

# Transport and Speciation of PAHs and PCBs in a River Ecosystem

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## Abstract

This paper presents the results of analysis of samples of river water and bottom sediments for PAH and PCB content using previously developed analytical procedures.

Conclusions are drawn as to the form and main places of occurrence of the above analytes in the various elements of the river ecosystem (water phase, suspension, bottom sediments).

The dependencies which were found between the PAH and PCB concentration in these three phases of the ecosystem suggest that:

- PAHs are almost entirely adsorbed on the suspension and their transport in river water occurs mainly with the suspended matter.
- PCBs are adsorbed to a lesser degree on the particles of suspended matter, which means that their transport in the river takes place both with the aqueous phase and with the suspended matter.
- PAHs accumulate in bottom sediments to a much greater extent than PCBs.

**Keywords:** polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), river ecosystem, speciation.

## Introduction

The environment is a system of a high degree of complexity, negatively influenced by different forms of human activity. The effects of these activities can cancel each other out or accumulate synergically *i.e.*, with an increased effect of the component mixture as compared with the sum of their individual effects, resulting in unpredictable final effects [1].

Water, *via* surface runoff to rivers and lakes, as well as groundwater, carries pollutants to plant and animal

organisms, and so in the long run also to the human organism, working as a carrier of polluting substances.

Water reservoirs, aside from collecting and holding water, are also places of accumulation of various sediments and function as storage tanks for both dissolved and solid matter.

The recognition of the dangers resulting from the pollution of different elements of the environment is therefore a very complex task, if only because of the aforementioned transportation processes, or biogeochemical cycles. They only appear to be hermetic and reversible. Some of the chemical compounds continually circulate in the live matter along the food chains,

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and after mineralization they are taken up by a new organism, entering a new food chain.

A whole spectrum of organic compounds can be identified within the river environment, from those soluble in water to those bound with suspended matter and those which are a part of the deposit formed due to sedimentation. They include carbohydrates, proteins, amino acids, esters, lipids, organic acids, detergents, aldehydes, ketones, alcohols, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and phenols, occurring at various concentration levels. Organic components such as PAHs and PCBs are widely distributed, and considered hazardous to the environment due to their high toxicity, carcinogenic and mutagenic properties, and their stability in the environment. Analytes from both groups (PAH and PCB) have been placed by the U.S. Environmental Protection Agency on the priority pollutant lists. The lipophilic character of polychlorinated biphenyls and their low susceptibility to degradation in the environment cause them to undergo the process of biocumulation at the higher levels of trophic chains. The low volatility and hydrophobic character of polycyclic aromatic hydrocarbons and polychlorinated biphenyls, on the other hand, make them susceptible to sorption on the surface of particles present in surface waters in the form of suspended matter [2-6].

Obtaining detailed knowledge concerning the processes which organic pollutants undergo in the river ecosystem is extremely important both for extending environmental knowledge as well as for the development of zoology and zootechnology, *i.e.*, the sciences concerned with the causes and effects of changes occurring in environmental systems as a result of human activities, and with the ways to prevent them and lessen their negative effects. The development of speciation analytics may be helpful in gaining this knowledge.

Two special types of speciation are: physical speciation and distribution speciation [7].

In the case of a river ecosystem the same analytes can occur in the following physical forms:

- dissolved
- adsorbed

There is also a certain state of equilibrium between the same analyte present in the suspended matter, water, bottom sediment, plant organisms and animal organisms.

Speciation studies can provide valuable data necessary for studying transportation processes, cumulation, *etc.*, as well as biological accessibility and toxicity of analytes in a water environment [8,9].

The characteristics of compounds belonging to the PAH and PCB groups lead to the conclusion that in surface waters the analytes belonging to these groups of organic compounds will collect mainly on solid particles suspended in water and accumulate in bottom sediments, but will be found less frequently in a dissolved state in water. In consequence there is a close correlation between the concentration level of PAHs and PCBs in the water

environment and pollution of the suspended matter.

Knowing the proportions in which these analytes occur in the different elements of the river environment is very important for evaluating the degree of environmental pollution, and at the same time it is a classic example of analytical studies in physical and distribution speciation. Such studies are a serious challenge for the analytical chemist and require new analytical tools.

The analysis of samples of river water and bottom sediments requires, as with most environmental samples, introducing to analytical procedures additional operations which are based chiefly on separating the analytes from the components of the original matrix and analyte enrichment. As a result, the whole procedure becomes more time and labour consuming, and ensuring proper quality of the results grows more difficult.

Additional difficulties are connected with:

- the dynamic character of the river ecosystem, which results in relatively large fluctuations in the proportions of the individual physical forms of the analytes;
- the necessity of determination of analytes from both groups of chemical compounds from a single extract.

These additional difficulties, of both hydrochemical and technical character, have caused the methodological problems to remain unresolved, and many analytical laboratories continue intensive work developing new or modifying old analytical methods that could be used in studies of river water samples and bottom sediment samples in order to determine trace amounts of analytes of the PAH and PCB groups.

The earlier studies conducted by van Noort and Wondergem (1985) [10] show that, during the filtration process, the analytes from the PAH group dissolved in the aqueous phase are adsorbed on elements of the filter and on the forming layer of suspension. Thus, the determined concentration of the PAH analytes in the filtrate does not correspond to their actual content in the aqueous phase. And similarly, the determined PAH concentration obtained after extracting the suspension does not correspond to the actual concentration in the suspension.

It seems, therefore, that the procedure for analysing surface water for the content of analytes from the PAH and PCB group should include a suspension separation stage, and requires the determination of these compounds in both phases: aqueous and suspended. The separation process should be conducted in such a manner as to ensure that from the same volume of surface water the filtrate and the suspension are analysed, and the mass of the suspension is determined.

## Material and Methods

In the analysis of water samples an original procedure was used, based on utilizing the kit for separating the suspension from the water samples [11,12]. The filtration vessel is directly connected with the SPE column, which allows for the filtration process to take place simultaneously

with the process of isolation and enrichment of PAHs and PCBs. Filling the filter with a bed of glass beads prevents it from becoming clogged. At the same time, the filtration and the enrichment of the analytes from 0.5 liter surface water samples containing 100 mg/l level of suspension does not take longer than three hours.

After the isolation stage, the vessel is placed in a lyophilising unit to dry its contents. The difference between the mass of the vessel after drying and its mass before the isolation stage corresponds to the suspended matter content in the analyzed water sample.

The **advantages** of the proposed construction of the filtration vessel include:

- simplicity of construction and use,
- utilising construction materials recommended for trace organic analysis,
- suspended matter separation and the isolation of the analytes dissolved in water simultaneously on an appropriate sorbent bed,
- the possibility of conducting the suspension separation and the isolation of analytes in field conditions.

It seems that applying lyophilisation at the stage of removal of water from the suspension and solvent extraction aided by ultrasounds is the best solution for getting the highest possible recoveries of analytes from suspension samples.

Figure 1 presents schematically the procedure of preparing a surface water sample while using small extraction cartridges together with a filtration vessel of our own construction.

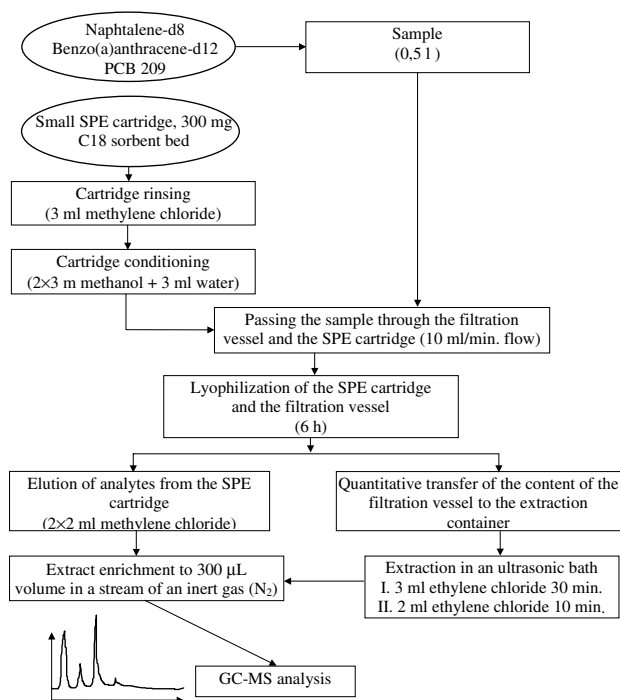


Fig. 1. The determination procedure for analytes of the PAH and PCB group in water samples employing small SPE cartridges together with a filtration vessel that allows separating the suspension.

Solvent extracts obtained from bottom sediment samples contain organic components belonging to different groups of chemical compounds at very different concentration levels. Chromatographic determination of analytes from both groups of compounds (PAHs and PCBs) in a single extract with very high concentrations of PAHs and comparatively low concentrations of PCBs becomes difficult if not impossible.

Procedure of sediments preparation for PAH and PCB analysis has been described in an earlier paper [13].

This procedure of preparation of bottom sediment samples enables us to:

- decrease the sample mass to 1 g, as compared to other methods described in literature, where the sample mass ranges from 5 to 100 g [14-17];
- simultaneously determine analytes from both groups (PAH and PCB) from a sample of a single solvent extract;
- minimise the consumption of solvents;
- decrease the time and labour related to the process.

It should be especially noted that this sample preparation procedure is characterised by accuracy and precision confirmed in an interlaboratory test.

### Validation of Analytical Procedures

During studies described here two new original analytical procedures of determination of PAHs and PCBs in water and suspended matter [11,12] and bottom sediments [13] were employed. These publications contain all the details of validation and statistical evaluation of analytical results.

The procedure of bottom sediment sample preparation has also been verified during an international interlaboratory study organised by the *International Atomic Energy Agency Marine Environment Laboratory* in 1998.

During the interlab test the method was evaluated in respect of accuracy defined as the difference between the expected value of the results of parallel determinations done employing the new procedure and the actual analyte content.

The interlaboratory study proves that the developed procedure for preparing bottom sediment samples for analysis for the content of analytes from the PAH and PCB group gives accurate and precise results.

### Results and Discussion

The procedures described above were used in studies of water and bottom sediment samples collected from the Odra River [18].

The aim of our research was speciation of analytes from the PAH and PCB group in the river ecosystem.

Tables 1–3 show the results of determinations of the sum of PAHs, benzo(a)pyrene and PCBs in samples of bottom sediment, suspension, and water.

A comparison of the content of the sum of analytes from the PAH group (Table 1) as well as benzo(a)pyrene

(Table 2) in bottom sediment [ $\mu\text{g}/\text{kg}$ ], in water filtered through the filtration vessel (taking the suspension into account) [ $\mu\text{g}/\text{l}$ ] and unfiltered water [ $\mu\text{g}/\text{l}$ ] leads to the conclusion that the concentration ratio is approximately:

$$10^6 : 10 : 1$$

assuming that 1 liter of water weighs 1 kilogram.

The ratio of the content of the sum of analytes from the PAH group in bottom sediments [ $\mu\text{g}/\text{kg}$ ] and in water filtered through the vessel (expressed as mass of suspended matter per 1 l of water) is approximately:

$$1 : 1$$

The above ratios suggest that PAHs are almost entirely adsorbed in the suspension, and their transport in surface waters takes place mainly with the suspended phase.

Similar calculations can be done for the sum of PCBs present in the analysed samples, but the concentration level of the analytes from this (PCB) group in the surface water samples being generally close to the determination limit makes the estimation of the ratio of the analyte content in the different phases less exact. The approximate relation of the content of the PCB sum in bottom sediment [ $\mu\text{g}/\text{kg}$ ], in water filtered through the vessel (taking the suspension into account), and in unfiltered water [ $\mu\text{g}/\text{l}$ ] can be described by the following ratio:

$$10^3 : 1 : 1$$

As opposed to PAHs, the analytes from the PCB group are to a lesser extent adsorbed on suspended matter, which means that the transport of PCBs in rivers occurs both with the aqueous phase and suspended matter.

Additionally, it may be concluded that PAHs accumulate mainly in bottom sediments, while PCBs undergo this process to a lesser extent.

Particular attention should be paid to the conclusion from the speciation studies of analytes from the PAH group in the river environment (confirmed by other authors) [10,19], pointing to the huge difference in analyte concentrations in the aqueous phase and the suspended phase. The equilibrium shifted so strongly towards the solid phase must necessarily pose and actually poses analytical problems during the determination of analytes from the PAH group in surface water samples.

The Polish standard, currently under preparation, based on a proposed ISO/DIS 7981-2 (1990) standard for determining 6 PAHs in water, including surface water, contains the following note: “*recovery from river waters is worse and probably varies strongly, depending on the kind and amount of suspension*”.

Also under preparation is another standard, based on a proposed ISO/DIS 17993 (2000) standard, for determining

Table 1. The results of determinations of the sum of PAHs in samples of bottom sediment, suspension, and water.

Sum of PAHs					
Sampling site and its distance from the source	Sediment [ $\mu\text{g}/\text{kg}$ ]	Suspension [ $\mu\text{g}/\text{kg}$ ]	Water + suspension [ $\mu\text{g}/\text{kg}$ ]	Water [ $\mu\text{g}/\text{l}$ ]	Mass of suspended matter [ $\mu\text{g}/\text{l}$ ]
Chałupki 21 km	38873	15811	0.567	0.415	35.86
Krapkowice 127 km	64381	34948	3.536	0.663	101.18
Opole 156 km	50729	26157	0.961	0.339	36.74
Oława 216 km	60937	138350	1.710	0.365	12.36
Brzeg Dolny 285 km	35076	54767	1.999	0.322	36.5
Mała Panew 158.5 km	3673	25887	0.248	0.257	9.58
Bystrzyca 266.5 km	60852	34037	0.806	0.229	23.68

Table 2. The results of determinations of benzo(a)pyrene in samples of bottom sediment, suspension, and water.

Benzo(a)pyrene					
Sampling site and its distance from the source	Sediment [ $\mu\text{g}/\text{kg}$ ]	Suspension [ $\mu\text{g}/\text{kg}$ ]	Water + suspension [ $\mu\text{g}/\text{kg}$ ]	Water [ $\mu\text{g}/\text{l}$ ]	Mass of suspended matter [ $\mu\text{g}/\text{l}$ ]
Chałupki 21 km	3627	864	0.031	0.018	35.86
Krapkowice 127 km	5521	2085	0.211	0.039	101.18
Opole 156 km	3634	2450	0.09	0.017	36.74
Oława 216 km	5204	23139	0.286	0.02	12.36
Brzeg Dolny 285 km	3090	4767	0.174	0.023	36.5
Mała Panew 158.5 km	379	835	0.008	0.002	9.58
Bystrzyca 266.5 km	5612	1394	0.033	0.016	23.68

Table 3. The results of determinations of the sum of PCBs in water and sediment samples.

Sum of PCBs			
Sampling site and its distance from the source	Sediment [ng/kg]	Water + suspension [µg/kg]	Water [µg/l]
Chałupki 21 km	6.2	0.006	0.017
Krapkowice 127 km	9.0	0.002	0.030
Opole 156 km	10.8	0.003	0.008
Oława 216 km	7.0	0.010	0.005
Brzeg Dolny 285 km	4.4	0.001	0.010
Mała Panew 158.5 km	7.6	0.002	0.001
Bystrzyca 266.5 km	3.7	0.002	0.025

15 PAHs in drinking, ground, and surface waters. In the sample preparation procedure included in this standard, there is no stage connected with sample filtration and, unfortunately, there is no mention of the possible problems of determining PAHs in water in the presence of suspension.

In the end it may be stated that considering the fact of interphase distribution of the analytes from the PAH group in collected water samples (aqueous phase and suspended phase), it is necessary to separately determine the analytes in these two components. A convenient method for isolating the suspension (for analytical purposes) is filtration, and total analyte content in the studied water samples will be the sum of the content of these analytes determined in "filtration cake" and in the filtrate.

### Conclusions

The results of our studies concerning speciation of PAHs and PCBs in a river ecosystem suggest that:

- PAHs are almost entirely adsorbed on the suspension and their transport in river water occurs mainly with the suspended matter.
- analytes from the PCB group are adsorbed to a lesser degree on the particles of suspended matter, which means that their transport in the river takes place both with the aqueous phase and with the suspended matter.
- PAHs accumulate in bottom sediments to a much greater extent than PCBs.

Further investigation should be continued in this direction aimed at the formation of optimal recommendations for surface water monitoring.

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