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Purgeable Aromatic Hydrocarbons in Water and Sediment from the River Morava Catchment (Slovakia)

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The Morava River receives discharges from both industrial and domestic sources. In the Morava catchment , the oil fields and sugar works are the main sources of industrial pollution. The Czech and Slovak 30 sugar works, mainly in the season of peak production, strongly pollute all the rivers entering the Danube such as the River Morava (Kovacs 1978).

The domestic wastes of the small cities which are situated on the different branches of Morava (Figure 1) (Myjava 73 km, Rudava 38 km, Malina 29 km and Mláka 11 km), enter the Morava River without being purified. There are 42 sources which discharge their wastewater to the River Morava (Horváthová and Madarászova 1990). The rough mass balance made by Water Research Institute in Bratislava shows that the input of organic matter and nutrients from point sources in Bratislava area are relatively low in relation to the amounts that are transported by the Morava River. Concentrations of nutrient and organic matter are higher in the water of Morava River than the Danube River (Jensen 1992). The rough estimate of loadings based on everage values indicate that the organic transport in Morava River is approximately 10-15 % of that of Danube River. These estimates indicate that the input of pollutants from Morava River can be significant contribution to the Danube at least for certain periods.

Volatile aromatic hydrocarbons constitute an important fraction of volatile organic compounds (VOCs) in the aquatic environment. More importantly, the volatile aromatic components benzene, toluene, ethylbenzene, and xylenes (BTEX) are generally considered to be the most mobile and toxic hydrocarbon constituents. Volatile aromatic compounds are present everywhere in estuaries accounting for between 48-74 % of all volatile organic compounds (VOCs) found in water samples, and 32-78 % of all VOCs in sediments, taking into account that some variation is due to sampling time and place (Bianchi 1991). BTEX are emited by industrial processes, automobile exhaust, raw sewage and road run-off. Toluene is the only volatile aromatic which has both natural (biogenic) and man-made (anthropogenic) sources. Volatile aromatic hydrocarbons are nonbiodegradable, low-molecular weight compounds and they are included in the list of refractory organic industrial wastes (Meyer *et al.* 1981), and in the USEPA purgeable priority pollutants list (USEPA 1989).

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Exposure to aromatic hydrocarbons can cause serious health problems. Benzene is known as to be leukaemic agent in humans (Vigliani 1976). The toxic properties of toluene, ethylbenzene, and xylenes have been frequently studied (Sittig 1980; Rinsky *et al.* 1987; Rastogi 1993).

The analysis of volatile aromatic compounds in water and sediment has become an important task in many environmental laboratories. Since Swinnerton and Linnenbom (1967), Grob (1973), Bellar and Lichtenberg (1974), purge and trap injection and gas chromatography analysis (PTI-GC) represents one of the most scientifically advanced techniques available for the detection of VOCs in water (Núñez *et al.* 1984). However, the direct application of these methods for analysing VOCs in sediments is not straightforward and must take into account complicating factors such as sediment composition, physico-chemical properties of sediments and organic compound classes involved (Bianchi *et al.* 1991). The purge and trap techniques specified in the USEPA method 503.1 (GC-conventional detectors) for monitoring volatile aromatic organic compounds in water require cryogenic refocusing in order to effectively transfer the analytes to capillary GC column (Supelco 1991). The Chrompack PTI system represents one of the newest advanced techniques to purge and trap VOCs from the water sample. The purged volatiles were trapped on fused silica cold trap, cooled with liquid nitrogen and injected into the capillary column of a gas chromatograph for analysis. This technique is invaluable in the analysis of VOCs at very low concentrations (ppb/ppt).

Bianchi (1991) modified the EPA method 503.1 open-loop dynamic headspace technique for stripping and trapping the VOCs from estuarine sediment. The method used 300-400 g wet weight of sediment. In this work, the sample preparation procedure of Bianchi (1991) has adapted. A sediment sample, 10-20 g wet weight, was transferred into the glass vial of the purge and trap injector, and purged with Chrompack PTI technique at 60 mL/min of pure nitrogen for 10 min at ambient temperature. Although some studies and reports of water quality have been made in the catchment of the River Morava, to date no studies have examined the presence of volatile aromatic compounds. This study aimed to evaluate the water quality of the River Morava with respect to volatile aromatic compounds. The present preliminary study was done to determine the concentration levels and the distribution of selected purgeable aromatics along the catchment of the River Morava.

MATERIALS AND METHODS

Ten stations were selected in the catchment of the River Morava to investigate the identity and quantity of the volatile aromatic compounds in water and sediment samples.

The samples were collected along the length of four main branches of the River Morava (Myjava, Rudava, Malina and Mláka), as in Fig.1. Three stations in the lower part of the Morava basin were chosen to study the effect of seasonal variation on the concentration levels and distribution of volatile aromatic

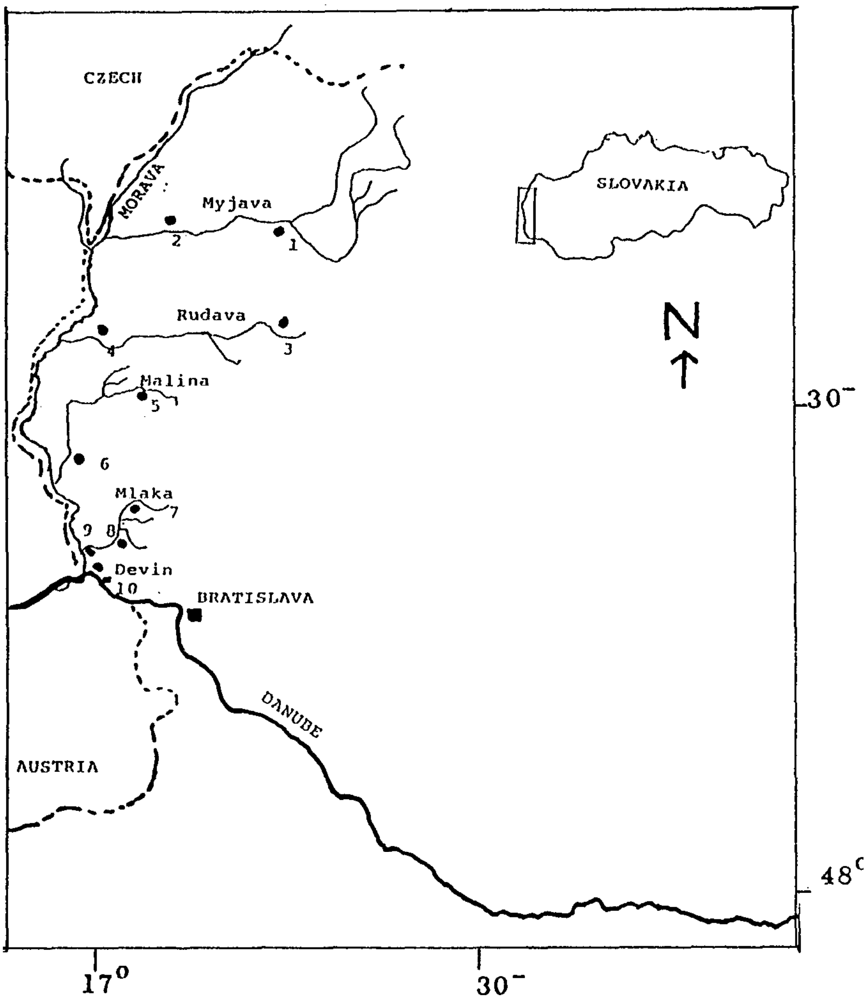

Figure 1. Map of the River Morava showing the locations of sampling station.

compounds. Water samples were collected in 1-L amber-glass bottles with aluminium foil-lined caps by filling the sample bottle to overflow from the sub-suface water. Sediment samples were collected in sealed glass containers (200-300 g wet weight) by using small shovel of 1 kg sediment. All glassware used were acetone-rinsed then oven-dried at 120 °C for about 24 hr prior to use. Both water and sediment samples were transported in cooled box to the laboratory for immediate analysis, by using PTI-GC.

Standards were prepared by using a commercial-grade aromatic hydrocarbons and methanol, both supplied by Lachema n.p. Brno, Czech Republic. The standard mixture contained target volatile aromatic components, which were added to stripped water as described by Bianchi (1991) and sediment for assessing recovery and method detection limits. These standards were used also for quantification of volatile aromatic compounds in water and sediment samples. Detection limits and recoveries were obtained from analysis of 7 replicates aqueous composite standard solutions at concentrations of 0.1, 1.0, 10, and 100 µg/L.

The purge and trap gas chromatograph used for this study was Chrompack CP9000, equipped with flame ionization detector (FID), 30 m x 0.25 µm ID, OV-1 wall-coated open-tubular fused silica capillary column 0.5 mm film thickness, rogrammed from 40 °C (for 2 min) to 150 °C at 10 C/min . According to the Chrompack PTI design, 20 mL of water sample was put into the purge vial. The sample was purged with pure nitrogen for 10 min. Purge flow was 60 mL/min nitrogen at the ambient temperature. The method of Bianchi (1991) for the analysis of sediment sample has adapted by using small size of sample to be applied with PTI-GC system from Chrompack CP 9000. The sediment samples were mixed with free-organic water at ratio 3:1 wet weight sediment to water. A 10-20 g wet weight of the prepared sediment was transferred into the purge vial, and then stripped under the same conditions previously described for water samples.

RESULTS AND DISCUSSION

The peak areas of seven replicates of four different concentrations of BTEX in reagent water, river water and sediments are given in Table 1. The precision of the peak areas for these measurements, expressed as relative standard deviation (RSD), were in the range of 2.8 to 16.7 %, which is acceptable for the determination of VOCs in water and sediment. The determination of peak areas for the concentration range from 0.1 to 100 µg/L in water and similar concentrations in sediments had no profound effect on the precision of the results . Linear relationship between the peak areas and the concentration of BTEX were obtained for the range of 0.1-100 µg/L.

The recoveries were calculated from the mean peak areas of volatile aromatics of river water and sediments in relation to those from reagent water (Table 1). Recoveries of BTEX in water ranged from 85.2 to 93.7 % and in sediment from 55.7 to 68.5 % (Table 2). The RSD of the recoveries varied from 3.4 to 6.5 for water and 9.0 to 13.6 for sediments .

The values of method detection limits (MDL) were calculated using the following equation and a 99 % confidence level

$$MDL = t_{n-0.01} . (SD)$$

where MDL equals the method detection limit; $t_{n-0.01}$ equals the Student's t value appropriate for 99 % confidence interval and a standard deviation estimate with n-l degree of freedom and SD equals the standard deviation of the 7 replicate analyses as used by USEPA. The MDL were in the range of 0.02-0.04 µg/L aromatics in water and 0.04-0.05 µg/kg wet weight in sediment samples. These results confirmed that the method used allowed the determination of BTEX were at sub-ppb concentrations.

The average concentration of volatile aromatics in water and sediment for two samples collected every season are given in Tables 3 and 4. The results show that the seasonal fluctuation in the concentration of volatile aromatics in water and sediment is primarily a function of temporal changes in volatile loadings (from

Table 1. The mean* of the peak areas and % RSD for different concentrations of volatile aromatics in water and sediment using PTI-GC

Conc.	0.1 µg/L, 0.1 µg/kg			1 µg/L, 1µg/kg			10 µg/L, 10 µg/kg			100 µg/L , 100 µg/kg		
Matrix	reagent water	river water	sediment	reagent water	river water	sediment	reagent water	river water	sediment	reagent water	river water	sediment
Compound	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD	area %RSD
Benzene	3522 10.7	2691 14.0	2624 11.5	24703 8.4	22436 16.7	19041 8.1	202933 6.0	185329 5.8	123826 8.6	1737242 5.1	1536483 4.0	1067022 9.8
Toluene	10431 13.7	8695 6.4	8404 15.6	32342 10.6	29041 15.7	33700 6.0	223910 7.6	20373 6.7	124503 6.7	1995014 5.2	1878516 2.8	1232255 10.2
Ethyl-benzene	2315 8.9	2263 10.7	1732 13.2	18273 9.4	16679 6.9	9291 7.6	163232 4.8	147741 5.4	73875 9.0	1352909 5.5	1327799 2.8	724698 10.0
p,m-Xylene	3303 7.2	2928 9.9	2672 11.1	25543 8.2	24303 13.2	13197 9.5	221999 7.3	202688 5.5	100292 9.7	1894793 4.1	1844985 2.8	1004350 10.3
o-Xylene	3294 12.4	2519 12.1	2563 13.3	22354 8.0	20106 14.2	11731 6.5	184285 7.1	157861 6.0	83189 11.5	1536684 3.2	1403809 3.3	832952 10.2

*mean is from 7 replicates.

Table 2. Recoveries and detection limits for 0.1 µg/L volatile aromatics in water and sediment using PTI-GC

Compound	water			sediment		
	recovery	% RSD	MDL[1]	recovery	% RSD	MDL[2]
Benzene	87.6	5.4	0.03	68.5	10.0	0.05
Toluene	89.4	6.5	0.05	63.5	9.9	0.05
Ethylbenzene	93.7	8.1	0.03	55.7	13.6	0.04
p,m-Xylene	93.0	3.4	0.02	57.6	9.0	0.04
o-Xylene	85.2	4.1	0.04	58.6	9.1	0.04

1 = MDL in mg /L for water

2 = MDL in mg /kg wet weight for sediment.

industrial and domestic waste-water) and the temperature variation in the river ecosystem. Major factors influencing volatile aromatic concentrations are temperature and concentration. The results in the Tables 3 and 4 show that there is a wide variation in the concentration of BTEX over the three seasons and the variation in concentrations is due to seasonal changes. For example, the minimum concentrations of volatile aromatics in sediment was observed in summer months (July, August). The higher average temperature in summer increases the evaporation of volatile aromatics from the water surface in comparison to the sorption and adsorption processes. In contrast, the lower temperatures of winter and spring months (January, February, March, April) combined with increases in organic matter added to the river from its sources, cause the increased accumulation of volatile aromatics in sediment. During the autumn season the natural inputs (leaf-fall) and anthropogenic inputs become greater (e.g., from increased rain fall run-off, increased used of fossil fuels and dry fallout), contributing additional volatile aromatics to the sediment. The effect of the autumn season on the concentration of volatile aromatics in water and sediments of the River Morava will be determined in a forthcoming study.

Tables 3 and 4 demonstrate that the total average concentration of volatile aromatics in sediments is in range from 6.19 to 295 µg/kg wet weight and from 0.30 to 8.61 µg/L for water samples. The average concentration of total volatile aromatics shows that the sediments contain levels about 30 times higher than that of water. The results are in agreement with the literature values cited by Bianchi (1991) and that sediments accumulate much higher levels of volatile aromatics than might normally be found in the water column. Table 5 shows the analytical results of one winter sample (Feb. 1993) of 7 stations from four main branches in the catchment of the Morava. These samples were analyzed in order to describe the main sources and the distribution of volatile aromatics along the catchment of the River Morava. Differences in the concentrations of volatile organic compounds between four branches of the Morava were observed. The River Myjava contained relatively higher concentrations of volatile aromatic compounds than the other branches of the River Morava . Table 5 shows that ethylbenzene and xylenes were not detected in the samples collected in winter 1993; however, in 1992 these compounds at the same stations were detected (Tables 3 and 4). The present study has shown that toluene was generally detected at the highest concentrations at all stations compared to the other volatile aromatics. This may be due to the several sources of toluene , and also because the toluene is the only volatile aromatic in water which has both natural (biogenic) and man-made sources (Bianchi 1991). The biogenic formation of toluene can take place by several biological pathways under microbiological mechanisms (Juttner 1986), especially in the weeks following the autumn leaf fall. Within certain stretches of water the natural source of toluene is dominant contributor to river concentrations.

Our data show that by using PTI-GC the concentrations of benzene, toluene, ethylbenzene, and xylenes in water and sediments of the catchment of the River Morava have been determined at ppb, respectively sub-ppb concentrations. The study shows also that the volatile aromatic compounds in water and sediment of the River Morava may originate from the natural and man-made sources. Relatively higher levels of aromatics were found in spring time. The river sediments were

Table 3. Seasonal variation in concentration of volatile aromatic compounds in water sampls in µg/L

Compound	Mláka 8			Mláka 9			Devin 10		
	winter	spring	summer	winter	spring	summer	winter	spring	summer
Benzene	0.50	1.89	ND	0.68	2.02	ND	ND	ND	ND
Toluene	0.58	3.49	ND	0.43	1.43	ND	0.03	1.05	ND
Ethylbenzene	ND	1.55	ND	ND	4.69	ND	ND	ND	ND
p,m-Xylene	0.16	0.97	ND	0.06	0.47	ND	ND	0.28	ND
o-Xylene	0.18	ND	ND	ND	ND	ND	ND	ND	ND
Total	1.42	7.90	ND	1.17	8.61	ND	0.03	0.31	ND

ND = not detected < MDL

Table 4. Seasonal variation in concentration of volatile aromatic compounds in sediment samples in µg/kg wet weight

Compound	Mláka 8			Mláka 9			Devin 10		
	winter	spring	summer	winter	spring	summer	winter	spring	summer
Benzene	0.32	0.66	ND	0.39	1.42	5.82	0.86	1.76	ND
Toluene	5.62	7.43	7.81	69.5	290	166	10.1	13.3	6.19
Ethylbenzene	ND	2.66	ND	6.84	1.88	ND	5.30	ND	ND
p,m-Xylene	1.47	1.53	ND	ND	0.34	ND	0.21	0.27	ND
o-Xylene	ND	0.29	ND	ND	ND	ND	ND	ND	ND
Total	1.41	12.6	7.81	76.7	294.6	171.8	16.4	15.2	6.19

ND = not detected < MDL

Table 5. The mean concentration* of volatile aromatic compounds in water and sediment from seven stations of four branches of the River Morava

Station	Benzene		Toluene		Ethylbenzene		Xylenes	
	water	sediment	water	sediment	water	sediment	water	sediment
Myjava 1	ND	0.58	1.61	86.15	ND	ND	ND	ND
Myjava 2	ND	0.75	2.20	192.3	ND	ND	ND	ND
Rudava 3	0.17	5.51	2.24	51.63	ND	ND	ND	ND
Rudava 4	0.31	4.31	0.64	13.93	ND	ND	ND	ND
Malina 5	ND	7.60	0.67	11.63	ND	ND	ND	ND
Malina 6	ND	3.63	0.75	9.03	ND	ND	ND	ND
Mláka 7	ND	ND	1.11	4.29	ND	ND	ND	ND

*concentration in µg/L for water samplesand in µg/kg wet weight for sediment
ND = not detected < MDL

identified as a sink of volatile organic compounds. Myjava and Rudava Rivers contained relatively higher concentrations of volatile aromatics than Malina and Mláka Rivers. The changes in water quality, which may occur with season, may have a direct relation on the accumulation and evaporation of volatile aromatics in water and sediment. The typical temperate ecosystem might show a spring season of a high run-off and a high water level causing turbid waters. Both these effects would tend to increase the concentration of volatile aromatics present in water and sediment. Because the volatile aromatic compounds routinely represent a large portion of total VOCs in water and sediment, by knowing their concentration in water and sediment one can evaluate the water quality of the River Morava.

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