

WP3- NA3: NA3: In-situ chemical, physical and optical properties of aerosols

Deliverable D3.3: Implementation of the existing EUSAAR standardization protocol for 3w-Neph and 1-w-AP

During the EUSAAR period, standardization protocols for 3-wavelengths nephelometers and 1-wavelength absorptions photometer were developed to determine the aerosol light scattering and absorption coefficients, respectively. Emphasis was given to harmonize correction schemes for the light absorption coefficient to obtain a harmonized data set. Furthermore, the aerosol conditioning in terms of drying to a relative humidity below 50% was a major task.

A technical meeting of ACTRIS WP3 (minutes are in the annex) was held at the Joint Research Center in Ispra, Italy, on October 24-28, 2011. At this meeting, the statuses of the station in terms light scattering and absorption measurements and the implementation of their standardization were discussed with people from EUSAAR and new ACTRIS observational stations (total of 55 participants from ACTRIS partner and associated partner institutions).

Following table presents the actual status of the implementation.

ACTRIS Partner #		Station	Station	Absorption type	Dryer	Scattering type
1	CNR	Monte Cimone, Italy	MTC	MAAP	not needed	Ecotech
2	CNRS	Puy de Dôme, France	PDD	MAAP	not needed	TSI 3563
2	CNRS	Sirta, France	SIRTA	Aethalomer (7w)	No dryer yet	Ecotech 9000
3	NILU	Birkenes, Norway	BIR	PSAP, home-made; PSAP 3w	Nafion	TSI 3563
3/AP15	NILU/SU	Zeppelin, Norway	ZEP	PSAP, home-made	not needed	TSI 3563
4	UHEL	Hyytiälä, Finland	SMR	Aethalometer	Nafion	TSI 3563
5	TUD	Cabauw, Netherlands	CESAR	MAAP	main inlet	TSI 3563
6	PSI	Jungfrauoch, Switzerland	JFJ	MAAP and Aethalomer (7w)	not needed	TSI 3563
7	IFT	Melpitz, Germany	MPZ	MAAP	main inlet	TSI 3563
10	UPC-UGR	Granada, Spain		MAAP, PSAP	Not defined yet	
12	ULUND	Vavihill, Sweden	VHL	PSAP, home-made	No info	Ecotech 9300 (3-wl)
13	CSIC	Montseny, Spain	MSY	MAAP	main inlet	Ecotech Aurora 3000
13	CSIC-AEMET	Izaña, Spain	IZO	MAAP.	Not needed	TSI 3563
14	NUIG	Mace Head, Ireland	MHD	Aethalometer & MAAP	No dryer yet	TSI 3563
15	NERC	Auchencorth Moss, UK		Aethalometer (1w)	Not defined yet	
16	FORTH	Finokalia, Greece	FKL	Aetholometer (7 w)	Main inlet with silica dryer	Radiance Research

17	JRC	JRC-Ispra, Italy	IPR	Aethalometer/MAAP	Nafion	TSI 3563
18	DWD	Hohenpeissenberg, Germany	HPB	MAAP, Aethalometer, PSAP	Nafion	TSI 3563
20	BEO	BEO Moussala, Bulgaria	BEO	n/a	Not needed	TSI 3563
26	UPAC	K-Puszta, Hungary	KPS	PSAP, Radianc Research	1:1 dilution with dry air at the main inlet	TSI 3563
ACTRIS Associated Partner #		Station	Station	Absorption type	Dryer	Scattering
AP4	FMI	Pallas, Finland	PAL	Aethalometer	not needed	TSI 3563
AP10	NCSR-D	Demokritos, Greece		Aethalometer 7w	Nafion	Ecotech Aurora 3000
AP11	NOA-IERSD	Navarino Environmental Observatory, Messenia, Greece		Aethalometer & SU home made PSAP	Not defined yet	Radianc Research M903
AP11	NOA-IERSD	Penteli Aerosol Station, Athens, Greece		PSAP	Not defined yet	Radianc Research M903
AP15	SU	Aspvreten, Sweden	ASP	PSAP, home-made	No dryer yet	Ecotech M9003
AP18	UNIBHAM	Harwell, United Kingdom		Aethalometer	No dryer yet	n/a
(not AP yet)	IPL	Preila, Lithuania	PLA	Aethalometer 7w	Diffusion dryer	

21 out of 28 partner and associated partner stations, i.e., 75%, comply with the EUSAAR/ACTRIS quality standards. The stations marked colored do not fully fulfill the EUSAAR/ACTRIS recommendations yet. The goal is to improve the implementation at these sites in the second year.

Following decisions were agreed on:

Nephelometer:

Data submission:

- Level-0: data as measured included RH, pressure etc.
- Level-2: Truncation and STP corrections

Truncation correction:

For 3-wavelength measurements:

- Angström exponent method (Anderson et al.)
- Recommendation for PM10 measurements: If Angstrom exponent is > 2 , there is a domination of sub-micron particle and for < 2 , there is a domination of supermicrometer particles

For 1-wavelength measurements:

- Determination via number size distribution.
- If the supermicrometer particles are missing, an increased uncertainty should be given.

Absorption Photometer:

Data submission:

- The datasets 2008-2010 have to be corrected according to a new corrections scheme and have to be re-submitted by end of January 2012.

References

Müller, T., B. Henzing, G. de Leeuw, A. Wiedensohler, A. Alastuey, H. Angelov, M. Bizjak, M. Collaud Coen, J. E. Engström, C. Gruening, R. Hillamo, A. Hoffer, K. Imre, P. Ivanow, G. Jennings, J. Y. Sun, N. Kalivitis, H. Karlsson, M. Komppula, P. Laj, S.-M. Li, C. Lunder, A. Marinoni, S. Martins dos Santos, M. Moerman, A. Nowak, J. A. Ogren, A. Petzold, J. M. Pichon, S. Rodriguez, S. Sharma, P. J. Sheridan, K. Teinilä, T. M. Tuch, M. Viana, A. Virkkula, E. Weingartner, R. Wilhelm and Y. Q. Wang (2011). "Characterization and Intercomparison of Aerosol Absorption Photometers: Result of two Intercomparison Workshops." *AMT* 4: 245–268.

Annex:
Minutes ACTRIS WP3 meeting, Ispra Oct 24-28, 2011

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Part I: Optical Properties

Station update:

ACTRIS Partner #		Station	Station	Absorption type	Dryer	Scattering type
1	CNR	Monte Cimone, Italy	MTC	MAAP	not needed	Ecotech
2	CNRS	Puy de Dôme, France	PDD	MAAP	not needed	TSI 3563
2	CNRS	Sirta, France	SIRTA	Aethalomer (7w)	No dryer yet	Ecotech 9000
3	NILU	Birkenes, Norway	BIR	PSAP, home-made; PSAP 3w	Nafion	TSI 3563
3/AP15	NILU/SU	Zeppelin, Norway	ZEP	PSAP, home-made	not needed	TSI 3563
4	UHEL	Hyytiälä, Finland	SMR	Aethalometer	Nafion	TSI 3563
5	TUD	Cabauw, Netherlands	CESAR	MAAP	main inlet	TSI 3563
6	PSI	Jungfrauoch, Switzerland	JFJ	MAAP and Aethalomer (7w)	not needed	TSI 3563
7	IFT	Melpitz, Germany	MPZ	MAAP	main inlet	TSI 3563
10	UPC-UGR	Granada, Spain		MAAP, PSAP	Not defined yet	
12	ULUND	Vavihill, Sweden	VHL	PSAP, home-made		Ecotech 9300 (3-wl)
13	CSIC	Montseny, Spain	MSY	MAAP	main inlet	Ecotech Aurora 3000
13	CSIC-AEMET	Izaña, Spain	IZO	MAAP.	Not needed	TSI 3563
14	NUIG	Mace Head, Ireland	MHD	Aethalometer & MAAP	No dryer yet	TSI 3563
15	NERC	Auchencorth Moss, UK		Aethalometer (1w)	Not defined yet	
16	FORTH	Finokalia, Greece	FKL	Aethalometer (7 w)	Main inlet with silica dryer	Radiance Research
17	JRC	JRC-Ispra, Italy	IPR	Aethalometer/MAAP	Nafion	TSI 3563
18	DWD	Hohenpeissenberg, Germany	HPB	MAAP, Aethalometer, PSAP	Nafion	TSI 3563
20	BEO	BEO Moussala, Bulgaria	BEO	n/a	Not needed	TSI 3563
26	UPAC	K-Puszt, Hungary	KPS	PSAP, Radiance Research	1:1 dilution with dry air at the main inlet	TSI 3563

ACTRIS Associated Partner #	Station	Station	Absorption	Dryer	Scattering
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				type		
AP4	FMI	Pallas, Finland	PAL	Aethalometer	not needed	TSI 3563
AP10	NCSR-D	Demokritos, Greece		Aethalometer 7w	Nafion	Ecotech Aurora 3000
AP11	NOA-IERSD	Navarino Environmental Observatory, Messenia, Greece		Aethalometer & SU home made PSAP	Not defined yet	Radianc Research M903
AP11	NOA-IERSD	Penteli Aerosol Station, Athens, Greece		PSAP	Not defined yet	Radianc Research M903
AP15	SU	Aspvreten, Sweden	ASP	PSAP, home-made	No dryer yet	Ecotech M9003
AP18	UNIBHAM	Harwell, United Kingdom		Aethalometer	No dryer yet	n/a
(not AP yet)	IPL	Preila, Lithuania	PLA	Aethalometer 7w	Diffusion dryer	

Nephelometer data:

Level-0: data as measured included RH, pressure etc.

Level-2: Truncation and STP corrections

Truncation correction:

For 3-wavelength measurements: Angström exponent method (Anderson et al.)

Recommendation for PM10 measurements: If Angstrom exponent is > 2 → domination of sub-micron particles, for < 2 → domination of supermicron particles

For 1-wavelength measurements: determination via size distribution (if the supermicron particles are missing → increase uncertainty)

Absorption Photometer data:

The dataset 2008-2010 has to be ready by end of January to be included in the IPCC. An Article will be written by Elisabetta Vignati.

Elisabetta Vignati will convert the data to 550 nm using a range of angstrom coefficient 1-1.5. On EBAS the data will be at level 2 with the original wavelength

Action Items:

1. Markus Fiebig: Give information about the nephelometer data in the old format. Stations should be contacted to resubmit the data in the new format
2. Ali Wiedensohler: Contact data providers to resubmit absorption data
3. Thomas Müller: Provide the aethalometer correction scheme
4. All: Everybody employs the correction scheme for the own data set

PART II Sampling and analysis of organic and elemental carbon

1. *Implementation of the EUSAAR standardized sampling and analysis protocols for organic and elemental carbon within ACTRIS*

Sampling train

- observations regarding sampling artifacts at PDD (K. Sellegri)
- performance of denuders for HiVol sampling (J. Cozic)
- planning a series of final tests to determine how much the EUSAAR denuder increases the negative artifact (JP. Putaud)
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K. Sellegri showed comparisons of the positive sampling artifacts determined using the Carbon monolith denuder recommended by EUSAAR and the “quartz behind Teflon” technique. Twelve 48 hr – integrated samples were collected simultaneously. Both techniques lead to comparable positive artifact estimates,

ranging from 15 to 80% of the particulate organic carbon (POC). But EC is observed also on back up filters, which indicates that positive artifacts might be overestimated. EC was never observed in back up filters during experiments in which no leaks occurred. Gyula KISS suggested that oligomerisation could produce EC like species over 48 hrs.

J. Cozic presented data obtained with a denuder prototype (3 monoliths of activated carbon in parallel) used at a face velocity of xxx cm/s. It is very efficient in removing O₃, and particle penetration is better than 90% for particles < 1 µm. Preliminary data obtained in Grenoble suggest that this denuder removes a close to constant concentration of 1.8 µg OC/m³ from a quartz fiber filter. However, the amount of EC in the denuded filter is also smaller (by 20%) than in the undenuded filter. Further testing is in progress. J. Cozic proposed to include the testing of High Vol denuders in the activities of ACTRIS. JP Putaud said that demonstrating the applicability of "EUSAAR – like" denuders to Hi Vol sampling would be an important achievement of ACTRIS, since Hi Vol sampling is necessary at the most remote monitoring station to collect enough mass for various analyses. J Cozic's proposal is acknowledged by the audience.

JP Putaud reminded that the EUSAAR sampling train for OC and EC determination was defined and described. It consists of a sampling head, a carbon monolith denuder, and two back to back quartz filters. The ultimate test to be performed regards the quantification of the magnification of the negative artifacts involved by the implementation of the denuder. This test has been carried out in Ispra only during EUSSAR. From the questionnaire sent before the meeting, and discussions during the meeting, nothing prevents these tests to be performed by Month 18 of ACTRIS (during summer if only one season is to be chosen) at the following sites: SIRTA (FR), Birkenes (NO), Montseny (ES), Kosetice (CZ), K-Puzsta (HU)

Optical correction of charring

- Lower / upper limits for which charring optical correction can be applied (F. Cavalli)
- Arguments in favor of light transmission vs. reflectance (J. Cozic, F. Cavalli)

Cavalli: Only upper limits for which charring optical correction can be applied have been investigated so far. For aerosol samples collected at IPR, F. Cavalli analyzed the attenuation ratio for EC (ratio between the blank filter attenuation and the initial attenuation) and for PyrC (ratio between the initial attenuation and the minimum attenuation value during the He-mode of the analysis) were analysed as a function of the corresponding EC and PyrC contents (in µg cm⁻² unit), respectively, as given by the calculation software. Both EC and PyrC attenuation ratio vs. corresponding xC concentration showed a log-like behavior. For EC, the attenuation ratio vs. xC concentration has the same log law in winter and summer. In contrast, the attenuation ratio vs. C concentration for PyrC follows the same behavior as that for EC for summer aerosol samples only: for winter samples, with higher EC concentrations, the PyrC attenuation / mass ratios are lower than those of EC for the same C concentrations. At EC concentrations higher than 6-8 µg cm⁻², the laser signal is almost saturated already at the beginning of the analysis such that a further attenuation caused by PyrC formation during the analysis is detected less accurately. Consequently, also the split between OC and EC will be less accurate.

J. Cozic presented a comparison between OC, EC and PyrC concentrations (concentration ranges for OC: 0-15µg/cm² and for EC: 0-26 µg/cm²) obtained using the same thermal protocol and applying both transmission and reflectance corrections for charring. EC_refl and EC_trans well correlate but EC_refl concentrations are 7% higher than EC_trans on average. Obviously, also OC_refl. and OC_trans. well correlate, with OC_refl concentrations being on average 8% lower than OC_trans.

Further, J. Cozic observed that for OC concentrations larger than ca. 10 µg/cm², PyrC_refl and PyrC_trans do not correlate anymore, and PyrC_trans is significantly lower than expected.

F. Cavalli presented correlations between EC measured on 24h aerosol samples by reflectance and transmission correction and online measurements of EBC (i.e. Aethalometer and MAAP). As correlation coefficients (R²) are equal on an annual basis for reflectance and transmission, there are, currently, no arguments in favor of one or the other correction in TOA analysis.

Action Items:

1. K. Sellegri to conduct further tests, comparing 48hr sampling plus off-line analysis and semi continuous on-line analyses.
2. LGGE is appointed for steering the action on Hi Vol denuders within ACTRIS.
3. A standard operating procedure will be made available by Partner 17 by the end of 2011.
4. Tests to be performed and analyzed at SIRTA, Birkenes, Montseny, Kosetice, K-Puzsta by the next WP3 meeting
5. ACTRIS recommend not to exceed $8 \mu\text{g cm}^{-2}$ EC for thermal-optical analyses
6. ACTRIS recommends saving OC and EC obtained by charring correction from both transmission and reflectance monitoring

2. Getting these protocols accepted as European and possibly international reference methods, and implemented in national and international (e.g. EMEP) air pollution monitoring networks (JP. Putaud)

The EMEP manual

The EMEP web site (<http://www.nilu.no/projects/ccc/manual/index.html>) states: "To be included in the EMEP Manual:

The EUSAAR protocol has been adapted as standard method for analysis of EC/OC within EMEP."

However, the draft EC/OC protocol does not include any reference to the methodologies developed with EUSAAR yet, and the link to the EUSAAR-2 protocol just lead to the EUSAAR home page.

Draft mandate from the European Commission (DG ENV) to CEN (European Committee for Standardisation)

A "summary description of planned mandated work of CEN/TC 264 in support to the implementation of ambient Air Quality legislation" has been drafted by the EC DG ENV. "This mandate is required to develop and validate standard measurement methods for the automated monitoring of particulate matter and for the measurement of its chemical composition, in order to ensure a harmonized implementation of Directive 2008/50/EC in the EU." Regarding the determination of OC and EC, "The validated method will focus on the harmonization and improvement of the data quality of thermal-optical measurement method for EC and OC used in monitoring networks, and develop guidance regarding the use of different protocols (analytical parameters) used currently within that method". When CEN receives the official mandate from DG ENV, it will be open a call and select a Institute to carry out the requested validation tests. JP Putaud declared he didn't feel like JRC should enter the competition, since he was strongly involved in the development of the EUSAAR_2 protocol (conflict of interest). In contrast, the audience proposed that the ACTRIS consortium should try to get involved in these validation test. However, only certified or accredited (?) laboratories are eligible.

Action Item:

1. Putaud to investigate if a consortium of ACTRIS partners could compete to get the validation job from CEN
2. Further work to be done by JP Putaud towards EMEP to have the EMEP manual updated.

3. Run regular quality assurance and control activities.

How can we define true values for OC and EC

- Separation of OC and EC for 14 C analyses (N. Perron)
- Seeking for reference materials: the Carbon Conference process (JP. Putaud)

Increasing our inter-comparability (F. Cavalli)

- Next intercomparison features
- What prevents the independent calibration with a standard gas from being more popular?

F. Cavalli presented the next intercomparison for OC and EC measurements

- i) 18 participants, namely 13 ACTRIS partners + 5 ACTRIS associates / EMEP laboratories, will take part in the 1st ACTRIS intercomparison for TC, OC and EC measurements.
- ii) In total 8 aerosol samples (2 samples from each sites BIR, IPR, MSY and KPS) have been distributed. In particular, ACTRIS partners will receive one punch of 2.4 cm x 2.4 cm and ATRIS associates / EMEP laboratories two punches of 1 cm x 1 cm. Considering that the homogeneity of the deposit on the filter is not guaranteed, FC advised to analyse as many aliquots as possible.
- iii) A third samples from each site will be devoted to investigate the homogeneity of the aerosol deposit area. Then filters from the same site will be assumed to have the same homogeneity. The study will be carried out by JRC –IPR.
- iv) A solution of phtalic acid ($1.52 \mu\text{gC } \mu\text{l}^{-1}$) has been distributed. Participants should use it as an external standard for checking their own liquid standard solution at the time of the intercomparison.
- iii) and iv) have been introduced in the attempt to explain the variability in TC that we observed in the previous intercomparison exercises.
- v) It has been recommended to perform also a calibration using external gaseous standard (e.g. injecting know amounts of CO_2 at each temperature steps in the He and He/Ox mode during an analysis run). As CO_2 does not degrade like sucrose, CO_2 calibration can results in a more accurate calibration factor. Further it would help interpreting the observed variability in EC/TC ratio. As an example, for the IPR Sunset lab analyzer, CO_2 injections at each T step in He and He/Ox-mode of the analysis showed that C concentrations are underestimated (at maximum 8%) in the He-mode and overestimated (at maximum 8%) in the He/Ox-mode leading to a maximum overestimation of 15% for the EC/TC ratio in IPR samples.

Currently, 6 out of 10 ACTRIS partners intend to calibrate their own instruments with an external gaseous standard.

Interferences from carbonate

- Paper on carbonate by ACTRIS partners (A. Alastuey)
- Expected progress on carbonate interferences within ACTRIS (JP. Putaud)

A. Alastuey presented the manuscript under review:

Karanasiou A. , Diapouli E. , Cavalli F. , Eleftheriadis K., Viana M., Alastuey A., Querol X., Reche C., On the quantification of atmospheric carbonate carbon by thermal / optical analysis protocols, Atmospheric Measurements Techniques, 2011.

Three temperature protocols were tested on filter samples containing known amounts of CaCO_3 prepared in a clean chamber: two NIOSH-like protocols suitable for the semi-continuous analyzer, i.e. RT-QUARTZ-840, with a maximum temperature in the He-mode = 840 °C and RT-QUARTZ-700 with a maximum temperature in the He-mode = 700 °C, and the EUSAAR_2 protocol maximum temperature in the He-mode 650 0C.

Carbonate carbon (CC) concentrations were quantified by manual integration of the sharp peak appeared at the maximum temperature step of the inert mode. High recoveries of ca. 90% of CC were achieved by all the thermal protocols. Using the EUSAAR-2 thermal protocol, more than 95% of CC evolved as OC during the maximum temperature step in inert atmosphere for CC amounts up to 56 $\mu\text{g(C)}$, corresponding to the mass of CC that would be collected during extreme desert dust events. Using the RT-QUARTZ-840 protocol specifically developed for on-line analyses, CC completely evolves as OC, regardless of the CC amount up 56 $\mu\text{g(C)}$.

Fumigation by HCl of a subset of samples shows that this treatment is able not only to eliminate CC, but also to cause losses of organic compounds like organic acids. Further, HCl residuals are known to seriously damage quartz oven of the OCEC analyzer.

For 14 atmospheric samples from Barcelona (urban site) and MSY (regional background site), CC concentrations obtained by the peak integration method using RT-QUARTZ-840 were compared to direct measurements of CC obtained by the H_3PO_4 acidification method used in JRC (EUSAAR deliverable NA2-D6)

The quantification of CC by the peak integration using RT-QUARTZ-840 implies a high level of uncertainty. CC concentrations obtained by this method were higher (33% as slope of linear regression)

than those obtained by the direct measurement. Further, the intercept indicates that a non-zero CC concentration is obtained from the thermogram peak integration also for samples not containing any CC.

JP Putaud suggested that the interference of carbonate should be further investigated within ACTRIS, since this might be an important criterion when the standard analytical protocol is selected by CEN. He proposed to first work with on existing samples, which are available from BIR (probably) and MSY.

Use of the database

- The OC and EC phenomenology (F. Cavalli)

F. Cavalli analyzed long time series (2008 and 2009) of TC, OC and EC concentrations (PM10 and/or PM2.5) and PM concentrations (from gravimetric analysis) for nine EUSAAR-ACTRIS stations (BIR, ASP, VHL, HWL, PDD, MSY, MPZ, OBK and IPR). The spatial and temporal variations (annual and seasonal averages) were analysed for the following variables: mass, TC, OC, EC, TC/Mass and EC/TC.

Ideally the TC, OC and EC concentrations database should be accurate/comparable and consistent/robust. This implies that:

i) Sampling

Carbonaceous aerosol samples should be collected using the same sampling train or corrected for positive artifact (possibly for the negative artifact).

In the present study:

-3 stations used a denuder (ASP, VHL and IPR_PM2.5)

-3 stations reported positive artifact correction:

PDD run a lvs and a parallel QBT train (in 2009 only). Comparison between denuded and QBT OC and EC concentration were presented by K. Sellegri (see 1.1);

MSY run a hvs. No estimates of the positive artifact contribution are currently available for hvs. Considering the high face velocity of 48.5 cm s⁻¹ of this hvs, positive artifact could possibly be considered negligible (?);

OBK run a lvs a parallel QBT train;

-3 stations did not use denuder and did not report for positive artifact contribution:

BIR (lvs), MPZ (hvs), HWL (lvs)

ii) Analysis

Carbonaceous aerosol samples should be analysed using the same analytical protocol.

In the present study, 7 EUSAAR stations applied the EUSAAR_2 protocol whereas 2 stations, i.e. HWL and MLP, applied the QUARTZ protocol and the VDI method, respectively.

Results from the 2008-2009-2010 EUSAAR intercomparison will be used to "harmonise", by means of asymmetrical error bars, station-to-station differences in EC/TC ratios.

iii) Concentrations from individual stations should show an interannual consistency.

In case of not negligible differences between 2008 and 2009 data, the station responsible will help F. Cavalli understand whether the observed differences are a methodological or a natural effect.

Action Items:

- JP Putaud and F. Cavalli to draft a contribution to the article, and refine the contribution (how can we define true values for OC and EC) to reflect "ACTRIS' view" on this question.
- Results of the intercomparison to be reported to F. Cavalli using the template file by Nov. 30th
- Results of the external calibration with a standard gas to be reported to F. Cavalli using the template file by Nov. 30th
- JP Putaud and F. Cavalli to come up with a SOP for measuring the transit time
- A. Alastuey takes the lead in organizing further investigations of interferences by carbonate.

Part III Particle number size distribution

Station status:

ACTRIS Partner #		Station	Station	S/DMPS	Charger	Equivalent length (loss correction)	Dryer	Dryer	Ion Spectrometer
					type&strength		aerosol	sheath air	type
1	CNR	Monte Cimone, Italy	MTC	home-made DMPS	Ni63	~ 3.5 m	Nafion	Diffusion	
2	CNRS	Puy de Dôme, France	PDD	home-made SMPS	Riebel		Diffusion	Diffusion	NAIS
2	CNRS	Sirta, France	SIRTA	SMPS GRIMM	Am241; 0.1 mCi	5m	silicagel	not needed	
3	NILU	Birkenes, Norway	BIR	home-made DMPS	Ni63, 370MBq	7cm	Nafion	Diffusion	
3/AP15	NILU/SU	Zeppelin, Norway	ZEP	home-made DMPS	Ni63, 370MBq	7cm	Nafion	Nafion	
4	UHEL	Hyytiälä, Finland	SMR	home-made TDMPS	C-14 370MBq	5m	no	Diffusion	NAIS
5	TUD	Cabauw, Netherlands	CESAR	IFT-modified TSI SMPS	Kr-85	9.6m	Nafion	Nafion	
6	PSI	Jungfraujoch, CH	JFJ	home-made SMPS	Kr85 / 185MBq	no info	not needed	not needed	-
7	IFT	Melpitz, Germany	MPZ	IFT TDMPS	Kr85 370MBq		Nafion	Diffusion	NAIS
10	UPC-UGR	Granada, Spain		TSI 3031	unipolar		not needed	not needed	
12	ULUND	Vavihill, Sweden	VHL	home-made TDMPS	Kr85	2 m	Nafion	Nafion	AIS
13	CSIC	Montseny, Spain	MSY	IFT SMPS	3077 TSI Kr85	4 m	Nafion	Nafion	
13	CSIC-AEMET	Izaña, Spain	IZO	TSI, not modified.	Kr-85; 10 mCi		not needed	not needed	
14	NUIG	Mace Head, Ireland	MHD	home-made SMPS	Krypton-85 2mC		Nafion	no	
15	NERC	Auchencorth Moss, UK		TSI SMPS with driers and RH probes	TSI 3077A (370 MBq Kr85)	3.5 m	inlet dryer	Nafion	
16	FORTH	Finokalia, Greece	FKL	IFT SMPS		4 m	Nafion	Nafion	
17	JRC	JRC-Ispra, Italy	IPR	home-made DMPS	Kr 85 / 2mCi	8.9 m	Nafion	Nafion	

18	DWD	Hohenpeissenberg, D	HPB	IFT SMPS	TSI 3077, 2 mCi		Nafion	Nafion	
20	BEO	BEO Moussala, Bulgaria	BEO	IFT SMPS	Am241 370MBq	4 m	Nafion	Nafion	
25	CHMI	Kosetice, Czech R.	OBK	IFT SMPS	Kr85 370 MBq	4m	Nafion	Nafion	
26	UPAC	K-Pusztá, Hungary	KPS	home-made UHEL-DMPS			Nafion	Nafion	

ACTRIS Associated Partner #		Station	Station	S/DMPS	Charger	Equivalent length	Dryer	Dryer	Ion Spectrometer
					type&strength	(loss correction)	aerosol	sheath air	type
AP4	FMI	Pallas, Finland	PAL	home-made DMPS	??		main inlet	Diffusion	
AP10	NCSR-D	Demokritos, Greece		mode made SMPS	Kr-85 10mCi	7 m (estim.)	Nafion	Nafion	
AP11	NOA-IERSD	Navarino Env. Obs., GR		home-made DMPS (SU)	??		Nafion	Nafion	
AP15	SU	Aspvreten, Sweden	ASP	home-made DMPS	Ni63, 10 mCi		Nafion	Nafion	
AP18	UNIBHAM	Harwell, United Kingdom		TSI SMPS	Kr85		main inlet	Nafion	
(not AP yet)	IPL	Preila, Lithuania	PLA	IFT SMPS	??	4m	Nafion	Nafion	

*The mobility spectrometers marked colored do not fully fulfill the EUSAAR/ACTRIS recommendations.

Decisions:

- We accept only high size resolution SMPS and DMPS preferably with a closed loop technique, using a particle counter as detector. This excludes e.g. systems such as the TSI 3031.
- Presently, the Grimm SMPS uses a weak Americium-241 bipolar charger, which produces an unknown bipolar charge distribution. We do not accept a general correction function to correct the number size distribution. This correction function won't be size distribution-independent.
- We suggest only using capable chargers, if possible with an activity of ~ 370MBq.
- The "Riebel bipolar charger" (presently used at PDD) cannot be accepted yet; it needs further investigations at which HV it should be operated and how the time-stability is.
- Presently, we do not accept the Soft-X-ray bipolar charger of TSI until we do know the bipolar charge equilibrium. This bipolar charge distribution is certainly different compared to the one produced in the traditional bipolar chargers. TSI provides a simple correction function, which can lead to large deviations.

Station status for data submission:

Several stations still keep the old data format for data submission. We need however to harmonize data submission. All the data have to be submitted in the new format with all the corrections.

From 2011 on, data have to be corrected for internal diffusion losses using the method of equivalent length. If possible, older data should be re-submitted including the correction for internal particle losses.

Data Submission for the 2008, 2009 and 2010:

As soon as possible, all the users should re-submit the previous years of data according to the previous statements.

Data corrected for diffusion losses.

Data submitted in the new format.

Aerosol charge Neutralizers inter-comparison:

Erik Swietlicki will send the Ni-63 radioactive sources to IFT to be intercompared with Kr85 radioactive sources.

Part IV Sampling and Inlets

Status of stations

ACTRIS Partner #	Station	Station	Inlet	Inlet Dryer	
1	CNR	Monte Cimone, Italy	MTC	Whole air, heated	no
2	CNRS	Puy de Dôme, France	PDD	Whole air, heated	no
2	CNRS	Sirta, France	SIRTA	TSP needs to be changed	no
2	CNRS	Maido, France	MAIDO	No information	
3	NILU	Birkenes, Norway	BIR	PM10, heated	no
4	UHEL	Hyttiälä, Finland	SMR	seperate, PM10	no
5	TUD	Cabauw, Netherlands	CESAR	4x PM10, nafion drye	Nafion
6	PSI	Jungfraujoch, Switzerland	JFJ	Whole air, heated	no
7	IFT	Melpitz, Germany	MPZ	PM10	Diffusion
10	UPC-UGR	Granada, Spain		Whole air, needs to be changed	Possibly dryer needed
12	ULUND	Vavihill, Sweden	VHL	3x PM10	Separate dryers
13	CSIC	Montseny, Spain	MSY	PM10	Nafion
13	CSIC-AEMET	Izaña, Spain	IZO	Whole Air inlet; PM10 impactors for neph and MAAP	no drier needed
14	NUIG	Mace Head, Ireland	MHD	whole air, PM10?	No, needs to be changed
15	NERC	Auchencorth Moss, UK	Eiko Nemitz	PM2.5, change to PM10?	Nafion
16	FORTH	Finokalia, Greece	FKL	PM1o	no
17	JRC	JRC-Ispra, Italy	IPR	High flow PM10	no
18	DWD	Hohenpeissenberg, Germany	HPB	PM10	Nafion
20	BEO	BEO Moussala, Bulgaria	BEO	Whole air, heated	not needed
25	CHMI	Kosetice, Czech	OBK	PM1o	no

		Republic			
26	UPAC	K-Pusztá, Hungary	KPS	NOAA PM10, DMPS separate	1:1 Dilution with dry air

ACTRIS Associated Partner #		Station	Station	Inlet	Inlet Dryer
AP4	FMI	Pallas, Finland	PAL	Custom, not defined?	no
AP10	NCSR-D	Demokritos, Greece		PM2.5	Nafion
AP11	NOA-IERSD	Navarino Env. Obs. GR		PM10	No, possibly needed
AP15	SU	Aspvreten, Sweden	ASP	size cut not defined	no
AP18	UNIBHAM	Harwell, United Kingdom		PM1 (SMPS + total CPC)	Nafion
(not AP yet)	IPL	Preila, Lithuania	PLA	PM10	no

Part V Organic Tracers

Introduction

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. The deliverables of this WP3 activity are:

- Expert workshop on organic tracer measurements (public report, M12)
- Standardized of the sampling and analysis of specific organic tracers (public report, M24)
- Implementation of organic tracer measurements at European sites (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

- Monosaccharide anhydrides as tracers for biomass combustion (levoglucosan, mannosan, galactosan)
- GC-MS molecular tracers (vehicles, petroleum, plant waxes, microbial, higher plants, meat cooking, tire wear...), and
- H-NMR spectral fingerprints (biomass etc) and 14C (modern/fossil carbon), HPLC, AMS, etc...

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 campaign 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 (¹⁴C, GC-MS, HPLC, HNMR, AMS)

Analytical techniques for organic tracers – French experiences

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 global 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 recommended and measured

Extraction:

- optimized for the simultaneous extraction of all compounds
- Average extraction depending of compounds in the majority 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:

- JJJ: capable of performing this on filter with PM as low as 15µg/m³
- 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 EUCAARI (Guyla Kiss):

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 semi-volatile)
- Sampling time (loss of semi-volatile)

Optimization and standardization of analysis:

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

The GC-MS approach has the advantage that it can identify and quantify a large number of organic tracers.

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, Sulliovatn 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 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 of traffic, energy production, tyre wear,... by using organic tracers
- The combination of techniques is necessary!!!!

Who will do it and 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:

Jean-Philippe: it is important to also consider the Aethalometer approach with the network that is already set up since we pushed for a 7-wavelength Aethalometer.

^{14}C fossil/modern carbon, possibilities and problems (Nolwenn Perron)

The ^{14}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 ^{14}C).

However, there are some artificial sources of ^{14}C :

- Nuclear bomb test
- Nuclear power plants
- Pharmaceutical industry

Aerosol samples are sometimes affected by ^{14}C contamination. There are cases when the aerosol radiocarbon analysis shows an unexpected excess in ^{14}C . Examples were shown from Lund, Sweden, where it was evident that there is significant ^{14}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}C ?

Conclusion:

- It is impossible to perform make ^{14}C based source apportionment in the surroundings of ^{14}C producing facilities.
- This makes most urban ^{14}C based source apportionment studies questionable.
- How far away do we have to go from the artificial ^{14}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}C values (high pMC) on your filters!! Reporting these could help others realizing the problems, 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}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)

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 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 ¹⁴C?

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 (2012/2013)

The summer campaign will take place from 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:

- 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) for the overall campaign coordination and André Prevot at PSI (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-puzta (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:

Jungfraujoch (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.

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

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 January 2012). 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

<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 CO₂.

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

Multi-variant 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 The Latin hypercube sampling (LHS) method. See Gelencser et al., 2007; Genberg et al, ACP 2011) for further information.

Examples of organic aerosols source apportionment

Organic aerosols source apportionment in France (Christine Piot)

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)

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- λ 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- λ 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}C ,...)

Questions/comments:

Discussion on whether it is possible to how 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- λ 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)

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}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)

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

Criteria for organic tracer compounds:

- Unique to a specific 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 within ACTRIS WP3:

- OC, EC
(YES) Methods → EUSAAR-2 protocol
- Biomass burning: Levoglucosan (mannosan, galactosan)
(YES) Methods → GC-MS, HPLC-ESI-MS/MS, HPLC-HRMS-TOF
- Modern/fossil carbon: ^{14}C (if possible on OC and EC separately)
(YES) Method → AMS (Accelerator Mass Spectrometry)
- Traffic (gasoline, diesel): PAH, hopanes, steranes
(YES) Method → GC-MS
- Mass spectrometric group analysis, several sources: (OC only)
(YES) Method → mini-AMS, HR-TOF-AMS (Aerodyne) by several groups
- Functional group analysis, several sources: (if possible on OC and EC separately)
(Probably) Method → HNMR (only at ISAC-CNR)

Methods and tracers that should be considered within ACTRIS WP3:

- Primary biogenic (Fungal spores): Mannitol, arabinol, trehalose
(Possible) Method → HPLC-HRMS-TOF
- 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 α -pinene (Müller et al, ACP 2012). It can be collected on filters and analyzed by liquid chromatography/mass spectrometry (LC/ESI-MS).

A series of methyl-nitrocatechol isomers (including 4-Methyl-5-nitro catechol) has been identified as a tracer for SOA originating from biomass burning (Linuma 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, α - and β -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.

PART VI CCN Counter

Calibrations

Temperature sensor "calibration":

- No calibration is required.
- Differences between nominal/set and actual temperature values may occur \Rightarrow see recommendations.

Recommendations:

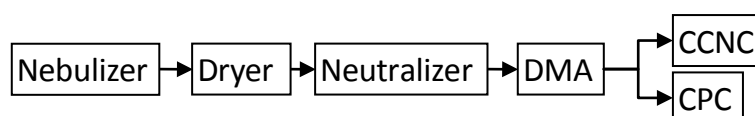
- Minimize differences between nominal/set and actual temperature values, if needed contact DMT. Note: a recalibration is required after adjusting the temperature gain parameter.
- Users should be consistent in either using the nominal/set or actual temperatures.

SS calibration:

- A target accuracy in supersaturation of $\pm 10\%$ (relative) is suggested at supersaturations above 0.2, for lower SS a different measure is needed (e.g. $\pm 0.03\%$ SS).

Recommendations:

- Calibration setup should consist of nebulizer, dryer, neutralizer, DMA, CCNC, CPC:



- Supersaturation calibrations should be performed at least every six month.
- Particle number concentrations larger than 2000 #/cc should be avoided during calibration.
- Calibration should be performed with ammonium sulfate particles.
- Proper column temperature for calculating surface tension should be used (action item for M. Gysel).
- Size- and temperature dependent critical supersaturation values of ammonium sulphate should be taken from the thermodynamic model ADDEM should be used and/or compared with own activity models (2% deviation to ADDEM is acceptable).
- A linear calibration curve (with non-zero axis intercept) should be applied when relating critical supersaturation to temperature gradient.

Action items:

- *Emanuel Hammer (PSI)*: Sends around calibration raw data and collects and compares calibration curves generated by CCNC operating groups.
- *All*: Generate calibration curve from raw data provided by PSI and send calibration curve to PSI.
- *Martin Gysel*: Sends around look-up table concerning droplet thermodynamics produced via ADDEM.
- *Frank Stratmann*: Provides calibration uncertainties from long term measurements.

Flow rate calibration

- Deviations between nominal and actual total and sample flows may occur if the differential pressure gages are not accurately calibrated.
- Deviations in total flow rate affect the actual supersaturation.
- Deviations in sample flow rate affect the measured droplet concentration. The plateau value of the activated fraction observed during calibration will be different from unity.

Recommendations:

- Total flow rate should be checked every time you are at site, at least every month.
- Sample flow should be checked at least every six month (this can be done by careful check of the plateau value of the activated fraction observed during calibration).

Counting efficiency / diffusion losses

- Diffusion losses occur at diameters below ~70 nm roughly.
- The diffusion losses will be ignored for monitoring measurements.

OPC calibration

- OPC calibration is optional.

SOP

Flow rate:

Recommendations:

- No recommendation is made whether temperature gradient stepping at constant flow rate or flow rate scanning at constant temperature gradient is the preferred operation mode for polydisperse measurements (decision post-poned, to get Erik's opinion, see below).
- Choice of total flow rate is free with a minimum of 0.2 and maximum of 1 l/min.
- Default value for the ratio of sample to total flow is 1/10, however values ranging from 1/5 to 1/15 should be feasible.

Action items:

- *Erik Swietlicki*: Confirms minimum and maximum total flow rates.
- *Erik Swietlicki*: Is willing to share code illustrating how to scan CCNC-flows and therefore supersaturation.
- *Erik Swietlicki*: Volunteered to provide a summary concerning the pros and cons of scanning flow for adjusting supersaturation.

Temperatures

Recommendations:

- It should be made sure that T1 it is below Tinlet and that T1 should be below 30°C.

Polydisperse vs. monodisperse measurements

- choice to be made by the stations

Polydisperse measurements

Recommendations:

- Common supersaturations for polydisperse measurements should be: 0.1, 0.2, 0.3, 0.5, 1.0 (1.0 for test purposes every now and then).

- If possible or desired a finer resolution can be considered: 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.5, 0.7, 1.0.
- Duration of a complete measurement cycle should be one hour or shorter.
- Enough time should be given concerning minimum duration per supersaturation to ensure good counting statistics.

Remarks:

- *Erik Swietlicki*: Equilibrium is not reached in scanning flow mode. Consequently the flow rate ramp has to be identical to that applied during calibration.
- *Markus Fiebig*: Report values always for the same supersaturation, even if interpolation is needed.

Monodisperse measurements

Recommendations:

- ACTRIS recommends D-scans.
- A neutralizer must be used in front of the DMA.
- The DMA should be operated as outlined in SOP for size distribution measurements.
- Diameter range to be covered during D-scans should be 40 – 300, or from zero activation to 300 nm (covering diameters larger than 300 nm is appreciated but not mandatory).
- Common supersaturations for monodisperse measurements should be 0.1, 0.2, 0.3, 0.5, 1.0 (1.0 for test purposes every now and then)
- Duration of measurement cycle should be around 1 to 1.5 hours.
- CCN-size distributions should be reported (rather than diameter dependence of activated fraction).

Data analysis procedures

Recommendations:

- Which temperature difference should be used as a reference for the supersaturation, e.g. T2-T1 or T3-T1? (Martin will get in contact with Thanos Nenes in order to make a recommendation.)
- No recommendation was made concerning which temperature should be used for calculating the surface tension (Martin will get in contact with Thanos Nenes in order to make a recommendation.)
- Diffusion losses, which become important below ~70 nm, should be ignored for now. Correction of polydisperse CCN measurements for diffusion losses would only be possible if parallel SMPS measurements are available. (A sensitivity study should possibly be performed).

Action items:

- *Martin Gysel*: Gets in contact with Thanos Nenes in order to identify the relevant temperature difference determining the SS.
- *Martin Gysel*: Gets in contact with Thanos Nenes concerning the temperature at the centre of the CCN's column at point of CCN activation.
- *Volunteer*: Performs a sensitivity study regarding the potential importance of considering the diffusion losses.
- *Groups possessing a code for inversion of monodisperse measurements*: It would be good to share the inversion code (in transparent form) with those groups that still need an inversion code for their monodisperse measurements.

Remarks:

- *Martin Gysel*: Stopping D-scans at D=300 nm implies that size distributions measured independently by an SMPS have to be used to estimate the number concentration of CCN above 300 nm.

- *Martin Gysel*: Verification of consistency between the calibrations of the SMPS and CCNC can be achieved as follows: polydisperse pure ammonium sulphate should be provided to the main inlet and the SMPS and CCNC should be operated in standard "monitoring" configuration. A closure study between SMPS and (polydisperse) CCNC can be done by integrating the SMPS above the critical diameter calculated for pure ammonium sulphate for the supersaturation applied in the CCNC.

EBAS Data format

Data filtering (open questions):

- Tolerance for deviations of total flow rate from nominal set point?
- Tolerance for actual supersaturation?

Level 0:

- Standard deviations for flow rate should be provided for later quality checks.
- Standard deviation for temperatures should be provided for later quality checks.
- Quality flags should be applied for flow rates (if flow is off during one set point, data should be rejected for level 1 and 2!). Acceptable tolerances: flow rate bias $<\pm 5\%$; relative standard deviation $<10\%$. Instruments operated in scanning flow rate operation will have to find their own reasonable quality criterion (corresponding to less than 10% relative uncertainty in the precision of the applied SS). Note, the flow rate control is susceptible to disturbance from other applications with high memory/CPU usage such as e.g. remote desktop login.
- Quality flags should be applied for the CCNC's flow ratio (sample : total): values between 1:5 and 1:15 should be acceptable.
- Quality flags should be applied for the maximum CCN number concentration (coincidence and water vapour depletion effects). Upper limit remains to be identified.
- Stable supersaturation should be assured (if SS is stepped). This can be achieved in different ways. A first option is filtering a sufficiently long time interval after setpoint changes based on careful tests of the equilibration times. A second test is to use the temperature readings to filter transient periods. The maximum temperature tolerance should correspond to less than 10% relative uncertainty in the precision of the applied SS. The type of stability criterion applied should be stated in the header of the file. Note, the CCNC's flag "temperatures stabilized" is not always sufficient.
- Nominal set point of total flow rate is missing in the instrument output and needs to be added by users when loading the raw data.
- Set points for supersaturation should be reported (either set point or reading should be indicated and used CONSISTENTLY).
- CCNC calibration data should be reported (requires flag marking data as "ambient" or "calibration").
- Monodisperse CCN data should contain the same quality parameters as SMPS data.
- Providing results for different supersaturations in one or different files? (In the former case, which time stamp should be used, in the latter native time should be used). Markus Fiebig will take a decision.

Action items:

- *Markus Fiebig*: Instructions concerning the level 0 data format will be distributed by the end of the year.
- *Frank Stratmann*: Check literature for upper limit CCN number concentration below which coincidence and water vapour depletion effects are negligible.

Level 1:

- Difference between level 0 and level 1 is mainly averaging

- Averaging time should be 1 hour.
- Monodisperse data must be inverted data and the inversion result must be quality checked.
- "Inversion" means at least correction for multiply charged particles, while considering effects of DMA transfer function is optional.
- Providing results for different supersaturations in one or different files? (In the former case, which time stamp should be used, in the latter native time should be used). Markus Fiebig will take a decision.
- If calibrations are different before and after a measurement period, those two calibrations should be averaged. 20 % difference is acceptable for now, if difference is larger, data should be flagged by provider.
- Calibration data are not included in level 1.

Level 2:

- Conversion to STP should be performed.
- Averaging time should be 1 hour for polydisperse and 3 hours for monodisperse measurements. (Time stamp refers to the end of the interval).
- The results for all supersaturations are provided in a single file.
- No information on variability will be provided, as the sampled subset is too small to provide statistically relevant information on the variability.