

## LETTER TO EDITOR

### POLYCYCLIC AROMATIC HYDROCARBON CONTENT IN THE SEDIMENTS OF WATER-BEARING SUBSIDENCE TROUGHS IN THE KARVINÁ REGION

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#### Abstract

*The pilot study deals with the monitoring of selected polycyclic aromatic hydrocarbon content (PAHs) in the sediments of water-bearing subsidence troughs in the Karviná Region. The significance of PAHs as an indicator of immission strain is also evidenced by the results of PAHs content monitoring of the air in the Karviná Region, namely with regard to the fact that PAHs are some of the typical organic pollutants in the overall Ostrava-Karviná industrial agglomeration. The assessed localities are water areas used for free-time fishing, as well as a locality with prevailing banking of waste rock, i.e. frequently used material for the redevelopment of the territory. For the purposes of the pilot study, only six PAH congeners were monitored in the sediments, namely: anthracene (ANT), benzo[a]-anthracene (BaA), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]-anthracene (DBahA), benzo[ghi]perylene (BghiPRL) and their sum. The obtained values of the monitored PAHs were compared with their contents in the air of the monitored territory.*

**Key words:** *polycyclic aromatic hydrocarbons, water-bearing subsidence troughs, sediments.*

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#### 1. Introduction

The Karviná Region belongs among the most strained territories in the Czech Republic. The surface of the Ostrava

Basin has been left with the traces of more than two-hundred-year mining activities. In many places subsidence troughs occur due to undermining, which are often saturated with water or they are used for

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the disposal of waste rock or industrial waste (the so-called settling pits).

Changes in the habitat must be considered as the decisive change-causing factor. They may be either gradual, at the slow formation of subsidence troughs with the changes in the water regime or relatively sudden, which are caused by banking the material during technical reclamation when, for example, wetland is substituted by a several-metre layer of banked waste rock and soil. The first type of impact cannot be practically eliminated if there are no changes in the spatial and time advance of extraction or mining of certain coal faces is not abandoned from economic or structurally geological reasons. The second type of changes can be quite well regulated by specific modifications of the projects of redevelopment-reclamation constructions (ARS).

It is the quality of water that is an important factor of the protection of natural water-bearing subsidence troughs. They are supplied with ground water or rainfall water. Ground water, compared to surface water in the industrial landscape, is considerably less contaminated by pollutants. The formed water areas thus create space for water and wetland biota, but simultaneously they also participate in the increase in the biological balance in the territory. Water-bearing subsidence troughs thus may become a principal stabilization element in an intensely disrupted environment [4]. With regard to the seriousness of the issue of water areas in the landscape, devastated by long-term mining activities, there is a number of research works pointing at the water quality, which are, however, predomi-

nantly focused on inorganic hydrochemical parameters. A more detailed monitoring of organic pollutants has not been implemented there yet.

One of the important indicators of anthropogenic environmental pollution may be polycyclic aromatic hydrocarbons (PAHs). It is the case of a well-known and wide-spread group of environmental organic pollutants. Polycyclic aromatic hydrocarbons are largely rather low reactive substances. Their reactivity is mainly conditioned by the presence of conjugated  $\pi$ -electron systems, while the differences between the individual congeners are given by the number and mutual position of the condensed nuclei. As for the environment, especially such reactions are interesting which influence their content in the air or other constituents of the environment, namely during own sample drawing, their storing and further laboratory processing.

However, the abundance of PAHs in the individual constituents is not even. Having entered the environment, PAHs are distributed into the individual constituents, which takes place e.g. through airflow from the areas with higher PAHs content, or resuspension and transport from contaminated sediments in the polluted territories. Polycyclic aromatic hydrocarbons are present in the environment in all its phases – i.e. in the air, water, organic matter (in sediments, humic acids in the soil and lipids and waxes in the biota). On the basis of its physical-chemical properties, PAHs either persist in the given constituent of the environment or are distributed among all its other constituents by volatilization or resuspension of particles. Wind and

water erosion thus represent important paths of redistribution mechanisms of PAHs in the environment. The time of their persistence in the different constituents of the environment varies, both in relation to the characteristics of the given substance as well as to the properties of the own environment, i.e. season, temperature, solar radiation, but also to the microbial activity. Along with the rising molecular weight of the individual PAHs (i.e. with the growth in the number of nuclei) there is a connection with the parameters affecting the mobility of such substances in the environment ( $K_{OW}$  n-octanol/water), their volatility and solubility in water which fall along with the growth in the number of nuclei.

The natural occurrence of PAHs in the hydrosphere is rather rare (e.g. infiltration of oil substances). As a rule, water is predominantly contaminated due to human activities, namely either directly (waste water, accident, spill, etc.), or secondarily from the atmosphere by dry or wet deposition. Among significant sources of contamination there is also drainage water from the road and motorway surface [2]. PAHs penetrate ground water as a result of an easy sorption onto solid matrixes only to a limited extent. Mainly PAHs with a low molecular mass are better soluble in water than PAHs with a higher molecular mass. Among the most soluble representatives of PAHs there is pyrene and fluoranthene, which are much more soluble than anthracene, but these are not usually metabolized by microorganisms. Chrysene, benzo[a]pyrene are almost insoluble in water.

Depending on their physical-chemical characteristics and environmental conditions, polycyclic aromatic hydrocarbons may evaporate from water, disperse in the water column, sediment or concentrate in the water biota [3]. Similarly to the atmosphere, the main transport mechanisms in the water is diffusion and convection. The most important processes that significantly affect PAHs degradation in the water medium are, first of all, photooxidation, chemical oxidation and aerobic biodegradation by water organisms [1]. This happens again in dependence on the environmental conditions, such as depth, transparency of an aqueous layer, temperature, quantity of oxygen, characteristics of microbial communities, etc. Degradation in the water environment takes place in a more slowly way than in the atmosphere.

Simonich and Hites [5] produced a model on which they demonstrated that approximately 54 % of PAHs emitted into the atmosphere is deposited in the soil and about 5 % is bonded in the water sediments. The time of persistence or half-life of the individual PAHs varies in the different types of environments. While they persist in the atmosphere usually only several days, in water it is several weeks and in the soil several months. In the sediments they may remain unchanged for several years.

The objective of the study was to assess the level of immission strain in the monitored area by selected PAHs, namely: anthracene (ANT), benzo[a]anthracene (BaA), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]-anthracene (DBahA), benzo[ghi]perylene (BghiPRL) and their sum. For the

illustration of the extent of pollution by the individual monitored PAHs the pilot study also includes the evaluation of the monitored PAHs content in the air for the identical period.

## 2. Materials and Methods

For the own monitoring of selected PAHs in the water-bearing subsidence trough sediments in the Karviná Region, which was implemented in 2008, three localities were chosen within the pilot study in a way the individual types of water areas present in the territory were represented. The studied set thus may be divided into the individual representatives characterizing the most frequent water areas:

- **Velký Loucký rybník** - used for fishing, a relatively clean locality, possible impact of emission from transport,
- **Barbora** - without further use, burdened with inorganic pollution,
- **Mokroš** - a former settling pit, burdened with inorganic pollution.

For the purpose of immission strain monitoring in the studied area by selected PAHs, sediments were drawn from the stated water-bearing subsidence troughs within the pilot study. The significance of PAHs as indicators of immissions is also evidenced by the results of PAHs content monitoring in the air in the Karviná Region, namely with regard to the fact that PAHs are some of the typical organic pollutants within the overall Ostrava-Karviná agglomeration (data for emission evaluation for the examined period was provided by the Czech Hydro-

meteorological Institute). The time of persistence of PAHs in the different segments of the environment varies, and it is closely connected with the characteristics of the given substance and environment. With respect to the fact that heat, ozone, nitrogen dioxide and ultra-red radiation cause degradation of PAHs, it was necessary to exclude such impacts not only during the time of sampling but also in the course of the overall handling of the samples. For the purposes of the pilot study only six congeners of PAHs were monitored in the sediments, namely: anthracene (ANT), benzo[a]anthracene (BaA), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[ah]anthracene (DBahA), benzo[ghi]perylene (BghiPRL) and their sum. Volatile two- and three-nuclei PAHs were eliminated from the set of the observed PAHs (naphthalene, acenaphthene, acenaphthylene, fluorene), namely with respect to the unbearably high losses during analytical determinations and thus dispersion of the results.

In the treatment of the samples and own analysis, verified methods of the laboratory of organic contaminants at the IEI HGF VŠB TU-Ostrava were adhered to. Having been extracted from the sediments, the analytes were placed in organic solvent (acetone) and after concentration they were determined using the method of high performance liquid chromatography (HPLC) with fluorescence detection (FLD). Correct function of the system was regularly checked, each sample was analyzed twice, including blind samples. The results were used for the calculation of PAHs concentrations in the given material. The repeatability

values ranged up to 8 % in the selected matrix samples. With regard to high demands of the analytical procedure, the obtained repeatability values may be considered satisfactory. PAHs analyses were carried out using a DIONEX machine with a programmable fluorescence detector.

The comparison of the total quantities of PAHs in the sediments with literature is very difficult as no adequate data is available. For reference comparison a methodical instruction of the Ministry of Environment was used, which states criteria for the pollution of soil, ground water and soil air. With regard to the fact that only six PAHs congeners were monitored within the pilot study, their contents were assessed only based on the pollution criteria A and B for the individual congeners of PAHs. (Procedure in the risk analysis processing, Zpravodaj MŽP ČR, 1996). For the illustration of the extent of pollution by the individual monitored PAHs the pilot study also includes the evaluation of the monitored PAHs content in the air for the identical period. A median value was used for the data assessment and Microsoft Office Excel 2007 was used for the graphic evaluation.

### 3. Results and Discussion

With regard to the characteristics of the studied territory, it may be assumed that the main source of contamination of the environment by PAHs will be combustion processes in the monitored localities, or emissions of such arising combustion products. It is well-known that mainly for this reason the atmospheric deposition

represents the main path for their transfer not only into the terrestrial but also the water ecosystem. Based on the above mentioned, it may be stated that the main transport medium of PAHs is the air.

Solubility of PAHs in water is, apart others, affected by other parameters too, namely temperature, presence of salt, which is the case of the monitored locality of Barbora, but also other organic matters. On the basis of this fact and with regard to the fact that within the model study mainly congeners with higher molecular mass were monitored, i.e. a higher number of nuclei, the water matrix of the monitored localities need not be burdened by those PAHs in identical measure.

The minimum values of all the six evaluated PAHs congeners (congeners with a higher molecular mass prevail) were taken in the period from May to September, i.e. in the period when the effects of climatic conditions are prominently demonstrated (i.e. temperature of the air, UR-radiation, presence of reactive pollutants, e.g. ozone). On the contrary, in winter when condensation of gaseous PAHs on the particle surface occurs preferentially, there is a distinguished increase in the monitored PAHs. In this case their follow-up deposition onto the earth's surface may be expected due to dry deposition in particular, horizontal wet deposition (fog, icing, dew) or vertical (rain, snow) and thus transfer from the air to water may occur, to the association with solid aerosol particles and organic soil fractions and sediment.

Rainfall is the basis of the atmospheric cycle of PAHs and PAHs have a characteristic distribution there. A mean

content of PAHs in the rainfall ranges in units to hundreds of  $\text{ng}\cdot\text{dm}^{-3}$  in dependence on their solubility in water (PAHs with a low molecular mass are soluble in water in the levels of  $\mu\text{g}\cdot\text{dm}^{-3}$ , with higher it is in the levels of  $\text{ng}\cdot\text{dm}^{-3}$ ). In general, it may be said that the PAHs identified in rainfall are higher in winter than in summer, which reflect the discovered seasonal variations of PAHs levels in the atmosphere in the Karviná Region. Snowing is also a much more effective method of PAHs removal from the atmosphere than rain. However, it must be pointed out that the PAHs levels in the environment show not only proved seasonal but also local changes. Higher PAHs in winter are attributed to the changes in the emission production (higher production of emission from household furnaces and car waste products) and changes in the meteorological conditions (shorter time of sunshine and lower temperature, temperature inversion). Those factors will also significantly affect the dispersion of air pollutants and variations in the phase distribution of PAHs (gaseous phase - particle) in the Karviná Region.

Concentrations of PAHs  $0.1\text{--}1\text{ ng}\cdot\text{m}^{-3}$  are considered as values complying with the background. Mean values in the air of the urban and industrial agglomeration range from  $0.3\text{--}6\text{ ng}\cdot\text{m}^{-3}$ , which corresponds to the found out facts. The mean values range rather near the upper limit of the given extent. It is apparent from Chart 2 that the highest abundance in the air is of benzo[a]anthracene (BaA=35 %) and anthracene (A=25 %); on the contrary, dibenzo[ah]anthracene (DBahA=2 %) has the lowest percentage abundance.

Logically, in the sediments where PAHs persist the longest their gradual concentration takes place. By means of PAHs content in the sediments it is possible to well characterize the total and mainly long-term strain of the monitored localities. In abiotic samples, PAHs are identified as complex blends with relatively unvarying proportions of the individual PAHs, characteristic for the individual matrixes - water, soil and air. It may be assumed that the geochemical character of the sediment may quite prominently influence the development of the ecosystem. In the territory of the Ostrava-Karviná industrial agglomeration the situation is rather complicated as sediments in the water-bearing subsidence troughs may be affected by a whole number of factors, such as immission strain, leaching from the subsoil rocks or leaching of the dumped waste material, which is used for redevelopment works in the territory. Monitoring of PAHs in the sediments in the selected water-bearing subsidence troughs thus may demonstrate the long-term immission strain of the studied territory, with regard to the fact that PAHs are some of the typical organic pollutants in the overall Ostrava-Karviná industrial agglomeration. The importance of PAHs as indicators of immission strain is also documented by the results of PAHs content monitoring of the air in the Karviná Region.

Table 1 provides the medians of the identified contents of the evaluated congeners of PAHs in the sediments for the studied localities which are very similar. Based on assumptions, no trends occurring in the air were identified as their degradation by physical-chemical paths is

much slower with respect to the absence of solar radiation and oxygen. Microbial degradation predominantly takes place there.

**Table 1.** Medians of the evaluated PAHs congener contents for the studied localities subject to MŽP criteria (Ministry of Environment)

Name	Velký Loucký rybník	Barbora	Mokroš	MŽP criterion	
				A	B
<b>mg/kg dry matter</b>					
ANT	0.11	0.28	0.46	0.10	40
BaA	0.50	0.78	1.89	0.10	4
BkF	0.25	0.28	0.25	0.05	4
BaP	0.46	0.63	1.38	0.10	1.5
DBahA	0.11	0.14	0.27	-	-
BghiPRL	0.45	0.56	1.26	0.05	20

#### 4. Conclusion

Based on the reference comparison of the individual PAHs contents in the sediments with the Methodical Instruction of the Ministry of Environment (Věstník MŽP 3/1996) it is clear that the individual PAHs contents in the sediments correspond to the reference criterion A (it approximately complies with the natural content of the observed substances in nature), while criterion B (its overrun must be dealt with as it may have a negative impact on human health and the individual constituents of the environment) was not exceeded. However, this evaluation cannot be considered decisive with regard to the fact that this methodical instruction is valid for soil and based on the literature it is known that PAHs contents in the soils are usually much higher than in fresh water sediments. In our opinion, based on the above mentioned the observed contents of PAHs in the monitored localities may be considered significant and it may be said

that the studied territory is considerably burdened with PAHs immissions.

Based on the implemented pilot study it was demonstrated that in the sediments where PAHs persists the longest, their gradual concentration takes place. The significance of PAHs as convenient indicators of immission strain was also proved by the results of the PAHs content monitoring of the air in the Karviná Region. It was found out that despite various types of water areas being selected, the content of the evaluated PAHs congeners in the sediments for the studied localities is analogous. In all the localities congruently higher abundances were identified, in particular benzo[a]anthracene, which though also corresponds to its increased content in the air in the Karviná Region. Nevertheless, a more serious finding is an approximately 5% higher content of carcinogenic benzo[a]pyrene in the sediments when compared with its content in the air, congruently in all the localities.

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**5. References**

1. Bertilsson, S., Widenfalk, A., Photochemical degradation of PAHs in freshwaters and their impact on bacterial growth - influence of water chemistry, *Hydrobiologia* 469, (2002), pp. 23-32.
2. Bryselbout, C. et al., Polycyclic aromatic hydrocarbons in highway plants and soils. Evidence for a local distillation effect, *Analysis* 28, (2000), pp. 290-293.
3. De Maagd et al., Physicochemical properties of polycyclic aromatic hydrocarbons: Aqueous solubilities, n-octanol/water partition coefficients, and Henry's Law constants, *Environ. Toxicol. Chem.* 17, (1998), pp. 251-257.
4. Pertile, E, *Hydrochemie aquifers subsidence basin in a defined territory Karviná*, Dissertation, (Czech), VŠB - TU Ostrava, (2007), p. 130.
5. Simonich, S. L., Hites, R. A., Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere, *Kature* 370, (1994), pp. 49-51.