Biomass burning tracers in urban and rural particles in Silesia - Poland

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Abstract

The major tracers are thermal degradation products from the biopolymer cellulose, namely the didehydromonosaccharide derivatives levoglucosan (LG), galactosan (GA) and mannosan (MN) and the resin acid derivative dehydroabietic acid, with minor β-sitosterol. The relative proportions of levoglucosan to mannosan (LG/MN) have been used for source reconstruction of combustion derived byproducts in atmospheric aerosols. Major tracers eg. levoglucosan, galactosan and mannosan were measured at two sites in Silesia region and health resort (Krynica) during winter season 2017/2018. Levoglucosan, mannosan and galactosan were quantified using a validated gas chromatography mass spectrometry (GC/MS) method described in detail by [Klejnowski et al, 2017]. The obtained results showed that mean concentrations of the total tracers determined in air in winter season were 522.6 ng/m^3 for Zabrze sampling point, 465.2 ng/m^3 in the case Rokitno and 156.75ng/m^3 for Krynica. Levoglucosan was most abundant tracer of biomass burning, it was 83.2 % of determined tracers in Zabrze, 78.1 % in Rokitno and 88.9 % in case of Krynica.

Keywords: biomass burning, tracers, winter season

1. Introduction

During the biomass burning, which consist mainly of cellulose, at a temperature above 300°C, the levoglucosan (LG, 1,6-anhydro-β-glucopyranose) is created, as well as the levoglucosan isomers, products of hemicellulose burning, mannosan (MN) and galactosan (GA) are formed. Levoglucosan, mannosan and galactosan are the biomass burning tracers. Those tracers are believed to be stable in the environment and resistant to photochemical oxidation. The objectives of this research was determination of changes in biomass burning tracers concentration for three sites – industry region, rural area and health resort, during winter season 2017/2018

2. Experimental

Atmospheric aerosol samples were collected on quartz filters in measurement stations in Zabrze (industry region), Rokitno (rural area) and Krynica (health resort) from December 2017 to March 2018. Samples were collected in accordance with the methodology described by Klejnowski et al, 2017 with the use of a low flow sampler with separating head PM$_{10}$ Atmoservice PNS3D15/LVS3d, with a stabilized flow of 2.3 m^3/h.

3. Methodology

In order to determine the concentration of biomass burning tracers: levoglucosan, mannosan and galactosan, a sample of atmospheric aerosol collected on a quartz filter was placed in a 4 ml dark glass vial. To the sample 2 ml of pyridine (POCH) and 50 μl of a derivatising agent: mixtures of N,O-bis(trimethylsilyl)trifluoro-acetamide and trimethylchlorosilane (BSTFA: TMCS, 99: 1, Supelco) were added. After the closure the vial was shaken for 1 minute and then placed in an oven at 40°C for 30 min. Extracts (1 ml), after filtration through a syringe filter (0.22 μm) were analyzed using a Shimadzu GC-2010 gas chromatograph coupled with a mass spectrometry detector equipped with an HP-5MS column (30 m, 0.25 mm, 0.25 µm). LOD was equal to 3.33 ng/ml for LG, 1.50 ng/ml for MN and 1.53 ng/ml for GA. LOQ was equal to 9.99; 4.51 and 4.58 ng/ml for LG, MN and GA, respectively. Precision expressed as a relative standard deviation was equal to 19%.

4. Result and Discussion

The results obtained for Zabrze, Rokitno and Krynica in the measurement campaign from December 2017 to March 2018 are presented in the table 1.

Table 1. Average concentration of biomass burning tracers in particular months (December 2017 - March 2018)

Mean	Month	Total, ng/m^3	LG	MN	GA
Krynica	December	*105.16*	91.06	11.54	2.56
	January	*194.87*	172.4	16.23	6.23
	February	*222.55*	194.29	19.27	8.99
	March	*104.45*	97.22	5.75	1.48
Rokitno	December	*439.94*	326.63	83.17	30.10
	January	*223.60*	188.19	27.92	7.49
	February	*1005.05*	805.84	119.22	79.98
	March	*192.29*	141.83	36.24	14.22
Zabrze	December	*902.44*	673.72	173.49	55.23
	January	*645.59*	501.54	111.19	32.86
	February	*95.25*	86.05	6.12	3.07
	March	*447.08*	403.22	30.23	13.63

The highest average concentration of biomass burning tracers for industry region in Zabrze was determined in December and was equal to 902.44 ng/m^3, while the lowest concentration equal to 95.24 ng/m^3 was determined in February. In the case of rural area - Rokitno, the highest concentration was recorded in February and the lowest in March, respectively 1005.05 and 192.29 ng/m^3. In the health resort, Krynica the highest concentration was determined in February and the lowest in December, 222.55 and 104.45 ng/m^3, respectively.

Table 2 shows the percentage of individual tracers in the total sum of determined compounds.

Table 2. Percentages of biomass burning tracers in the total sum of compounds in particular months (December 2017 - March 2018)

	Month	LG. %	MN. %	GA. %
Krynica	December	86.59	10.98	2.43
	January	88.47	8.33	3.20
	February	87.30	8.66	4.04
	March	93.08	5.51	1.42
Rokitno	December	74.25	18.91	6.84
	January	84.16	12.49	3.35
	February	80.18	11.86	7.96
	March	73.76	18.85	7.40
Zabrze	December	74.66	19.22	6.12
	January	77.69	17.22	5.09
	February	90.35	6.43	3.22
	March	90.19	6.76	3.05

In the industry region (Zabrze) the LG was on average 83.22%, MN was 12.41% and GA was 4.37%. For Rokitno, rural area the mean percentage of individual tracers in the total sum was 78.09%, 15.53% and 6.39% for LG, MN and GA, respectively. In case of health resort Krynica mean LG percentage in total sum was 88.86%, mean MN percentage was 8.37% and for GA was 2.77%.

The relative proportion of levoglucosan to mannosan (LG/MN) may be utilized to distinguish the smoke emission from different fuel types. The ratios of LG/MN are presented in table 3.

Table 3. LG/MN ratios in particular months (December 2017 - March 2018)

	Month	LG/MN
Krynica	December	7.89
	January	10.62
	February	10.08
	March	16.91
Rokitno	December	3.93
	January	6.74
	February	6.76
	March	3.91
Zabrze	December	3.88
	January	4.51
	February	14.06
	March	13.34

The mean value of LG/MN ratio for industry region was equal to 6.7, for rural area was 5.03 and for health resort was equal to 10.62.

5. Conclusions

In December, January and March the average biomass burning concentration was highest in industrial region, while the lowest concentration was determined in health resort.

In the February the highest biomass tracers concentration was determined in rural area, while the smallest concentration was determined in industrial area. Among the determined biomass burning tracers levoglucosan is the most abundant compound, its mean percentage in total sum of tracers varies from 78.09% to 88.86%. While galactosan was least frequent, its mean percentage in total tracers sum varies from 2.77% to 6.39%.

Obtained results for LG/MN ratios indicates that in case of industrial region and rural area monosaccharides are most likely emitted from softwoods burning. As for health resort the LG/MN ratios may indicate the co-firing of hard coal and hardwoods.

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