthalene (mNAP) and benzo(e)pyrene) in Danube and Moson Danube waters (~30 cm below the surface) were monitored at the permanent national sampling sites under the authority of the Győr-Moson-Sopron County, Environmental Protection Laboratory. A total of 98 and 49 surface water samples for trace metal(loid)s and PAHs were collected in the period of 2014–2015, respectively. However, only five sediment samples (~10 cm deep) were collected in the examined period (see also Table I and II). Moreover, the dissolved trace metal(loid)s determined in a number of 18 and also 18 water samples of Rába and Marcal rivers, respectively. The metal(loid)s and PAHs analysis are presented in our earlier studies [10], [11]. The sediment concentrations are given in dry weight (d. w.) in this study.

III. Results and Discussions

A. Concentration levels of Trace Metals and Arsenic in Surface Waters

The ranges of trace metals and arsenic concentrations in the water samples from the examined surface waters in the period of 2014–2015 are summarized in Table I. The calculated mean concentrations for As, Cu, Ni, Zn, Pb and Cd are shown in Fig. 2. The observed maximum and annual average concentrations were compared with the European Union

environmental quality standards (EQS) for dissolved trace metal(loid)s in the inland surface water [12], [13] (Table III). In Hungary, the prevalent regulation corresponds to the European Union EQS [14]. The EQS values of Cd, Zn and Cu are dependent upon the hardness of the surface water. Generally, in freshwater, as the hardness increases, the trace metal toxicity decreases due to competition between the trace metal and Ca^{2+} and Mg^{2+} ions for the uptake sites of organisms [11]. In the study area, the water hardness is higher than the value of ≥100 mg L^{-1} as $CaCO_3$.

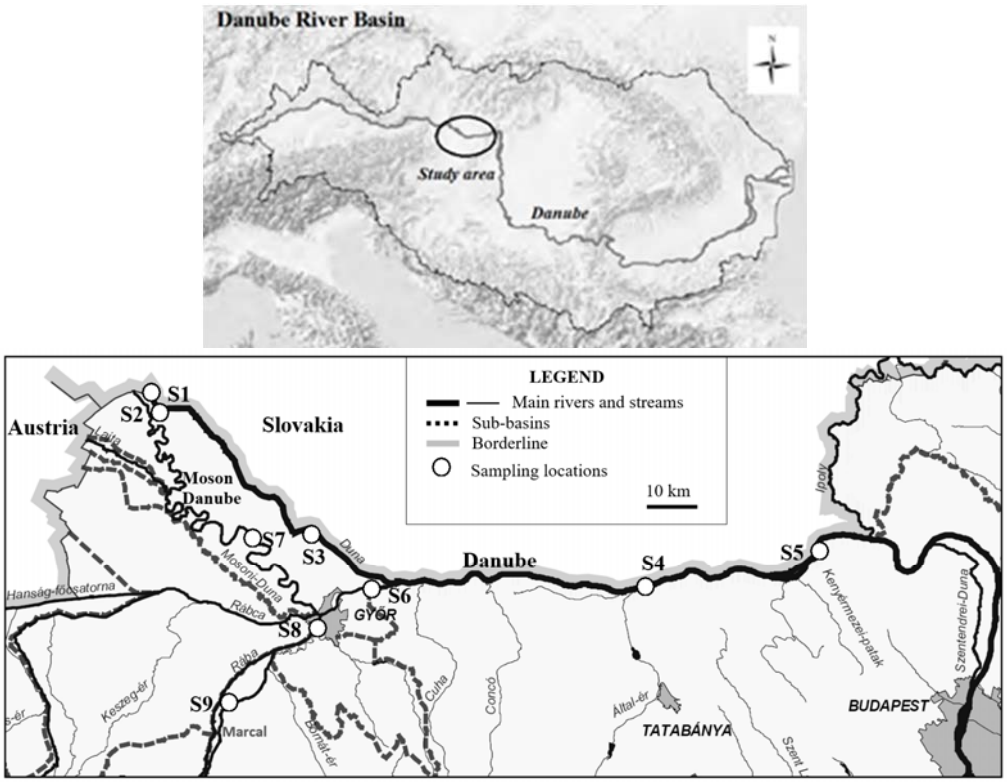


Fig. 1 The location of study area and sampling sites

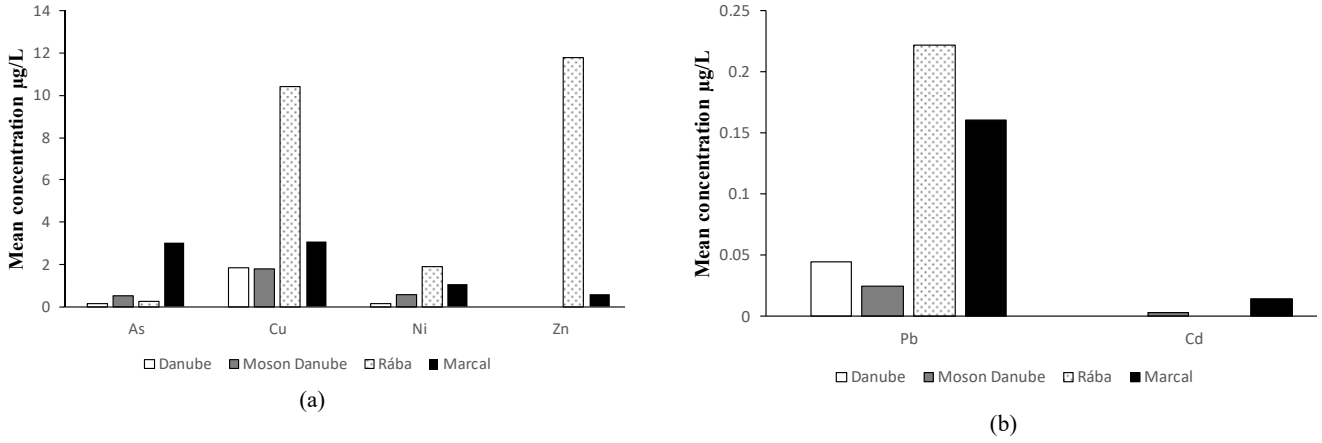


Fig. 2 Mean concentration of some trace metals and arsenic (a) and also Pb and Cd (b) in surface water samples

The total chromium was not detected in the water samples. The Hg was detected in only one sample collected from the Danube. Usually, the highest concentrations of other trace elements were measured in water samples collected from Rába and Marcal rivers. The highest concentrations for Cu, Ni, Zn and Pb were measured for Rába River. The highest As and Cd maximum and mean concentrations were found in the Marcal water samples. However, the annual average and maximum concentrations of trace elements in all years were below the permitted levels of EQS.

B. Concentration Levels of PAHs in Surface Waters

Table II shows the concentration levels of individual PAHs and total PAHs in the surface water from the Danube and Moson Danube for the examined period. The total PAH

concentrations in the river water of the Danube ranged from 0.016 to 0.131 µg/L with the mean value of 0.056 µg/L. Similar concentration levels for total PAHs were observed for Moson Danube with the range of 0.023–0.133 µg/L and the mean value of 0.058 µg/L.

The compositional pattern of total PAHs is shown in Figs. 3 and 4. The low molecular weight PAHs (two and three rings, LMW-PAHs) are the most abundant PAHs, which averaged 80 and 74 % of total PAHs in surface water of the Danube and Moson Danube, respectively. The four-ring PAHs constituting the middle molecular weight PAHs (MMW-PAHs) averaged 18 and 24 % of total PAHs. Naphthalene (NAP) and mNAP were the major species in water samples followed by phenanthrene (PHE), fluoranthene(FLT) and pyrene (PYR). The five- and six-ring PAHs constituting the high molecular weight PAHs (HMW-PAHs) were the least present. These compounds altogether averaged 2% of total PAHs for both surface waters.

TABLE I
CONCENTRATION RANGES OF TRACE METALS AND ARSENIC IN SURFACE WATER AND SEDIMENTS IN THE PERIOD OF 2014–2015

Trace metal (loid)	Surface water (µg/L)				Sediment (mg/kg d.w.)	
	Danube River,1848, 1806, 1766 and 1717 rkm (N = 61)	Moson Danube, 2.4 and 45 rkm (N = 37)	Marcal River, 18.4 rkm (N = 18)	Rába River, 1.9 rkm (N = 18)	Danube, Helenai Arm, 1845.5 rkm (N = 1)	Moson Danube, 2.4 rkm (N = 4)
As	<0.9–2.6 (n = 56)	<0.9–6.2 (n = 31)	<0.9–7.9 (n = 3)	<0.9–1.5 (n = 15)	7.6	10.6–14.1
Cu	<0.5–9 (n = 11)	<0.5–7.3 (n = 28)	<0.5–9.8 (n = 3)	<0.5–118 (n = 3)	22.8	22.1–39.4
Pb	<0.7–1.5 (n = 59)	<0.7–0.9 (n = 36)	<0.7–1.2 (n = 15)	<0.7–2.3 (n = 15)	19	12.9–32.2
Ni	<0.7–2 (n = 52)	<0.7–3.5 (n = 24)	<0.7–2.1 (n = 5)	<0.7–17.7 (n = 14)	23.4	31.8–43.0
Cr	<1.7	<1.7	<1.7	<1.7	20.4	43.2–63.4
Cd	<0.1	<0.1–0.1 (n = 36)	<0.1–0.14 (n = 16)	<0.1	1	<0.02–0.06 (n = 3)
Hg	<0.02–0.02 (n = 60)	<0.02	<0.02	<0.02	0.08	0.22–0.49
Zn	<10	<10	<10–10.6 (n = 17)	<10–175 (n = 16)	186	197–388

N = Number of total samples, n = Number of samples with concentration below the detection limit.

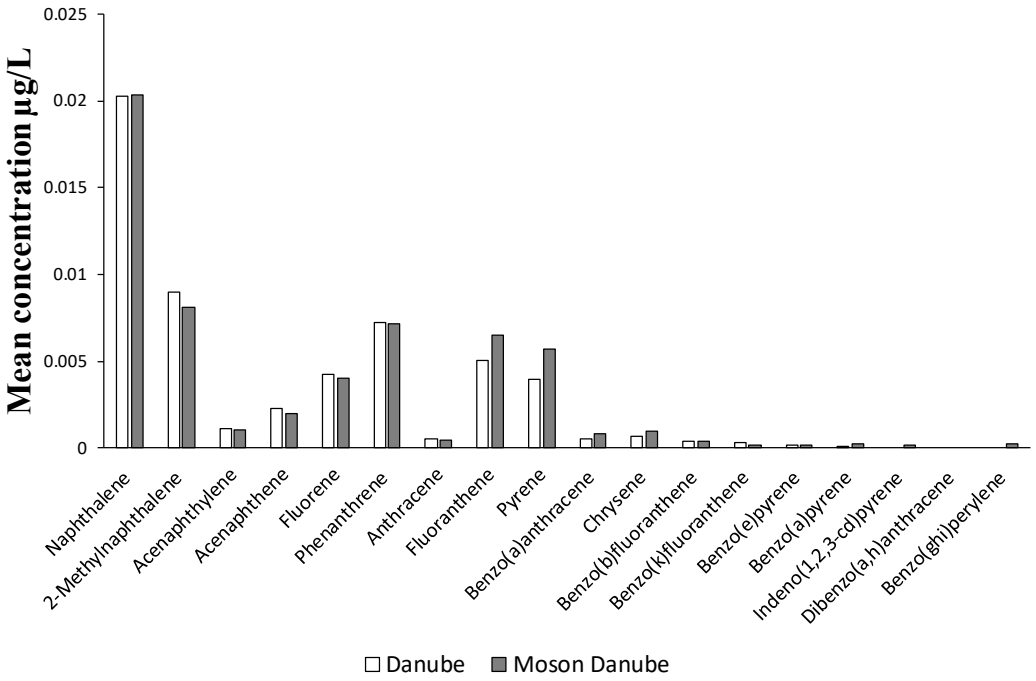


Fig. 3 Mean concentration of PAHs in surface water samples

TABLE II
CONCENTRATION RANGES OF PAHS IN SURFACE WATER AND SEDIMENTS IN THE PERIOD OF 2014–2015

PAH compound (total rings)	Surface water (μg/L)		Sediment (mg/kg d.w.)	
	Danube River, 1848, 1806 and 1766 rkm (N = 24)	Moson Danube, 2.4 and 45 rkm (N = 25)	Danube, Helenai Arm, 1845.5 rkm (N = 1)	Moson Danube, 2.4 rkm (N = 4)
Naphthalene (2)	0.001–0.074	0.007–0.048	0.00772	0.00155–0.00354
2-Methylnaphthalene (2)	0.002–0.032	0.003–0.025	0.00527	0.00071–0.00180
Acenaphthylene (3)	<0.001–0.003 (n = 8)	<0.001–0.004 (n = 14)	0.00321	0.00204–0.00368
Acenaphthene (3)	0.001–0.007	0.001–0.004	0.00217	0.00036–0.00073
Fluorene (3)	0.001–0.010	0.002–0.009	0.00341	0.00106–0.00215
Phenanthrene (3)	0.002–0.017	0.002–0.017	0.01520	0.00309–0.00596
Anthracene (3)	<0.001–0.003 (n = 14)	<0.001–0.002 (n = 16)	0.00807	0.00177–0.00601
Fluoranthene (4)	0.003–0.012	0.002–0.016	0.03661	0.01490–0.03230
Pyrene (4)	0.001–0.009	0.002–0.013	0.03102	0.01283–0.02452
Benzo(a)anthracene (4)	<0.001–0.002 (n = 13)	<0.001–0.003 (n = 9)	0.01872	0.00956–0.01481
Chrysene (4)	<0.001–0.003 (n = 9)	<0.001–0.003 (n = 8)	0.02130	0.00655–0.01553
Benzo(b)fluoranthene (5)	<0.001–0.002 (n = 16)	<0.001–0.002 (n = 18)	0.02927	0.00754–0.03034
Benzo(k)fluoranthene (5)	<0.001–0.002 (n = 18)	<0.001–0.001 (n = 21)	0.02637	0.00404–0.02845
Benzo(e)pyrene (5)	<0.001–0.002 (n = 21)	<0.001–0.001 (n = 21)	0.02285	0.00511–0.02387
Benzo(a)pyrene (5)	<0.001–0.001 (n = 22)	<0.001–0.001 (n = 20)	0.03020	0.00620–0.03689
Indeno(1,2,3-cd)pyrene (6)	<0.001	<0.001–0.001 (n = 21)	0.01479	0.00363–0.01481
Dibenzo(a,h)anthracene (5)	<0.001	<0.001	0.00196	0.00035–0.00206
Benzo(ghi)perylene (6)	<0.001	<0.001–0.001 (n = 20)	0.00486	0.00140–0.00801
Total PAHs	0.016–0.131	0.023–0.133	0.2830	0.11780–0.21930

N = Number of total samples, n = Number of samples with concentration below the detection limit.

TABLE III
ENVIRONMENTAL GUIDELINES OF TRACE METALS AND PAHS USED IN THIS STUDY FOR THE ASSESSMENT OF SURFACE WATER QUALITY [12], [13]

Pollutant	AA-EQS (μg/L)	MAC-EQS(μg/L)
As	25	-
Cu	5 or 30[a]	-
Pb	1.2	14
Ni	4	34
Cr(III)	4.7	32
Cr(VI)	3.4[b]	-
Cd	≤0.08–0.25[c]	≤0.45–1.5[c]
Hg	-	0.07
Zn	8 or 50 or 100[d]	-
Anthracene	0.1	0.1
Fluoranthene	0.0063	0.12
Naphthalene	2	130
Benzo(a)pyrene	0.00017	0.27
Benzo(b)fluoranthene	-	0.017
Benzo(k)fluoranthene	-	0.017
Benzo(ghi)perylene	-	0.0082

AA = annual average concentration, MAC = maximum allowable concentration, EQS = environmental quality standard.

[a]Where the result for total chromium is less than the EQS for Cr(VI), no further investigation is deemed necessary. Where there is a risk of Cr(VI) contamination, speciation studies should be included in the monitoring program.

The European Union EQS of PAHs for inland surface water are also shown in Table III. The measured concentrations of individual PAHs in all of water samples of Danube and Moson Danube were below the permitted levels of MAC-EQS. The annual average concentrations of anthracene (ANT), FLT, NAP and benzo(a)pyrene (BaP) in the Danube were less than the AA-EQs listed in Table III. The AA-EQs value of FLT was reached in the water samples of Moson Danube for the year of 2014. The calculated annual average concentration was 0.0065 μg/L. Relatively higher FLT concentrations were measured in winter and autumn sampling periods compared to spring or summer. However, the annual average concentrations of ANT, NAP and BaP were below the limit values of AA-EQS.

C. Sediment Quality

The concentration ranges of trace metals and PAHs in the examined sediment samples are also shown in Tables I and II. Figs. 5 and 6 illustrate the mean concentration data. The Hungarian limit values which were established for protection of the geological medium were used in this study for the assessment of sediment quality (Table IV) [15].

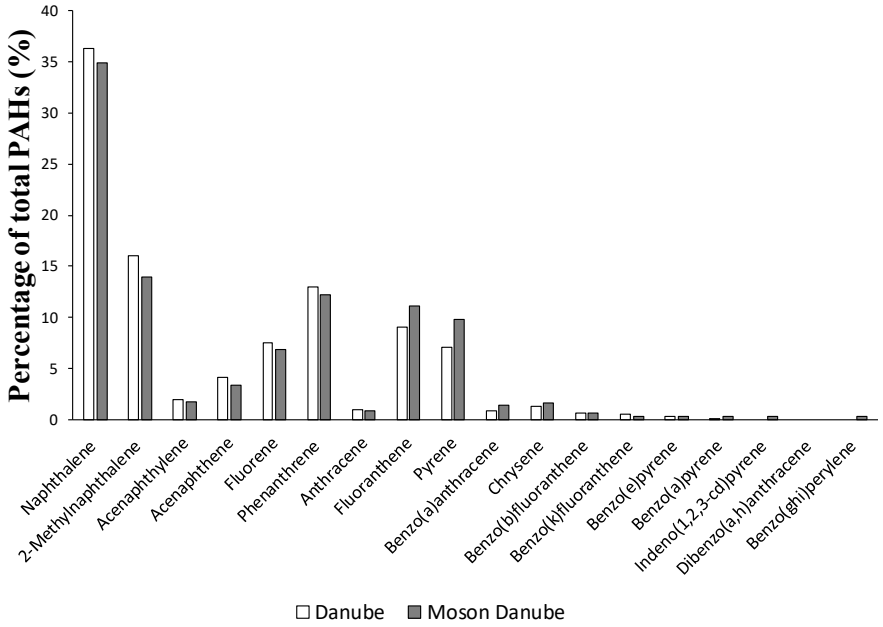
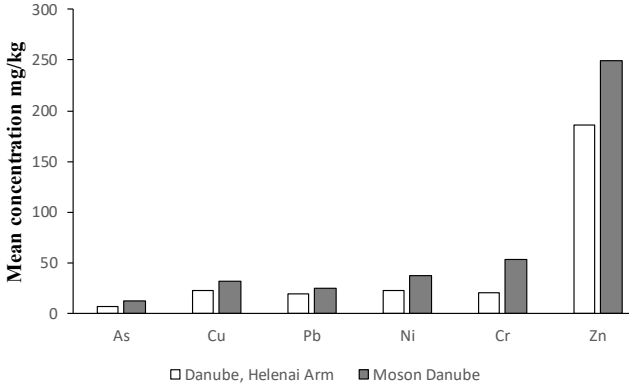
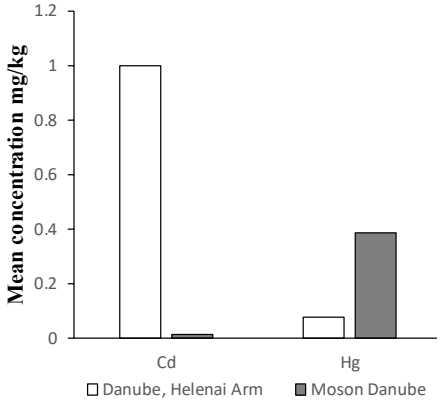


Fig. 4 Mean contribution of individual PAHs to total PAHs in surface water samples



(a)



(b)

Fig. 5 Mean concentration of some trace metals and arsenic (a) and also Cd and Hg (b) in sediment samples

All of the examined trace elements and PAH compounds were detected in the sediment samples. The mean percentage of individual PAHs to total PAHs is shown in Fig. 7. The HMW and MMW-PAHs were the most abundant compounds to total PAHs in the Helenai Danube arm (46 and 38 %) and Moson Danube (46 and 43%). FLT and PYR were the major species in sediment samples followed by BaP, benzo(b)fluoranthene and benzo(k)fluoranthene. However, the total PAH concentration in all sediment samples was below the limit value of 1 mg/kg. Furthermore, the molecular diagnostic ratios of ANT / ANT + PHE (0.25–0.53), FLT / FLT + PYR (0.54–0.60), benzo(a)anthracene (BaA) / BaA + chrysene (0.47–0.60), indeno(1,2,3-cd)pyrene (IND) / IND + benzo(ghi)perylene (0.54–0.76) were calculated [10]. These concentration ratios show that the PAHs found in sediments were of pyrolytic origins.

The sediments were also unpolluted for As, Cu, Ni, Cr and Hg according the Hungarian standards. The guideline value of 1 mg/kg for Cd was reached in only the one sediment sample of Helenai Danube arm. The guideline value of 200 mg/kg for Zn was exceeded in three sediment samples of the Moson Danube. However, the maximum concentration for Zn was nearly two time less than a wieldy used intervention value (720 mg/kg) for sediment quality assessment studies defined by the Dutch regulation [16]-[18]. Also, the highest Cd concentration (1 mg/kg) was less than the intervention value (12 mg/kg) according to the Dutch regulation [16], [17].

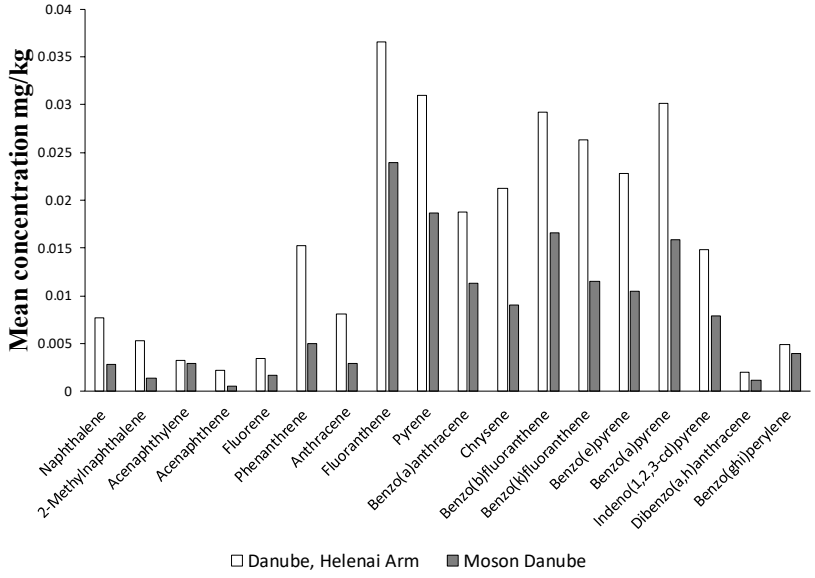


Fig. 6 Mean concentration of PAHs in sediment samples

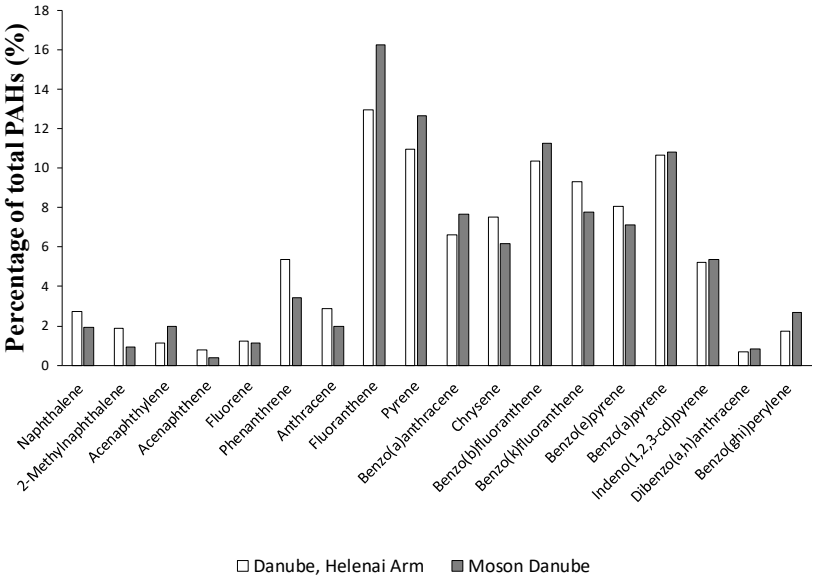


Fig. 7 Mean contribution of individual PAHs to total PAHs in sediment samples

TABLE IV
ENVIRONMENTAL GUIDELINES OF TRACE METALS AND PAHS USED IN THIS STUDY FOR THE ASSESSMENT OF SEDIMENT QUALITY [15]

Pollutant	Guideline[a] (mg/kg d.w.)
As	15
Cu	75
Pb	100
Ni	40
Total Cr	75
Cr(VI)	1
Cd	1
Hg	0.5
Zn	200
Total PAHs[b]	1

[a]The Hungarian limit values were established for protection of the geological medium; [b]Sum of the concentrations of 16 US EPA priority PAHs, 1-methylnaphthalene, 2-methylnaphthalene and benzo(e)pyrene.

IV. CONCLUSION

The available concentration data suggest that the surface water monitoring program in Hungary is probably enough to get a picture of the dissolved trace metal(loid)s and PAHs concentration levels in the examined surface waters. The results of this study have revealed that relatively low concentration levels of trace metal(loid)s and PAHs were detected in the water samples according to the European Union standard values. Also, the examined sediment samples were mainly unpolluted for PAHs and the most trace metals and arsenic in the period of 2014–2015. However, the sediment quality monitoring can be found insufficient based on relatively low number of samples.

ACKNOWLEDGMENT

This work was supported by the ÚNKP-17-4 New National Excellence Program of the Ministry of Human Capacities. We are grateful for the monitoring data and site information of our cooperation group members (especially for József Erdős) in Government Office for Győr-Moson-Sopron County, the Environmental Protection Laboratory (Győr, Hungary).

REFERENCES

[1] A. J. Horowitz, *A primer on sediment-trace element chemistry, 2nd edition.* United States Geological Survey: Denver, Open-File Report 91-76, 1991.
[2] ATSDR, *Toxicological profile for polycyclic aromatic hydrocarbons.* Agency for Toxic Substances and Disease Registry (ATSDR): Atlanta, GA, U.S. Department of Health and Human Services, 1995.
[3] E. Manoli, and C. Samara, "Polycyclic aromatic hydrocarbons in natural waters: sources, occurrence and analysis," *Trends Anal. Chem.,* vol. 18, no. 6, pp. 417–428, 1999.
[4] K. Srogi, "Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review," *Environ. Chem. Lett.*, vol. 5, pp. 169–195, 2007.
[5] E. C. Okafor; and K. Opuene, "Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments," *Int. J. Environ. Sci. Tech.,* vol. 4, no. 2, pp. 233–240, 2007.
[6] J. Ruelas-Inzunza, P. Spanopoulos-Zarco, and F. Páez-Osuna, "Cd, Cu, Pb and Zn in clams and sediments from an impacted estuary by the oil industry in the southwestern Gulf of Mexico: Concentrations and bioaccumulation factors," *J. Environ. Sci. Health A,* vol. 44, no. 14, 1503–1511, 2009.
[7] G. Beasley, and P. E. Kneale, "Investigating the influence of heavy metals on macro-invertebrate assemblages using Partial Cononical Correspondence Analysis (pCCA)," *Hydrol. Earth Syst. Sci. Discuss.,* vol. 7, no. 2, pp. 221–233, 2003.
[8] S. Zrncic, D. Oraic, M. Caleta, Z. Mihaljevic, D. Zanella, and N. Bilandzic, "Biomonitoring of heavy metals in fish from the Danube River," *Environ. Monit. Assess.,* vol. 185, no. 2, 1189–1198, 2013.
[9] O. O. Ajiboye, A. F. Yakubu, and T. E. Adams, "A review of polycyclic aromatic hydrocarbons and heavy metal contamination of fish from fish farms," *J. Appl. Sci. Environ. Manage.,* vol. 15, no. 1, 235–238, 2011.
[10] A. S. Nagy, G. Simon, J. Szabó, and I. Vass, "Polycyclic aromatic hydrocarbons in surface water and bed sediments of the Hungarian upper section of the Danube River," *Environ. Monit. Assess.,* vol. 185, no. 6, 4619–4631, 2013.
[11] A. S. Nagy, J. Szabó, and I. Vass, "Evaluation of trace metal levels in surface water and sediments of the Hungarian upper section of the Danube River and its tributaries," *J. Environ. Sci. Health A,* vol. 51, no. 14, pp. 1248–1261, 2016.
[12] EU Directive, *European Communities environmental objectives (surface waters) regulations 2009.* S.I. No. 272 of 2009.
[13] EU Directive, *European Union environmental objectives (surface waters) (amendment) regulations.* S.I. No. 386 of 2015.
[14] Hungarian Decree, *49/2015. (IX. 8.) BM 17. §, 8. Amendments to Ministerial Decrees on Water and Water Protection.* Hungarian Ministry of Interior: Budapest, 2015. (In Hungarian).
[15] Hungarian Decree, *6/2009. (IV. 14.) KvVM-EüM-FVM. KvVM-EüM-FVM common decree on the pollution threshold limit values for geological medium and groundwater protection and pollution measuring.* Ministry of Environment and Water Management, Ministry of Health and Ministry of Agriculture: Budapest, 2009. (In Hungarian).
[16] Dutch Guidelines, *Circular on target values and intervention values for soil remediation.* Ministry of Housing, Spatial Planning and Environment Directorate-General for Environmental Protection: Netherlands, 2000.
[17] P. Woitke, J. Wellmitz, D. Helm, P. Kube, P. Lepom, and P. Litheraty, "Analysis and assessment of heavy metal pollution in suspended solids and sediments of the river Danube," *Chemosphere,* vol. 51, no. 8, 633–642, 2003.
[18] D. M., Crnkovic, N. S. Crnkovic, A. J. Filipovic, L. V. Rajakovic, A. A. Peric-Grujic, and M. D. Ristic, "Danube and Sava river sediment monitoring in Belgrade and its surroundings," *J. Environ. Sci. Health A,* vol. 43, no. 12, pp. 1353–1360, 2008.