Introduction of the OrGanic Tracers and Aerosol Constituents - Calibration Centre (OGTAC-CC)

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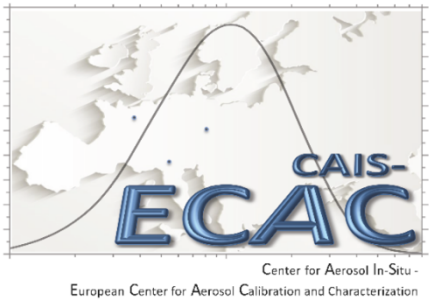
1st OGTAC-CC community meeting within the framework of the ECAC-CAIS CF 04/2024

Leibniz Association

TROPOS
Leibniz Institute for Tropospheric Research

Overview

1) Introduction ACTRIS-D
2) ACTRIS @TROPOS and ACTRIS @Atmospheric Chemistry Department (ACD)
3) Organic Tracers and Aerosol Constituents – Calibration Centre (OGTAC-CC) @ACTRIS
   - Former activities within Eurochamp-2020
   - Ongoing work and current status
   - Planned activities



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ACTRIS-D

The German contribution to the European Research Infrastructure for aerosol, clouds and trace gases

ACTRIS @TROPOS
ACTRIS @TROPOS ACD

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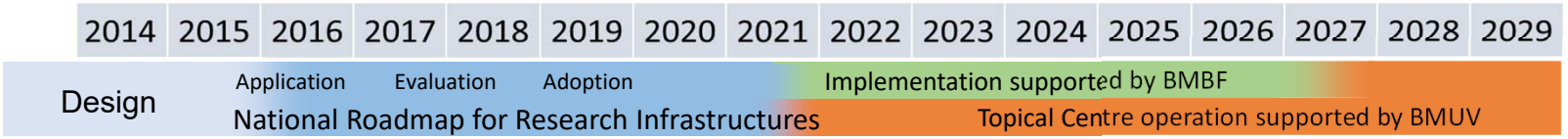
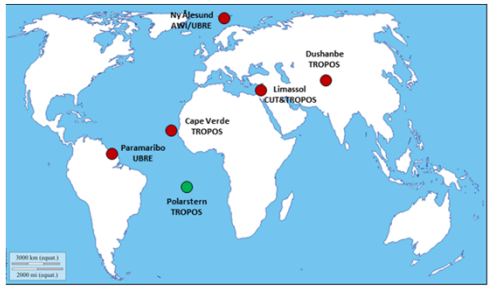
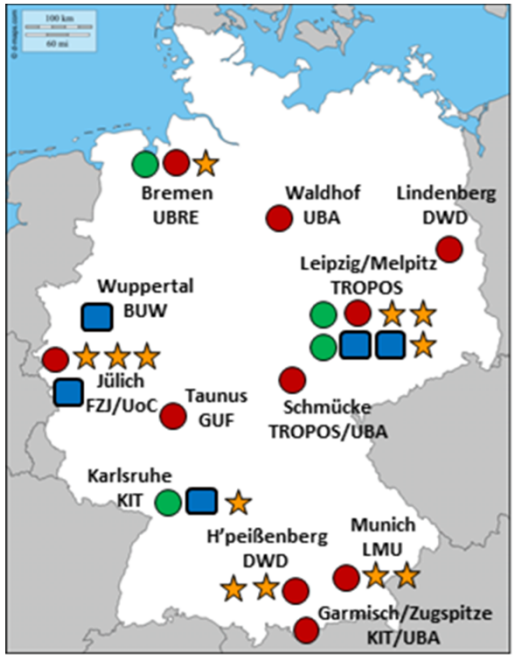
ACTRIS-D



- ACTRIS-D started in 2021 with 11 German partner institutions, led by TROPOS
- Implementation phase 2021-2026 is supported with 86 Mio. Euro by the BMBF (Federal Ministry of Education and Research)
- 27 NFs and 12 TCs in total
  - ➢ 15 Observational platforms
  - ➢ 5 Atmospheric simulation chambers
  - ➢ 7 Mobile platforms

  } Exploratory platfoms





- Operation supported by the BMUV (Federal Ministry for the Environment, Nature, Conservation, Nuclear Safety and Consumer Protection) since the **European Research Infrastructure Consortium (ERIC) was established** in March 2023

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TROPOS facilities

Topic Centre Units

World Calibration Center for Aerosol Physics (WCCAP)

OrGanic Tracers and Aerosol Constituents - Calibration Centre (OGTAC-CC)

Centre for Cloud Water Chemistry (CCWaC)

Observational Platforms

Melpitz Research Station

PollyNET

German Ultrafine Aerosol Network (GUAN)

Cape Verde Atmospheric Observatory (CVAO)

Schmücke Cloud Observatory (SCO)

Exploratory Platforms

Atmospheric Chemistry Department Chamber (ACD-C)

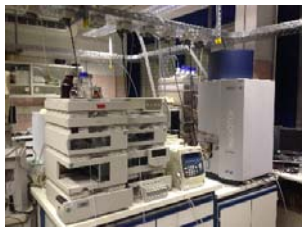
Turbulent Leipzig Aerosol Cloud Interaction Simulator (LACIS-T)

Leipzig Aerosol and Cloud Remote Observations System (LACROS)

Mobile shipborne facility (OCEANET)

Mobile shipborne facility on Polarstern-2 (OCEANET-2)

Aerosol from ground to Cloud Mobile Experiment (ACME)











Overview of former, current and planned activities of the OrGanic Tracers and Aerosol Constituents - Calibration Centre (OGTAC-CC)

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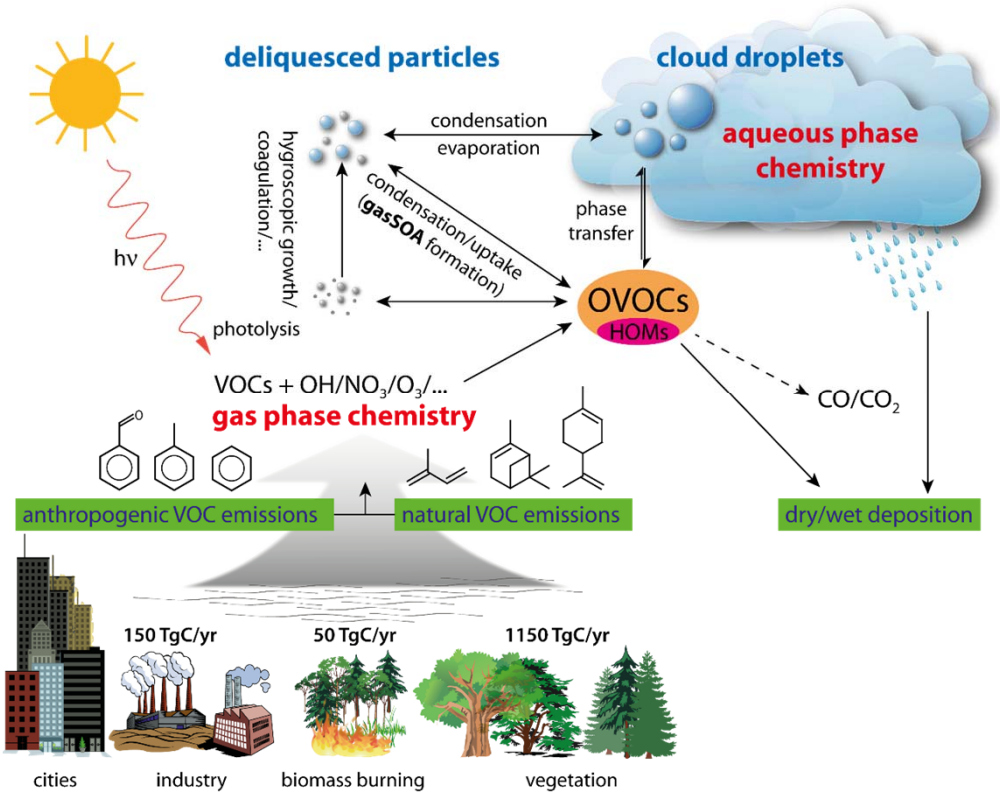
General overview

Why measuring organic tracers and aerosol constituents?

- Aerosol, clouds and trace gas understanding need the information on physical and chemical aerosol properties
- Gain detailed knowledge on aerosol chemical composition
- Improve the understanding on evolution in the atmosphere (transformation processes)
- Provide important compound specific input data for high quality source apportionment of organic aerosol and PM in addition to OC/EC and ACSM/AMS data



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General overview – former activities

Established as training/calibration centre within EUROCHAMP-2020

EUROCHAMP 2020

2 main activities:

- Training
- Interlaboratory comparisons

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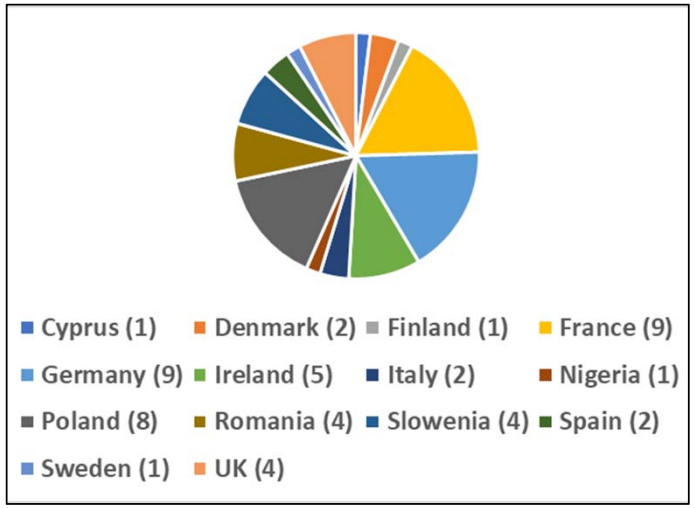
TRAINING

- 14 training sessions conducted within EUROCHAMP-2020 with 53 participants

- Individual trainings via TNAs or group trainings in forms of hands-on training workshops
- Lectures in atmospheric particle related chemical analysis
- Training sessions for the analysis of atmospherically relevant particulate products: filter collection, extraction, derivatization and enrichment procedures, analysis and quantification using state-of the-art instrumentation LC/MS; GC/MS and HPAEC/PAD

- 35% of users from EUROCHAMP partners



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General overview – former activities

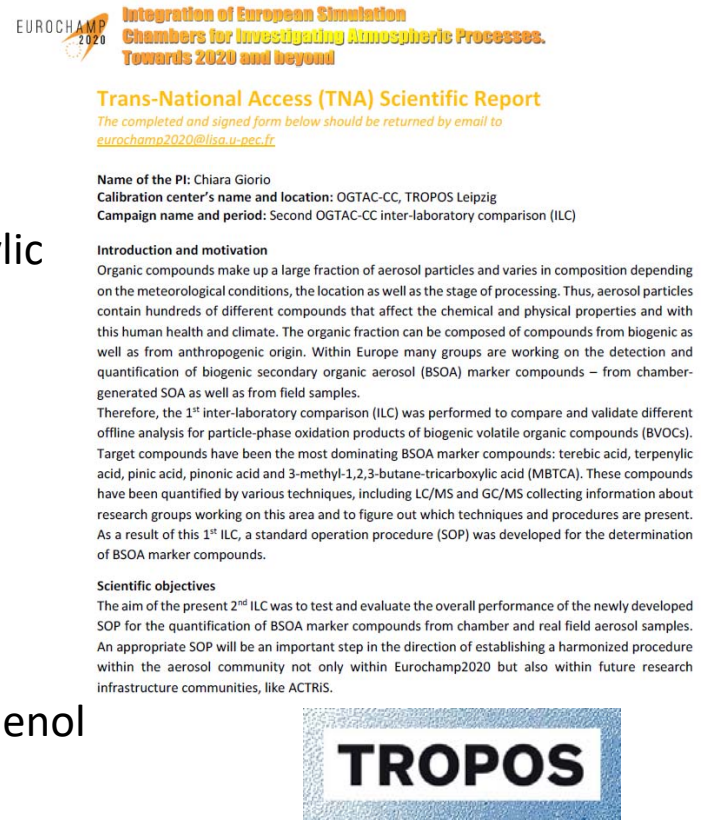
Interlaboratory comparisons (ILCs)

3 ILCs performed within the EUROCHAMP-2020 project:

→ Data evaluation according to ISO 13528 and ISO 5725-2

- **1st ILC on BSOA marker compounds w/o SOP (2018/2019)**
  - 9 participants (6 from Europe and US, 2 from Germany and TROPOS)
  - *MBTCA (3-methyl-1,2,3-butanetricarboxylic acid)*, terebic acid, terpenylic acid, pinic acid and pinonic acid
- **2nd ILC on BSOA marker compounds w/ draft SOP (2019-2021)**
  - 5 participants (4 from Europe and US and TROPOS)
- **3rd ILC on ASOA marker compounds w/o SOP (2021)**
  - 5 participants (4 from Europe and US and TROPOS)
  - syringaldehyde, 4-nitrophenol, 4-nitrocatechol and 2-methyl-4-nitrophenol

Collaboration between EUROCHAMP-2020 and ACTRIS-2 (WP3 Lead Erik Swietlicki (ULUND))



EUROCHAMP 2020 Integration of European Simulation Chambers for Investigating Atmospheric Processes. Towards 2020 and beyond

Trans-National Access (TNA) Scientific Report

The completed and signed form below should be returned by email to eurochamp2020@lisa.u-pec.fr

Name of the PI: Chiara Giorio
Calibration center's name and location: OGTAC-CC, TROPOS Leipzig
Campaign name and period: Second OGTAC-CC inter-laboratory comparison (ILC)

Introduction and motivation

Organic compounds make up a large fraction of aerosol particles and varies in composition depending on the meteorological conditions, the location as well as the stage of processing. Thus, aerosol particles contain hundreds of different compounds that affect the chemical and physical properties and with this human health and climate. The organic fraction can be composed of compounds from biogenic as well as from anthropogenic origin. Within Europe many groups are working on the detection and quantification of biogenic secondary organic aerosol (BSOA) marker compounds – from chamber-generated SOA as well as from field samples.

Therefore, the 1st inter-laboratory comparison (ILC) was performed to compare and validate different offline analysis for particle-phase oxidation products of biogenic volatile organic compounds (BVOCs). Target compounds have been the most dominating BSOA marker compounds: terebic acid, terpenylic acid, pinic acid, pinonic acid and 3-methyl-1,2,3-butane-tricarboxylic acid (MBTCA). These compounds have been quantified by various techniques, including LC/MS and GC/MS collecting information about research groups working on this area and to figure out which techniques and procedures are present. As a result of this 1st ILC, a standard operation procedure (SOP) was developed for the determination of BSOA marker compounds.

Scientific objectives

The aim of the present 2nd ILC was to test and evaluate the overall performance of the newly developed SOP for the quantification of BSOA marker compounds from chamber and real field aerosol samples. An appropriate SOP will be an important step in the direction of establishing a harmonized procedure within the aerosol community not only within Eurochamp2020 but also within future research infrastructure communities, like ACTRiS.

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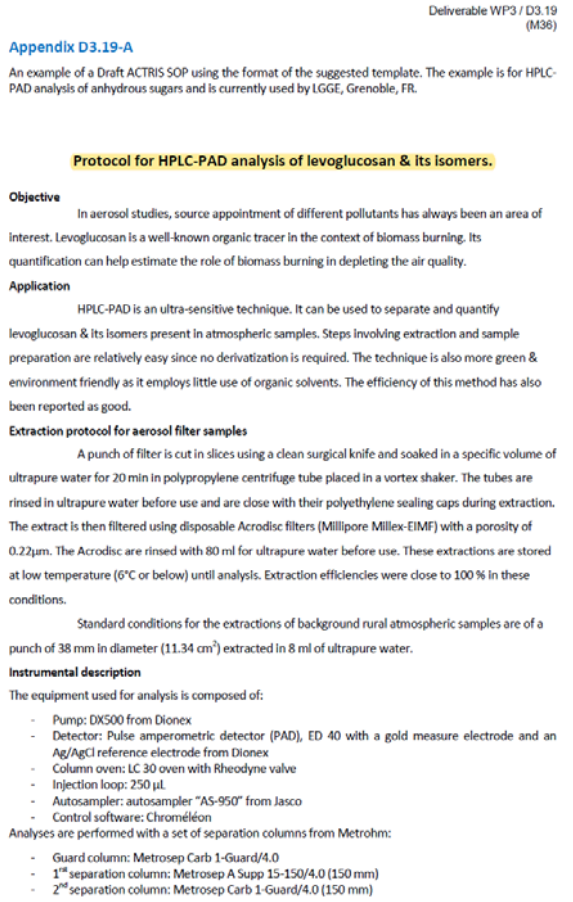
Former ACTRIS activities

By Erik Swietlicki, Karl Espen Yttri, Jean-Luc Jaffrezo et al.

Biomass Burning as source:

- Levoglucosan, Mannosan, Galactosan – ILC performed within ACTRIS-2 [1] → Methods: HPLC/ESI-MS, HPAEC-PAD, GC/MS
- ➢ Analytical methods are significantly different regarding sample preparation (extraction, derivatization), separation and detection
- ➢ All methods seem to be reliable making a general European SOP complex
- ➢ Draft SOP (protocol) available from ACTRIS PPP WP3-NA3 Deliverable D3.19 using HPLC-PAD
- ➢ Publication "An intercomparison study of analytical methods used for quantification of levoglucosan in ambient aerosol filter samples" in AMT 2015



Deliverable WP3 / D3.19
(M36)

Appendix D3.19-A

An example of a Draft ACTRIS SOP using the format of the suggested template. The example is for HPLC-PAD analysis of anhydrous sugars and is currently used by LGGE, Grenoble, FR.

Protocol for HPLC-PAD analysis of levoglucosan & its isomers.

Objective

In aerosol studies, source appointment of different pollutants has always been an area of interest. Levoglucosan is a well-known organic tracer in the context of biomass burning. Its quantification can help estimate the role of biomass burning in depleting the air quality.

Application

HPLC-PAD is an ultra-sensitive technique. It can be used to separate and quantify levoglucosan & its isomers present in atmospheric samples. Steps involving extraction and sample preparation are relatively easy since no derivatization is required. The technique is also more green & environment friendly as it employs little use of organic solvents. The efficiency of this method has also been reported as good.

Extraction protocol for aerosol filter samples

A punch of filter is cut in slices using a clean surgical knife and soaked in a specific volume of ultrapure water for 20 min in polypropylene centrifuge tube placed in a vortex shaker. The tubes are rinsed in ultrapure water before use and are close with their polyethylene sealing caps during extraction. The extract is then filtered using disposable Acrodisc filters (Millipore Millex-EIMF) with a porosity of 0.22µm. The Acrodisc are rinsed with 80 ml for ultrapure water before use. These extractions are stored at low temperature (6°C or below) until analysis. Extraction efficiencies were close to 100 % in these conditions.

Standard conditions for the extractions of background rural atmospheric samples are of a punch of 38 mm in diameter (11.34 cm^2) extracted in 8 ml of ultrapure water.

Instrumental description

The equipment used for analysis is composed of:

- Pump: DX500 from Dionex
- Detector: Pulse amperometric detector (PAD), ED 40 with a gold measure electrode and an Ag/AgCl reference electrode from Dionex
- Column oven: LC 30 oven with Rheodyne valve
- Injection loop: 250 µl
- Autosampler: autosampler "AS-950" from Jasco
- Control software: Chromeleon

Analyses are performed with a set of separation columns from Metrohm:

- Guard column: Metrosep Carb 1-Guard/4.0
- 1st separation column: Metrosep A Supp 15-150/4.0 (150 mm)
- 2nd separation column: Metrosep Carb 1-Guard/4.0 (150 mm)

[1] K.E. Yttri, J. Schnelle-Kreis, W. Maenhaut, G. Abbaszade, C. Alves, A. Bjerke, N. Bonnier, R. Bossi, M. Claeys, C. Dye, M. Evtyugina, D. Garcia-Gacio, R. Hillamo, A. Hoffer, M. Hyder, Y. Iinuma, J.L. Jaffrezo, A. Kasper-Giebl, G. Kiss, P.L. Lopez-Mahia, C. Pio, C. Piot, C. Ramirez-Santa-Cruz, J. Sciare, K. Teinila, R. Vermeylen, A. Vicente, R. Zimmermann, An intercomparison study of analytical methods used for quantification of levoglucosan in ambient aerosol filter samples, Atmos. Meas. Tech., 8 (2015) 125-147.

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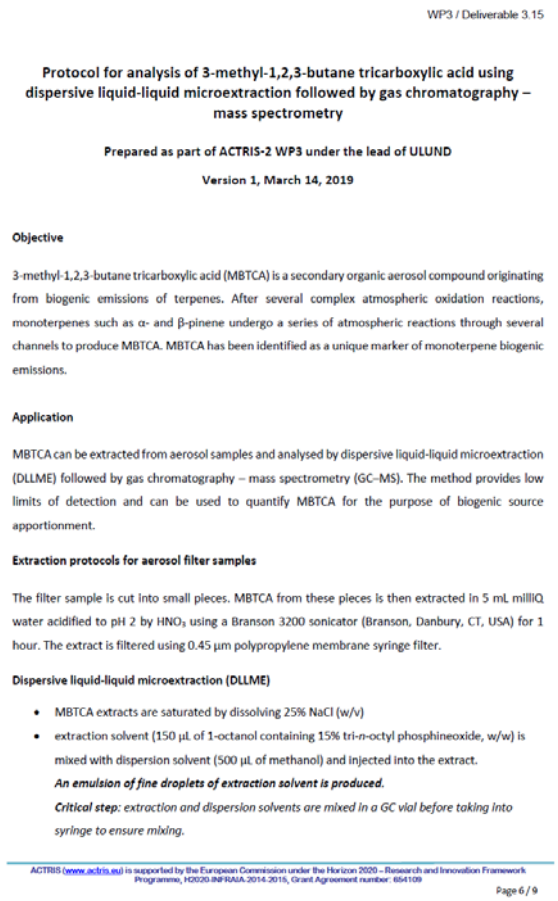
Former ACTRIS activities

By Erik Swietlicki, Karl Espen Yttri, Jean-Luc Jaffrezo et al.

Biogenic secondary organic aerosol (BSOA):

- MBTCA (3-methyl-1,2,3-butanetricarboxylic acid) – 2 ILCs performed in collaboration of EUROCHAMP2020 and ACTRIS-2
- Target compounds besides MBTCA: terebic acid, terpenylic acid, pinonic acid and pinic acid
- Methods: LC/MS, GC/MS
- Draft SOP (protocol) available for MBTCA within ACTRIS-2 WP3 Del. 3.15 using GC/MS after liquid-liquid microextraction
- Draft SOP (protocol) on the full process starting from the filter sample, extraction procedure and final analysis by LC/MS was tested within the 2nd ILC of EUROCHAMP-2020



WP3 / Deliverable 3.15

Protocol for analysis of 3-methyl-1,2,3-butane tricarboxylic acid using dispersive liquid-liquid microextraction followed by gas chromatography – mass spectrometry

Prepared as part of ACTRIS-2 WP3 under the lead of ULUND

Version 1, March 14, 2019

Objective

3-methyl-1,2,3-butane tricarboxylic acid (MBTCA) is a secondary organic aerosol compound originating from biogenic emissions of terpenes. After several complex atmospheric oxidation reactions, monoterpenes such as α- and β-pinene undergo a series of atmospheric reactions through several channels to produce MBTCA. MBTCA has been identified as a unique marker of monoterpene biogenic emissions.

Application

MBTCA can be extracted from aerosol samples and analysed by dispersive liquid-liquid microextraction (DLLME) followed by gas chromatography – mass spectrometry (GC–MS). The method provides low limits of detection and can be used to quantify MBTCA for the purpose of biogenic source apportionment.

Extraction protocols for aerosol filter samples

The filter sample is cut into small pieces. MBTCA from these pieces is then extracted in 5 mL milliQ water acidified to pH 2 by HNO_3 using a Branson 3200 sonicator (Branson, Danbury, CT, USA) for 1 hour. The extract is filtered using 0.45 µm polypropylene membrane syringe filter.

Dispersive liquid-liquid microextraction (DLLME)

- MBTCA extracts are saturated by dissolving 25% NaCl (w/v)
- extraction solvent (150 µL of 1-octanol containing 15% tri-*n*-octyl phosphineoxide, w/w) is mixed with dispersion solvent (500 µL of methanol) and injected into the extract.

An emulsion of fine droplets of extraction solvent is produced.

Critical step: *extraction and dispersion solvents are mixed in a GC vial before taking into syringe to ensure mixing.*

ACTRIS (www.actris.eu) is supported by the European Commission under the Horizon 2020 – Research and Innovation Framework Programme, H2020-INFRAIA-2014-2015, Grant Agreement number: 654109

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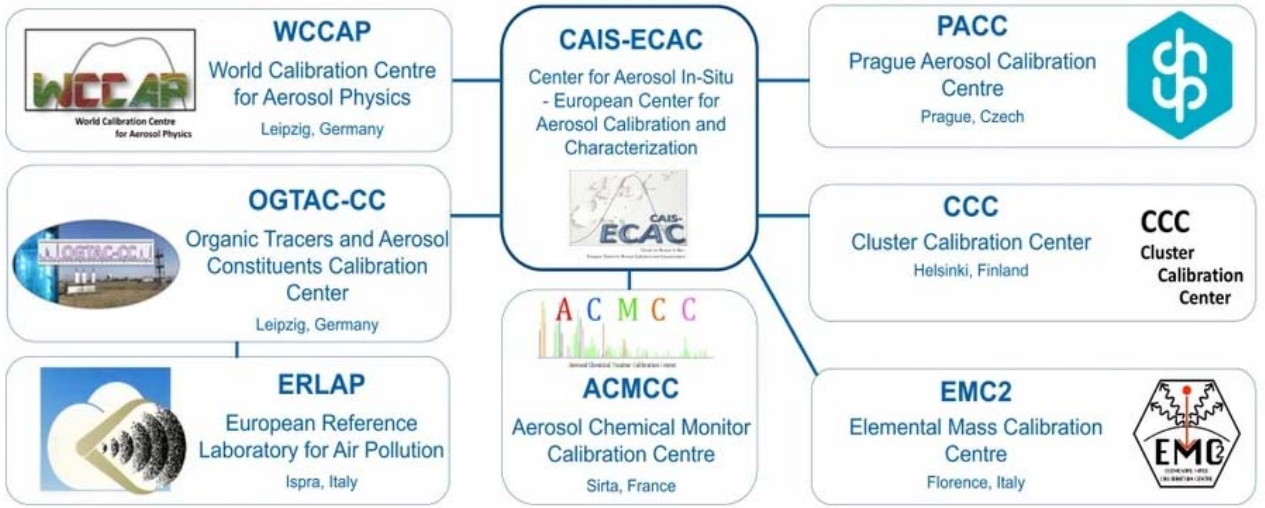
General overview – current status

- Within ACTRIS OGTAC-CC became an Aerosol in situ TC unit as one partner of the Center for Aerosol In Situ-European Center for Aerosol Calibration and Characterizatio (CAIS-ECAC)
- TC parameter: Mass concentration of particulate organic tracer compounds



CAIS-ECAC is a consortium, consisting of seven facilities. The WCCAP (World Calibration Center for Aerosol Physics), PACC (Prague Aerosol Calibration Center), and CCC (Cluster Calibration Center) are responsible for aerosol microphysical and optical aerosol variables. The OCTAC-CC (Organic Tracer and Aerosol Constituents - Calibration Center), ERLAP (European Reference Laboratory for Air Pollution), the ACMCC (Aerosol Chemical Monitor Calibration Center) and EMC2 (Element Mass Calibration Center) are in charge of the chemical & elemental aerosol variables.

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General overview – current status

ACTRIS Standard Procedures for In-Situ Aerosol Sampling, Measurements, and Analyses at ACTRIS Observatories

ACTRIS-ERIC Version 1.0; January, 2024
Center for Aerosol In-Situ Measurement
European Center for Aerosol Calibration and Characterization (CAIS-ECAC).

ACTRIS aerosol in-situ variables

Five out of the 12 ACTRIS aerosol in-situ variables are obligatory for NFs (observatories). The number of obligatory variables for exploratory and mobile platforms may differ and is explained elsewhere.

Obligatory ACTRIS aerosol in-situ variables for observatories:

- Particle number concentration D_{P50} = 10 nm (EN-16976)
- Particle number size distribution – mobility diameter 10 to 800 nm (CEN/TS-17434) [1)]
- Particle light scattering & backscattering coefficient - multi-wavelength [2)]
- Particle light absorption coefficient and/or equivalent black carbon concentration [2)]
- At least one additional variable from the list below, preferably a variable on particle chemical or elemental composition, considering the scientific program of the NF.

TROPOS

General overview – current status

ACTRIS Standard Procedures for In-Situ Aerosol Sampling, Measurements, and Analyses at ACTRIS Observatories

ACTRIS-ERIC Version 1.0; January, 2024
Center for Aerosol In-Situ Measurement
European Center for Aerosol Calibration and Characterization (CAIS-ECAC).

Other ACTRIS aerosol in-situ variables:

- Nano-particle number concentration (D_{P50} < 10 nm)
- Nano-particle number size distribution < 10 nm
- Particle number size distribution - aerodynamic diameter 0.8 to 10 µm [3)]
- Cloud condensation nuclei number concentration
- Mass concentration of particulate organic tracers / unit: (ng m^{-3})
- Mass concentration of particulate organic and elemental carbon [4)]
- Mass concentration of non-refractory particulate organics and inorganics within PM1 fraction [5,6)]
- Mass concentration of particulate elements [2)]

OGTAC-CC @TROPOS

subcontracting

European Reference Laboratory for Air Pollution – ERLAP, Italy

Dr. Fabrizia Cavalli
(fabrizia.cavalli@ec.europa.eu)

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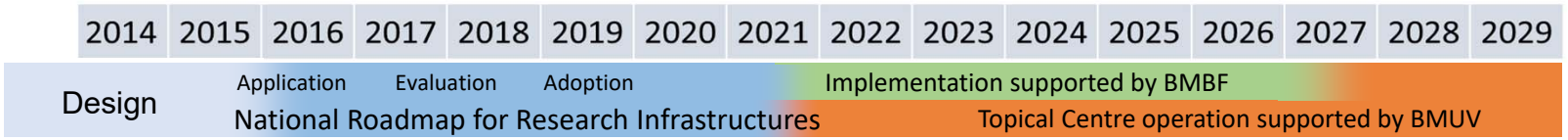
Current status within implementation phase



2 main pillars remain:

1) Training of operators and scientists – operational activity

2) Calibration Centre Activities – task chain

a) implementation → b) operation

\+ Trans National Access (TNA), but currently no official project running

TROPOS

Hands-on training workshop March and November 2023 @TROPOS ACD, Leipzig (Germany)

1) Training of operators and scientists

1st training within ACTRIS performed in March 2023 @TROPOS

2nd training @TROPOS in November 2023

<u>Topic:</u> Theory and practice - determination of organic tracers and aerosol constituents from sampling to the final result demonstrated for the future ACTRIS platforms Melpitz (observational) and ACD-C (exploratory)

Planned activities within implementation phase

2) Calibration Centre Activities – task chain

- Definition of target compounds, e.g., biomass burning or on secondary organic aerosol constituents of biogenic and anthropogenic origin
- Set up technical requirements, for all steps from sampling to the quantitative result, set Data Quality Objectives (DQO)
- Development of measurement guidelines based on the technical requirements and Interlaboratory Comparisons (ILCs)
- Standard Operating Procedure (SOP) templates needs to be finalized by each NF individually together with the calibration centre
- NF individual SOP will finally need approval by the calibration centre
- Define QA/QC procedures, e.g., performance test by ILCs
- Develop workflow for offline data submission

→ All in close collaboration with the NFs!!!

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Agenda

1st OGTAC-CC community meeting 2024 (online) – Agenda Tuesday April 9	
13:00 - 13:15	Welcome
13:15 - 13:45	Introduction of OGTAC-CC
13:45 - 14:30	Presentation of the Technical Requirements and discussion part 1
	- Draft list of target compounds
	- Sampling procedure
	- Sample pre-treatment, storage and transport
	- Maintenance (Sampling)
14:30 - 14:45	Coffee break
14:45 - 15:30	Presentation of the Technical Requirements and discussion part 2
	- Data resolution, coverage and provision
	- Sample handling and preparation in the laboratory
	- Recommended and supported analytical techniques
15:30 - 16:00	Outlook on the Measurement Guidelines
16:00 - 16:15	Coffee break
16:15 - 16:45	Introduction ILC autumn 2024
16:45 - 17:00	Time for further discussion

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