Anthropogenic Pollutants in Extracts from Maritsa Iztok Dumps

Maya Stefanova[1], Zlatka Milakovska[2], Stefan Marinov[1]

[1] Institute of Organic Chemistry with Centre of Phytochemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., Bldg. 9, Sofia 1113 Bulgaria
[2] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev str., Bldg. 24, Sofia 1113 Bulgaria

maia@orgchm.bas.bg

Abstract. Coals are suspected for many human health problems and are an object of the new discipline - "medical geology". Potential human health risk of organic compounds with coal/lignite provenance includes endocrine disruption, nephrotoxicity, cancer, etc. Recent investigations proved that different organic components, i.e. hydrocarbons, phenols etc. move through/release out of the dump area as a result of alteration processes of the organic matter (OM) caused by the wash-out and/or drainage processes. The timeliness of the present study is based on the scarcity of information on organic geochemistry of dump materials from open pit coal mines and weathered lignites in particular. The limited number of studies on dumps clarifies that even for the "short" time span (some tens of years) in geological point of view, processes of transformation of the extractable OM are detectable. The secondary phases, a result of the OM transformations, move through and out of the dump area and could be potential contaminants for the surface/underground waters and soils in the area. Another environmental problem comes from the air-born VOCs and products of the modern chemical industry. By GC-MS in the slightly polar fractions of the chloroform extracts of dump samples a broad set of components was determined, i.e. phthalates (dominant), *i*-propyl palmitate, *i*-propyl myristate, *n*-hexyl benzoates, etc. These organic contaminants could be regarded more likely as anthropogenic (originating from plasticizers, industrial pollutants, etc.).
Presently, it seems that the identified compounds do not represent an acute toxic risk from an environmental viewpoint. However, some compounds could raise concerns and further attention is needed to be focused on them.

1. Introduction

The problems and measures on environmental protection are increasingly demanding better and more versatile knowledge of the problems and processes that cause them. In this respect, studies affecting mainly the mineral composition of coal and dump waste materials were published [1], while the organic components were systematically neglected. Respectively, organic components in dumps are still "opaque" substances. One explanation is their low content and complicated systematic method to isolate and analyze. The rapid development of instrumental analytical technique allows detailed organic matter (OM) characterization and tracking of the alterations developed under the influence of natural and/or anthropogenic factors. One of the priority areas of the national strategy, that should focus more and more effective investment, is "handling and control of harmful and hazardous household and industrial waste", i.e. the waste materials of energy production, [2]. Scientific research provided herein is related to the development and testing of methods to identify potential organic pollutants included in the list of priority hazardous substances of the EU.

Studies on the organic geochemistry of dump materials from open-pit lignite mining in the scientific world are just beginning. There are some achievements in the field of organic geochemistry of natural and anthropogenic weathering of OM and they have attracted our attention on these processes. The challenge in the study on Bulgarian samples is that they are immature (Miocene-Pliocene in Age) and buried at very shallow depth (150 m), so, the OM from Mini Maritsa Iztok EAD samples is extremely immature. In comparison, the objects of other working teams with similar studies and topics of interest are deeply buried (Tournaisian marine black shale [3], Triassic marine clays [4], sediments and fossil (Middle Jurassic) wood [5], wastes from high-rank coal exploitation [6, 7]. The OM characteristics of the objects of the present study predetermine the variety of spectral and instrumental equipment of high sensibility and resolution. Based on the previous investigation [8], it is necessary to adapt the methodological approach for fossil fuels (coal, oil, shales, etc.) analyses to dump materials. The main goal of the investigation is a quantitative tracking of a set of organic compounds, some of them with natural, other - of anthropogenic origins.

The limited number of studies on the issue [7-9] clearly indicates that even for the "short" time span (some tens of years) in geological point of view, processes of transformation of the extractable OM are detectable. The secondary phases, a result of the transformations, move through into and out of the dump area during the water drainage and wash-out [6, 7] could be potential contaminants for the surface/underground waters and soils in the area. Another problem comes from the air and some wastes as potential mobile organic compounds of the modern chemical industry. Plasticizers, antioxidants, stabilizers and other organic compounds (e.g. 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, triacetine, isopropyl palminate, isopropyl myristate, tributyl-, triethyl- and trioctylphosphates, N,N-dibutylformamide, methyl dihydrojasmonate, nonylphenols and bumetrizole) have been detected in the surface/underground waters and soils around the lignite fields [10]. These new data and processes established gave us the reason to make an attempt to appreciate by geochemical methods organic pollutants in extracts from Maritsa Iztok dumps of the largest coal basin in Bulgaria.

2. Experimental

Mini Maritsa Iztok EAD is the main coal mining company in the Republic of Bulgaria, exploiting the Maritsa Iztok lignite field (240 km^2) 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 (figure 1), 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 long wall 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 m^3 of overburden removed and backfilled (www.marica-iztok.com; Annual report 2013).

Lignite reserves in the Maritsa Iztok Basin (MIB), used as a source of electric power generation, are projected to last for at least the next fifty to sixty 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 a potential to lead to environmental problems. The term "dump" is used according to the Annual Report of 2013, found at www.marica-iztok.com; the term "materials" is considered more neutral or more correct, rather than "overburden redeposited", "landfill" or "waste", since it concerns sediments (overburden) excavated and removed by continuous operation of bucket wheel excavators, transported by rubber-belt conveyors and free-heaped by belt spreaders *(*www.marica-iztok.com*)* in a dump area, i.e. artificially reworked and redeposited sediments. The locations of dump samples studied are indicated on Figure 1.

Figure 1. Mini Maritsa Iztok layout (www.marica-iztok.com) and dump samples locations

Dumps samples (*ca.* 40 g) were Soxhlet extracted by chloroform HPLC grade (~300 ml) for 30 h. Soluble organic matter (SOM) was concentrated and asphaltenes were precipitated by pouring into cold *n*-hexane (1:100 v/v), while the soluble portions (maltenes) were concentrated and subsequently separated *via* column chromatography. Mini-glass column (10×1 cm) with Kieselgel (35–70 mesh ASTM) was used. The following fractions were prepared: neutral, aromatic/slightly polar, and polar. Subsequently first two fractions were studied by gas-chromatography-mass spectrometry (GC-MS).

GC-MS analyses was carried out on a Hewlett-Packard 6890 GC system plus HP 5973 MSD equipped with a HP-5 MS column (30m×0.25mm×0.25µm film thickness) with flame ionization detector (300^{o}C). A split/splitless capillary injector (300^{o}C) is used in the splitless mode (valve reopened 1 min after injection). After 0.5 min isothermal period at 85^{o}C the oven temperature was increased to 200^{o}C at 20^{o}C/min and then to 320^{o}C at 5^{o}C/min. The MSD was operated in the electron impact mode with energy of 70 eV and scan range from 50 to 650 Daltons.

The 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 Xcalibur software was used. MS were quantitatively interpreted by internal standard application. Contents were normalized in µg/g TOC or mg/g TOC of dumps.

3. Results and discussions

By GC-MS separation of the slightly polar fractions of SOM from dump samples of open pit lignite mines of Maritsa East lignite a broad set of components was determined, i.e. phthalates (dominant), *i*-propyl palmitate, *i*-propyl myristate, *n*-hexyl benzoates, etc. (Figure 2).

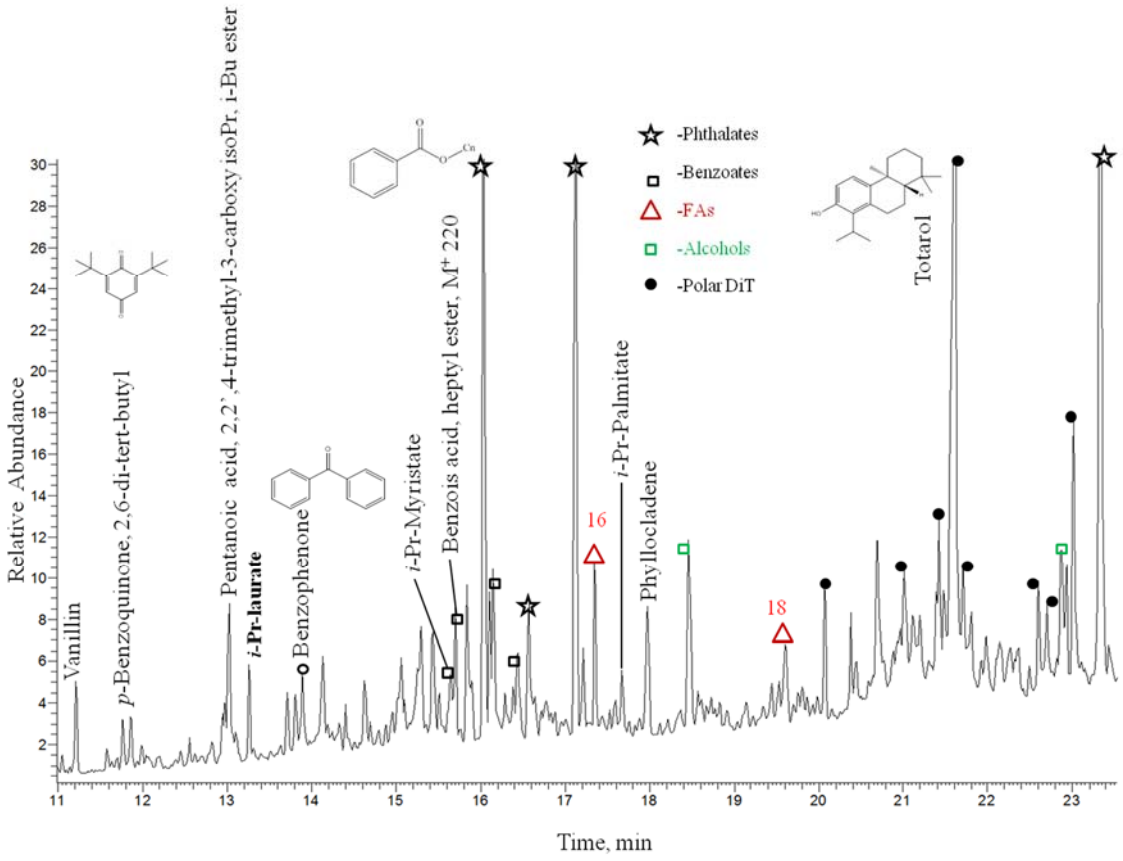

Figure 2. GC-MS separation of slightly polar fraction of dump C. (FA – fatty acid; numbers correspond to atoms in fatty acids; DiT– diterpenoid)

Ministry of Environment and Waters in Bulgaria has stated regulations for the amounts of organic components in soils (Reg. № 3) and in groundwater (Reg. № 8). They concern polycyclic aromatic hydrocarbons (PAH), Cl-containing organic compounds, petroleum products, fungicides, pesticides, etc. At the same time more organic compounds are monitored in the EU. Our study aims to assess the changes in dump OM posing a potential environmental hazard. In the organic geochemistry there are new data published for the mobility of the alteration product of the dump OM resulting from the water drainage and wash-out processes [7]. New fundamental knowledge about the composition of OM and ongoing secondary changes resulting from the research will add new data to acquire a clear and accurate picture of the nature and mechanisms of these changes. The study is important because some of the new forms produced by alteration could be mobilized and infiltrate into surface/groundwater and soils. Even in very low amounts organic pollutants should be under controls as the problem for human health is not in their absolute concentrations but in the long exposure to their harmful impact.

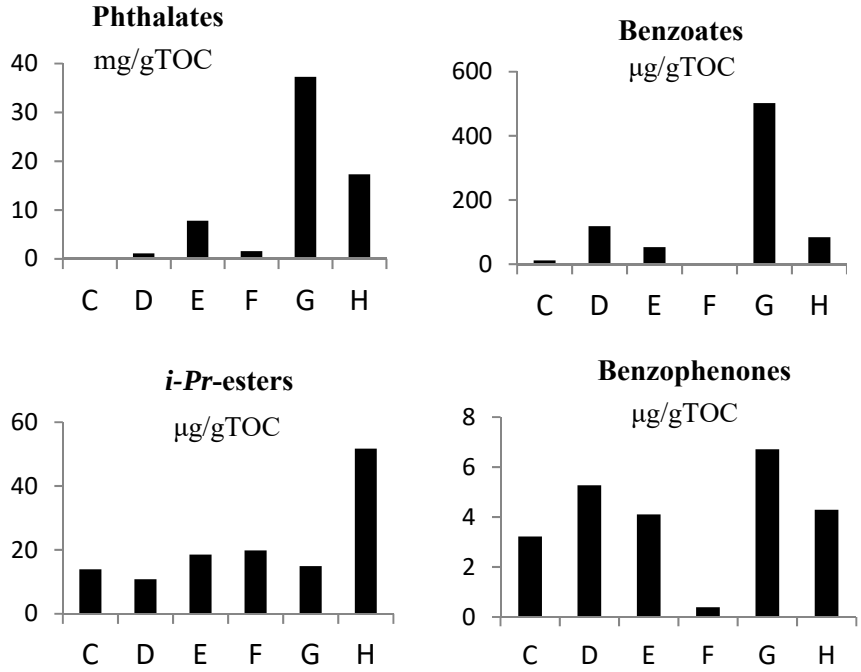

Figure 3. Contents of organic pollutants in dumps studied normalized to gTOC (Capital letters correspond to dumps with locations indicated in Figure 1)

In table 1 is listed the possible origin of some of registered industrial pollutants and their relative abundance in samples studied. Our data demonstrate the high predominance of phthalates in the slightly polar fractions. They are the major industrial pollutants of our civilization scattered all over the world.

Table 1. Possible origin for organic pollutants.

Pollutants	Industrial application	Abundance
Phthalates	Plasticizers	(++++)
Benzoates	Flavor ingredients	(+++)
i-Pr-esters, C_{15},C_{17},C_{19}	Emollients, moisturizers, thickening agents, anti-statics, lubricants	(++)
Benzophenone	UV-stabilizer	(++)
Pentanoic acid, 2,2',4-trimethyl-3-carboxy, *i-Pr*,*i-Bu* ester	Plasticizers	(+)
n-Hexyl salicylate	Floral fragrance	(+)
p-Benzoquinone, 2,6-di-*t-Bu*	Antioxidant	(+)

(+) - low; (++) - average; (+++) - high; (++++) - very high;

In a regional aspect, Mini Maritsa Iztok EAD seeks and develops new technologies for "humus-free" remediation due to insufficient quantity of humus required for humus remediation of damaged terrains. New technologies [11] have been suggested in order of faster restoration of damaged areas after the open lignite mining, incl. application of agricultural and industrial wastes, zeolites and organo-zeolitic

products, soft wood wastes, biochemical methods for soil remediation. For a successful implementation of the technologies listed, it is necessary to determine the OM characteristics in the dump materials and the secondary processes taking place. This need fixes the main objective of the present study on industrial pollutants present in damaged territories.

4. Conclusions

Slightly polar organic matter extracted from dumps was investigated. The identified organic compounds with a potential environmental relevance were quantified and normalized per g TOC of dump. Some differences in total pollutants contents among dumps studied were depicted. All organic contaminants were of anthropogenic origin - originating from plasticizers, industrial pollutants, etc. Dump-derived organic compounds were represented predominantly by polar diterpenoids (ferruginol derivatives). These compounds are not harmful for human health. Therefore, no influence of the dump organic matter itself to the environment could be deduced. Respectively, industrial pollutants should be presented in the list of monitored substances in the regulation norms for dump organic matter environmental estimate.

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