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Citation style: Rybicki Maciej, Marynowski Leszek, Bechtel Achim, Simoneit Bernd R.T. (2020). Variations in $\delta^{13}\text{C}$ values of levoglucosan from low-temperature burning of lignite and biomass. "Science of the Total Environment" (Vol. 733 (2020), Art. No. 138991), doi 10.1016/j.scitotenv.2020.138991



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Variations in $\delta^{13}\text{C}$ values of levoglucosan from low-temperature burning of lignite and biomass



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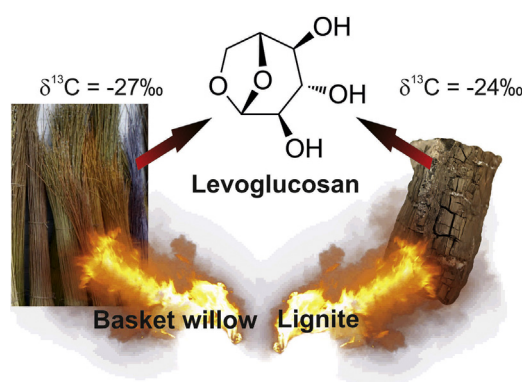
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HIGHLIGHTS

- Low-temperature combustion of lignite is a source of levoglucosan in the ambient air.
- Levoglucosan $\delta^{13}\text{C}$ values from lignite are heavier than those from biomass burning.
- Thermally unstable hopanes in atmospheric PM are tracers of lignite combustion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 March 2020

Received in revised form 21 April 2020

Accepted 23 April 2020

Available online 7 May 2020

Editor: Pingqing Fu

Keywords:

Levoglucosan
Carbon isotope
Lignite
Biomass burning
Coal burning
Aerosol

ABSTRACT

Levoglucosan, an anhydrosaccharide, is commonly used as an organic tracer for biomass burning, but has also been identified from coal smoke particulate matter (PM) including lignites. Here we showed that stable carbon isotope analysis specifically of levoglucosan may be one possible way to determine the relative contributions from coal combustion versus biomass burning sources. PM samples were collected from low-temperature burning/smoldering of Miocene lignites from Poland and basket willow (*Salix viminalis* L.) representative of biomass. The calculated levoglucosan $\delta^{13}\text{C}$ values of xylites varied from -23.6 to -21.6‰ , while for detritic coal samples they ranged from -24.2 to -23.1‰ , with means of -22.7 and -23.7‰ , respectively. The calculated levoglucosan $\delta^{13}\text{C}$ value of basket willow wood was -27.1‰ . Values of willow wood mixtures with xylite varied from -25.8 to -23.4‰ (with an increasing proportion of xylite), while values of mixtures of willow and detritic coal ranged from -26.9 to -24.6‰ (with an increasing proportion of detritic coal). The $\delta^{13}\text{C}$ values for the mixtures changed proportionally to the contents of individual components with $R^2 = 0.88$ and 0.89 for willow with xylite and detritic coal, respectively. The hopanoid distributions characteristic for low-temperature lignite/peat burning, with a predominance of $22R$ - α,β -homohopane, $\beta\beta$ -hopanes and hopenes, as well as low or very low values of the homohopane index, were observed in smoke PM from most lignite samples and absent in the basket willow sample. Thus, the relatively high content of hopanes (with the occurrence of $22R$ - α,β -homohopane, $\beta\beta$ -hopanes and hopenes) in atmospheric PM samples can be treated as additional tracers of lignite combustion.

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1. Introduction

The problem of poor air quality is a global phenomenon that has an adverse effect on human health. Pollution from particulate matter (PM) creates a substantial burden of disease, and reduction of life expectancy by almost 9 months on average in Europe (WHO, 2013). To be able to effectively counteract air pollution, one must first know the sources of various harmful substances. In recent decades, in the field of atmospheric chemistry, organic tracers which allow the source apportionment of organic pollutants occurring in aerosols are gaining importance (e.g. Cass, 1998; Simoneit, 1984, 1999; Liu et al., 2008; Caseiro et al., 2009; Thurston et al., 2011; Sun et al., 2016). Levoglucosan (1,6-anhydro- β -D-glucopyranose), derived from cellulose burning (Simoneit et al., 1999; Fabbri et al., 2008, 2009), as well as mannosan (1,6-anhydro- β -D-mannopyranose) and galactosan (1,6-anhydro- β -D-galactopyranose), originating from thermal degradation of hemicellulose (e.g. Nolte et al., 2001; Fine et al., 2002, 2004), are considered as the major and most robust tracers of biomass burning. However, research conducted in recent years indicates that levoglucosan, mannosan and to a lesser extent also galactosan can be emitted into the atmosphere during the burning of coals, especially lignites (Fabbri et al., 2008, 2009; Yan et al., 2018; Rybicki et al., 2020). This is particularly important, because in some countries, e.g. China or Poland, emission of black and brown carbon PM is highly connected with coal burning (Yan et al., 2017, 2018; Górká et al., 2014; Lubecki et al., 2019), which links the origin of a portion of levoglucosan with coal burning.

In Poland, brown coal (lignite) is mined in four large and one smaller mine, with a total of nine opencasts. The deposits mined are of the Lower and Middle Miocene age. These coals are used in five power plants, and their energy generated represents about 31% of the national energy mix (Ehrenhalt, 2019). Additionally, many households, especially those in the close proximity to lignite mines, use that coal in home furnaces, which are one of the most important sources of low temperature PM emissions, including smog. Brown coal was available for retail sale in Poland until the end of 2019. Therefore, it seems currently to be difficult to correctly identify the source of levoglucosan in aerosols during winter in Poland.

Stable carbon isotope analysis measured directly on levoglucosan can be considered as one possibility to distinguish its emission sources. Because this compound is a thermal decomposition product of cellulose (Simoneit et al., 1999), the carbon isotope signal of levoglucosan measurements should correspond to the $\delta^{13}\text{C}$ values determined for cellulose. According to literature data, the $\delta^{13}\text{C}$ values of cellulose differ significantly between Miocene lignite samples and recent biomass (e.g. McCarroll and Loader, 2004; Bechtel et al., 2008; Taylor et al., 2008). These differences are due to considerable climate change since the Middle Miocene. The climate in the northern hemisphere was much warmer and wetter during the Lower and Middle Miocene compared to recent years (Piwocki and Ziemińska-Tworzydło, 1997; Bechtel et al., 2008), which is recorded as decreasing $\delta^{13}\text{C}$ values since the Middle Miocene (e.g. Farmer, 1979; Saurer et al., 1995; Loader et al., 2007; Dodd et al., 2008). Therefore, the $\delta^{13}\text{C}$ measurements carried out directly on levoglucosan derived from various sources (lignite and biomass combustion) should potentially show different isotopic signals.

Our main goal in this study was to show that the $\delta^{13}\text{C}$ values measured directly on levoglucosan derived from Polish Miocene lignite and biomass burning differ from each other. Levoglucosan-specific stable carbon isotope analyses are a potential way to deconvolute the sources of levoglucosan in the ambient air, especially in lignite mining and processing regions. To represent biomass, we used basket willow wood (*Salix viminalis* L.), a fast-growing shrub commonly occurring in Europe that is also grown for use in the energy sector. Additionally, the molecular compositions of PM originating from low-temperature burning of lignite, willow wood and their proportional mixtures were compared in order to show differences between these sources of PM.

2. Materials and methods

2.1. Samples

Seven samples of Polish lignite of Miocene age and one sample of basket willow (*Salix viminalis* L.) were collected for burn test analysis. Two samples (one xylite and one detritic coal) from the Józwin IIB opencast mine were chosen to make mixtures with the willow wood. The series of mixtures (xylite with willow and detritic coal with willow) were prepared in various proportions (from 10% to 90% of each component, for example the prefix JD10W90 indicates the sample contains 10% detritic coal and 90% willow, while JX90W10 indicates the sample contains 90% xylite and 10% willow). All samples are listed in Table 1. The mean huminite reflectances for the lignites from the mines are: Józwin Rr = 0.19% ($n = 13$), Kazimierz Rr = 0.19 ($n = 24$) and Bełchatów Rr = 0.2% ($n = 21$) (Fabińska, 2007). General background information about the Polish lignite deposits can be found in Widera (2016).

2.2. Burn tests

PM₁₀ samples were taken by high-volume filtration of smoke from low-temperature, open-fire burning/smoldering of the lignites and willow wood. The measured temperature of combustion ranged from 190 to 330 °C with lower temperatures for detritic coals, higher for xylites and about 260 °C for basket willow. The smoke was generated by placing 50 g of the powdered sample (lignite, willow and their mixtures) in a ceramic crucible and leaving it to burn down until the fire went out. After the fire was started with a gas torch, the smoke was collected on a precleaned, quartz fiber filter with a Hi-Vol air sampler (Atmoservice LVS-3D) at a constant flow of air of 2.3 m³/h. A blank sample of the ambient air from the burn room contained only small amounts of *n*-hexadecanoic and *n*-octadecanoic acid with a trace of additional other *n*-fatty acids.

2.3. Extraction and derivatization

The quartz fiber filter samples were extracted using a dichloromethane (DCM)/methanol mixture (1:1, v:v) by agitation with an ultrasonic bath. Aliquots of the total extract of selected samples were dried under nitrogen in 2 mL vials with a Biotage TurboVap® LV and then converted to trimethylsilyl (TMS) derivatives by reaction with *N,O*-bis-(trimethylsilyl)trifluoroacetamide (BSTFA), 1% trimethylchlorosilane, and pyridine for 3 h at 70 °C. The excess reagent was then removed under blow-down with dry nitrogen and the sample mixture dissolved in an equivalent volume of *n*-hexane. A blank sample (silica gel) was analyzed using the same procedure. Trace amounts of phthalates, *n*-fatty acids and *n*-alkanols were found.

2.4. Gas chromatography - mass spectrometry

Gas chromatography - mass spectrometry (GC-MS) analyses were carried out with an Agilent Technologies 7890A gas chromatograph and Agilent 5975C Network mass spectrometer with Triple-Axis Detector (MSD). Helium (6.0 Grade) was used as a carrier gas at a constant flow of 2.6 ml/min. Separation was obtained on a J&W HP5-MS (60 m \times 0.32 mm i.d., 0.25 μm film thickness) fused silica capillary column, coated with a chemically bonded phase (5% phenyl, 95% methylsiloxane), for which the GC oven temperature was programmed from 45 °C (1 min) to 100 °C at 20 °C/min, then to 300 °C (hold 60 min) at 3 °C/min, with a solvent delay of 10 min.

The GC column outlet was connected directly to the ion source of the MSD. The GC-MS interface was set at 280 °C, while the ion source and the quadrupole analyzer were set at 230 and 150 °C, respectively. Mass spectra were recorded from 45 to 550 da (0–40 min) and

Table 1

Carbon isotopic compositions of levoglucosan, ratio of levoglucosan to (galactosan + mannosan), hopane to levoglucosan ratio, total organic carbon content and total sulfur content in the samples.

Sample	Location	Coal type	LG $\delta^{13}\text{C}$ (‰, PDB)	LG $\delta^{13}\text{C}$ (‰, PDB) calculated	LG $\delta^{13}\text{C}$ (‰, PDB) calculated for lignite/willow mixture	LG/(GA + MN)	Σ hopanes/levoglucosan x 100%	TOC (%)	TS (%)
Benzoic Acid (TMS)	Standard		-29.63						
Benzoic Acid	Standard		-26.44	-37.08					
Levoglucosan (TMS)	Standard		-30.39						
Levoglucosan	Standard		-27.16	-36.85					
			mean	-36.97					
B1426_75-81BT	Bełchatów	Detritic	-28.23	-23.87		189.32	n.d.	56.94	1.4
B1426_87-93BT	Bełchatów	Detritic	-27.71	-23.09		98.01	n.d.	58.16	1.38
IBB10BBT	Józwin IIB	Xylite	-27.14	-22.23		19.27	0.16	56.64	3.1
J10CBT	Józwin IIB	Charcoal	-26.73	-21.62		73.76	1.30	58.68	2.2
K1BT	Kazimierz	Xylite	-28.06	-23.61		12.02	n.d.	65.03	2.01
JX	Józwin IIB	Xylite	-27.84	-23.28		24.53	n.d.	57.24	2.12
JD	Józwin IIB	Detritic	-28.42	-24.15		45.65	10.24	54.47	1.55
JX90WL10	Józwin IIB/Willow		-27.90	-23.37	-23.75	24.81	n.d.	n.d.	n.d.
JX80WL20	Józwin IIB/Willow		-27.81	-23.24	-24.05	20.75	n.d.	n.d.	n.d.
JX70WL30	Józwin IIB/Willow		-28.08	-23.64	-24.43	n.d.	n.d.	n.d.	n.d.
JX60WL40	Józwin IIB/Willow		-28.14	-23.73	-24.81	22.61	n.d.	n.d.	n.d.
JX50WL50	Józwin IIB/Willow		-28.58	-24.39	-25.19	19.44	n.d.	n.d.	n.d.
JX40WL60	Józwin IIB/Willow		-29.57	-25.88	-25.58	25.36	n.d.	n.d.	n.d.
JX30WL70	Józwin IIB/Willow		-29.25	-25.40	-25.96	22.09	n.d.	n.d.	n.d.
JX20WL80	Józwin IIB/Willow		n.d.	n.d.	-26.34	17.10	n.d.	n.d.	n.d.
JX10WL90	Józwin IIB/Willow		-29.51	-25.79	-26.72	17.46	n.d.	n.d.	n.d.
WL	Willow		-30.39	-27.10		13.70	n.d.	n.d.	n.d.
JD10WL90	Józwin IIB/Willow		-30.26	-26.91	-26.81	11.86	0.23	n.d.	n.d.
JD20WL80	Józwin IIB/Willow		-29.65	-26.00	-26.51	9.73	0.47	n.d.	n.d.
JD30WL70	Józwin IIB/Willow		-29.40	-25.62	-26.22	10.56	0.74	n.d.	n.d.
JD40WL60	Józwin IIB/Willow		-29.18	-25.29	-25.92	10.31	1.01	n.d.	n.d.
JD50WL50	Józwin IIB/Willow		-29.24	-25.38	-25.63	9.47	1.79	n.d.	n.d.
JD60WL40	Józwin IIB/Willow		-28.92	-24.90	-25.33	10.82	2.77	n.d.	n.d.
JD70WL30	Józwin IIB/Willow		-28.87	-24.83	-25.04	9.73	2.40	n.d.	n.d.
JD80WL20	Józwin IIB/Willow		-29.01	-25.04	-24.74	8.57	5.77	n.d.	n.d.
JD90WL10	Józwin IIB/Willow		-28.74	-24.63	-24.45	15.64	9.00	n.d.	n.d.

LG = levoglucosan.

GA = galactosan.

MN = mannosan.

n.d. = not determined.

50–700 da (> 40 min). The MS was operated in the electron impact mode, with an ionization energy of 70 eV.

2.5. Quantification and identification

An Agilent Technologies MSD ChemStation E.02.01.1177 and the Wiley Registry of Mass Spectral Data (9th edition) software were used for data collection and mass spectra processing. Levoglucosan was confirmed by analysis of a reference standard.

2.6. Stable carbon isotope measurements and calculations

The $\delta^{13}\text{C}$ values of benzoic acid and levoglucosan standards (underivatized and derivatized), as well as levoglucosan from burning

experiments of detritic coal, xylites and their mixtures with willow, were measured in duplicate using a Trace GC-Ultra gas chromatograph attached to a Thermo Fischer Delta-V isotope ratio mass spectrometer (irMS) via a combustion interface (GC Isolink, Thermo Fischer). The GC coupled to the irMS was equipped with a 30 m DB-5MS fused silica capillary column (i.d. 0.25 mm; 0.25 μm film thickness). The GC oven temperature was programmed from 70 to 300 °C at a rate of 4 °C/min, followed by an isothermal period of 15 min. Helium was used as the carrier gas. The sample was injected in the splitless mode at 275 °C. Raw isotope values were initially converted to the international standard VPDB and scale using the Thermo Isodat 3.0 software. Pulses of the CO reference gas were measured at the beginning and end of each analysis. Sample $\delta^{13}\text{C}$ values were further corrected using the slope and intercept of the measured and known values of the C3 n -

alkane standard mix (which contains the n -C₁₇, n -C₁₉, n -C₂₁, n -C₂₃, and n -C₂₅ alkanes) from Arndt Schimmelmann (Indiana University, USA) which was run at the beginning and end of each sequence, as well as after every 8 to 10 sample injections. Analytical reproducibility was in the range of 0.2–0.4‰.

The obtained $\delta^{13}\text{C}$ values of underivatized and derivatized benzoic acid and levoglucosan were used to calculate $\delta^{13}\text{C}$ of the derivatization trimethylsilyl group from the reagent (BSTFA: mean $\delta^{13}\text{C}$ of -37.0‰ ; Table 1). The isotopic shift due to the carbon introduced to levoglucosan by derivatization was corrected by the following relationship (Ballentine et al., 1998):

$$\delta^{13}\text{C}_{\text{LC(TMS)}} = f_{\text{LC}} \delta^{13}\text{C}_{\text{LC}} + f_{\text{TMS}} \delta^{13}\text{C}_{\text{TMS}}$$

where $\delta^{13}\text{C}_{\text{LC(TMS)}}$, $\delta^{13}\text{C}_{\text{LC}}$ and $\delta^{13}\text{C}_{\text{TMS}}$ are the carbon isotope composition of the levoglucosan (TMS), the levoglucosan, and the BSTFA used for derivatization, respectively; and f_{LC} and f_{TMS} are the carbon fractions in the levoglucosan (TMS) due to the underivatized levoglucosan and BSTFA, respectively.

3. Results and discussion

3.1. Levoglucosan-specific stable carbon isotope compositions and relative contributions from coal combustion versus biomass burning

The calculated levoglucosan $\delta^{13}\text{C}$ values of the xylites vary from -23.6 to -21.6‰ , while for the detritic coal samples they range from -24.2 to -23.1‰ , with mean values of -22.7 and -23.7‰ , respectively (Table 1). These $\delta^{13}\text{C}$ values for levoglucosan are clearly lower than the $\delta^{13}\text{C}$ values for cellulose extracted from fossil wood remains of the Lubstów opencast which range from -22.6 to -19.5‰ , with a mean of -20.8‰ (Bechtel et al., 2007). The calculated levoglucosan $\delta^{13}\text{C}$ value of the basket willow is -27.1‰ , which is significantly lower than those measured for numerous southeastern Chinese plants with levoglucosan $\delta^{13}\text{C}$ values ranging from -25.6 to -22.2‰ (Sang et al., 2012). However, the climate in southeastern China is much warmer and wetter compared to central Europe which has a significant impact on the values of stable carbon isotopes (e.g. Lipp et al., 1991; Diefendorf et al., 2010; Werner et al., 2012).

The next step of our study was the measurement of levoglucosan $\delta^{13}\text{C}$ values for mixtures of lignite and basket willow to check changes in carbon isotope values depending on the percentage of individual components of the mixture. Values of willow mixtures with the Józwin IIB xylite vary from -25.8 to -23.4‰ (with an increasing proportion of xylite), while values of mixtures of willow and detritic coal from the Józwin IIB opencast range from -26.9 to -24.6‰ (with an increasing proportion of detritic coal, Table 1, Fig. 1). The $\delta^{13}\text{C}$ values for the mixtures change proportionally to the content of individual components with $R^2 = 0.88$ and 0.89 for the mixtures with xylite and detritic coal, respectively.

Such relevant differences in $\delta^{13}\text{C}$ values of levoglucosan between lignites and biomass suggest that carbon isotope values can be useful for determining the PM source in environmental studies. So far, data of levoglucosan carbon isotope values for aerosols from urban to rural areas are limited to China. The $\delta^{13}\text{C}$ values for levoglucosan measured for rural, suburban and urban areas of Guangdong province, China were between -25 to -20‰ , generally higher for urban and lower for rural areas (Fig. 1 in Gensch et al., 2018). Higher values (-23 to -20‰) correspond to emissions from brown coal burning (Table 1), and because urban environments are strongly impacted by such burning (Yan et al., 2017, 2018) an origin of levoglucosan (at least part of it) from such emissions is highly probable. Values of $\delta^{13}\text{C}$ for levoglucosan from burning of biomass samples in South China were measured by Sang et al. (2012) and ranged from -26.5 to -22‰ , with a mean of -25‰ (Table 2 in Sang et al., 2012). This in turn corresponds to the $\delta^{13}\text{C}$ values of -27‰ measured for basket willow

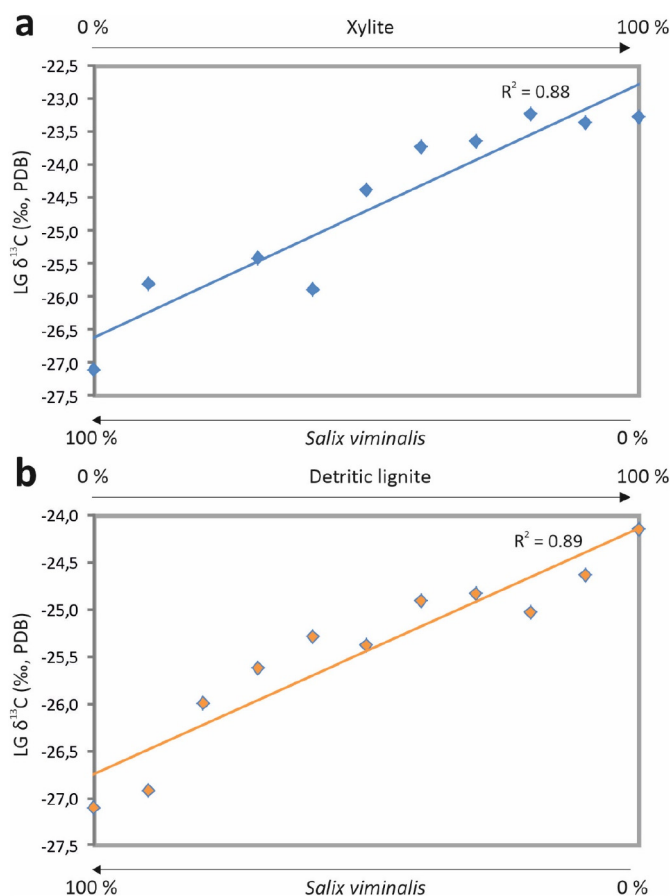


Fig. 1. Cross correlation of (a) the $\delta^{13}\text{C}$ values of levoglucosan from xylite/willow smoke mixtures and (b) the $\delta^{13}\text{C}$ values of levoglucosan from detritic lignite/willow smoke mixtures vs the xylite/detritic lignite and willow wood contents in the smoke samples.

(Table 1). More data, especially from different aerosol regions and combustion sources, is needed to unequivocally confirm these observations, but hitherto the results seem promising.

For carbon isotope measurements of levoglucosan it is important to consider that at burn temperatures up to 300 °C the isotope values can change ($\pm 1.5\text{‰}$), which is related to the preferential decomposition of compounds with heavier or lighter $\delta^{13}\text{C}$ values in C4 and C3 plant biomass, respectively (Ballentine et al., 1998; Wiesenberg et al., 2009). Above 300 °C further isotopic fractionation does not occur (Wiesenberg et al., 2009). This additional temperature factor indicates that the results obtained cannot be regarded as precise and only ranges of specific $\delta^{13}\text{C}$ values can be used for assessing the sources of levoglucosan. The other important factor is the stability of levoglucosan. Current data are very divergent, characterizing the ambient stability of levoglucosan from 0.7–2 days to much >10 days (see review in Bhattarai et al., 2019). Influences of processes such as photooxidation or degradation by reaction with OH radicals can change the isotopic signal of levoglucosan. Gensch et al. (2018) noticed that the $\delta^{13}\text{C}$ of ambient levoglucosan was heavier than the average $\delta^{13}\text{C}$ of levoglucosan found in source samples from C3-plant combustion. Here we show that an alternative source of heavy levoglucosan can be burning of lignite and maybe also other kinds of coal.

3.2. Organic tracers of lignite and biomass burning

Levoglucosan is the main compound in almost all smoke PM samples. Mannosan is also present in all samples but in lesser amounts,

while galactosan occurs only in traces (Fig. 2). The levoglucosan to (galactosan + mannosan), LG/(GA + MN), ratio values vary from 12 to 74 for xylites (31 to 92 for xylites in Fabbri et al., 2009) and from 46 to 189 for detritic coals (Table 1). Such a significant preponderance of levoglucosan over mannosan and galactosan is probably due to the fact that cellulose is more abundant in plants, and more resistant to hydrolysis and diagenetic (bio)degradation than hemicelluloses (e.g. Sundqvist, 2004; Lechien et al., 2006; Yang et al., 2007; Marynowski et al., 2018). However, the effect of burn temperature should also be taken into account (see below). Thus, in lignite smoke PM levoglucosan, a product of the thermal degradation of cellulose, clearly dominates over mannosan with only traces of galactosan. The LG/(GA + MN) ratio in willow smoke PM is 13.7 which is typical for hardwood (Nolte et al., 2001; Fine et al., 2002; Sang et al., 2012) although it is dependent on the hardwood species and some reported results of the ratio were lower (Engling et al., 2006; Schmidl et al., 2008). The values of the LG/(GA + MN) ratio in smoke PM from xylite/willow mixtures vary from 17.1 (sample with 80% of willow) to 24.8 (sample with 90% of xylite). Moreover, the LG/(GA + MN) ratio is highly dependent on temperature of combustion, and differences in the values between burning and smoldering have been noticed (Engling et al., 2006; Kuo et al., 2011; Vicente and Alves, 2017; Bhattarai et al., 2019; Křůmal et al., 2019). The concentrations of mannosan and galactosan decreased more rapidly than levoglucosan with temperature increases and all these compounds disappear above ca. 350 °C (Kuo et al., 2011; but also see Bhattarai et al., 2019; Suciú et al., 2019). That may explain the diverse values of the LG/(GA + MN) ratios for smoke PM from detritic lignite/willow mixtures. Polish detritic lignites (Miocene) usually contain significantly lower amounts of cellulose (and probably only trace amounts of hemicelluloses) than xylites (Marynowski et al., 2018). Thus, their LG/(GA + MN) ratio values are very high (see detritic coals in Table 1) but also the burn temperatures of detritic coals are lower than those recorded during burning of willow with/or xylite. Therefore, the addition of even a small amount of willow to the detritic coal caused a significant decrease in the LG/(GA + MN) ratio values (Table 1). Moreover, an increase in the burn temperature caused by the addition

of willow, resulted in a reduced emission of mannosan and galactosan. Consequently, despite an increase in willow content in the willow/detritic coal mixture, which contains significantly more hemicellulose than detritic coal alone, the LG/(GA + MN) ratio remains at a similar level (Table 1). As indicated in previous studies, the hopanoid distributions with an enhanced enrichment of $\beta\beta$ -hopanes and hopenes, as well as high levels of 22R- α,β -homohopane, are characteristic for smoke from low-temperature burning of peat and lignite (Oros and Simoneit, 2000; Abas et al., 2004; Rybicki et al., 2020), whereas those compounds are not observed in products from biomass burning (Rogge et al., 1998; Oros and Simoneit, 2001a, 2001b; Simoneit, 2002; Medeiros and Simoneit, 2008). The homohopane index, 22S/(22S + 22R), the ratio between 22S-17 α (H),21 β (H)-homohopane and its 22R-epimer, is used to assess this input to aerosol PM. In our PM samples from low-temperature burning/smoldering of lignite the values of the 22S/(22S + 22R) homohopane ratio are low or very low (in samples JD and J10CBT the 22S-epimer is absent) with a dominance of $\alpha\beta$ -homohopane, $\beta\beta$ -hopanes and hopenes (e.g. Fig. 3). No hopanes are detectable in some samples (B1426_75-81BT, B1426_87-93BT, JX, K1_BT and basket willow). The relationship between the relative content of the total hopanes as a ratio with the content of levoglucosan, which is the main compound in each willow/detritic coal sample, is plotted in Fig. 4. A positive correlation ($R^2 = 0.96$) is observed between the relative content of hopanes and the proportion of detritic coal in the burn samples. Importantly, detritic coal is a raw material used in power production and domestic furnaces, while xylite is usually treated as waste. For this reason, the relatively high content of hopanes (with an enrichment of the compounds specific to lignite) in atmospheric PM samples can be treated as tracer of brown coal combustion. If anhydrosugars (including levoglucosan) are present in ambient aerosol PM, there is a high probability that a portion of those compounds are derived from brown coal and not only biomass combustion.

Moreover, most coal smoke PM samples contain terpenoids like cadalene, ferruginol, 6,7-dehydroferruginol, sugiol, *des-A*-allobetulin and phyllocladane, which are typical conifer-derived compounds (Simoneit

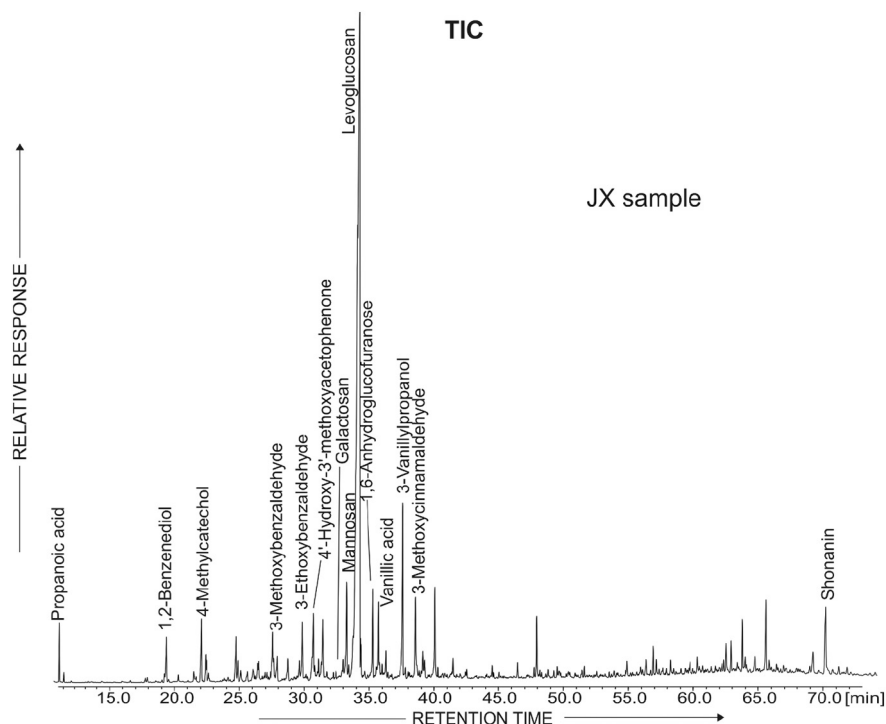


Fig. 2. Total ion current (TIC) chromatogram from GC-MS analysis of the PM extract of the JX xylite burn test sample showing the organic compound distributions.

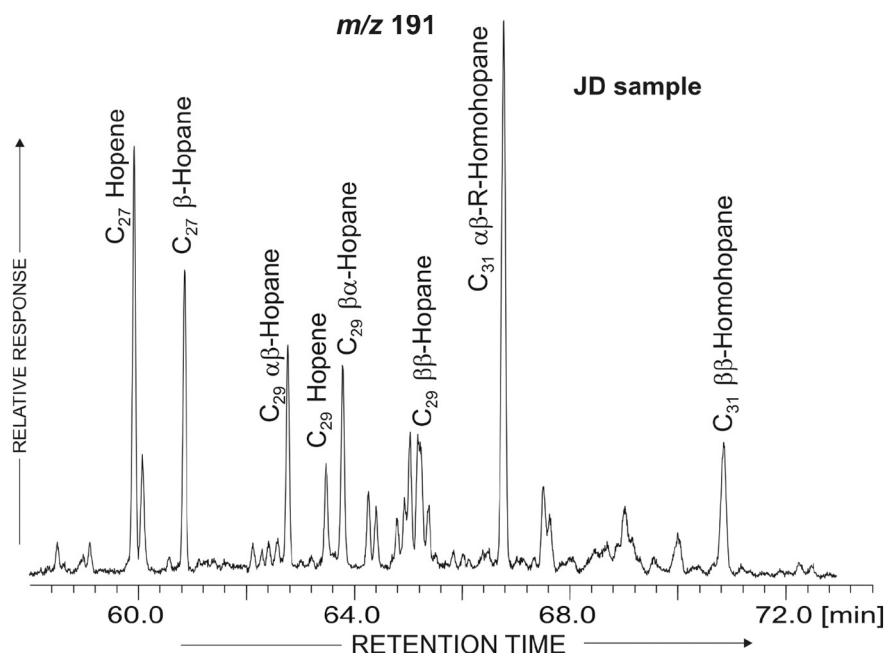


Fig. 3. Partial m/z 191 mass chromatogram for the PM extract of the JD lignite burn test sample showing the typical hopane distribution, with high concentrations of $\beta\beta$ -hopanes and hopenes.

and Mazurek, 1982; Otto and Simoneit, 2001; Marynowski et al., 2007). Friedelin, a pentacyclic triterpenoid common epicuticular plant wax, is observed in detritic coal smoke samples (Oros and Simoneit, 2000). Shonanin, a lignan that occurs in conifers (e.g. Yamamoto et al., 2004; Fabbri et al., 2009) is present in minor amounts in two xylites (JX and K1_BT). Although all these compounds if present in aerosol PM would suggest an origin from lignite burning, they can be also generated by burning of gymnosperm wood (Oros and Simoneit, 2001a, 2001b). However, the co-occurrence of these compounds with hopanoids, which indicate an immature OM character, and levoglucosan characterized by $\delta^{13}\text{C}$ values between ca. -23 to -20% , can suggest a carbonaceous component in smoke PM from burning of lignite.

4. Conclusions

1. Values of $\delta^{13}\text{C}$ measured for levoglucosan generated from burning of Miocene lignites are ca. 3–4‰ heavier than values measured for levoglucosan from biomass burning, and range from -24 to -22% .

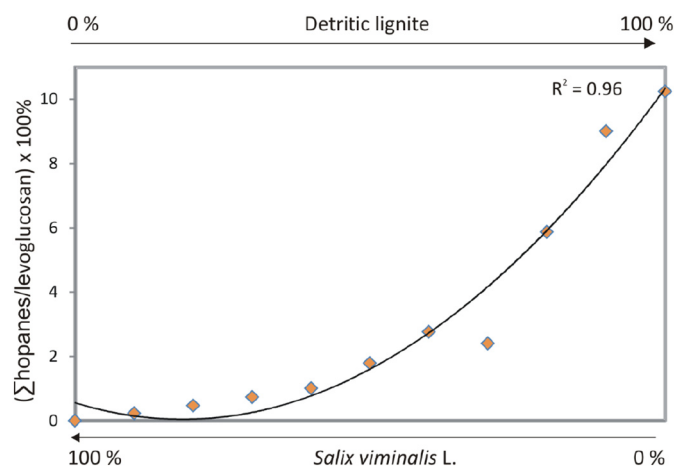


Fig. 4. Cross correlation of the total hopanes/levoglucosan ratio to the proportional detritic lignite and willow smoke contents in the samples.

2. Values of the LG/(GA + MN) ratio depend on temperature and type of combustion. The measured temperature of combustion of Polish lignites (Miocene) ranged from 190 to 330 °C with lower temperatures for detritic coals, higher for xylites and about 260 °C for basket willow.
3. Co-measurement of stable carbon isotope values for levoglucosan, the LG/(GA + MN) ratio, as well as the presence of thermally less stable hopanes in aerosols can be potentially useful to assess the sources of levoglucosan.
4. More source and field data is needed to specifically confirm that stable carbon isotope measurements of levoglucosan can be used as a tool to determine the relative contributions from coal combustion versus biomass burning sources, especially in the ambient environment.

CRedit authorship contribution statement

Maciej Rybicki: Data curation, Formal analysis, Writing - original draft. **Leszek Marynowski:** Methodology, Visualization, Writing - original draft. **Achim Bechtel:** Formal analysis, Writing - review & editing. **Bernd R.T. Simoneit:** Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by NCN grant 2015/19/B/ST10/00925 to LM.

References

- Abas, M.R., Rahman, N.A., Omar, N.Y.M.J., Maah, M.J., Samah, A.A., Oros, D.R., Otto, A., Simoneit, B.R.T., 2004. Organic composition of aerosol particulate matter during a haze episode in Kuala Lumpur, Malaysia. *Atmos. Environ.* 38, 4223–4241.
- Ballentine, D.C., Macko, S.A., Turekian, V.C., 1998. Variability of stable carbon isotopic compositions in individual fatty acids from combustion of C_4 and C_3 plants: implications for biomass burning. *Chem. Geol.* 152, 151–161.

- Bechtel, A., Widera, M., Sachsenhofer, R.F., Gratzler, R., Lücke, A., Woszczyk, M., 2007. Biomarker and stable carbon isotope systematic of fossil wood from the 2nd Lusatian lignite seam of the Lubstow deposit (Poland). *Org. Geochem.* 38, 1850–1864.
- Bechtel, A., Gratzler, R., Sachsenhofer, R.F., Gusterhuber, J., Lücke, A., Püttmann, W., 2008. Biomarker and carbon isotope variation in coal and fossil wood of Central Europe through the Cenozoic. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 262, 166–175.
- Bhattarai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., Kang, S., Zhang, O., Zhang, Y., Wu, G., Wang, X., Kawamura, K., Fu, P., Cong, Z., 2019. Levoglucosan as a tracer of biomass burning: recent progress and perspectives. *Atmos. Res.* 220, 20–33.
- Caseiro, A., Bauer, H., Schmidl, C., Pio, C.A., Puxbaum, H., 2009. Wood burning impact on PM10 in three Austrian regions. *Atmos. Environ.* 43, 2186–2195.
- Cass, G.R., 1998. Organic molecular tracers for particulate air pollution sources. *Trends Anal. Chem.* 17, 356–366.
- Diefendorf, A.F., Mueller, K.E., Wing, S.L., Koch, P.L., Freeman, K.H., 2010. Global patterns in leaf ^{13}C discrimination and implications for studies of past and future climate. *Proc. Natl. Acad. Sci.* 107, 5738–5743.
- Dodd, J.P., Patterson, W.P., Holmden, C., Brasseur, J.M., 2008. Robotic micromilling of tree-rings: a new tool for obtaining subseasonal environmental isotope records. *Chem. Geol.* 252, 21–30.
- Ehrenhalt, W., 2019. Assumptions for the energy strategy in Poland. ZPP 1–63 (in Polish).
- Engling, G., Carrico, C.M., Kreidenweis, S.M., Collett Jr., J.L., Day, D.E., Malm, W.C., Lincoln, W.C., Hao, W.M., Iinuma, Y., Herrmann, H., 2006. Determination of levoglucosan in biomass combustion aerosol by high-performance anion exchange chromatography with pulsed amperometric detection. *Atmos. Environ.* 40, 299–311.
- Fabbri, D., Marynowski, L., Fabińska, M.J., Zatoń, M., Simoneit, B.R.T., 2008. Levoglucosan and other cellulose markers in pyrolysates of Miocene lignites – geochemical and environmental implications. *Environ. Sci. Technol.* 42, 2957–2963.
- Fabbri, D., Torri, C., Simoneit, B.R.T., Marynowski, L., Rushdi, A.I., Fabińska, J., 2009. Levoglucosan and other cellulose and lignin markers in emissions from combustion of Miocene lignites. *Atmos. Environ.* 43, 2286–2295.
- Fabińska, M., 2007. Organic Geochemistry of Brown Coals from the Selected Polish Basins (Geochemia Organiczna węgla Brunatnych Wybranych złóż Polski). University of Silesia, Katowice, nr. 2468, 319 pp. (in Polish).
- Farmer, J.G., 1979. Problems in interpreting tree-ring $\delta^{13}\text{C}$ records. *Nature* 279, 229–231.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2002. Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the southern United States. *Environ. Sci. Technol.* 36, 1442–1451.
- Fine, P.M., Cass, G.R., Simoneit, B.R.T., 2004. Chemical characterization of fine particle emissions from the fireplace combustion of wood types grown in the Midwestern and Western United States. *Environmental Engineering Science* 21, 387–409.
- Gensch, I., Sang-Arlt, X.F., Laumer, W., Chan, C.Y., Engling, G., Rudolph, J., Kiendler-Scharr, A., 2018. Using $\delta^{13}\text{C}$ of levoglucosan as a chemical clock. *Environ. Sci. Technol.* 52, 11094–11101.
- Górka, M., Rybicki, M., Simoneit, B.R.T., Marynowski, L., 2014. Determination of multiple organic matter sources in aerosol PM10 from Wrocław, Poland using molecular and stable carbon isotope compositions. *Atmos. Environ.* 89, 739–748.
- Křůmal, K., Mikuška, P., Horák, J., Hopan, F., Krpec, K., 2019. Comparison of emissions of gaseous and particulate pollutants from the combustion of biomass and coal in modern and old-type boilers used for residential heating in the Czech Republic, Central Europe. *Chemosphere* 229, 51–59.
- Kuo, L.-J., Louchouart, P., Herbert, B.E., 2011. Influence of combustion conditions on yields of solvent-extractable anhydrosugars and lignin phenols in chars: implications for characterizations of biomass combustion residues. *Chemosphere* 85, 797–805.
- Lechien, V., Rodriguez, Ch., Ongena, M., Hilgismann, S., Rulmont, A., Thonart, P., 2006. Physicochemical and biochemical characterization of non-biodegradable cellulose in Miocene gymnosperm wood from the Entre-Sambre-et-Meuse, southern Belgium. *Org. Geochem.* 37, 1465–1476.
- Lipp, J., Trimborn, P., Fritz, P., Moser, H., Becker, B., Frenzel, B., 1991. Stable isotopes in tree ring cellulose and climatic change. *Tellus B: Chemical and Physical Meteorology* 43 (3), 322–330.
- Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., Tang, D., 2008. Source profiles of volatile organic compounds (VOCs) measured in China: part I. *Atmos. Environ.* 42, 6247–6260.
- Loader, N.J., McCarroll, D., Gagen, M., Robertson, I., Jalkanen, R., 2007. Extracting climatic information from stable isotopes in tree rings. In: Dawson, T.E., Siegwolf, R.T.W. (Eds.), *Stable Isotopes as Indicators of Ecological Change*. Elsevier, pp. 27–48.
- Lubecki, L., Oen, A.M.P., Breedveld, G.D., Zamojska, A., 2019. Vertical profiles of sedimentary polycyclic aromatic hydrocarbons and black carbon in the Gulf of Gdańsk (Poland) and Oslofjord/Drammensfjord (Norway), and their relation to regional energy transitions. *Sci. Total Environ.* 646, 336–346.
- Marynowski, L., Otto, A., Zaton, M., Philippe, M., Simoneit, B.R.T., 2007. Biomolecules preserved in ca. 160 million year old fossil conifer wood. *Naturwissenschaften* 94, 228–236.
- Marynowski, L., Bucha, M., Smolarek, J., Wendorff, M., Simoneit, B.R.T., 2018. Occurrence and significance of mono-, di- and anhydrosaccharide biomolecules in Mesozoic and Cenozoic lignites and fossil wood. *Org. Geochem.* 116, 13–22.
- McCarroll, D., Loader, N.J., 2004. Stable isotopes in tree rings. *Quat. Sci. Rev.* 23, 771–801.
- Medeiros, P.M., Simoneit, B.R.T., 2008. Source profiles of organic compounds emitted upon combustion of green vegetation from temperate climate forests. *Environ. Sci. Technol.* 42, 8310–8316.
- Nolte, C.G., Schauer, J.J., Cass, G.R., Simoneit, B.R.T., 2001. Highly polar organic compounds present in wood smoke and in the ambient atmosphere. *Environ. Sci. Technol.* 35, 1912–1919.
- Oros, D.R., Simoneit, B.R.T., 2000. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel* 79, 515–536.
- Oros, D.R., Simoneit, B.R.T., 2001a. Identification of emission factors of molecular tracers in organic aerosols from biomass burning: part 1. Temperate climate conifers. *Appl. Geochem.* 16, 1513–1544.
- Oros, D.R., Simoneit, B.R.T., 2001b. Identification of emission factors of molecular tracers in organic aerosols from biomass burning: part 2. Deciduous trees. *Appl. Geochem.* 16, 1545–1565.
- Otto, A., Simoneit, B.R.T., 2001. Chemosystematics and diagenesis of terpenoid in fossil conifer species and sediment from the Eocene Zeititz formation, Saxony, Germany. *Geochim. Cosmochim. Acta* 65, 3505–3527.
- Piwocki, M., Ziemińska-Tworzydo, M., 1997. Neogene of the Polish Lowlands – lithostratigraphy and pollen-spore zones. *Geological Quarterly* 41, 21–40.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1998. Sources of fine organic aerosol: 9. Pine, oak and synthetic log combustion in residential fireplaces. *Environ. Sci. Technol.* 32, 13–22.
- Rybicki, M., Marynowski, L., Simoneit, B.R.T., 2020. Composition of organic compounds from low-temperature burning of lignite and their application as tracers in ambient air. *Chemosphere* <https://doi.org/10.1016/j.chemosphere.2020.126087>.
- Sang, X.F., Gensch, I., Laumer, W., Kammer, B., Chan, C.Y., Engling, G., Wahner, A., Wissel, H., Kiendler-Scharr, A., 2012. Stable carbon isotope ratio analysis of anhydrosugars in biomass burning aerosol particles from source samples. *Environ. Sci. Technol.* 46, 3312–3318.
- Saurer, M., Siegenthaler, U., Schweingruber, F., 1995. The climate carbon isotope relationship in tree-rings and the significance of site conditions. *Tellus, Ser. B* 47, 320–330.
- Schmidl, C., Marr, I.L., Caseiro, A., Kotianová, P., Berner, A., Bauer, H., Kasper-Giebl, A., Puxbaum, H., 2008. Chemical characterisation of fine particle emissions from wood stove combustion of common woods growing in mid-European Alpine regions. *Atmos. Environ.* 42, 126–141.
- Simoneit, B.R.T., 1984. Organic matter of the troposphere - III. Characterization and sources of petroleum and pyrogenic residues in aerosols over the western United States. *Atmos. Environ.* 18, 51–67.
- Simoneit, B.R.T., 1999. A review of biomarker compounds as source indicators and tracers for air pollution. *Environ. Sci. Pollut. Res.* 6, 159–169.
- Simoneit, B.R.T., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 17, 129–162.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of the troposphere - II. Natural background of biogenic lipid matter in aerosols over the rural western United States. *Atmos. Environ.* 16, 2139–2159.
- Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos. Environ.* 33, 173–182.
- Suciu, L.G., Masiello, C.A., Griffin, R.J., 2019. Anhydrosugars as tracers in the Earth system. *Biogeochemistry* 146, 209–256.
- Sun, Y., Du, W., Fu, P., Wang, Q., Li, J., Ge, X., Zhang, Q., Zhu, C., Ren, L., Xu, W., Zhao, J., Han, T., Worsnop, D.R., Wang, Z., 2016. Primary and secondary aerosols in Beijing in winter: sources, variations and processes. *Atmos. Chem. Phys.* 16, 8309–8329.
- Sundqvist, B., 2004. Colour Changes and Acid Formation in Wood during Heating. Ph.D. Thesis. Luleå Tekniska Universitet, Luleå, Sweden, p. 154.
- Taylor, A.M., Brooks, J.R., Lachenbruch, B., Morrell, J.J., Voelker, S., 2008. Correlation of carbon isotope ratios in the cellulose and wood extractives of Douglas-fir. *Dendrochronologia* 26, 125–131.
- Thurston, G.D., Ito, K., Lall, R., 2011. A source apportionment of U.S. fine particulate matter air pollution. *Atmos. Environ.* 45, 3924–3936.
- Vicente, E., Alves, C., 2017. An overview of particulate emissions from residential biomass combustion. *Atmos. Res.* 199, 159–185.
- Werner, C., Schnyder, H., Cuntz, M., Keitel, C., Zeeman, M., Dawson, T., Badeck, W., Brugnoli, E., Ghashghaie, J., Grams, T., Kayler, Z., Lakatos, M., Lee, X., Mágua, C., Ogée, J., Rascher, K., Siegwolf, R., Unger, S., Welker, J., Wingate, L., Gessler, A., 2012. Progress and challenges using stable isotopes to trace plant carbon and water relations across scales. *Biogeosciences* 9, 3083–3111.
- WHO, 2013. Mental Health Action Plan 2013–2020. World Health Organization.
- Widera, M., 2016. Genetic classification of Polish lignite deposits: a review. *Int. J. Coal Geol.* 158, 107–118.
- Wiesenberg, G., Lehdorff, E., Schwark, L., 2009. Thermal degradation of rye and maize straw: lipid pattern changes as a function of temperature. *Org. Geochem.* 40, 167–174.
- Yamamoto, S., Otto, A., Simoneit, B.R.T., 2004. Lignans in resin of *Araucaria angustifolia* by gas chromatography/mass spectrometry. *J. Mass Spectrom.* 39, 1337–1347.
- Yan, C., Zheng, M., Bosch, C., Andersson, A., Desyaterik, Y., Sullivan, A.P., Collett, J.L., Zhao, B., Wang, S., He, K., Gustafsson, Ö., 2017. Important fossil source contribution to brown carbon in Beijing during winter. *Sci. Rep.* 4, 43182.
- Yan, C., Zheng, M., Sullivan, A.P., Shen, G., Chen, Y., Wang, S., Zhao, B., Cai, S., Desyaterik, Y., Li, X., Zhou, T., Gustafsson, Ö., Collett, J.L., Jr., 2018. Residential coal combustion as a source of levoglucosan in China. *Environ. Sci. Technol.* 52, 1665–1674.
- Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C., 2007. Characteristics of hemicelluloses, cellulose and lignin pyrolysis. *Fuel* 86, 1781–1788.