SEMI-VOLATILE ORGANIC TRACE QUANTIFICATION OF EMISSION SAMPLES WITH PTR-TOF-MS

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INTRODUCTION

Carbonaceous compounds represent a major fraction of atmospheric aerosols. This holds true for ambient particulate matter, but is even more obvious when emission samples from residential wood combustion are evaluated. Moreover, biomass combustion is also a source for volatile organic compounds (VOCs) which may interact with carbonaceous compounds in particulate matter. Routinely carbonaceous compounds are quantified with a thermal-optical method, differentiating between organic and elemental carbon. In this study, we will investigate the impact of semi-volatile organics on the evolution of elemental carbon with this method.

STUDY DESIGN

This study focusses on the amount of semi-volatile organic trace compounds in emission samples from different firewood combustion devices. Sampling differentiated between hot and cooled total suspended particle (TSP) samples, “cooled-phase samples” were diluted with compressed air. A comprehensive chemical characterization of both sample fractions was carried out. The analysis of organic carbon (OC) and elemental carbon (EC) was performed in duplicates by an OCEC analyzer (Sunset Laboratory Inc.), applying the EUSAAR_2 protocol in the transmission mode[1]. Different contributions of the carbonaceous aerosol fractions could be observed in both sample fractions. Hot-phase samples consist primarily of EC while OC concentrations dominate cooled-phase samples. For hot-phase samples the filter transmittance signal was very low caused by the relative high filter loadings, which made OC charring difficult to detect. Based on a first evaluation, hot-phase samples were divided into samples showing “early burning EC” (EB-EC) and “late burning EC” (LB-EC). EB-EC samples showed a rapid evolution of EC during the first temperature step and right after switching to the oxidative phase. While LB-EC samples showed the opposite effect, where the evolution of EC took place during the last and highest temperature step within the oxidative phase.

Liu et al. reported that the presence of oxygenated species in particulate matter samples may be associated with premature EC evolution [2]. To investigate this effect for emission samples under evaluation, semi-volatile trace quantification of both sample fractions will be carried out using a Proton Transfer Reaction “Time-of-Flight” Mass Spectrometer (PTR-TOF-MS). This method couples high sensitivity with high mass resolution for multiple semi-volatile organics emitted from biomass burning.

PRELIMINARY RESULTS

This study evaluates the separation between the carbonaceous fraction EC and OC and its dependence on other constituents of particulate matter formed during biomass combustion of different residential firewood devices. Special focus will be put on semi-volatile organics. PTR-TOF-MS enables a real-time detection of semi-volatile organics during the different temperature steps which were used for OC and EC quantification. Results will be compared with data from the thermal-optical method. Statistical analysis will be performed with mentioned data and will give insights in the impact of semi-volatile organics on the premature evolution of EC. Detailed interaction of VOCs and carbonaceous fraction emitted from residential firewood combustion devices will be presented at the symposium.

CONCLUSIONS AND OUTLOOK

Here we will present the comprehensive characterisation of emission samples, which serves as a basis for the calculation of up to date emission factors. The obtained results will give insights in the interaction of semi-volatile organics and elemental carbon.

Furthermore, this work aims to establish awareness on the advantages and limitations of the quantification of OC and EC with a thermal-optical method.

REFERENCES

[1] Cavalli et al., Toward a standardized thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Techn.3, p. 79-89, 2010

[2] Liu et al., Uncertainties in thermal-optical measurements of black carbon: Insights from source and ambient samples, Science of the Total Environment, p. 239-249, 2019