



TNA User Report

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Project title	Training in Chemical Analysis of SOA Constituents Using High-Resolution Mass Spectrometry II
Name of the accessed chamber	OGTAC CC
Number of users in the project	1
Project objectives (max 100 words)	The aim of the visit to the Calibration Centre for Organic Tracers and Particulate Aerosol Constituents (OGTAC CC) of the Atmospheric Chemistry Department (ACD) at TROPOS was to gain detailed knowledge on the chemical analysis of organic aerosol constituents with LC/MS through an intensive hands-on training course with a special focus on high-resolution mass spectrometry data.
Description of work (max 100 words):	During the training course, particle sampling techniques, sample preparation and compound separation by LC/MS were described and explained in detail, focusing on data processing of high-resolution mass spectrometry data. Sample preparation (i.e., filter extraction) was completed under expert supervision. Quantification and data interpretation were conducted for a large number of chamber-generated samples. Special attention was paid to artifact formation from gas-phase SO ₂ during detection and quantification of organosulphates.

Principal Investigator's and group's information	
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User status ³	Academic
New user	Yes

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 EXP= Engineer; ACA= Academic; TEC= Technician.

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: Matthieu Riva

Chamber name and location: OGTAC CC at TROPOS ACD

Campaign name and period: Training in Chemical Analysis of SOA Constituents Using High-Resolution Mass Spectrometry II

Text:

Introduction and Motivation

The OGTAC CC is a calibration centre for the analysis of atmospheric organic tracers and particle-phase constituents. This is the first of its kind worldwide, focusing on main constituents of and tracers for secondary organic aerosol (SOA) of biogenic and anthropogenic origin. This individual training course is dedicated to the application of high-resolution mass spectrometry (HRMS) in combination with ultra-high pressure liquid chromatography (UHPLC) to atmospherically relevant aerosol particles and gases. The training mainly covered targeted as well as untargeted screening methods using UHPLC-ESI/Orbitrap MS and complementary techniques. A special focus of this training course was the analysis of sulphur-containing organic compounds, in particular organosulphates and nitrooxy organosulphates, which are a ubiquitous class of compounds in atmospheric aerosol particles. However, these compounds are rarely analysed on a routine basis because their measurement is typically hampered by a lack of authentic standards and the abundance of yet unidentified compounds.

In addition, artefact formation during particle sampling and sample analysis is only rarely considered, which might lead to biased results.

Scientific objectives

Within the two weeks, filter samples were prepared in a number of chamber experiments, subsequently extracted and analysed. Particulate organosulphates and nitrooxy-organosulphates were identified and quantified using high-resolution Orbitrap mass spectrometry in combination with ultra-high performance liquid chromatography (UHPLC). Special attention was paid to artifact formation from gas-phase SO₂ during detection and quantification of organosulphates.

Reason for choosing the simulation chamber/ calibration facility

The OGTAC CC was the ideal location to perform this offline chemical analysis as it has the required instrumentation and necessary protocols, as well as the expertise to train and guide visitors. Following training, sample preparation, analysis, and quantification was completed under expert guidance and supervision. In particular, a dual filter sampling setup developed at TROPOS allows the investigation of artefacts from reactive trace gases during particle sampling. A UHPLC-HRMS system in combination with a well-established non-target screening (NTS) approach¹ enabled the applicant to achieve detailed and comprehensive insights into the chemical composition of organic compounds in aerosol samples. Moreover, in complementary targeted analyses, quantification of single compounds were carried out with high sensitivity and low detection limits.²

Method and experimental set-up

The filter samples were generated in the aerosol chamber at TROPOS ACD (see Table 1 for details) by oxidizing α -pinene under various conditions, in the presence of NO_x and SO₂. A detailed description of the chamber can be found elsewhere.³ For each experimental run, several filter samples were taken at 18 L/min with a sampling time of 30 min. To investigate artefacts from SO₂, a dual filter sampling unit enabled both particle sampling in the presence and in the absence of SO₂. All samples were directly stored at below -18 °C until extraction and analysis. During sample preparation, half of the filter was extracted by ACN/H₂O. Subsequently, the extract was analysed by UHPLC-HRMS according to Brüggemann et al. (Environ. Chem. 2019). Relative quantification of sulphur-containing monoterpene oxidation products was conducted using Xcalibur 4.1 (Thermo Fisher Scientific, USA) from peak areas of the corresponding [M-H]⁻ ion signals in full scan mode (m/z 50–750, R = 70k). In a NTS approach, all LC-HRMS data obtained in full scan and ddMS2 mode were analyzed using the open-source software package MZmine 2.51 (<http://mzmine.github.io>).^{4,5} The automated workflow comprised followed the protocol of Brüggemann *et al.*,¹ i.e., signal detection in MS and MS/MS spectra, filtering of shoulder peaks in the mass spectra, chromatogram building, chromatogram deconvolution, grouping of isotopes / adducts / complexes, and retention time alignment. Additionally, MFs were assigned using the SIRIUS module, which considers isotopic patterns and MS/MS fragmentation spectra during formula prediction of detected compounds.

Table 1: Overview on the chamber runs. Commonly, 60 ppb α -pinene, 15 ppb SO_2 , and 15 ppb NO were present in the chamber. All experiments were conducted at 50% RH and 20 °C. Seed particles were injected by nebulizing aqueous sodium sulfate solutions with different acidities.

experiment	Oxidant	Seed Acidity (pH)
1	NO_3	acidic (2)
2	NO_3	neutral
3	OH	NPF
4	NO_3	acidic (2)
5	O_3	acidic (1.2)
6a	OH	acidic (2)
6b	OH	acidic (1.2)
7a	OH	neutral
7b	OH	neutral
8a	OH	neutral
8b	OH	neutral
9a	NO_3	neutral
9b	NO_3	neutral
10a	OH	NPF
10b	OH	NPF
10c	OH	acidic (1.2)
10d	NO_3	acidic (1.2)
11a	NO_3	acidic (1.2)
11b	OH	acidic (1.2)
11c	OH	acidic (1.2)
12	O_3	neutral

Preliminary results

From the chamber experiments in combination with the dual sampling setup, differences in particle mass-normalized abundances of organosulphates of more than three orders of magnitude were observed, indicating a strong effect of gaseous SO_2 on the abundance of organosulphates.

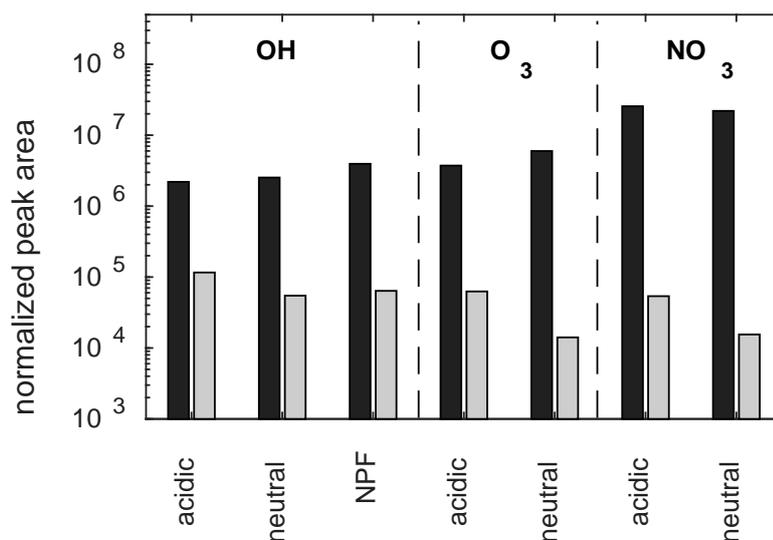


Figure 1. Total peak areas of detected OSs normalized to the total particle mass without (black bars) and with SO_2 removal (grey bars).

Overall, the effect of SO₂ removal on OS abundance was significantly enhanced under neutral conditions. Since SO₂ dissolution is known to be favored under more basic conditions,⁶ this pH dependency suggests that SO₂ solubility plays a key role in additional OS formation on the filter material. Similarly, the total number of organosulphates significantly decreased when SO₂ was absent during particle collection on the filter substrate (Figure 2).

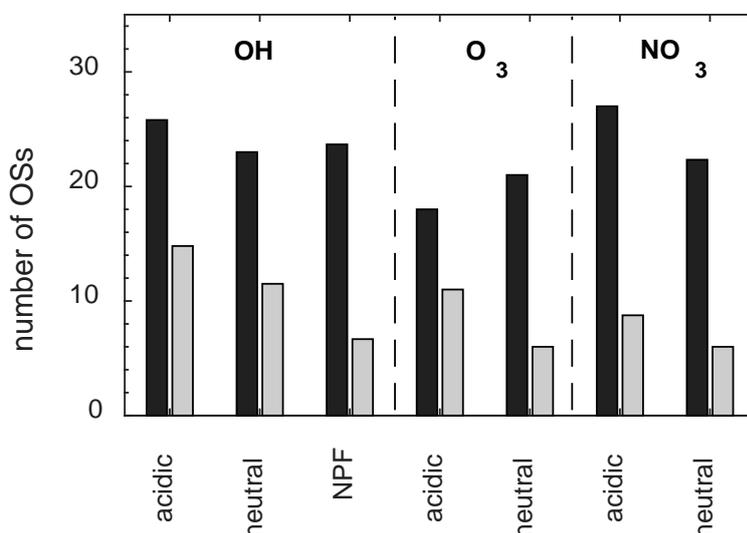


Figure 2. Total number of detected OSs without (black bars) and with SO₂ removal (grey bars).

Since neutral seed particles were isotopically labeled (i.e., ³⁴S), all detected organosulphates must be derived, directly or indirectly, from gaseous SO₂. Contributions of isotopically labeled organosulphates were not larger than the natural abundances of ³⁴S. The same conclusion applies to new particle formation experiments. Because no particulate sulfate was added in these experiments, all observed organosulphates must originate from gas-phase SO₂. Nevertheless, it is important to note that organosulphates were not exclusively formed on the filter substrate but also through well-known multiphase and heterogeneous chemistry (involving S(IV) and/or S(VI)), as organosulphates were also detected in SOA particles collected after SO₂ removal. However, the large differences between denuder and non-denuder samples demonstrate that without SO₂ removal prior to particle collection, organosulphate abundances and numbers are artificially enhanced.

Outcome and future studies

The main objectives of the proposed TNA activity were successfully completed. A high level of training was received and each of the samples were analysed, generating a reliable data set. The findings of this project will provide new insights into chemical composition. More efforts will be spent to evaluate and corroborate the findings of this project.

References

- (1) Brüggemann, M.; van Pinxteren, D.; Wang, Y.; Yu, J. Z.; Herrmann, H. Quantification of Known and Unknown Terpenoid Organosulfates in PM₁₀ Using Untargeted LC–HRMS/MS: Contrasting Summertime Rural Germany and the North China Plain. *Environmental Chemistry* **2019**. <https://doi.org/10.1071/EN19089>.
- (2) Mutzel, A.; Rodigast, M.; Iinuma, Y.; Böge, O.; Herrmann, H. Monoterpene SOA – Contribution of First-Generation Oxidation Products to Formation and Chemical Composition. *Atmospheric Environment* **2016**, *130*, 136–144. <https://doi.org/10.1016/j.atmosenv.2015.10.080>.
- (3) Mutzel, A.; Poulain, L.; Berndt, T.; Iinuma, Y.; Rodigast, M.; Böge, O.; Richters, S.; Spindler, G.; Sipilä, M.; Jokinen, T.; Kulmala, M.; Herrmann, H. Highly Oxidized Multifunctional Organic Compounds Observed in Tropospheric Particles: A Field and Laboratory Study. *Environmental Science & Technology* **2015**, *49* (13), 7754–7761. <https://doi.org/10.1021/acs.est.5b00885>.
- (4) Pluskal, T.; Castillo, S.; Villar-Briones, A.; Oresic, M. MZmine 2: Modular Framework for Processing, Visualizing, and Analyzing Mass Spectrometry-Based Molecular Profile Data. *BMC bioinformatics* **2010**, *11* (1), 395. <https://doi.org/10.1186/1471-2105-11-395>.
- (5) Pluskal, T.; Uehara, T.; Yanagida, M. Highly Accurate Chemical Formula Prediction Tool Utilizing High-Resolution Mass Spectra, MS/MS Fragmentation, Heuristic Rules, and Isotope Pattern Matching. *Analytical Chemistry* **2012**, *84* (10), 4396–4403. <https://doi.org/10.1021/ac3000418>.
- (6) Seinfeld, J. H.; Pandis, S. N. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*; Wiley: New York, 2006.