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# SEZONOWA ZMIENNOŚĆ STĘŻEŃ MARKERÓW SPALANIA BIOMASY I WĘGLA ORGANICZNEGO W WYBRANYCH FRAKCJACH PYŁU ATMOSFERYCZNEGO

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# Extended abstract

In recent decades, more effort is put on searching for alternative energy sources such as biomass combustion. Biomass burning is a global phenomenon resulting from fires and from forest burning for agricultural purposes. Moreover the agricultural waste and by-products of the wood industry are used for heating purposes in individual boiler and combined heat and power (CHP) plants, either by direct combustion or co-firing. Particulate matter (PM) from biomass combustion, when mixed with particles emitted from other sources such as transport, becomes difficult to identify. A number of studies around the world show that air pollutants, due to their physical and chemical properties, have a huge impact on climate change and human health. Due to this facts, it is necessary to study air quality in terms of concentrations of hazardous as well as indicator/marker substances in the air. Biomass burning is an important source of a wide range of organic compounds, which can also be produced by other processes. However, the anhydrosaccharides: levoglucosan (LG) and its isomers, mannosan (MN) and galactosan (GA), are mainly formed by pyrolysis and the combustion of cellulose and hemicellulose. In addition, they show relatively long stability under certain environmental conditions. Taking into consideration the above anhydrosaccharides are called biomass burning markers. The emission of these compounds and their relative amount in the environment is influenced by the temperature efficiency of anhydrosugars formation, which depends on the type of vegetation. As cellulose is found in plants in higher quantities than hemicellulose, the pyrolytic efficiency of levoglucosan formation is higher than that of its isomers. Futhermore hemicellulose is much more structurally diverse than cellulose. Therefore, more mannan derivatives, such as galactosan and mannosan, can be obtained when coniferous wood is burned compared to burning hardwoods. By comparing the ratios of galactosan to levoglucosan and mannosan to levoglucosan in the flue gas, the type of biomass burned can be identified.

Currently, there is no large-scale measurement of concentrations of biomass burning markers in atmospheric aerosols in Poland. It is known that knowledge of local emission sources, including biomass burning, can affect a larger area of the country. To date, the recommended analytical technique for the determination of biomass burning markers, the method of sample preparation and the particulate fraction of atmospheric aerosol most representative in the study of their concentrations have not been presented. This study presents

the results of a long-term campaign to determine the concentrations of biomass combustion markers in the air, taking into account seasonality. Considering the correlations between dust concentrations and organic carbon.

The main scientific objective of the thesis was to determine changes in the concentrations of biomass burning markers such as levoglucosan, mannosan and galactosan in relation to (i) atmospheric aerosol fractions, i.e. PM1 and PM2.5, and (ii) organic carbon content. Furthermore, the study attempts to determine correlations between marker concentrations and $PM_1$ and $PM_{2.5}$ as well as organic carbon concentrations associated with PM1 and $PM_{2.5}$, taking into account seasonality (heating and non-heating periods).

As part of the study, research was conducted to apply and validate an analytical procedure for the determination of the biomass burning markers: levoglucosan, mannozan and galactosan in atmospheric aerosol samples. Two PM fraction were determined according to a procedure of simultaneous extraction and derivatisation and quantitative analysis by gas chromatography coupled to a mass spectrometry detector.

The object of the study was 102 weekly compositional samples of $PM_1$ and $PM_{2.5}$ particulate matter, 51 samples each of $PM_1$ and $PM_{2.5}$, respectively. The atmospheric aerosol samples were collected in Zabrze at the measurement station belonging to IPIŚ PAN between 26.05.2020 and 30.05.2021. In the samples, concentrations of $PM_1$ and $PM_{2.5}$, organic carbon and biomass burning markers associated with particulate matter fraction were determined. In addition, correlations were established between (i) concentrations of biomass burning markers and concentrations of $PM_1$ and $PM_{2.5}$, (ii) the concentration of biomass burning markers and the concentration of organic carbon associated with $PM_1$ and $PM_{2.5}$. Moreover, the influence of the heating season on the level of concentrations of PM fractions, organic carbon and biomass burning markers was determined. Furthermore, the contribution of organic carbon from biomass burning was calculated based on levoglucosan concentrations, and identification of combustion sources was undertaken based on the ratios of the concentrations of the markers determined.

As part of the study, the concentration of the $PM_1$ and $PM_{2.5}$ and their components, i.e.: organic carbon and biomass burning marker concentration, were determined. The average concentration of $PM_1$ during the measurement campaign was 10.2 $\mu g/m^3$, while that of $PM_{2.5}$

was 25.5 μg/m$^3$. The determined average concentration of organic carbon associated with the $PM_1$ during the measurement campaign was 4.66 μg/m$^3$. For the $PM_{2.5}$, the mean organic carbon concentration during the campaign was determined to be 10.3 μg/m$^3$. As part of the work, concentrations of biomass burning markers were determined. The average sum of their concentrations associated with the $PM_1$ and $PM_{2.5}$ during the measurement campaign was 34.1 and 157 ng/m$^3$, respectively. The same relationship can be seen for the individual biomass combustion markers levoglucosan, mannosan and galactosan in both PM fractions. Furthermore, the highest concentrations in the dust samples were determined for levoglucosan. In contrast, of all the markers tested, galactosan occurs at the lowest concentrations.

During the study, higher concentrations of $PM_1$ and $PM_{2.5}$ as well as organic carbon and biomass burning markers associated with both particulate fractions were observed during the winter season. The differences between the heating season and the non-heating season are probably related to the increase in emissions from fuel combustion for heating purposes. Furthermore, higher concentrations of $PM_{2.5}$ and OC associated with this particulate fraction were determined throughout the measurement campaign. In addition, the decrease in temperature during the autumn period resulted in an increase in the sum of biomass burning marker concentrations due to the higher proportion of biomass combustion. As in the case of PM and organic carbon concentrations, we can observe an increase in the sum of markers, as well as individual compounds, for the $PM_{2.5}$ fraction. Among the biomass burning markers, levoglucosan is the dominant compound in each PM fraction, while galactosan is the marker found in the lowest concentrations.

In ongoing studies on the concentration of biomass burning markers in atmospheric aerosol, attempts were made to establish a correlation between the concentration of levoglucosan and the concentration of PM and organic carbon associated with the $PM_1$ and $PM_{2.5}$. However, these showed a lack of linear correlation between the sum of biomass burning marker concentrations and the concentration of PM and organic carbon. This most likely indicates the varying characteristics of the combusted fuels used for heating purposes in the vicinity of the sampling point. However, it can be observed that an increase in the concentration of organic carbon associated with both $PM_1$ and $PM_{2.5}$ results in an increase in the sum of biomass burning markers concentrations associated with the respective particulate fractions.

Biomass burning markers are included in the total organic carbon content. The known concentration of levoglucosan allows the calculation of the percentage of organic carbon from biomass burning in the determined organic carbon according to the formula of Sang et al. [152] as well as the estimated concentration of organic carbon from biomass burning according to the formula proposed by Puxbaum [15] and Fuller [153]. For the calculated percentage of organic carbon from biomass burning in the determined organic carbon in $PM_1$ and $PM_{2.5}$, the highest percentages were estimated in the 41st week of 2020, i.e. 5-11.10.2020, amounting to 23.2% and 62.3%, respectively. In addition, the highest estimated organic carbon concentrations from biomass burning were also observed in week 41 of 2020, being 0.696 and 4.02 $\mu g/m^3$, representing 26.5 and 55.1% respectively of the determined OC content associated with $PM_1$ and $PM_{2.5}$.

In order to distinguish between sources from the different types of biomass, the relative ratios of levoglucosan to mannosan (LG/MN) and levoglucosan to the sum of mannosan and galactosan (LG/(MN+GA)) were determined. In the $PM_{2.5}$ samples, for the winter season, the LG/MN ratio was 9.2 and LG/(MN+GA) was 9.0 indicating the combustion of a mixture of coniferous and hardwood. For the non-heating season, the average LG/MN and LG/(MN+GA) ratios are equal and are 10.7 (due to the fact that galactosan concentrations were below the limit of quantification) indicating combustion of a predominantly hardwood mixture.

The work also undertook to establish a target PM fraction for the determination of biomass burning markers. For this purpose, the correlations between the biomass burning markers, i.e. MN vs LG, GA vs LG and GA vs MN, were determined. The correlation coefficient of these ratios could only be determined for the $PM_{2.5}$ and indicated the highest linear fit of above 0.9. This considers the $PM_{2.5}$ to be considered suitable for the analysis of levoglucosan, mannosan and galactosan.