Article

Assessment of Emission of Selected Gaseous Components from Coal Processing Waste Storage Site

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Abstract: Coal mine waste dumps are often thermally active objects with exhalation zones emitting exhaust gases, both inorganic and organic, including polycyclic aromatic hydrocarbons, phenols and BTEX hydrocarbons. The genotoxic, mutagenic and carcinogenic properties of polycyclic aromatic hydrocarbons make the monitoring of their emissions of particular importance. In this paper, the emissions of polycyclic aromatic hydrocarbons from exhalation zones of selected mine waste dumps located in Poland are presented. The experimental data set was analyzed with the application of the Hierarchical Clustering Analysis. The compounds of two- and three-cyclic hydrocarbons, such as naphthalene, acenaphthene, fluorene, phenanthrene and anthracene, were quantified in the gaseous samples tested. The compounds with a greater number of aromatic rings, such as fluoranthene, pyrene, benzo[a]anthracene and chrysene were characteristic only for some of the mine waste dumps tested.

Keywords: coal mine waste; PAHs; emission; hierarchical clustering analysis

1. Introduction

For several decades, large amounts of gangue have been extracted and stored on the surface in Polish coal mining plants. This deposited waste material also contains shales, as well as coal and other combustible materials. It is estimated that, on average, approximately 0.4–0.5 Mg of waste material is produced for each 1 Mg of extracted coal, and some part of it is deposited in coal mining waste dumps [1]. In the past, because of technical limitations and poorly developed waste management methods, much waste was stored haphazardly. Many factors, including non-fulfillment of the basic principles of fire prevention, the use of improper technologies, as well as the absence of waste segregation and compaction in the storage process, resulted in self-ignition of mine waste dumps. Coal and pyrite included in waste material are oxidized when exposed to air and water vapor, which leads to self-heating of the deposited material, and in consequence to fires [2,3]. Coal mine waste dumps are therefore often thermally active objects characterized by high internal and surface temperatures and presence of exhalation zones emitting exhaust gases [4]. These exhaust gases may contain both inorganic (e.g., CO, SO2, H2S) and organic compounds, like, e.g., polycyclic aromatic hydrocarbons (PAHs), phenols and BTEX hydrocarbons (Benzene, Toluene, Ethylbenzene, Xylene) [5]. Strong genotoxic, mutagenic and carcinogenic properties of PAHs impose the need for constant monitoring of the content of these hydrocarbons in water, soil and air [6,7]. In the literature, the issues concerning fire hazard within the mine waste dumps, including the analysis of the causes of fire occurrence, description of ecological aspects of this phenomenon, as well as the proposition of prevention techniques, have been presented [3,8,9]. The phenomenon of endogenic
fire formation has complex mechanisms, and their description has been attempted on the basis of theoretical considerations, experimental results and process data related to spontaneous ignition of coal and underground fires in coal mines [10–12]. However, the studies defining the scale of gas emission from exhalation zones of thermally active dumps, describing the method of samples collection, and examining the content of the above mentioned gases in mixtures emitted from the mine waste dumps are extremely limited [4]. In this study, PAH emission from exhalation zones of burning mine waste dumps located within the Upper Silesian Coal Basin, Poland was presented. Chemometric analysis was employed in the experimental data exploration to trace the similarities between the objects (gaseous samples tested) in the parameter space and between the parameters in the object space.

2. Materials and Methods

2.1. Materials

Twenty four gas samples were collected from each of the three selected mine waste dumps, denoted as DI, DII and DIII, located within the Upper Silesian Coal Basin, Poland (72 samples in total) (see Figure 1). The mine waste dumps subjected to the study were thermally active and had numerous exhalation zones. The major differences characterizing the particular examined areas included the shape, manner of construction and reclamation level.

![Figure 1. Location of sampling sites.](image)

2.2. Gas Sampling and Analytics

The sampling system applied in the study for quantification of PAH compounds consisted of a sampling device with a solid PUF (polyurethane foam) sorbent, quartz fiber filter, SKC Airchek2000 aspirator and cooler cable. Gas samples were collected with a flow rate of 3 L min⁻¹ and sampling time of 20 min. The components adsorbed were extracted using ASE (Accelerated Solvent Extraction) and the DIONEX ASE 200 extractor with hexane. The extraction stage consisted of a series of pre-heating (5 min) and static extraction (5 min) at 100 °C under a pressure of 1.5 MPa. The extract was next
purified using the SPE (Solid Phase Extraction) technique, concentrated by evaporation under a stream of nitrogen, and dissolved in 1 mL of acetonitrile. All tested samples were analyzed with the use of High-Performance Liquid Chromatography (HPLC) with a Fluorescence Detector (FLD) (excitation/emission spectra of 225/350 nm) (Figure 2).

A HPLC 1200 Series liquid chromatograph from Agilent Technologies with ZORBAX Eclipse PAH column (4.6 mm × 150 mm, 3.5 µm; 250 °C) was applied at a flow rate of 1.2 L min⁻¹, along with a mobile phase of acetonitrile (A)/water (B) at 50/50. The gradients used were: 50% B (0–1 min), 0% B (16–27 min) and 50% (28 min). In order to verify the correctness of the method employed, studies on the recovery of fifteen PAH compounds (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene and indeno[1,2,3-cd]pyrene) were also carried out. The studies concerning the recovery of particular PAHs were carried out by taking into account all stages of preparation of samples for the analysis and three concentration levels, of 0.1 ng, 1 mg and 5 µg, using extraction in hexane and in the mixture of hexane and acetone (90:1) [7]. The average recovery efficiency of fifteen PAHs ranged from 86 to 97% for the extraction with hexane, and from 88 to 104% in case of extraction with the mixture of hexane and acetone. Since the differences between the extraction with hexane and hexane-acetone mixture were insignificant, the first type of extraction was applied in further studies, which also meets the requirements of the US Environmental Protection Agency [7].

2.3. Experimental Data Exploration

The experimental data set on polycyclic aromatic hydrocarbons emission from the thermally active mine waste dumps was analyzed with the use of the Hierarchical Clustering Analysis (HCA) method [13–19]. This method of data exploration allows the exploration of the structure of data by tracing the similarities between the objects in the parameter space and between the parameters in the object space. HCA methods vary in terms of the similarity measure applied and the way of clustering. The most commonly applied similarity measure is the Euclidean distance. Among the methods of clustering, Single Linkage Method, Complete Linkage Method, Average Linkage Method, and Centroid Linkage Method, as well as Ward’s linkage method, may be distinguished. The results of the data exploration are presented in the form of dendrograms, where the x-axis describes the order in which the objects were linked with each other, and the y-axis defines their mutual similarity. The clustering analysis does not allow for the simultaneous interpretation of the dendrograms representing the objects in the parameter space and the parameters in the object space. However, complementing the cluster analysis with a color map of experimental data showing the values of measured parameters ordered in accordance with the order of organization of the objects and parameters on the dendrograms enables this problem to be overcome [17–21]. Simultaneous interpretation of dendrograms, complemented with a color map of experimental data, enables more in-depth interpretation of the data structure.
3. Results and Discussion

The average concentrations of PAHs in gas samples from mine waste dumps DI–III are given in Table 1. The highest average concentration was reported for naphthalene, irrespective of the mine waste dump considered. The naphthalene content amounted to over 90% of the total average PAH concentration in the cases of DI and DII, and over 70% for samples collected from mine waste dump DIII. The high concentration of naphthalene in the gaseous phase may be attributed to its having the highest volatility among all PAH group compounds. Higher amounts of fluorene and phenanthrene were also characteristic for gases emitted from mine waste dumps DI and DII, while in the case of DIII, the second-largest contribution to the total average PAHs concentration was for acenaphthene. The average concentrations of pyrene, benzo(a)anthracene (BaA) and chrysene were well below 1 µg m$^{-3}$ for all mine waste dumps examined.

Table 1. Average PAH concentrations in gas samples from mine waste dumps DI–III.

| No | Compound             | Carcinogenicity | Number of Rings | Average Concentration µg m$^{-3}$ |
|----|----------------------|-----------------|----------------|---------------------------------|
|    |                      |                 |                | DI     | DII    | DIII   |
| 1  | Naphthalene (NAP)    | 0.001           | 2              | 534.43 | 991.06 | 83.21  |
| 2  | Acenaphthene (AcP)   | 0.001           | 3              | 2.14   | 8.38   | 29.28  |
| 3  | Fluorene (Flu)       | 0.001           | 3              | 14.50  | 12.33  | 0.89   |
| 4  | Phenanthrene (PA)    | 0.001           | 3              | 24.10  | 12.89  | 2.62   |
| 5  | Anthracene (Ant)     | 0.010           | 3              | 4.05   | 0.40   | 0.19   |
| 6  | Fluoranthene (FluT)  | 0.001           | 4              | 0.55   | BDL    | 1.72   |
| 7  | Pyrene (Pyr)         | 0.001           | 4              | 0.30   | BDL    | 0.14   |
| 8  | Benzo(a)anthracene (BaA) | 0.001       | 4              | 0.16   | BDL    | 0.02   |
| 9  | Chrysene (Chr)       | 0.001           | 4              | 0.22   | BDL    | BDL    |

1 Relative carcinogenicity of particular PAH [20].

The experimental data on polycyclic aromatic hydrocarbons emission from the thermally active mine waste dumps was analyzed with the application of Hierarchical Clustering Analysis. The experimental data set was organized in a matrix $X(72 \times 6)$, whose rows describe gaseous samples collected from three mine waste dumps and the columns describe the contents of naphthalene, acenaphthene, fluorene, phenanthrene, anthracene and fluoranthene in gas samples from mine waste dumps DI–III.

For the experimental data organized in matrix $X(72 \times 6)$, dendrograms were developed with the use of Ward’s linkage method and Euclidean distance (see Figure 3). In the Ward’s linkage method, two groups of objects are clustered in a manner that minimizes the sum of squared deviations of all objects from these two groups from the center of gravity of the new group that will be created as a result of their clustering. Figure 3 shows also a color map of experimental data ordered in accordance with the order of objects and measured parameters obtained on the dendrograms.

The dendrogram shown in Figure 3a allows grouping the tested samples into four clusters:

- cluster A, including all gas samples collected from the mine waste dump DIII (objects 49–72),
- cluster B, including 12 gas samples collected from the mine waste dump DI (objects 1–12) and 16 samples collected from the dump DII (objects 25–27, 29–40 and 42),
- cluster C, including the remaining 8 gas samples collected from the mine waste dump DII (objects 28, 41, 43–48), and
- cluster D, including the remaining gas samples collected from the mine waste dump DI (objects 13–24).

Additionally, within the distinguished clusters, subgroups of similar objects were identified. Within cluster A, a subgroup A1 including objects 49–64, 66 and 68–72, as well as subgroup A2 composed of objects 65 and 67 were distinguished. Within cluster B, three subgroups were identified:

- subgroup B1, including objects 1–6,
- subgroup B2, including objects 25–27, 29–37 and 42, and
- subgroup B3, including objects 7–12 and 38–40.

Within cluster C, a subgroup including objects 28, 41 and 43–47 was distinguished, and also the specific nature of object 48 was indicated, and within the cluster D, two subgroups were found:
- subgroup D1, including objects 13–19 and 24, and
- subgroup D2, including objects 20–23.

The dendrograms for 6 measured parameters in the space of 72 objects are shown in Figure 3b. This allows the parameters measured to be grouped into classes including parameters 3, 4 and 5, describing the concentrations of fluorene, phenanthrene and anthracene (Class A), and parameters 1 and 6, describing the concentrations of naphthalene and fluoranthene (Class B), along with one ungrouped parameter 2, describing the concentration of acenaphthene.

The results of the cluster analysis made it possible to divide the examined samples with regard to the place of their collection. A clear difference between the samples collected from the mine waste dump III and samples collected from the mine waste dumps DI and DII was observed. Moreover, a distinct division between the samples collected from the same mine waste dump was observed and evidenced by the fact that the cluster B includes a portion of samples from the mine waste dumps DI and DII. The remaining samples from the mine waste dump DI were grouped into cluster D, and the samples from the mine waste dump DII were grouped into cluster C. Simultaneous interpretation of the dendrogram for 72 gas samples from three different mine waste dumps in the space of 6 measured PAHs with a color map of experimental data makes it possible to state that the objects 49–72 grouped in cluster A are characterized by having the lowest concentrations of naphthalene, fluorene, phenanthrene...
(parameters 1, 3 and 4), low concentration of fluoranthene (parameter 6), and a relatively high concentration of acenaphthene (parameter 2) compared to the samples collected from dumps DI and DII. The specific nature of objects 65 and 67 included in the subgroup A2 was associated with high concentration of acenaphthene (parameter 2). The objects 1–12, 25–27 and 29–40 included in cluster B were characterized by low concentrations of naphthalene, fluorene, phenanthrene, anthracene and fluoranthene (parameters 1 and 3–6), and the lowest concentration of acenaphthene (parameter 2). Subgroup B1, including objects 1–6, was characterized by having the highest, within cluster B, concentration of fluoranthene (parameter 6). The objects 25–27, 29–36, and 42 had relatively higher concentrations of naphthalene (parameter 1) within cluster B, and the objects 7–12 and 38–40 showed the highest concentrations of naphthalene, fluorene and phenanthrene (parameter 1, 3 and 4). Cluster C, including 8 samples collected from the mine waste dump DII (objects 28, 41, 43–48), was characterized by having relatively higher concentrations of naphthalene and fluoranthene (parameters 1 and 6) in comparison to the other samples tested. At the same time, the specific nature of sample 48, collected from the waste dump DII, was attributed to its having the highest, among all the tested samples, concentrations of naphthalene, acenaphthene, fluorene and fluoranthene (parameters 1–3 and 6). Other samples collected from the mine waste dump DI (objects 13–24) included in cluster D were characterized by having the highest concentrations of phenanthrene and anthracene (parameters 4 and 5), among all the samples tested. In addition, the specific nature of the objects 20–23 included in subgroup D2 was reported, and was characterized by having the highest concentration of fluorine (parameter 3) for this sub-group.

4. Conclusions

In the experiments performed, mostly compounds of the so called “lighter PAH” group, two- and three-cyclic compounds, such as naphthalene, acenaphthene, fluorene, phenanthrene and anthracene, were quantified in the tested gaseous samples collected from mine waste dumps. The compounds with a greater number of aromatic rings, such as fluoranthene, pyrene and benzo[a]anthracene, were quantified for samples taken from mine waste dumps DI and DIII. Chrysene was detected only in samples from mine waste dump DI.

PAHs emitted into the atmosphere from self-heating and fire processes occurring on mine waste dumps may undergo various transformation and reactions with, e.g., sulfur dioxide or nitrogen oxides emitted along with carbon monoxide and hydrogen sulfide from thermally active mine waste dumps. These transformations may result in the generation of compounds of increased carcinogenicity. The measurements of PAH concentrations in the atmosphere are therefore important in terms of the assessment of environmental and health safety in the vicinity of such mine waste dumps.

The application of Hierarchical Clustering Analysis allowed the grouping of the tested gas samples into four clusters. The first one included all gas samples collected at the mine waste dump DIII, the second cluster included 12 samples acquired from the mine waste dump DI and 16 samples taken at the mine waste dump DII. Clusters C and D included the remaining samples collected at the mine waste dumps DI and DII, respectively. The Hierarchical Clustering Analysis performed for the parameters (concentrations of PAHs) in the space of objects (tested gaseous samples) allowed the division of the examined parameters into two groups; the first group included parameters representing the concentration of fluorene, phenanthrene and anthracene, and the second included the parameters representing the concentrations of naphthalene and fluoranthene. There was also one ungrouped parameter describing the concentration of acenaphthene.

It was found that all objects included in cluster A were characterized by the lowest concentrations of naphthalene, fluorene, and phenanthrene, low concentration of fluoranthene, and relatively high concentration of acenaphthene compared to the samples taken from the other mine waste dumps. The samples included in cluster B differed from the remaining samples due to low concentrations of naphthalene, fluorene, phenanthrene, anthracene and fluoranthene, and the lowest concentration of acenaphthene, while the samples of cluster C were characterized by having relatively higher
concentrations of naphthalene and fluoranthene compared to the other samples tested. It was also found that the samples included in cluster D had higher concentrations of phenanthrene and anthracene than all other samples tested.

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