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Polycyclic Aromatic Hydrocarbons in Bottom Sediments from Three Water Reservoirs, Slovakia

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Abstract Thirty-four sediment samples were collected in three water reservoirs from the Slovak Republic to investigate polycyclic aromatic hydrocarbon (PAH) distribution and predict their possible sources. The results showed that the highest total PAH concentrations were associated with sediments from the Velke Kozmalovce, ranging from 7,910 to 29,538 ng/g of dry weight. On the other hand, the lowest total PAH concentrations (84–631 ng/g of dry weight) were found in sediments of the Zemplinska Sirava, an important recreational area in eastern Slovakia. The distribution of individual PAHs was consistent within the three water reservoirs, and this together with diagnostic PAH ratios suggests mainly pyrolytic contamination of the sediments. However, petrogenic inputs appear to be important in the Zemplinska Sirava sediments.

Keywords Polycyclic aromatic hydrocarbons · Distribution · Sediment · Sources · Water reservoir

Water reservoirs in the Slovak Republic are exposed to a constant silting up as a result of soil erosion and suspended sediment loads from rivers (Abaffy and Lukác 1991). In order to prevent the reduction of accumulation capacity and the risk of flooding, bottom sediments accumulated in a water reservoir should have to be dredged periodically. As the bottom sediments play an important role as sinks for many persistent organic pollutants (Warren et al. 2003), they may pose a risk for the environment after dredging and disposal of to land. To better predict environmental risks relating to the dredged contaminated sediments, it is necessary to determine in the first step the concentrations and sources of persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons are common environmental pollutants and may exhibit a wide range of hazardous effects to living organisms including mutagenicity and carcinogenicity (Delistraty 1997). There are numerous industrial, economical and social activities associated with combustion processes and discharges of oil derivates in Slovakia, which may produce large amounts of PAHs, contaminating gradually the environment. However, no data on PAH contamination of sediments in the water reservoirs of Slovakia are available to date.

The present study gives an overview on the contamination level of bottom sediments with PAHs in the three important water reservoirs from Slovakia, namely the Ruzin, the Velke Kozmalovce, and the Zemplinska Sirava. The water reservoirs are suspected to be contaminated with PAHs in river-borne suspended materials. Relative distributions and diagnostic ratios were also analyzed for the identification of possible sources of the PAH contamination.

Materials and Methods

The Ruzin reservoir with an area of 3.9 km^2 and a water volume of 59 × 10^6 m^3 lies at the northwest of Kosice,

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eastern Slovakia (Fig. 1). Two rivers flow into the reservoir: Hornad a Hnilec. The two rivers drain the Spiš-Gemer Rudohorie Mts., the area with long-time mining activities, ore-treatment and procesing industrial activities. Moreover, numerous urban waste discharges drain directly into the rivers. The reservoir of Velke Kozmalovce with an area of 0.62 km^2 and a total water volume of 2.7×10^6 m^3 lies on the River Hron near the village of Stary Tekov, western Slovakia (Fig. 1). The River Hron receives organic pollutants from direct discharges of industrial waste waters and atmospheric deposition. The largest reservoir is Zemplinska Sirava with an area of 15.1 km^2 and a water volume of 185×10^6 m^3. It lies at the northeast of Michalovce in eastern Slovakia and serves for flood-control, irrigation and recreational purposes. Kocan et al. (2001) have shown that the Zemplinska Sirava is highly contaminated with polychlorinated biphenyls produced by the Chemko chemical factory (Strazske) during the period of 1959–1984.

Samples were collected in June 2005. The sampling locations are shown in Fig. 1. Totally 34 sediment samples to a depth of 20 cm were collected using a stainless-steel corer. After collection, all samples were transferred to a glass jars and stored at −20°C until extraction. Frozen aliquots of sediment samples were air dried and then ground and sieved through a 2 mm sieve. A 10 g of sediment was extracted by sonication for 60 min with 20 mL mixture of *n*-hexane and acetone (1:1 v/v) in two cycles. The extracts were centrifuged at 4,000 rpm for 15 min and combined. A 5 mL of supernatant was removed and passed through 10 g of anhydrous Na_2SO_4 column to remove residues of water, and then eluted with 5 mL *n*-hexane and acetone mixture (1:1 v/v). The combined extracts were concentrated using Turbovap evaporator (Zymark, USA) to

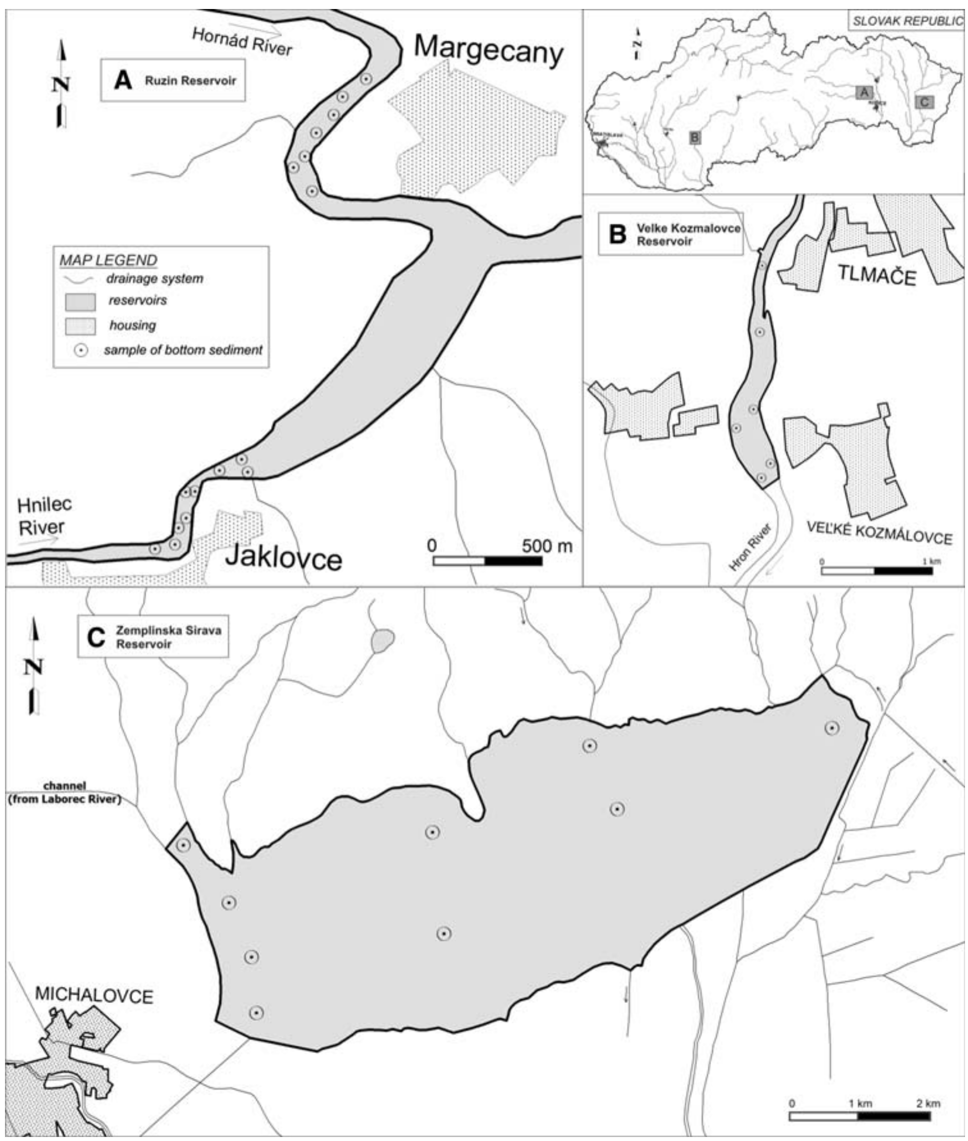

Fig. 1 Sampling locations of the sediments

approximately 2 mL and purified in a silica gel column. The column was eluted by 10 mL mixture of dichloromethane and *n*-hexane (1:10 v/v). The extracts were evaporated to dryness and the residues were dissolved in acetonitrile. The PAH extracts of the sediment samples were analyzed by HPLC (Agilent 1100 series) system equipped with fluorescence detector (HP 1046A) and a data station with HP ChemStation software package. The LiChrospher PAH column (250 mm × 4 mm) designed for the high resolution separation of PAHs was used. The mobile phases were acetonitrile and Milli Q + water in a linear gradient program. The flow rate of the mobile phases was kept at 1.0 mL/min and the injection volume was 20 μL. The response of the fluorescence detector was measured at various excitation and emission wavelengths which were optimal and specific for individual PAH substances. By this method, fifteen PAH substances were determined with the limit of detection of about 1 ng/g and relative standard deviation of 10%. To control analytical reliability and determine recovery efficiency, analyses were conducted on spiked sediment samples with known quantities of PAH mixture and reference material BCR-535 (freshwater harbour sediment). Recovery efficiences ranged from 76% up to 97% depending on the individual PAH substances. Total organic carbon (TOC) contents were determined using a CS analyser (Metalyt CS 100/100, Eltra, FRG).

Results and Discussion

The mean concentrations of each PAH and total PAH (expressed as the sum of the concentrations of 15 parent PAH compounds and denoted as ΣPAH) are given in Table 1. The total PAH concentrations in sediments varied widely among the three water reservoirs. The maximum concentrations of total PAH were recorded in sediments from the Velke Kozmalovce (7,910–29,538 ng/g), followed by sediments from the Ruzin (2,697–756 ng/g). The lowest total PAH concentrations, ranging from 84 to 631 ng/g were observed in sediments from the Zemplinska Sirava. The high contamination level of the Velke Kozmalovce sediments with PAHs and also relatively high TOC contents in these sediments could be ascribed to the direct discharges of organic-rich waste waters from heavy industry into the River Hron which supplies the reservoir with water. Atmospheric deposition might be also a significant source of PAHs as the whole catchment area of the River Hron is highly industrialized with activities associated with the consumption of coals, e.g., ore-procesing, wood and petrochemical industries. The total PAH concentrations covering wide range of contamination levels observed in this study are comparable with those from other studies. For example, data published by Boháček et al. (2003) in the Horní Bečva reservoir (Czech Republic) showed a total PAH concentrations ranging from 3,550 up to 80,400 ng/g in sediments collected to the depth of 30 cm. Even the sediments from high altitude lakes of the High Tatra Mts. (Slovakia) appear to be contaminated with PAHs (18,000 ng/g) (Fernández et al. 1999) comparatively to the sediments from Velke Kozmalovce. On the other hand, Baran et al. (2002) reported lower contamination with PAHs in sediments from the River Narew (Poland), ranging from 21 to 600 ng/g, with an overall level lower than 160 ng/g for most of the sediments. When total PAH concentrations from the three water reservoirs were combined, a significant correlation was found between total organic carbon content and PAH concentration ($r = 0.671$; $p < 0.001$). However, this was not a case when the three water reservoirs were considered separately. Therefore, it is suggested that the observed distribution of PAHs in sediments was not governed mainly by sediment organic matter contents, but it might be related to the location and strength of sources from which PAHs originate. This is in close agreement with other studies where no correlation between TOC and ΣPAU was observed (Storelli and Marcotrigiano 2000; El Deeb et al. 2007).

Polycyclic aromatic hydrocarbons naturally occur in complex mixtures. Their composition may be used to characterize and identify the possible sources of contamination. This was done by calculation of PAH distributions (expressed as weight percentages of the total PAH concentrations) and several diagnostic PAH ratios indicating the source of PAHs. In most of the sampling sites almost identical PAH distributions were observed. Figure 2 shows the mean PAH distributions in sediment samples from the three water reservoirs investigated. This uniformity in the PAH distributions with predominant fluoranthene and pyrene suggests a similar source of PAHs in most of the sediment samples regardless of the reservoir location. The ratio of low molecular weight PAHs to high molecular weight PAHs (LMW/HMW) can be used as an indication for petrogenic or pyrolytic origin of PAHs (Soclo et al. 2000). The low values of the LMW/HMW ratios in the sediments (Table 1) suggest that high temperature processes are the predominant source of PAHs. To characterize PAH sources further, the selected diagnostic ratios were calculated (Fig. 3) as proposed by Yunker et al. (2002). The Fl/Fl + Py ratios were higher than 0.50 and almost the same in the sediments. This indicates that pyrolitic inputs are the major source of PAHs in the reservoir sediments. Additional ratios were also determined simultaneously in order to give a better estimate of PAH sources. It could be seen from Fig. 3 that PAHs in the sediments seemed to be of pyrolytic origin, although some petrogenic inputs were important for PAH contamination

Table 1 Concentrations and standard deviation (SD) of individual and total PAHs (ng/g of dry sediment) and total organic carbon contents (%) in the sediment samples

	Ruzin			Velke Kozmalovce			Zemplinska Sirava		
	Mean	Range	SD	Mean	Range	SD	Mean	Range	SD
Na	55.4	26–85	15.7	123	59–296	90.2	11	5–15	3.94
Ac	26.6	11–83	17.3	308	122–665	194	ND[a]		
Ph	373	212–654	119	1464	662–2604	713	58	19–100	28.7
A	90.6	48–229	44.6	361	150–597	163	5.89	1–9	3.26
F	37.2	19–91	17.2	466	198–910	254	11	6–18	4.21
Fl	887	492–1569	258	6982	2580–11720	3250	69.1	9–103	35.6
Py	725	417–1227	203	4861	1808–8270	2387	54.9	4–87	31.6
BaA	372	211–580	94.2	1671	654–2440	675	13.8	1–27	8.2
Chr	398	229–585	101	1132	521–1630	409	31.3	3–51	17.4
BbF	385	227–544	88.6	512	336–678	124	43.4	8–70	22.8
BkF	236	122–374	71	282	173–382	73.1	18.4	2–27	9.45
BaP	450	272–680	110	473	294–636	129	34.6	5–55	18.7
IP	389	227–583	90.2	223	194–282	31.2	44.3	6–71	19.9
DA	49.7	32–72	10.8	33.2	26–44	6.37	5.78	3–9	2.17
BP	242	152–354	60.5	145	119–193	26.6	31.1	12–48	13.9
ΣPAH	4719	2697–7561	1232	19034	7910–29538	8227	434	84–631	205
TOC[b]	4.95	2.26–7.40	1.55	7.28	6.12–8.72	0.89	2.13	0.74–3.93	0.89
LMW[c] HMW	0.14	0.12–0.19	0.018	0.17	0.13–0.21	0.033	0.29	0.16–0.59	0.13

[a] *ND* below detection limit, *Na* naphthalene, *Ac* acenaphthene, *Ph* phenanthrene, *A* anthracene, *F* fluorene, *Fl* fluoranthene, *Py* pyrene, *BaA* benzo(*a*)anthracene, *Chr* chrysene, *BbF* benzo(*b*)fluoranthene, *BkF* benzo(*k*)fluoranthene, *BaP* benzo(*a*)pyrene, *IP* indeno(1,2,3-*cd*)pyrene, *DA* dibenzo(*a*,*h*)anthracene, *BP* benzo(*g*,*h*,*i*)perylene, [b]*TOC* total organic carbon, [c]*LMW/HMW* ratio of low molecular weight PAHs to high molecular weight PAHs = (Na + Ac + Ph + A + F)/(Fl + Py + BaA + Chr + BbF + BkF + BaP + IP + DA + BP)

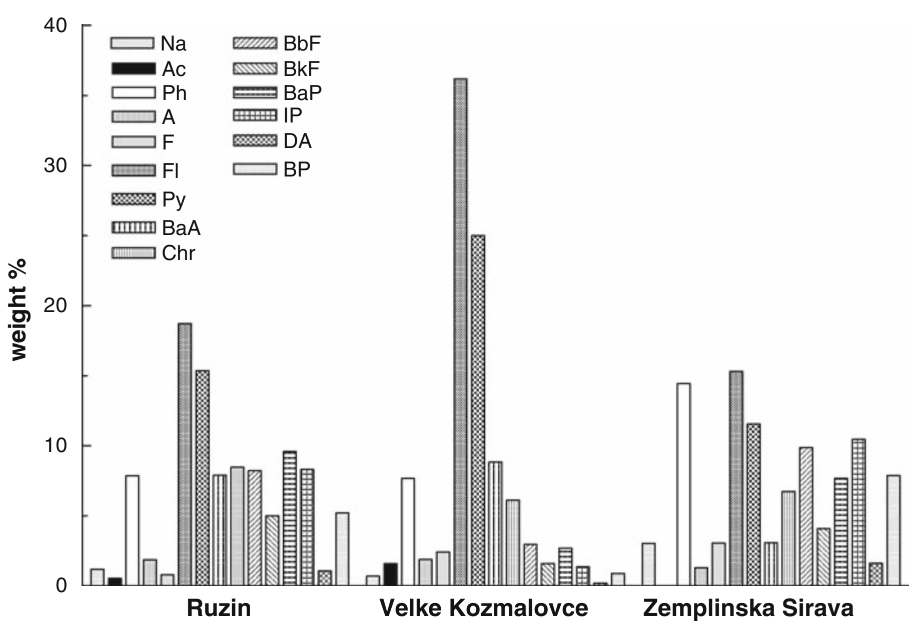

Fig. 2 Mean distributions (in weight percentages) of individual PAHs in the sediments of the Ruzin, Velke Kozmalovce and Zemplinska Sirava water reservoirs

in the Zemplinska Sirava reservoir as the A/A + Ph and BaA/BaA + Chr ratios were below 0.1 and 0.35, respectively, and phenanthrene became the predominant constituent (Fig. 2). The Zemplinska Sirava reservoir is a well-known recreational area with many auto-camps, yacht-clubs and shipping activities. Therefore, accidental

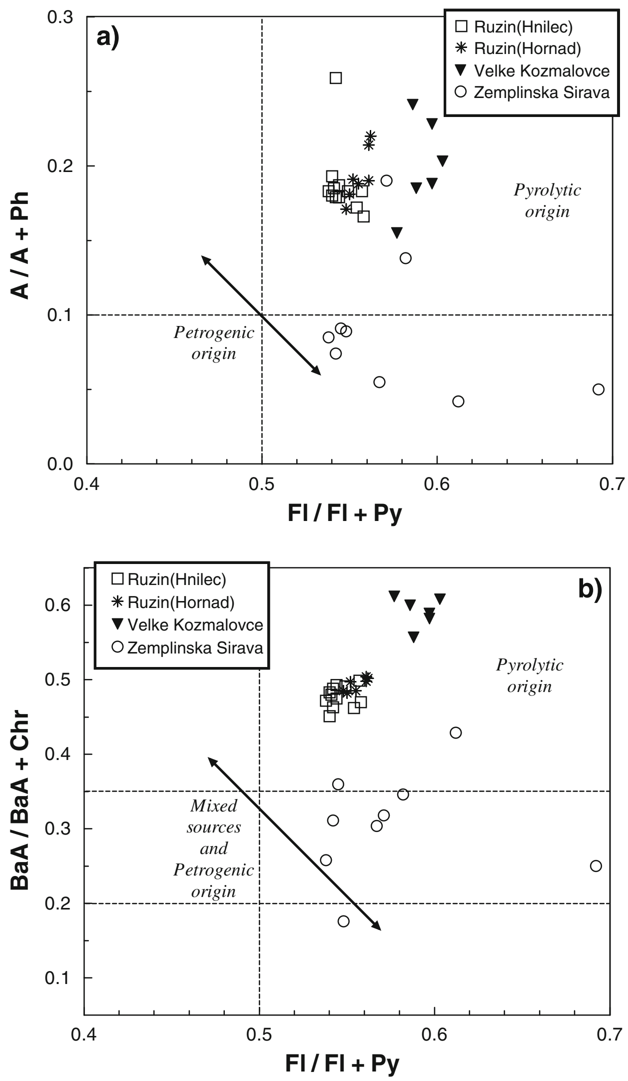

Fig. 3 Plots of selected diagnostic ratios for the identification of sources of polycyclic aromatic hydrocarbons in the sediments of the water reservoirs

and intended seepages of fuels during the loading and repairing might contribute to the petrogenic origin of PAHs in these sediments.

In summary, our study demonstrated that the total PAH concentrations in bottom sediments varied greatly among the three water reservoirs. The contamination with PAHs decreased in the following order: Velke Kozmalovce > Ruzin > Zemplinska Sirava and seemed to be related directly to the extent of industrialization in surroundings of the water reservoirs. The major inputs of PAHs are of pyrolitic origin, although petrogenic origin of PAHs occurs in the Zemplinska Sirava sediments.

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