WP3: Task 3.1

Subtask on:

Organic tracer measurements

Erik Swietlicki, ULUND

ACTRIS-2 WP3

Athens, Greece

10 Nov 2015

European Commission

JRC REFERENCE REPORTS

European Guide on Air Pollution Source Apportionment with Receptor Models

Claudio A. Belis, Bo R. Larsen, Fulvio Amato, Imad El Haddad, Olivier Favez, Roy M.Harrison, Philip K. Hopke, Silvia Nava, Pentti Paatero, André Prévôt, Ulrich Quass, Roberta Vecchi, Mar Viana

2014

Report EUR 26080 EN

Joint Research Centre

Organic Tracers – ACTRIS-2

Proposal and Grant Agreement, Task 3.1:

. . . with the aims
to **increase the amount and quality of delivered data**,
to **control implementation of existing Standard Operation Procedures (SOP)** and
to **eventually propose revisions**.

This will be achieved via
- **inter-laboratory comparison exercises** (round-robin),
- **use of ACTRIS TNA** (WP8) . . .

ACTRIS-2 will maintain and further optimize the procedures when necessary.
In addition to **core variables** controlled in ACTRIS (Organic/Elemental carbon – OC/EC-, . . . and **specific organic tracers**), ACTRIS-2 will implement control procedures for . . . , and **one additional organic tracer** for which SOPs were recently agreed upon in ACTRIS.

Organic Tracers – ACTRIS-2

Proposal and Grant Agreement, Task 3.1:

The frequency of QA/QC activities follows ACTRIS implementation plan and covers **at least one exercise in two different years of the project for each considered variable**.

. . . , **inter-laboratory comparison (ILC) studies will be also performed for selected organic aerosol (OA) tracers** used **for OA source apportionment**.

Organic Tracers – ACTRIS-2

Proposal and Grant Agreement, Task 3.1:

The ILC will use both **synthetic standards and ambient air test samples** to

- **support the establishment of SOPs** for variables not already addressed by ACTRIS, such as

- **tracers for primary and secondary OA from biogenic sources**, as well as
- **traffic OA**,

and to

- **determine the quality performance of the participating laboratories.**

Deliverables

WP3 – Task 3.1 Organic Tracers

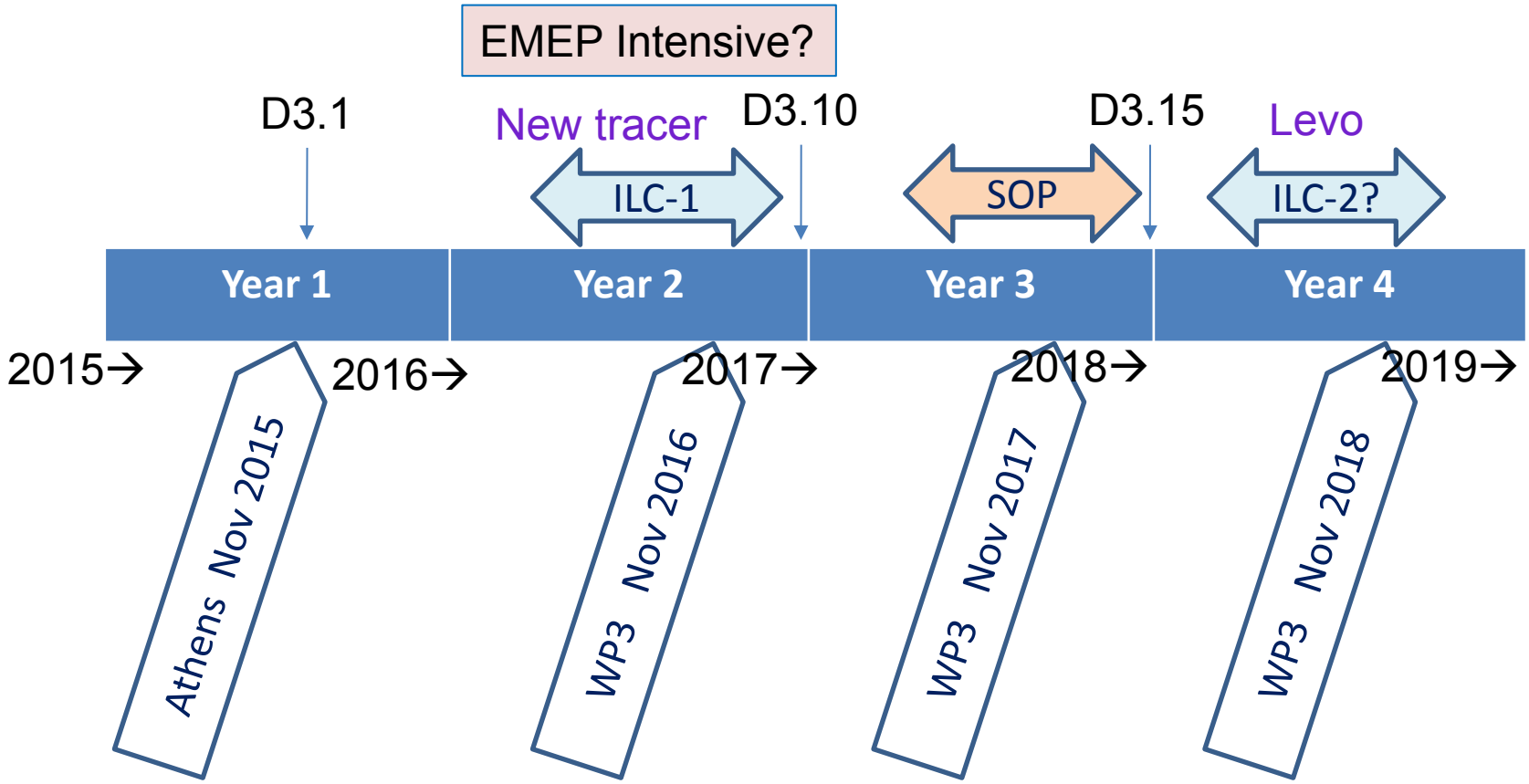
Lead Partner: ULUND, Duration: M1-M48

Deliv#	Title	Dissemination	Delivery date
D3.1	**Expert workshop to determine the targeted set of OA tracers (TROPOS)** Athens Nov 2015	Public Report	M6 Nov-Dec 2015
D3.10	**Inter-laboratory comparison (ILC)** studies for the targeted set of OA tracers (CNRS)	Confidential	M24
D3.15	**Standard Operating Procedures (SOPs)** for the targeted set of OA Tracers (ULUND)	Public Report	M36

ACTRIS-2 Deliverables

WP3 – Task 3.1 Organic Tracers

Lead Partner: ULUND, Duration: M1-M48



ACTRIS-1 Deliverable D3.19

Intercomparisons

Intercomparison studies are essential elements of ACTRIS, since they are the tool by which to determine the applicability of a certain SOP across the ACTRIS network.

Ideally, all suggested SOPs for organic tracers should be subjected to regular intercomparison studies, as is the case already for OC/EC.

Two intercomparison studies for organic tracers have been performed within ACTRIS (levoglucosan and 14C).

WP3 - Organic Tracers

Levoglucosan and isomers

ACTRIS conclusion from intercomparison studies of anhydrous sugars

There is adequate information regarding the interlaboratory applicability and suitability of anhydrous sugars (levoglucosan, mannosan, galactosan) as tracers for biomass burning for ACTRIS to suggest **Draft SOPs** for these compounds using GC, LC and HPAEC analytical techniques.

WP3 - Organic Tracers

Radiocarbon (14C) for fossil/modern carbon

ACTRIS conclusion from intercomparison studies of radiocarbon

There is adequate information from the radiocarbon intercomparison study for ACTRIS to suggest **Draft SOPs** for analysis of 14C as tracer for the fraction of modern versus fossil carbon in the organic aerosol.

SOPs are given for the analytical procedures for graphitization (normal ion source followed by 14C analysis on TC) and for a gas ion source and 14C analysis of OC/EC separately.

Suggested Organic Tracers – ACTRIS-1

Tracers/methods that should be implemented within ACTRIS WP3:

OC, EC (To be apportioned to sources)
(**YES**) Methods → Thermal-optical Analysis - EUSAAR-2 protocol

SOPs ready!

Biomass burning: Levoglucosan (mannosan, galactosan)
(**YES**) Methods → GC, LC, HPAEC

SOPs ready! ILC + ILC

Modern/fossil carbon: ^{14}C on TC (if possible on OC and EC separately)
(**YES**) Method → AMS (Accelerator Mass Spectrometry)

ACTRIS-2 SOP, ILC

Traffic (gasoline, diesel): PAH, hopanes, steranes
(**YES**) Method → GC

ACTRIS-2 SOP, no ILC

Mass spectrometric group analysis, several sources: (OC only)
(**YES**) Method → ACMS, HR-TOF-AMS (Aerodyne)

ACTRIS-2 SOP!

Suggested Organic Tracers – Task 3.1

Tracers and methods that should be further considered within ACTRIS-2 WP3:

Biogenic sources

Suggested for ACTRIS-2

Biogenic SOA formed from BVOC

3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA) (LC/ESI-MS)
Unique tracer compound for terpene BSOA. (low-volatility product).
Oxidation product of α-pinene (pinonic acid).

Primary biogenic (Fungal spores): Mannitol, arabitol, trehalose
(**Probably**) Method → LC, HPAEC

Option for ACTRIS-2

Primary biogenic (Plant debris): Cellulose
(**Probably not**) Method → Enzymatic method by Kunit and Puxbaum (1996).

Suggested tracers require ILC to support SOPs !

Suggested Organic Tracers – Task 3.1

Tracers and methods that should be further considered within ACTRIS-2 WP3:

Traffic sources (no really ideal tracer in remote air)

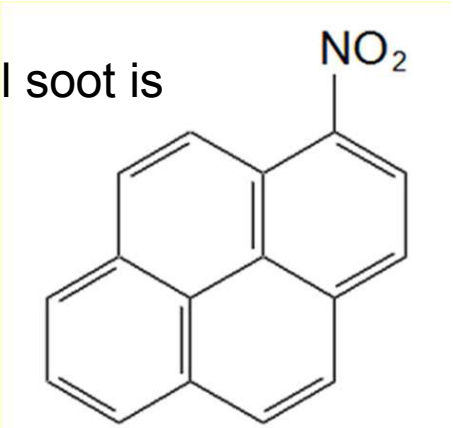
No new organic tracer suggested (for ILC)

PAH: Not unique for traffic (SOP for GC-MS exist)

Hopanes, steranes: Unique (oil products) but low concentration in remote air.

Nitro-PAH: In many European countries Diesel soot is the main source of direct Nitro-PAH emissions. Low concentration in remote air.

1-Nitropyrene (particle bound)



Additional Organic tracers that were considered – D3.7/D3.14

- Cholesterol (meat cooking)
- Methoxyphenols (tracer for combustion of lignin in wood)
- Glucose (biomass burning, fungi, soil biota)
- Ergosterol (fungi)
- Erythritol (lichens)
- Fructose (lichens)
- Mannose and galactose (soil biota)
- Organosulphates (anthropogenic/biogenic source mixing)
- Methane sulfonic acid (MSA, marine SOA)
- Methyltetrols, terpenoic acids (BSOA)

Suggested Organic Tracers – D3.7/D3.14

The criteria for organic tracer compounds are that they should:

- be unique to a specific source and emitted in sufficient quantities from this source;
- be possible to sample and analyze with reasonable accuracy, precision and cost;
- have low vapour pressures (so that they partition preferentially to the particle phase);
- be stable (at least a few days lifetime in particulate phase).

Additional Organic tracers to be considered – D3.7/D3.14

Biogenic SOA formed from BVOC

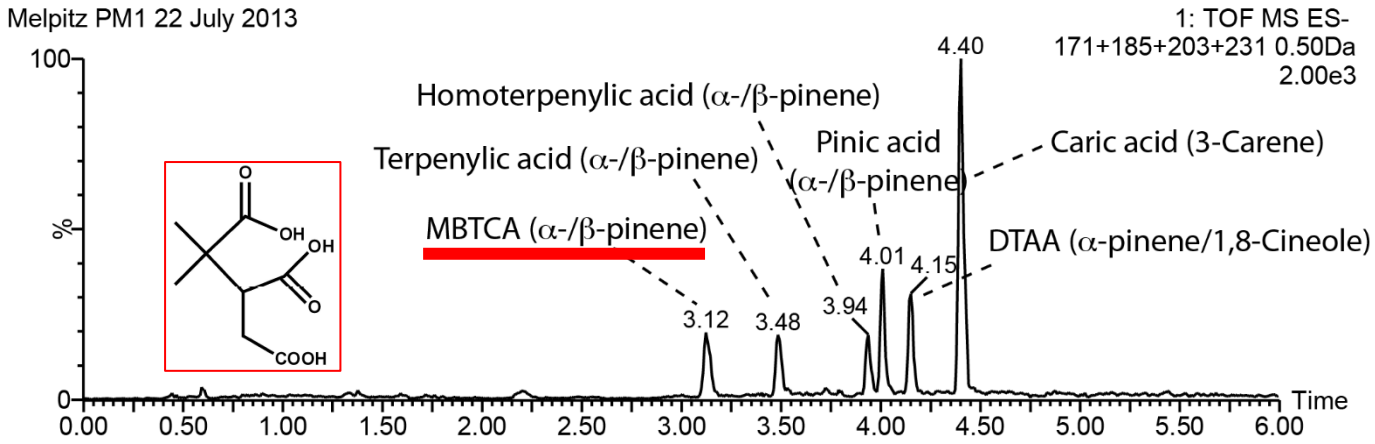
3-methyl-1,2,3-butanetricarboxylic acid (3-MBTCA) (LC/ESI-MS)
Unique tracer compound for terpene BSOA. (low-volatility product).
Oxidation product of α-pinene.

Issues:

- The relative yields of BSOA components are not adequately known or constrained;
- There is a lack of authentic standard compounds;
- There is as yet no standardized analytical procedure;
- Smog chamber BSOA may differ significantly from ambient BSOA;
- Many BSOA peaks are not identified;
- Structural elucidation is an extremely daunting task;
- BVOCs that are significant contributors to ambient BSOA may have been overlooked.

BSOA

An example of extracted ion chromatogram from LC/MS analysis in Melpitz sample



- A number of BSOA marker compounds in both July 2013 and May 2014 samples
- They can be attributed to α-pinene, β-pinene and 3-carene originating BSOA compounds
  - Very intensive 3-carene SOA peaks

TROPOS

Atmos. Chem. Phys., 12, 1483–1496, 2012
www.atmos-chem-phys.net/12/1483/2012/
doi:10.5194/acp-12-1483-2012

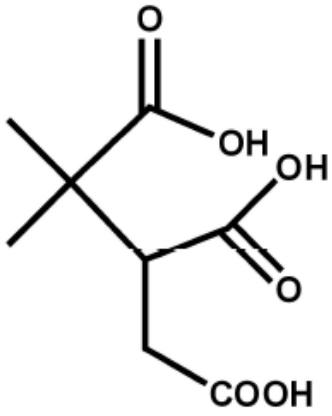
Atmospheric Chemistry and Physics

Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid – a mass spectrometric study of SOA aging

L. Müller[1], M.-C. Reinnig[1], K. H. Naumann[2], H. Saathoff[2], T. F. Mentel[3], N. M. Donahue[4], and T. Hoffmann[1]

Conclusions

This study confirms 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) as an important low volatility aging product of the gas-phase oxidation of pinonic acid.



MBTCA was observed and characterized by . . . filter analysis via **liquid chromatography-ESI-mass spectrometry**.

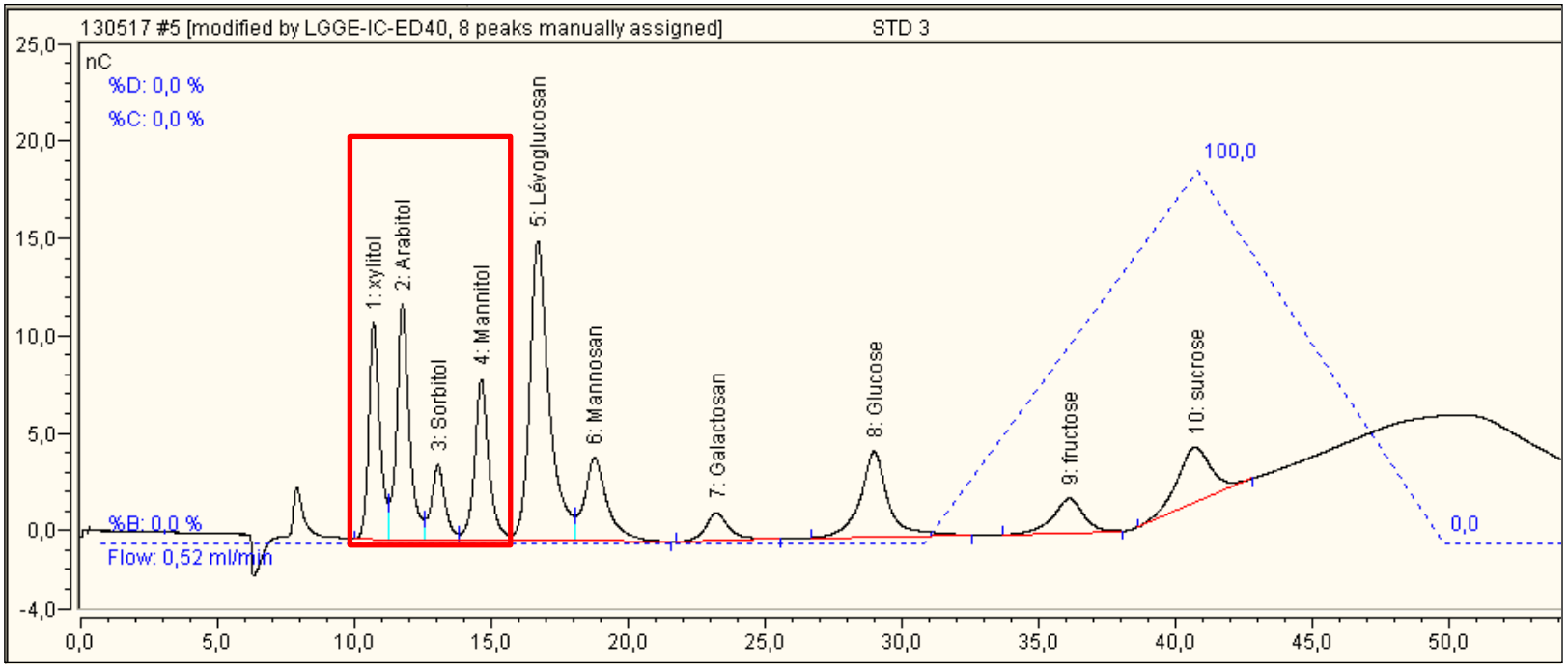
The formation of **MBTCA explains about 10% of the newly formed SOA mass**.

The experimental **yield** was determined to be **about 0.61 %.**

Additional Organic tracers to be considered

Primary biogenic (Fungal spores, soil biota):
Mannitol, arabitol, sorbitol (polyols)
(**Possible**) Method → LC (same as for levoglucosan), (HPAEC)

From ACTRIS SOP for levoglucosan (HPLC-PAD, Jean-Luc Jaffrezo)



WP3 - Organic Tracers

Lead Partner: ULUND, Duration: M1-M48

What is the level of OA source apportionment we need to achieve?

A more general separation would be according to the following categories:

- Fossil/modern combustion (for OC/EC)
- Natural versus anthropogenic sources (for OC/EC)
- Primary/secondary OA

On a more specific level, the following OA source categories are of interest:

- Traffic (diesel, gasoline, possibly also biofuels)
- Residential wood burning, agricultural fires, forest fires
- Cooking OA
- Marine OA
- Possibly also fixed combustion sources

Suggested Organic Tracers – Task 3.1

Tracers and methods that should be further considered within ACTRIS-2 WP3:

Biogenic sources

Suggested for ACTRIS-2

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Option for ACTRIS-2

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(**Probably not**) Method → Enzymatic method by Kunit and Puxbaum (1996).

No new organic tracer for traffic suggested (for ILC)

Suggested tracers require ILC to support SOPs !