

Organic components in leachates from some Bulgarian lignites

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Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

The information on composition of lignite water-soluble fractions, the so-called leachates, formed during coal mining, storage and exploration is scarce. The aim of the present study is to characterize by wet chemical and spectral methods leachates from some Bulgarian lignites and to estimate their role as potential organic pollutants in groundwaters. In this study, lignites from Thrace- and Sofia- coal basins, i.e. Maritza-East and Stanjanci mines, were subjected to water sequential extraction by distilled water at 25 °C for 10 weeks. The freeze-dried extracts (leachates) were characterized by yields (1.4% for Stanjanci lignites and 1.7% for Maritza-East lignites), technical and elemental analysis. Soluble in dichloromethane portions of leachates, 330 mg/kg Maritza East (ME) lignites and 75 mg/kg Stanjanci (Stan) lignites, were analyzed by GC-MS. Two groups of components were identified: ketophenols, 12 mg/kg ME lignite and 1.2 mg/kg Stan lignite, were 5,6-dehydroferruginol, hinokione, 7-ketototarol and sugiol were the main extracted polar diterpenoids. Oxygenated polar diterpenes of abietane-type are widely distributed in the plant realm. They are not harmful for the environment. Keto- and unsaturated steranes were the other group of compounds in leachates. They are not harmful to human health as well. The study will continue with application of instrumental technique capable to analyze at molecular level essential portion of leachates organic matter. Data from the various approaches will be compared and their joint interpretation will allow making reasonable conclusions for potentially harmful/harmless components in coal leachates.

Key words: lignites, leachate, organic matter, ketophenols, ketosteranes

INTRODUCTION

Currently there is a little information about harmful to human health persistent organic compounds that are leached from coals in the environment. The amounts of leached inorganic substances are under regulation and some organic impurities in surface waters, i.e. industrial pollutants like phthalates, chlorinated products, PAHs, etc., are under control [1]. In order to assess the potential impact of interactions between coal and water that might occur in the environment it is necessary to have more information on the composition of lignite water-soluble fractions, the so-called leachates. They could be formed during coal washing processes, dump storage piles exposed to rain and/or water spray, transport in coal water slurry, disposal of coal, and deposition of waste materials from energy production in thermal power plants, etc. [2-4]. It is proved that during secondary transformations of organic matter proceeding in dumps, mainly oxidation, the content of polar constituent increases, and susceptibility to water run-off arises [5]. It is of utmost importance

to know the type and amount of leachates infiltrated in the environment during coal storage and maintenance.

Coals themselves are not mutagenic, but water-soluble organic matter from lignite produced an appreciable mutagenicity [6-8]. Some studies have reported that groundwater can leach organic matter from Pliocene lignite and they can be hazardous to human health (e.g., urinary tract cancer, tubulointerstitial nephropathies). Long-term exposure to low concentrations of organic compounds leached from Pliocene lignite is probably one of factors in the etiology of the disease so-called Balkan endemic nephropathy (BEN) [9].

In order to appreciate the potential impact of interactions between coal and water that might occur in the environment it is necessary to have information on the composition of lignite water-soluble fractions. The aim of the present study is comparative characterization of organic soluble portions in dichloromethane of leachates from two Bulgarian lignites in view to depict presence/absence of harmful components.

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EXPERIMENTAL

Lignite samples from Thrace- and Sofia-coal basins, i.e. “Maritsa-East” (ME) and “Stanjanci” (Stan) mines were subjected to water sequential extraction at 25 °C for 10 weeks. The protocol at certain extent was adopted from Doskočil *et al.* [10]. Briefly, 10 g of grounded lignite samples at < 0.2 mm and 150 ml of distilled water were placed into a 200 ml Erlenmeyer flask. The slurry was regularly agitated by magnetic stirrer. Each 7 days, the leachate was separated from lignite by centrifugation for 10 min at 4000 rpm at 25^o C. Experiments were performed in duplicate. Subsequently the supernatant was filtered to remove the finest particles eventually penetrated during manipulations. Leachates were freeze-dried and subjected to characterization by chemical and instrumental methods [11].

For isolation of material soluble in organic solvents, freeze-dried leachates were refluxed 3x50 ml for half an hour with dichloromethane (DCM). Soluble portions were combined, dried over CaSO₄, filtrated, concentrated at reduced pressure and studied by GC-MS. Scheme of isolation is illustrated in Fig. 1.

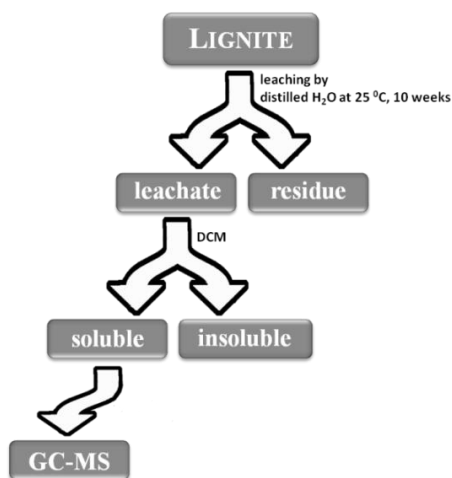


Fig.1. Scheme of extraction and leachate analyses

GC-MS analyses was carried out on a Hewlett-Packard 6890 GC system plus HP 5973 MSD equipped with a HP-5 MS column (0.25mm×30m×0.25µ film thickness) with flame ionization detector (300°C). A split/splitless capillary injector (300°C) is used in the splitless mode (valve reopened 1 min after injection). After 0.5 min isothermal period at 85°C the oven temperature was increased to 200°C at 20°/min and then to 320°C at 5°/min. The MSD was operated in the electron impact (EI) mode with energy of 70 eV and scan range from 50 to 650 Daltons. The 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 spectra tracking Xcalibur software was used. MS were quantitatively interpreted by internal standard application, deuterated *n*C₂₄. Amounts were normalized in mg/kg..

RESULTS AND DISCUSSION

Leachates conductivity (2000-4000 µS) demonstrated that extracts from the first two weeks were characterized by high amount of salts, 60-70% ash [11]. Data are in accordance with results for leaching of South Moravian lignites where leachates conductivity from the first weeks was very high [10]. Later on conductivity gradually decreased from 60 to 15 µS and measured total organic carbons, (TOCs 316-380 g/kg) were comparable. Therefore, based on conductivity in our experiment [11] and literature data [10], only leachates enriched in TOCs were further studied by GC-MS. Respectively, leachates from 3 to 10 weeks were combined, freeze-dried and analyzed. Relatively lower residue amounts, 33-36 % (comparing to the first two leachates with ashes 63-70 %,) and high oxygen content, 31-43 %, were determined for the combined leachates.

In Table 1 are shown yields of leachates, in %. Data were recalculated on “dry, ash free basis” and amounts of organic matter in leachates, in % daf, were obtained. Extractability of leachates in DCM were 330 mg/kg for ME lignites and 75 mg/kg for Stan lignites.

Table 1. Yields of leachates and amounts of organic matter, in %

Lignite	Leachate yield	W ^a	Residue	LOM (% ^{daf})
Maritsa-East	1.7	15.93	35.9	0.82
Stanjanci	1.4	11.45	32.8	0.78

LOM= Leachate organic matter

In Figure 2 is illustrated GC-MS separation of DCM extractable organic matter in ME leachate. Identified structures are given in Table 2. In both extracts GC-MS study of DCM extracts has depicted two groups of organic compounds: (i) polar diterpenoids, (ii) and, ketosteranes. Structures of identified compounds are illustrated in Appendix (Fig.3). GC-MS data for polar diterpenoids were quantitatively interpreted and their amounts are given in Table 2.

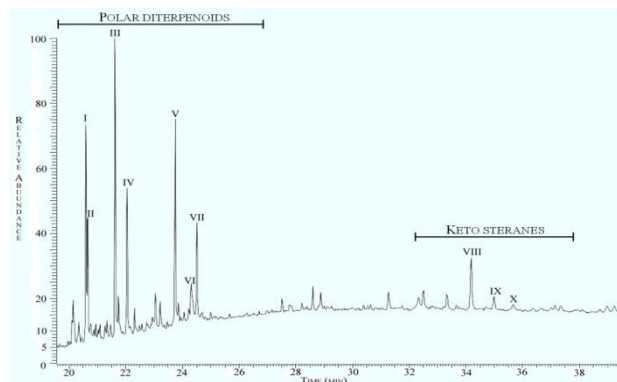


Fig. 2. GC-MS separation of DCM soluble portion of Maritsa East lignite leachate (Structures in Table 2 and Appendix)

Both DCM extracts compositions were comparable. There were differences only in compounds proportions: (i) tenfold higher amount of polar diterpenoids (Polar-Di) for ME lignites, 12 mg/kg, comparing to 1.2 mg/kg for Stan lignites; (ii) and, higher amount of ketosteranes for Stan lignite, 2.6 mg/kg coal, comparing to 1.5 mg/kg coal for ME lignite (Table 2).

A specific flora was growing on our territory during the Tertiary, in a subtropical, warm and humid climate, as proved our studies on biomarker compositions [12-14]. Marshland vegetation including water grass and species of plants and trees (*Taxodium*, *Sequoia*, *Glyptostrobus*, etc.) were presented at the edges of shallow lakes and lagoons. The dead vegetation was buried by sediment and decayed mainly under anaerobic conditions. A systematic study of Pliocene aged lignites in Balkan Peninsula as a reason for the kidney disease abundant only in the territories of Serbia, Romania, Bulgaria, Croatia, has been performed [6-9]. Leachates from the endemic area lignites include aliphatic (mainly cycloalkanes/alkenes and steranic structures) and aromatic (mono- and polyaromatic terpanes, polycyclic aromatic hydrocarbons) structures. By spectral methods, i.e. ^{13}C NMR, GC-MS, was proven that many of these compounds have attached O- functional groups, i.e. phenolic OH, keto groups, OCH_3 , etc., and some of them contain heterocyclic N or NH_2 groups, structural features that could make them nephrotoxic and carcinogenic.

The preservation potential of terpenoids as phenols or ketones is appreciable. In particular diterpenoids were used as (palaeo)chemosystematic indicators for the systematics and phylogeny of conifers. Polar diterpenoids, i.e. ferruginol and its

dehydrogenated analogue, are common constituents of modern species of *Cupressaceae/Taxodiaceae* and *Podocarpaceae*. Their chemotaxonomic value has already been discussed in studies of Bulgarian Neogene lignites where the vegetation in the palaeoswamps was dominated by such conifers [12-15].

Oxygenated polar diterpenes of abietane-type are widely distributed in the plant realm. Potential cytotoxic, antifungal, and antibacterial activities for them have been reported by Kusumoto *et al.* [16,17]. In a suite of studies the authors have enhanced the pharmacological prospects of the natural abietane-type diterpenoids extracted from conifer cones. According to these finding polar diterpenoids of abietane type were not harmful for the environment and possess pharmacological properties with well expressed antioxidant activity, anti-fungal, anti-termitic, anti-ulcerogenic properties, etc.

Among the steroid ketones (ketosteranes) the most abundant are stigmastan-3,5-diene-7-one (VIII) 24-ethylcholest-4-en-3-one (stigmast-4-en-3-one) (IX), with lower contributions of 24-methylcholest-4-en-3-one (ergost-4-en-3-one), 24-methylcholestan-3-one (ergostanone), and 24-ethylcholestan-3,5-dien-7-one (not indicated in Fig.2 and not quantified in Table 2). One diketo sterane, stigmastan-3,6-dione (X), was identified as well. There were some negligible amounts of di- and tri- unsaturated steranes, i.e. stigmastan-3,5-diene, M^+396 , m/z 147 (100%) and stigmastan-3,5,22-triene, M^+394 , m/z 255 (100%). All keto- and unsaturated steranes are typical for coal extractable matter and denote terrigenous input [12]. They are not harmful to human health as well.

CONCLUSION

This study was inspired by the necessity of information on the organic matter composition of coal leachates. Two Bulgarian lignites were leached by distilled water at 25°C for 10 weeks. GC-MS study of organic extractable matter in leachates has revealed the presence of two groups of polar organic compounds: (i) polar diterpenoids, 1.2-12 mg/kg coal, i.e. 5,6-dehydroferruginol, hinokione, 7-ketototarol, sugiol; (ii) and, ketosteranes of terrigenous origin, 1.5-2.6 mg/kg coal. Both groups of compounds are not harmful for human health. The study will continue with application of other instrumental technique capable to analyse leachates essential portions at molecular level.

Compound	Formula	M ⁺	m/z (100%)	Leachate	
				ME	Stan
Polar diterpenoids*, i.e.					
6,7-Dehydroferruginol (I)	C ₂₀ H ₂₈ O	284	202	2.3	0.3
Ferruginol (II)	C ₂₀ H ₃₀ O	286	271	1.3	0.2
Hinokione (III)	C ₂₀ H ₃₀ O ₂	300	189	3.0	0.2
7-Ketototarol (IV)	C ₂₀ H ₂₈ O ₂	300	285	1.5	0.2
Sugiol (V)	C ₂₀ H ₂₈ O ₂	300	285	2.3	0.2
Salvinolone (VI)	C ₂₀ H ₂₆ O ₃	314	244	0.6	-
5,6-Dihydrosugiol (VII)	C ₂₀ H ₂₆ O ₂	298	213	1.0	0.1
TOTAL				12.0	1.2
Keto steroids*, i.e.					
Stigmastan-3,5-diene-7-one (VIII)	C ₂₉ H ₄₆ O	410	174		
Stigmastan-4-en-3-one (IX)	C ₂₉ H ₄₈ O	412	124		
Stigmastan-3,6-diene-dione (X)	C ₂₉ H ₄₈ O ₂	428	245		
TOTAL				1.5	2.6

*- structures in Appendix

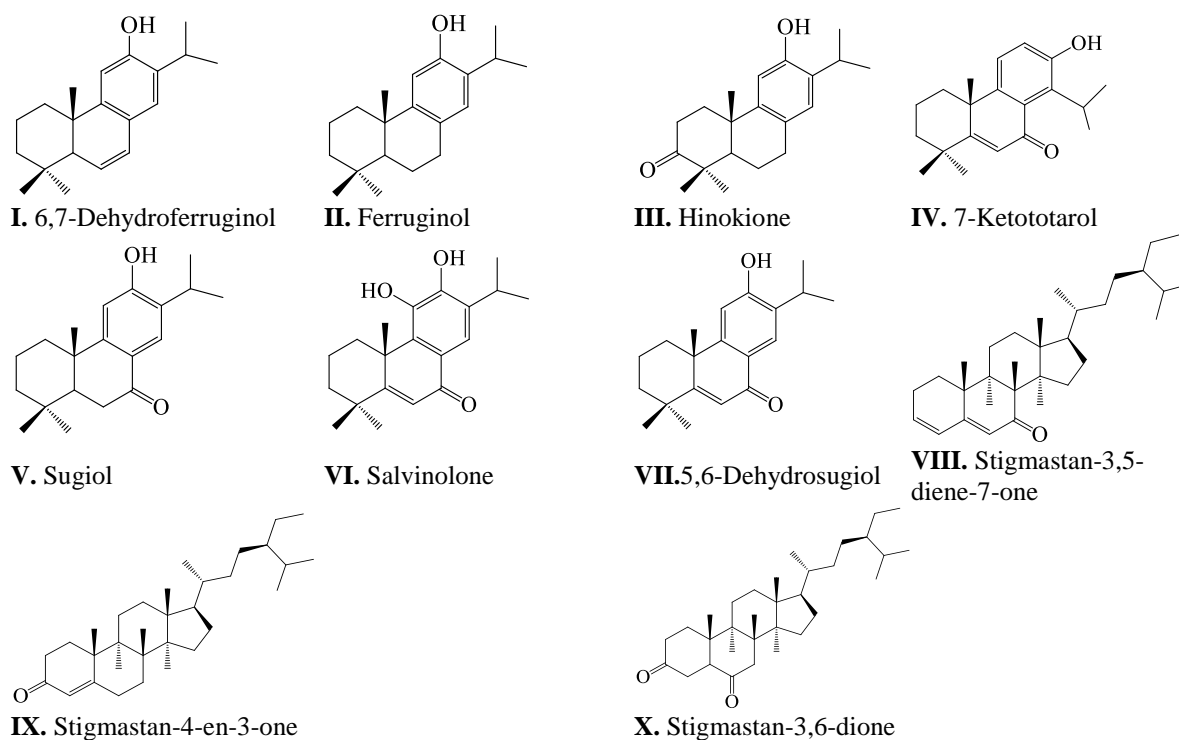


Fig. 3. Appendix: Chemical structures cited in the text

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ОРГАНИЧНИ ВЕЩЕСТВА ОТ ИЗЛУГВАНЕ НА НЯКОИ БЪЛГАРСКИ ЛИГНИТИ

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(Резюме)

Понастоящем информацията за състава на лигнитните водоразтворими фракции образувани по време на добив на въглища, съхраняването им и тяхната експлоатация, т. н. инфилтрати, е ограничена. Цел на настоящото изследване е охарактеризирането чрез химически и спектрални методи на инфилтрати от български лигнити и оценката им като потенциални органични замърсители на подпочвени води. Лигнити от Тракийския и Софийския въглищни басейни, в т.ч. мини „Марица Изток” и „Станянци”, бяха подложени на последователна екстракция с дестилирана вода при 25 °С, в продължение на 10 седмици. Лиофилизираните екстракти (инфилтрати) са охарактеризирани с добив 1.4% за Станянски лигнити и 1.7% за лигнити от Марица-Изток, технически и елементни анализи. Разтворимите в дихлорметан порции на инфилтратите, съответно 330 mg/kg за Марица Изток (ME) и 75 mg/kg за Станянци (Stan) бяха анализирани чрез газ хроматография/маспектрометрия (GC-MS). Определени са две групи съединения - кетофеноли, 12 mg/kg за ME лигнити и 1.2 mg/kg за Stan-лигнитни въглища. Основните полярни дитерпеноиди присъстващи в екстрактите са 5,6-дехидроферужинол, хинокон, 7-кетототарол и сужиол. Кислород съдържащите полярни дитерпени от абиетанов тип са широко разпространени в растителния свят и е доказано, че не са вредни за околната среда. Другата група съединения са кето- и ненаситени стерани. Те също са безвредни за човешкото здраве. Изследването ще продължи с търсене и прилагането на инструментални техники, подходящи да се изучи на молекулно ниво представителна част от органичните вещества в изследваните инфилтрати. Данните от различните подходи ще бъдат сравнени, а тяхното съвместно интерпретиране ще позволи да се направят заключения относно присъствието на потенциално вредни/безвредни компоненти в каменовъглените инфилтрати, получени при излугване на лигнитни въглища.