



TNA User Report

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Project title	Understanding secondary aerosol formation from wood burning and coal combustion through the application of ultra-high performance liquid chromatography coupled to electrospray ionization ultra-high resolution mass spectrometry
Name of the accessed chamber	PACS-C3 (Paul Scherrer Institute, Villigen, Switzerland)
Number of users in the project	2
Project objectives (max 100 words)	We demonstrate molecular level characterization of the secondary aerosol formation from wood and coal burning emissions in the PACS-C3 smog chamber. The objectives of this study were to identify oxidation products in the complex mixtures of coal- and wood-burning aerosol and compare the identified products with single VOC oxidation experiments, in which cresol and toluene was oxidized with different seed aerosol composition. Chromatographic separation of the individual oxidation products from the complex mixture and from single VOC experiments enabled us to attribute single oxidation products and their contribution to the total observed signal in the coal- and wood biomass-oxidation experiments. Furthermore, we investigated whether we observe evidence for the formation of organosulfates under different aerosol acidity conditions.
Description of work (max 100 words):	Particle filter samples of cresol and toluene oxidation experiments with different seed aerosol composition were sampled, as well as filters from coal and wood burning emissions. Secondary organic aerosol formation was achieved by OH generation of HONO photolysis. Different seed aerosols served as condensational sink for low- and semi-volatile oxidation products. Particle filters were sampled and analyzed by ultra-high performance liquid chromatography coupled to ultra-high resolution mass spectrometry (UHPLC/UHRMS). Non-targeted data analysis of negative electrospray ionization modes revealed the abundance of several CHNO-containing compounds from cresol oxidation. Coal- and wood-burning aerosols revealed complex spectra and their chemical transformation (aging) trajectories during photo-oxidation were visualized.

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¹ Physics; Chemistry; Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.

² UNI= University and Other Higher Education Organisation;

RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);

SME= Small and Medium Enterprise;

PRV= Other Industrial and/or Profit Private Organisation;

OTH= Other type of organization.

³ UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher ENG= Engineer; ACA= Academic; TEC= Technician.

⁴ Reproduce the table for each user who accessed the infrastructure

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Alexander Vogel

Chamber name and location: PACS-C3

Campaign name and period:

**Secondary organic aerosol from cresol oxidation,
coal combustion and wood burning emissions
(3.4.2018-20.4.2018)**

Introduction and motivation

Organic compounds are major constituents in both primary and secondary atmospheric particulate matter (PM). The organic fraction in atmospheric aerosols varies between 20 and 90 % of the total suspended mass and undergoes continuous chemical transformation (aging) in the atmosphere (Jimenez et al., 2009). The combustion of biomass (wood and coal) is of global relevance for aerosol loadings due to its strong natural (wildfires) and anthropogenic (heating, cooking activities in developing countries) sources. While the molecular composition of primary emissions has been studied extensively, the knowledge of aging processes of primary emissions remains limited (Bertrand et al., 2018). Aging of primary emissions can occur in two ways: (1) gas-phase oxidation of co-emitted gases and of evaporated components from the particles, following re-condensation of the oxidized products, and (2) photochemical oxidation by reactive species that are formed in the condensed phase upon irradiation (e.g. photosensitized oxidation) or reactive uptake of oxidants. Both mechanisms can lead to increased formation of particulate matter, and can furthermore modify the physicochemical properties of aerosol particles. Mechanistic understanding of the dominant aging processes of biomass burning aerosols needs to be achieved, in order to improve our predictive

capability of aerosol loadings under future scenarios and develop effective mitigation strategies of PM pollution.

Scientific objectives

The scientific objectives of the project are to characterize secondary organic aerosol (SOA) composition from coal combustion, wood combustion and single aromatic volatile organic compounds (VOCs) as precursor gases. The coal and wood combustion experiments shall simulate the chemical transformation of primary emissions under different aging conditions, such as aging by OH radicals under UV or by NO₃ radicals in the dark. The single VOC experiments shall shed light onto which products in the particle phase are formed from the precursor gases cresol and toluene. Comparison to the fresh and aged SOA in the biomass combustion experiments shall reveal to which extent we can use a molecular fingerprint-approach for the determination of the contribution of individual VOC oxidation products to total SOA. Furthermore, we want to investigate the formation of organosulfates from cresol oxidation with different sulfate seed aerosol particles and their abundance in the SOA formed from coal burning emissions.

Reason for choosing the simulation chamber

The PACS-C3 cool chamber is a Teflon chamber with a volume of 9 m³. It allows studying biomass burning emissions and their atmospheric transformation at a different temperatures and relative humidity in time scales of up to ~8-10 hours (depending on the sampling flow rate). The Teflon bag is installed on flexible suspension points, which allows to fill the chamber at the beginning of the experiment, following sampling the air inside the bag without the need to dilute with zero air in order to compensate for the sampled volume. The chamber is furthermore equipped with the necessary infrastructure, such as a stove for the combustion of the biomass, an emission dilution system, a UV system, a scanning mobility particle sizer (SMPS) and a suite of gas monitors (O₃, NO_x, SO₂).

Method and experimental setup

Chamber experiment

At the beginning of the experiments the VOC (cresol/ toluene) and seed aerosol (ammonium sulfate, ammonium bisulfate) was injected into the chamber until the desired levels (~50 ppb and ~30-40 µg/m³, respectively). After equilibration, HONO and d9-Butanol were added as the OH source and as a tracer for monitoring OH concentration, respectively. Formation of SOA was initiated by switching on the UV light and thus starting HONO photolysis.

The particle filter sampling for offline analysis was conducted inside the thermal housing of the chamber in order to avoid analyte losses by evaporation. Filters were usually sampled twice in each experiment for 20 min at a flow rate of 20 l/min with the first filter during the initial SOA formation and a second filter during a later stage of the experiment. Blank filters were sampled from the chamber for the same duration and flowrate, but before the UV was turned on (w/ and w/o seed aerosol present). Filters were stored at -18 °C until analysis.

During the campaign, three different online mass spectrometers measured *in-situ* the gas- and particle-phase composition:

- (1) A proton transfer reaction-mass spectrometer (PTR-MS) for measuring the gas phase precursor concentration and d9-butanol decay to measure OH exposure.
- (2) An aerosol mass spectrometer (AMS) for quantitatively measuring the seed aerosol concentration, the primary organic aerosol from biomass combustion, and the formation of secondary organic aerosol.

(3) An extractive electrospray ionization time-of-flight mass spectrometer (EESI-ToF) for the highly time resolved measurement of single organic compounds, without fragmentation of the organic molecular ions.

Filter extraction and UHPLC/UHRMS analysis

A circular punch (16 mm) of each filter was transferred into a 1.5 mL HPLC vial (TruView, LC-MS certified, Waters) and covered with 0.5 mL of ultrapure methanol (hypergrad for LC-MS, LiChrosolv®, Merck). 10 µL of a 100 µM solution of ¹³C-labelled vanillin (Vanillin-(phenyl-¹³C₆), 99 atom% ¹³C, Sigma-Aldrich) was added as internal standard for quality control. The vial was closed and agitated for 10 minutes in a laboratory shaker. Afterwards, the methanol extract was transferred together with the soaked filter material into a centrifugal filter unit (Ultrafree – MC, 0.22 µm GV Durapore, Merck Millipore). The filter units were centrifuged for 3 x 1 minute and the clear methanol filtrate was transferred into HPLC vials for UHPLC/UHRMS analysis. The chromatographic separation was conducted on a UHPLC (Ultimate 3000, Thermo Fisher Scientific) with a reversed phase column (Accucore C₁₈ RP-MS, 50 x 2.1 mm, 2.6 µm particle size, Thermo Fisher Scientific). A 16 minute gradient of two solvents was applied by a binary pump system (solvent A: 1% v/v MeOH, 1% MeCN, 0.2% Formic acid, 97.8% ultrapure water, solvent B: 100 % MeOH), starting with 99% solvent A and linearly increasing to 99% solvent B between minute 2 and 12 of the chromatographic run. The flow rate was set to 400 µL / min. 20 µL were injected for each UHPLC/UHRMS analysis. The ionization for mass spectrometric analysis was done by electrospray ionization on an ultra-high resolution Orbitrap mass analyzer (Q-Exactive Focus, Thermo Fisher Scientific). Each sample was measured in positive and negative mode of the electrospray ionization. Data acquisition was done in the data-dependent acquisition mode, in which after each full scan (m/z 70 -1000 amu), the three most intense ions are selected for MS/MS.

Data description and analysis

Data from the smog chamber experiments comprise online measurements of particle size distribution (SMPS), aerosol chemical composition (AMS, EESI-ToF) and gas-phase composition (PTR-MS, gas monitors). The objective of this project is the chemical analysis of filter samples by UHPLC/UHRMS. The data comprise full scan spectra (m/z 70-1000 amu) of the chromatograms, including MS/MS spectra of the most intense molecular ions. The utilized mass spectrometer provides high-resolution and accurate-mass (HR/AM) spectra (R~70,000 at m/z 400 and mass accuracy better than 2 ppm).

The presented data analysis was carried out utilizing the open-source software mzmime2 (mzmime.github.io). This software provides an algorithm for non-targeted compound detection. It extracts all ions from the raw data above a certain threshold, builds and deconvolutes chromatograms, attributes ion signals from isotopes, clusters and adducts to the molecular ions, aligns peak lists of different experiments and predicts molecular formulas based on the exact mass and isotopic pattern. The development of the workflow of this analysis is an essential part of the work conducted within this project. So far, the data analysis only comprises measurements that were acquired in the negative ESI mode. Results from positive ionization have been collected and are subject to future analysis.

Preliminary results and conclusions

The analysis of particle filter samples requires a solid evaluation of chamber blanks. Figure 1 (a) shows the identified signals in a chamber blank filter that includes organic compounds introduced by the seed aerosol particles. Especially the region between 200 and 400 amu, and between 10 and 13 minutes shows several CHOS containing molecules, which are likely introduced by the seed aerosol. These compounds have high H/C ratios and are likely organic sulfate esters or sulfonates with alkyl chains.

Figure 1 (b) shows a filter from the same experiment after turning on the UV light source and letting cresol being oxidized by HO and NO radicals from HONO photolysis. In the region between 150-250 amu and 4-9 minutes, several CHNO containing molecules arise. These compounds all contain 6-8 carbon atoms with low H/C ratios, with the highest ion signals from C7-compounds. These signals are likely oxidation products of cresol, such as different isomers of methyl-nitrocatechol ($C_7H_7NO_4$). Comparing the different seed aerosol conditions ($(NH_4)_2SO_4$ vs. NH_4HSO_4 vs. no seed) revealed no significant differences between these experiments. In none of the cresol oxidation experiments, we identified significant contribution of organic sulfates that can be attributed unambiguously to cresol.

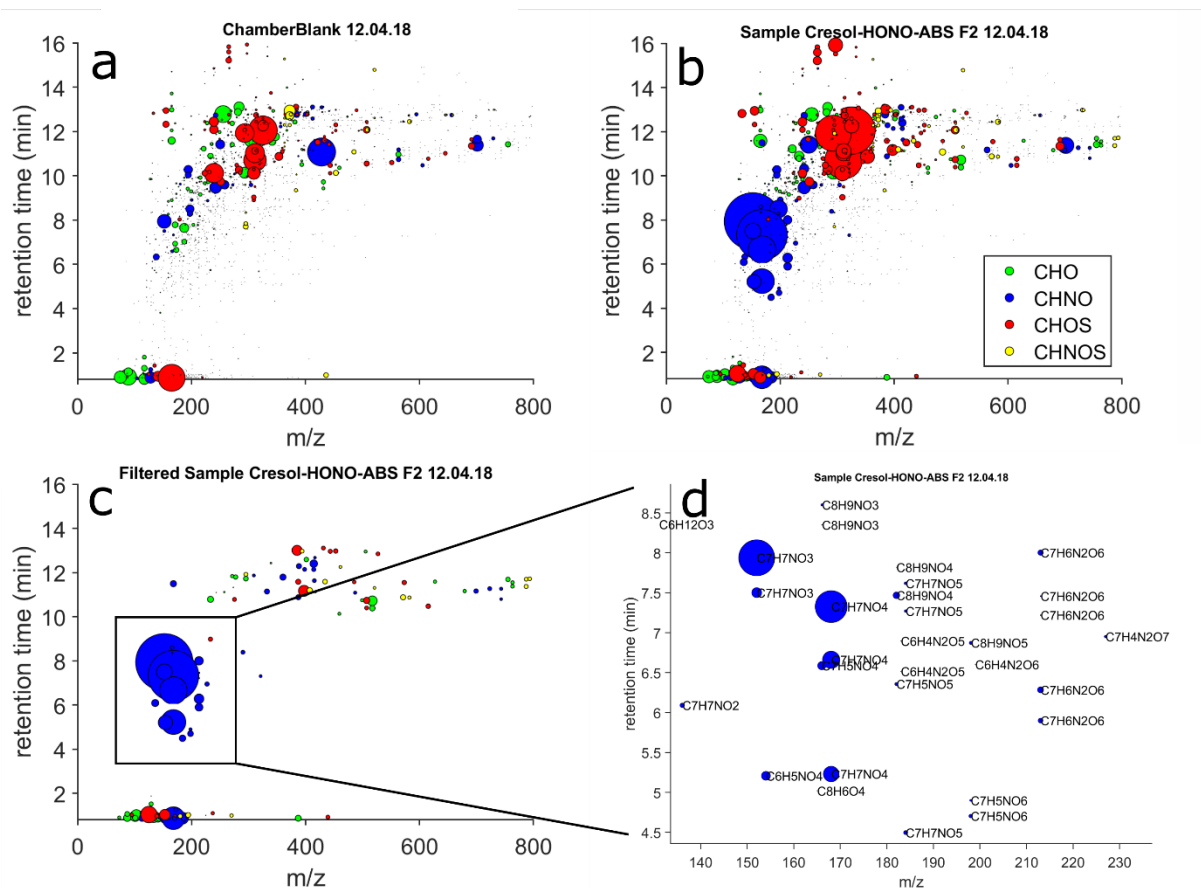


Figure 1. Mass-over-charge (m/z) vs. retention time plots of (-)ESI measurements. Each circle represents an ion signal for which an elemental formula could be determined based on the measurement of the exact mass and the isotopic pattern. The size of the circles represent the signal intensity, and the color codes the elemental composition group according to the legend in (b). (a) Ion signals from the chamber blank filter, including the presence of cresol and NH_4HSO_4 seed aerosol. (b) Ion signals from a sample filter, after cresol has been photochemically oxidized. (c) Filtered plot showing only compounds which have 10 x higher signal in the sample filter compared to the chamber blank filter. (d) Zoom into the region of cresol oxidation products.

While the identified secondary oxidation products of cresol comprises only a few (~20) compounds, the molecular fingerprint of the coal and wood burning experiments is much more complex.

Figure 2 (a) and (d) depict the identified ion signals from primary (fresh) and secondary (aged) compounds, respectively. The chemical transformation during aging of the coal aerosol emissions becomes visible by comparing Figure 2 (a-c) vs. Figure 2 (d-f). We observe the disappearance of compounds of the CHO class with relatively high carbon numbers ($\#C=13-23$, Figure 2 (b)) and low O/C and H/C ratios ($O/C < 0.3$ and $H/C < 1$, Figure 2 (c)). These compounds are likely aromatic compounds in the primary aerosol emission, which disappear during photochemical transformation. Since these compounds are likely not very volatile due to their high mass, one might speculate that these compounds are degraded by chemical transformation processes (e.g. through photosensitized chemistry) occurring in the condensed phase.

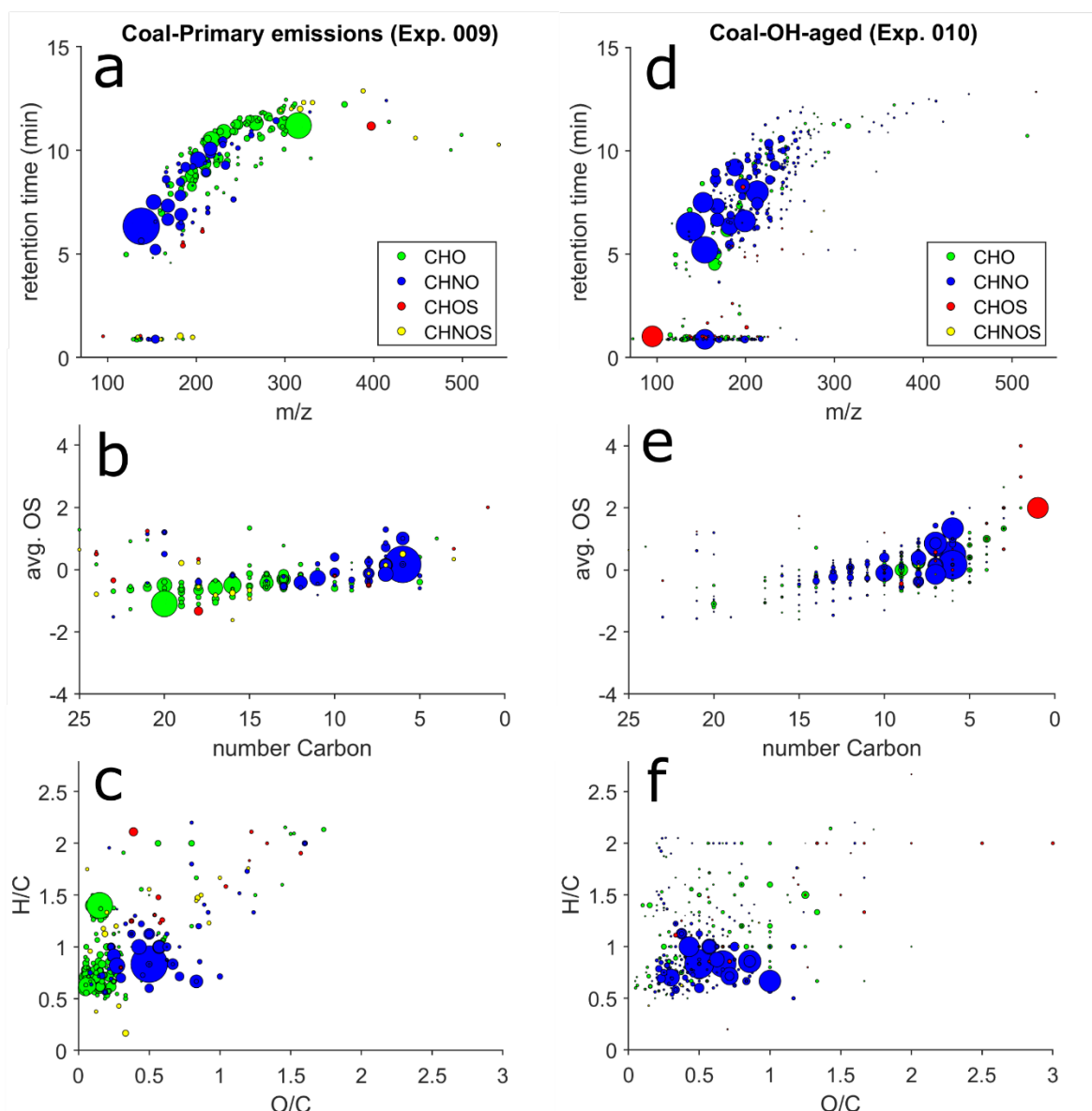


Figure 2. (a-c) Composition of primary aerosol from coal burning experiments under dark conditions. (d-f) Composition of the photochemically aged primary aerosol including the secondary oxidation products. The marker size of d-f was divided by a factor 5 compared to the intensities shown in a-c for better graphical representation. (a, d) mass/charge vs. retention time plot (as introduced in Figure 1 for cresol oxidation). (b, e) Kroll-plot based on the elemental formulas : number of carbon vs. the average oxidation state ($avgOS = 2 \cdot O/C - H/C$), after Kroll et al. (2011). (c, f) Van-Krevelen Diagram : compounds with $H/C < 1$ have an aromatic character.

In the aged coal-burning aerosol we observe mostly compounds of the CHNO class with carbon numbers < 15 and on average a higher O/C ratio compared to the fresh coal emissions. On average, the H/C ratio did not change significantly. It is worth noting that the ion intensities in Figure 2 (d-f) were divided by a factor 5 compared to Figure 2 (a-c) for a better graphical illustration- the overall higher signal in Figure 2 (d-f) is in line with the observed mass increase during aging of the coal burning aerosol.

The qualitative comparison between coal burning aerosol and SOA from cresol oxidation is shown in Figure 3. Due to the analysis using chromatographic separation, we are now able to state similarities between different experiments on the molecular-resolved level. Although we observe different ion intensities between the coal burning and cresol experiments, we do observe a number of cresol oxidation products in the complex molecular fingerprint of both primary and secondary aerosol from coal burning. It will be subject to discussion whether we can now use the fraction of compounds, which are in common between single VOC and coal burning experiments, as a direct measure for the contribution of cresol oxidation in the complex emission mixture to the total aerosol mass.

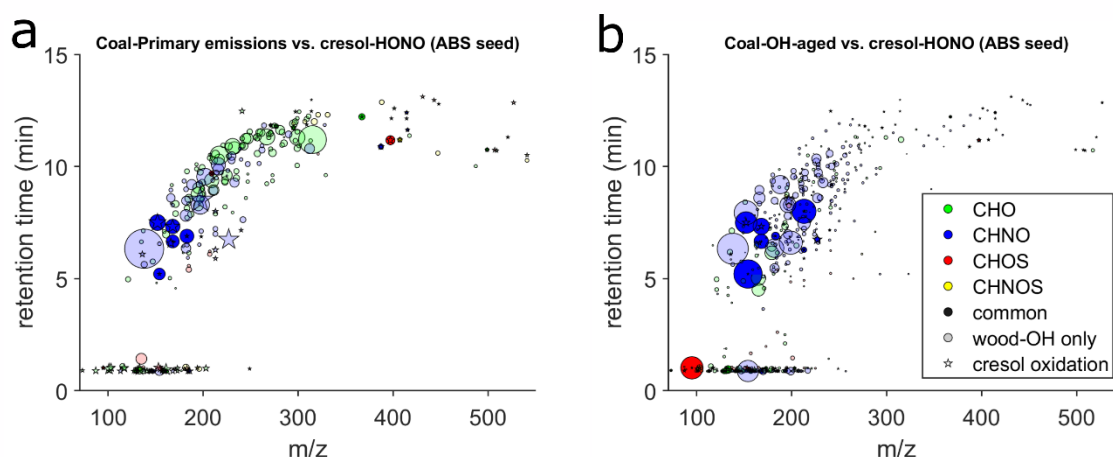


Figure 3. Molecular fingerprint comparison between primary coal burning aerosol and cresol-SOA (a) and secondary coal burning aerosol and cresol-SOA (b). Transparent circles show compounds that are detected only in the coal burning aerosol, transparent stars are compounds detected in cresol SOA and non-transparent circles are compounds detected in both coal burning aerosol and cresol-SOA (signal intensity from the coal burning experiment). The marker size (ion intensity) of (b) was divided by a factor 5 compared to the intensities shown in (a) for better graphical representation.

Outcome and future studies

All of the shown data are preliminary and require further analysis. However, we have already shown the molecular fingerprints of primary, fresh and secondary aged aerosol from coal-burning emissions. We have also shown comparisons on the molecular level between the coal burning experiments and the composition of SOA from cresol oxidation.

We did not observe the formation of organic sulfates from cresol oxidation with different seed aerosol acidity, nor did we identify organic sulfates (except methanesulfonic acid) from coal burning aerosol.

Future analysis will comprise data analysis of the positive ion mode measurements as well as the molecular fingerprints from toluene oxidation. Comparison to extractive electrospray ionization measurements (EESI-ToF) might provide further insights into the dynamics of the chemical transformation of both single VOC precursor experiments as well as complex biomass burning studies.

References

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