

BIOGENIC AND ANTHROPOGENIC MARKERS IDENTIFIED IN THE PARTICULATES FROM 'CHUKUROVO' LIGNITE COMBUSTION, BULGARIA

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Abstract. Peculiar series of organic compounds in particulates from lignite FBC in pilot installation have been detected. In the present paper an extract of the particulates collected in the cyclone was under consideration. The species present could be derived from two main sources: biological detritus (e.g. plant waxes) and anthropogenic emissions (e.g. combustion, oils, synthetics, etc.). The distinguishable compound pattern of distribution for organic extracts is unique and allowed emitted compounds to be related to the proper sources. The main products detected in the cyclone trap extract were the following: i) *n*-alkanoic/alkenoic acids with a strong dominance of 'even' carbon numbers homologues. They are interpreted to be of biogenic origin. The acid couples $C_{16}/C_{16:1}$ and $C_{18}/C_{18:1}$ are highly abundant inasmuch they are ubiquitous in biota. The unsaturated counterparts are an indication for destruction; ii) biomarkers for the parent vegetation embrace sugiol and products of its oxidation. The diterpenoid dehydroabietic acid is present as well and is considered as an indication for partially altered product from resin acids, source specific for *Gymnosperm* progenitors; iii) phytosterols and their thermally altered products from sterol precursors were identified; iv) dominant series of wax esters, C_{30} - C_{40} , C_{max} at C_{36} (ester of $C_{16:1}$ acid with C_{20} alcohol). All abovementioned products could not be considered as products of combustion. They might be regarded as products of smoldering ($T < 300^\circ\text{C}$) where organic compounds and altered products are released by a volatilisation/entrainment stripping effect.

Keywords: coal combustion, emissions, PAH, wax esters.

AIMS AND BACKGROUND

The study addresses the possible coal combustion contribution to atmospheric chemistry. The problem is rather complicated as all emissions, i.e. biomass burning, wild fires, municipality incinerations, house-hold heating, volcanic eruptions, etc., all of them influence air quality. The problem is additionally aggravated as organic species could be adsorbed on particulate matter and transported by winds in accordance to their caprices. The spreading depends on weather,

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geographic peculiarities, etc., all of them under study. The phenomenon is described as 'transboundary' pollution and we shall keep this classification.

All registered volatiles, directly emitted or thermally altered, might be used as specific traces for emissions monitoring and applied for legislation purposes. The organic matter carry 'fingerprints' for source inputs, transport mechanism and receptor fate in samples of atmospheric fine particulate matter. Organic matter in atmosphere is derived from two major sources, biogenic and abiogenic, each one characterised by source specific indicators. Their proper description is out of the scope of this study but more information could be found in Refs 1 and 2 where emissions of *Angiosperms*, *Gymnosperms* and *Gramineae*s burning were compared. In this work first data on some peculiar series of organic compounds found in particulate matter from lignite combustion is described. The paper is one more illustration of the fact that the problem of clean air is very difficult to resolve. Results attained demonstrate once again that to fulfill legislation limits there are still unexhausted sources for harmful compounds in atmosphere, like products release by volatilisation/entrainment of fuels.

EXPERIMENTAL

'Chukurovo' lignite coal ($Ash^{daf} = 11.50\%$; $C^{daf} = 72.50\%$; $H^{daf} = 6.75\%$; $S_t^d = 0.93$) was burnt in laboratory scale installation. Experiments were performed in a fluidised bed pilot plant (2800 W), laboratory scale, consisting of a continuous feeder (30-300 g/h), which allows to modify the burnt coal amount. The fluidised bed reactor is made of Kanthal steel (ID 6.7 cm, H 76 cm), a furnace $T_{max} - 1000^\circ\text{C}$ and a preheater (up to 800°C). The pilot plant worked at atmospheric pressure. The entry air was divided into two gas stream flows: one enough to fluidise the bed and introduced by the bottom of the reactor; the second one introduced by the top of the continuous feeder, making easier the entry of the fuel fed into the reactor. Both air flows were controlled by the corresponding mass flow controller and the rot meter, respectively.

The combustion experiments were performed keeping constant the total air flow (800 l/h air flow enough for a good fluidisation avoiding slugging regime), the percentage of excess oxygen (3%), combustion temperature (850°C) and the nature bed (sand). The combustion experience was repeated three times in order to attain good reproducibility.

The combustion gases were forced to pass through a system formed by two cyclones and a condenser in order to avoid moisture condensation problems in the sampling system. At the exit of the condenser an aliquot of combustion gases was forced to pass through the sampling system formed by Teflon filter ($1\ \mu\text{m}$) and an adsorbent, XAD-2 resin.

Four samples were taken from each experience during a period of 3 h. The sampling points were: cyclones, condenser, teflon filter, and XAD-2 resin; all samples were kept in a refrigerator and protected from sunlight until extraction and analysis to eliminate photo-degradation reactions. The samples from cyclone were extracted by sonication three times with 25 ml of dimethylformamide (DMF) for 15 min. The sample of condenser was preliminary treated for water evaporation. All samples were filtered and concentrated in a rotary vacuum until final volume of 10 ml.

Experimental conditions for determination by synchronous fluorescence are described in Refs 3 and 4. A second analytical technique (GC-MS) was used and mutual confirmation for PAH and their heteroanalogues was achieved⁵⁻⁷. Chromatographic conditions can be found there. Briefly, a Hewlett-Packard 6890 GC instrument equipped with 5973 MS detector was used. Column Resteck-XTI 5 column (30 m × 0.25 mm i.d. and 0.25 film thickness). The oven temperature up to 320° C. Samples were analysed using full scan acquisition (m/z 40-600 with cycle time of 1 s).

RESULTS AND DISCUSSION

Table 1 contains results on polycyclic aromatic hydrocarbons (PAH) determined by fluorescence spectroscopy in synchronous mode. The data are for one experiment. Two others were run as well and data were in accordance with those present in Table 1. For comparison, the total sum of µg PAH/kg coal measured in other experiment were 0.56 and 0.83 µg/kg. The main observation is the lack of PAH in condenser for all experiments. In all of them the main quantities were gathered in cyclone trap, magnitudes in the range of 0.36-0.93 µg/kg for the three determinations. One of the samples of cyclone trap was subjected to subsequent chromatographic separation. The protocol of fractionation could be found in our previous studies³⁻⁵.

Table 1. Concentrations of PAH (mg/kg) in emission of burned lignite 'Chukurovo' determined by synchronous fluorescence spectroscopy

Polycyclic aromatic hydrocarbon	Teflon	Condenser	Cyclon	Total
Fluorene	n.d.	n.d.	0.62	0.62
Benzo[a]pyrene	n.d.	n.d.	n.d.	n.d.
Pyrene	0.99	n.d.	0.18	1.17
Chrysene	n.d.	n.d.	0.13	0.13
Total	0.99	0.00	0.93	1.92

Note: n.d. – not detected.

All compounds registered in cyclone extract and characterised by GC-MS are presented in Table 2. Species were grouped in homologue series and their relative quantities, expressed in relative %, were given as well.

Table 2. Compounds in cyclone extract determined by GC-MS

RT (min)	Compound	Content (%)	Structure
1	2	3	4
<i>n</i> -Alkanoic/ <i>n</i> -alkenoic acids (11.66%):			
7.42	C ₁₄	1.20	
8.91	C _{16:1}	1.75	
9.10	C ₁₆	4.44	
10.96	C _{18:1}	2.63	
11.22	C ₁₈	1.64	
Polycyclic aromatic compounds (< 1%):			
7.50	9-fluorenone		
7.84	phenanthrene/anthracene		
10.69	pyrene/fluoranthene		
Wax esters (54.53%)			
	(acid/alcohol)		
23.92	C ₃₀ (C _{16:1} /C ₁₄)	M+ 450	1.70
25.10	C ₃₁ (C _{16:1} /C ₁₅)	M+ 464	1.00
26.31	C ₃₂ (C _{16:1} /C ₁₆)	M+ 478	3.02
26.56	C ₃₂ (C ₁₆ /C ₁₆)	M+ 480	1.65
27.18	C ₃₃ (C _{16:1} /C ₁₇)	M+ 492	3.15
27.43	C ₃₃ (C ₁₆ /C ₁₇)	M+ 494	1.00
28.44	C ₃₄ (C _{16:2} /C ₁₈)	M+ 504	2.18
28.61	C ₃₄ (C _{16:1} /C ₁₈)	M+ 506	8.67
28.81	C ₃₄ (C ₁₆ /C ₁₈)	M+ 508	1.80
30.56	C ₃₆ (C _{16:2} /C ₂₀)	M+ 532	6.32
30.79	C ₃₆ (C _{16:1} /C ₂₀)	M+ 534	7.67
30.98	C ₃₆ (C ₁₆ /C ₂₀)	M+ 536	1.00
31.43	C ₃₇ (C _{16:2} /C ₂₁)	M+ 546	1.40
31.69	C ₃₇ (C _{16:1} /C ₂₁)	M+ 548	2.20
31.98	C ₃₇ (C ₁₆ /C ₂₁)	M+ 550	1.00
33.11	C ₃₈ (C _{16:2} /C ₂₂)	M+ 560	3.20
33.39	C ₃₈ (C _{16:1} /C ₂₂)	M+ 562	2.70
33.50	C ₃₈ (C ₁₆ /C ₂₂)	M+ 564	0.50
36.88	C ₄₀ (C _{16:1} /C ₂₄)	M+ 590	3.44
37.20	C ₄₀ (C ₁₆ /C ₂₄)	M+ 592	1.00

to be continued

1	2	3	4
Steroids (13.7%)			
anthropogenic origin (7.9%)			
24.19	cholesterol	M+ 386	I
20.82	cholesta-3,5-diene	M+ 368	II
24.74	cholesta-3,5-diene-7-one	M+382	III
biogenic origin (5.8%)			
26.40	5 α -stigmasteran-3-one	M+ 414	IV
23.08	24-ethyl-19-norcholesta-1,3,5(10)-triene	M+ 394	V
27.41	stigmaster-4-en-3-one	M+ 412	VI
Diterpenoids (< 1%)			
13.48	dehydroferruginol	M+ 284	VII
14.03	hinokione	M+ 300	VIII
16.30.1	abieta-8,11,13-triene-7-one	M+ 284	IX
17.43	sugiol	M+ 300	X
Triterpenoids (<1%)			
26.69	3-keto-urs-12-ene	M+ 424	XI

The main products detected in the cyclone trap extract were the following: i) *n*-alkanoic/alkenoic acids with a strong dominance of 'even' carbon numbers homologues. They are interpreted to be of biogenic origin (Table 3). The acid couples $C_{16}/C_{16:1}$ and $C_{18}/C_{18:1}$ are highly abundant inasmuch they are ubiquitous in biota. The unsaturated counterparts are indications for destructions; ii) biomarkers for the parent vegetation embrace sugiol and products of its oxidation. The diterpenoid dehydroabietic acid is present as well and is considered as an indication for partially altered product from resin acids, source specific for *Gymnosperm* progenitors; iii) sterols and their thermally altered products from sterol precursors were identified; iv) dominant series of wax esters, C_{30} - C_{40} , C_{max} at C_{36} (ester of $C_{16:1}$ acid with C_{20} alcohol); esters amounted to ~ 54 rel.% of the

Table 3. Major compound groups identified and their potential sources, according to Ref. 2

Compound group (rel. %)	Plant source	Product
<i>n</i> -Alkanoic acids, 11.7%	internal lipid substance	natural (biogenic)
Diterpenoids, < 1%	gymnosperm resins	natural (biogenic)
Triterpenoids, < 1%	angiosperm wax	natural (biogenic)
PAC, < 1%	combustion	altered (anthropogenic)
Steroids, 16.3%	internal lipid substance	natural/altered
Wax esters, 53.8%	lipid membrane, wax	natural (biogenic)

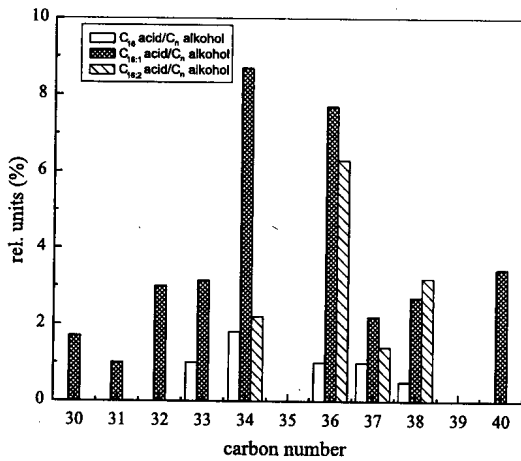


Fig. 1. Pattern of wax esters distribution

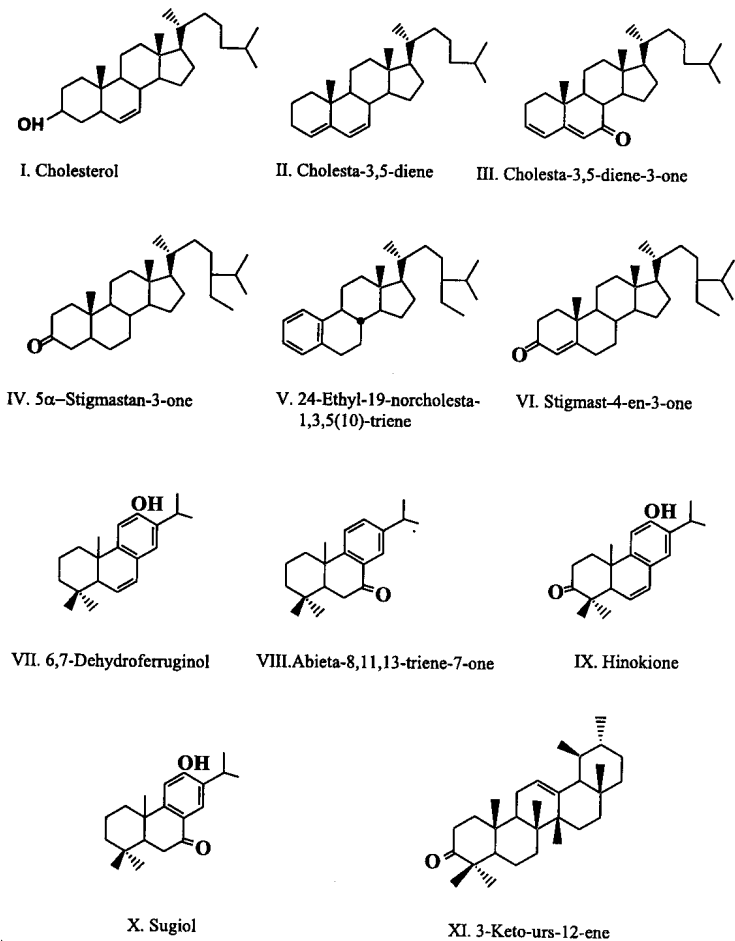


Fig. 2. Structures

total cyclone extract and are in a strong dominance. Their pattern of distribution is illustrated in Fig. 1. Structures of di-/triterpenoids and steroids determined in cyclone trap are gathered in Fig. 2.

The composition of cyclone trap extract strongly resembled epicuticular wax of conifer origin. The identification of plant wax constituents have been of utility for chemotaxonomic purposes, as indicators for determining pollutant exposure, in studies of environmental influences on plant development, etc. They have been used for source reconciliation studies of urban, rural and remote aerosols and for characterisation of fuel sources in biomass burning⁸. The chemical composition of epicuticular waxes for conifers depends on the constitution of the dominant initial species. Respectively, we can assume that the waxes for the dominant coal precursor of the lignite paleoplant community was dominated by C₃₄ and C₃₆ homologues, all esters of C_{16:1} acid (Fig. 1). Esters of polyunsaturated acid, C_{16:2}, were registered as well. We can not insist on the fact that there were not higher homologues of esters as this was the limit of our equipment of conventional capillary columns. For the study of the longer chain wax esters we needed high-temperature GC-MS where esters up to C₆₀ were capable of identification².

CONCLUSIONS

The study shows the extreme variety of organic compounds emitted and/or existing in the atmosphere. Polycyclic aromatic compounds were in negligible quantities. The more abundant products contained in the particulate matter trapped in the cyclone could not be considered as typical for coal combustion. They might be regarded as a result of devolatilisation process at temperature ~300°C where organic compounds are released by entrainment. Nevertheless, they are emitted in atmosphere and should obtain proper attention.

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REFERENCES

1. D. R. OROS, B. R. T.SIMONEIT: *Fuel*, **79**, 515 (2000).
2. B. R. T. SIMONEIT: *Envir. Sci. and Pollut. Res.*, **6**, 159 (1999).
3. A. M. MASTRAL, M. S. CALLEN, T. GARCIA, M. STEFANOVA, S. P. MARINOV: *J. Envir. Prot. and Ecology*, **2** (1), 190 (2001).
4. A. M. MASTRAL, M. S. CALLEN, T. GARCIA, M. STEFANOVA, S. P. MARINOV: *J. Envir. Prot. and Ecology*, **3** (2), 335 (2002).
5. M. STEFANOVA, S. P. MARINOV, A. M. MASTRAL, M. S. CALLEN, T. GARCIA: *Fuel Proc. Tech.*, **77-78**, 89 (2002).
6. A. M. MASTRAL, M. S. CALLEN, T. GARCIA, M. STEFANOVA, S. P. MARINOV: *J. Envir. Prot. and Ecology*, **4** (3), 594 (2003).
7. S. MARINOV, M. STEFANOVA, P. GADJANOV, I. KOSTOVA, VI. STAMENOVA: *J. Envir. Prot. and Ecology*, **5** (1), 43 (2004).

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