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Occurrence and determination of organic pollutants in aerosol, precipitation, and sediment samples collected at Lake Balaton

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Abstract

The results of the determination of different organic pollutants [organic acids, polycyclic aromatic hydrocarbons (PAHs), *n*-alkanes, volatile hydrocarbons] in aerosols, precipitation, atmosphere, and sediment samples collected at Lake Balaton are presented. Different chromatographic methods were used: capillary zone electrophoresis (CZE) for organic acids, GC–MS for *n*-alkanes, solid-phase extraction (SPE) and HPLC for PAHs and thermal desorption–GC for BTEX (benzene, toluene, ethylbenzene, *m*- and *p*-xylene) compounds. For the determination of the size distribution of organic compounds aerosol was collected by an 8-stage Berner-type low-pressure impactor. Low-molecular mass organic acids were extracted in water in an ultrasonic bath and analysed by CZE. *n*-Alkanes were extracted by *n*-hexane, cleaned up on a silica cartridge and analysed by GC–MS. For analysis of PAHs in aerosols, samples were extracted in dichloromethane and acetone, cleaned on a Sep-Pak C₁₈ cartridge and analysed by HPLC–fluorescence detection. Enrichment of PAHs of the precipitation samples was accomplished by SPE on a C₁₈ cartridge. PAHs were eluted with dichloromethane and analysed by HPLC–fluorescence detection. The detection limit was <1 ng l⁻¹ for several PAHs. Well dried and sieved (500-μm sieve) sediment samples were extracted with dichloromethane and acetone. The extracts were cleaned and analysed by HPLC–fluorescence detection. Fourteen PAHs were determined and fluoranthene was found to have the highest concentration at 24 μg kg⁻¹. BTEX compounds were collected by diffusive sampling on Carboxpack adsorbent. Samples were analysed by a GC–thermal desorber method and one magnitude higher concentration of volatile compounds was found among the different locations. © 1997 Elsevier Science B.V.

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1. Introduction

Lake Balaton is the largest lake of Central Europe with a surface of about 600 km² and an average depth of 3 m. The shallow lake is one of the most valuable and important recreation zones. That is why the lake and its surroundings have been studied in several phases since the beginning of this century. Monitoring of the lake for organic pollutants is

fundamental to the solution of environmental protection problems. Most of the pollutants are transferred into the aquatic ecosystem, but for the complete picture, the investigation of atmospheric aerosols is also of great significance. Therefore, along with the analysis of sediments, samples of rain and snow, as well as volatile organic pollutants of the atmosphere should be investigated. Based on the results the mass balance of the compounds can be estimated.

Low-molecular-mass monocarboxylic and dicarboxylic acids are one of the main organic com-

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ponents in the atmosphere found in gas phase, aerosols and precipitation. Direct sources of organic acids include automotive exhaust, biomass combustion and biogenic emission. Organic acids can also be formed indirectly in the atmosphere from primary pollutants by gas-phase chemical and photochemical reactions. The concentration of these species in the atmosphere is relatively high compared to the other organics. Recently, several papers have been dedicated to the determination of organic acids in the atmosphere [1–8]. The techniques used were mostly ion chromatography [1,9–17], ion-exclusion chromatography [6,18–20] and gas chromatography [3,21–24]. Nowadays, capillary zone electrophoresis (CZE) has also been proved as a powerful technique because of high separation efficiency, short analysis time and small sample volume requirement [25,26]. The possibility of on-line sample preconcentration and simultaneous determination of inorganic ions and organic acids is a great advantage.

Similarly, *n*-alkanes present in aerosol samples can be derived from both biogenic and anthropogenic sources. A key parameter associated with *n*-alkanes is the carbon preference index (CPI) which considers the relative abundance of compounds containing odd and even number of carbon atoms [27]. This parameter is known to show the source of the hydrocarbons in the atmosphere. In the range C_{19} – C_{35} $CPI > 5$ indicates natural sources (primarily cuticular waxes of higher plants), whereas $CPI \approx 1$ implies anthropogenic influence (combustion of fossil fuels). It was also found that *n*-alkanes originating from higher plant sources preferentially turn up in the larger size fraction while *n*-alkanes of anthropogenic origin favour the fine particles.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous pollutants of anthropogenic origin. They can be detected in the atmosphere as well as in surface waters, sediments and soils. The hydrophobic character of PAHs exhibits a strong adsorption affinity on solid particles in aqueous matrices. The low concentration of PAHs requires thorough sample preparation which can be performed by solid-phase extraction (SPE) on C_{18} cartridges [28–35]. Sample preparation is followed by reversed-phase HPLC separation of the individual aromatic hydrocarbons.

In this paper we present the methods and results of the determination of different organic pollutants

[organic acids, *n*-alkanes, BTEX compounds (benzene, toluene, ethylbenzene, *m*- and *p*-xylene), PAHs] in samples of aerosols, precipitation and sediment. Along with the determination of total concentration their size distribution in atmospheric aerosols was also investigated.

2. Experimental

2.1. Sampling and sample preparation

The sampling sites were in Tihany (Lake Balaton) and Veszprém. Tihany is a village located about 25 km from Veszprém directly at Lake Balaton. Veszprém is a small town in the central western part of Hungary with a population of around 65 000, where there are no considerable industrial sources. The sampling schedule was decided in order to cover seasonal differences and samples were usually collected weekly. The volume of the sampled air was determined by preliminary experiments considering the detection limit of an individual analyte.

2.1.1. Determination of organic acids in atmospheric aerosols by CZE

Samples were collected on Whatman GF/F glass microfibre filters of 4.7-cm diameter using low volume sampler ($1.2 \text{ m}^3 \text{ h}^{-1}$) (Millipore, USA). The sampling time was 60 h in Veszprém and 48 h in Tihany, the volume of the air sampled was about 100 m^3 and 60 m^3 , respectively. The samples were collected at 20 m above the surface in Veszprém and 2 m in Tihany from November 1995 to January 1996. For the determination of the size distribution of organic acids, aerosol was separately collected on aluminum foils in a 8-stage Berner-type low-pressure impactor in Veszprém. With a flow-rate of 31.2 l min^{-1} the aerodynamic cut-off diameters of the stages (at 50% efficiency) are as follows: 0.0625, 0.125, 0.250, 0.50, 1.0, 2.0, 4.0 and $8.0 \mu\text{m}$. In a 60 h sampling period 120 m^3 air was sampled. Ten samples were collected between September 1995 and February 1996.

Samples were extracted in ultrasonic bath with 10 ml of Milli-Q water for 30 min. The ionic composition of the extracts was analysed by CZE. Waters Quanta 4000 capillary electrophoresis system was

used with fused-silica capillary of 60 cm×75 µm I.D. The background electrolyte contained 6 mM sodium chromate, 0.25 mM tetradecyltrimethylammonium bromide, 0.25 mM tris(hydroxymethyl)aminomethane and 0.125 mM potassium hydrogophthalate. The pH of the electrolyte was 8.0–8.1. The samples were introduced into the capillary by hydrostatic injection. The sample vial was lifted 10 cm above the electrolyte level for 30 s. Amperostatic separation was applied and the separation current was 25 µA. Indirect UV detection was used at 254 nm wavelength. Theoretical plate numbers were found as 300 000–500 000 for inorganic anions and 70 000–100 000 for organic acids. For the migration time the relative standard deviation (R.S.D.) was <0.5%, while for corrected peak area at 2 ppm organic acid R.S.D. was <2%. The precision of the method was 5–10% at the detection limit of 0.1–0.2 ppm concentration.

2.1.2. Determination of *n*-alkanes from atmospheric aerosol samples by GC

Samples were collected weekly with a Whatman GF/F filter in Tihany, using low volume sampler (1.2 m³ h⁻¹) (Millipore, USA) for 48 h. Samples were also collected with a Berner-type 8-stage cascade impactor on top of a five-storied building in Veszprém. The filters were extracted in an ultrasonic bath with 3 times 10.0 ml of *n*-hexane (Aldrich) for 15 min. The extracts were cleaned up on a 500-mg silica cartridge (Baker) then evaporated to 1.0 ml. After the addition of 20 ml of internal standard solution (*n*-undecane in *n*-hexane), 1.0 ml was injected into the gas chromatograph connected to a mass spectrometer in splitless mode. The column was a SPB-1 fused-silica capillary of 30 m×0.32 mm I.D. and 0.25-µm film thickness. The temperature program applied was 40°C for 1 min, then 8°C min⁻¹ to 300°C, held for 10 min. GC-MS analysis was carried out with a TRIO-1000 instrument of Fisons (UK). The mass spectrometer was operated in SIR mode, monitoring ions of 57 and 85 u.

2.1.3. Determination of PAHS from atmospheric aerosol, precipitation and sediment samples by HPLC

Aerosol samples were collected on glass fiber

filters (Whatman, USA) using a high volume sampler (60 m³ h⁻¹) for 24 h, or a low volume sampler (1.2 m³ h⁻¹). Sampling sites: S1: K-puszta, a background station on the Great Hungarian Plain, sampling height: 5 m, sampling time 24 h. S2: Tihany, sampling height: 2 m, sampling time 48 h. S3: Veszprém, sampling height: 18 m, sampling time 60 h. S4: Szombathely, (a town in West-Hungary), sampling height: 1.5 m, sampling time 4 h (from 8 to 12 a.m., high traffic). The filters were extracted in organic solvents, dichloromethane and acetone. The extract was cleaned on a C₁₈ SPE cartridge (Sep-Pak Plus, Waters, Milford MA, USA) to protect the HPLC column from long chain aliphatic compounds and finally, it was evaporated to 0.5–1 ml prior to HPLC analysis.

Collection of precipitation samples was performed by a wet-only sampler with a cross-sectional area of 452 cm². The precipitation was collected through a glass funnel into a glass beaker. Samples were analyzed within some hours after the rain. Concentration of the precipitation samples was performed by SPE on a Sep-Pak C₁₈ SPE cartridge [37] using 2-propanol as organic modifier and dichloromethane followed by methanol as eluent. The sample size was reduced with gentle nitrogen stream.

Sediment samples were collected from the top 20-cm layer of the bottom of Lake Balaton. Samples were dried at room temperature, then stones and plant fragments were removed by passing the dried sample through a 2-mm sieve. The sieved sample was powdered and finally passed through a 500-µm sieve. A 20-g sample of the fine powder was sonicated twice in 30 ml of extracting solvent for 20 min. The extract was filtered through a glass fiber filter (Whatman GF/D type, cut-off=2.7 µm) and cleaned by SPE Samplex C₁₈ (250 mg, Baker) cartridge. The cleaned extract was injected into the liquid chromatograph equipped with fluorescence detector.

For analysis of PAHs, HPLC-grade acetonitrile (Romil, UK) and water (supplied by a Milli-Q water purification system, Waters) were applied. Eluent was composed as follows: linear gradient from 40% acetonitrile in water to 100% acetonitrile in 20 min then 100% acetonitrile for 15 min with a flow-rate of 1 ml min⁻¹. The column was LiChrospher PAH, 250 mm×4 mm, 5-µm polymeric type C₁₈ packing.

Waters 600E HPLC pump, a Rheodyne 7125 injector (sample volume 20 μl) and Waters 470 fluorescence detector with programmed wavelength changes were used. PAH mixture 610 M standard solution of the 16 US Environmental Protection Agency (EPA) PAHs (100–2000 $\mu\text{g ml}^{-1}$) (Supelco, Bellefonte, PA, USA) was used as standard. To compare the selectivity and sensitivity of UV and fluorescence detection a Waters 490 multiwavelength UV detector at 254 nm and 280 nm was used. Data acquisition and processing were carried out by a Maxima 820 chromatography software.

2.1.4. Determination of BTEX compounds from the atmosphere by GC

Samples were taken by diffusive sampling with standard Perkin–Elmer sample tubes ($A=0.2\text{ cm}^2$; $L=1.5\text{ cm}$) filled with Carbo-pack adsorbent. Carbo-pack (mesh size 20–40, BET specific surface area $100\text{ m}^2\text{ g}^{-1}$), obtained from Supelco, is a graphitized carbon black. The evaluation of the diffusive sampler for the determination of BTEX compounds was discussed in detail elsewhere [36]. It was found that Carbo-pack was the optimum adsorbent for passive sampling of toluene at exposure doses up to at least 40 ppm min [37]. The sampling sites were selected to cover a wide range of sampling locations from heavily polluted downtown areas to non-polluted rural locations. The sampling locations were the following (in the order of decreasing level of pollution):

Site 1: The 350 long road tunnel ‘Lánchíd’ in the downtown of Budapest, subject to heavy traffic all day long. No trespassing is allowed through the tunnel for health considerations. The samplers were fixed at a height of 1.5 m at the center of the tunnel. The concentrations of BTEX compounds are expected to be a sort of ‘integrated emission values’ of the Hungarian car fleet.

Site 2: In Budapest, 30 m away from the busy motorway M0, 2 m above the ground in the direction of the prevailing wind. The site is thought to be heavily polluted.

Site 3: In the center of Veszprém, near a busy crossroads, 6 m above ground level.

Site 4: Near Veszprém, 30 m away from the main road 8, in the direction of the prevailing wind. Apart from the road traffic no urban pollution is expected.

Site 5: In the suburb of Szombathely, a site of moderate traffic (access only), 2 m above ground level.

Site 6: In Balatonalmádi, a small town at Lake Balaton, in a quiet resort area with little traffic.

Site 7: At the bank of the river Dráva, South Hungary, 1.5 km away from the main road 6. No traffic is allowed.

Site 8: In the middle of the Bakony mountains, more than 5 km away from main roads, not accessible for vehicles.

At each sampling site 3 sampling tubes were applied simultaneously. Samples were analyzed with a gas chromatograph coupled to a Perkin–Elmer ATD 400 automatic thermal desorber. Desorption parameters were: desorption temperature 250°C, desorption time 2 min, trap low temperature -30°C , trap high temperature 250°C, trap hold time 5 min. The gas chromatograph was a GC 6000 Vega Series 2, with column SPB-1, $15\text{ m}\times 0.53\text{ mm I.D.}$, film 1.5 μm . The temperature program applied was 40°C for 1 min, 4°C min^{-1} to 100°C, $10^\circ\text{C min}^{-1}$ to 270°C. Flame ionization detection was applied, temperature was 270°C. The carrier gas was helium (T55, Messer Griesheim) at a flow-rate of 3.45 ml min^{-1} . Standard tubes loaded with known amounts of BTEX compounds were purchased from TNO Department of Environmental Sciences, Delft, Netherlands.

3. Results and discussion

3.1. Determination of organic acids in atmospheric aerosols by capillary electrophoresis

Five organic acids were identified in the samples: monocarboxylic acids formic and acetic acid and dicarboxylic acids oxalic, malonic and succinic. The concentrations of organic acids in samples collected on glass fiber filter in Veszprém and in Tihany (Lake Balaton) are shown in Figs. 1 and 2, respectively.

In Veszprém the most abundant acid was oxalic acid followed by succinic and formic acids. Oxalic acid was found in all samples and the concentration was about 1.5–3 times higher than the amount of the other dicarboxylic acids. This result is in accordance with those of Sempéré et al. [38]. Formic acid was also detected in almost each sample, except if heavy

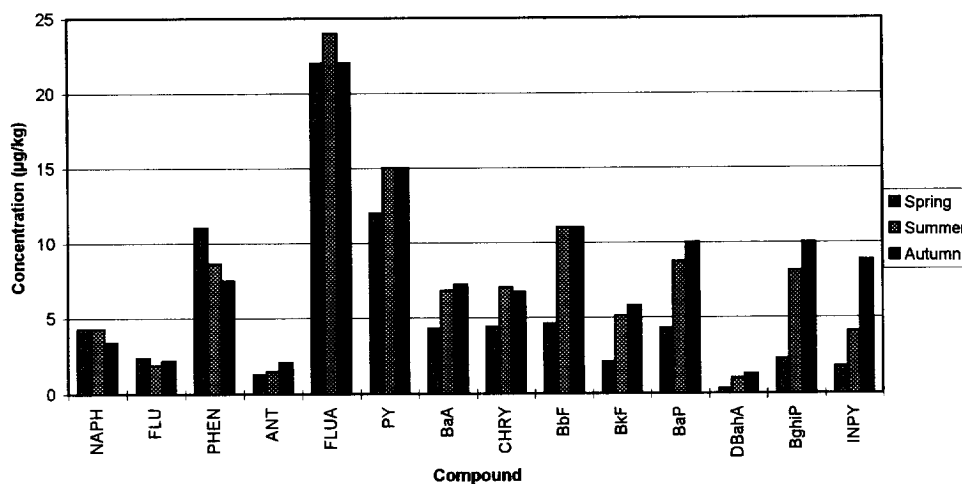


Fig. 1. Concentration of organic acids in atmospheric aerosols collected in Veszprém.

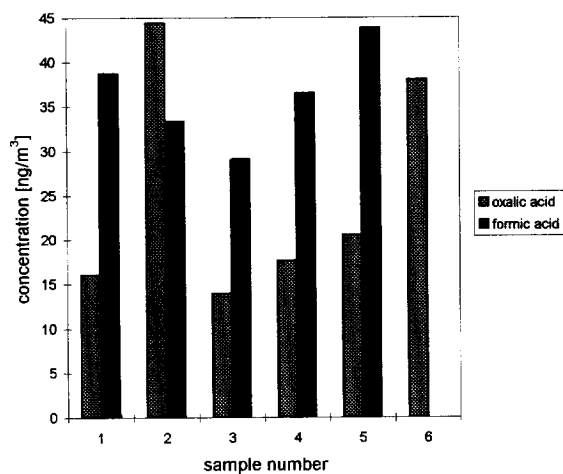


Fig. 2. Concentration of organic acids in atmospheric aerosols collected in Tihany (Lake Balaton).

snow occurred during the sampling (samples 5 and 11). Formic acid is easily removed from the aerosol by wet deposition due to its high water solubility.

Malonic and acetic acid were detected in the half of the samples only. In aerosol samples collected at Tihany only oxalic and formic acids were identified and the concentration of formic acid slightly exceeded the concentration of oxalic acid. In Veszprém the absolute and the relative concentrations of the five acids changed considerably in the three month periods, while in Tihany, the concentrations of the two acids, especially those of the formic acid, were more stable. The average concentration of the oxalic acid found in Veszprém was about 3 times higher than it was at the Lake Balaton. The concentration of formic acid, however, was only about 70% compared to the samples collected in Veszprém. The differences in the species and the amount of the acids between the two sampling sites may be due to the different intensity of anthropogenic sources and to the different magnitude of the public transport.

The results of the size distribution of the acids are shown in Table 1. The data are for the average mass concentrations of the acids at three different particle

Table 1
Size distribution of organic acids in atmospheric aerosol (ng/m³)

Particle diameter (µm)	Oxalic acid	Malonic acid	Succinic acid	Formic acid	Acetic acid
0.0625–0.25	5.5	2.4	3.7	3.9	nd
0.25–2	113.0	20.5	20.3	23.7	9.3
2–16	12.4	7.0	9.3	16.9	nd
Total concentration	130.9	29.9	33.3	44.5	9.3

size ranges. It can be seen that each of the acids was mostly concentrated in the $0.25 < d < 2 \mu\text{m}$ particle size range. A significant portion of acids, like 92% of oxalic acid, 77% of malonic acid, 72% of succinic acid, 62% of formic acid and the total amount of acetic acid was found on the fine particles ($d < 2 \mu\text{m}$). Therefore, these organic species were formed by gas-to-particle conversion. Since the size distribution of the acids was very similar to each other, they might come from the same sources. Similar size distribution of PAHs was obtained in the atmospheric aerosol collected at the same sampling site [39].

3.2. Determination of *n*-alkanes from atmospheric aerosol samples by GC

Samples taken in Tihany during the growth season were analyzed for *n*-alkanes. From the concentrations of individual compounds the total concentration of *n*-alkanes, the carbon preference index (CPI) and the mass median average carbon number (N_{max}) were calculated. These parameters are shown in Table 2, with reference to the date of sampling. It can be seen that the parameters varied considerably during the sampling period. The most significant changes were observed in the CPI. There is some correlation between CPI and N_{max} values. From the series of observations three distinct types of distributions can be differentiated on the basis of the parameters.

Table 2

The calculated total concentration of *n*-alkanes, their carbon preference index (CPI) and mass median carbon number (N_{max}) in the summer samples

No.	Date	c_{total} (ng/m^3)	CPI	N_{max}
1	12–14 June 1995	29.2	1.09	24.1
2	19–21 June 1995	41.6	1.15	24.3
3	26–28 June 1995	14.6	4.97	28.1
4	21–23 June 1995	18.9	6.79	28.8
5	13–15 July 1995	24.7	1.54	26.1
6	27–29 July 1995	34.6	1.79	26.3
7	07–09 August 1995	19.3	2.01	27.3
8	21–23 August 1995	31.0	1.47	25.6
9	04–06 September 1995	23.9	1.98	27.2
10	18–20 September 1995	34.4	2.33	27.5
11	02–04 October 1995	26.2	1.67	24.8
12	16–18 October 1995	18.7	2.12	26.9

Table 3

The calculated total concentration of *n*-alkanes, their carbon preference index (CPI) and mass median carbon number (N_{max}) in the fractions of a cascade impactor sample taken in February 02–05, 1996

Fraction	Cut-off (μm)	c_{total} <i>n</i> -alkanes (ng/m^3)	CPI	N_{max}
1	0.0625	12.4	1.52	24.4
2	0.125	1.5	0.93	24.8
3	0.25	2.3	0.95	23.5
4	0.5	3.4	1.10	24.2
5	1	2.6	1.05	24.5
6	2	6.1	1.17	24.7
7	4	9.9	1.21	25.4
8	8	6.6	1.27	24.8

The results of the analyses with a Berner-type cascade impactor are presented in Table 3. Data show that no significant increase of CPIs can be observed with particle size. The total concentrations of *n*-alkanes in the fractions varied with particle size. The majority of the *n*-alkanes were found in the smallest and the three largest particle size fractions, exhibiting a bimodal distribution. In the smallest size fraction compounds of anthropogenic origin are expected to be abundant whereas larger fractions contain, to a larger extent, biogenic *n*-alkanes.

3.3. Determination of PAHs from atmospheric aerosol samples by HPLC

3.3.1. Investigation on the extraction parameters

The efficiency of the sonication of the aerosol samples was primarily investigated. The volume of extracting solvent, number and duration of extractions were optimized. The low concentration (pg/m^3 to ng/m^3) of PAHs in atmospheric aerosol samples requires efficient extraction with the least organic solvent volume and the minimum time of sample preparation. A 15-cm^2 piece of filter was extracted four times with 5 ml of dichloromethane for 20 min. Each extract was analyzed for PAHs. It was found that 80–90% of the PAHs were in the first two extracts and only some percents were detected in the fourth one. So, this extraction procedure proved to be

efficient, however, it took 80 min. Next, the filter was extracted four times with 5 ml of dichloromethane for only 10 min. The results were similar to those obtained in the previous experiments showing that 40 min was enough for the efficient extraction.

The effect of the amount of organic solvent on the reproducibility of the sample preparation was further investigated. Three equal-sized pieces of a filter were extracted four times with dichloromethane as described above. The solvent/filter ratio was 0.75 ml solvent/cm² of filter. Then, 3 equal-sized pieces of another filter was extracted with a ratio of 2.5 ml solvent/cm² of filter. The average and the relative standard deviation of the concentration values for both experiments are shown in Table 4.

High R.S.D. values (10–30%) were obtained at solvent/filter ratio of 0.75 showing that the amount of the solvent was insufficient. Increasing the solvent/filter ratio to 2.5 resulted in R.S.D. values around 5% with only one exception (in case of anthracene an unresolved compound made the evaluation of the anthracene peak less reliable). Dichloromethane and acetone were compared as efficient organic solvents for the extraction of PAHs from solid samples. From the same filter 3 pieces were cut and extracted with both solvents. The concentration and R.S.D. values showed that no significant departure was found in the average con-

centrations, so dichloromethane can be substituted by acetone with R.S.D. of 3–14%.

3.3.2. Determination of PAHs in atmospheric aerosol samples

The concentration of the PAHs in atmospheric aerosol samples was determined at different sites and results are summarized in Table 5. The limit of quantitation (LOQ) and the limit of determination (LOD) of PAHs in aerosol samples are summarized in Table 6.

It has been found that PAHs were mostly adsorbed on soot at a particle size of <3 μm [40–43]. Kertesz-Saringer et al. [41] observed that 70% of benzo[a]pyrene was adsorbed on aerosol particles of <0.3 μm. Since the residence time of the particles of 0.1–0.5 μm is about 10 days (without wet deposition), the compounds adsorbed on their surface can travel long distance before they are deposited from the atmosphere. Data showed that PAHs concentration in samples collected in Greenland was <5 pg/m³ on average, except for fluoranthene and pyrene, but they did not surpass the 30 pg/m³ either [44]. Comparing the results to the measurement taken at the Mediterranean Sea and Baltic Sea, one to four magnitudes higher concentration of PAHs, respectively, was obtained [45,46]. In this work the most polluted area was found at Site 4, where during

Table 4
Effect of organic solvent amount/filter size ratio on the reproducibility of the sample preparation

Compound	0.75 ml solvent/cm ² filter		2.5 ml solvent/cm ² filter	
	Average concentration (ng/m ³ , n=3)	R.S.D. (%)	Average concentration (ng/m ³ , n=3)	R.S.D. (%)
Fluorene	0.70	21	0.13	8.19
Phenanthrene	1.7	10	1.7	6.8
Anthracene	0.41	22	0.07	15
Fluoranthene	1.2	15	2.9	7.7
Benz[a]anthracene	2.8	30	5.6	4.8
Chrysene	3.6	24	6.3	2.8
Benzo[b]fluoranthene	4.6	20	7.4	1.4
Benzo[k]fluoranthene	2.2	21	3.4	1.9
Benzo[a]pyrene	4.7	22	7.3	5.2
Dibenz[a,h]anthracene	0.44	17	0.81	1.5
Benzo[ghi]perylene	9.5	27	11	3.4
Indeno[1,2,3-cd]pyrene	5.6	21	6.6	3.2

Table 5
Concentration of PAHs (ng/m³) determined in atmospheric aerosol samples at different sampling sites

Compound	Sampling site			
	K-pusztá	Tihany	Veszprém	Szombathely
Naphthalene	0.44	0.51	0.93	0.8
Fluorene	0.018	0.033	0.11	0.13
Phenanthrene	0.13	0.23	0.28	2.6
Anthracene	0.005	0.003	0.024	0.17
Fluoranthene	0.20	0.35	0.46	8.4
Pyrene	0.15	0.26	0.43	13
Benz[a]anthracene	0.051	0.058	0.57	8.3
Chrysene	0.099	0.35	0.58	9.0
Benzo[b]fluoranthene	0.16	0.44	0.73	12
Benzo[k]fluoranthene	0.066	0.14	0.38	5.7
Benzo[a]pyrene	0.13	0.17	0.61	11
Dibenz[a,h]anthracene	0.014	0.045	0.093	1.9
Benzo[ghi]perylene	0.16	0.20	0.80	13
Indeno[1,2,3-cd]pyrene	0.13	0.083	0.13	9.9

R.S.D. = 5–15%.

n = 3.

day time (from 8 to 12 a.m.), the high pollution can be assigned to the heavy traffic. At other sampling sites no extremely high concentrations have been found due to the less polluted environment.

3.4. Determination of PAHs from precipitation samples by HPLC

The concentration and the percentage of the

Table 6
The limit of quantitation (LOQ) and the limit of determination (LOD) of PAHs in aerosol samples

Compound	LOQ (pg/m ³)	LOD (pg/m ³)
Naphthalene	67	30
Acenaphthene	67	30
Fluorene	33	3
Phenanthrene	17	5
Anthracene	1.7	0.8
Fluoranthene	130	50
Pyrene	67	30
Benz[a]anthracene	6.7	3
Chrysene	6.7	3
Benzo[b]fluoranthene	1.7	1
Benzo[k]fluoranthene	1.7	0.3
Benzo[a]pyrene	3.3	2
Dibenz[a,h]anthracene	13	3
Benzo[ghi]perylene	13	6
Indenopyrene	67	30

individual compounds in winter samples are summarized in Table 7. Naphthalene was excluded from the percentage calculation because its concentration was greater by one or two orders of magnitude than that of the other compounds. The concentration of PAHs ranged from 1–930 ng l⁻¹ in winter precipitation samples. Naphthalene, phenanthrene, fluoranthene and pyrene were found in the highest concentration (190–680 ng l⁻¹) both in rain and snow samples. The concentration of the other compounds was frequently less, ranged between 4 and 37 ng l⁻¹. The concentration profile of the PAHs did not change substantially in the observed period. This was caused by the similar origin of the pollutants and the mixing processes in the atmosphere. The correlation between the movement of air masses (characterized by isentropic trajectories) and concentration data was discussed elsewhere [40].

3.5. Determination of PAHs in sediment samples by HPLC

Sediment samples were extracted using acetone and dichloromethane. It was found that the concentration values obtained with acetone were comparable to those obtained with dichloromethane. Acetone is more polar than dichloromethane, therefore, less apolar compounds (e.g. aliphatic hydro-

Table 7
Concentration (ng l⁻¹) of PAHs in precipitation samples

Compound	Concentration (%)	
	Rain (n=5)	Snow (n=2)
Naphthalene	680 (-)	930 (-)
Fluorene	37 (4.9)	29 (4.8)
Phenanthrene	230 (31.5)	100 (17.1)
Anthracene	3.9 (0.5)	4.8 (0.8)
Fluoranthene	190 (25.4)	120 (20.1)
Pyrene	190 (25.4)	170 (28.5)
Benz[a]anthracene	<1 (-)	2.8 (0.5)
Chrysene	29 (3.9)	51 (8.5)
Benzo[b]fluoranthene	19 (2.6)	44 (7.4)
Benzo[k]fluoranthene	6.1 (0.8)	14 (2.3)
Benzo[a]pyrene	4.6 (0.6)	6.7 (1.1)
Dibenz[a,h]anthracene	8.7 (1.2)	<3 (-)
Benzo[ghi]perylene	24 (3.2)	53 (8.9)
Total	1422.3(100)	1525.3 (100)

carbons) can be extracted which should be removed on octadecyl-silica columns before analysis. Standard solution of PAHs dissolved in acetone was diluted with water and the solution was passed through a SPE cartridge with cyclohexyl or amino stationary phase. Since the recovery of the PAHs is influenced by the organic modifier content, first, the volume of water used for dilution was investigated. A 40-ml volume of standard solution (as a hypotheti-

cal extract) was diluted with water to maintain 10, 15, and 20% (v/v) of acetone in water. Results for cyclohexyl phase and amino phase are shown in Table 8, respectively.

It can be concluded that 15% (v/v) acetone content is sufficient for the cyclohexyl column (recovery of PAHs was between 65% and 97%), while 10% acetone is appropriate for the amino column (recovery of PAHs was between 6% and

Table 8
Recovery (%) of PAHs from aqueous standard solution with different acetone content using cyclohexyl-silica (a) or amino-silica (b) SPE cartridge (n=3)

Organic modifier content	10% acetone, V=400 ml		15% acetone, V=267 ml		20% acetone, V=200 ml	
	a	b	a	b	a	b
Naphthalene	53	6	65	6	54	6
Acenaphthene	66	15	79	11	73	10
Fluorene	72	25	85	19	74	16
Phenanthrene	82	51	88	28	86	26
Anthracene	73	48	85	35	79	28
Fluoranthene	85	66	97	42	86	35
Pyrene	83	68	95	45	88	37
Benz[a]anthracene	84	83	93	65	91	66
Chrysene	84	85	93	62	90	65
Benzo[b]fluoranthene	82	83	97	74	89	71
Benzo[k]fluoranthene	78	78	93	75	87	76
Benzo[a]pyrene	81	80	95	65	92	75
Dibenz[a,h]anthracene	71	75	89	68	85	75
Benzo[ghi]perylene	78	69	96	57	92	71
Indeno[1,2,3-cd]pyrene	73	68	89	60	85	78

Table 9

Recovery of PAHs (%) on SPE cartridges of different types from sediment extracts (15% acetone content, $V=267$ ml, $n=3$)

Compound	Cyclohexyl	Amino	Octadecyl
Fluorene	80	26	92
Phenanthrene	76	25	94
Anthracene	76	33	80
Fluoranthene	82	40	82
Pyrene	77	48	80
Benz[<i>a</i>]anthracene	73	57	75
Chrysene	77	59	75
Benzo[<i>b</i>]fluoranthene	85	63	83
Benzo[<i>k</i>]fluoranthene	94	68	86
Benzo[<i>a</i>]pyrene	92	69	81
Dibenz[<i>a,h</i>]anthracene	93	61	79
Benzo[<i>ghi</i>]perylene	94	54	64
Indeno[1,2,3- <i>cd</i>]pyrene	90	54	75

91%). Since the time of sample loading was longer by 50% in case of 10% (v/v) acetone ($V=400$ ml) than that of 15% (v/v) acetone ($V=267$ ml), the last composition was selected for further investigation. In the real experiment sediment extracts were diluted with water to maintain a 15% acetone content and SPE was performed on cyclohexyl, amino and octadecyl columns. Results are summarized in Table 9. It can be concluded that the octadecyl column yielded the highest recovery for the 3–4-ring PAHs, while the cyclohexyl column resulted in the excellent recoveries for the 5–6-ring compounds.

The concentration of PAHs was determined in sediment samples of Lake Balaton. Samples were taken in different seasons of the year. Results are compared in Fig. 3. The concentration of naph-

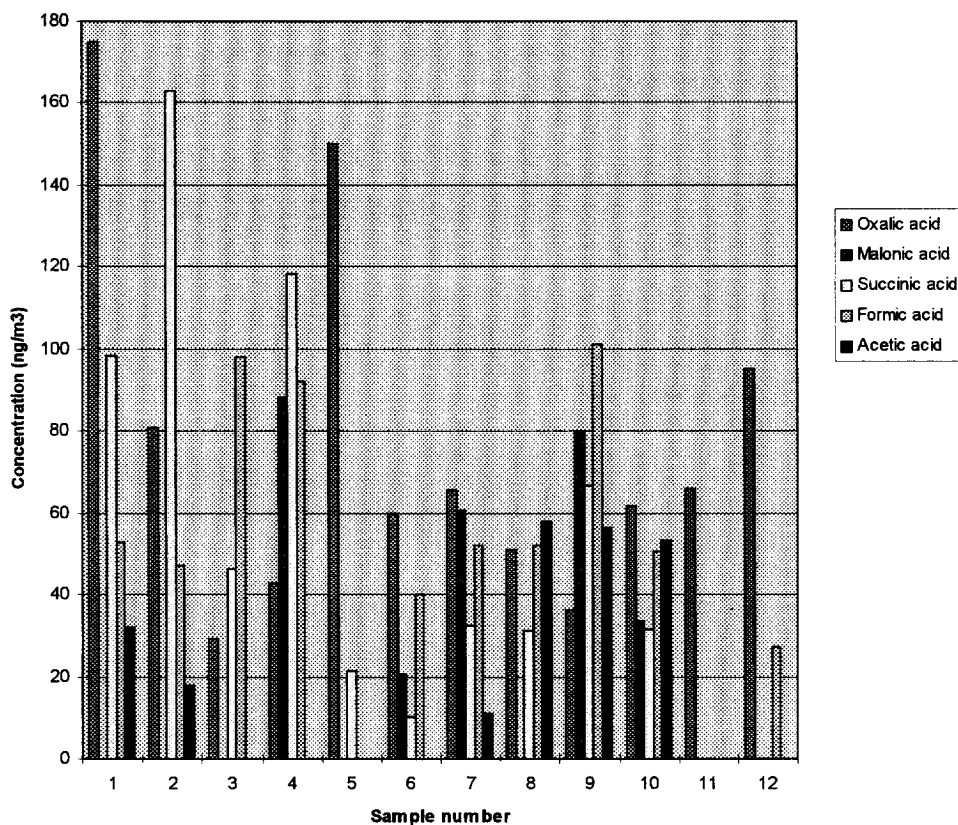


Fig. 3. Concentration of PAHs in sediment samples collected in the Lake Balaton.

thalene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene did not change over time, however, the concentration of the other compounds increased from spring to autumn. A chromatogram of a sediment sample obtained by HPLC with programmed fluorescence detection after solid-phase extraction is shown in Fig. 4. Concentrations of PAHs were found one to three magnitudes higher in sediment samples collected at polluted rivers, estuaries and harbors in Canada, Australia, and USA, respectively [47–49].

3.6. Determination of BTEX compounds by GC

The time weighted average (TWA) concentrations of BTEX compounds and their 95% confidence intervals together with the duration of sampling are summarized in Table 10.

The absolute concentrations of compounds vary by orders of magnitude from heavily polluted urban

location to unpolluted background areas. In less polluted areas it is sometimes difficult to determine the degree of pollution solely on the basis of absolute concentrations: sampling sites 5–8 show quite similar concentration values. It is difficult to compare the results because they were obtained under different conditions and for different periods of time. The target compounds are not stable in the atmosphere; they are subject to photochemical reactions with OH radicals during the day: e.g. toluene is 5 times more reactive than benzene; their relative concentrations are, therefore, changing continuously while being transported in the atmosphere. So, the relative concentrations of selected compounds, e.g. toluene to benzene, are more characteristic of the level of pollution: this ratio changes from 2.0 to 1.1 moving from the most polluted location (Site 1) to the least polluted one (Site 8). This is in accordance with the fact that toluene is depleted faster than benzene in

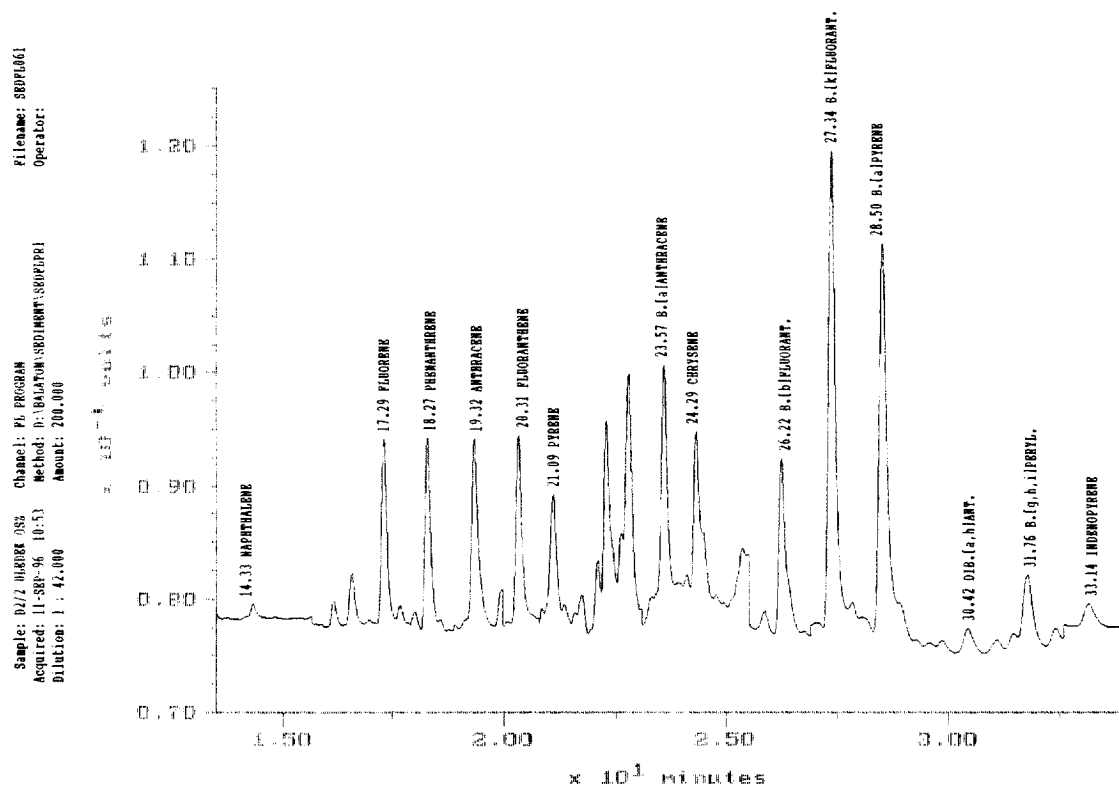


Fig. 4. HPLC chromatogram of a sediment sample collected in the Lake Balaton (Autumn, 1996).

Table 10

The duration of sampling and time weighted average (TWA) concentrations of benzene, toluene, ethylbenzene and *m,p*-xylene and their 95% confidence intervals

Site	Duration (min)	C_{benzene} ($\mu\text{g}/\text{m}^3$)	C_{toluene} ($\mu\text{g}/\text{m}^3$)	$C_{\text{ethylbenzene}}$ ($\mu\text{g}/\text{m}^3$)	$C_{\text{m,p-xylene}}$ ($\mu\text{g}/\text{m}^3$)
1	116	129±4	260±22	97±8	233±6
2	10 080	27±2	42±1	21±3	47±5
3	1907	9.4±0.4	16±1	7.3±1.1	14±2
4	10 255	10±2	15±4	8.6±1.4	13±2
5	10 144	2.3±0.2	3.4±0.1	2.1±0.3	3.2±0.6
6	10 080	2.8±0.1	4.2±0.6	2.4±0.4	3.7±0.7
7	1920	3.6±0.3	3.8±0.5	2.3±0.5	2.9±0.4
8	10 255	2.6±0.5	2.7±0.2	1.9±0.3	2.2±0.3

the atmosphere. The monitoring of the ratio of these abundant pollutants can be an indication of the level of pollution at a given location.

4. Conclusions

Based upon the results of a systematic investigation on the environmental condition of the Lake Balaton it can be concluded that there is no serious pollution from anthropogenic compounds originating from municipal and industrial activities or from agriculture. In aerosol samples organic acids were identified and, in samples collected in Veszprém, the most abundant acid was oxalic acid followed by succinic and formic acids. In the samples collected at the Lake Balaton only oxalic and formic acids were identified. The results of the size distribution of the acids showed that each of the acids was mostly concentrated in the particles of <2 μm size range. Therefore, it is possible that these organic species are formed by gas-to-particle conversion.

Samples taken in Tihany (Lake Balaton) during the growth season were analyzed for *n*-alkanes and the carbon preference index (CPI) and the mass median average carbon number (N_{max}) were calculated. The most significant changes were observed in the CPI. Some correlation was found between CPI and N_{max} values and from the series of observations three distinct types of distributions can be differentiated. Data showed that no significant increase of CPIs could be observed with particle size. The total concentrations of *n*-alkanes in the fractions varied

with particle size. The majority of the *n*-alkanes were found in the smallest and the three largest particle size fractions, exhibiting a bimodal distribution. The concentration of the PAHs in atmospheric aerosol samples was determined at different sites: The most polluted area was found at Szombathely, where the high pollution (13 ng/m^3 benzo[ghi]perylene) can be assigned to the heavy traffic. At other sampling sites (e.g. at the Lake Balaton and K-pusztá) no very high concentrations were found due to the less polluted environment. The concentration of PAHs in sediment samples of Lake Balaton was found one to three magnitudes smaller than those in sediment samples collected at polluted rivers, estuaries and harbors. The absolute concentrations of BTEX compounds varied by orders of magnitude from heavily polluted urban location to unpolluted background areas. The monitoring of the concentration and calculation of the ratio of these pollutants might be an indication of the level of pollution. The proposed methods have been successfully used for determination of distinct organic compounds in different environmental media.

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