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Levoglucosan and other cellulose and lignin markers in emissions from burning of Miocene lignites

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ABSTRACT

Levoglucosan (L), mannosan (M), galactosan (G) and other cellulose and lignin markers from burn tests of Miocene lignites of Poland were determined by gas chromatography–mass spectrometry (GC–MS) to assess their distributions and concentrations in the smoke. Their distributions were compared to those in the pyrolysis products of the lignites. Levoglucosan and other anhydrosaccharides are products from the thermal degradation of cellulose and hemicellulose and are commonly used as tracers for wood smoke in the atmosphere. Here we report emission factors of levoglucosan in smoke particulate matter from burning of lignite varying from 713 to 2154 mg kg^{-1}, which are similar to those from burning of extant plant biomass. Solvent extracts of the lignites revealed trace concentrations of native levoglucosan (0.52–3.7 mg kg^{-1}), while pyrolysis yielded much higher levels (1.6–3.5 $\times$ 10^4 mg kg^{-1}), indicating that essentially all levoglucosan in particulate matter of lignite smoke is derived from cellulose degradation. The results demonstrate that burning of lignites is an additional input of levoglucosan to the atmosphere in regions where brown coal is utilized as a domestic fuel. Interestingly, galactosan, another tracer from biomass burning, is not emitted in lignite smoke and mannosan is emitted at relatively low concentrations, ranging from 7.8 to 70.5 mg kg^{-1}. Thus, we propose L/M and L/(M + G) ratios as discriminators between products from combustion of lignites and extant biomass. In addition, other compounds, such as shonanin, belonging to lignans, and some saccharides, e.g., α- and β-glucose and cellobiose, are reported for the first time in extracts of bulk lignites and of smoke particulate matter from burning these lignites.

1. Introduction

Vegetation is the major biomass being burned by natural and man-made fires. Recent studies have shown that levoglucosan (1,6-anhydro-β-D-glucopyranose), the major product from thermal alteration of cellulose, is a dominant organic component emitted in fine smoke particulate matter from burning of biomass (Simoneit et al., 1999, 2004a; Simoneit and Elias, 2000; Simoneit, 2002). This compound, together with other thermal decomposition products from cellulose and hemicellulose (e.g., mannosan, galactosan and 1,6-anhydro-β-glucofuranose) were utilized as tracers for biomass burning (Simoneit et al., 1999, 2004a,b,c; Simoneit and Elias, 2000; Oros et al., 2002; Graham et al., 2002; Zdráhal et al., 2002; Simpson et al., 2004; Medeiros et al., 2006; Engling et al., 2006; Medeiros and Simoneit, 2007, 2008; Puxbaum et al., 2007; Alfarra et al., 2007; for review see Simoneit, 2002; Schkolnik and Rudich, 2006; Jordan et al., 2006). On the other hand, levoglucosan and other tracers from cellulose have not been reported in smoke particulate matter from coal and other fossil fuels (e.g., Oros and Simoneit, 2000; Simoneit et al., 2007). Our recent study has shown that levoglucosan and other cellulose markers are present in pyrolysates from Miocene lignites, which are utilized as fuels in many regions of Poland (Fabbri et al., 2008).

Here we report the occurrence of relatively high concentrations of levoglucosan in lignite smoke particulate matter. Moreover, we provide comparison of results obtained from open burning and

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off-line analytical pyrolysis of lignites from Miocene brown coals of Poland. These results suggest that caution should be exercised when utilizing levoglucosan as a tracer in modeling wood smoke and coal smoke emissions.

2. Materials and methods

The detailed description of the samples was provided elsewhere (Fabbri et al., 2008). Briefly, the lignites selected in this investigation come from the Konin Brown Coal Basin (Jóźwin mine – Jsp11, Lubstów mine – Lst6) and the Western Brown Coal Basin (Sieniawa mine – S6s). These lignite samples were burned for source tests to determine the tracer emission factors in the smoke for use in air quality modeling and were also characterized using pyrolysis methods.

2.1. Coal burning tests

Three coal samples were burned as bulk fuel (Lst6 and S6s) and as powder (Jsp11). The burns were open, controlled fires under both flaming (active flame) and smoldering (glowing, no flame) conditions. The mass of fuel burned was determined by weighing the initial coal and the residual ash. The emitted smoke was collected on organically clean quartz fiber filters (annealed at 550 °C for 3 h prior to use; 100% particle retention for diameters > 1.5 μm, i.e., sampled total suspended particles, TSP) with a high volume air sampler. Its location was adjusted to collect all the smoke emissions about 1.0–1.5 m above and to the side of the small fire. Smoke was sampled for about 3–6 min at a suction flow rate of 1.13 $m^3\ min^{-1}$. After sampling, a portion of each filter (8 cm^2) was cut out and set aside for elemental carbon (EC) analysis. The collection filters were then placed in precleaned 300 ml jars with Teflon lined lids to which 10 ml of dichloromethane (CH_2Cl_2) was added. The jars were stored at 4 °C until chemical extraction was conducted.

Each filter was extracted using ultrasonic agitation for three 20 min periods using 200 ml of CH_2Cl_2 and methanol (MeOH) mixture (3:1, v/v, nannograde, glass distilled). The solvent extract was filtered using a Gelman Swinney filtration unit containing an annealed glass fiber filter for the removal of insoluble particles. The filtrate was first concentrated by use of a rotary evaporator and then a stream of filtered nitrogen gas. The final volume was adjusted to exactly 2.0 ml by addition of CH_2Cl_2 and MeOH mixture. Aliquots (20 μl) were taken for conversion to the trimethylsilyl (TMS) derivatives. The reaction of the extract aliquot with *N*,*O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA, 20 μl) plus 1% trimethylchlorosilane (TMCS) and pyridine (5 μl) was carried out for approximately 3 h at 70 °C prior to analysis. This transforms alcohol and phenol hydroxyls to TMS ethers and alkanoic acids to TMS esters. The reagents were removed by blow down with N_2 and the products dissolved in hexane prior to GC–MS.

2.2. Off-line analytical and preparative pyrolysis

Lignite samples (10 mg weighed exactly) were pyrolyzed with a filament coil pyrolyser at 700 °C (set temperature) for 100 s. The evolved products were trapped onto an XAD-2 resin and eluted with 5 ml acetonitrile (ACN). An aliquot of the solution (50 μl) was combined with internal standard (2.5 μg methyl-β-arabinopyranoside in 50 μl ACN), silylated with BSTFA/TMCS/pyridine for 2 h at 60 °C, and analyzed by GC–MS. The non-silylated solution was spiked with internal standard (2-bromonaphthalene 40 μg in 0.1 ml ACN) prior to GC–MS analysis.

Lignite sample Lst6 (3.00 g) was pyrolyzed with a bench tubular quartz reactor at 500 °C for 10 min under nitrogen flow (for details of the apparatus see Fabbri et al., 2007). Condensable gas (tar) was collected in cold traps and dissolved into 50 ml ACN. Aliquots of this solution were analyzed as described below.

2.3. Gas chromatography–mass spectrometry (GC–MS)

Sample solutions were injected under splitless conditions into the injector port maintained at 250 °C of an Agilent 6850 gas chromatograph connected to an Agilent 5975 quadrupole mass spectrometer. Analytes were separated by an MDN-5S (Supelco) fused-silica capillary column (stationary phase poly[5% diphenyl/95% dimethyl]siloxane, 30 m, 0.25 mm i.d., 0.25 μm film thickness) with the following temperature program: from 50 °C (hold for 10 min) to 310 °C (hold 5 min) at 10 °C min^{-1}, using helium as carrier gas. Mass spectra were recorded under electron impact ionization (70 eV) at a frequency of 1 scan s^{-1} over a mass range of 50–450 da.

Quantitation was performed from the peak areas in the total ion mode of analytes and internal standard by using the response factor of 2-furaldehyde for furans, 3-methylphenol for (methoxy)phenols and levoglucosan for silylated compounds. Relative standard deviations of calculated percentage yields ranged from 1 to 30% (16% on average) for silylated compounds, and from 0.5 to 16% (8% on average) for non-silylated compounds.

2.4. Analysis of extracted (anhydro)sugars

Lignite samples (100–200 mg) spiked with internal standard (2.5 μg methyl-β-arabinopyranoside in 50 μl ACN) were extracted twice with 15 ml MeOH under ultrasonic agitation. The mixture was centrifuged and the methanolic solution dried by rotary evaporation. The residue was dissolved in 0.5 ml ACN and treated with 0.1 ml BSTFA with 1% TMCS and 0.02 ml pyridine for 2 h at 60 °C. The solution was finally combined with 2-fluorobiphenyl (11.3 μg in 0.1 ml ACN) and analyzed by GC–MS as above. A comparison was made with the GC–MS analysis of persilylated levoglucosan, D-glucose and cellobiose. Blank analyses were performed using the same procedure in the absence of a lignite sample.

3. Results and discussion

3.1. Bulk petrographic and molecular background

The lignites are composed of the xylitic, xylodetrital, detroxylitic, detrital and fusinic lithotypes and the predominant macerals in the samples belong to the huminite group (47–79%, see Fabbri et al., 2008 for supporting information). Textinite, the maceral with the highest content in all samples, occurs in the range of 30–60%, while ulminite, mostly textoulminite, is in the range of 17–34%. Euulminite is generally absent, indicating a low gellification level. The cellular structure of the wood tissue is well preserved in all samples. The lignite maturities are comparatively low in all analyzed samples. Random vitrinite reflectance – Rr is in the range of 0.15–0.23%. GC–MS analysis of biomarker distributions in extracts of the lignites indicate that all samples investigated are derived from conifer wood (Fabbri et al., 2008). The features in those biomarker distributions for samples Jsp11 and S6s are characterized by the presence of ferruginol and sugiol, which are typical for the Podocarpaceae or Cupressaceae (Otto and Wilde, 2001; Otto et al., 2002; Otto and Simoneit, 2001; Marynowski et al., 2007). On the other hand, sample Lst6 contains abietic acid, dehydroabietic acid and their degraded polar products, which suggest that this lignite originated from Pinaceae wood (e.g., Otto et al., 2002, 2007). More detailed information was published elsewhere (Fabbri et al., 2008).