

Determination of Polycyclic Aromatic Hydrocarbons in Water (Including Drinking Water) of Łódź

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are more dangerous xenobiotics, very carcinogenic for animals and humans. They are found in air, water, sediments, and plant and animal tissues. Most PAHs in the environment are derived during incomplete combustion of organic substances at temperatures lower than 700° C. Total emission of all PAHs is very difficult to estimate but the global emission of benzo[a]pyrene is estimated at about 8600 tons/year. Most PAHs are lipophilic compounds that can be bioaccumulated to high levels. Microbial biodegradation and sunlight decomposition are the main mechanisms for PAH removal from sediments and water. In the present paper the authors will try to determine concentrations of 16 PAHs from the US EPA list in river water and drinking water of the Łódź area to be compared with bibliographic data obtained by other chromatographic methods.

Keywords: polycyclic aromatic hydrocarbons (PAHs), benzo[a]pyrene (B[a]P), high performance liquid chromatography (HPLC), water concentrations of PAHs.

Introduction

Polycyclic aromatic hydrocarbons (Polynuclear aromatic hydrocarbons -PAHs) are perhaps the most extensively studied components in polluted air, water, soil, and foodstuffs. This is a consequence of PAHs having been shown to be carcinogenic and mutagenic to laboratory animals as well for man [1-3]. PAHs are found in air, soil, and water, in many members of both animal and plant kingdoms, marine and non-marine sediments and also as spectrum of foods, including smoked foods, processed rice, roasted coffee, baked goods, barbecued meat, raw agricul-

tured commodities (such as oranges), and products such as commercial waxes and paraffins, mineral oil and solvents. The majority of PAHs in the environment is derived during incomplete combustion of organic substances at high temperature and under pyrolytic conditions. At temperatures of 400-500°C organic components are partially cracked smaller and relatively unstable molecules (radicals) which then recombine to form larger and more stable PAHs [4-6]. If the starting material also contains heteroatoms (eg. oxygen, nitrogen and sulphur) then heteroaromatics are formed in addition to PAHs. The total emission of PAHs has been estimated at 8,600 tons per year in the USA and

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about 14,100 ton/year in Europe (Table 1). Investigation of the concentration of PAHs from Greenland showed that the present level of these compounds is about 50 times higher than in the preindustrial period [7,12].

PAHs are a group of about 500 compounds present in environment. In nature, they assume many structural forms, covering a wide range of molar masses. Besides B[a]P at least 11 very carcinogenic polycyclics have been found in urban air: chrysene, benzo[a]anthracene, benzo[a]pyrene, benzo[e]pyrene, indeno-[1,2,3-c,d]pyrene, benzo[e]acephenanthrylene, benzo[j]fluoranthene, dibenzo[e,l]pyrene, dibenzo[a,h]pyrene, dibenzo[a,j]pyrene, dibenzo[a,h]acridine, and dibenzo[a,j]acridine [13-15]. In Europe the highest concentrations of B[a]P in air were found in the former Czechoslovakia (1.9 µg/1000 m³), Hungary (1.9 µg/1000 m³), Germany (1.5 µg/1000 m³), Poland (1.4 µg/1000 m³) and Austria (1.3 µg/1000 m³). The lowest concentrations are in Finland (0.034 µg/1000 m³), Sweden (0.040 µg/1000 m³), Norway (0.042 µg/1000 m³), and Portugal (0.067 µg/1000 m³) [7,11]. In general the concentrations of B[a]P are ranged between 0.01-10.0 µg/1000 m³ and concentrations of all 16 PAHs are about 10 times higher than B[a]P for central Europe and is about 10-30 µg/1000 m³ [5,7,10,16].

The concentrations of PAHs in polluted areas is lower than 600 µg/kg (I degree), in polluted (II degree) is about 600-1,000 µg/kg and strong polluted soil (III degree) the concentrations of PAHs ranged between 1,000-5,000 µg/kg. In Poland for Zabrze area concentrations of 6 PAHs are about 7,000 µg/kg [17], for Poznań area the concentrations ranged between 184-494 µg/kg [18-24], in Kraków about 930 µg/kg [25] and 60-650 µg/kg in Łódź [26,27]. But for industrial areas the concentrations of B[a]P only were: Płock Petrochemical Works 11,000-15,000 µg/kg, Czechowice Refinery 33,100 µg/kg, Zabrze-Bytom area 1,000-2,600 µg/kg [26].

Concentrations of PAHs in surface water very often ranged between 0.1-830 ng/L (2.5-9.0 ng/L tap water, 1.0-10.0 ng/L ground water, 2.7-7.3 ng/L rain water and about 10-830 ng/L for surface water) [28] and their presence has been detected in wastewater, runoff or rain water and also in drinking water [29]. Condensed aromatics are mostly nonpolar or very weak polar solids and their solubility in water is very low and is decreasing as the number of aromatic rings in PAH increases. Generally, the high molecular weight compounds (≥ 4 aromatic rings) are less water-soluble, less volatile and more lipophilic than lower molecular weight ones (PAHs ≤ 3 rings 0.07-32 mg/L; PAHs ≥ 4 rings 0.003-0.26 mg/L) [7,11,30-33]. The determination of B[a]P and other PAHs in lakes in National Wielkopolski Park have shown concentrations of B[a]P to be between 0-25 ng/L (mean 5.6 ng/L) and $\Sigma 6$ PAHs were ranged between 2-123 ng/L (mean 5.6 ng/L) [34]. In Gdańsk urban region the concentration of B[a]P in runoff water were 0.41-7.7 ng/L in summer season and between 2.56-25.0 ng/L in heating season. Concentrations of total PAHs ranged between 79-393 ng/L (summer season) and 169-891 (heating season) [35]. In comparison, in 1985-1991 the mean concentrations of B[a]P in Warta river were 6.9-31.2 ng/L and mean $\Sigma 6$ PAHs were 75.9-312.4 [36].

The surface of water accompanied by the organic layer formed on the water by chemical and biological components together form a unique environment for microorganisms (surface biofilm). Since B[a]P and various other PAHs are lipophilic and these compounds can be bioaccumulated to high levels. For example, high accumulation of B[a]P in clams was reported (24 h exposure to 0.0305 ppm ¹⁴C-B[a]P in sea water) the tissue concentration of 7.2 ppm indicating a 236 fold bioaccumulation over exposure water concentration [37]. Fritsche [38] revealed that about 20% of microorganisms have the facility to decompose hydro-

Table 1. Annual emission of PAHs in different countries [7].

Country	Emission of PAHs [tonnes/year]						References
	Stationary fuel combustion		Industrial processes	Transport	Incineration	Total	
	Domestic heating	Power stations					
USA	1380	400	3500	2170	1150	8600	[8]
Sweden	142	2	313	47	4	510	[8]
Sweden	x	x	x	x	x	200	[9]
Poland	265	118	320	80	5	800	[2]
Poland	464 (*)	x	67	35	x	566	[10]
England	604	6	19	80	6	712	[6]
Germany	x	x	x	x	x	8218	[9]
Netherlands	x	x	x	x	xx	1116	[9]
EUROPE	9863		324	845	x	14090	[11]

(*) combined domestic heating and power stations

carbons through metabolism. Among them were such bacterial strains such as: *Pseudomonas*, *Achromobacter*, *Alcaligenes*, *Flavobacterium* and *Micrococcus*. B[a]P is oxidized by microorganisms, for example *Beijerinckia* sp. to form 7,8-dihydroxy-7,8-dihydrobenzo[a]pyrene and 9,10-dihydroxy-9,10-dihydrobenzo[a]pyrene with further more extensive degradation. Microbial degradation is a major mechanism for compound removal in sediments and bacteria capable of degrading heteroaromatic systems have also been isolated. Generally B[a]P metabolizing cultures are microorganisms with long exposure to B[a]P growth rates of bacteria on PAHs are directly related to the solubilities of the PAHs. The yields of PAH degradation by neustonic and planktonic bacteria in Jeziorak Lake were 44.4% for anthracene in surface microlayer and 38.2% for subsurface water and for naphthalene 59.6% and 57.2% [39]. The half-life of B[a]P in river, ponds and lakes after oxidation is about 340 h, but half-life volatilization in river is about 140 h, 350 h in ponds and about 700 h for eutrophic and oligotrophic lakes. Sunlight decomposition is faster ranged between 0.2-14.1 h (anthracene/benzo[k]-fluoranthene) and ranged 0.15-5.38 in the presence of ozone. Also, biological decomposition of PAHs is used in most petroleum refineries [40,41].

Gas chromatography (GC-MS) with capillary and high performance liquid chromatography (HPLC) with DAD and fluorescence detector are the most widely used methods in PAH analysis. According to very low concentrations of PAHs in water and foods very important is preconcentration process. Solid-Phase Extraction (SPE) microcolumns off-line or on-line and C18 extraction discs of different matrices have been used as alternative techniques for the isolation and preconcentration of PAHs with liquid-liquid extraction [42-45]. Recovery of 2- and 3-ring PAHs from different chemically bonded phases has been compared [46-48], and the application of bonded octadecyl phase yielded recoveries of 64-100%. Brouwer et al., [48] compared the extraction efficiency of C18 stationary phase and found similar recoveries for 3-6 ring PAHs. Kiciński et al. [49] published recoveries of 16-70% for 2-3 ring PAHs and 71-90% for 4-6 ring PAHs on C18 SPE microcolumn. In another study decreasing recoveries were reported with increasing ring number (naphthalene 85%, anthracene 55% and pyrene 37%) [50]. The low yields of adsorption on SPE from natural water is the result of PAH adsorption on humic and fulvic acid, lipids and proteins forming dissolved organic matter (DOM). The presence of suspended particular matter (SPM) during transport and storage can reduce PAH recoveries by about 20-70% [51].

The present paper aims to determine concentrations of 16 PAHs according to the US EPA procedure using the RP-HPLC technique in surface water and drinking water of the Łódź area. In addition, the authors compared the experimental results with bibliographic data obtained by other authors using thin layer chromatography (TLC), high performance thin layer chromatography (HPTLC) and gas

chromatography (GC) techniques for different Polish lakes and rivers.

Experimental

Materials and Reagents

The water samples were collected in 2.0 L dark glass bottles: from Sulejów artificial lake in Bronisławów, from the Brzustówka river near the Pilica river, from the Łódź-Stoki reservoir of drinking water, from Tomaszów town water intake and from the Łódź-Chojny area in period 07.1999-12.2000 (Table 2). Water samples were stored at +4°C with the addition of 0.05% (w/v) sodium azide (NaN₃).

For preconcentration of PAHs by solid phase extraction (SPE) Bakerbond C18 microcolumns (6.0 mL, 1000 mg) and Speedisk Bakerbond SPE-50 (C18) from J.T.Baker (USA) were used. Additionally single-use microfilters type Millex-HV (0.45 µm) from Millipore (USA) were used.

For conditioning of SPE columns and speedisks, removal of PAHs and separation by liquid chromatography solvents for HPLC separation (HPLC grade: water, acetonitrile, dichloromethane, methanol, ethanol, and isopropanol) from J.T. Baker (USA) were used.

As a standard the mixture of 16 PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo-[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-c,d]pyrene (purity 97.4-99.9%) in concentrations 10.0 mg/L of each from Ehrenstorfer (Germany) and standard of benzo[a]pyrene in concentration 100.0 mg/L ACN (purity 97.5%) from Sigma (USA) were used in experiments.

All processes were done using single-use equipment and automatic pipets.

Preconcentration of PAHs by SPE Method

The Bakerbond C18 microcolumns and Speedisks SPE-50 (C18) at the beginning were eluted (activated) by: 10.0 mL dichloromethane, 10.0 mL of isopropanol, 10.0 mL of ethanol, 10.0 mL of methanol and finally 10.0 mL of distilled and deionized water from Millipore system.

The samples of water (1.0 L) were preconcentrated on Bakerbond C18 microcolumns (drinking water) or on Speedisk SPE-50 (C18) (lake or river water) with a flow rate of 2-3 mL/min. For preconcentration the SPE technique (SPE-12G from J.T. Baker) was used. The microcolumns and speedisk at the beginning were eluted by: 10.0 mL of distilled water, 10.0 mL of methanol, 10.0 mL of ethanol and 10.0 mL of isopropanol. Later were eluted by: 10.0 mL of ACN and 10.0 mL of CH₂Cl₂ at a flow rate 2-3 mL/min. Both fractions eluted by ACN and CH₂Cl₂ were collected and dried at inert gas flow at 28°C. The dried samples were resolved in 1.0 mL of CH₂Cl₂.

For the measure of recovery of PAHs by SPE method 1.0 mL of solutions of 16 PAHs was added to 100 mL of

distilled water. The samples were separated and preconcentrated by microcolumns Bakerbond C18 and by Bakerbond Speedisk SPE-50 (C 18) as environmental samples and were determined by RP-HPLC method. The yields of recovery were calculated according to concentrations of all PAHs in standard solutions from Ehrenstorfer (Table 3).

Separation of PAHs by HPLC Method

The samples preconcentrated by SPE were separated by RP-HPLC method (HP 1050 with UV/VIS detector from Hewlett-Packard, USA) on the column Spherisorb 5S ODS2 250x4 mm ID with precolumn Spherisorb 5S ODS2 4x4 mm ID (Hewlett-Packard, USA). Samples were separated by US EPA method [52-54] with application of gradient elution: (a) H₂O:ACN (50% v/v ACN), (b) at 6 min. start gradient elution by 5.0 min from 50% ACN in water to 100% CAN and (c) 100% ACN for 20.0 min. with a flow rate 0.5 mL/min., volume of injection loop 20.0 µL, column

temperature 25°C, absorbance at 254 nm was determined (Figures 1-3). The mean elution times were calculated from n=10 injections and the mean recovery of SPE method and concentration of PAHs were calculated from n=5 measurements in comparison with area of standard peaks [55,56].

Results and Discussion

The concentrations of all 16 PAHs determined in 1999/2000 are presented in Figures 4a-4l. The mean quarterly concentrations of all 16 PAHs and total concentrations of carcinogenic PAHs are given in Tables 4-8.

The general recovery of different PAHs obtained by SPE and RP-HPLC methods (Figures 1-3) ranged between 28.28-104.32% of applied doses. The lower recovery were for naphthalene (28.28%) and also benzo[b]fluoranthene and benzo[k]fluoranthene (32.42%). The highest recovery were received for fluorene (92.09%) and phenanthrene (104.32%) (Table 3). The detection limits were ranged

Table 2. Characterization of water samples.

No.	Data	Place	Characteristic of water samples	Volume
1.	07.1999-12.2000	Stoki-Łódź	Drinking water	2.0 L
2.	07.1999-12.2000	Tomaszów	Drinking water	2.0 L
3.	07.1999-12.2000	Bronisławów	Artificial lake water	2.0 L
4.	07.1999-12.2000	Brzustówka	River water	2.0 L
5.	07.1999-12.2000	Chojny-Łódź	Drinking water	2.0 L

Table 3. The characterization of PAHs determined in water samples (*).

No.	PAHs	Abbreviation	t _r [min] (**)	SD [min] (**)	Recovery [%] (***)	Detection limit[ng/L]
1.	Naphtalene	Nfl	12.822	0.610	28.28	5
2.	Acenaphtylene	Acyl	13.368	0.577	51.97	2
3.	Acenaphthene	Ac	14.136	0.533	76.18	1
4.	Fluorene	Fln	14.649	0.476	92.09	0.01
5.	Phenanthrene	Fen	14.931	0.438	104.32	0.1
6.	Anthracene	Ant	15.537	0.373	89.38	0.1
7.	Fluoranthene Pyrene	Flu Pir	16.101	0.343	87.70	1
8.	Benzo[a]anthracene Chrysene	B[a]A Chn	16.783	0.321	63.72	1
9.	Benzo[b]fluoranthene Benzo[k]fluoranthene	B[b]F B[k]F	18.246	0.297	32.42	1
10.	Benzo[a]pyrene	B[a]P	19.448	0.399	81.19	1
11.	Dibenzo[a,h]anthracene Benzo[g,h,i]perylene	Db[a,h]A B[g,h,i]P	21.690	0.547	52.06	2
12.	Indeno[1,2,3-c,d]pyrene	I[1,2,3-c,d]P	22.427	0.583	48.51	5

(*) The characterization of PAHs was based on mixture of 16 standards of PAHs prepared by Ehrenstorfer (Germany) with concentrations of 10.0 mg/L of each with purity 97.4-99.9%, determined by EPA 550.1. procedure.

(**) The mean retention time values were calculated on n=10 injections.

(***) The mean recoveries of SPE method were calculated on n=5 measurements.

between 0.01-5 ng/L. The lower detection limit was for fluorene (0.01 ng/L) but the highest (5 ng/L) were for naphthalene and for indeno[1,2,3-c,d]pyrene (Table 3). The chromatogram of 16 PAH standards (PAH Mix-16) are presented in Figure 1. In most commercial available C18 type columns separation of all 16 PAHs is impossible. The retention times of B[k]F, B[b]F, B[g,h,i]P, I[1,2,3-c,d]P or even B[a]A and Chn are very similar and there is a problem with a good separation and selectivity on C18 type chromatographic columns [57-59].

The highest concentrations of benzo[a]pyrene and all the carcinogenic PAHs for drinking water were observed in July-September 1999 and July-August 2000 (Łódź-Chojny); July-September 1999 and July, August and October 2000 (Łódź-Stoki), and in July-September 1999, February-March 2000, June and November-December 2000 (Tomaszów Mazowiecki) (Tables 4-6, Figures 4a-4l). In all this period the concentrations of B[a]P in drinking water from Łódź-Chojny, Łódź-Stoki and Tomaszów Mazowiecki in practice in most samples were lower than 15 ng/L as recommended by WHO, The European Commission and International Agency for Research on Cancer (IARC) [60-63]. The last WHO document for drinking water recommended concentrations of B[a]P lower than 0.7 µg/L (700 ng/L) for additional carcinogenic risk 10^{-5} for all life [64]. The concentrations of B[a]P were:

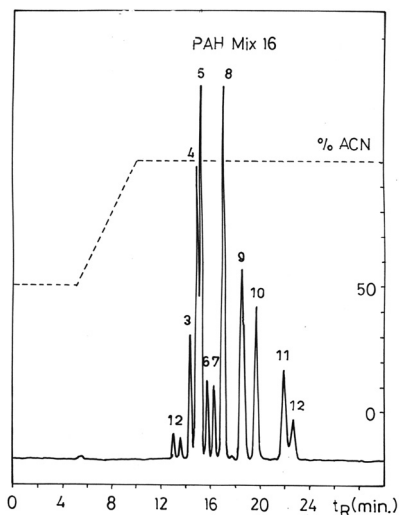


Fig.1. Separation of mixture of 16 PAH standards (separation by gradient elution on column Spherisorb 5S ODS2 250x4 mm ID with precolumn Spherisorb 5S ODS2 4x4 mm ID from Hewlett-Packard, USA, flow-rate 0.5 mL/min., volume of injection loop 20.0 µL, column temperature 25°C, absorbance at 254 nm was determined) where: (1) naphthalene; (2) acenaphylene; (3) acenaphthene; (4) fluorene; (5) phenanthrene; (6) anthracene; (7) fluoranthene and pyrene; (8) benzo[a]anthracene and chrysene; (9) benzo[b]fluoranthene and benzo[k]fluoranthene; (10) benzo[a]pyrene; (11) dibenzo[a,h]anthracene and benzo[g,h,i]perylene; (12) indeno[1,2,3-c,d]pyrene.

0-15 ng/L (mean 8+/-5 ng/L) for Łódź-Chojny, 0-16 ng/L (mean 7+/-5 ng/L) for Łódź-Stoki and 0-18 ng/L (mean 8+/-5 ng/L) for Tomaszów Mazowiecki and were similar to results obtained for Bydgoszcz, Gdańsk, Katowice, Kraków, Lublin, Warszawa and Wrocław, where the mean concentrations of B[a]P ranged between 4.00-8.33 ng/L [65]. The determination of B[a]P concentrations in drinking water at Kobiernice (Tresna artificial lake), showed the mean concentration range between 10-20 ng/L and were higher than for Łódź and Tomaszów Mazowiecki towns [66]. In all drinking water samples the contents of Σ8 PAHs were lower than 200 ng/L (Tables 4-6, Figures 4a-4l), recommended by WHO [62]. The mean contents of Σ8 PAHs for Łódź-Chojny (57+/-59 ng/L), Łódź-Stoki (45+/-

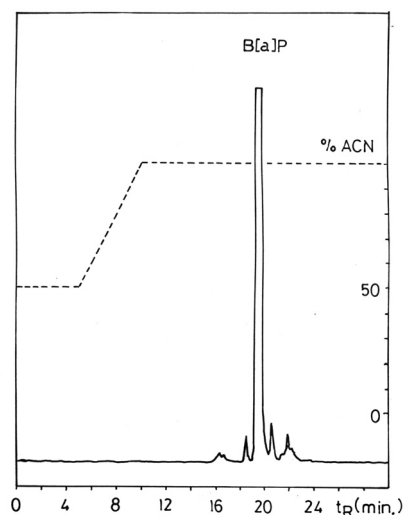


Fig.2. Separation of benzo[a]pyrene standard (condition of RP-HPLC separations as in Fig.1.).

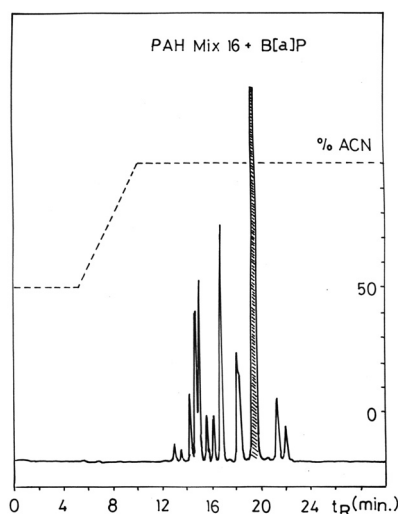


Fig.3. Separation of mixture of 16 PAHs standards and benzo[a]pyrene standard (1: 10) (conditions of RP-HPLC separation as in Fig.1.).

Table 4. Mean concentrations of PAHs in drinking water in the Łódź-Chojny area.

PAHs	The mean concentrations of PAHs in water [ng/L] (*)						
	07-09.1999	10-12.1999	01-03.2000	04-06.2000	07-09.2000	10-12.2000	1999/2000
Naphtalene	0-2587 1210+/-1302	0-224 75+/-129	0-225 5+/-130	35-179 122+/-76	0-706 372+/-355	0-301 100+/-174	0-2587 326+/-632
Acenaphthylene	0-5180 1867+/-2877	0 0	0-242 129+/-122	0 0	258-821 454+/-318	7-1035 401+/-554	0-5180 478+/-1210
Acenaphthene	0-128 48+/-68	0-86 55+/-47	25-66 46+/-20	0 0	22-107 54+/-46	0-66 24+/-36	0-128 38+/-41
Fluorene	246-770 489+/-264	120-186 145+/-36	78-120 101+/-21	52-89 67+/-19	37-189 95+/-82	18-241 153+/-119	18-770 175+/-181
Phenanthrene	16-119 52+/-58	0-8 3+/-5	0-11 4+/-6	0 0	0-10 5+/-5	0-15 10+/-8	0-119 12+/-27
Anthracene	0-887 313+/-498	0-40 13+/-23	0-37 23+/-20	0 0	0-53 23+/-27	27-56 46+/-16	0-887 69+/-205
Fluoranthene	0-77 47+/-41	0-40 13+/-23	6-19 8+/-10	0 0	0-21 12+/-11	0-138 50+/-76	0-138 22+/-37
Benzo[a]anthracene	5-260 116+/-131	0-15 5+/-9	0 0	0 0	12-45 26+/-17	0-6 4+/-3	0-260 25+/-62
Chrysene	52-71 63+/-10	13-28 18+/-8	0-94 31+/-54	0 0	0-56 19+/-32	0-28 13+/-14	0-94 24+/-30
Benzo[b]fluoranthene	0-13 8+/-7	2-8 4+/-3	7-11 9+/-2	0-4 2+/-2	10-15 12+/-2	6-12 10+/-3	0-15 8+/-5
Benzo[k]fluoranthene	0-13 4+/-7	0 0	0 0	0 0	0-14 7+/-7	0 0	0-14 2+/-4
Indeno[1,2,3-c,d]pyrene	0-18 6+/-10	0 0	0 0	0 0	0-12 4+/-7	0 0	0-18 2+/-5
Σ 8 PAHs (**)	65-179 128+/-58	16-61 36+/-23	7-124 49+/-65	0-42+/-2	25-108 54+/-47	25-161 73+/-76	0-179 57+/-59
Σ 16 PAHs	785-9815 4223+/-4885	144-469 331+/-168	158-825 427+/-352	126-235 191+/-58	374-1837 1084+/-732	127-1851 811+/-915	126-9815 1178+/-2247

(*) in table are presenting ranges of PAHs concentrations from minimum to maximum in presenting period and mean concentrations with standard deviations (SD),

(**) the concentrations of 8 cancerogenic PAHs (benzo[a]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, [indeno1,2,3-c,d]pyrene, benzo[a]anthracene, chrysene and dibenzo[a,h]anthracene).

Table 5. Mean concentrations of PAHs in drinking water in the Łódź-Stoki area.

PAHs	The mean concentrations of PAHs in water [ng/L] (*)						
	07-09.1999	10-12.1999	01-03.2000	04-06.2000	07-09.2000	10-12.2000	1999/2000
Naphtalene	710-1717 1157+/-513	0-368 194+/-185	38-161 104+/-62	0-96 61+/-53	0-252 119+/-127	0-569 190+/-328	0-1717 304+/-455
Acenaphthylene	350-1893 1160+/-774	0 0	45-275 179+/-119	0-239 80+/-138	0-159 101+/-88	0-898 346+/-483	0-1893 311+/-517
Acenaphthene	0-117 70+/-62	0-36 12+/-21	0-37 16+/-19	0-44 15+/-25	14-49 26+/-20	0-37 13+/-21	0-117 25+/-34
Fluorene	65-406 179+/-197	62-214 125+/-79	17-116 55+/-53	20-110 58+/-47	16-245 121-116	135-446 259+/-165	16+/-446 133+/-126
Phenanthrene	11-64 30+/-29	0-12 7+/-6	3-13 7+/-5	0-7 4+/-3	0-6 2+/-3	0-19 6+/-11	0-64 9+/-15
Anthracene	0-501 218+/-257	0 0	0-67 32+/-34	0-134 45+/-77	0-32 11+/-18	20-76 40+/-31	0-501 56+/-121
Fluoranthene	0-59 20+/-34	0-118 39+/-68	0-33 20+/-18	0 0	0-43 14+/-25	0-34 20+/-18	0-118 19+/-31
Pyrene	0-19 9+/-10	0 0	0 0	0 0	0-43 18+/-22	0-72 25+/-40	0-72 9+/-19
Benzo[a]anthracene	0-62 21+/-36	20-30 26+/-5	0 0	0 0	0-11 4+/-6	0-17 6+/-10	0-62 9+/-17
Chrysene	0-16 10+/-9	6-9 7+/-2	4-13 8+/-5	0-2 1+/-1	0-9 5+/-4	8-11 10+/-1	0-16 7+/-5
Benzo[b]fluoranthene	0-97 32+/-56	0 0	0 0	0 0	0-31 18+/-16	0 0	0-97 8+/-24
Benzo[k]fluoranthene	0 0	0 0	0-26 9+/-15	0 0	0 0	0 0	0-26 1+/-6
Indeno[1,2,3-c,d]pyrene	15-172 83+/-81	29-154 73+/-70	6-58 37+/-27	0-2 1+/-1	22-59 40+/-18	11-61 35+/-25	0-172 45+/-48
Σ 8 PAHs (**)	1358+/-4192 2906+/-1435	139-772 411+/-326	321-595 429+/-146	122-536 307+/-211	70-668 438-322	195-4356 1641+/-2353	70-4356 1022+/-1378

(*) in table are presenting ranges of PAHs concentrations from minimum to maximum in presenting period and mean concentrations with standard deviations (SD),

(**) the concentrations of 8 cancerogenic PAHs (benzo[a]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, [indeno1,2,3-c,d]pyrene, benzo[a]anthracene, chrysene and dibenzo[a,h]anthracene).

Table 6. Mean concentrations of PAHs in drinking water in Tomaszów Mazowiecki.

PAHs	The mean concentrations of PAHs in water [ng/L] (*)						
	07-09.1999	10-12.1999	01-03.2000	04-06.2000	07-09.2000	10-12.2000	1999/2000
Naphtalene	28-1647 724+/-833	0-264 135+/-132	0-341 221+/-191	0-527 176+/-304	0-221 104+/-111	0-969 357+/-533	0-1647 286+/-426
Acenaphthylene	692-1762 1109+/-573	0 0	0-567 315+/-289	0-837 279+/-483	66-124 92+/-30	94+/-262 181+/-84	0-1762 329+/-466
Acenaphthene	27-310 129+/-157	0-66 22+/-28	0-69 23+/-40	0-65 22+/-37	0-26 13+/-13	0-57 26+/-29	0-310 39+/-73
Fluorene	76-197 154+/-68	40-124 91+/-45	53-232 134+/-91	38-201 99+/-89	101-177 148+/-41	152-346 217+/-111	38-346 141+/-78
Phenanthrene	10-121 48+/-63	0 0	0-17 9+/-8	0-10 3+/-6	0-8 3+/-5	0 0	0-121 10+/-28
Anthracene	0-965 324+/-555	0-32 11+/-18	0-50 30+/-27	0 0	0-25 8+/-14	0-160 53+/-92	0-965 71+/-226
Fluoranthene Pyrene	0-92 40+/-47	0-89 30+/-51	0-19 12+/-10	0-4 1+/-2	0-27 9+/-16	0-59 26+/-30	0-92 20+/-30
Benzo[a]anthracene Chrysene	0-37 19+/-18	0 0	0-81 30+/-45	0 0	1-7 4+/-3	0-8 3+/-5	0-81 9+/-20
Benzo[b]fluoranthene Benzo[k]fluoranthene	33-56 43+/-12	17-86 40+/-39	0-84 28+/-48	0-21 7+/-12	0-60 25+/-31	0 0	0-86 24+/-30
Benzo[a]pyrene	12-13 12+/-1	0-10 5+/-5	8-18 11+/-6	0-13 5+/-7	0-7 4+/-4	5-10 8+/-3	0-18 8+/-5
Dibenzo[a,h]anthracene Benzo[g,h,i]perylene	26-39 35+/-7	0 0	0 0	0-9 3+/-5	0-22 10+/-11	0 0	0-39 8+/-14
Indeno[1,2,3-c,d]pyrene	0-16 10+/-9	0 0	0 0	0 0	0-17 6+/-10	0 0	0-17 3+/-6
Σ 8 PAHs (**)	94-195 140+/-49	17-111 75+/-50	8-121 51+/-61	0-47 16+/-27	9-133 54+/-68	10-68 34+/-30	0-195 62+/-58
Σ 16 PAHs	1193-4953 2646+/-2020	319-362 334+/-24	61-1292 813+/-659	38-1687 594+/-946	311-541 426+/-115	483-1248 72+/-379	38-4953 948+/-1142

(*) in table are presenting ranges of PAHs concentrations from minimum to maximum in presenting period and mean concentrations with standard deviations (SD),

(**) the concentrations of 8 cancerogenic PAHs (benzo[a]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, [indeno1,2,3-c,d]pyrene, benzo[a]anthracene, chrysene and dibenzo[a,h]anthracene).

Table 7. Mean concentrations of PAHs in water at Sulejów Artificial Lake.

PAHs	The mean concentrations of PAHs in water [ng/L] (*)						
	07-09.1999	10-12.1999	01-03.2000	04-06.2000	07-09.2000	10-12.2000	1999/2000
Naphtalene	923-2374 1674+/-722	376-5234 3269+/-2558	0-2326 878+/-1263	0-409 157+/-220	0 0	0-3324 1346+/-1750	0-5234 1221+/-1627
Acenaphthylene	1036-8495 3721+/-4145	0-1126 597+/-560	0-365 217+/-192	0-428 143+/-247	0 0	0-711 237+/-410	0-8495 819+/-1977
Acenaphthene	0-910 433+/-457	0-522 299+/-269	31-120 90+/-51	0-272 91+/-157	0-2 1+/-1	0-22 7+/-13	0-910 153+/-251
Fluorene	268-2073 1335+/-946	140-3726 2189+/-1847	77-1237 794+/-626	0-1298 435+/-747	3-46 20+/-23	27-2267 965+/-1164	0-3726 956+/-1131
Phenanthrene	12-69 40+/-28	10-48 32+/-20	0-13 8+/-7	0-22 7+/-13	0-8 3+/-5	0-39 13+/-22	0-69 17+/-21
Anthracene	48-181 128+/-71	0-108 67+/-58	0-50 21+/-26	0-293 98+/-169	0 0	0-349 129+/-191	0-349 73+/-107
Fluoranthene Pyrene	143-794 366+/-370	0-192 119+/-104	0-73 24+/-42	0-65 22+/-37	0 0	0-39 13+/-22	0-794 91+/-188
Benzo[a]anthracene Chrysene	0-16 8+/-8	0 0	0 0	0 0	2-64 23+/-35	0-5 2+/-3	0-64 6+/-15
Benzo[b]fluoranthene Benzo[k]fluoranthene	0-56 19+/-32	28-84 61+/-29	0 0	0-1 1+/-1	0-12 4+/-7	0-2 1+/-1	0-84 14+/-27
Benzo[a]pyrene	28-119 62+/-50	64-82 73+/-9	95-120 108+/-12	1-31 16+/-15	0-55 34+/-29	48-413 188+/-197	0-413 80+/-91
Dibenzo[a,h]anthracene Benzo[g,h,i]perylene	13-22 18+/-4	0 0	0 0	0-9 3+/-5	0-11 4+/-6	0 0	0-22 4+/-7
Indeno[1,2,3-c,d]pyrene	0 0	0 0	0 0	0-15 5+/-9	0 0	0 0	0-15 1+/-3
Σ 8 PAHs (**)	189-845 464+/-340	102-344 253+/-131	95-193 132+/-53	2-120 46+/-65	0-78 41+/-39	51-452 202+/-218	0-845 190+/-210
Σ 16 PAHs	2671-13832 7817+/-5631	628-10022 6704+/-5270	217-4263 2139+/-2030	22-2842 976+/-1616	51-110 87+/-31	78-6503 2901+/-3283	22-13832 3437+/-4210

(*) in table are presenting ranges of PAHs concentrations from minimum to maximum in presenting period and mean concentrations with standard deviations (SD),

(**) the concentrations of 8 cancerogenic PAHs (benzo[a]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, [indeno1,2,3-c,d]pyrene, benzo[a]anthracene, chrysene and dibenzo[a,h]anthracene).

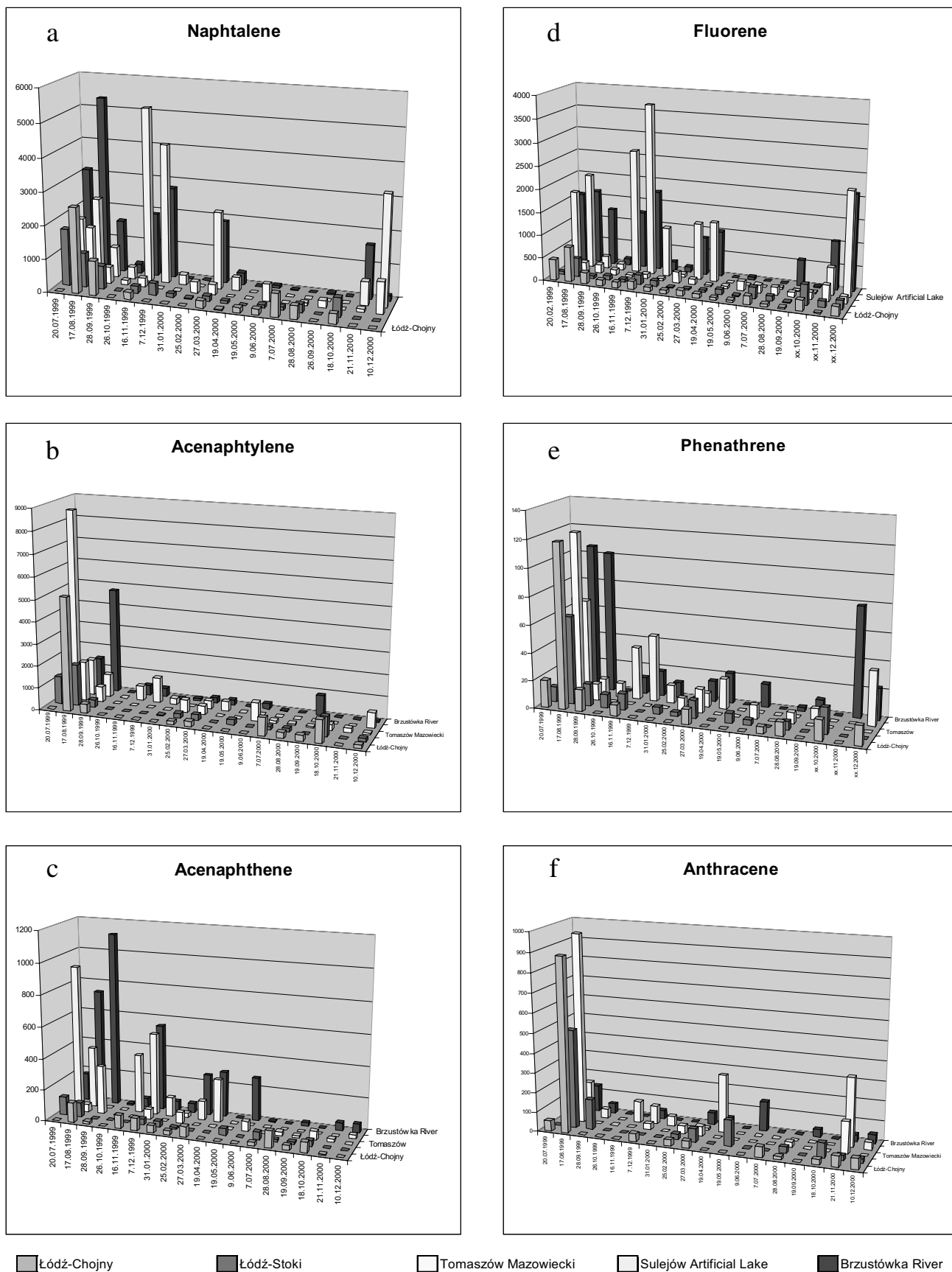
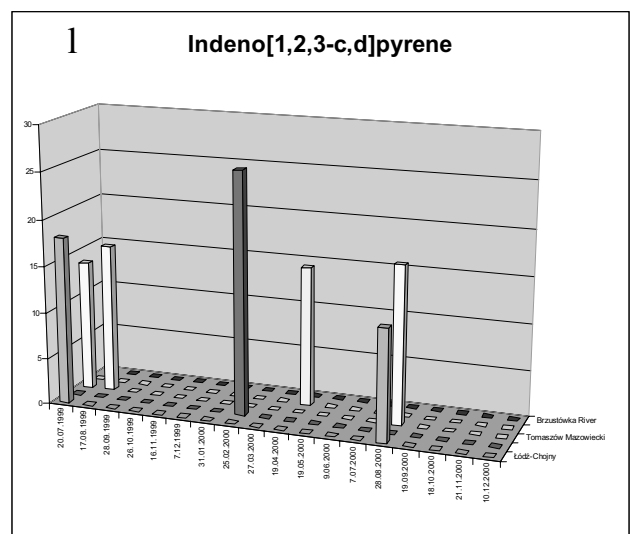
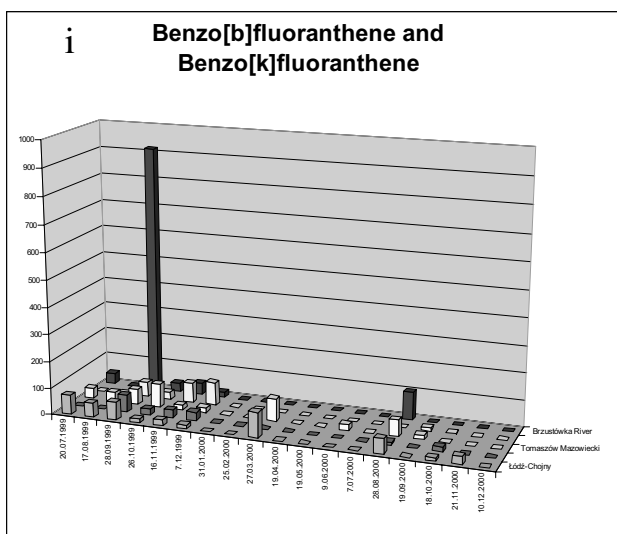
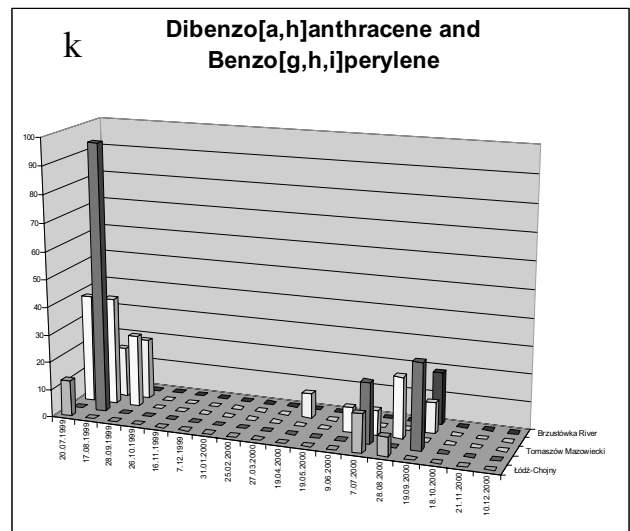
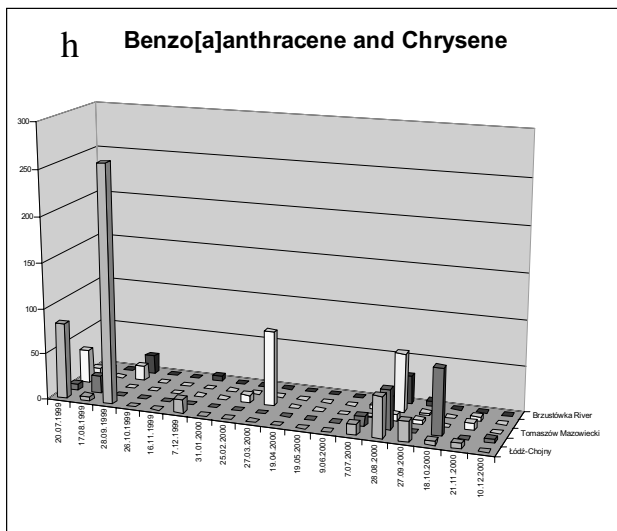
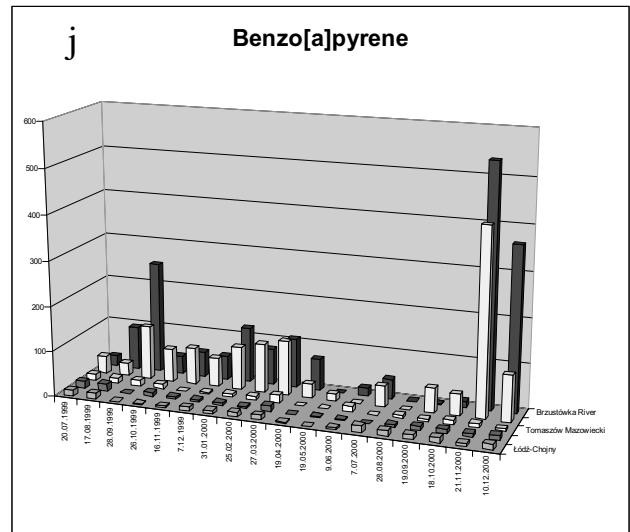
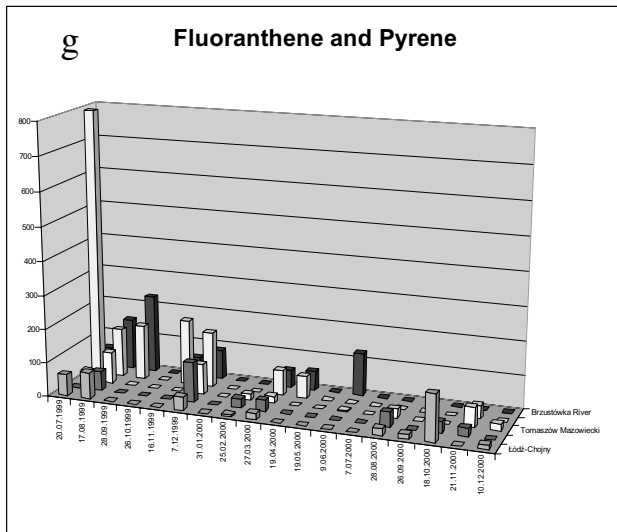


Fig. 4. Concentrations of 16 PAHs in water from Łódź-Chojny reservoir of drinking water, Łódź-Stoki, Tomaszów Mazowiecki, Sulejów Artificial Lake and Brzustówka River in period from 07.1999-12.2000, where (a) naphthalene, (b) acenaphtylene, (c) acenaphthene, (d) fluorene, (e) phenanthrene, (f) anthracene.



Łódź-Chojny
 Łódź-Stoki
 Tomaszów Mazowiecki
 Sulejów Artificial Lake
 Brzustówka River

Fig. 4. Concentrations of 16 PAHs in water from Łódź-Chojny reservoir of drinking water, Łódź-Stoki, Tomaszów Mazowiecki, Sulejów Artificial Lake and Brzustówka River in period from 07.1999-12.2000, where (g) fluoranthene and pyrene, (h) benzo[a]anthracene and chrysene, (i) benzo[b]fluoranthene and benzo[k]fluoranthene, (j) benzo[a]pyrene, (k) dibenzo[a,h]anthracene and benzo[g,h,i]perylene, (l) of indeno[1,2,3-c,d]pyrene.

Table 8. Mean concentrations of PAHs in water from Brzustówka river.

PAHs	The mean concentrations of PAHs in water [ng/L] (*)						
	07-09.1999	10-12.1999	01-03.2000	04-06.2000	07-09.2000	10-12.2000	1999/2000
Naphtalene	1586-5323 3341+/-1878	290-2754 1650+/-1252	0-1891 630+/-1092	0-367 156+/-190	0-46 23+/-23	0-1604 589+/-882	0-5323 1065+/-1490
Acenaphthylene	781-4773 2346+/-2131	0-456 282+/-246	0-240 118+/-120	0-246 153+/-134	0-903 307+/-516	0-47 16+/-27	0-4773 537+/-1131
Acenaphthene	176-1112 674+/-471	10-548 204+/-299	58-257 125+/-114	0-289 187+/-162	0-23 10+/-12	0-55 35+/-30	0-1112 206+/-305
Fluorene	1246-1631 1468+/-199	136-1748 1041+/-824	120-819 376+/-385	0-944 350+/-558	2-560 189+/-322	22-2106 1059+/-1042	0-2106 747+/-714
Phenanthrene	67-106 92+/-21	0-18 10+/-9	0-15 9+/-8	0-22 13+/-11	0-10 4+/-5	0-79 34+/-41	0-106 27+/-36
Anthracene	48-324 169+/-141	0-42 14+/-24	0-63 21+/-36	0-150 66+/-77	0-39 13+/-22	0-45 26+/-23	0-324 51+/-82
Fluoranthene	56-230 145+/-87	0-88 49+/-45	0-50 17+/-29	0-125 60+/-63	0-9 3+/-5	0 0	0-230 46+/-66
Benzo[a]anthracene	0-22 14+/-12	0-6 2+/-3	0 0	0 0	0-31 12+/-16	0 0	0-31 5+/-9
Chrysene	0-917 319+/-518	20-44 32+/-12	0 0	0 0	0-104 35+/-60	0 0	0-917 64+/-214
Benzo[b]fluoranthene	23-248 122+/-115	40-56 49+/-8	80-123 104+/-22	0-71 29+/-37	0-43 15+/-24	14-535 304+/-266	0-535 104+/-142
Benzo[k]fluoranthene	0-31 10+/-18	0 0	0 0	0 0	0-19 6+/-11	0 0	0-31 3+/-8
Indeno[1,2,3-c,d]pyrene	0 0	0 0	0 0	0 0	0 0	0 0	0 0
Σ 8 PAHs (**)	151-1395 597+/-692	72-160 130+/-50	80-159 121+/-40	0-142 89+/-78	30-104 59+/-39	14-535 304+/-266	0-1395 217+/-321
Σ 16 PAHs	6162-10282 8701+/-2221	508-5666 3334+/-2614	372-3444 1400+/-1770	0-2059 1015+/-1030	93-1617 617+/-866	36-3351 2064+/-1777	0-10282 2855+/-3221

(*) in table are presenting ranges of PAHs concentrations from minimum to maximum in presenting period and mean concentrations with standard deviations (SD),

(**) the concentrations of 8 cancerogenic PAHs (benzo[a]pyrene, benzo[g,h,i]perylene, benzo[b]fluoranthene, benzo[k]fluoranthene, indeno[1,2,3-c,d]pyrene, benzo[a]anthracene, chrysene and dibenzo[a,h]anthracene).

48 ng/L) and Tomaszów Mazowiecki (62+/-58 ng/L) were higher than for drinking water in Poznań obtained from the Warta river. In 1985-1991 the mean annual concentrations of Σ6 PAHs were ranged between 10.3-53.0 ng/L [67,68]. The Σ6 PAHs in tap water in Bytom and Zabrze were 3.715+/-0.697 ng/L and 16.876+/-1.296 ng/L [69]. Obtained results are a little bit different in comparison with our results because 6 PAHs and pollutants were determined by TLC or HPTLC methods. The contents of all 16 PAHs in drinking water ranged between 126-9,815 ng/L (1,178+/-915 ng/L) for Łódź-Chojny, 70-4,356 ng/L (1,022+/-1,378 ng/L) for Łódź-Stoki and 38-4,953 ng/L (948+/-1,142 ng/L) for Tomaszów Mazowiecki (Tables 4-6, Figures 4a-4l). The comparison of results obtained by GC and TLC method show that results obtained for B[a]P by TLC method were about 41-56% lower than those obtained by GC. Similar results were obtained for other PAHs, where the concentration of PAHs determined by TLC were about 35-60% lower than for GC. The differences between GC and HPLC did not exceeded by about 5-10% [70]. The highest concentrations presented in our article are probably the results of applying HPLC.

The concentration of B[a]P in Sulejów Artificial Lake in Bronisławów ranged 0-413 ng/L, (mean 80+/-90 ng/L) and between 0-535 ng/L (mean 104+/-142 ng/L) for the Brzustówka River (Tables 7 and 8, Figures 4a-4l). The levels of B[a]P were higher than for lakes in Wielkopolski

National Park (Witobelskie, Dymaczowskie, Lipno, Chomęcickie, Rosnowskie Małe, Rosnowskie Duże, Jarosławickie, Góreckie, Skrzyńka and Budzyńskie), where the mean concentration of B[a]P were ranged between 0-12 ng/L and in Warta, which is the eastern border of the national park, where content were ranged 0-16 ng/L [34]. The concentration of B[a]P in the Warta river near Poznań (Dębin and Dębiec) in 1985-1991 were about 6.9-31.2 ng/L and were lower than for the Brzustówka River [67]. Results obtained by Zawadzka et al., [71] show that concentrations of B[a]P in the Wisła at Kraków (115 ng/L and 130 ng/L) were similar to our results obtained for Sulejów and Brzustówka, but in the Wisła at Warsaw (20-54 ng/L) and in the Warta at Poznań (2-12 ng/L) were lower than our results. The Σ8 PAHs in Sulejów artificial lake and Brzustówka river were between 0-845 ng/L (mean 190+/-210 ng/L) and 0-1395 ng/L (mean 217+/-321 ng/L) (Tables 7 and 8, Figures 4a-4l). The Σ6 PAHs in protected area of Wielkopolski National Park were about 5-90 ng/L and were lower than results obtained in our laboratory [34]. In 1985-1991 Σ6 PAHs in Warta were about 75.9-312.4 ng/L and were similar to our results [67]. The results obtained by Zawadzka et al., [71] (710 and 730 ng/L for Wisła/Kraków; 190-294 ng/L for Wisła/Warsaw and 124-269 ng/L for Warta/Poznań) were higher and similar to our results, even though analysis was done by the TLC method [70-72].

The main components of PAH mixtures are: naphthalene, acenaphthylene, fluorene and anthracene. Dibenzo[a,h]anthracene, benzo[g,h,i]perylene, indeno[1,2,3-c,d], benzo[a]anthracene and also chrysene are components with the lower concentrations in natural water (river and lake water) and drinking water in Łódź and Tomaszów Mazowiecki areas (Tables 4-8). The highest contents of all PAHs, for all samples, were observed in the rainy summer of 1999 and in autumn-winter 2000, which correlated with very extensive rainfall and snowfall (Figures 4a-4l). The strong changes of PAH concentrations, in lakes and rivers is the result of the high content of PAHs in runoff and rain water at the beginning of raining time. The concentrations of all 16 PAHs in rain and snow can be about 500-20,000 ng/L [35,73-75]. After this the concentrations of PAHs in river and lakes can increase more than 100 times in comparison to normal state.

Conclusions

The level of benzo[a]pyrene and other PAHs in drinking water in the Łódź area is similar to results for other towns and are lower than concentrations of PAHs recommended by WHO and the European Commission.

Concentrations of benzo[a]pyrene and other PAHs in water at Brzustowka river and Sulejów Artificial Lake is high in comparison with levels determined in Polish lakes and rivers obtained by other authors.

The differences in concentrations of PAHs in tap and river water in the area of Łódź and others can be the result of sensitivity of TLC or HPTLC methods and HPLC method used in experiments.

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