

# Monitoring the Production of Selected PAHs on PM<sub>10</sub> from Thermally Active Dump Hermanice Ostrava (Czech Republic)

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**Citation:** Vastyl M, Leher V, Balcarik L, Valova B (2018) Monitoring the Production of Selected PAHs on PM<sub>10</sub> from Thermally Active Dump Hermanice Ostrava (Czech Republic). *J Environ Pollut Manag* 1: 102

**Article history:** Received: 16 February 2018, Accepted: 12 March 2018, Published: 13 March 2018

## Abstract

Black coal mining in the Ostrava-Karvina district is responsible for the creation of at least six mining diggers. The material that touched both carbon and aggregates from the mined areas. As a result of the imperfect separation and ignorance of modern technologies, a high percentage of coal is imposed. Due to processes such as pressure (due to compaction), sulfur content (pyrite, chalkopyrite) and high humidity, self-ignition of the dump occurred. The dredging it self was great environmental burden, but the thermally active dump increased the level of danger. Thermal waste incineration processes result in increased dust, but also greenhouse gases and PAHs. Measurement at Hermanice Dump (Czech Republic) was performed by HPLC. Pollutants of PAHs were measured. The measurements were carried out from June 2016 to June 2017. The mean concentration of  $\Sigma 16$  PAH was  $1\ 353.81\ \text{mg kg}^{-1}$  in the Hermanice wasteland. Concentrations have been found to be no different in the course of the year. For minor factors, the differences are only minimal. Due to the nature of the weather conditions, the city of Ostrava and the adjacent areas are the most affected.

**Keywords:** PM<sub>10</sub>; Air pollution; PAHs, Dump

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) belong to groups of organic pollutants. Pollutants of PAHs occur in different environmental compartments due to the communication between them. PAHs are monitored as pollution indicators at combustion halls. Therefore, it was chosen to identify characteristic pollutants in this old ecological damage.

Hermanice dump is located in Silesian Ostrava (Ostrava, Czech Republic). The history of the construction dates back to 1907. The area of dump  $8,8 \cdot 10^5\ \text{m}^2$  is the largest in the Ostrava-Karvina district and the volume is  $18 \cdot 10^6\ \text{m}^3$  and height 20-70 m. The Dump contains coal residues from the Hermanice mine, which have been stored until 1970 [1-3].

There are plenty of flammable materials of various kinds in which focal points of burning are created in places with oxygen air access. These outbreaks are recorded at different depths, and the most critical sites are on the edges of the dump in the south-east, south and west [2-5].

This study follows the following selected PAHs: Naphthalene, Acenaphthalene, Acenaften, Fluoren, Fenantrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysen, Benzo(b)fluoranthene, Benzo(ah)anthracene, Benzo(ghi)perylene, Indeno(1,2,3-cd)pyrene [3].

## Methods and area description

Hermanice dump. The total number of sampling places 20 (marked as H1, H2, ..., H20) was selected in Hermanice warehouses to be as representative as possible and to have a good predictive value for PAH at 2016-2017, (Figure 1) [3].

## Sampling

Among the most important factors influencing the analytical determination are the sampling. Passive sampling was selected for this study. The principle is the distribution of the analyte among the present media. There is a diffusion of the chemicals from the phase with the highest fugacity to the phase with lower fugacity. The material transfer rate is qualified by the total mass transfer coefficient. Free flow of compounds takes place until equilibrium is reached throughout the system or until the sampling process

is completed. For sampling PAHs, white polyurethane foam (PUF) filters with a density of  $0.030 \text{ g cm}^{-3}$ , 150 mm in diameter and 15 mm thick, were placed in two bowl-shaped stainless steel containers. Sampling time lasted 28 days, which is the recommended time for passive sampling using PUF to monitor PAHs. Attention was drawn to factors that could influence passive sampling, i.e. exposure time and ambient temperature [4-8].

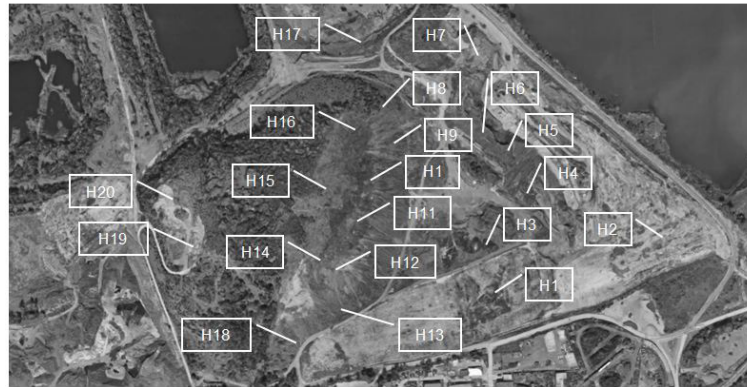


Figure 1: Sampling Points on the Hermanice Dump

### Extraction

The analyte was extracted with Soxhlet extract in 110 ml of n-hexane (POCH for HPLC) and acetone (1:1) for 15 hours. The same solvent ratio was used for extraction in the mixture n-hexane and n-pentane. After extraction, the samples were purified using a silica gel column.

### Purification and fractionation

Purification was performed to separate the alkane fraction from simple aromatic hydrocarbons. Alkanes were eluted with 1.0 ml of n-pentane, the aromatic compounds were collected in a mixture of n-pentane (10 ml) and dichloromethane (7:3). Subsequently, they were dried with a stream of argon. Activation of the silica gel for fractionation was carried out at  $130 \text{ }^\circ\text{C}$  for 24 hours. Silica gel mixed with distilled water was used to deactivate the silica. After vigorous shaking, the silica was homogenized at room temperature for 12 hours. After this time, methyl chloride was added to suspend the silica gel. The column for fractionation was made of flame retardant glass, equipped with glass wool and a PTFE faucet at the bottom pre-filled with dichloromethane. Activated anhydrous  $\text{Na}_2\text{SO}_4$  (4 g) was added to the top of silica gel. The chromatography column was pre-eluted with hexane / pentane (40:40). The solvent present in the samples was evaporated with a stream of nitrogen. The sample was then redissolved in 2 ml of acetonitrile and 1 ml transferred to the HPLC analysis column. All chemicals used were pure for Penta analysis (p.a.) [6-9].

### HPLC analysis

The sample thus prepared was analyzed on a DIONEX fluorescence detector. Analyzes of PAHs were performed using an HPLC column which worked with a clean extract (1 ml) dissolved in acetonitrile with a  $10 \text{ } \mu\text{l}$  spray. Analysis was performed at column temperatures  $25 \text{ }^\circ\text{C}$ , a flow rate of  $0.5 \text{ ml min}^{-1}$ , and the detection limit was 210 nm. The lowest measurable concentration with this method is  $0.01 \text{ } \mu\text{l / m}^3$ .

The correct function of the system was checked regularly, each sample was analyzed twice, including blank samples. The results were used to calculate the concentrations of PAHs in the material. Reproducibility values varied in samples of the selected matrix up to 8% [9].

### Results and discussion

The dump material is very inhomogeneous and the concentration of the individual  $\Sigma 16$  PAHs varies greatly from point to point. Therefore, all the results presented in Table 1 and Table 2 are reported as average values of all 20 points that were created at the Hermanice dump. Due to the spatial distribution of the measuring points, the attendance could not be affected by individual points.

Of the total average number of  $\Sigma 16$  PAHs =  $1\,353.81 \text{ } \mu\text{g kg}^{-1}$  / year, two and three nuclear ( $1344.95 \text{ } \mu\text{g kg}^{-1}$  per year) and four nuclear and more nuclear ( $8.86 \text{ } \mu\text{g kg}^{-1}$  were most frequently found in Hermanice per year) PAHs. PAHs such as Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, Dibenzo(ah)anthracene, Benzo(ghi)perylene, indeno(1,2,3-cd)pyrene. These PAHs are under the detection limit.

Evaluation of the results of determination of the concentrations of sixteen representatives of PAHs according to US EPA on dust particles  $\text{PM}_{10}$  taken from Hermanice dump. Prior to the analysis of PAHs on  $\text{PM}_{10}$  particles, the composition of the mineral phases of the collected dust particle samples was determined. A pyrite content of 0.9% was detected among the detected minerals, which at such a low content is oxidized in the burning material to form iron hydroxides or thermally degraded, and indicates the susceptibility of the deposited material to self-ignition.

| PAHs                   | July 2016    | August 2016  | September 2016 | October 2016  | November 2016 | December 2016 |
|------------------------|--------------|--------------|----------------|---------------|---------------|---------------|
| Naphthalene            | 16,18        | 18,21        | 17,48          | 15,37         | 19,58         | 18,35         |
| Acenaftylene           | 0,00         | 0,00         | 0,00           | 0,00          | 0,10          | 0,00          |
| Acenaften              | 24,59        | 30,28        | 29,25          | 28,35         | 33,89         | 31,26         |
| Fluoren                | 18,33        | 21,13        | 30,39          | 32,20         | 35,38         | 34,12         |
| Phenanthrene           | 21,35        | 25,38        | 28,69          | 27,85         | 26,52         | 26,17         |
| Antracene              | 2,30         | 2,18         | 2,23           | 2,38          | 2,78          | 2,59          |
| Fluoranten             | 1,14         | 1,25         | 1,47           | 1,54          | 1,11          | 1,48          |
| Pyrene                 | 0,33         | 0,70         | 0,53           | 0,52          | 0,99          | 0,46          |
| Benzo(a)anthracene     | 0,07         | 0,03         | 0,06           | 0,04          | 0,05          | 0,04          |
| Chrysen                | 0,09         | 0,06         | 0,06           | 0,01          | 0,01          | 0,02          |
| Benzo(b)fluoranthene   | 0,08         | 0,04         | 0,08           | 0,05          | 0,07          | 0,06          |
| Benzo(k)fluoranthene   | 0,00         | 0,00         | 0,00           | 0,00          | 0,00          | 0,00          |
| Benzo(a)pyrene         | 0,00         | 0,00         | 0,00           | 0,00          | 0,00          | 0,00          |
| Dibenzo(ah)anthracene  | 0,00         | 0,00         | 0,00           | 0,00          | 0,00          | 0,00          |
| Benzo(ghi)perylene     | 0,00         | 0,00         | 0,00           | 0,00          | 0,00          | 0,00          |
| Indeno(1,2,3-cd)pyrene | 0,00         | 0,00         | 0,00           | 0,00          | 0,00          | 0,00          |
| <b>Total</b>           | <b>84,46</b> | <b>99,26</b> | <b>110,24</b>  | <b>108,31</b> | <b>120,48</b> | <b>114,55</b> |

**Explanatory note:**

- beyond detection limits
- results are given in  $\mu\text{g}/\text{m}^3$

**Table 1:** Results of concentrations of  $\Sigma$  16 PAHs monitored at Hermanice July 2016 - December 2016

| PAHs                   | January 2017  | February 2017 | March 2017    | April 2017    | May 2017      | June 2017     |
|------------------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Naphthalene            | 16,18         | 18,21         | 17,48         | 15,37         | 19,58         | 19,12         |
| Acenaftylene           | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          | 0,12          |
| Acenaften              | 32,89         | 34,10         | 32,90         | 35,10         | 33,85         | 33,50         |
| Fluoren                | 36,12         | 35,47         | 35,21         | 35,98         | 33,72         | 35,52         |
| Phenanthrene           | 27,80         | 27,45         | 27,83         | 26,74         | 29,21         | 28,69         |
| Antracene              | 2,39          | 2,57          | 2,14          | 2,89          | 2,54          | 2,60          |
| Fluoranten             | 1,36          | 1,59          | 1,89          | 1,35          | 1,34          | 1,30          |
| Pyrene                 | 0,49          | 0,54          | 0,61          | 0,83          | 0,24          | 0,48          |
| Benzo(a)anthracene     | 0,07          | 0,08          | 0,06          | 0,09          | 0,07          | 0,06          |
| Chrysen                | 0,02          | 0,03          | 0,04          | 0,05          | 0,20          | 0,01          |
| Benzo(b)fluoranthene   | 0,05          | 0,08          | 0,07          | 0,08          | 0,09          | 0,07          |
| Benzo(k)fluoranthene   | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          |
| Benzo(a)pyrene         | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          |
| Dibenzo(ah)anthracene  | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          |
| Benzo(ghi)perylene     | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          |
| Indeno(1,2,3-cd)pyrene | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          | 0,00          |
| <b>Total</b>           | <b>117,37</b> | <b>120,12</b> | <b>118,23</b> | <b>118,48</b> | <b>120,84</b> | <b>121,47</b> |

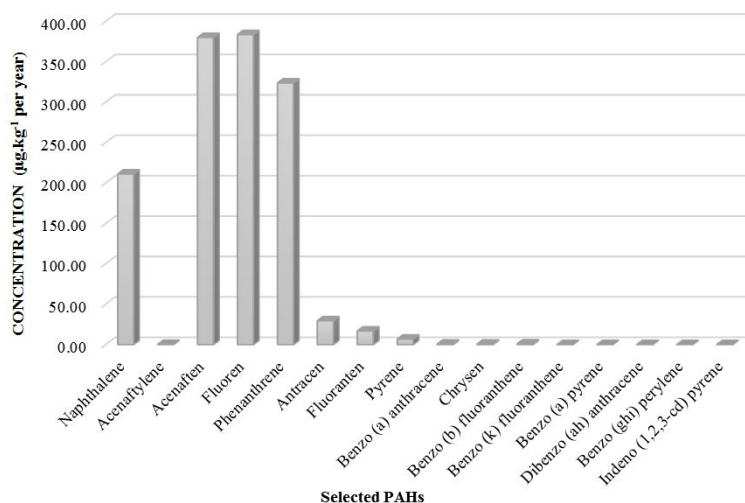
**Explanatory note:**

- beyond detection limits
- results are given in  $\mu\text{g}/\text{m}^3$

**Table 1:** Results of concentrations of  $\Sigma$ 16 PAHs monitored at Hermanice January 2017 - June 2017

During the PAHs analysis, many homologous lines were detected on many samples n-alkanes and also phenanthrene and pyrene, which can be considered as high-temperature pyrogenic processes. For all species, there is a non-homogeneous composition of dump material where the concentration of individual PAHs from point to point can be dramatically changed. For the sake of clarity, therefore, a percentage of PAHs adsorbed on  $\text{PM}_{10}$  particles at Hermanice was plotted in Figure 2.

The measured values that come from Tables 1 and 2 tell us that in terms of the representation of individual PAHs, Naphthalene (min: 15.37  $\mu\text{g kg}^{-1}$  - 1 max: 19.58  $\mu\text{g kg}^{-1}$ ), Acenaftylene (min: 24.59  $\mu\text{g kg}^{-1}$  max: 35.10  $\mu\text{g kg}^{-1}$ ), Fluoren (min: 18.33  $\mu\text{g kg}^{-1}$  max: 36.12  $\mu\text{g kg}^{-1}$ ), Phenanthrene (min: 21.35  $\mu\text{g kg}^{-1}$  max: 29.21  $\mu\text{g kg}^{-1}$ ).



**Figure 2:** Results of concentrations of  $\Sigma 16$  PAHs monitored at Hermanice June 2016 - November 2017

This implies that they are mainly PAHs with 2-3 nuclei. It is known that low molecular weight PAHs (2-3 benzene nuclei) are contained in the atmosphere only in the gas phase as diffusion-moving molecules, while at higher molecular weights they are bound to aerosol particles or sorbed on organic matter. This represents more than 95.5% of the total PAHs.

In the air, PAHs are preferably bonded to the surface of PM particles where they are fed by condensation and adsorption mechanisms. During emission, adsorption occurs on the resulting solid particles, which are then coupled by condensation when the emissions are cooled. Dependency has been determined whether this dependency can be demonstrated on the monitored sites. A linear regression evaluation was carried out, which evaluated the possible dependence of quantitative variables (the detected concentration of PAHs on the heats of Hermanice depending on the PM<sub>10</sub> particle concentrations).

From an overall perspective, it can be estimated that the Ostrava thermally active dumps do have a significant impact on air quality and human health, as they are located in locations close to residential enclosures. Gradual blasting of a variety of dump material, the process of extraction or changing weather conditions can result in a change in the concentrations and character of the pollutants that are produced. It is therefore in place to develop a comprehensive monitoring that will deal not only with substances that are produced by rolling but also with thermal activity within the interior of the body. In conclusion, we could find out how the thermal activity inside the body changes in connection with the emergence of new contaminants.

## Conclusion

Analyzes of  $\Sigma 16$  selected PAHs monitored on PM<sub>10</sub> particles at 20 points on the hermanice dump. Concentrations were found to be no different in the course of the year. For minor factors, the differences are only minimal. Due to the nature of the weather conditions, the city of Ostrava and the adjacent areas are the most affected. The best available analysis methods were used to extract and analyze PAHs.

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