

3249

# Behaviour of polycyclic aromatic hydrocarbons and triazine herbicides in water and aquifer material of a drinking water recharge plant

## II. Polycyclic aromatic hydrocarbons (PAHs) in surface water of the Ruhr and in ground water\*

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**Summary.** In part I of this series the area of investigation and the determination methods for the investigated analytes were introduced. In this second part the results of a routine PAH determination in Ruhr surface water and ground water covering a two-years period at two-weekly intervals are presented. It could be established that the highest PAH concentrations in surface water occurred at an increased Ruhr water outlet. The hydrochemically dependent concentrations of suspended matter in the surface water are defined as the responsible determinants for the measured PAH concentrations. Decreasing concentrations were observed in particular for the higher molecular PAHs in the investigation of three different underground flow sections (transects).

### 1 Introduction

The knowledge about the behaviour of PAHs in surface water and ground water of a drinking water plant is of great importance for securing a good drinking water quality. In operating a drinking water recharge plant it has to be ensured according to the German Drinking Water Decree (TVO) that the sum concentration of 6 PAHs in water is below 200 ng after purification [1]. In the present project the behaviour of 11 PAHs in the course of the flow section and purification section of the drinking water recharge plant "Insel Hengsen" in Schwerte-Geiseke is studied.

### 2 Ruhr surface water

The PAH concentrations in the surface water of the Ruhr are of importance as input concentrations for the drinking water recharge plant.

In the surface water all investigated PAHs could be detected. As the concentrations showed significant correlations between the individual PAHs at ranges for the correlation coefficient between 0.64 and 0.96, the occurrence of the PAHs in the Ruhr can be regarded jointly (cf. Table 1).

The PAH concentrations varied during the measuring period. The highest concentrations were always found in the winter months. By the formation of averages of the concentrations in the winter and summer half-years the seasonal effects in the appearance of the PAHs were investigated. The selected periods were for the winter half-year from November till April and for the summer half-year from May to October. The averages of the concentrations in three winter and two summer half-years for three PAHs are exemplary shown in Fig. 1.

The average concentrations showed a maximum in the winter half-year 1987–1988. In the following mild winters the average concentrations did not exceed more than the threefold of those measured in summer. The lower molecular PAHs like anthracene, fluoranthene and pyrene did not show any seasonal differences. With increasing molecular size and decreasing water solubility [2] there is a tendency that greater concentration differences were measured in the winter and summer half-years.

#### 2.1 Determinants for the PAH concentrations in the Ruhr

Compared with the summer, more energy from fossil fuels is produced during the heating period in the winter half-year. The pyrolytic formation of PAHs yielding higher atmospheric concentrations in the winter months is a sufficiently investigated subject [3–8].

The contamination pathway by wet deposition is supported by measuring high PAH concentrations in rain, fog and snow during the winter months [9–12]. Hence the seasonally increased anthropogenic emission can be regarded as a determinant for the enhanced concentration in the surface water. Another determinant is of greater importance for the high concentrations in the surface water. Due to its hydrophobic properties a great part of the PAHs are associated with particulate matter [13–17]. The concentration of suspended matter depends on the hydromechanical state of the river [18]. The concentration of suspended matter increases with increasing flow volume per time unit [19].

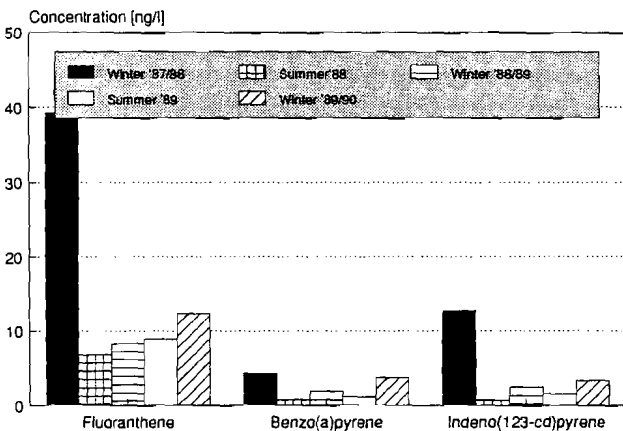
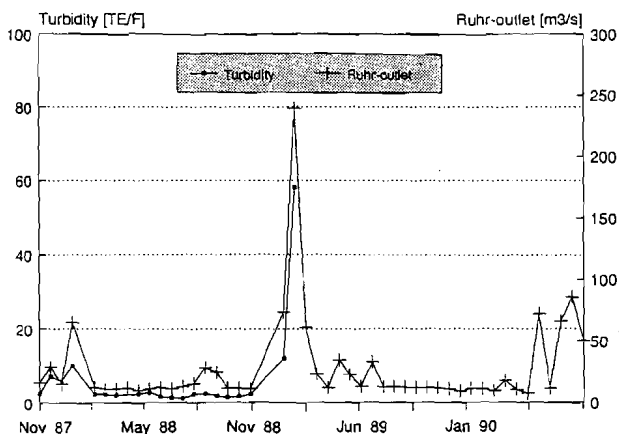
The relationship between the effluent volume and the load of suspended matter or turbidity (DIN 38404 part 2 [20]) is represented for the river Ruhr in Fig. 2.

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**Table 1.** Correlation coefficients of PAH concentrations in surface water of the Ruhr in the measuring period May 1988–April 1990

	Fla	Cry	Bbf	Bap	Ind
Fla		0.80	0.83	0.68	0.64
Cry			0.96	0.94	0.91
Bbf				0.92	0.88
Bap					0.90
Ind					

n: 46 pairs of values  
Statistical certainty: 99%

**Fig. 1.** Mean PAH concentrations in the Ruhr in the winter and the summer half-years from November 1987 till April 1990**Fig. 2.** Turbidity and Ruhr-outlet in the measuring period from November 1987 till April 1990

The linear regression showed a correlation coefficient of  $r = 0.99$  (at 20 pairs of values). The parameter Ruhr-outlet was chosen for the further considerations because there exists a greater data density as in case of the turbidity (Table 2).

The PAHs showing significant correlation with the Ruhr-outlet are the substances with low solubility in water and with a high octanol-water distribution coefficient ( $K_{ow}$ ) (see Table 3). These substances are nearly completely particle-bound [21].

The significance of the relationship between PAH concentration and the load of suspended matter (Ruhr-outlet)

**Table 2.** Correlation coefficients of the PAH concentrations versus Ruhr-outlet

	Ant	Fla	Pyr	Baa	Cry	Bbf	Bkf	Bap	Dbp	Bgh	Ind
R	0.27	0.21	0.31	0.16	0.47	0.48	0.54	0.55	0.44	0.58	0.58
	not significant				significant						

R: Correlation coefficient  
n: 44 pairs of values  
Statistical certainty: 99%

**Table 3.** Water solubilities and octanol-water distribution coefficients of the investigated PAHs (a [22]), (b [23])

	Structure number of rings	Water solubility		$\log K_{ow}$ (a)
		$\mu\text{g/l}$ (a)	$\mu\text{g/l}$ (b)	
Ant	3	70	45	4.45
Fla	3	260	206	5.53
Pyr	4	140	132	5.53
Baa	4	14	9.4	5.61
Cry	4	2	1.8	5.61
Bbf	5	1.2	1.5	6.53
Bkf	5	0.55	0.8	6.84
Bap	5	3.8	1.6	6.04
Dbp	5	0.5	0.7	5.95
Bgh	6	0.26	0.5	7.23
Ind	6		0.2	7.66

$\log K_{ow}$ : logarithm of the octanol-water coefficient

becomes plausible by the properties water solubility and octanol-water coefficient.

### 3 Ground water (underground passage)

All the PAHs found in the Ruhr were detected in the transects. Analogous to the results in surface water it was established that all the substances occurred jointly [24].

The measured PAH-concentrations at the measuring points in the transects were investigated with respect to seasonal effects because these effects were observed in the surface water of the Ruhr. Therefore the values of the measured concentrations were arranged according to winter and summer half-years and represented as seasonal averages. In the winter half-year the period from November till April and in the summer half-year the period from May till October were chosen. The period from May 1988 till April 1990 was taken into account. For the presentation of the results there are three substances selected to be representative for the investigated PAHs at the points of the underground passage:

- Fluoranthene (4 rings),
- Benzo(a)pyrene (5 rings),
- Indeno(1,2,3-cd) pyrene (6 rings).

#### 3.1 Transect I

Transect I carries pure bank filtrate. The relative slightly water soluble PAHs anthracene, fluoranthene and pyrene do not show any changes of the half-year medians in the course of the flow section in the underground. Only an average decrease of concentrations between the measuring point Ruhr and I/A was observed.

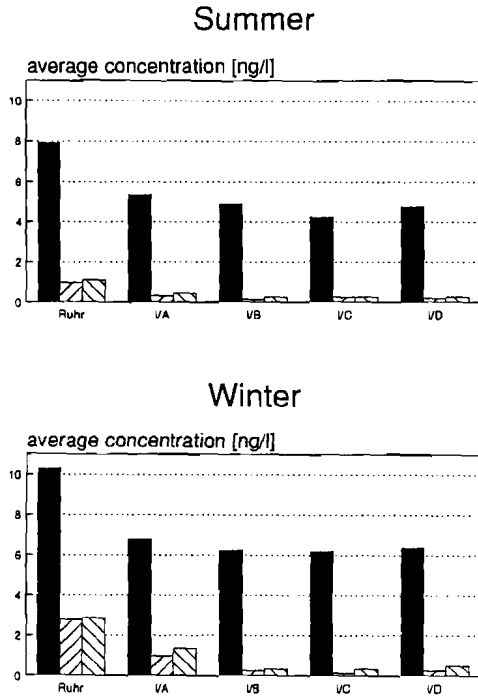


Fig. 3. PAHs in the course of the transect I. ■ Fluoranthene; ▨ Benzo(a)pyrene; ▩ Indeno(1,2,3-cd)pyrene

The other PAHs, which have a lower water solubility (1–2 decimal powers) in comparison with the compounds as mentioned above (see Table 3) show a concentration decrease compared with the Ruhr concentration by the factor 3–10 in the course of the transect. No principle seasonal differences are established but in summer the concentration level of these compounds is significant lower (see Fig. 3).

**3.1.1 Characteristic states.** On 25th January, 1990 and 28th June, 1990, comparable hydraulic states could be investigated for transect I. The measuring values showed in both states an increasing Ruhr water-outlet. Hence, similar hydraulic states in a different season could be studied.

In contrast to the routine sampling at the measuring points (I/B), (I/C), (I/D) the samples were taken in different depths so that a differentiation by depth was possible on the basis of the PAH concentration. The detailed description of the measuring points and the sampling depth is given in Table 4.

The comparison of the measuring data from the comparable characteristic states in winter and in summer shows a similar concentration decrease in the course of the flow section. The concentration drop of the PAHs with low water solubility at the measuring points I/B–I/D below the determination limit is extraordinarily clear (see Fig. 4). This phenomenon is explained by the fact that the water level of the tail race of the Ruhr increases at an increasing outlet of the Ruhr. This leads to a flat potential gradient of the ground water levels, causing a lower flow velocity in the underground [25]. Hence, a greater part of the particle bound PAH is deposited by sedimentation.

Differences exist in the concentration decrease between the measuring point Ruhr and I/A. In winter nearly all PAHs were quantifiable there, but the concentrations were under the determination limit in summer. The high fluoranthene

Table 4. Measuring points and sampling depths for the characteristic states in transect I

Measuring point		Sampling depth (meters below the top edge of the well)
Name	Number of the well	
I/A	I/A1	7.0
I/B	I/B4	4.0
I/B	I/B3	4.6
I/B	I/B2	6.5
I/C	I/C3	4.0
I/C	I/C2	5.0
I/C	I/C1	6.5
I/D	I/D4	4.5
I/D	I/D3	5.5
I/D	I/D2	6.5
Ruhr		1 m below the water surface

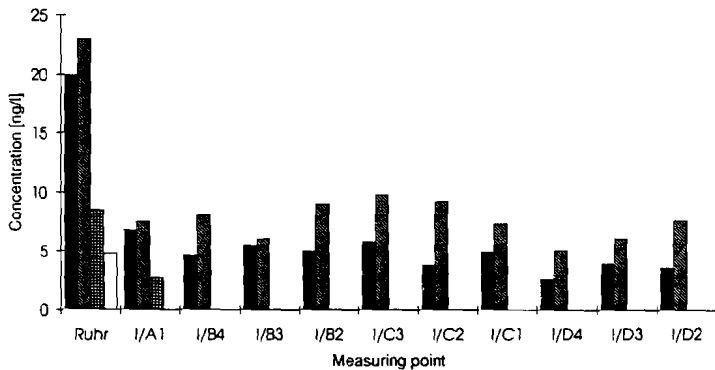


Fig. 4. Concentrations of benzo(a)pyrene and fluoranthene at increasing flow of the Ruhr water in transect I. ■ Fluoranthene 25. 1. 90; ▨ Fluoranthene 28. 6. 90; ▩ Benzo(a)pyrene 25. 1. 90; □ Benzo(a)pyrene 28. 6. 90

concentrations in the surface water of the Ruhr and in ground water of the transect during the summer (see Fig. 4) are probably due to the improved solubility of the substances at higher water temperatures.

The concentration gradients of the PAHs between the individual sampling depths do not indicate an inhomogeneous aquifer with different water layers, because the concentration differences were partially not significant and not confirmed by a second characteristic situation [24].

### 3.2 Transect II

The course of transect II is influenced by the bank filtration in its upper part and by artificial infiltration water in its lower part (see part I, chapter 2.1.2). The flow rate in the underground depends on the operating conditions of the plant. Especially the measuring points II/D and II/E are effected by these conditions (compare part I).

The relatively slightly water soluble PAHs, e.g. fluoranthene, show only little decreases in concentration comparing the measuring points Ruhr and II/A in contrast to the comparison of the heavy soluble substances with significant concentration drops. In the following course of transect II the mean concentrations of the heavy soluble PAHs

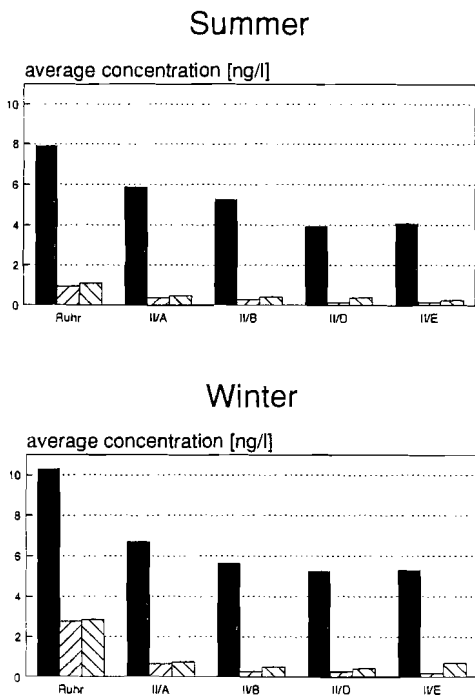


Fig. 5. PAHs in the course of the transect II. ■ Fluoranthene; ▨ Benzo(a)pyrene; ▩ Indeno(1,2,3-cd)pyrene

decrease below the determination limit whereas the fluoranthene concentrations remain constant at the concentration level at the measuring point II/A (Fig. 5).

### 3.3 Transect III

Transect III is mainly flown through by artificial water (see part I, chapter 2.1.3). For the representation in Fig. 6 data were exclusively used which were measured during the operation of the main filter so that a definite flow direction from the surface water of the Ruhr over the primary filter and main filter (MF) through the underground of the transect (measuring points III/A and III/B) can be considered. The arrangement of the measuring points and the selection of the measuring values permit an evaluation of the efficiency of the primary filter and the main filter system in case of artificial infiltration. The concentration difference between the measuring points Ruhr and MF corresponds with the concentration drop by the primary filter. The main filter/slow sand filter is responsible for the decrease in concentration between the measuring points MF and III/A.

The relative good water soluble PAHs, like fluoranthene, show a continuous slight decrease as an average of a half-year in the course of the flow section of the infiltration water. The other PAHs, which have a 1–2 decimal power lower water solubility, show an even clearer concentration decrease in the course of the transect. In winter this concentration decrease in the transect can amount to the factor 20 with respect to the mean PAH concentration in the Ruhr. The concentration decreases occur in summer and in winter as well, whereas the inlet concentrations (surface water of the Ruhr) of the sparingly soluble PAHs are higher in winter. The highest decrease in the PAH concentration was determined in a comparison of the measuring points MF and III/A (see Fig. 4), especially for the PAHs with high molecular

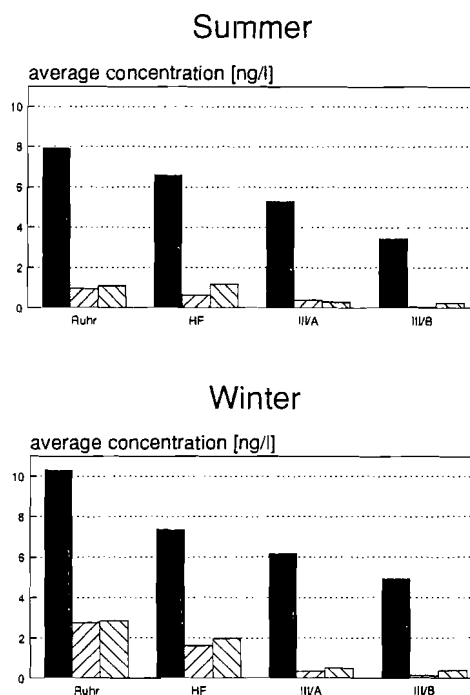


Fig. 6. PAHs in the course of the transect III. ■ Fluoranthene; ▨ Benzo(a)pyrene; ▩ Indeno(1,2,3-cd)pyrene

weight, benzo(a)pyrene and indeno(1,2,3-cd)pyrene, in the mean of the winter half-year. In contrast to that, the difference between the Ruhr concentrations and those of the measuring point MF is lower, i.e. the performance of the main filter is the most effective element of the transect.

### 3.4 Comparison of the transects

Drawing a comparison between transect I and transect II which both exclusively carry bank filtrate in the upper area for the measuring points I/A and II/A, differences were found for the sparingly soluble PAH in winter. The means of the PAH concentrations in I/A are higher than the level of the values for II/A. In summer these differences are less significant.

There are no significant differences between the anaerobic transect I (bank filtrate) and the aerobic transect III (artificial filtrate) with respect to the relative concentration decrease in the course of the transects.

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