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NMR AEROSOLOMICS STUDY OF WATER-SOLUBLE ORGANIC COMPOUNDS IN SIZE-RESOLVED PARTICULATE MATTER

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INTRODUCTION

Organic aerosols (OA) account for a significant fraction (10 – 90%) of atmospheric particulate matter (Hallquist et al., 2009). The composition of organic aerosols is very complex and is usually characterized by their water solubility (Decesari et al., 2006). Water-soluble organic compounds (WSOC) constitute a large fraction of OA (10 – 80%) and consist of chemical species containing oxygenated functional groups such as hydroxyl, carboxyl, or carbonyl groups. NMR spectroscopy represents an alternative to commonly used techniques (gas chromatography-mass spectrometry, liquid chromatography-based techniques) for WSOC analysis. Our recently introduced method, called NMR aerosolomics, allows quantitative analysis of dozens of individual compounds from different aerosol samples (Horník et al., 2020).

An important part of the characterization of aerosols is their classification by particle size. The analysis of individual compounds in the size-resolved fractions of the WSOC class has been performed only in a few studies that focus mainly on a particular subclass of compounds or use multiple analytical techniques (Barbaro et al., 2019; Xu et al., 2020).

EXPERIMENTAL SETUP

Aerosol samples were collected in a suburb area of Prague-Suchdol in the campus of the Institute of Chemical Process Fundamentals (50° 7'39'' N, 14° 23'4'' E, 277 m a.s.l.). A homemade prototype of high-volume cascade slit impactor with five stages (flow rate 370 l/min) and a back-up filter was used for aerosol sampling. Four aerosol samples were separated into six different fractions: < 0.11 μm (1), 0.11 – 0.40 μm (2), 0.40 – 0.87 μm (3), 0.87 – 2.30 μm (4), 2.30 – 4.68 μm (5), and 4.68 – 20.0 μm (6). Impactor stages 1 – 4 correspond to the fine aerosol fraction, while stages 5 – 6 correspond to the coarse fraction. Two sample series were collected in summer 2015; the winter series were collected in two campaigns, one in 2017, the other in 2018. Three samples were collected as multi-day (2 – 8 days) samples, while one summer sample was collected on the same medium during several summer mornings and afternoons when new particle formation events could be collected, especially organics related to particle growth.

The sample medium was cut into pieces and extracted in 15 mL of deionized water. Extraction was performed for 30 minutes in an ultrasonic bath and for 2 hours on a shaker. The extract was then filtered and freeze-dried. Subsequently, the obtained material was dissolved in deuterated water (99.96% D) containing a known amount of DSS (dimethyl silapentane sulfonate, 0.8 mM) as a reference for chemical shift and line shape. Finally, after dissolution, the sample was transferred to a 5 mm NMR tube and

immediately inserted into the NMR spectrometer. Chenomx NMR Suite software was used to identify and quantify the compounds. In this approach, each compound in the ^{1}H NMR spectrum is identified based on the precise chemical shift of the individual signals.

RESULTS AND CONCLUSIONS

In this study, NMR aerosolomics was used to analyze WSOC in size-resolved particulate matter. Advanced analysis based on compound profiling in the ^{1}H NMR spectra allowed quantification of 31 – 45 compounds in each sample. A total of 73 individual compounds were assigned in the samples. The concentration data were subjected to multivariate statistical analysis, which revealed significant differences in chemical composition between the two seasons and in the main characteristics of the fine and coarse aerosols. Levoglucosan was identified as the major factor in group separation by season of sampling. Clustering based on particle size was mainly determined by the content of carbohydrates in the coarse aerosol fractions.

of the individual compounds showed that some of the compounds were present in all fractions in both the summer and winter samples, while some of the compounds were more specific to a particular season or to a particular particle size. The concentration profiles of the size-resolved aerosol showed an association of certain compounds across different classes that could be attributed to a common source or degradation pathway. A correlation of carbohydrates with trimethylglycine and choline was found in the coarse summer aerosol derived from various biogenic sources. Similar distribution profiles were observed for several compounds associated with solid fuel combustion (methylsuccinic acid, maleic acid, fumaric acid, phthalic acid, and imidazole) in the 2018 winter series with the highest concentration in the accumulation mode. A similar distribution profile in both winter series was found for glucose and levoglucosan, indicating a common origin, most likely biomass burning. Further details of this work were recently published in Horník et al. (2021).

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