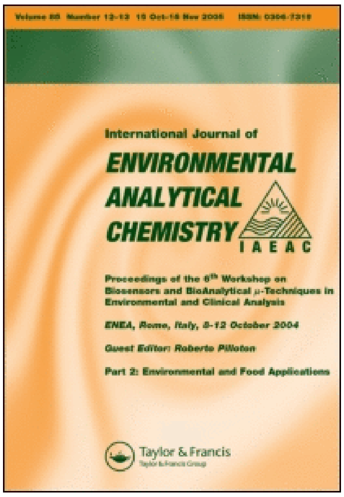

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# TEMPORAL TRENDS OF POLYCYCLIC AROMATIC HYDROCARBONS IN PRECIPITATION OF POZNAŃ AND ITS VICINITY (POLAND)

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Samples of precipitation: rain, sleet and snow, were collected at the centre of the city of Poznań and in the Wielkopolski National Park. Samples were collected from 26 Nov. 1996 to 20 Nov. 1999. PAHs were isolated by extraction in the system liquid-solid state (columns for SPE and a Speedisk-adsorbent $C_{18}$). Determination was performed on a liquid chromatograph HPLC. The breakdown curves for naphthalene (SPE, Empore and Speedisk) were given. The main PAHs occurring in the samples from the city and from the National Park area were naphthalene and anthracene. The other PAH compounds occurred at much lower concentrations. The content of benzo[*a*]pyrene did not exceed the permissible level. Significant differences were noted in the content of certain PAHs depending on the kind of precipitation. Differences in PAHs concentrations were also observed between the precipitation samples collected in winter and spring.

The results of PAH determinations over the few years of observation, from 1996 to 1999, prove a decrease in the contents of the majority of PAHs in precipitation, which is directly related to intense modernisation of the system of central heating and the changeover from coal to gas heating.

*Keywords:* Polycyclic aromatic hydrocarbons; Precipitation; Solid Phase Extraction; Poland

## INTRODUCTION

The development of industry and motorization has been responsible for introducing into the environment many substances which did not occur there earlier or occurred in very small amounts. Such substances include polycyclic aromatic

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hydrocarbons (PAHs) which are commonly found in surface – and groundwater, soil, air, and even in plants and food products [1,2]. An analysis of their content in ice monoliths from Greenland showed a substantial increase in their amount in the period of the rapid development of industry [3]. The established mutagenic and carcinogenic properties of PAHs [4,5] prompted the US Environmental Protection Agency (EPA) to recommend a control of the level of 16 compounds from this group in the environment [6].

The air is the element most threatened with contamination by PAHs as they are introduced into it directly from the sources of emission. Complicated reactions taking place in the air under the influence of light, ozone and temperature hinder the establishment of the pathway of conversion of these compounds [7]. It has been estimated that the recent emission of benzo[*a*]pyrene from industrial sources in Poland has amounted to 21 tonnes per year [8]. The total annual emission of PAHs in Poland has been estimated at 2.56 $kg/km^2$, which is twice the amount emitted in the USA and Sweden [9]. PAHs introduced into the atmosphere are frequently adsorbed on dust particles, and with them can be dispersed over long distances or fall down. In unfavourable atmospheric conditions they can accumulate in a given area and remain there in the form of haze and aerosol.

In Poland a few reports have been published on the content of PAHs in the air in the most industrialised and most contaminated region of Upper Silesia [10,11] and central Poland [7,12,13], and in precipitation [9,14]. Atmospheric precipitation plays an important role in the removal of these compounds from the air [15,16]. The content of PAHs in precipitation differs significantly depending on the kind of precipitation (rain, hail, snow, mist) [11], its frequency and volume, as well as geographic location [17,18,19]. Their content also shows seasonal changes [10,20].

The results reported in this paper provide information on changes in the level of the most important PAHs in precipitation depending on the degree of urbanisation of an area and the season of the year.

## EXPERIMENTAL

### Precipitation collection sites

Samples of precipitation: rain, sleet and snow, were collected at the centre of the city of Poznań, at a site a little off the main roads, and outside the city, in the Wielkopolski National Park, about 20 km SW from Poznań (Figure 1). Samples were collected from 26 Nov. 1996 to 20 Nov. 1999, into dark glass vessels of 2.5 L capacity and fixed with chloroform in the amount of 3 mL per 1 L [21].

FIGURE 1 Location of sampling sites

## Isolation of PAHs from the wet matrix and selection of the extraction method

The PAH extraction was performed in the liquid-solid systems indicated in Table I and Table II.

TABLE I Characterisation of the sorptive systems for naphthalene

| *Technique* | *Type of support* | *Parameters of support* | *Type of phase* | *Mean recovery [%]* |
|---|---|---|---|---|
| SPE | Silica | capacity 3 mL. 500 mg | $C_{18}^{aqua}$ | 80 – 100 |
| Empore® disks | PTFE (10%)<br>Silica (90%) | depth of support 1 mm<br>diameter 45 mm | $C_{18}^{aqua}$ | 55 –75 |
| Speedisk® | Silica | depth of support 3 mm<br>membrane thickness 1 mm<br>diameter 50 mm | $C_{18}^{aqua}$ | 80 – 90 |

TABLE II Outline of the procedure

| Sample preparation: | | |
|---|---|---|
| 15% 2-propanol is added to 1L of water sample | | |
| Solid Phase Extraction | EMPORE disks | Speedisk |
| Conditioning: | | |
| Wash column with 6 mL 2-propanol and 6 mL of water/2-propanol mixture (9:1 v/v); support should not get dry. | Wash disk with 5 mL of (1:1) mixture of methyl dichloride/ methyl acetate. Leave mixture for 3 min., filter off, dry disk. Add 5 mL of methanol and leave for 3 min. | Deposit 1ml of methyl dichloride on disk. Leave for 1min., filter off, dry disk. Deposit 10 mL of methanol, leave 1ml, filter off with care so as not to dry disk. Add 10 mL of water (HPLC purity). |
| Deposition: | | |
| Deposit sample on support and filter off at 5 mL /min rate. Wash support with 2 mL of (9:1) water/2-popropanol mixture. Dry in vacuum. | Filter water sample through disk. Dry in vacuum for 15 min. | Deposit water sample and filter it through disk. Dry in vacuum for about 20 min. |
| Elution: | | |
| Elute 4 x 0.5 mL of methylene chloride, evaporate to 1 ml volume. | Elute 2 x 5 mL methylene dichloride, leave for 3 min., filter off. Dry extract over anhydrous $Na_2SO_4$. Evaporate to 1 mL volume. | Elute 5 ml acetonitrile, add 2 x 5 mL methyl dichloride. Dry extract with anhydrous $Na_2SO_4$. Evaporate to 1 mL volume. |

A comparative study of the isolation of naphthalene (a representative of PAHs) from water by SPE columns and membrane disks Speedisk and Empore was conducted according to the recommended method [22,23,24], using a BakerBond $PAH_{aqua}$ column which according to EPA, is selective towards 16 PAHs (Table I). An outline of particular stages of the procedure is given in Table II. The column ensured the best and reproducible results (Recovery 80–90%, RSD<3%). The analysis of the breakdown curves for naphthalene shown in Figure 2 (concentration $c_N = 1.2 \cdot 10^{-6}$ g/L), plotted for the three sorption systems studied, proved that the highest recovery was obtained for the SPE column (R = 92 ±2%). The results are in agreement with the earlier published data [24]. With an Empore type disk as a sorptive medium the values were about 10% lower.

The highest value of threshold breakdown was noted for Speedisk. The threshold value of the column breakdown ($c/c_0$) was 80% for the analyte volume $V_e$ of 900 mL. For the Empore disk and SPE column the corresponding values were 30% for $V_e = 600$ mL and 75% for $V_e = 500$ mL. As follows from this comparison, the recovery values change in inverse proportion to the permeability of supports of particular sorptive systems. This fact is important when determining large-volume environmental samples. Despite the highest value of recovery obtained on SPE columns, the permeability of the support decreased by as much

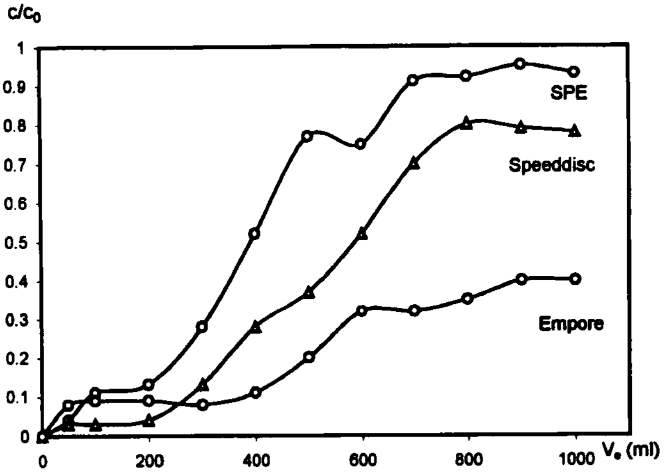

FIGURE 2 The breakdown curves for naphtalene for the three sorption systems: SPE, Speedisk and Empore

as 40% (the highest threshold value of the time of sample/support contact) in relation to Speedisk. The lowest R values obtained for the Empore disk, in relation to those obtained for Speedisk and SPE, are understandable because of a short time of contact (the depth of the sorptive layer is 1 mm – see Table I).

On the basis of the preliminary results we decided to use Speedisk (adsorbent $C_{18}$) and SPE columns. The results reported were obtained after experimental optimisation of the process of PAH isolation and enrichment.

## Analytical procedures

Qualitative and quantitative determination were performed on a liquid chromatograph HPLC type LC 10A made by Schimadzu (Kyoto, Japan) composed of a gradient pump, a UV – VIS diode array detector of variable wavelength ($\lambda = 190 - 600$ mm), a Rheodyne Co. (Berkeley CA, USA) injection valve (20 μL) and a fluorescence detector type RF – 10A.

The system was equipped with an analytical column Supelcosil™ LC – PAH (150 × 4.6 mm ID) filled with a 5 μm silica type adsorbent (Supelco, Bellefonte, PA, USA). The solvents used were acetonitrile and methanol, both of HPLC purity. Water was prepared by a Milli Q / RO type device, made by Millipore Ltd.

The whole HPLC set-up was controlled by a PC 486 DX2 with the ChemStation 2 program (Schimadzu), designed for controlling the set-up, data collection and processing.

### Standard mixture

A standard mixture of 16 PAHs in acetonitrile (J.T. Baker) was used. The standards were prepared at three levels of dilution: 1:50, 1:100 and 1:200, in order to check the linearity of the calibration curve. Each time the procedure was performed for the standard dissolved at 1:100 in a single injection of 20 μL.

## RESULTS AND DISCUSSION

The analysis of precipitation performed in the period 26 Nov. 1996 – 20 Feb. 1997 proved that the main PAH occurring in the samples from the city and from the National Park area was anthracene, whose concentration amounted to 177 ng/L (Table III). The second most important PAH was naphthalene, whose concentration was slightly over 100 ng/L. The other PAH compounds occurred in much lower concentrations. The content of benzo[*a*]pyrene in the investigated different kinds of precipitation averaged 5.3 ng/L and did not exceed the permissible level (20 ng/L). The analysis showed much higher average concentrations of naphthalene and anthracene (107.1 ng/L and 148.6 ng/L, respectively) in snow than in rain (60.6 ng/L and 92.6 ng/L, respectively). The results did not confirm the expected lower pollution outside the city, which was probably due to a close neighbourhood of sources of emission from house furnaces and elimination of local boiler houses in the city.

The results obtained 2 years later confirmed that among PAHs occurring in all kinds of precipitation, the concentration of naphthalene was from 4.0 ng/L to 198.2 ng/L, with 71 ng/L on average (Figure 3). The concentration of anthracene varied from 5.1 to 83.3 ng/L (21 ng/L on average), and fluorene, from 2.6 to 98.2 ng/L (31.7 ng/L on average). The concentration of benzo[*a*]pyrene was low and varied from 0.1 to 3.9 ng/L (1.8 ng/L on average) (Figure 4). Significant differences were noted in the content of certain PAHs depending on the kind of precipitation. The concentrations of naphthalene (198.2 ng/L) and fluorene (83.2 ng/L) in snow samples were much higher than in rain samples (52.0 and 23.1 ng/L, respectively); in sleet the relevant concentrations took intermediate values (72.7 and 38.3 ng/L, respectively).

TABLE III Concentrations [ng/L] of PAHs in the precipitation samples (different forms) collected in Poznań and in Wielkopolski National Park

| *PAHs* | *Wielkopolski National Park 26 Nov. 96 rain* | *Poznań 26 Nov. 96 rain* | *Wielkopolski National Park 15 Dec. 96 sleet* | *Wielkopolski National Park 9 Jan. 97. snow* | *Poznań 20 Feb. 97 snow* |
|---|---|---|---|---|---|
| Naphthalene | 81.0 | 40.2 | 100.0 | 108.0 | 106.2 |
| Acenaphthene | 13.4 | 4.6 | 30.6 | 25.7 | 3.3 |
| Fluorene | 14.8 | 10.3 | 23.3 | 25.2 | 7.2 |
| Phenanthrene | 9.2 | 1.6 | 10.6 | 17.8 | 0.8 |
| Anthracene | 97.7 | 87.2 | 176.8 | 167.4 | 129.8 |
| Fluoranthene | 2.5 | 16.3 | 13.0 | 16.3 | 10.2 |
| Pyrene | 14.0 | 2.4 | 20.2 | 20.2 | 3.3 |
| Benzo[*a*]anthracene | 13.6 | 17.5 | 28.0 | 28.9 | 13.4 |
| Chrysene | 11.6 | 2.7 | 15.4 | 15.6 | 3.1 |
| Benzo[*b*]fluorene | 7.2 | 12.5 | 6.2 | 6.6 | 13.5 |
| Benzo[*k*]fluorene | 5.0 | 1.8 | 3.0 | 3.8 | 1.8 |
| Benzo[*a*]pyrene | 4.5 | 4.9 | 6.2 | 5.5 | 5.4 |
| Dibenzo[*ah*]anthracene | 1.1 | 1.8 | 1.8 | 1.7 | 1.8 |
| Benzo[*ghi*]perylene | 0.3 | 2.3 | 3.3 | 3.2 | 1.2 |
| Indeno[1,2,3-*cd*]pyrene | 0.0 | 2.1 | 3.8 | 4.3 | 2.5 |

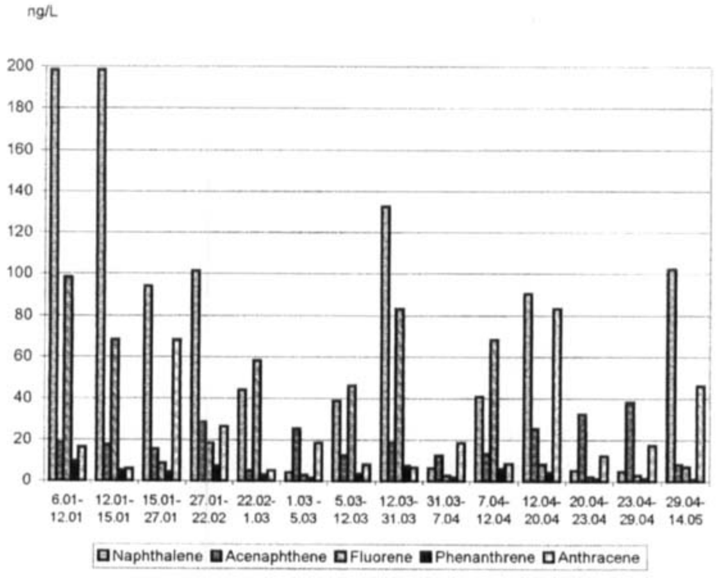

FIGURE 3 Concentrations of selected PAHs in samples of precipitation collected in Poznań from 6 Jan. to 14 May 1999 (ng/L)

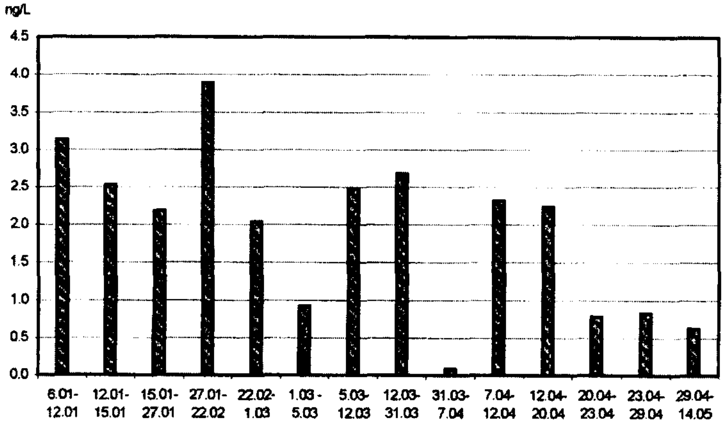

FIGURE 4 Concentrations of benzo[*a*]pyrene in the precipitation samples collected in Poznań from 6 Jan. to 14 May 1999 (ng/L)

Significant differences in PAH concentrations were also observed between the precipitation samples collected in winter and late spring. In the samples collected on 1 May 1998, i.e. after the house-heating season, only 6 out of 16 PAHs were detected. Acenaphtene was found in a concentration of 29 ng/L, fluorene in 3.2 ng/L, phenenthrene in 1.7 ng/L, while the concentrations of the other PAHs were lower than 1 ng/L [19].

The results of PAH concentration determinations over the few years of observation, from 1996 to 1999, show a decrease in the content of the majority of PAHs in precipitation. This tendency was most pronounced for anthracene, fluoranthene, pyrene and benzo[*a*]pyrene, whereas the mean level of naphthalene remained at about 70 ng/L, and the concentration of fluorene increased from 14 to 32 ng/L. The total amount of PAHs in precipitation in 1996 was 280 ng/L as against 169 ng/L in 1999, which is directly related to intense modernisation of the system of central heating and the changeover from coal to gas heating.

A comparison of our results with literature data reveals differences in the kinds of PAHs reported by different authors. Differences are noted both in qualitative and quantitative compositions and reach even a few orders of magnitude. The results of a study carried out in Gdańsk (north Poland) [14], a large industrial centre, proved a significant variation in concentrations of particular PAHs reaching four orders of magnitude, e.g. the concentration of benzo[*b*]fluoranthene varied from 11 to 12 800 ng/L. The mean values of PAH concentrations obtained in this period indicate that the dominant PAH was fluoranthene whose mean concentration was 679 ng/L, then chryzene with a mean concentration of 478 ng/L, pyrene (408 ng/L), and benzo[*b*]fluoranthene (452 ng/L). All these values are much higher than those obtained for Poznań. The concentration of the most dangerous benzo[*a*]pyrene varied from 0.34 to 573 ng/L, with an average of 76 ng/L, i.e. a value 20 times higher than in Poznań. Perhaps, the reason for so high values is the presence of a crude oil refinery and the high level of urbanisation of the area.

The concentrations of PAHs in precipitation reported by Kowalczyk (central Poland) [9] indicate differences depending on the month of sample collection. From December to February the mean total amount of PAHs was 1844 ng/month, while in April it was only 91 ng/month. Higher concentrations were reported from Germany [20]. The highest concentration was that of naphthalene in the range of 0.26 to 6.6 μg/L (2.0 μg/L on average). There were also high concentrations of fluorene (1.3 μg/L), phenanthrene (1.2 μg/L), and fluoranthene (1.2 μg/L). The total amount of PAHs averaged 9.5 μg/L. The authors emphasise seasonal variations in the content of PAHs and significant variations over time in the same kind of precipitation. The content of PAHs in the first millimetre of precipitation was even 6 times greater than in the second one.

Somewhat lower values were reported from Hannover [18], where the amount of fluoranthene was on average 149 ng/L and pyrene 84 ng/L, and the total amount of PAHs was 525 ng/L. The concentration of benzo[*a*[pyrene was 29 ng/L, that is, 16 times greater than its average concentration in Poznań, while naphtalene and anthracene, occurring in substantial amounts in Poznań, were not detected in the precipitation in Hannover. As follows from the studies performed in Hungary, the precipitation samples collected there contained also naphthalene in the highest amount, and its concentration was higher than in Poznań [25].

In conclusion, the results of PAH determination in the precipitation samples from Poznań and the National Park 20 km from the city, reveal their presence in low concentrations, both when analysing particular PAHs and their total amount. The results confirmed that greater amounts of PAHs occur in snow and sleet than in rain, as already indicated in the literature [15,16]. The concentrations of benzo[*a*]pyrene, the most harmful compound among the PAHs studied, were much below the Polish standard (20 ng/L). A comparison with the results of similar reports from other places in Europe proves that the amount and composition of PAHs in precipitation strongly depends on local conditions.

Taking into account that PAH concentrations are differently associated to the dissolved and suspended phases, a further study is planned including phase speciation of particular components.

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