

**WP3- NA3: In-situ chemical, physical and optical properties of aerosols**  
**Deliverable D3.7: Expert workshop for organic tracer**  
**measurements**

**Compiled by Erik Swietlicki (ULUND) after comments from ACTRIS partners.**  
**Minutes are based on notes taken by Julie Cozic (LGGE).**

The expert workshop for organic tracer measurements was held at the European Commission's Joint Research Centre in Ispra, Italy, from 25-26 October 2011 as part of the ACTRIS WP3/WP4 technical workshop.

The overall goal of this workshop was to initiate the work within ACTRIS to develop standardized operation protocols (SOP) for sampling and quantification of organic tracers for source identification and apportionment. Furthermore, the workshop drew up plans regarding the implementation of sampling and analysis of organic tracers for source identification.

At the time of the Expert workshop and the submittal of this deliverable (D3.7 in M12), we judge it to be premature to establish the SOPs for organic tracers. Although SOPs do exist for various EU nations, these differ in their respective details and are not straightforward to harmonize on the European scale. Furthermore, the meeting debated whether SOPs should indeed be settled within the time frame of ACTRIS, since the field of analytical chemistry and organic aerosol analysis is rapidly developing. Fixing operation procedures within Europe might hinder this development, which might then be detrimental for future studies on organic aerosols and their apportionment.

Nevertheless, this workshop marks the start of the process leading forward towards more standardized procedures in Europe, realizing that there must be room for further development within the ACTRIS community and beyond. The second deliverable of this WP3 effort is due in M24, and will report on the further progress of this activity during the second year of ACTRIS (D3.14; "Standardization of sampling and analysis of specific organic tracers", public report, M24).

The agenda and participant list from the meeting can be downloaded from the ACTRIS intranet:  
<http://www.actris.net/Members/Meetings/WPMeetings/tabid/4637/Default.aspx>

The presentations and minutes are also found there:  
<http://www.actris.net/Members/Meetings/WPMeetings/WP3meeting2428Oct2011/tabid/5013/Default.aspx>.

## Minutes from the Meeting

### Introduction (Erik Swietlicki)

(ppt presentation available for more details)

Erik Swietlicki summarized the objectives and tasks for WP3 Organic tracers:

- To develop standardized protocols for sampling and quantification of organic tracers for source identification
- Implementation of sampling and analysis of organic tracers for source identification

This Ispra meeting constitutes the “Expert workshop on organic tracer measurements” that was scheduled for Year-1 (latest M12). A report of this workshop will also be the first deliverable of this activity (D3.7, M12). The related WP3 deliverables are:

- Expert workshop on organic tracer measurements (D3.7, public report, M12)
- Standardization of sampling and analysis of specific organic tracers (D3.14, public report, M24)
- Implementation of organic tracer measurements at European sites (D3.19, public report, M36)

According to the *original plans*, the source apportionment of the organics aerosol mass (OA) fraction will be performed on the basis of

- a) Monosaccharide anhydrides as tracers for biomass combustion (levoglucosan, mannosan, galactosan),
- b) Molecular tracers (vehicles, petroleum, plant waxes, microbial, higher plants, meat cooking, tire wear...),
- c) Spectral fingerprints and H-NMR (biomass etc), AMS, and
- d)  $^{14}\text{C}$  (modern/fossil carbon)

New analytical techniques and methodologies for OA source apportionment should nevertheless be considered, and scrutinized with regard to their suitability within ACTRIS.

### Planning actions for the 3 years

Throughout the meeting, discussions took place regarding the workplan for the next three years of ACTRIS, and included basically four topics.

#### **Topic 1: Complete the review of activities in Europe**

- particularly on source apportionment comparisons
- opportunities of campaigns in order to realize comparisons

#### **Topic 2: Realization of comparisons of analytical methods**

- Comparisons and consideration of uncertainties and artifacts

#### **Topic 3: Proposition / definition of a common measurement campaign**

- Discussion on how to proceed with WP3 to meet objectives and milestones
- Decision on who will undertake OA tracers sampling (not funded by ACTRIS).

#### **Topic 4: Synthesis, definition of standardized methods**

- Identification of obstacles and additional research that need to be undertaken.
- How to proceed on establishing SOPs for the chosen analytical methods?

### Source apportionment: Analytical methods for organic tracers ( $^{14}\text{C}$ , GC-MS, HPLC, HNMR, AMS etc...)

#### **Analytical techniques for organic tracers – French experiences**

(ppt presentation available for more details)

Christine Piot (LGGE) presented the work of three French groups. These have developed, and are currently implementing, well established sampling and analytical protocols that are suitable for AQ networks. These protocols can serve as a basis for the future ACTRIS protocols. Their purpose is to

- gain better knowledge of chemical composition and evolution in the atmosphere

- to perform source apportionment of OA and PM

The protocols are designed with the explicit aim to enable a comprehensive determination and organic speciation on the same filter, including filters taken at rural background sites.

Sampler used: Hi-Vol and Low-Vol, daily sampling

Type (inlet): PM10 and PM2.5

Compounds: OC, EC, ions, metals and trace elementals, radioactive isotopes of C, organic speciation

Instrumentation for organic fraction: GC-MS, HPLC-fluo, HPLC-ESI-MS/MS

16 PAH were recommended and measured.

Extraction:

- optimized for the simultaneous extraction of all compounds
- Average extraction efficiency was between 90-100%

Quantification parameter:

- Authentic high quality standard
- External calibration for liquid chromatography
- Internal calibration for gas chromatography

Inorganic compounds quantified:

- Ionic species: sulfate, nitrate, chloride, ammonium, calcium, sodium, magnesium, potassium
- 50 metals and trace elements using ICP-MS

Contamination of filters during sampling and treatment

- Cleaning prior to sampling; 500°C during 10h

Questions to Christine:

- JLJ: capable of performing this on filter with PM as low as 15µg/m<sup>3</sup>
- Filter type: PALLXP56, TISSUQUARTZ QAT-UP 2500 150 MM
- HPLC-ESI-MS/MS for levoglucosan is done with the electrospray ionization

### **Organic tracers investigated in EU FP6 EUCAARI (Gyula Kiss)**

(ppt presentation available for more details)

Within WP2.4 of the EU FP6 Integrated Project EUCAARI, several analytical methods were applied for OA source apportionment.

Sources of carbonaceous aerosol identified:

- Variety of sources: fossil fuel (traffic and energy production), BB (also stubble field and agricultural waste burning), biofuel combustion, and waste burning, residential heating, cooking, biogenic emissions...
- Anthropogenic – biogenic (or both)
- Primary/secondary
- Coarse/fine
- Modern/fossil

Organic tracers investigated in EUCAARI: A large number of compounds, representative of a variety of different sources, different molarity, polar/non polar compounds.

Method development for sample preparation prior to GC-MS analysis:

- Separation into 5 fractions based on polarity
- GC-MS analysis of the 5 fractions separately

Optimization and standardization of sampling:

- Sampling media (loss of semivolatiles)

- Sampling time (loss of semivolatile)

Optimization and standardization of analysis:

- Sample preparation (recovery)
- Derivatization (agent, conditions, efficiency, degradation)
- GC-MS separation and quantification

The GC-MS approach has the advantage that it can identify and quantify a large number of organic tracers. However, it is time-consuming and requires rather expensive standards.

Problems with OA source apportionment based on organic tracers:

- Specific emission factors are not constant
- Tracers are not always stable in the atmosphere e.g. levoglucosan (M. Cruz)
- specific emission factors (levo/OC BB) vary ca 0.03-0.46 (mostly 0.06-0.016) (Fine et al, 2004, Goncalves, 2010, Schmidl et al, 2008, Sullivan et al., 2008)
- Levoglucosan can be photochemically oxidized (Hennigan et al, 2010; Cubison et al., 2011)

Combination of different approaches needed!!!!

*A possible approach:*

- Modern carbon : Biomass burning (BB)+ biogenic emission (+ cooking)  
OC-BB and EC-BB calculated from levoglucosan  
Rest of modern carbon originates from primary and secondary biogenic emission (+ cooking)  
Fossil carbon: traffic, energy production
- New challenge: biofuel (cars) combustion = modern carbon coming from traffic, This is an increasing source (ethanol, rapeseed oil)
- Modern carbon: BB + biogenic emission (+ cooking) + biofuel combustion  
Tracers from biofuel combustion are necessary!

*What do we need?*

- C14 for the separation of modern and fossil carbon (EC/OC is even better)  
*Modern carbon:*
  - Quantification of BB combustion by using organic tracers and HNMR
  - Quantification of possible contribution of biofuel burning and cooking by using organic tracers*Fossil carbon:*
  - Quantification of the contribution from traffic, energy production, tyre wear, etc by using organic tracers
- The combination of techniques is necessary!

Who within ACTRIS will do it??

Who will pay for it?

There is limited funding within ACTRIS for the actual implementation of the OA source apportionment across Europe. We therefore will have to rely on additional funding at the national level.

Question/Comment:

Jean-Philippe: it is important to also consider the 7-wavelength Aethalometer approach with the network that is already set up, since the ACTRIS DoW includes multi-wavelength light absorption measurements.

## **<sup>14</sup>C fossil/modern carbon, possibilities and problems (Nolwenn Perron)**

(ppt presentation available for more details)

The <sup>14</sup>C radioactive carbon isotope has proven to be useful for the apportionment of sources of aerosol carbon to either modern or fossil sources (which are depleted of <sup>14</sup>C).

However, there are some artificial sources of <sup>14</sup>C, of which the most important are:

- Nuclear bomb test

- Nuclear power plants
- Pharmaceutical industry

Aerosol samples are sometimes affected by  $^{14}\text{C}$  contamination. There are cases when the aerosol radiocarbon analysis shows an unexpected excess in  $^{14}\text{C}$ . Examples were shown from Lund, Sweden, where it was evident that there is significant  $^{14}\text{C}$  contamination, most likely from pharmaceutical companies near-by the sampling site. Is this a contribution from adsorbed gases such as semi-volatile VOC rich in  $^{14}\text{C}$ ?

Conclusion:

- It is impossible to perform  $^{14}\text{C}$  based source apportionment in the surroundings of  $^{14}\text{C}$  producing facilities.
  - This makes most urban  $^{14}\text{C}$  based source apportionment studies questionable.
- How far away do we have to go from the artificial  $^{14}\text{C}$  sources with our aerosol sampling?

Remaining issues:

- What about measurements with high pMC (percentage modern carbon) values, but still below the natural maximum? Should we reconsider our former measurements?
- Which tracers could help us to track sources of contamination?

Advice:

Do not hesitate to report high  $^{14}\text{C}$  values (high pMC) on your filters!! Reporting these could help others realizing this problem, and help us to avoid sources of contamination.

Ideas:

It might be possible to use inverse modeling to determine the origin of the contaminated air mass and to identify the sources.

Is it possible to get an estimated  $^{14}\text{C}$  flux from industry? Total usage of radiocarbon substances should be available, but the tricky thing is to convert this to emissions, since they vary considerably over time.

## **HNMR methods for estimating the biomass burning contribution to organic aerosol mass concentrations (Stefano Decesari)**

(ppt presentation available for more details)

### ***Concept of the method***

What is the origin of the oxygenated organic compounds in biomass burning (BB) aerosols?

- Traditional view: POA from unburned/pyrolyzed fuel (e.g. anhydrosugars)
- Emerging view: SOA (e.g. Donahue et al, 2011)
- Both can be correct: How to discriminate between them?

A possible way is to look at the aerosol WSOC functional group distribution and use this for source attribution. The analytical method used for WSOC functional group analysis is HNMR. The NMR spectra can be seen as a multivariate problem. Several methods can be used to deduce factors (sources) from the NMR spectra. PMF has shown great promise in this respect.

### ***NMR factors (from PMF)***

- They can be described in terms of "lumpings" of functional groups
- They are conceptually analogous to the AMS factors
- They are experimental specific, while we are looking for universal factor

### ***Experience from the EUCAARI project***

There are several publications in preparation describing the results from the OA apportionment based on HNMR and complementary methods.

*S. Pietro capofiume 2008 (Saarikoski et al., to be submitted)*

HR-ToF-AMS observations: BBOA not completely correctly correlated to levoglucosan, on average levoglucosan = 43% of the BBOA, but together with OOA-b the contribution of levoglucosan was 14%. We need more factors to follow the BB contribution from AMS at that site. NMR can capture a lot of contribution.

Where are the SOA in biomass burning aerosol? The aromatics appear to be stable, while there are losses of phenols, and oxygenated aliphatic are growing with aging. The PMF analysis gives an HNMR spectrum that is very similar to that of HULIS. This may also be an indicator of BB.

**Conclusions:**

- Factor analysis applied to HNMR spectra collections can provide an apportionment of the BB fraction of oxygenated OC
- More than one factor is needed to account for compounds of probable secondary origin
- Similar but somewhat non coincidental results are provided by HR-ToF-AMS
- In general, problems in comparing NMR with AMS factors may arise when
  - o WSOC is not a good proxy of OOC
  - o Sampling artifacts are significant
  - o Time integrated sampling do not capture the essential variability

**Discussion:**

There was a discussion about the atmospheric stability of levoglucosan. There are still big uncertainties on the levoglucosan inventory and efficiency of production.

Inorganic tracers of BB are potassium, sulfur and chlorine, that show up in fairly stable elemental ratios in BB smoke.

- Is there any other group in the world doing the same type of HNMR on aerosols? There are a few papers, but in Europe ISAC-CNR in Bologna is the only one.
- How does the measurement of the background affect your samples and analysis? Sampling is quite long and helps being above the noise level.

## Summary of the presentations on OA analytical techniques and protocols

- **Positive artifacts are a major problem. We really need a denuder in front of the Hi-Vol.**
- Quite a large number of samples is needed to apply PMF, which is one of the limitations since it requires a lot of work.

What are the issues?

- What is the time frame we want to address, what are the processes we want to address?
- Source region, evolution of the seasonality...
- Probably no need of fast online measurement yet.
- We all thought that with the high-resolution instruments now present we could get a really good deconvolution of the OA, but is it sufficient to reach what we want within ACTRIS?
- There are 6-7 stations that will have the mini-AMS. We need to address the source apportionment on those sites, making full use of the AMS data.
- Should we go also for more detailed methods such as HNMR?
- We have to think of a set of methods that can be applicable for long-term monitoring stations.
- What is the level of OA source apportionment we need to achieve?
- What is the required degree of details in the OA apportionment? Things like fossil or modern OC/EC is important, but politicians want to know also which mobile source that is responsible (cars, mopeds, trucks, etc...).
- Should the same level of details used also at the remote sites?
- Could we ask to the industry to add marker in there biofuel?!
- Ideally, we should separate into the source categories that the modelers can use.

We should probably have several levels of source apportionment methods. For BB source apportionment, a 7-wavelength Aethalometer could be used as a first screening method. It can also be used to improve the time resolution, and study plumes of BB smoke within a residential area. Nevertheless, it has to be complemented and evaluated against other methods for BB apportionment.

*Would it not be easier to have specific analytical centers for organic tracers, such as those for <sup>14</sup>C?*

It appears important to have sites of excellence, since instrument-heavy analytical methodologies are not easy to implement. With only a few sites of experts on the various analytical techniques, then we could avoid having to do too many intercomparison studies. It would also facilitate the use of standardized procedures.

## Discussions with Paolo Laj regarding WP3 OA source apportionment

### Paolo:

Key to our success with ACTRIS as an atmospheric research infrastructure are:

1. Improving the state of the infrastructure
2. Increasing the number of data users (e.g. AEROCOM, MACC, ...)
3. Clear positioning in the EU context (WP6)
4. Good governance/management

All WPs within ACTRIS need to show how things have progressed and improved. Furthermore, we need to show how and where our data have been used. OA source apportionment within WP3 is no exception from this rule.

We have to make sure that our recommendations on OA source apportionment are passed along throughout the entire organic aerosol community, also outside ACTRIS members. Examples are partners within projects such as PEGASOS or CHARMEX.

We must make full use of the future EMEP summer and winter campaigns on organic aerosols. Actually, EMEP counts on the active participation from strong research environments such as ACTRIS. Examples in the recent past are the EMEP campaigns where EUSAAR and EUCAARI researcher played an important role. The upcoming EMEP campaigns should have a big ACTRIS stamp all over them.

Regarding the use of standardized methods, some groups may be really reluctant to have a common method and will claim their method is the best. This was the case for also OC/EC before EUSAAR, but EUSAAR showed that a new standard protocol can indeed be introduced and gain wide acceptance.

We are not going to ask the people to change their methods. For instance, there is no need to buy a new GC-MS if the analysis using an existing HPLC-ESI-MS/MS instrument gives comparable results. What is important is that we need documentation of comparison between methods.

### ACTRIS participation in the upcoming EMEP intensive measurement periods (EIMPS 2012/2013)

The summer campaign will take place between June 8 to July 17 2012. The winter campaign is not defined yet but it is planned to be from around January 15 - February 15 2013. These represent a major effort to conduct European-scale coordinated aerosol measurements and to perform OA source apportionment. All ACTRIS partners are greatly encouraged to take active part in both these campaigns.

### Action Item:

1. All partners with an interest in OA source apportionment should promptly report their willingness to take active part in both the two EMEP intensive measurements campaigns. Contact persons are Wenche Aas at NILU ([Wenche.Aas@nilu.no](mailto:Wenche.Aas@nilu.no)) for the overall campaign coordination and André Prevot at PSI ([Andre.Prevot@psi.ch](mailto:Andre.Prevot@psi.ch)) specifically for the AMS measurements during these campaigns.

Partners and stations that, during the WP3 OA tracer meeting at Ispra, declared their willingness to participate with measurements aimed at OA source apportionment are:

- Auchencorth (GB), Cabauw (NL), Melpitz (DE), Puy de Dôme (FR), SIRTA (FR), Hyytiälä (FIN), K-pusztá (HU), Monseny (ES), JRC-Ispra (IT), Venice (IT), Monte Cimone (IT), Vavihill (SE),

Additional stations that are likely to participate are:

- Birkenes (NO), Kosetice (CZ) and possible also Pallas (FIN).

In addition, a number of sites will operate an ACSM (mini-AMS) during the two EMEP intensive measurements campaigns as part of ACTRIS. These are:

- Jungfrauoch (CH), Finokalia (GR), Mace Head (IRL), Melpitz (DE), Hyytiälä (FIN), Cabauw (NL).

Several other sites will operate other versions of the Aerodyne AMS instruments (Q-AMS, ToF-AMS). A full list of AMS sites active during the EMEP intensives is being compiled by André Prevot. The AMS data will be analyzed using the PMF (ME-2) source receptor model.

#### **Parameters to be measured:**

Since we intend to apportion OA to its various relevant sources, it is absolutely essential that OC and EC are measured at all participating sites. These measurements should adhere to the EUSAAR standards for “artifact-free” sampling and analysis (EUSAAR-2 protocol). Partners should also participate regularly in the ACTRIS OC/EC round-robin intercomparisons. Apportionment of PM necessitates also parallel PM measurements.

#### **Action Item:**

- All partners carrying out OA source apportionment within the two EMEP intensive measurements campaigns should perform OC/EC sampling and analysis in compliance with the EUSAAR standards. The OC/EC sampling should preferably be on a daily basis, if aerosol loadings permit.

To further improve the EC time resolution, it is preferred that ACTRIS partners also operate light absorption measurements in parallel (MAAP, PSAP, Aethalometer). In particular multi-wavelength light absorption measurements – using for instance the 7-wl Aethalometer – are of great interest with regard to the apportionment of EC to traffic versus wood combustion sources.

The EUSAAR sampling protocol requires a denuder (for the positive artifacts) and is thus limited to low-volume flow rate sampling only.

#### **Filter sampling**

LV-sampling:

- All ACTRIS partners already operate low-volume filter samplers.
- In addition, sites with LV-sampling that may participate are: Venice (IT), Athens (GR), SIRTA (FR).

HV-sampling:

There are also several sites where HV-sampling is performed. The HV-sampling is in many cases needed to ensure the collection of adequate OA mass filter loadings for the subsequent OA tracer analyses.

#### **Action Item:**

- It must be determined whether the partners operating HV-samplers have also equipped with them with denuders, and if so, to ascertain and document the denuder efficiency. Erik Swietlicki coordinates with Wenche Aas and ACTRIS partners.

The OA sampling procedure is also important. Previous EMEP campaigns have used 1-week sampling periods without denuder to minimize positive OC artifacts. Improved time resolution should be weighed against OA tracer analytical sensitivity.

We must ensure that the OA-related data that will be acquired during the EMEP intensives will be useful for the subsequent OA source apportionment studies.

#### **Action Item:**

- The OA sampling procedures and sampling periods must be determined. Erik Swietlicki coordinates with Wenche Aas and ACTRIS partners.

## **Statistical evaluation methods available**

(ppt presentation available for more details)

Erik Swietlicki presented the various statistical evaluation methods that are available and currently in use for aerosol source apportionment, including organic tracers.

In relation to this, Claudio Belis (JRC Ispra) advertised an ongoing initiative within the “European intercomparison for receptor modeling of air pollutants”. Workshops on this topic are arranged at Ispra (4-5 November 2010 and 17-18 January 2012, “The Use of Receptor Models in the Source Apportionment of Air Pollutants”). It is certainly in the interest of ACTRIS to coordinate the efforts with regard to receptor modeling procedures with the initiative coordinated by Claudio Belis. Minutes from the meetings and other related information can be found on the web (e.g. <http://www.harmo.org/Conferences/Proceedings/Kos/publishedSections/H14-182.pdf>).

### **Source apportionment**

Source apportionment is a quantitative estimate of the impact of each relevant source on the concentrations observed at the receptor site.

Source–receptor models are a complement to the atmospheric dispersion models that estimate source impacts in the forward direction (source to receptor), while source–receptor models work in the “backward” direction using the receptor site data to estimate source contributions. Studies employing a combination of both methodologies, source–receptor models and atmospheric dispersion models, are optimum. Inverse modeling has also been used, for instance for CO<sub>2</sub>.

### ***CMB (Chemical Mass Balance)***

This is one of the first types of source–receptor models to be developed and used, and several types of software are available. It is based on a multiple linear regression of receptor site data against a predetermined number of sources of known composition (source profiles). Uncertainties in both receptor data and source profiles can be used as weights in the regression.

Pros:

- + CMB can be performed on single samples separately

Cons:

- Number of sources must be known beforehand
- Source profiles (composition) must be known beforehand (source profile library needed)
- Collinearity between sources of similar composition causes problems in some cases

### ***Multivariate source–receptor models:***

The source profiles are inferred from the co-variation between the pollutants measured at the receptor site. Aged sources can also be accounted for. The purpose of the multivariate source–receptor models is to:

- Find the true dimensionality of the receptor site data (=number of relevant sources, m)
- describe the composition of the sources from the receptor data only (source profiles)
- calculate the contribution from each source for each sampling occasion

The multivariate source–receptor models have advantages and disadvantages compared with the CMB models:

Pros:

- + No source inventory required
- + Transformations of source profiles during atmospheric transport included in model

Cons:

- Requires a large number of samples needed ( $n > m$ )
- Interpretation of “factors” as physical sources can be problematic
- Meteorology gives co-variation
- Collocated sources may be hard to separate (need to have different temporal behavior)
- “Infinite” number of solutions possible
- Number of relevant sources not unambiguous

Examples of multivariate source–receptor models are:

- APCA: Absolute Principal Components Analysis;

- PMF: Positive Matrix Factorization
- COPREM: Constrained Physical Receptor Model

APCA (and related varieties) are based on Principal Components Analysis or Factor Analysis, which essentially is an eigenvector solution of the correlation matrix. PMF and COPREM are basically multivariate regression models with possibilities to impose constraints on the solutions, such as requirements for strictly non-negative solutions. It is often informative to apply different receptor models to the same data set.

### **The Latin hypercube sampling (LHS) method**

An alternative for source apportionment is the Latin hypercube sampling (LHS) method. See Gelencser et al., 2007; Genberg et al, ACP 2011; Yttri et al, ACP 2011) for further information.

## **Examples of organic aerosols source apportionment**

### **Organic aerosols source apportionment in France (Christine Piot)**

(ppt presentation available for more details)

Christine Piot (LGGE) presented examples of OA source apportionment from campaigns in France and Switzerland (EMPA, study funded by FOEN). Several research programs were coordinated to use the same protocols for sampling and analysis:

- **MEGAPOLI** (Megacities: Emissions, urban, regional, Global Atmospheric POLLution and climate effects, and Integrated tools for assessment and mitigation)
- **FORMES** (ORganic Fraction of urban aerosols: Source apportionment MEthod)
- **Particul'Air** (Inter-Regional study of the particulate pollution in rural air, in collaboration with air quality networks)
- **CAMERA** and **ANDRA** (Long-term monitoring programs French in rural background, > 3 years, 1 filter/week)
- **APICE** (Marine site ; Common Mediterranean strategy and local practical Actions for the mitigation of Port, Industries and Cities Emissions)
- **Research studies in collaboration with French Air Quality Networks** (at French Alpine valley sites)

The French protocol for filter sampling with the purpose of conducting subsequent tracer analyses is made available as an example of future possible ACTRIS SOPs.

Several methods for source apportionment calculations were applied to the data. In cases where only a few number of samples were available, CMB was chosen. For this purpose, source profiles of the relevant sources need to be developed and evaluated. The following organic tracers were chosen, since they were able to distinguish between sources and could be analyzed on the filter samples:

### **Tracers compounds used in French studies:**

- EC
- Alkanes (27 to 31 carbon)
- 3 PAHs (Benzo[e]pyrene, Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene)
- 3 hopanes (for diesel and gasoline vehicles)
- levoglucosan

Three heavy PAHs were used for traffic profile. Heavy PAH are likely to be present in the particulate phase. For biomass burning, it was found that the American hardwood profile showed a better fit to ambient data than the Schmidl et al. (2008) profile with a mix of hardwood and softwood (which should otherwise be reflected in the ambient levoglucosan/mannosan ratio).

### **The source profiles adopted were essentially those found in literature:**

- biomass burning: hardwood (Fine et al., 2004)
- direct vehicular emissions: light-duty vehicles in tunnel (El Haddad et al., 2009)
- vegetative detritus (Rogge et al., 1993a)
- natural gas combustion (Rogge et al., 1993b)

To further evaluate the source profiles used for CMB, several examples were shown that compared the CMB source apportionment with that of other methods. See also El Haddad et al. (2011a,b).

**Evaluation against other methods was based on:**

- radiocarbon (modern/fossil carbon)
- PCA applied on the same data base as for CMB
- PMF applied on major fraction + trace elements/metals
- 7- $\lambda$  Aethalometer (on-line measurement)
- AMS-PMF (on-line measurement)

When applying PMF to the trace metal data, OC was underestimated compared with the CMB apportionment, while EC showed similar apportionment using both metals (PMF) and organics (CMB) as tracers. The 7- $\lambda$  Aethalometer apportionment of the biomass burning source agreed well with that of CMB, while AMS-PMF showed lower biomass burning contribution.

In conclusion, the French studies have demonstrated a capability to apportion OA based on a limited number of tracers. A CMB source profile library was established. Nevertheless, some issues still remain:

**Advantages and limits**

- Source profiles need to be adapted to the site in question
- New tracers and profiles are needed for additional sources
- On-line methods should be developed and employed for faster apportionment
- Approaches for SOA need to be developed
- It is likely that several approaches need to be combined (PMF,  $^{14}\text{C}$ ,...)

**Questions/comments:**

Discussion on whether it is possible to make our apportionment data available in the MACC/GMES system. [Background: MACC - Monitoring Atmospheric Composition and Climate - Interim Implementation - is the current pre-operational atmospheric service of the European GMES programme. MACC provides data records on atmospheric composition for recent years, data for monitoring present conditions and forecasts of the distribution of key constituents for a few days ahead. MACC-II combines state-of-the-art atmospheric modelling with Earth observation data to provide information services covering European Air Quality, Global Atmospheric Composition, Climate, and UV and Solar Energy.] ACTRIS data should optimally find its way to the near real-time data products of MACC: <http://www.gmes-atmosphere.eu/data/>.

It was stressed again that we need to consider carefully the possibilities to use on-line methods such as the 7- $\lambda$  Aethalometer, which is in principle able to provide instantaneous apportionment of traffic versus biomass burning BC. Furthermore, it is relatively inexpensive and easy to operate. The new mini-AMS may be able to provide similar on-line information for OC, but is more expensive to purchase and requires more skills in handling and data evaluation.

**Nordic examples of OA source apportionment studies (Erik Swietlicki)**

(ppt presentation available for more details. See also Genberg et al ACP(2011), Yttri et al, ACP(2011a,b) Erik Swietlicki described the results from OA apportionment studies in the Nordic countries.

In a study in southern Sweden (Vavihill site; Genberg et al ACP(2011)), OC and EC were apportioned separately to various sources based on the analysis of OC/EC (EUSAAR-2 protocol),  $^{14}\text{C}$  (on TC) and levoglucosan. **The Latin hypercube sampling (LHS) method** was applied to estimate source contributions (similar approach to that in the CARBOSOL EU project). Several ratios (for instance the levoglucosan to OC ratio in biomass burning) were defined with an uncertainty interval. The LHS method then gave a range of source attributions for each sample taken. The source contributions were compared with the EMEP OA model predictions, showing that the wood combustion emissions are probably underestimated in Europe. This study shows that OC/EC source apportionment can be performed using only a fairly limited number of tracers.

In a Nordic summertime study (Yttri et al, ACP(2011)13339; 4 stations), additional tracers were also used to refine the apportionment, in particular regarding the primary biogenic (cellulose, mannitol) and SOA components (organosulphates and nitrooxy-organosulphates). The biogenic secondary organic aerosol (BSOA) was the single most important summertime source of OC (48–57%), and the primary biological aerosol particles (PBAP) were the

second most important source (20–32%). The Latin hypercube sampling (LHS) method was applied also in this study. These Nordic studies clearly show the predominance of modern carbon on OA (wood combustion in wintertime, BSOA and primary biogenic in summertime).

### **Summary (Erik Swietlicki)**

(ppt presentation available for more details)

Erik Swietlicki briefly summarized the discussions regarding WP3 Organic tracers. A discussion followed.

#### **Criteria for organic tracer compounds:**

- Unique to a specific source and emitted in sufficient quantities from this source
- Possible to sample and analyze with reasonable accuracy and precision
- Low vapour pressure (partitions preferentially to the particle phase)
- Stable (at least a few days lifetime in particulate phase)

Also there should be a clear willingness and capacity of partners to carry out the work needed.

There are studies indicating that levoglucosan as well as hopanes and steranes may degrade within a few days in the atmosphere.

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

What sources do we need to distinguish and apportion?

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

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

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

- Traffic (diesel, gasoline, biofuels?)
- Residential wood burning, agricultural fires, forest fires
- Marine OA? (MSA)
- Fixed combustion sources?

Tracers and methods that should be implemented or further considered within ACTRIS WP3:

- **OC, EC**  
(YES) Methods → Thermal-optical Analysis - EUSAAR-2 protocol
- **Biomass burning**: Levoglucosan (mannosan, galactosan)  
(YES) Methods → GC and LC
- **Modern/fossil carbon**: <sup>14</sup>C on TC (if possible on OC and EC separately)  
(YES) Method → AMS (Accelerator Mass Spectrometry)
- **Traffic (gasoline, diesel)**: PAH, hopanes, steranes  
(YES) Method → GC
- **Mass spectrometric group analysis, several sources**: (OC only)  
(YES) Method → mini-AMS, HR-TOF-AMS (Aerodyne)
- **Functional group analysis, several sources**: (if possible on OC and EC separately)  
(Probably) Method → HNMR (only at ISAC-CNR)
- **Primary biogenic (Fungal spores)**: Mannitol, arabitol, trehalose  
(Possible) Method → LC
- **Primary biogenic (Plant debris)**: Cellulose  
(Possible) Method → Enzymatic method by Kunit and Puxbaum (1996).

In addition, the following tracers may be considered:

**Methoxyphenols** are emitted from combustion of lignin in wood. This tracer may serve as a complement to levoglucosan (pyrolysis product of cellulose) for biomass burning.

**Cholesterol** is often used as a tracer for meat cooking (GC-MS).

The compound **3-methyl-1,2,3-butanetricarboxylic acid** (3-MBTCA) was shown to be a unique tracer compound for terpene BSOA. It is a low-volatility product formed by OH-radical gas-phase oxidation of pinonic acid, a well-known oxidation product of  $\alpha$ -pinene (Müller et al, ACP 2012). It can be collected on filters and analyzed by liquid chromatography/mass spectrometry (LC/ESI-MS).

**Ergosterol** is a widely used biomarker for determining the fungal biomass, in addition to the sugar polyols mannitol and arabitol. Ergosterol is a primary fungal membrane sterol and is almost exclusively found in fungi, and is therefore an efficient biomarker. GC-MS is the most efficient method for determination of ergosterol (for instance Burshtein et al, ACP 2011).

A series of **methyl-nitrocatechol** isomers (including 4-Methyl-5-nitro catechol) has been identified as a tracer for SOA originating from biomass burning (Iinuma et al, 2010). The precursor for these methyl-nitrocatechols is m-cresol, which is emitted from biomass burning at significant levels.

**Organosulphates and nitrooxy-organosulphates** have lately been suggested as tracers of biogenic SOA aged in air masses with anthropogenic influence. These organosulphate compounds are formed from several BVOC (isoprene,  $\alpha$ - and  $\beta$ -pinene and limonene).

In addition, the AMS community in Europe can also help in the source apportionment of OA, especially with respect to the degree of atmospheric aging (HOA vs OOA). Due to the fragmentation in the AMS, only a few compounds and sources can be quantified (for instance biomass burning, PAHs). This data is nevertheless highly complementary to the specific organic tracers.

With the organic tracer compounds presented during the meeting, we still need to consider whether we are lacking tracers for important source categories.

**ACTRIS WP3 / WP4 technical Workshop JRC, Ispra, Italy - 24-28 Oct 2011**  
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# FILTER SAMPLING PROTOCOL FOR TRACERS MEASUREMENTS

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## 1. Objective

This protocol defines the standard operational procedure (SOP) for filter sampling of ambient particulate matter below 10  $\mu\text{m}$  in diameter (PM<sub>10</sub>) for the analysis of inorganic species, elemental and organic carbon fractions, and organic speciation for tracer quantification.

## 2. Application domain

This procedure is applicable for aerosol high volume sampling (HVS, High Volume Sampler) and the analysis of a large set of compounds.

## 3. Bibliography

EMEP Manual for sampling and chemical analysis, EMEP/CCC.

## 4. Sampling principal

Sampling of PM<sub>10</sub> is performed daily on a quartz fiber filter with a high volume sampler. Exposed filters are then sent to the laboratory where they are punched for the different analyses:

- Analysis of OC and EC with a thermo-optical method.
- Extraction and analysis of the major ion species by ionic chromatography
- Extraction and analysis for organic speciation.

## 5. Sampling system

PM<sub>10</sub> sampling is performed with a manual Digital HVS equipped of a PM<sub>10</sub> head. Schematic of the sampler is presented on Figure 1. Sampling flow is regulated to 30  $\text{m}^3/\text{h}$  ( $\pm 2\%$ ) at ambient atmospheric temperature and pressure. Regulation of the pump is ensured in front of the filter with a flow-meter.

Some inorganic and organic aerosols are particularly volatile and this volatility depends of the condition of pressure and temperature. In order to limit the losses the sampler must be placed in a controlled temperature room as close as possible to 20°C. Temperature and pressure must be recorded next to the sampler.

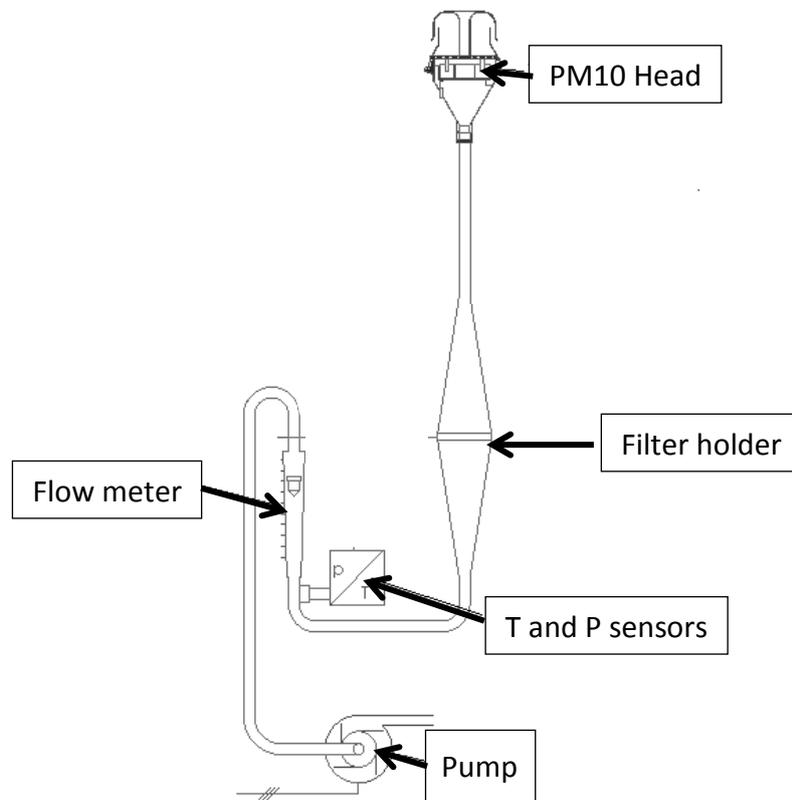


Figure 1 : Schematic and principal of the sampling system

## 6. Frequency of sampling

The sampling frequency will depend upon the program, but one sample per week, or more often when possible, is recommended.

## 7. Filter material

In order to analyze a large set of species from inorganic to organic compounds, quartz fiber filter are used (PALLFLEX TISSUQUARTZ QAT-UP 2500 150 MM) and are pre-heated to 500°C for 10h.

## 8. Filter manipulation

Every manipulation is done with new gloves (powder free).

Filters should be manipulated with clean tweezers. Use some Milli-Q water to clean tweezers and dry it with clean room tissues. Manipulation should be performed in a room far from contamination, for instance far from cigarette smoke. We recommend proceeding at the

unpacking of the sampled filter directly at the station. Manipulation should be done on a clean surface, optimal in a laminar flow box.

## 9. Filter holder cleaning and packing

- Filter holder should be cleaned at least once a month, if possible every time in between each sample.
- Remove the filter tighter, the white join from the filter holder using the adapted tweezers.



- Wash with MilliQ water the 3 pieces by scrubbing with a clean room tissue (don't mix the different parts with another filter holder).
- Let it dry in a laminar flow box (~12h to be dry) and finish the cleaning with a clean room tissue. If no laminar flow box, place it in a room as clean as possible, on the clean side of an open plastic band.
- Place a new clean filter in the filter holder, reinstall the white join (in the same direction each time), and finally add the filter tighter.
- Pack the filter holder in clean aluminum foil, and in a Ziploc to protect from contamination before sampling.

## 10. Filter treatment after sampling

After sampling, packing of the filter should be done at the station on a table prepared for it. The packing kit should be prepared before unpacking:

- Manipulation should be done on a clean surface, using the **clean side of an open plastic band**.
- Every manipulation is done with **new gloves** (powder free).
- Filters should be manipulated with **clean tweezers** (tweezers should be cleaned previously and packed in a Ziploc bag).
- Aluminum foil and Ziploc for packing the filter
- Sampling sticker

How to pack the filter:

Carefully remove the filter tighter, the white join and the filter from the filter holder

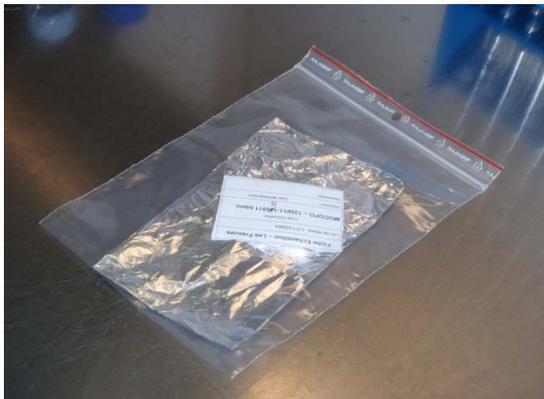
Place the filter on the none exposed face on an aluminum foil

Bend in 2 the filter, using the 2 tweezers, in order that the exposed side of the filter doesn't touch the aluminum foil



Pack the aluminum foil around

Insert it in a Ziploc bag with the sample sticker.



Samples should be stored and transported as follow.

## 11. Sample transport and storage

During transport, filters should not be brought to temperature above 20°C. Transport should thus be done in a cooling box with ice packs. Before shipment to the analytical laboratory, samples should be stored at negative temperature (freezer or at least frig).

## 12. Field blank

Field blanks are collected at least once a month. They are performed by placing the filter in the collector without starting the sampling pump. These filters are thus put into the same conditions

as a samples and are therefore subjected to the same potential contamination from manipulation, storage, transport...

### 13. Sending frequency for analysis

Samples should be sent at least every 2-3 months for analysis following the transport procedure.

### 14. Sampling information

Sampling information note must come with each sample. This note summarizes the major information:

STATION NAME	
Filter series :	LOT 56664
Operator :	
Filter type :	<input type="checkbox"/> Sample <input type="checkbox"/> Field blank
Sampling Date (dd/mm/yyyy) :	
Sampling Volume (in ambient T, P conditions):	m <sup>3</sup>
Temperature :	°C
Pressure :	mmBar
Observations :	

In addition a summarize file should report all the collected information and be sent by email.

### 15. Sampling Kit

Sampling material sent to the station :

- Plastic sheet (to be used for clean sampling area by cutting a piece, cutting one side in order to be able to open the band and place the inside face toward the sample)
- 2 tweezers (to manipulate filters)
- 1 special tweezers to open the filter holder
- Some aluminum to pack the filters (1 roll)
- Ziploc bags (2 sizes) for packing the filters and the small material that must stay clean (for instance the tweezers) (300)
- Cooling packs that must be cooled prior to use and then use for the transport of the filters (4)
- Sample stickers for entering all the sampling information
- Several packs of free powder gloves which need to be change after every manipulation (3 packs)
- Sampling filters (50)

### 16. Checking of the system

Maintenance of the sampling system should be done by the person responsible of the site following the following table.

**Table 1 : Maintenance and control of the sampling system**

<b>Operation</b>	<b>Recommended periodicity</b>
Cleaning of the sampling head	1 month
Leak test	3 months
Calibration of the sample flow	
Calibration of the temperature and pressure sensor	
Maintenance of the sampling pump	12 months

**END OF THE PROCEDURE**