Guidelines for comparison of ACSM measurements with co-located external data

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1 INTRODUCTION

Airborne particles (or aerosols) are ubiquitous pollutants in ambient air, with significant impacts on the Earth's climate, ecosystems and human health. A better understanding of these effects requires high quality measurements of the aerosol physical and chemical properties, especially within the fine fraction (e.g. particles with aerodynamic diameters less than 1 or 2.5 µm (PM_1 and $PM_{2.5}$, respectively)). In the last decade, the Aerosol Chemical Speciation Monitor (ACSM, *Aerodyne Res. Inc.*) has been deployed at a growing number of monitoring stations and research facilities. This instrument provides near real-time measurements of the major chemical components of non-refractory submicron particles (NR-PM_1). It was built on the same operating principles than the Aerodyne Aerosol Mass Spectrometer (AMS), but with the advantage of being cheaper, simpler and more robust. It is therefore particularly well suited for continuous networking in situ observation activities. One of the main goals of the COLOSSAL COST Action CA16109 (https://www.costcolossal.eu/) is to establish common ACSM standard operation procedures, to guarantee comparability of measurements over Europe and to facilitate the implementation of research infrastructure such as ACTRIS (https://www.actris.eu/).

In this context, the present document provides guidelines for the comparison of quadrupole or time-of-flight ACSM data with external data obtained from relevant co-located measurements. Such comparison exercises are essential to assess the validity of tuning and calibration parameters applied for ACSM operation. They include so-called "chemical mass closure", where the sum of major chemical species is compared to total PM mass concentration measurements or estimates. In this case, **NR-PM_1 ACSM measurements should be combined with refractory species mass concentrations, starting with Elemental or equivalent Black Carbon** (EC and eBC, respectively) and possibly including sea salt and/or mineral dust measurements. Comparisons of individual chemical species concentrations with external data are also highly recommended. More generally, the use of any available co-located measurements is worth considering. Nevertheless, the two following principles should always be kept in mind:

- **Priorities should be given to comparisons with other instruments which measure mass concentrations directly** (rather than instruments allowing for the estimation of mass concentrations using theoretical and/or empirical conversion factors or algorithms).
- Due to the low time-resolution and significant artefacts possibly affecting offline filter-based measurements[1,2,3], **comparison with complementary online data is preferred**, when available.

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[1] EN 12341:2014 Ambient air - Standard gravimetric measurement method for the determination of the PM_{10} or $PM_{2.5}$ mass concentration of suspended particulate matter.

[2] EN 16909:2017 Ambient air - Measurement of elemental carbon (EC) and organic carbon (OC) collected on filters.

[3] EN 16913:2017 Ambient air - Standard method for measurement of NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+} in PM2,5 as deposited on filters.

For comparison purposes, coherence in measurements conditions between ACSM and co-located instruments should be preserved. This includes T and RH in the inlet line and measured aerosol size fraction(s). Moreover, installation of a common primary sampling inlet should be considered for the ACSM and relevant co-located instruments, when appropriate (i.e., coherence within the measured size fraction(s) and preservation of a constant and laminar flow entering each individual instrument) and possible (e.g., in the case of long-term measurements at observatory platforms).

Before achieving comparison exercises, an important parameter to be considered is the ACSM collection efficiency (CE), which translates how efficiently the sampled particles eventually reach and are impacted onto the vaporizer. **COLOSSAL recommendations include to apply the procedure proposed by Middlebrook et al. (2012) to accurately estimate CE under various conditions,** as detailed in ACSM standard operation procedures.[4,5]

Examples of comparison exercises commonly achieved within the scientific community are given in sections 3 and 4 of the present document, in order of appearance determined by both general principles described above. Section 2 provides general guidance on the type of regressions to be considered when performing these comparisons.

2 GENERAL RECOMMENDATIONS FOR COMPARISON DATA TREATMENT

Comparison results can notably be presented and investigated by compiling timeseries in a single graph or using scatterplots. Here, it is recommended to use both. The first display may help to easily and precisely identify when outliers or suspicious periods occur. The second one allows improved quantification of the amplitude of the correlation and/or deviations that could be observed between the compared datasets. In this case, **it is highly recommended to use an orthogonal regression**, as, generally, none of the compared datasets may be considered to be without error.

It is preferable to get and use external data obtained for the same size fraction as ACSM measurements (most commonly PM_1). In this case, orthogonal regressions - in the form '$y = ax + b$' - are expected to show satisfactory correlations (typically, $r^2 > 0.8$), with b (intercept) close to 0 and a (slope) close to 1, depending on the combined instruments' uncertainties. For major species (i.e., organic matter, nitrate, sulfate and ammonium) as well as for NR-PM_1 concentrations, overall ACSM measurement uncertainties on the order of 20-35% have been proposed by various studies.[6,7,8]

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[4] Middlebrook et al. (2012) Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Science and Technology, 46:3, 258-271.

[5] Current SOP version available from COLOSSAL website (https://www.costcolossal.eu/).

[6] Budisulistiorini et al. (2014) Intercomparison of an Aerosol Chemical Speciation Monitor (ACSM) with ambient fine aerosol measurements in Downtown Atlanta, Georgia. Atmos. Meas. Tech., 7, 1929-1941.

When comparing datasets corresponding to different size fractions, one does not aim at having *b* (intercept) close to 0 nor *a* (slope) close to 1. The determination of acceptable thresholds and criteria should then be left to the operator's appraisal, notably based on his/her knowledge of the sampling environment and expected aerosol size distribution at the sampling site.

In any case, **a sudden change in the slope needs to be investigated**, as it might be caused by a modification of the ACSM voltages, calibration factors, CE or by a technical failure (valve, filter, pump, etc.).

Comparisons of individual chemical species concentrations with external data can support the identification of the optimal CE value, which can depend on the type of sampled aerosols. For instance, Alfarra et al. suggested CE value equal to 0.7 when high relative contributions of organic matter from biomass combustion are present.[9]

Moreover, a growing concern is currently related to the accuracy of the Relative Ionisation Efficiency (RIE) of organic aerosols (RIE_{org}), which is set by default to 1.4. Unlike for other main chemical species (i.e., nitrate, sulfate and ammonium), this RIE value is usually neither calibrated nor empirically validated (e.g., checking for the ion balance as in the case of inorganic species), and its fluctuation could have a substantial influence on organic and NR-PM_1 mass concentrations derived from the ACSM. Just as an example, Reyes-Villegas et al.[10] recently showed that cooking organic aerosols might display RIE values up to 3 in ambient air. Therefore, if scientifically sound and relevant evidences are obtained, this RIE_{org} value might be adjusted upon user's appraisal - and clearly documented - in specific case studies.

Nevertheless, discrepancies between the ACSM and the co-located instrument datasets should always be interpreted with caution since biases may also come from co-located instrument(s). Moreover, the accuracy of mass concentrations delivered by the ACSM notably rely on three parameters which are applied in the same way to each chemical species, namely the NO_3 Response Factor (RF_{NO3}), the collection efficiency CE and the Air Beam signal. Then, **once all ACSM technical validations have been carried out**, including checking for the use of accurate RIE values, **discrepancies with external data should not lead to systematic invalidation of the relative distribution of the chemical species.**

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[7] Crenn et al. (2015) ACTRIS ACSM intercomparison - Part 1: Reproducibility of concentration and fragment results from 13 individual Quadrupole Aerosol Chemical Speciation Monitors (Q-ACSM) and consistency with co-located instruments. Atmos. Meas. Tech., 8, 5063-5087.

[8] Bahreini et al. (2009) Organic Aerosol Formation in Urban and Industrial Plumes Near Houston and Dallas, Texas. *J. Geophys. Res.* 114:D00F16.

[9] Alfarra et al. (2007) Identification of the Mass Spectral Signature of Organic Aerosols from Wood Burning Emissions. Environ. Sci. Technol., 41, 5770-5777.

[10] Reyes-Villegas et al. (2018) Online Chemical Characterization of Food-Cooking Organic Aerosols: Implications for Source Apportionment. Environ Sci Technol, 52, 5308-5318.

Another important point to be carefully considered for comparisons is **the coherence of the time-period corresponding to each data point**. Generally, a common timeframe should be determined by the lowest time-resolution of the different datasets to be compared. Furthermore, one should make sure that time stamps are coherent, i.e. each compared data point are actually corresponding to the same time-period.

Note #1: for Q-ACSM, the time stamp of a given data point corresponds to the end of this data point averaging period; while for ToF-ACSM, it roughly corresponds to the beginning of the averaging period (depending on the selected number of "filter valve closed measurements", which are disregarded for time stamping).

Note #2: dedicated Igor procedures are notably available on request at acmcc@lsce.ipsl.fr or from Aerodyne Res. Inc. in order to process and estimate ACSM concentration timeseries on a different timeframe than the one corresponding to the actual sampling timeframe.

3 CHEMICAL MASS CLOSURE

It is possible to "reconstruct" PM mass concentrations as the sum of major chemical species, including NR species measured by the ACSM. To do so, it is highly recommended to also account for equivalent black carbon or elemental carbon concentrations (eBC and EC, respectively) in the calculations. Indeed, this latter compound is the main refractory species within the fine aerosol fraction. eBC data is commonly obtained from absorption photometers (e.g., aethalometers, *Magee Scientific*); while EC is generally measured using online or offline filter-based thermal-optical devices (preferably using the EUSAAR2 protocol, according to EN 16909). Online eBC/EC measurements should be preferred as they will allow comparisons at a higher time resolution.

Therefore, in the most common case of submicron measurements and using an absorption photometer, the following equation should be applied:

$$PM_{1,\ chem} = NO_3 + SO_4 + NH_4 + Cl + Org + eBC \qquad \textit{(Eq. 1)}$$

where NO_3, SO_4, NH_4, Cl and Org are nitrate, sulfate, ammonium, chloride and organic aerosol concentrations obtained from the ACSM after CE corrections, and eBC concentrations are derived from absorption photometer measurements.

"$PM_{1,\ chem}$" can then be compared to co-located measurements, using orthogonal regression analysis as described in section 2.

In any case, *Eq. 1* is only valid when no other chemical species significantly contributes to total PM mass. Even if most commonly present in the coarse aerosol mode, sea salt and mineral dust might need to be considered in this equation, notably at coastal and semi-arid environments (Figure 1), respectively.

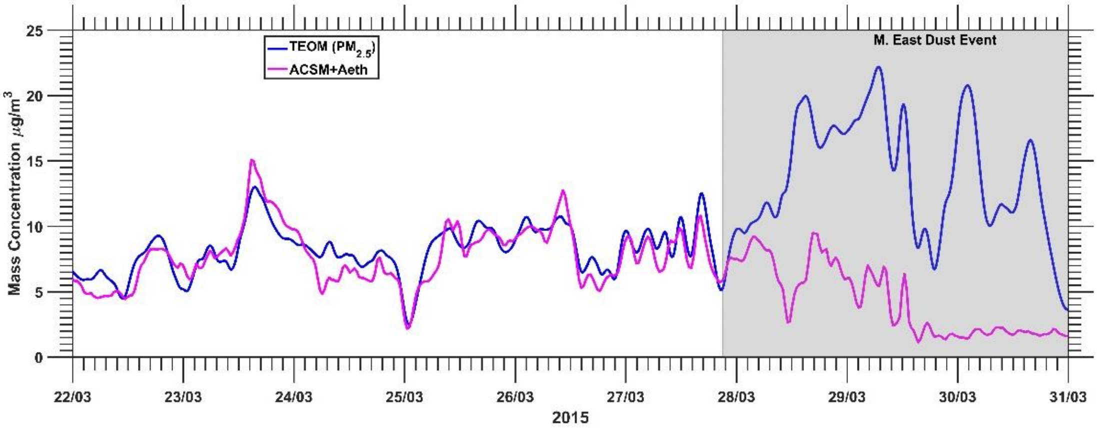

Figure 1. Comparison of ACSM (PM_1) and Aethalometer (PM_{10}) datasets with TEOM-FDMS ($PM_{2.5}$) measurements before and during a mineral dust event at Ayia Marina Xyliatou observatory platform (courtesy of M. Pikridas, The Cyprus Institute).

3.1 Comparison with PM mass concentration analyzers

Ideally, mass closure exercises should be achieved by comparison to direct online measurements of PM mass concentrations within the same aerosol size fraction than the one sampled through the ACSM lens (either PM_1 or $PM_{2.5}$). Candidate PM analyzers include the Tapered Element Oscillating Microbalance equipped with Filter Dynamic Measurement System (TEOM-FDMS, *Thermo*) and beta gauge devices.

It should be considered that PM mass concentration analyzers used for regulatory monitoring in the frame of the European Directives on ambient air shall be able to operate with a maximum expanded measurement uncertainty of 25%.[11]

When PM mass concentration measurements are not available for the aerosol size fraction used by ACSM measurements, different size fractions can be compared. Hence, it is possible to compare $PM_{1,\ chem}$ with online $PM_{2.5}$ regulatory measurements, keeping in mind that the difference in aerosol size fractions can substantially influence the correlation. Comparisons with PM_1 mass concentration estimates from Mobility Particle Size Spectrometers (MPSS, see section 4.2) or optical devices (section 4.3) are also highly recommended.

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[11] EN 16450:2017 Ambient air - Automated measuring systems for the measurement of the concentration of particulate matter (PM10; PM2.5).

3.2 Comparison with Mobility Particle Size Spectrometers

Particle number size distribution (PNSD) is usually measured in parallel to the ACSM using Mobility Particle Size Spectrometer (MPSS). A chemical mass closure exercise can then be achieved between $PM_{1,\ chem}$ (see Eq. 1) and an estimated PM_1 mass concentration derived from the MPSS measurements. To do so, MPSS volume size distribution can be converted into mass concentration, assuming particles to be spherical and calculating time-dependent gravimetric density based on the following equation from Salcedo et al. (and references therein)[12]:

$$density = \rho = \frac{[Total_{AMS} + eBC]}{\frac{[NO_3^-] + [SO_4^{2-}] + [NH_4^-]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[Org]}{1.2} + \frac{[eBC]}{1.77}} \qquad \textit{(Eq. 2)}$$

where time-dependent chemical composition is coming from ACSM, with respective densities of 1.75g cm^{-3} for nitrate, sulfate and ammonium, 1.52 g cm^{-3} for chloride, and 1.2 g cm^{-3} for organic matter.[13] For the latter one, as stated by Turpin and Lim[14], significant contributions of carboxylic acids and/or polycyclic aromatic hydrocarbons as well as a significant presence of amines and amino acids would increase the organic aerosol density, while higher concentrations of n-alkanes and/or n-alkanoic acids would result in a decrease of the density. Finally, for eBC, a default density of 1.77 g cm^{-3} can be applied, while additional information is also available in Poulain et al.[15]

Alternatively, ACSM data can be converted into volume concentrations - by dividing each species mass concentrations by its expected density (see above) and adding them together - and then compared to volume MPSS data.

In both cases, the consistency (or discrepancy) of the overall size fractions sampled by the ACSM and the MPSS should be investigated and documented. To do so, mobility diameters used within MPSS can be converted into vacuum aerodynamic diameters used within ACSM ($D_{va} = \rho.D_m$).[16]

Deviations could be observed in the correlations due to temporal variation (typically seasonal and/or diurnal variations) of the particle size distribution. Particle volume size distribution (PVSD) must be systematically investigated in case of discrepancy between the two methods or datasets (that coming from MPSS and that coming from ACSM). In the presence of coarse mode particles, the low transmission efficiency of the aerodynamic lenses of the ACSM might induce an underestimation of the total mass

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[12] Salcedo et al. (2006) Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmos. Chem. Phys., 6, 925-946.

[13] See also: Cross et al. (2007) Laboratory and ambient particle density determinations using light scattering in conjunction with aerosol mass spectrometry, Aerosol Sci. Technol., 41, 343-359.

[14] Turpin and Lim (2001) Species Contributions to $PM_{2.5}$ Mass Concentrations: Revisiting Common Assumptions for Estimating Organic Mass, Aerosol Science & Technology, 35:1, 602-610.

[15] Poulain et al. (2014) Chemical mass balance of 300 degrees C non-volatile particles at the tropospheric research site Melpitz, Germany, Atmos. Chem. Phys., 14, 10145-10162.

[16] DeCarlo et al. (2014) Particle morphology and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, Aerosol Sci. Technol., 38, 1185-1205.

compared to the MPSS. An instrument-dependent sensitivity can be expected depending on each aerodynamic lens.

Finally, as for *Eq. .1*, *Eq. 2* is only valid when no other chemical species (e.g., sea salt and/or mineral dust) is significantly influencing the sampled aerosol total mass concentration.

3.3 Comparison with optical devices

We refer here to optical particle sizers/counters measuring the number of medium and coarse particles (typically, 200 nm - 20 µm) within as many size classes as possible (notably including *PALAS*, *Grimm*, and other devices). These instruments commonly propose PM_1 and $PM_{2.5}$ mass concentration estimates based on assumptions empirically determined and implemented in the device's software by the manufacturer.

The use of these devices should preferably be accompanied with external calibration set-up, i.e., regularly achieving parallel gravimetric validation exercises (ideally, following EN 16450 and EMEP sampling procedures[17]). Alternatively, *Eq. 2* might also be used to validate or to correct mass concentration estimates provided by the optical system based on the number of particles counted in each size class.

3.4 Comparison with gravimetric offline methods

Even if affected by low time resolution and various sampling artefacts, the offline filter-based gravimetric method is still recommended for direct measurements of PM mass concentration. Obtained results are also of interest for testing the chemical mass closure proposed by *Eq. 1*.

Ideally, this method should be used following EMEP sampling procedures and/or EN 12341 handling, sampling, weighing, transport and storage recommendations.

4 INDIVIDUAL CHEMICAL SPECIES

4.1 Comparison with online chemical analyzers

To limit the risk of sampling artefact influence, it is preferable to compare ACSM chemical species concentration to corresponding dataset obtained from online measurements, rather than off-line filter-based chemical speciation.

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[17] https://www.unece.org/fileadmin/DAM/ie/capact/ppp/pdfs/rws2/emep_man_e.pdf (as accessed on November 19th, 2019): EMEP manual for sampling and chemical analysis, EMEP/CCC-Report 1/ (ref: O-7726), revised Nov. 2001.

External data may originate from another aerosol mass spectrometer instrument (e.g., validation campaigns using an extra ACSM, or co-located measurements using a High-Resolution AMS system). It may also originate from other type of technology and/or methodology, as described below.

Most commonly, co-located automated measurements of inorganic species can be achieved using ion chromatography upstream of Particle-Into-Liquid Sampler (PILS) or Steam Jet Aerosol Collector (SJAC) systems. In both cases, the removal or subtraction of gaseous inorganic species should be achieved to deliver proper measurement in the particulate phase. As examples of commercially available and commonly used instruments, one can mention the MARGA (*Metrohm AG*) and the AIM (*Thermo*) devices.

Moreover, for sulfate and chloride, several online X-ray fluorescence apparatuses are now able to propose near-real time and in situ reliable measurements of total S and/or Cl concentrations.

For organic aerosol, online thermal-optical measurements of organic carbon (OC) are currently proposed by two manufacturers (namely, Sunset Inc. and DRI-Magee Scientific). Near-real time and in situ measurements of total carbon (TC) are nowadays developed by different companies and/or academic laboratories. When coupled with automated eBC measurements (such as from absorption photometers), such devices may provide estimates of OC concentrations in near-real time. This is for instance possible with the Total Carbon Analyzer (TCA) recently developed by *Aerosol d.o.o.* and commercialized by *Magee Scientific*. Here, an expected OC-to-OA conversion factor should be assumed (see below).

Depending on the investigated species, the following cautions should be considered:

- Ammonium nitrate and ammonium chloride

As these species are semi-volatile, same cautions as the ones taken for ACSM measurements should be considered for setting-up online ion chromatography sampling lines.[18]

- Refractory salts

In locations where sources of marine aerosols contribute to the fine aerosol mass, refractory salts (in particular, sodium chloride and sodium sulfate) as well as those resulting from atmospheric reactions (e.g., sodium nitrate) present challenges when comparing between ACSM and other measurement approaches. Their high melting points mean the 600°C ACSM vaporizer will not result in their evaporation and ionization. However, it is possible to adjust SO_4 measured using the ion chromatography measurements (or XRF measurements, assuming S as a tracer for SO_4), using Na (or Mg)

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[18] Poulain et al. (2019) Multi-year ACSM measurements at the central European research Station Melpitz (Germany) Part 1: instrument robustness, quality assurance, and impact of upper size cut-off diameter, Atmos Meas. Tech. Discuss., doi: 10.5194/amt-2019-361.

as a tracer for sea salt to provide an assessment of non-sea salt sulfate (nss-SO_4), to be eventually compared with ASCM measurements.[19] Similarly, non-sea-salt chloride concentrations may be derived from online ion chromatography, but the validity of expected Na/Cl or Mg/Cl sea salt ratios should be questioned for measurements at non-coastal sites and/or considering possible chloride depletion during air mass transport.

- Organic aerosol

According to EN 16909, organic carbon (OC) is corresponding to the mass concentration of carbon atoms (C) which is volatilised or oxidised to CO_2 in He or He + O_2 at temperature up to 850°C, and which is not detected as elemental carbon. Therefore, its comparison with organic aerosol mass concentrations (OA) measured by the ACSM requires assumptions on the quantity of heteroatoms (non-C) which are present with organic aerosols. If the comparison is perfect, the slope of the linear regression of OA vs OC corresponds to the OA-to-OC ratio. This ratio is dataset-specific. Some best-guess values can be found in dedicated studies.[20,21]

4.2 Comparison with offline filter-based measurements

When comparing individual chemical species with co-located filter-based offline measurements, sampling artefacts should be carefully considered. For example, it is extremely difficult to properly compare the ACSM-nitrate mass concentration with nitrate mass concentration from filter samples during summertime since ammonium nitrate evaporates from the filter. Similarly, ammonium, chloride and organic aerosol concentrations may be highly influenced by negative sampling artefacts. Positive sampling artefacts could also occur on filters, especially for organic aerosol.

Therefore, it is recommended to **mainly focus on comparison obtained for sulfate**, which may be less affected by positive and/or negative filter sampling artefacts. As for online co-located measurements, ACSM-sulfate concentrations have then to be preferably compared to nss-SO_4 concentrations.

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[19] Tremper et al. (2018) Field and laboratory evaluation of a high-time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols, Atmos. Meas. Tech., 11, 3541-3557.

[20] Aiken et al. (2008) O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols using of high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42 (12), 4478-4485.

[21] Canagaratna et al. (2015) Elemental ratios measurements of organic compounds using aerosol mass spectrometry: characterizations, improved calibrations, and implications, Aerosol Chem. Phys., 15, 253-272.