A Thorough Study for PAHs in Dump Materials from Open-pit Lignite Mining, Maritsa Iztok Basin, Bulgaria

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) in six samples from Bulgarian Lignite Dumps Maritsa Iztok are tracked and amounts are determined. For isolation of soluble organic matter (SOM) ca. 40 g of powdered dump samples were Soxhlet extracted by chloroform. After asphaltenes precipitation, maltenes were separated via column chromatography. The first two fractions were further analyzed. Gas chromatography-mass spectrometry (GC-MS) was applied to appreciate organic matter sources and to identify and quantify PAHs in the samples. The set of PAHs determined pointed out that 3 and 4 ring unsubstituted PAHs as dominant in the dump extracts. Total organic carbon (TOC) values of the samples varied in the range 1.18-5.63 wt.%. Phenanthrene + Methylphenanthrene amounts were in the range 0.44-2.98 mg/kg TOC, while for Fluoranthene + Pyrene were in the range 0.06-0.52 mg/kg TOC. Total amounts of PAHs varied in the range 7-41 microg/kg sample. Values were compared with the legislation norms for PAHs in soils. All magnitudes were under the regulation norms for harmful substances in soil published by the Bulgarian National Legislation (2008). In conclusion, the study is in an equivocal proof for the negligible amounts of PAHs in dump materials from Maritsa Iztok lignite mining. However, their amounts in dumps should be measured and monitored bearing in mind the huge territories covered by these waste materials of mining industry.

1. Introduction

Presence of polycyclic aromatic hydrocarbons (PAHs) in the environment is directly related to health and quality of life on the Earth [1]. Their existence is responsible for development of various diseases in humans and animals. Hence, study and monitoring environmentally harmful compounds are of great importance. PAHs are part of the group of volatile organic compounds (VOCs) originating from the solid and liquid energy sources like coal, shale, oil, etc. PAHs originate from natural and anthropogenic sources, or fall on Earth from the space. The most important contributors of PAHs are fossil fuels combustion, i.e. industrial and domestic and a number of chemical industries making a significant impact to the emission of pollutants in the atmosphere [2]. Natural sources of PAHs are volcanic activity, forest fires, etc. Leakage of organic compounds from dump coal materials as a result of groundwater flushing or natural erosion of coal seams [3,4], as well as releases from coal mining and transportation could be regarded as other potential sources for PAHs at mining areas. PAHs,
regardless of their origin, are characterized by a broad range of action. Of especial concern are the so-called PAHs with “trans-border action”. Due to the fine particulate matter as carriers of adsorbed pollutants on them PAHs can be emitted to long, long distances. This makes people particularly sensitive to any source of PAHs.

Mini Maritsa Iztok EAD is the largest coal mining company in the Republic of Bulgaria, exploiting the Maritsa Iztok lignite basin and of decisive importance for the national energy strategy. Three open-cast mines currently operate in the coalfield: Troyanovo-1, Troyanovo-North and Troyanovo-3, with a combined annual production of about 20 million tons. Reserves are estimated at about 2027 billion tons (as of 31.12.2013). The total length of the longwall of the three mines is some 10 km. From the beginning of operations in 1962 until 31.12.2013, 1,038,217,911 tons of coal had been extracted, with 4,278,655,232 m³ of over-burden removed and backfilled [5]. Lignite reserves in the Maritsa Iztok Basin (MIB), used as a source of electric power generation, are previewed to last for at least the next 50-60 years. Carried out in the form of long opencast exploitation, mining works in the basin have generated a huge volume of dump materials that have the potential to provoke environmental problems.

The aim of the study is to determine qualitatively/quantitatively PAHs in some samples extracted from Maritsa Iztok dumps, Bulgaria. The present work is a kind of prolongation of our previous study on the organic pollutants in extracts of Maritsa Iztok mining dumps [6] where some VOCs were quantitatively identified.

2. Material and Methods

Six samples of Bulgarian Maritsa Iztok dumps with different location of drills were investigated. The sampled dump materials were taken from the internal dumps Troyanovo-North Mine, Staroselets Dump, United North Dumps and Dryanovo outpost dump of the Trojanovo mine [6]. In Table 1 are gathered Rock Eval data of samples studied.

| Sample location and Index | TOC | S₁ | S₂ | S₃ | Tₘₐₓ | HI | OI | PI | RC | PC |
|--------------------------|-----|----|----|----|------|----|----|----|----|----|
| Troyanovo-North Mine     |     |    |    |    |      |    |    |    |    |    |
| C                        | 1.18 | 0.04 | 0.51 | 1.85 | 415  | 43 | 157 | 0.07 | 1.04 | 0.14 |
| H                        | 1.26 | 0.04 | 0.85 | 1.27 | 426  | 67 | 101 | 0.04 | 1.11 | 0.15 |
| Dryanovo Dump            |     |    |    |    |      |    |    |    |    |    |
| D                        | 1.27 | 0.02 | 0.72 | 1.33 | 423  | 57 | 105 | 0.03 | 1.13 | 0.14 |
| E                        | 3.63 | 0.03 | 3.69 | 3.37 | 434  | 102 | 93  | 0.01 | 3.13 | 0.5  |
| Staroselets Dump         |     |    |    |    |      |    |    |    |    |    |
| F                        | 5.63 | 0.09 | 7.76 | 6.14 | 414  | 138 | 109 | 0.01 | 4.65 | 0.98 |
| United North Dumps       |     |    |    |    |      |    |    |    |    |    |
| G                        | 1.46 | 0.04 | 0.96 | 2.85 | 379  | 66 | 195 | 0.04 | 1.24 | 0.22 |

Dump samples, ca: 30 g were Soxhlet extracted by chloroform. Soluble organic matter (SOM) was concentrated and asphaltenes were removed. Soluble portions, maltenes, were subsequently separated via column chromatography by mini-glass column with Kieselgel. The following fractions were prepared: neutral (n-He eluent), aromatic/slightly polar (DCM eluent), and polar (Ac eluent). Saturated and aromatic hydrocarbons were further analysed by a gas chromatography–mass spectrometer (GC-MS). Finnigan MAT GCQ, equipped with a DB-5MS silica capillary column (30 m, 0.25 mm i.d.,
0.25 µm film thickness) was used. Oven temperature was programmed from 70–300 °C with steps of 4 °C/min, followed by an isothermal period of 15 min. Helium was used as carrier gas. The device was set in electron impact mode with a scan rate of 50–650 Daltons (0.7 s/scan). MS data were acquired and processed with the HP software. Individual compounds were determined by comparison of mass spectra (MS) with literature and library data, comparison of MS and GC retention times with those of authentic standards or interpretation of mass spectra. For MS tracking X-calibur software was used. MS was quantitatively interpreted by internal standard application.

3. Results and Discussions
The determined values for TOCs varied from 1.18 to 5.63 wt. %. The highest TOC value was measured for sample from “Staroselets Dump” and the lowest TOC for the sample from “Troyanovo North-Mine” (Table 1). The high TOC has reflected in the highest yield of extracted SOM (sample F) and the lowest yield of maltenes for the sample C. The results for fractional compositions of the samples studied are given in Table 2.

| Sm.       | SOM wt.% | Fractional composition of maltenes, % | Asphaltenes,% |
|-----------|----------|--------------------------------------|---------------|
| C Tr-2,1983 mp | 0.26     | I fr. 7.9, II fr. 12.0, III fr. 20.8, Losses 9.9 | 49.4          |
| D Dump,Dr-E-m | 0.12     | I fr. 9.4, II fr. 15.4, III fr. 22.2, Losses 7.4 | 45.6          |
| E Dump,Dr-S-m | 0.23     | I fr. 12.4, II fr. 22.0, III fr. 35.4, Losses 3.6 | 26.6          |
| F Dump,Staros. | 0.79    | I fr. 6.8, II fr. 14.2, III fr. 32.7, Losses 8.4 | 37.8          |
| G Dump,G-5 | 0.08     | I fr. 21.6, II fr. 27.7, III fr. 23.1, Losses 11.8 | 15.8          |
| H Tr-2,1983 m clay | 0.17 | I fr. 11.0, II fr. 12.0, III fr. 34.0, Losses 8.0 | 35.0          |

* - % of SOM;

The first two fractions of maltenes (saturated hydrocarbons and aromatic/slightly polar compounds) were further GC-MS analyzed. Identified organic compounds with a potential environmental relevance were quantified and normalized per kg TOC of dump and per kg of dump. Some differences in total PAH amounts among dumps were depicted. PAHs determined pointed out that 3 and 4 ring unsubstituted PAHs are dominant in the dump extracts. This is in accordance with the study of Apostolova et al. [7, 8] on amounts and compositions of native PAHs in coals with different rank. In Figure 2 is illustrated a typical GC separation of Phenanthrene (Ph) and Methylphenanthrenes (MPh). Since the absolute amounts of individual 3 and 4 ring PAHs were insignificant, we combined the contents of 3 cyclic with their alkyl substituted derivatives (Ph + MPh) and also 4 cyclic PAHs Fluoranthene (Fl) + Pyrene (Py). Table 3 lists the determined quantities of the two groups of PAHs, 3 and 4 cyclic. Further values were normalized to mg compound in kg total organic carbon (mg/kg TOC). In view to compare with norms for soils determined in Bulgarian legislation the total sum of the PAHs was expressed in microg/kg sample (Table 3). The values ranged from 7 to 41 microg/kg sample. For comparison Regulation norms for PAHs in soil announced in Regulation № 3 of the Ministry of Environment and Water, Ministry of Health and Ministry of Agriculture and foods determines the limit for allowable content of harmful substances in soils. Therein the background for the sum of 16 priority PAHs [9] should be below 150 microg/kg dry soil. The maximal admissible concentration for the Σ16PAHs in Regulation is 4000 microg/kg dry sample. From the data in Table 3, it is obvious that the determined amounts of PAHs are several times lower than the norms for soils in the Regulation.
Figure 1. GC-MS separation of Ph and MePh isomers in sample C (Tr-2, 1983 mp).

Table 3. PAHs in dump samples and calculated MPI-3 indexes

| Sm | mg/kg TOC | microg/kg Total PAHs | MPI-3* |
|----|-----------|----------------------|--------|
|    | Ph + MePh | Fl + Py  |                  |
| C  | 2.98      | 0.52    | 41                | 1.45   |
| D  | 0.83      | 0.14    | 12                | 1.26   |
| E  | 1.24      | 0.21    | 52                | 0.87   |
| F  | 0.54      | 0.06    | 33                | 1.09   |
| G  | 1.05      | 0.14    | 17                | 1.37   |
| H  | 0.44      | 0.16    | 7                 | 0.81   |

* Methylphenanthrene Index (MPI-3) = (2-MeP+3-MeP)/(9+4MeP+1MeP) [10]

There are not systematic studies on the content and composition of PAHs in Bulgarian coals. However, the recent investigation of Apostolova et al. [8] should be mentioned. Therein the total amount of PAHs in Maritsa East lignites was determined 11.06 microg/g TOC. For comparison, the comprehensive study of PAHs in the flying ashes from thermal power plant (TPP) Maritza East-2 burning the same low rank coal (lignites), the total sum of determined PAHs was 17 microg/kg [11]. The studies pointed out the low total amount of Σ 16 PAHs with distribution pattern dominated by 3-4 cyclic PAHs.

4. Conclusions
This study is of significant environmental impact as some organic pollutants, i.e. PAHs from coal mining dumps could leach by ground waters. Respectively, PAHs could be mobilized and infiltrated into surface/ground water and soils. Even in very low concentrations organic pollutants should be under controls as the problem for human health is not only in their absolute concentrations but also in the long exposure to their harmful impact.
In conclusion, the study is in an equivocal proof for the presence of negligible amounts of PAHs in dump materials from Maritsa Iztok lignite mining. However, their amounts in dumps should be measured and monitored bearing in mind the huge territories covered by these waste materials of coal mining.

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