The study by Poulain et al. presented a comprehensive evaluation of the ACSM measurements based on the inter-comparisons with other collocated measurements for more than 5 years. The robustness, the limits, and the potential sources of uncertainties of the ACSM measurements for different aerosol species were well discussed. The results are very important for broad ACSM users to understand the long-term measurement uncertainties. The manuscript is well written, and I recommend it for publication.

We would like to thank the referee for his/her constructive comments and suggestions made to improve and clarify our manuscript. Our responses are given below. For clarity, comments from the referee are in black, our responses in blue, and change on the text of the manuscript in **bold blue**.

The authors would like to mention here that two additional co-authors were added to the initial list regarding to their contributions on the revision of the manuscript.

I have a few comments:

R1. The ACSM was calibrated twice at ACMCC, and also could be several times at the TROPOS research station Melpitz. How robust of the relative ionization efficiencies of ammonium and sulfate were. This is also an important information for long-term measurements.

A1: Thanks for bringing up this interesting and important point. To consider this, the following text has been added to the ACSM description (section 2.2) that discussed calibration and stability of the ionization efficiency (IE) and relative ionization efficiency (RIE) of ammonium and sulfate:

“The ACSM was regularly calibrated according to the manufacturer's recommendations at that time with 350 nm monodispersed ammonium nitrate and ammonium sulfate particles selected by a DMA and using the jump scan approach. It is important to note that since recently, the recommended calibration method has changed to a full scan approach (Freney et al., 2019). The total particle number concentration was systematically set below 800 # cm^{-3} to limit the artefact due to multiple charged particles. An overview of the ionization efficiency (IE) and relative ionization efficiency (RIE) for ammonium and sulfate can be found in Figure SI-1. On average, all performed calibration provides a mean IE value of 4.93 (± 1.45) 10^{-11} (mean ± std. dev.) and mean RIEs for ammonium and sulfate were 6.48 ± 1.26 and 0.68 ± 0.13, respectively. These values are very close to the ones used for the data evaluation as indicated in Figure SI-1. Overall, no clear trend for IE and RIE of sulfate can be observed over the period, while a small decrease in the RIE of ammonium can be reported. The lowest RIE of ammonium was reported just after the replacement of the filament indicated a possible need for degassing and stabilization period. However, it is difficult to conclude if these tendencies could be associated with a possible aging effect of the instrument since it corresponds to a single instrument. Similar observations on various other individual ACSMs would be needed to allow for stating such a conclusion and a more systematic investigation of potential trends should then be performed with a large number of ACSM.”

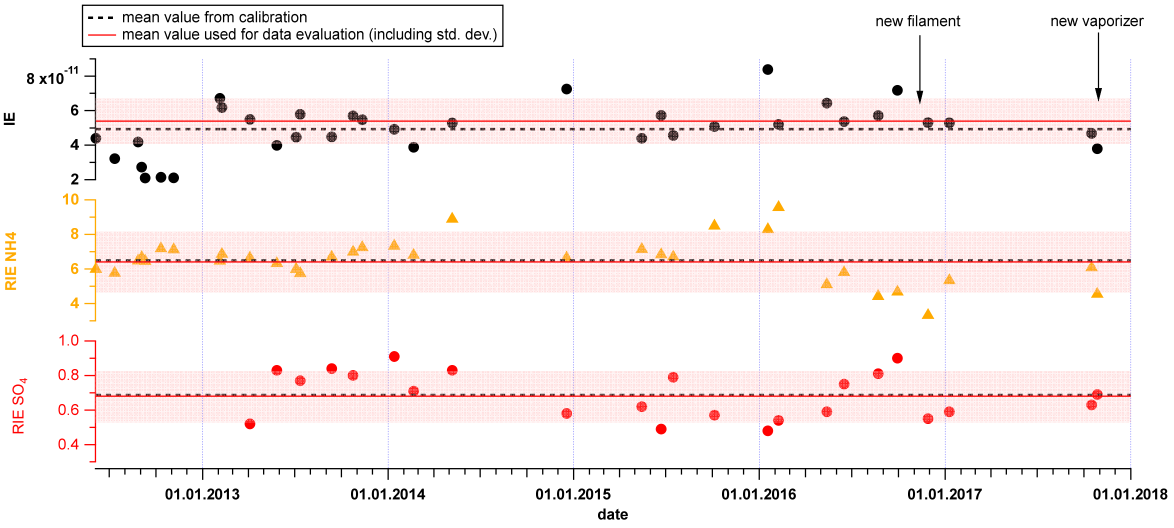


Figure SI-1: Time variation of the IE and RIE for ammonium and sulfate. The single points correspond to calibration, the dashed black line to the mean value from the calibration, and the full red line the mean value from the data analysis (shaded area corresponds to the standard deviation). Major maintenance (change of filament and vaporizer) are including.

R2. The format of ions should be consistent throughout the manuscript, e.g., page 7, line 15 – 25, use “+” for all ions.

A2: Charge was added to all mass spectra fragments.

Following correction were made:

P7, L 15-27: “[…] same m/z (for example, **$C_6H_8^+$** and/or **$C_5H_4O^+$** at m/z 80 for **SO_3^+**, or **$C_6H_9^+$** and **$C_5H_5O^+$** at m/z 81 for HSO_3^+) […] change of SO_3^+/SO^+ and HSO_3^+/SO^+ […]”

P 9, L 11: “[…] at m/z 30 (**NO^+**) and m/z 46 (**NO_2^+**), as well as on a minor contribution of N^+ and HNO_3^+ ions […] ”

P11, l31: “[…] a possible artefact on the CO_2^+ signal itself.”

R3. Page 15, line 25 – 26, “ACMS” to “ACSM”

A3 Corrected

References

Freney, E., Zhang, Y., Croteau, P., Amodeo, T., Williams, L., Truong, F., Petit, J.-E., Sciare, J., Sarda-Esteve, R., Bonnaire, N., Arumae, T., Aurela, M., Bougiatioti, A., Mihalopoulos, N., Coz, E., Artinano, B., Crenn, V., Elste, T., Heikkinen, L., Poulain, L., Wiedensohler, A., Herrmann, H., Priestman, M., Alastuey, A., Stavroulas, I., Tobler, A., Vasilescu, J., Zanca, N., Canagaratna, M., Carbone, C., Flentje, H., Green, D., Maasikmets, M., Marmureanu, L., Minguillon, M. C., Prevot, A. S. H., Gros, V., Jayne, J., and Favez, O.: The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations, Aerosol Sci. Technol., 1-25, 10.1080/02786826.2019.1608901, 2019.

The paper by Poulain et al. reports on long-term ACSM measurements at an established central European location and discuss different aspects of measurement quality assurance. The paper is well developed with data thoroughly analysed and as such is worth publishing in AMT. However, there are several issues to be resolved before it can be accepted for publication. Last but not least English of the paper should be improved following numerous suggestions. Special attention should be given to Figure captions which are often inconsistent and awkwardly worded.

We would like to thank the referee for his/her constructive comments and suggestions made to improve and clarify our manuscript. Our responses are given below. For clarity, comments from the referee are in black, our responses in blue, and change on the text of the manuscript in **bold blue**.

The authors would like to mention here that two additional co-authors were added to the initial list regarding to their contributions on the revision of the manuscript.

Major comments

R.1: Particle mass closure is already a routine requirement requested by reviewers when considering different aspects of AMS/ACSM performance. But what is missing in the abstract and little attention is given in the paper, is the impact of RH and inlets (impactor type or cyclones) affecting comparability. There is no question of the usefulness to cross-checking ACSM with online PM mass or offline PM speciation, but this paper should take a much more comprehensive approach to sampling inlets as crucial factors for maintaining stability and consistency of online chemical speciation monitors, more specifically isokinetic sampling and wet/dry cut-off effects in size selective inlets.

A1: The reviewer points out several important questions that will be answered separately.

1. The impact of RH when comparing measurements made at ambient RH (typically offline samplers) with the ones made at dry conditions.

We agree that mentioning this aspect is missing in the manuscript. However, we would like to draw the attention of the referee that our group already published a paper specifically discussing this question: Chen, Y., Wild, O., Wang, Y., Ran, L., Teich, M., Gross, J., Wang, L. N., Spindler, G., Herrmann, H., van Pinxteren, D., McFiggans, G., and Wiedensohler, A.: The influence of impactor size cut-off shift caused by hygroscopic growth on particulate matter loading and composition measurements, Atmos. Environ., 195, 141-148, 2018. Based on this study, the cut-off shift due to aerosol hygroscopic growth should play a minor role at Melpitz, as this effect was estimated to influence the comparison by 2 % for marine air-mass and 1 % for continental air-mass for PM_1 (7.2 % and 1.1 %, respectively for the $PM_{2.5}$). Overall for the European background station, the cut-off shift represents less than 10 % for PM_1 and 20 % for $PM_{2.5}$ particle mass loading. However, the cut-off shift can be stronger for marine or coastal stations (up to 43 % for PM_1 and 62 % for $PM_{2.5}$) and must consequently be considered when doing such a comparison.

The following sentences have been added at the beginning of section 3.1 before starting discussing the comparisons between ACSM and offline samplers:

“It is also important to note here that the comparison between ACSM and offline samplers generally consists of comparing dry aerosol online measurements to offline analyses of samples collected at ambient RH. A direct consequence is that the offline results might suffer from a cut-off shift due to aerosol hygroscopic growth when ambient RH is high (Chen et al., 2018). Based on

this study, the cut-off shift due to aerosol hygroscopic growth should play a minor role at Melpitz, as this effect was estimated to influence the comparison by 2 % for marine air-mass and 1 % for continental air-mass. For European background stations, such a cut-off shift has been estimated to represent less than 10 % for PM$_1$ and 20 % for PM$_{2.5}$ particle mass loading, while it is stronger for marine or coastal stations (up to 43 % for PM$_1$ and 62 % for PM$_{2.5}$). Therefore, such artefact has to be considered when comparison ACSM with offline measurements."

The following sentence has been added to the conclusion:

"Therefore, for such a comparison, the limitations due to the different size cuttings must be considered. **Moreover, possible cut-off shift due to ambient relative humidity effect on the offline measurements could represent a non-negligible parameter and has to be considered during such an exercise, especially for marine stations.**"

2. Inlet type (impactor or cyclone): we agree with the referee on the importance of the type of the inlet for aerosol measurements and later comparison. However, this effect was not investigated in this study since only one inlet was used. Nevertheless, inlet system for offline filter-based analyses are defined on the Air Quality Directive EN 12341 of the European Union. For the online instruments, the WMO/GAW recommend to use either a cyclone or an impactor with an upper cut point of 10 µm (WMO/GAW, 2016). The use of such a high cut point inlet makes the influence of the inlet type for sub-µm particle negligible.

3.Isokinetic sampling:

Because all the instruments connected to the main sampling line do not have the same flow rate, it is mandatory to ensure that the splitting sampling flow between all of them is made in a representative way. This is the reason why the sampling flow distribution at Melpitz is made by an isokinetic splitter (Fig. 1) following the GAW and ACTRIS recommendation (https://www.wmo-gaw-wcc-aerosol-physics.org/files/actris-recommendation-for-aerosol-inlets-and-sampling-tubes.pdf).

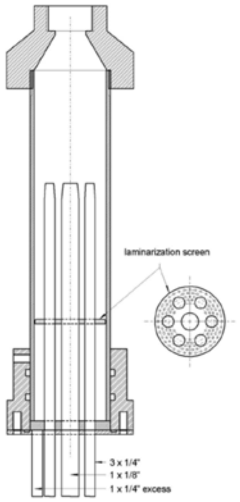


Figure 1: Example sketch of the isokinetic splitter similar to the one used on the sampling line at Melpitz (copy from https://www.wmo-gaw-wcc-aerosol-physics.org/files/actris-recommendation-for-aerosol-inlets-and-sampling-tubes.pdf).

We have corrected the text (section 2.1) to mention the isokinetic splitter on the station description as follows:

"the aerosol flow is divided among a set of instruments" was changed to "**The aerosol flow is divided among a set of instruments by an isokinetic splitter (WMO/GAW, 2016) ensuring a representative sampling between the instruments**."

In conclusion, the following sentence was added: "**For such an exercise, it is fundamental to ensure isokinetic flow splitting between the different instruments connected to the main sampling line to ensure a homogeneous distribution of the air sample**."

Finally, the following changes have also been made on the abstract and the introduction:

"**The Aerosol Chemical Speciation Monitor (ACSM) is nowadays widely used to identify and quantify the main component of fine particles in ambient air. As such, its deployment at observatory platforms is fully incorporated within the European Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS). To ensure the consistency** of the dataset, as well as instrumental performance and variability, regular intercomparisons are organized at the Aerosol Chemical Monitoring Calibration Center (ACMCC, part of the European Center for Aerosol Calibration, Paris, France). However, in-situ quality assurance remains a fundamental tracking point of the instrument's stability. **Here, we present and discuss the main outputs of long-term quality assurance efforts achieved for ACSM measurements at the research station Melpitz (Germany) since 2012 onwards. In order to validate the ACSM measurements over the years and to characterize the seasonal variations, nitrate, sulfate, ammonium, organic, and particle mass concentrations […]**"

"For this purpose, a European **distributed facility of ground-based Aerosol Chemical Species Monitor (ACSM, Ng et al., 2011) is operated within ACTRIS (European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases, http://www.actris.eu). Complementary, the COST Action CA16109 Chemical On-Line cOmpoSition and Source Apportionment of fine aerosol (COLOSSAL, https://www.costcolossal.eu) is gathering a wide community of European research groups (with even further international inputs, as well as participation of some regional air quality monitoring networks) interested in the fine aerosol fraction. One of the main objectives of these coordinated programs is to investigate and understand the spatial variability […]**"

R2: Page 3. Line 26. Volume cannot be converted to mass without the use of average density which is derived from ACSM/AMS measurements making the MPSS derived mass and ACSM-MAAP mass the dependent variables. Instead, ACSM/AMS and MAAP mass can be correctly converted to volume, because individual species mass and density is known (with some exception of organics and black carbon perhaps) making no prior reference to MPSS and keeping both variables independent of each other. All of the above assumes fully internally mixed aerosol which may not always be the case necessitating AMS and BC size distribution.

A2: It is true that using the density derived from the chemical composition of the ACSM-MAAP to determine the MPSS-derived mass concentration makes the two measurements dependent on each other. However, atmospheric aerosol measurements are generally performed in mass concentration making the quantification of a potential discrepancy more apprehensible in terms of mass (µg m^{-3}) than in volume (µm^3 cm^{-3}). This may be the reason why the mass approach is more common in the literature than the volume one. Nevertheless, and as suggested by the referee, we reinvestigated all our comparisons using volume concentration and assuming spherical particles, fully internally mixed and identical chemical composition over the entire size distribution. As shown in Figure 2, changing the unit does not influence the slopes between the two instruments and did not affect our conclusions. As a consequence, regarding our sampling place, the two approaches appear to be similar.

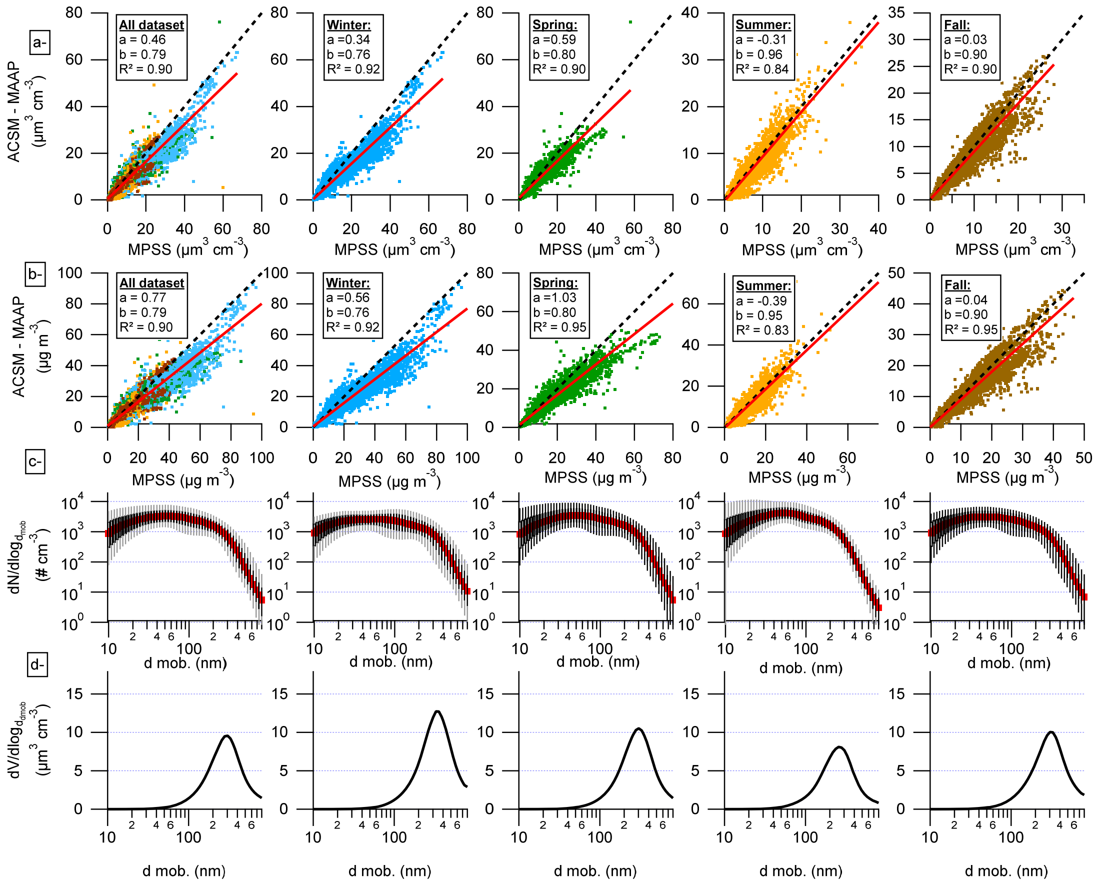


Figure 2: Comparison between measured ACSM-MAAP and MPSS for the entire period and seasonal variability: volume-closure (a), mass-closure (b), median number size distribution (red) with 10-90 (grey line) and 25-75 (black boxes) percentiles (c), median volume size distribution (d). The correlation curves (red line) were calculated using the least orthogonal distance fit method.

The text at the beginning of section 3.2.2. has been changed as follow:

"The PNSD has been continuously measured in parallel to the aerosol mass spectrometer and can, therefore, be used to perform mass closure analysis between ACSM-MAAP and PNSD (ranging from 10 to 800 nm, mobility diameter). To ensure a robust comparison between the two systems, two approaches are reported in the literature: the first one consists of converting the ACSM-MAAP mass concentration into volume and the PNSD in volume concentration. The second one consists of converting the PNSD into mass concentration. Both approaches are based on the same assumptions of (i) spherical, (ii) fully internally mixed particles, and (iii) an identical chemical composition over the entire size distribution to estimate a chemical time-dependent gravimetric particle density based on the following equation from Salcedo et al. (2006):

$$density = \frac{[Total_{AMS} + eBC]}{\frac{[NO_3^-]+[SO_4^{2-}]+[NH_4^+]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[Org]}{1.2} + \frac{[eBC]}{1.77}} \quad (1)$$

Here, the density was assumed to be 1.75 g cm^{-3} for ammonium nitrate and ammonium sulfate (Lide, 1991), 1.52 g cm^{-3} for ammonium chloride (Lide, 1991), and 1.2 g cm^{-3} for organic matter (Turpin and Lim, 2001). Finally, a density of 1.77 g cm^{-3} (Park et al., 2004) was applied for eBC. A discussion of eBC density can be found in Poulain et al. (2014).

It is important to note that for the volume concentration approach, both measurements (ACSM-MAAP and MPSS) remain independent between each other, which is not the case when using mass concentration. However, only a few numbers of papers reported a comparison between AMS or ACSM and MPSS in volume concentration (e.g. DeCarlo et al., 2008;Elsasser et al., 2012). Even though the two variables are non-independent on the mass concentration approach, it remains the most commonly used. A possible reason is that the mass concentration unit remains easier to use and interpreted as the volume concentration since atmospheric measurements are usually made in mass concentration.

Here, we investigated comparison results obtained using each of these approaches. Results are summarized in Figure 9.a for the volume concentration approach and Figure 9.b for the mass concentration one.

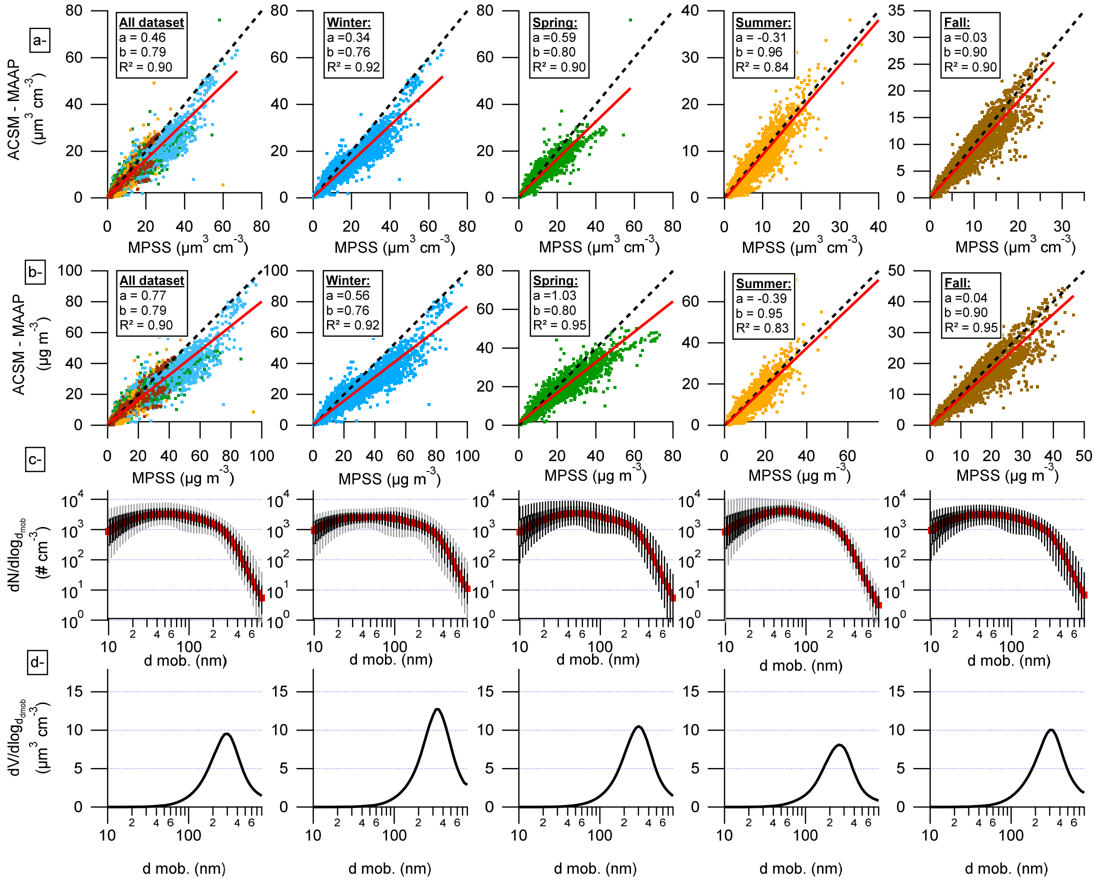


Figure 9: Comparison between measured ACSM-MAAP and MPSS for the entire period and seasonal variability: volume-closure (a), mass-closure (b), median number size distribution (red) with 10-90 (grey line) and 25-75 (black boxes) percentiles (c), median volume size distribution (d). The linear regressions (red lines) were calculated using the least orthogonal distance fit method.

Over 5.5 years of measurements, the ACSM-MAAP-derived volume or mass concentration correlates well with the estimated volume or mass concentration of the MPSS with the same slope of 0.79 (R² = 0.90, Fig. 9a and 9b). This matches similar previous comparisons at the same place with an AMS (Poulain et al., 2014). **Therefore, the selected method (volume or mass) did not substantially influence the comparison results. In the conditions of the present study both approaches could be applied for the station of Melpitz. Since comparison in mass concentration is the more commonly used, we will focus on it in the following discussions."**

In summary, the following comment was added:

"It can be performed by converting the ACSM-MAAP mass concentration into volume concentration or by converted the MPSS volume concentration into mass concentration both using time-dependent density and assuming spherical and fully internally mixed particles. The volume approach is the most robust since it enables a strictly independent method. Being more interpretable, the mass approach may be used instead of for error quantification as long as it agrees with the volume approach. For the present dataset, the selected method did not substantially influence the comparison results."

R3: Page 10. Line 22. I do not follow this reasoning. Sulfuric acid is a stronger acid and ammonia is preferentially neutralizing stronger acid when compared to nitric acid. Therefore, it needs to be checked for degree of neutralization taking into account that ammonium ion has to balance sulfate first and only then the nitrate. Small amounts of organosulfate or organonitrate do not violate the above general pattern at significant sulfate and nitrate concentrations.

A3: As suggested by the referee, a discussion on the neutralization of ammonium by nitrate, sulfate, and chloride species for both ACSM and PM_1 filters was added in section 3.1.3 before discussing the comparison of the two methods.

The section has been rewritten and a Figure has been added to the Supplementary information as follow:

"The ammonium mass concentration measured by the ACSM mostly corresponds to ammonium nitrate and ammonium sulfate salts. Before comparing ACSM and offline PM_1 ammonium mass concentration, the neutralization state of the particles was estimated for both datasets assuming a full neutralization by nitrate, sulfate, and chloride as described in e.g. Sun et al. (2010). In both approaches, particles can be considered as fully neutralized during the entire period with no seasonality (Fig. SI-7) in agreement with previous AMS measurements made at the same place (Poulain et al., 2011). Correlations with offline systems fall somewhere between the two previously discussed ions. During the cold season, the ACSM ammonium mass concentration matches the PM_1 (slope 1.02, $R^2 = 0.83$), which supports the larger fraction of ammonium nitrate in the total PM as well as the size effect of sulfate during wintertime (Fig. 1 and Fig. 2). During the warm season, the evaporation of ammonium nitrate as discussed before will also induce a loss of ammonium on the filter samples compared to the online measurements leading to an under-estimation of the ammonium concentration on the offline sampler as well as a poor correlation ($R^2 = 0.49$). Similar conclusions can also be drawn when comparing it to the $PM_{2.5}$ ammonium mass concentration Fig. SI-1 & SI-2)."

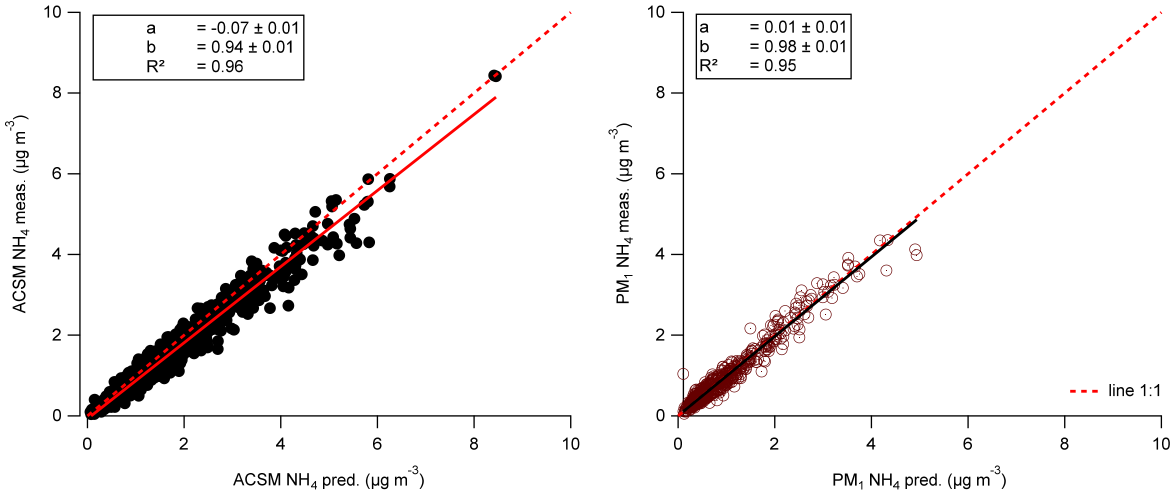


Figure SI-5: Comparison of the measured ammonium with the predicted ammonium mass concentration for the ACSM (left) and offline PM$_1$ samples assuming a full neutralization by nitrate, sulfate, and chloride. The linear regressions were calculated using the least orthogonal distance fit method (y = a x + b).

R4: Line 30. Estimation of the ratio can only be done after validating ACSM/PM1 agreement which should be done by an independent variable. Otherwise what is the reasoning of using ACSM/PM1or2.5 comparison for sulfate uncovering discrepancies, but assuming that ACSM OM measurements are fine and ready for deriving OM/OC ratio? Later the authors do comparison by retrieving OC from f44, but that is rather arbitrary given little confidence with regard to AMS measurements done elsewhere and with different instrument. In any event the authors should not start OM comparison going straight to discussing OM:OC ratios before all other technical matters were discussed. And I doubt that ACSM/PM1 comparison can inform about the OM:OC ratio, only AMS/PM1 can, because only AMS can provide OC mass after laborious data processing.

A4: We agree with the first part of this comment. A direct comparison of the organic mass concentration measured by the ACSM with collocated organic mass concentration would be the ideal case and would allow us to proceed on a comparable approach as for the inorganic species. However, this approach is not possible, since no other instrument has provided direct OM measurements at the station. Consequently, the best way to directly compare organic measurements together is to either use the OM:OC ratio or to compare OC values. Nevertheless, we agree that limitations on both measurements must be first discussed further. For this purpose, Figure 6c of the manuscript was modified to consider temperature effect on filter samples. Consequently, the text of the manuscript was modified and reorganized following the reviewer's suggestions.

We would like to underline here that using the contribution of the CO_2^+ signal to the total organic signal (f_{44}) as a surrogate to estimate the OM:OC ratio is commonly used within the AMS community when working on Unit Mass Resolution organic mass spectra (e.g. Chen et al., 2015 and reference therein). A comparison with the elemental analysis approach using high-resolution organic mass spectra of the HR-ToF-AMS was successfully made by Aiken et al. (2008) and Canagaratna et al. (2015). The latter one concluded on the accuracy of 13 % of the f_{44} method compared to the elemental analysis one for the SOA compounds, while this accuracy is decreasing for primary OA standards having an $f_{44} < 4\%$ on average. Considering that m/z 44 dominates the organic mass spectra, it is reasonable to consider the 13 % accuracy as the highest accuracy that can be obtained for unit mass resolution AMS results. Consequently considering, that m/z 44 is systematically the dominant fragment of the organic mass spectra for ambient measurements and that the ACSM is based on similar principle than the AMS, it is still relevant to apply the f_{44} approach on the ACSM organic results as a proxy for ambient OC, and compare the results with the well-established offline OC method. Finally, on a longer perspective, presenting and discussing results from such a comparison whenever possible is also important in the frame of the standardization process, currently trying to establish guidelines for investigating possible equivalence towards the standard EC-OC offline method of any type of alternative measurement technique.

As a result, the text on section 3.1.4 was changed as follows:

“The ACSM provides organic aerosol (OA) mass **concentrations but contrary to the inorganic species no direct comparison with collocated organic mass measurements is possible. Actually, only ACSM or AMS systems are nowadays able to provide such measurements and other methods - primarily based on the thermal and/or optical properties of carbonaceous aerosols - are estimating organic carbon (OC) mass concentration instead of OA. Here, offline OC measurements are available from the thermal-optical analyses of filter punches, allowing for comparing both parameters over the entire period of the study. In the following, the limitations of both methods are discussed. First of all, the organic aerosol mass concentration is defined as the sum of the non-attributed inorganic species fragments from the aerosol mass spectra as defined by Allan et al. (2004). A wrong assignment or correction of the fragmentation table during the data analysis process could be a source of mis-quantification of the organic mass concentration. For example, the fragment CO_2^+ (m/z 44) is the major signal on the organic mass spectra. It can suffer from substantial measurement biases, i.e., the so-called Pieber effect (Pieber et al., 2016;Freney et al., 2019) associated with interference due to nitrate signal. This artefact can lead to an overestimation of the m/z 44 and consequently directly affects the total organic mass concentration. Unfortunately, a thorough quantification of this effect on the present dataset is not possible, as the relevant method to do so includes regular full scan calibrations which has been proposed only recently, and further works are still needed to define associated correction procedures (Freney et al., 2019). Another main source of uncertainty for OA concentration estimates is linked to the assumption of a constant RIE. Here, it has been set at its 1.4 default value during the whole period of the study while it is known that RIE-organic and/or its CE can be influenced by the chemical composition of the organic (Xu et al., 2018). As already mentioned, organic is not included in the CDCE estimation method from Middlebrook et al. (2012), which might also have a potential impact on the resulting mass concentration. Overall, an uncertainty of 19 % in the ACSM organic mass concentration can be considered based on the ACSM reproducibility analysis made by Crenn et al. (2015).**

OC mass concentrations derived from the offline analyses of filter samples are also subject to measurement uncertainties They are obtained according to a specific method (here the EUSAAR2 thermal-optical protocol). Applying another method will directly influence the OC concentration (Cavalli et al., 2010;Zanatta et al., 2016;Chiappini et al., 2014). Moreover, the samplers used for this study were sitting outside and were not temperature controlled. A direct consequence is that the evaporation of the more semi-volatile organic during warm days must be expected, which similarly impacted the measured OC concentration than for ammonium nitrate discussed above.

Keeping in mind all the mentioned uncertainties on each method, the OA mass concentration was compared to the offline OC mass concentration, which can, therefore, be considered as a **fair** estimation of the OM:OC ratio (Fig. 6-a). Correlation between OA and OC is not significantly impacted by the PM_1:$PM_{2.5}$ threshold ratio of 0.6 as for inorganics (Table SI-1). This supports the fact that organic is mainly distributed on the sub-µm size range throughout the year (Fig. SI-4). As expected, a lower OM:OC ratio was obtained in winter (slope = 1.29, $R^2 = 0.78$), which corresponds with the period with the largest anthropogenic influence. The highest OM:OC ratio was obtained in summer (slope = 2.74, $R^2 = 0.68$), corresponding with the SOA formation maximum. **Although such a seasonal variation is coherent with a priori expectations (notably considering higher SOA contribution at summertime), biases related to instrumental uncertainties should still be considered. In a similar way than for nitrate, ambient temperature affects the OC leading to a systematic extreme OM:OC ratio during summer (Fig. 6c). Consequently, the summer’s slope of 2.74 is certainly overestimated. However, some extreme values are found also for some winter days, which can therefore not be associated with a temperature artefact on the offline samplers. Such wintertime**

discrepancies might rather be attributed to the above-mentioned ACSM uncertainties related to RIE for organics, CE estimation and/or substantial influence of the so-called Pieber effect."

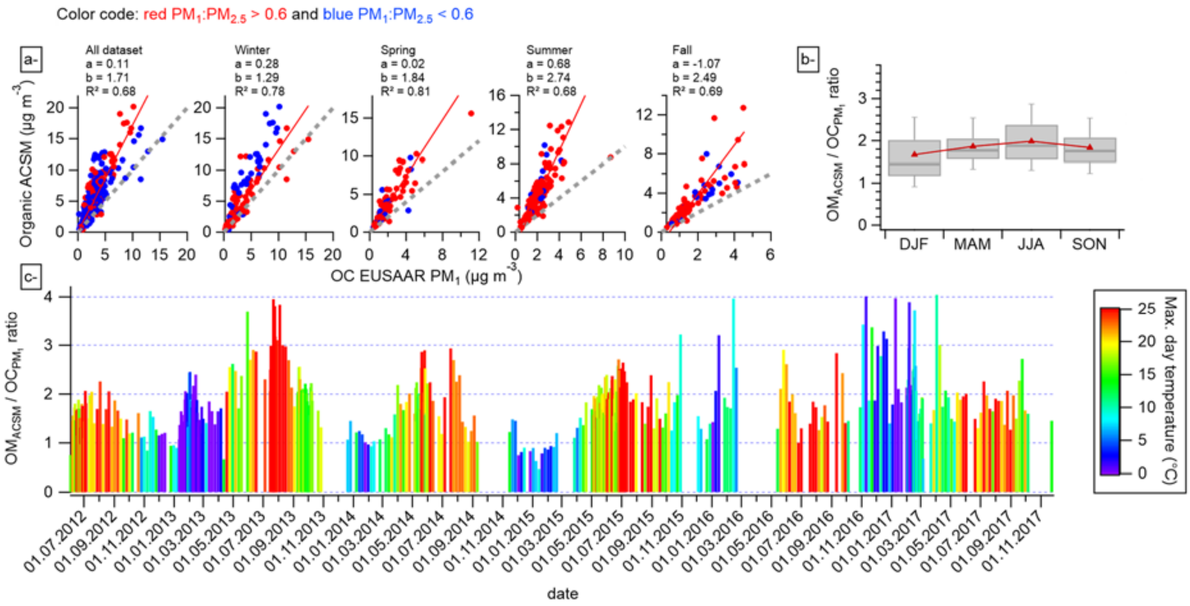


Figure 6: Correlation between ACSM organic mass concentrations and off-line OC PM_1 (a); seasonal variability of the estimated OM_{ACSM}:OC_{PM1} ratio (b), and the entire time series colored by maximum daily temperature (c).

Another way to compare ACSM measurements to OC concentrations could be envisaged based on some previous works using AMS systems. Indeed, the estimation of the OM:OC ratio from AMS measurements is normally not done on a direct comparison of organic particle mass concentrations with collocated OC measurements but rather estimated based on the elemental analysis of the high-resolution organic mass spectra Aiken et al. (2007) and Aiken et al. (2008) or the variability of the f_{44}, the contribution of mass m/z 44 (mostly CO_2^+) to the total organic signal when only unit mass resolution mass spectra are available (Aitken et al., 2008, Ng et al., 2010). Both methods were reinvestigated and improved by Canagaratna et al. (2015) providing the following equations to convert the f_{44} signal of an AMS into O:C and OM:OC ratios:

$$O{:}C = 0.079 + 4.31\ \times\ f_{44} \tag{1}$$

$$OM{:}OC = 1.29\ \times O{:}C + 1.17 \tag{2}$$

By a systematic comparison of the two approaches, the elemental analysis, and the f_{44}, Canagaratna et al. (2015) concluded to an accuracy of 13 % of the f_{44} proxy for SOA traces decreasing for primary OA standards having an $f_{44} < 4$ % on average. Considering that m/z 44 is systematically the dominate fragment of the organic mass spectra for ambient measurements and that the ACSM is based on similar principle than the AMS, it is relevant to apply the f_{44} approach on the ACSM organic results as a proxy for ambient OC, and compare the results with the well-established off-line OC method. Therefore, equations 1 and 2 were applied in the present dataset to estimate OC mass concentrations from the measured ACSM organic mass concentration (OC_{ACSM}) and to compare them to the OC-PM_1 (for the entire dataset: slope = 0.65, $R^2 = 0.73$, Fig. 7). As previously shown, a seasonal trend can also be observed here, with a unity regression slope obtained during summer periods (slope = 0.99, $R^2 = 0.64$), whereas a lower slope (0.56, $R^2 = 0.82$) was obtained in winter (Fig. 7 and Table SI-1). Here, the different instrumental and technical uncertainties have to be considered. Contrary to nitrate, temperature seems to have a less significant impact on the ratio between the OC_{ACSM}

and the OC_{PM1}, as can be seen in figure SI-8. **However, the extreme OC_{ACSM}:OC_{PM1} ratio values mostly happened during warm days supporting our previous conclusion on the temperature artifact on the OM_{ACSM}:OC_{PM1} ratio. As was mentioned above, the extreme ratio values during winter might result from a possible variability of the organic RIE as well as a possible co-call Pieber effect on the m/z 44 that directly affects the estimation of the OC_{ACSM}.** Despite this agreement between ACSMs, Crenn et al. (2015) showed a large variability concerning the f_{44} signal itself during the ACSM intercomparison exercise. This variability was attributed to an instrument-dependent difference of the vaporization conditions. For this reason, the authors did not recommend to systematically use the f_{44} approach to estimate the O:C ratio, as it can be achieved with the AMS and done here, or to interpret the resulting O:C ratios with caution. Since the OC_{ACMS} results are well supported by the offline analysis, we can conclude that our ACSM provides a relatively realistic value of the f_{44} over the considered timeframe and consequently, a reasonable proxy for the OM:OC ratio. However, we cannot rule out that a similar approach would provide the same results when using another ACSM at Melpitz and/or when applying the present method in another location. Further systematic comparisons between the ACSM and collocated OC-PM_1 measurements should be performed in order to better investigate and characterize the suspected instrument vaporization dependency and/or a possible matrix effect depending on the dominant type of aerosol chemical composition at the considered sampling site, which might influence both the CO_2^+ signal and the organic RIE."

The following sentence on the conclusion "Nevertheless, more systematic comparisons should be performed in a similar way in different environments to validate our results and to better identify f_{44} instrumental variability „ has been rewritten as follow: "Nevertheless, **the method might be difficult to apply for short time measurements (e.g. a few weeks only), where low/high extreme ratios may be misinterpreted, and results interpreted with cautions, such OA-OC comparison and OC_{ACSM}:$OC_{offline}$ methods shall then preferably be used on long term continuous measurements. Finally, it should also be noted that OC is the only regulated organic aerosol-related variable commonly monitored within current air quality networks (Directive 2008/50/CE, 2008;WMO/GAW, 2016) whereas equivalent methods for a better OA quantification at high-time resolution are still to be standardized, reinforcing the need for much more systematic comparison exercises at various locations."**

R5: Page 11. Line 2. Very high ratio of 2.74 (or even higher observed by Ripoll and Minguillon) suggests that ACSM is probably overestimating OM as well as in the case of sulfate or nitrate with the remainder attributed to OM:OC ratio. Can the authors support such a high oxidation ratio from the literature? I would be very curious to see those studies from the ambient atmosphere as even theoretically the ratio should not exceed ~3 (CO2 would have 3.66 and it is a gas). It is irrelevant that seasonal OM:OC ratios make sense if they are made from averaging unrealistic values. If so, the authors should not talk about OM:OC ratios before examining slopes carefully and discussing what is and is not theoretically possible. Perhaps consideration of CDCE by neglecting OM is a likely source of overestimation too.

A5: We agree with the referee and invite the referee to read our answer A4, which also includes a discussion on the uncertainties of the two approaches (ACSM and offline).

Minor comments

R6: Page 2. Line 7. Spell MPSS for those who read abstract only.

A6: added "[…] of the Mobility Particle Size Spectrometer (MPSS) […]"

R5: Line 25. . . .composition

A7: corrected

R8: Page 3. Line 8. Ovadnevaite et al. have published a rare study that reports...longterm... Do authors suggest in the following sentence that several years (e.g. three) is not sufficiently long period, but their own five years long period is sufficiently long? Please reword or clarify.

A8: Three years is indeed long enough to check the stability of an instrument. However, the authors compared their near-PM_1 HR-ToF-AMS data with $PM_{2.5}$ samples and did not discuss the variability of the correlation over these 3-years. Therefore, we considered that our approach provides more understanding of such a systematic comparison to identify sources of deviation and artefacts.

We have clarified it as follows: "Ovadnevaite et al. (2014) have written a rare published work that reports long-term AMS comparisons **(3-years). Even though the authors successfully compared it with offline $PM_{2.5}$ filter samples, they did not discuss the variability of the correlation and potential source of uncertainties.**"

R9: Line 18. within the scope, not focus

A9: Changed

R10: Line 33. TEOM-FDMS never provides PM1 mass and, even worse, separation in size typically occurs at ambient RH while the mass measurement occurs after drying at room temperature.

A10: We are not certain to fully understand this comment. The size cutting of a TEOM-FDMS depends on the aerosol inlet used. When connecting to PM_1 inlet, the TEOM-FDMS will provide PM_1 aerosol mass concentration. Moreover, it is true that the inlet cut-off occurs at ambient RH, while the mass measurements after drying at room temperature, which is a general issue for all online aerosol measurements. The use of an impactor after conditioning the sampling air, while being certainly more efficient for keeping a constant cutoff on the measurement.

Please refer to our answer A1 for the discussion on the effect of RH on aerosol sampling. Nevertheless, discussing the interaction on the RH to the TEOM-FDMS measurements made during the cited study is behind the scope of the present manuscript.

R11: Page 4. Line 9. the impact, not effect.

A11: Changed

R12: Line 18. Is the RH actively monitored or indirectly maintained? Is the aerosol flow divided/split isokinetically or randomly? Significant losses can occur if split randomly due to different instrument flow rates.

A12: RH is actively monitored on the sampling line by an automatic aerosol diffusion dryer to keep the relative humidity on the sampling line below 40 %. A detailed description of the drying system can be found on the cited reference of Tuch et al., 2009.

The text has been changed to include the word "actively":

"This inlet line consists of a PM_{10} Anderson impactor located approximately 6 m above ground level and directly followed by an automatic aerosol diffusion dryer to **actively** keep the relative humidity on the sampling line below 40 % (Tuch et al., 2009)."

As mentioned in our answer to the first major comment (A1), an isokinetic splitter (Fig. 1) is used to ensure a representative sampling between all the connected instruments.

The text has been changed as follows:

"**The aerosol flow is divided among a set of instruments by an isokinetic splitter (WMO/GAW, 2016) ensuring a representative sampling between the instruments**."

R13: Page 5. Line 14. ACSM data capture was 80% during deployment at Melpitz.

A13: Text was corrected as suggested

R14: Line 18. CDCE is Composition Dependent Collection Efficiency as used in the original Middlebrook et al paper. It is also important to note that CDCE algorithm does not take OM into account which can be a potential error source.

A14: We agree with the comments and the text was changed to: "The ACSM data was analyzed following the recommendation of manufacturer and applying **a composition dependent collection efficiency (CDCE) correction** based on the algorithms proposed by Middlebrook et al. (2012) to correct particle loss due to bouncing off the vaporizer before flash vaporization. **It is important to note that the CDCE algorithm includes inorganic species only and did not consider a possible effect of the organics on the collection efficiency estimation**".

R15: Line 23. … collect particles with size selective PM2.5 and PM10 inlets on preheated...

A15: replaced "cutting" by "**selective**"

R16: Line 24. Samples were collected on a daily basis...

A16: replaced "performed in" by "collected on"

R17: Page 6. Line 15. It is probably meant by "within Planetary Boundary Layer", but I do not quite understand what is meant by "above 500m" and why.

A17: The air mass trajectory analysis was set with an altitude of 500 m above the research station. Because Planetary Boundary Layer (PBL) is dynamic and its altitude is changing over time, it is critical to consider only air mass trajectories results that are connected with the measurements. In our case, if the PBL is located at an altitude below 500 m, the calculated air mass trajectory is reaching the station at an altitude above the PBL level. Consequently, this trajectory cannot be associated with the ground level measurements made at this time and will be not considered further in the analysis.

The text was changed as follows:

“Finally, the meteorological conditions as available from the HYSPLIT output for each trajectory calculation were also examined. Although backward trajectories were started at a height of 500 m, the Planetary Boundary Layer at the trajectory starting time could be at a lower altitude making the association between the ground-based measurements and the inflowing air mass difficult. Therefore, only air mass trajectories with a HYSPLIT-estimated PBL height above 500 m were further considered for analysis.”

R18: Page 7. Line 2. ...mass concentration comparison is suggesting overestimation by ACSM when compared to offline PM1.

A18: The sentence was changed as suggested

“Over the entire period, the regression slope of the sulfate mass concentration comparison **is suggesting overestimation** by ACSM when compared to offline PM_1.”

R19: Line 6. influenced by three specific periods in January 2015 and February 2017 (...).

A19: The sentence was corrected as suggested

R20: Line 10. The overestimation can be caused by either size selective inlet or(and) sodium sulfate mainly residing in coarse particles. However, I am not sure that is good enough explanation of very contrasting comparison between PM1 and PM2.5. Judging from slopes (1.45 for PM1 and 0.68 for PM2.5) that is suggesting 100% difference between PM1 and PM2.5 - that is massive and not necessarily related to ACSM.

A20: It is true that the overestimation of the ACSM sulfate mass concentration, when compared to $PM_{2.5}$ offline samples, can be caused by either the difference of the respective size inlet and/or presence of coarse sodium sulfate as mentioned on the manuscript (“This overestimation could be associated with the size-cutting difference between the two methods and the presence of not detected sulfate species on the coarse mode, such as sodium sulfate.”). However, the difference between PM_1 and $PM_{2.5}$ is not as massive as suggested by the referee. On average over the 5.5 years, the ratio sulfate PM_1 to $PM_{2.5}$ is of 0.77, as can be seen in Figure SI-3. As it is discussed in the manuscript, the difference of slopes is strongly related to specific days showing an important coarse fraction as demonstrated by the sensitivity analysis (Fig. 3). By considering only days with a PM_1:$PM_{2.5} > 0.6$, the slopes between ACSM-SO_4 and PM_1-SO_4 is 0.96. consequently, the difference between the slopes for PM_1 and $PM_{2.5}$ agrees with the difference between the sulfate mass concentration on PM_1 and $PM_{2.5}$ samples.

R21: Line 18. That is correct theoretical explanation, but given huge discrepancy during "outlier" days the organic fragment signals should be of very significant magnitude to inorganic ones. Do authors have hints from the multiple campaigns when high resolution AMS was deployed at the site?

A21: We agree with the comment that the contribution of organic fragments to the sulfate signal is an absolute theoretical explanation and cannot be solved due to the unit mass resolution of the ACSM. However, based on the previous HR-ToF-AMS, we can confirm the presence of organic fragments on m/z 80 and 81. Based on the summer, fall, and winter HR-ToF-AMS measurements made at Melpitz and published in Poulain et al. (2011), $C_6H_9^+$, $C_5H_5O^+$ fragments were found at m/z 81 with concentrations closed to the one of HSO_3^+ on some time. The comparison between UMR-SO_4 and HR-SO_4 however, shows a different < 10 % for the campaigns published in Poulain et al., 2010.

As a result, the following sentence was added on the manuscript:

"Therefore, an increase of the organic signal at this m/z might lead to an overestimation of the ACSM sulfate mass concentration. **Although our previous measurements using High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) at Melpitz (Poulain et al., 2011) support the presence of organic fragments on the UMR sulfate signal. The difference between the sulfate mass concentration based on UMR (as for ACSM) and the one obtained on the high-resolution (i.e. excluding the contribution of organic fragments on the sulfate signal) is below 10% indicating a minor impact of the organic to the sulfate signal**."

R22: Line 27. coincides, not corresponds.

A22: replaced

R23: Line 31. PM1 cannot contribute to PM2.5 it is an inherent part of it. Is it not simply a ratio?

A23: Yes, it is. We changed the sentence by replacing "PM_1 contribution to $PM_{2.5}$" by "**PM_1:$PM_{2.5}$ ratio**" and homogenize the nomenclature on the entire manuscript.

R24: Page 8. Line 1. Consider that wet PM1 size segregation will inevitably pass less submicron particles. However, if that is the plausible culprit then ACSM should perfectly compare with PM2.5 which even in wet cut-off conditions should well correspond to dry ACSM PM1.

A24: This problem is inherent to all aerosol inlet system. However as discussed before on our answer A1, the cut-off shift due to aerosol hygroscopicity growth should play a minor role at Melpitz

The following sentence has been added to the text: "Therefore, the discrepancy between the ACSM and the PM_1 can be attributed to the individual upper size cutting of the two instruments, and it highlights the limits of such a comparison. **As already mentioned, a minor effect of the RH to the cut-off shift of the offline samplers can be expected at Melpitz (Chen et al., 2018)."**

R25: Line 5. The effect may still be there, but masked by the evaporation effect and NaNO3 effect on filters. Is this sentence out of place as it is becomes confusing whether the following sentences regard to sulfate or nitrate?

A25: We agree with the comment and the corresponding sentence was removed.

R26: Line 19. Please explain what air mass density means.

R26: The air mass density is a proxy of the occurrence of the trajectory within each cell. For clarity, it was replaced by the term "**trajectory density**", as defined in Petit et al. (2017).

R27: Line 20. This confirms the predominantly shallow PBL...

A27: Corrected

R28: Line 28. ...to slightly overestimate... The overestimation is very small and within the error margin compared to massive overestimation in Minguillon et al. I see this as a contrast from previous studies, not similarity.

A28: The text has been changed as follows: "The ACSM nitrate mass concentration tends to **slightly** overestimate the offline PM_1 nitrate throughout the entire period (slope = 1.16, $R^2 = 0.80$; Fig. 1 and 2). **This overestimation is very small and within the error margin compared to massive overestimation in** Ripoll et al. (2015) with a slope of 1.35 ($R^2 = 0.77$) and Minguillon et al. (2015) with a slope 2.8 ($R^2 = 0.80$)."

R29: Page 9. Line 5. I see more evidence in Figure 5. First, a lot of nitrate evaporation is visible at low ambient temperature as many of the points are clearly above ratio of 1.0. That is not surprising considering evaporation from particles already collected on the filter. However, the effect in summer seems to be larger, but concentrations are much lower in summer suggesting that evaporation can be near constant (as long as filter temperature is maintained similar during all seasons which needs to be confirmed). As more nitrate loaded particles are deposited on filter during winter they become buried under new layers of particles before being significantly evaporated. During summer there is little nitrate on particles and less particles altogether resulting in more absolute evaporative losses until particles buried under the new layers of particles.

A29: We thank the referee for his/her pertinent comments. The temperature effect described in figure 5 is linked to the evaporation from particles already collected on the filter only. The high-volume samplers are sitting outside and are not temperature controlled. Consequently, the inside temperature of the sampler is depending as well as of the outside temperature but also of the solar radiation that can contribute to warm-up the instrument. Both factors might explain the fact that the discrepancy between the two methods is already visible at low ambient temperature. Additionally, this leads to different inside temperature conditions during winter and summer periods making impossible a direct comparison of the evaporation process between summer and winter. This is the reason why we plotted Figure 5 using outside temperature.

The following text has been added on the manuscript:

"In an intercomparison study of different sampling supports, Schaap et al. (2004) demonstrated that a quartz filter ($PM_{2.5}$ and PM_{10}) is a suitable material for sampling nitrate as long as temperature does not exceed 20 °C. **The high-volume samplers are sitting outside and are not temperature controlled. Therefore, the inside temperature of the sampler is influenced by the outside temperature.** This temperature artefact is clearly illustrated in Figure 5, when the variation of the ACSM:PM_1 nitrate ratio and the maximum temperature measured during the sampling day are compared. For ambient maximum temperatures above 10 °C, an increase of the ACSM:PM_1 ratio can be observed. Here it is imperative to note that the ambient maximum temperature did not reflect the temperature inside the sampler, **solar radiation may also contribute to warm up the sampler**."

R30: Page 10. Line 20. ...with off-line measurements fall somewhere in between the two previously discussed ions.

A30: corrected as suggested

R31: Page 12. Line 10. in another location.

A31: replaced "on" by "**in**"

R32: Line 25. The first comparison is correct by comparing mass with mass, but the second comparison is not, because particle mass derived from PNSD and MPSS will rely on ACSM for estimating average density making the two variables dependent. Therefore, only volume, not mass comparison of ACSM-MAAP and PNSD can be done correctly.

A32: Please see our previous answer (A2) on this comment for more details on this topic.

The sentence has been reworded as follows:

"The resulting total PM_1 mass, later referred to as the ACSM-MAAP-derived mass concentration, was then compared to the particle mass concentration obtained by weighting filters (PM_1 and $PM_{2.5}$) as well as to the calculated particle **volume and** mass concentration from the PNSD of the MPSS.

R33: Page 13. Line 3. Therefore, it is not possible to conclude whether....depends on the location or the presence of larger coarse mode.

A33: the sentence was corrected as suggested.

The text has been changed as follows: "**Therefore**, it is not possible to conclude whether this difference in correlation results between the two studies **depends on the** location or the presence of more coarse mode. Moreover, a possible loss of the more volatile compounds."

R34: Line 9. … cannot typically account for the entire mass

A34: The sentence was corrected as suggested.

R35: Line 12. It is inappropriate to arbitrarily choose specific OM:OC ratio when the above paragraphs discussed wildly different ratios.

A35: We agree that it would make more sense to apply a time-depend OM:OC ratio to convert the OC into OM. However, applying a time-depend OM:OC ratio based on the results discussed in the manuscript could lead to the introduction of bias on the offline mass closure. Indeed, it could be seen as directly replacing the OC results by the ACSM organic mass concentration. However, and as discussed in section 3.1.4, the ratio ACSM organic to offline OC is not free of artefact and uncertainties. The more key ones are the RIE-CE and Pieber effect for the ACSM, and the evaporation of volatile organic compounds during warm days for the filter samples. Moreover, the total PM mass concentration measured on the filter samples also include this temperature effect. Therefore, replacing the OC by the ACSM organic appears to be inappropriate for us. Nevertheless, and as mentioned by the referee, a constant OM:OC ratio could be considered as a too simple approach regarding the variability of the ratio. In consequence and to consider the aforementioned limitations, the seasonal OM:OC ratio presented on Figure 6-b was used since these values are resulting from a long dataset and should be less influenced by the day-to-day uncertainties.

Accordingly, the Figures 8 and SI-9 were replotted and the text changed as follows:" Here, the residual mass fraction was calculated as the difference between the weighted filter mass and the sum of the detected compounds **(Fig. SI-9). It is important to note here, that to properly convert the OC into OM and to consider all the different limitations inherent to both online and offline approaches, the seasonal means OM:OC ratio values (Fig. 6b) were applied**".

Figure caption SI-7 (now Fig. SI-9) was changed as follows: **“Time series of the Digitel PM_1 chemical composition. Conversion of OC into OM was made based on the seasonal OM:OC ratio presented in figure 6.”**

R36: Line 32. Incorrect method. See above.

A36: Please refer to our answer A2 and the corresponding corrections/changes made on the manuscript.

R37: Page 14. Line 24. This artefact may plausibly explain the seasonality of the mass closure (it should be volume closure instead).

A37: The sentence was corrected as suggested and we refer to your previous answer (A2) regarding the discussion between volume and mass closure analysis

R38: Page 15. Line 1. By the same principle ACSM size range is 1um/1.6=0.625um (dvac/density=dmob) and discrepancies between size ranges of ACSM and MPSS should be irrelevant. Please reconsider and reflect in conclusions.

A38: The vacuum aerodynamic diameter of 1 µm indeed corresponds to approximately 625 nm (assuming a constant density of 1.6, spherical particle under free molecular regime). However, this assumption considered several approximations making the comparison potentially inaccurate. First, it assumes that the size cutting of the ACSM is absolute at 1 µm, which is not the case. The transmission of the aerodynamic lenses at 1 µm is ranging from 40 to 60% depending on the lens and the pressure (Liu et al., 2007). Moreover, and as already mentioned by the referee, the density is not constant over time, resulting in a time dependence of the equivalent diameter, which is ranging for Melpitz after monthly averaging over the entire period, from ca. 600 and 700 nm. Consequently, following the suggestion, it would be necessary to consider a time dependence on the upper size range for the MPSS to be properly accurate. Last but not least, applying such an approach will bring us back to the discussion on the volume- / mass-closure analysis bringing a dependency on the ACSM measurements to the MPSS dataset. This dependency might strongly impact the results since it is considered twice one for rescaling the MPSS measurement and second for the unit conversion (ACSM to volume or MPSS to mass).

Consequently, applying such correction on the MPSS data would certainly improve the correlation between the two instruments by smoothing the respective size effect, but it might be better for the wrong reasons. Then again, for certain specific environments, like a station with high coarse mode concentration (marine, dust environment), assumptions for cutting the MPSS scan-range before comparing with ACSM would make sense to avoid interference from super-micrometer multiple charged particles. This is important in case there is not APSS measurement available to perform a proper multiple charge correction.

R39: Line 31. Can this be called an artefact? It depends whether organo-nitrate belongs to organics class or nitrate. Nitrate functional group is still a nitrate even if bound to organic species. Quite contrary, off-line inorganic and offline OC/EC analysis completely misses nitrate bound to organics making the use of the term “artefact” justified. Ideally, one would want a clear distinction of organo-nitrate compound which would be out of reach by off-line inorganic techniques unless specifically measured for OrgNO3.

A39: We agree with the comment and replace “artefact” by “**uncertainty**”.

R40: Figure 1. I recommend changing PM to ACSM-MAAP or ACSM+eBC for consistency with further Figures.

A40: We disagree with the suggestion as Figure 1 shows the time series of the particulate mass concentration from the ACSM-MAAP but also PM mass concentration of the filter samples. Therefore, the use of PM appears to us as the most relevant.

R41: Figure 2. ...and solid black lines represent regression fit by least orthogonal distance (y=a+bx)

A41: corrected

R42: Figure 3. change "data coverage" to "data capture".

A42: We updated Figure 3

R43: Figure 4. ...for days where sulfate concentration difference between PM2.5 and PM1 exceeded 1ug/m3: (a) overpassing trajectory density; (b) potential source contribution function??; (c) time series of sulfate concentration difference, PBL height above 2000m, precipitation events exceeding 1mm/h and PBL formation above the station altitude.

A43: Text was changed as follows: "**Trajectory analysis for days where sulfate concentration difference between $PM_{2.5}$ and PM_1 exceeded 1 µg m^{-3}: (a) overpassing trajectory density; (b) results of the potential source contribution function (PSCF) analysis; (c) time series of sulfate mass concentration difference, trajectory altitude above 2000 m, precipitation events exceeding 1 mm h^{-1} and PBL above the station < 500 m.**"

R44: Figure 6. ...and off-line OC PM1 (a); seasonal variability....(b) and the entire time series (c).

A44: Corrected

R45: Figure 7. Awkward Figure caption. Please rewrite according to suggested above.

A45: Figure caption was rewritten as follows:

"Correlations between the estimated OC_{ACSM} and the offline OC mass concentration over the entire period and seasonality for PM_1 (a), and $PM_{2.5}$ (b). Black lines show the least orthogonal linear fit and the red dotted lines the 1:1 line."

R46: Figure 9. Incorrect graph as it should be volume comparison. Awkward Figure caption. Please rewrite according to suggested above.

A46: The figure was modified as follows:

"Comparison between measured ACSM-MAAP and MPSS for the entire period and seasonal variability: volume-closure (a), mass-closure (b), median number size distribution (red) with 10-90 (grey line) and 25-75 (black boxes) percentiles (c), median volume size distribution (d). The linear regressions (red lines) were calculated using the least orthogonal distance fit method.".

R47: Figure S1. Make PM axis consistent with further Figures

A47: Please refer to our answer A40 which is dealing with the same comment

R48: Figure S2. ...to daily PM2.5 mass.

A48: Figure caption was changed to "**Scatter plot of the ACSM species mass concentration measurements compared to corresponding daily $PM_{2.5}$ mass concentration over the entire period and seasonality.**"

R49: Figure S5. ...corrected for organo-nitrate contribution during days with PM1:PM2.5 < 0.6

A49: The figure caption was changed to **"Scatter plot of the winter (DJF) ACSM nitrate mass concentration corrected for organo-nitrate contribution during days with a PM_1:$PM_{2.5}$ < 0.6 compared to PM_1 nitrate mass concentration. The linear regressions (red lines) were calculated using the least orthogonal distance fit method."**

References

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental analysis of organic species with electron ionization high-resolution mass spectrometry, Anal. Chem., 79, 8350-8358, doi:10.1021/ac071150w, 2007.

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478-4485, doi:10.1021/es703009q, 2008.

Allan, J., Delia, A. E., Coe, H., Bower, K. N., Alfarra, R. M., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35, 909 - 922, doi:10.1016/j.jaerosci.2004.02.007, 2004.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Ruiz, L. H., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, doi 10.5194/acp-15-253-2015, 2015.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J. P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79-89, DOI 10.5194/amt-3-79-2010, 2010.

Chen, Q., Heald, C. L., Jimenez, J. L., Canagaratna, M. R., Zhang, Q., He, L. Y., Huang, X. F., Campuzano-Jost, P., Palm, B. B., Poulain, L., Kuwata, M., Martin, S. T., Abbatt, J. P. D., Lee, A. K. Y., and Liggio, J.: Elemental composition of organic aerosol: The gap between ambient and laboratory measurements, Geophys. Res. Lett., 42, 4182-4189, 2015.

Chen, Y., Wild, O., Wang, Y., Ran, L., Teich, M., Gross, J., Wang, L. N., Spindler, G., Herrmann, H., van Pinxteren, D., McFiggans, G., and Wiedensohler, A.: The influence of impactor size cut-off shift caused by hygroscopic growth on particulate matter loading and composition measurements, Atmos. Environ., 195, 141-148, 2018.

Chiappini, L., Verlhac, S., Aujay, R., Maenhaut, W., Putaud, J. P., Sciare, J., Jaffrezo, J. L., Liousse, C., Galy-Lacaux, C., Alleman, L. Y., Panteliadis, P., Leoz, E., and Favez, O.: Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter, Atmos. Meas. Tech., 7, 1649-1661, 10.5194/amt-7-1649-2014, 2014.

Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Frohlich, R., Belis, C. A., Aas, W., Auml;ijala, M., Alastuey, A., Artinano, B., Baisnee, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillon, M. C., Mocnik, G., O'Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Esteve, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prevot, A. S. H., Jayne, J. T., and Favez, O.: 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, 2015.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 8, 4027-4048, 2008.

Directive 2008/50/CE: Ambient air quality and cleaner air for Europe, OJL 152, 11.6.2008, 2008.

Elsasser, M., Crippa, M., Orasche, J., DeCarlo, P. F., Oster, M., Pitz, M., Cyrys, J., Gustafson, T. L., Pettersson, J. B. C., Schnelle-Kreis, J., Prevot, A. S. H., and Zimmermann, R.: Organic molecular markers and signature from wood combustion particles in winter ambient aerosols: aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany, Atmos. Chem. Phys., 12, 6113-6128, 10.5194/acp-12-6113-2012, 2012.

Freney, E., Zhang, Y., Croteau, P., Amodeo, T., Williams, L., Truong, F., Petit, J.-E., Sciare, J., Sarda-Esteve, R., Bonnaire, N., Arumae, T., Aurela, M., Bougiatioti, A., Mihalopoulos, N., Coz, E., Artinano, B., Crenn, V., Elste, T., Heikkinen, L., Poulain, L., Wiedensohler, A., Herrmann, H., Priestman, M., Alastuey, A., Stavroulas, I., Tobler, A., Vasilescu, J., Zanca, N., Canagaratna, M., Carbone, C., Flentje, H., Green, D., Maasikmets, M., Marmureanu, L., Minguillon, M. C., Prevot, A. S. H., Gros, V., Jayne, J., and Favez, O.: The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations, Aerosol Sci. Technol., 1-25, 10.1080/02786826.2019.1608901, 2019.

Lide, D. R.: CRC Handbook of Chemistry and Physics, CRC Press Inc., USA, 1991.

Liu, P. S. K., Deng, R., Smith, K. A., Williams, L. R., Jayne, J. T., Canagaratna, M. R., Moore, K., Onasch, T. B., Worsnop, D. R., and Deshler, T.: Transmission efficiency of an aerodynamic focussing lens system: Comparison of model calculations and laboratory measurements for the aerodyne aerosol mass spectrometer, Aerosol Sci. Technol., 41, doi10.1080/02786820701422278, 2007.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci. Technol., 46, 258-271, doi:10.1080/02786826.2011.620041, 2012.

Minguillon, M. C., Ripoll, A., Perez, N., Prevot, A. S. H., Canonaco, F., Querol, X., and Alastuey, A.: Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor, Atmos. Chem. Phys., 15, 6379-6391, 10.5194/acp-15-6379-2015, 2015.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Technol., 45, 780-794, doi 10.1080/02786826.2011.560211, 2011.

Ovadnevaite, J., Ceburnis, D., Leinert, S., Dall'Osto, M., Canagaratna, M., O'Doherty, S., Berresheim, H., and O'Dowd, C.: Submicron NE Atlantic marine aerosol chemical composition and abundance: Seasonal trends and air mass categorization, Journal of Geophysical Research-Atmospheres, 119, 11850-11863, 10.1002/2013jd021330, 2014.

Park, K., Kittelson, D. B., Zachariah, M. R., and McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates, J. Nanopart. Res., 6, 267-272, doi:10.1023/B:NANO.0000034657.71309.e6, 2004.

Petit, J. E., Favez, O., Albinet, A., and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind and trajectory analyses, Environ. Modell. Softw., 88, 183-187, 10.1016/j.envsoft.2016.11.022, 2017.

Pieber, S. M., El Haddad, I., Slowik, J. G., Canagaratna, M. R., Jayne, J. T., Platt, S. M., Bozzetti, C., Daellenbach, K. R., Frohlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jimenez, J. L., Worsnop, D. R., Baltensperger, U., and Prevot, A. S. H.: Inorganic Salt Interference on CO2+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies, Environ. Sci. Technol., 50, 10494-10503, 10.1021/acs.est.6b01035, 2016.

Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A., and Herrmann, H.: Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT research station Melpitz, Atmos. Chem. Phys., 11, 12579-12599, doi:10.5194/acp-11-12579-2011, 2011.

Poulain, L., Birmili, W., Canonaco, F., Crippa, M., Wu, Z. J., Nordmann, S., Spindler, G., Prevot, A. S. H., Wiedensohler, A., and Herrmann, H.: Chemical mass balance of 300 degrees C non-volatile particles at the tropospheric research site Melpitz, Germany, Atmos. Chem. Phys., 14, 10145-10162, doi:10.5194/acp-14-10145-2014, 2014.

Ripoll, A., Minguillon, M. C., Pey, J., Jimenez, J. L., Day, D. A., Sosedova, Y., Canonaco, F., Prevot, A. S. H., Querol, X., and Alastuey, A.: Long-term real-time chemical characterization of submicron aerosols at Montsec (southern Pyrenees, 1570 m a.s.l.), Atmos. Chem. Phys., 15, 2935-2951, 10.5194/acp-15-2935-2015, 2015.

Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Muller, K., Bruggemann, E., Chi, X., Putaud, J. P., Hitzenberger, R., Puxbaum, H., Baltensperger, U., and ten Brink, H.: Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL, Atmos. Environ., 38, 6487-6496, 10.1016/j.atmosenv.2004.08.026, 2004.

Sun, J. Y., Zhang, Q., Canagaratna, M. R., Zhang, Y. M., Ng, N. L., Sun, Y. L., Jayne, J. T., Zhang, X. C., Zhang, X. Y., and Worsnop, D. R.: Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, Atmos. Environ., 44, 131-140, doi:10.1016/j.atmosenv.2009.03.020, 2010.

Tuch, T. M., Haudek, A., Müller, T., Nowak, A., Wex, H., and Wiedensohler, A.: Design and performance of an automatic regenerating adsorption aerosol dryer for continuous operation at monitoring sites, Atmos. Meas. Tech., 2, 417-422, doi:10.5194/amt-2-417-2009, 2009.

Turpin, B. J., and Lim, H.-J.: Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 302-610, doi:10.1080/02786820119445, 2001.

WMO/GAW: Aerosol Measurement Procedures, Guidelines and Recommendation, 2016.

Xu, W., Lambe, A., Silva, P., Hu, W. W., Onasch, T., Williams, L., Croteau, P., Zhang, X., Renbaum-Wolff, L., Fortner, E., Jimenez, J. L., Jayne, J., Worsnop, D., and Canagaratna, M.: Laboratory evaluation of species-dependent relative ionization efficiencies in the Aerodyne Aerosol Mass Spectrometer, Aerosol Sci. Technol., 52, 626-641, 10.1080/02786826.2018.1439570, 2018.

Zanatta, M., Gysel, M., Bukowiecki, N., Muller, T., Weingartner, E., Areskoug, H., Fiebig, M., Yttri, K. E., Mihalopoulos, N., Kouvarakis, G., Beddows, D., Harrison, R. M., Cavalli, F., Putaud, J. P., Spindler, G., Wiedensohler, A., Alastuey, A., Pandolfi, M., Sellegri, K., Swietlicki, E., Jaffrezo, J. L., Baltensperger, U., and Laj, P.: A European aerosol phenomenology-5: Climatology of black carbon optical properties at 9 regional background sites across Europe, Atmos. Environ., 145, 346-364, 2016.

Relevant changes made in the manuscript

Page 1:

-line 5: added 2 new co-authors: Jean-Eudes Petit[2,3], Olivier Favez[4,3],

-line 7: added affiliation of the 2 new co-authors:

[2] Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, IPSL, Université Paris-Saclay, 91191 Gif-sur-Yvette, France
[3] Aerosol Chemical Monitor Calibration Centre (ACMCC), Batiment 701 CEA Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France
[4] Institut national de l'environnement industriel et des risques (INERIS), Parc Technol Alata, BP2, F-60550 Verneuil En Halatte, France

Abstract :

Line10 : replaced : « The Aerosol Chemical Speciation Monitor (ACSM) is an instrument for identifying and quantifying the influence of air quality mitigations. For this purpose, a European ACSM network has been developed within the research infrastructure project ACTRIS (European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases). To ensure the uniformity of the dataset, as […]"
By "The Aerosol Chemical Speciation Monitor (ACSM) is nowadays widely used to identify and quantify the main component of fine particles in ambient air. As such, its deployment at observatory platforms is fully incorporated within the European Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS). To ensure the consistency of the dataset […]"

Line 16: added the following sentence: "Here, we present and discuss the main outputs of long-term quality assurance efforts achieved for ACSM measurements at the research station Melpitz (Germany) since 2012 onwards."

Line 16: change the sentence "In order to check the robustness of the ACSM over the years and to characterize the seasonality effect, nitrate, sulfate, ammonium […]" by "In order to validate the ACSM measurements over the years and to characterize seasonal variations, nitrate, sulfate, ammonium […]"

Line 22: added "Mobility Particle size Spectrometer (MPSS)"

1. Introduction

Page 2, Line 22: modified and added a sentence "For this purpose, a European network of ground-based Aerosol Chemical Species Monitor (ACSM, Ng et al., 2011) is operated within the European Research Infrastructure ACTRIS (European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases, http://www.actris.eu). One of the main objectives of this coordinated ACSM network is to investigate and […]" by ". For this purpose, a European distributed facility of ground-based Aerosol Chemical Species Monitor (ACSM, Ng et al., 2011) is operated within ACTRIS (European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases, http://www.actris.eu). Complementary, the COST Action CA16109 Chemical On-Line cOmpoSition and Source Apportionment of fine *aerosol* (COLOSSAL, https://www.costcolossal.eu) is gathering a wide community of European research groups (with even further international inputs, as well as participation of some regional air quality monitoring networks) interested in the fine aerosol fraction. One of the main objectives of these coordinated programs is to investigate and […]"

Page 3, Line 8: replace "Ovadnevaite et al. (2014) have written a rare published work that reports long-term AMS comparisons." By "Ovadnevaite et al. (2014) have written a rare published work that reports long-term AMS comparisons (3-years). Even though the authors successfully compared it with offline $PM_{2.5}$ filter samples, they did not discuss the variability of the correlation and potential source of uncertainties.

Page 3, Line 18: replace "focus" by "Scope"

2.1 Research observatory Melpitz

Page 4, line 9: replace "effect" by "impact"
Line18 added "actively" in "[…] automatic aerosol diffusion dryer to actively keep the relative humidity […]"

Page 4, Line 18: Replaced the sentence "The aerosol flow is divided among a set of instruments" by "The aerosol flow is divided among a set of instruments by an isokinetic splitter (WMO/GAW, 2016) ensuring a representative sampling between the instruments".

2.2 ACSM

Page 5, Line 14: replace "covers" by "capture"

Page 5, Line 15: the following text has been added "The ACSM was regularly calibrated according to the manufacturer's recommendations at that time with 350 nm monodispersed ammonium nitrate and ammonium sulfate particles selected by a DMA and using the jump scan approach. It is important to note that since recently, the recommended calibration method has changed to a full scan approach (Freney et al., 2019). The total particle number concentration was systematically set below 800 # cm^{-3} to limit the artefact due to multiple charged particles. An overview of the ionization efficiency (IE) and relative ionization efficiency (RIE) for ammonium and sulfate can be found in Figure SI-1. On average, all performed calibration provides a mean IE value of 4.93 (±1.45) 10^{-11} (mean ± std. dev.) and mean RIEs for ammonium and sulfate were 6.48±1.26 and 0.68±0.13, respectively. These values are very close to the ones used for the data evaluation as indicated in Figure SI-1. Overall, no clear trend for IE and RIE of sulfate can be observed over the period, while a small decrease in the RIE of ammonium can be reported. The lowest RIE of ammonium was reported just after the replacement of the filament indicated a possible need for degassing and stabilization period. However, it is difficult to conclude if these tendencies could be associated with a possible aging effect of the instrument since it corresponds to a single instrument. Similar observations on various other individual ACSMs would be needed to allow for stating such a conclusion and a more systematic investigation of potential trends should then be performed with a large number of ACSM."

Page 5, Line 18: replaced "chemical time-dependent collection efficiency" by "composition dependent collection efficiency (CDCE)"

Page 5, Line 19: the following sentence has been added ". It is important to note that the CDCE algorithm includes inorganic species only and did not consider a possible effect of the organics on the collection efficiency estimation."

2.4 Air mass trajectory analysis

Page 6, line 14: The sentence "Finally, the meteorological conditions as available in HYSPLIT during each trajectory were also examined and only the trajectories ending with a Plenary Boundary Layer height (PBL) above 500 m were further considered for analysis" was replaced by "Finally, the meteorological conditions as available from the HYSPLIT output for each trajectory calculation were also examined. Although backward trajectories were started at a height of 500 m, the Planetary Boundary Layer at the trajectory starting time could be at a lower altitude making the association between the ground-based measurements and the inflowing air mass difficult. Therefore, only air mass trajectories with a HYSPLIT-estimated PBL height above 500 m were further considered for analysis."

3.1 Comparison with offline chemical composition

Page 6, line 29: The following sentence was added: "It is also important to note here that the comparison between ACSM and offline samplers generally consists of comparing dry aerosol online measurements to offline analyses of samples collected at ambient RH. A direct consequence is that the offline results might suffer from a cut-off shift due to aerosol hygroscopic growth when ambient RH is high (Chen et al., 2018). Based on this study, the cut-off shift due to aerosol hygroscopic growth should play a minor role at Melpitz, as this effect was estimated to influence the comparison by 2 % for marine air-mass and 1 % for continental air-mass. For European background stations, such a cut-off shift has been estimated to represent less than 10 % for PM_1 and 20 % for $PM_{2.5}$ particle mass loading, while it is stronger for marine or coastal stations (up to 43 % for PM_1 and 62 % for $PM_{2.5}$). Therefore, such artefact has to be considered when comparison ACSM with offline measurements."

3.1.1 Sulfate

Page 7, line 19: The following sentence was added ". Although our previous measurements using High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) at Melpitz (Poulain et al., 2011) support the presence of organic fragment on the UMR sulfate signal. The difference between the sulfate mass concentration based on UMR (as for ACSM) and the one obtained on the high-resolution (i.e. excluding the contribution of organic fragments on the sulfate signal) is below 10% indicating a minor impact of the organic to the sulfate signal."

Page 8, line 3: the following sentence was added "As already mentioned, a minor effect of the RH to the cut-off shift of the offline samplers can be expected at Melpitz (Chen et al., 2018)."

Page 8, line 5: The following sentence was removed: ". Interestingly, the PM1:PM2.5 ratio has a minor influence on nitrate and OC correlation parameters, as will be discussed later on".

3.1.2 Nitrate

Page 8, line 29: Replaced "Such an overestimation of nitrate mass concentrations by the ACSM has already been shown by Ripoll et al. (2015) […]" by "This overestimation is very small and within the error margin compared to massive overestimation in […]"

Page 9, line 4: Added "The high-volume samplers are sitting outside and are not temperature controlled. Therefore, the inside temperature of the sampler is influenced by the outside temperature."

3.1.3 Ammonium

Page 10, line 19: This section was completely rewritten as follows "The ammonium mass concentration measured by the ACSM mostly corresponds to ammonium nitrate and ammonium sulfate salts. Before comparing ACSM and offline PM_1 ammonium mass concentration, the neutralization state of the particles was estimated for both datasets assuming a full neutralization by nitrate, sulfate, and chloride as described in e.g. Sun et al. (2010). In both approaches, particles can be considered as fully neutralized during the entire period with no seasonality (Fig. SI-7) in agreement with previous AMS measurements made at the same place (Poulain et al., 2011). Correlations with offline systems fall somewhere between the two previously discussed ions. During the cold season, the ACSM ammonium mass concentration matches the PM_1 (slope 1.02, $R^2 = 0.83$), which supports the larger fraction of ammonium nitrate in the total PM as well as the size effect of sulfate during wintertime (Fig. 1 and Fig. 2). During the warm season, the evaporation of ammonium nitrate as discussed before will also induce a loss of ammonium on the filter samples compared to the online measurements leading to an under-estimation of the ammonium concentration on the offline sampler as well as a poor correlation ($R^2 = 0.49$). Similar conclusions can also be drawn when comparing it to the $PM_{2.5}$ ammonium mass concentration Fig. SI-2 & SI-3)."

3.1.4 OM and OC

Page 10: the section from line 28 to page 12 line 3 was rewritten as follows "The ACSM provides organic aerosol (OA) mass concentrations but contrary to the inorganic species no direct comparison with collocated organic mass measurements provided organic mass concentration is possible. Actually, only ACSM or AMS systems are nowadays able to provide such measurements and other methods - primarily based on the thermal and/or optical properties of carbonaceous aerosols - are estimating organic carbon (OC) mass concentration instead of OA. Here, offline OC measurements are available from the thermal-optical analyses of filter punches, allowing for comparing both parameters over the entire period of the study. In the following, the limitations of both methods are discussed. First of all, the organic aerosol mass concentration is defined as the sum of the non-attributed inorganic species fragments from the aerosol mass spectra as defined by Allan et al. (2004). A wrong assignment or correction of the fragmentation table during the data analysis process could be a source of mis-quantification of the organic mass concentration. For example, the fragment CO_2^+ (m/z 44) is the major signal on the organic mass spectra. It can suffer from substantial measurement biases, i.e., the so-called Pieber effect (Pieber et al., 2016;Freney et al., 2019) associated with interference due to nitrate signal. This artefact can lead to an overestimation of the m/z 44 and consequently directly affects the total organic mass concentration. Unfortunately, a thorough quantification of this effect on the present dataset is not possible, as the relevant method to do so includes regular full scan calibrations which has been proposed only recently, and further works are still needed to define associated correction procedures (Freney et al., 2019). Another main source of uncertainty for OA concentration estimates is linked to the assumption of a constant RIE. Here, it has been set at its 1.4 default value during the whole period of the study while it is known that RIE-organic and/or its CE can be influenced by the chemical composition of the organic (Xu et al., 2018). As already mentioned, organic is not included in the CDCE estimation method from Middlebrook et al. (2012), which might also have a potential impact on the resulting mass concentration. Overall, an uncertainty of 19 % in the ACSM organic mass concentration can be considered based on the ACSM reproducibility analysis made by Crenn et al. (2015).

OC mass concentrations derived from the offline analyses of filter samples are also subject to measurement uncertainties They are obtained according to a specific method (here the EUSAAR2 thermal-optical protocol). Applying another method will directly influence the OC concentration (Cavalli et al., 2010;Zanatta et al., 2016;Chiappini et al., 2014). Moreover, the samplers used for this study were sitting outside and were not temperature controlled. A direct consequence is that the evaporation of the more semi-volatile organic during warm days must be expected, which similarly impacted the measured OC concentration than for ammonium nitrate discussed above.

Keeping in mind all the mentioned uncertainties on each method, the OA mass concentration was compared to the offline OC mass concentration, which can therefore be considered as a fair estimation of the OM:OC ratio (Fig. 6-a). Correlation between OA and OC is not significantly impacted by the PM_1:$PM_{2.5}$ threshold ratio of 0.6 as for inorganics (Table SI-1). This supports the fact that organic is mainly distributed on the sub-µm size range throughout the year (Fig. SI-4). As expected, a lower OM:OC ratio was obtained in winter (slope = 1.29, R^2 = 0.78), which corresponds with the period with the largest anthropogenic influence. The highest OM:OC ratio was obtained in summer (slope = 2.74, R^2 = 0.68), corresponding with the SOA formation maximum. Although such a seasonal variation is coherent with a priori expectations (notably considering higher SOA contribution at summertime), biases related to instrumental uncertainties should still be considered. In a similar way than for nitrate, ambient temperature affects the OC leading to a systematic extreme OM:OC ratio during summer (Fig. 6c). Consequently, the summer's slope of 2.74 is certainly overestimated. However, some extreme values are found also for some winter days, which can therefore not be associated with a temperature artefact on the offline samplers. Such wintertime discrepancies might rather be attributed to the above-mentioned ACSM uncertainties related to RIE for organics, CE estimation and/or substantial influence of the so-called Pieber effect.

Another way to compare ACSM measurements to OC concentrations could be envisaged based on some previous works using AMS systems. Indeed, the estimation of the OM:OC ratio from AMS measurements is normally not done on a direct comparison of organic particle mass concentrations with collocated OC measurements but rather estimated based on the elemental analysis of the high-resolution organic mass spectra Aiken et al. (2007) and Aiken et al. (2008) or the variability of the f_{44}, the contribution of mass m/z 44 (mostly CO_2^+) to the total organic signal when only unit mass resolution mass spectra are available (Aitken et al., 2008, Ng et al., 2010). Both methods were reinvestigated and improved by Canagaratna et al. (2015) providing the following equations to convert the f_{44} signal of an AMS into O:C and OM:OC ratios:

$$O{:}C = 0.079 + 4.31 \times f_{44} \quad (1)$$

$$OM{:}OC = 1.29 \times O{:}C + 1.17 \quad (2)$$

By a systematic comparison of the two approaches, the elemental analysis, and the f_{44}, Canagaratna et al. (2015) concluded to an accuracy of 13 % of the f_{44} proxy for SOA traces decreasing for primary OA standards having an $f_{44} < 4$ % on average. Considering that m/z 44 is systematically the dominate fragment of the organic mass spectra for ambient measurements and that the ACSM is based on similar principle than the AMS, it is relevant to apply the f_{44} approach on the ACSM organic results as a proxy for ambient OC, and compare the results with the well-established offline OC method. Therefore, equations 1 and 2 were applied in the present dataset to estimate OC mass concentrations from the measured ACSM organic mass concentration (OC_{ACSM}) and to compare them to the OC-PM_1 (for the entire dataset: slope = 0.65, $R^2 = 0.73$, Fig. 7). As previously shown, a seasonal trend can also be observed here, with a unity regression slope obtained during summer periods (slope = 0.99, $R^2 = 0.64$), whereas a lower slope (0.56, $R^2 = 0.82$) was obtained in winter (Fig. 7 and Table SI-1). Here, the different instrumental and technical uncertainties have to be considered. Contrary to nitrate, temperature seems to have a less significant impact on the ratio between the OC_{ACSM} and the OC_{PM1}, as can be seen in figure SI-8. However, the extreme OC_{ACSM}:OC_{PM1} ratio values mostly happened during warm days supporting our previous conclusion on the temperature artifact on the OM_{ACSM}:OC_{PM1} ratio. As was mentioned above, the extreme ratio values during winter might result from a possible variability of the organic RIE as well as a possible co-call Pieber effect on the m/z 44 that directly affects the estimation of the OC_{ACSM}"

3.2.1 Mass closure with offline filters

Page 13, line 10: the sentence "Here, the residual mass fraction was calculated as the difference between the weighted filter mass and the sum of the detected compounds applying a constant OM:OC ratio of 1.8 to convert OC into OM (Fig. SI-7)" was rewritten as follows "Here, the residual mass fraction was calculated as the difference between the weighted filter mass and the sum of the detected compounds (Fig. SI-9). It is important to note here, that to properly convert the OC into OM and to consider all the different limitations inherent to both online and offline approaches, the seasonal means OM:OC ratio values (Fig. 6b) were applied.".

3.2.2 Mass closure with PNSD

Page 13: the section from page 13 line 29 to page 14 line 12 was rewritten as follows: "The PNSD has been continuously measured in parallel to the aerosol mass spectrometer and can, therefore, be used to perform mass closure analysis between ACSM-MAAP and PNSD (ranging from 10 to 800 nm, mobility diameter). To ensure a robust comparison between the two systems, two approaches are reported in the literature: the first one consists of converting the ACSM-MAAP mass concentration into volume and the PNSD in volume concentration. The second one consists of converting the PNSD into mass concentration. Both approaches are based on the same assumptions of (i) spherical, (ii) fully internally mixed particles, and (iii) an identical chemical composition over the entire size distribution to estimate a chemical time-dependent gravimetric particle density based on the following equation from Salcedo et al. (2006):

$$density = \frac{[Total_{AMS} + eBC]}{\frac{[NO_3^-] + [SO_4^{2-}] + [NH_4^-]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[Org]}{1.2} + \frac{[eBC]}{1.77}} \quad (1)$$

Here, the density was assumed to be 1.75 g cm^{-3} for ammonium nitrate and ammonium sulfate (Lide, 1991), 1.52 g cm^{-3} for ammonium chloride (Lide, 1991), and 1.2 g cm^{-3} for organic matter (Turpin and Lim, 2001). Finally, a density of 1.77 g cm^{-3} (Park et al., 2004) was applied for eBC. A discussion of eBC density can be found in Poulain et al. (2014).

It is important to note that for the volume concentration approach, both measurements (ACSM-MAAP and MPSS) remain independent between each other, which is not the case when using mass concentration. However, only a few numbers of papers reported a comparison between AMS or ACSM and MPSS in volume concentration (e.g. DeCarlo et al., 2008;Elsasser et al., 2012). Even though the two variables are non-independent on the mass concentration approach, it remains the most commonly used. A possible reason is that the mass concentration unit remains easier to use and interpreted as the volume concentration since atmospheric measurements are usually made in mass concentration.

Here, we investigated comparison results obtained using each of these approaches. Results are summarized in Figure 9.a for the volume concentration approach and Figure 9.b for the mass concentration one. Over 5.5 years of measurements, the ACSM-MAAP-derived volume or mass concentration correlates well with the estimated volume or mass concentration of the MPSS with the similar slopes of 0.79 and 0.77, respectively ($R^2 = 0.90$, Fig. 9a and 9b). This matches similar previous comparisons at the same place with an AMS (Poulain et al., 2014). Therefore, the selected method (volume or mass) did not substantially influence the comparison results. In the conditions of the present study both approaches could be applied for the station of Melpitz. Since comparison in mass concentration is the more commonly used, we will focus on it in the following discussions."

4 Summary and conclusion

Page 15, line 16: Added: "For such an exercise, it is fundamental to ensure isokinetic flow splitting between the different instruments connected to the main sampling line to ensure a homogeneous distribution of the air sample."

Page 16, line 9: Replaced "Nevertheless, more systematic comparisons should be performed in a similar way in different environments to validate our results and to better identify f44 instrumental variability" by "Nevertheless, the method might be difficult to apply for short time measurements (e.g. a few weeks only), where low/high extreme ratios may be misinterpreted, and results interpreted with cautions, such OA-OC comparison and OC_{ACSM}:$OC_{offline}$ methods shall then preferably be used on long term continuous measurements. Finally, it should also be noted that OC is the only regulated organic aerosol-related variable commonly monitored within current air quality networks (Directive 2008/50/CE, 2008;WMO/GAW, 2016) whereas equivalent methods for a better OA quantification at high-time resolution are still to be standardized, reinforcing the need for much more systematic comparison exercises at various locations."

Page 16, line 15: Added the following sentence "Moreover, possible cut-off shift due to ambient relative humidity effect on the offline measurements could represent a non-negligible parameter and has to be considered during such an exercise, especially for marine stations."

Page 16, line 22: Added the following sentence "It can be performed by converting the ACSM-MAAP mass concentration into volume concentration or by converted the MPSS volume concentration into mass concentration both using time-dependent density and assuming spherical and fully internally mixed particles. The volume approach is the most robust since it enables a strictly independent method. Being more interpretable, the mass approach may be used instead of for error quantification as long as it agrees with the volume approach. For the present dataset, the selected method did not substantially influence the comparison results."

Figures

Figure 3: corrected labelling right y-axis

Figure 4: replaced the figure capture by “Trajectory analysis for days where sulfate concentration difference between $PM_{2.5}$ and PM_1 exceeded 1 µg m^{-3}: (a) overpassing trajectory density; (b) results of the potential source contribution function (PSCF) analysis; (c) time series of sulfate mass concentration difference, trajectory altitude above 2000 m, precipitation events exceeding 1 mm h^{-1} and PBL above the station < 500 m.”

Figure 6: the figure was corrected and the figure caption was changed to “Correlation between ACSM organic mass concentrations and offline OC PM_1 (a); seasonal variability of the estimated OM_{ACSM}:OC_{PM1} ratio (b), and the entire time series colored by maximum daily temperature (c).“

Figure 7: the figure caption was changed to “Correlations between the estimated OC_{ACSM} and the offline OC mass concentration over the entire period and seasonality for PM_1 (a), and $PM_{2.5}$ (b). Black lines show the least orthogonal linear fit and the red dotted lines the 1:1 line.“

Figure 8 The figure was corrected

Figure 9 : the figure was remade and the figure caption was changed accordingly to “Comparison between measured ACSM-MAAP and MPSS for the entire period and seasonal variability: volume-closure (a), mass-closure (b), median number size distribution (red) with 10-90 (grey line) and 25-75 (black boxes) percentiles (c), median volume size distribution (d). The linear regressions (red lines) were calculated using the least orthogonal distance fit method. “

Supplementary information

Co-authors and corresponding affiliation lists were corrected.

Two new figures were added:

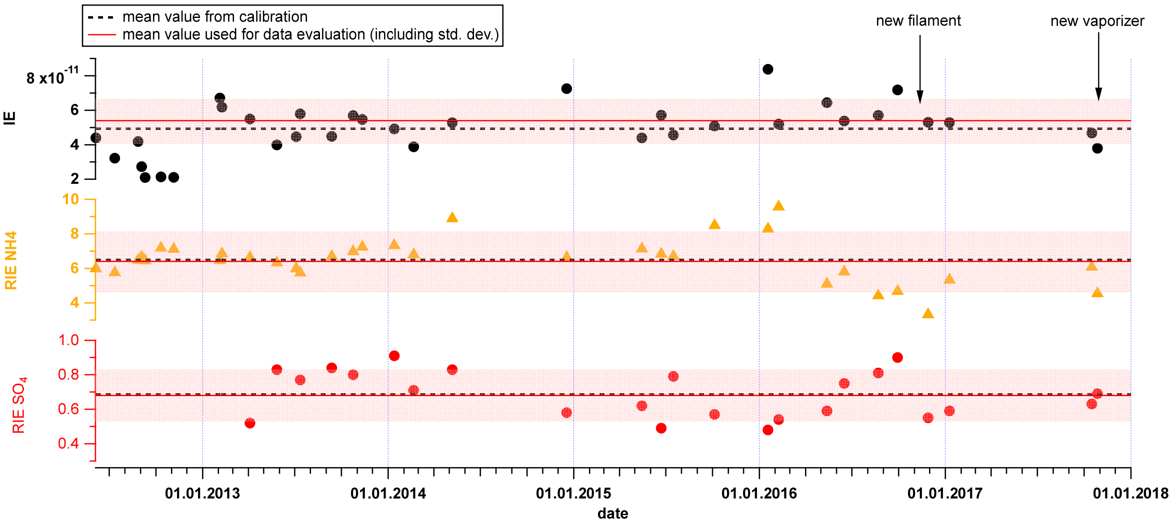


Figure SI-1: Time variation of the IE and RIE for ammonium and sulfate. The single points correspond to calibration, the dashed black line to the mean value from the calibration, and the full red line the mean value from the data analysis (shaded area corresponds to the standard deviation). Major maintenance (change of filament and vaporizer) are including.

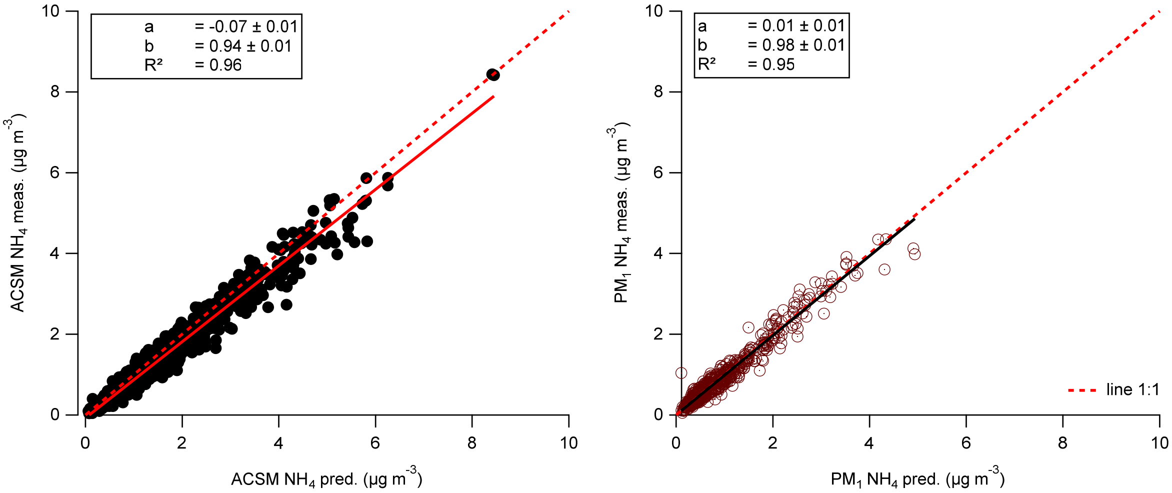


Figure SI-7: Comparison of the measured ammonium with the predicted ammonium mass concentration for the ACSM (left) and offline PM_1 samples assuming a full neutralization by nitrate, sulfate, and chloride. The linear regressions were calculated using the least orthogonal distance fit method (y = a x + b).

Figure SI-2: the figure caption was changed as follows "Scatter plot of the ACSM species mass concentration measurements compared to corresponding daily $PM_{2.5}$ mass concentration over the entire period and seasonality."

Figure SI-5: the figure caption was changed as follows "Scatter plot of the winter (DJF) ACSM nitrate mass concentration corrected for organo-nitrate contribution during days with a PM_1:$PM_{2.5}$ < 0.6 compared to PM_1 nitrate mass concentration. The linear regressions (red lines) were calculated using the least orthogonal distance fit method."

Figure SI.7: the figure was corrected according to referee comment and the figure caption updated accordingly as follows "Time series of the Digitel PM_1 chemical composition. Conversion of OC into OM was made based on the seasonal OM:OC ratio presented in Figure 6."

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental analysis of organic species with electron ionization high-resolution mass spectrometry, Anal. Chem., 79, 8350-8358, doi:10.1021/ac071150w, 2007.

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478-4485, doi:10.1021/es703009q, 2008.

Allan, J., Delia, A. E., Coe, H., Bower, K. N., Alfarra, R. M., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35, 909 - 922, doi:10.1016/j.jaerosci.2004.02.007, 2004.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Ruiz, L. H., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, doi 10.5194/acp-15-253-2015, 2015.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J. P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79-89, DOI 10.5194/amt-3-79-2010, 2010.

Chen, Y., Wild, O., Wang, Y., Ran, L., Teich, M., Gross, J., Wang, L. N., Spindler, G., Herrmann, H., van Pinxteren, D., McFiggans, G., and Wiedensohler, A.: The influence of impactor size cut-off shift caused by hygroscopic growth on particulate matter loading and composition measurements, Atmos. Environ., 195, 141-148, 2018.

Chiappini, L., Verlhac, S., Aujay, R., Maenhaut, W., Putaud, J. P., Sciare, J., Jaffrezo, J. L., Liousse, C., Galy-Lacaux, C., Alleman, L. Y., Panteliadis, P., Leoz, E., and Favez, O.: Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter, Atmos. Meas. Tech., 7, 1649-1661, 10.5194/amt-7-1649-2014, 2014.

Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Frohlich, R., Belis, C. A., Aas, W., Auml;ijala, M., Alastuey, A., Artinano, B., Baisnee, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillon, M. C., Mocnik, G., O'Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Esteve, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prevot, A. S. H., Jayne, J. T., and Favez, O.: 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, 2015.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 8, 4027-4048, 2008.

Directive 2008/50/CE: Ambient air quality and cleaner air for Europe, OJL 152, 11.6.2008, 2008.

Elsasser, M., Crippa, M., Orasche, J., DeCarlo, P. F., Oster, M., Pitz, M., Cyrys, J., Gustafson, T. L., Pettersson, J. B. C., Schnelle-Kreis, J., Prevot, A. S. H., and Zimmermann, R.: Organic molecular markers and signature from wood combustion particles in winter ambient aerosols: aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany, Atmos. Chem. Phys., 12, 6113-6128, 10.5194/acp-12-6113-2012, 2012.

Freney, E., Zhang, Y., Croteau, P., Amodeo, T., Williams, L., Truong, F., Petit, J.-E., Sciare, J., Sarda-Esteve, R., Bonnaire, N., Arumae, T., Aurela, M., Bougiatioti, A., Mihalopoulos, N., Coz, E., Artinano, B., Crenn, V., Elste, T., Heikkinen, L., Poulain, L., Wiedensohler, A., Herrmann, H., Priestman, M., Alastuey, A., Stavroulas, I., Tobler, A., Vasilescu, J., Zanca, N., Canagaratna, M., Carbone, C., Flentje, H., Green, D., Maasikmets, M., Marmureanu, L., Minguillon, M. C., Prevot, A. S. H., Gros, V., Jayne, J., and Favez, O.: The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations, Aerosol Sci. Technol., 1-25, 10.1080/02786826.2019.1608901, 2019.

Lide, D. R.: CRC Handbook of Chemistry and Physics, CRC Press Inc., USA, 1991.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci. Technol., 46, 258-271, doi:10.1080/02786826.2011.620041, 2012.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Technol., 45, 780-794, doi 10.1080/02786826.2011.560211, 2011.

Ovadnevaite, J., Ceburnis, D., Leinert, S., Dall'Osto, M., Canagaratna, M., O'Doherty, S., Berresheim, H., and O'Dowd, C.: Submicron NE Atlantic marine aerosol chemical composition and abundance: Seasonal trends and air mass categorization, Journal of Geophysical Research-Atmospheres, 119, 11850-11863, 10.1002/2013jd021330, 2014.

Park, K., Kittelson, D. B., Zachariah, M. R., and McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates, J. Nanopart. Res., 6, 267-272, doi:10.1023/B:NANO.0000034657.71309.e6, 2004.

Pieber, S. M., El Haddad, I., Slowik, J. G., Canagaratna, M. R., Jayne, J. T., Platt, S. M., Bozzetti, C., Daellenbach, K. R., Frohlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jimenez, J. L., Worsnop, D. R., Baltensperger, U., and Prevot, A. S. H.: Inorganic Salt Interference on CO2+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies, Environ. Sci. Technol., 50, 10494-10503, 10.1021/acs.est.6b01035, 2016.

Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A., and Herrmann, H.: Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT research station Melpitz, Atmos. Chem. Phys., 11, 12579-12599, doi:10.5194/acp-11-12579-2011, 2011.

Poulain, L., Birmili, W., Canonaco, F., Crippa, M., Wu, Z. J., Nordmann, S., Spindler, G., Prevot, A. S. H., Wiedensohler, A., and Herrmann, H.: Chemical mass balance of 300 degrees C non-volatile particles at the tropospheric research site Melpitz, Germany, Atmos. Chem. Phys., 14, 10145-10162, doi:10.5194/acp-14-10145-2014, 2014.

Sun, J. Y., Zhang, Q., Canagaratna, M. R., Zhang, Y. M., Ng, N. L., Sun, Y. L., Jayne, J. T., Zhang, X. C., Zhang, X. Y., and Worsnop, D. R.: Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, Atmos. Environ., 44, 131-140, doi:10.1016/j.atmosenv.2009.03.020, 2010.

Turpin, B. J., and Lim, H.-J.: Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 302-610, doi:10.1080/02786820119445, 2001.

WMO/GAW: Aerosol Measurement Procedures, Guidelines and Recommendation, 2016.

Xu, W., Lambe, A., Silva, P., Hu, W. W., Onasch, T., Williams, L., Croteau, P., Zhang, X., Renbaum-Wolff, L., Fortner, E., Jimenez, J. L., Jayne, J., Worsnop, D., and Canagaratna, M.: Laboratory evaluation of species-dependent relative ionization efficiencies in the Aerodyne Aerosol Mass Spectrometer, Aerosol Sci. Technol., 52, 626-641, 10.1080/02786826.2018.1439570, 2018.

Zanatta, M., Gysel, M., Bukowiecki, N., Muller, T., Weingartner, E., Areskoug, H., Fiebig, M., Yttri, K. E., Mihalopoulos, N., Kouvarakis, G., Beddows, D., Harrison, R. M., Cavalli, F., Putaud, J. P., Spindler, G., Wiedensohler, A., Alastuey, A., Pandolfi, M., Sellegri, K., Swietlicki, E., Jaffrezo, J. L., Baltensperger, U., and Laj, P.: A European aerosol phenomenology-5: Climatology of black carbon optical properties at 9 regional background sites across Europe, Atmos. Environ., 145, 346-364, 2016.

Multi-Year ACSM measurements at the Central European Research Station Melpitz (Germany) Part I: Instrument Robustness, Quality Assurance, and Impact of Upper Size Cut-Off Diameter

Laurent Poulain[1], Gerald Spindler[1], Achim Grüner[1], Thomas Tuch[1], Bastian Stieger[1], Dominik van Pinxteren[1], Jean-Eudes Petit[2,3], Olivier Favez[4,3], Hartmut Herrmann[1], and Alfred Wiedensohler[1]

[1] Leibniz Institute for Tropospheric Research (TROPOS), Permoserstr. 15, 04317 Leipzig, Germany
[2] Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, IPSL, Université Paris-Saclay, 91191 Gif-sur-Yvette, France
[3] Aerosol Chemical Monitor Calibration Centre (ACMCC), Bâtiment 701 CEA Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France
[4] Institut national de l'environnement industriel et des risques (INERIS), Parc Technol Alata, BP2, F-60550 Verneuil En Halatte, France

Correspondence to: L. Poulain (poulain@tropos.de)

Abstract. The Aerosol Chemical Speciation Monitor (ACSM) is nowadays widely used to identify and quantify the main component of fine particles in ambient air. As such, its deployment at observatory platforms is fully incorporated within the European Aerosol, Clouds and Trace Gases Research Infrastructure (ACTRIS). ~~is an instrument for identifying and quantifying the influence of air quality mitigations. For this purpose, a European ACSM network has been developed within the research infrastructure project ACTRIS (European Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases).~~ To ensure the ~~uniformity~~ consistency of the dataset, as well as instrumental performance and variability, regular intercomparisons are organized at the Aerosol Chemical Monitoring Calibration Center (ACMCC, part of the European Center for Aerosol Calibration, Paris, France). However, in-situ quality assurance remains a fundamental tracking point of the instrument's stability. Here, we present and discuss the main outputs of long-term quality assurance efforts achieved for ACSM measurements at the research station Melpitz (Germany) since 2012 onwards. In order to ~~check~~ validate the ~~robustness of the~~ ACSM measurements over the years and to characterize ~~the seasonality effect~~seasonal variations, nitrate, sulfate, ammonium, organic, and particle mass concentrations were systematically compared with collocated measurements including daily off-line high-volume PM_1 and $PM_{2.5}$ filter samples. Mass closure analysis was made by comparing the total particle mass (PM) concentration obtained by adding the mass concentration of equivalent black carbon (eBC) from the Multi-Angle Absorption Photometer (MAAP) to the ACSM chemical composition, to that of PM_1 and $PM_{2.5}$ during filter weighting, as well as to the derived mass concentration of particle number size distribution measurements (PNSD). A combination of PM_1 and $PM_{2.5}$ filter samples helps identify the critical importance of the upper size cut-off of the ACSM during such exercises. The ACSM-MAAP-derived mass concentrations systematically deviate from the PM_1 samples when the mass concentration of the latter represents less than 60 % of $PM_{2.5}$, which is linked to the transmission efficiency of the aerodynamic lenses of the ACSM. The best correlations are obtained for sulfate (slope 0.96, $R^2 = 0.77$) and total PM (slope 1.02, $R^2 = 0.90$). Although, sulfate does not exhibit a seasonal dependency, total PM mass concentration shows a small seasonal effect associated with an increase in non-water-soluble fractions. The nitrate suffers from a loss of ammonium nitrate during filter collection, and the contribution of organo-nitrate compounds to the ACSM nitrate signal make it difficult to directly compare the two methods. The contribution of m/z 44 (f_{44}) to the total organic mass concentration was used to convert the ACSM organic mass to OC by using a similar approach as for the AMS. The resulting estimated OC_{ACSM} was compared with the measured OC_{PM1} (slope 0.74, $R^2 = 0.77$), indicating that the f_{44} signal was relatively free of interferences during this period. The $PM_{2.5}$ filter samples use for the ACSM data quality might suffer from a systematic bias due to a size cutting effect as well as to the presence of chemical species that cannot be detected by the ACSM in coarse mode (e.g. sodium nitrate and sodium sulfate). This may lead to a systematic underestimation of the ACSM particle mass concentration and/or a positive artefact that artificially decreases the discrepancies between the two methods. Consequently, ACSM data validation using $PM_{2.5}$ filters has to be interpreted with extreme care. The particle mass closure with the PNSD was satisfying (slope 0.77, $R^2 = 0.90$ over the entire period), with a slightly overestimation of the Mobility Particle Size Spectrometer (MPSS) ~~MPSS~~ derived mass concentration in winter. This seasonal variability was related to a change on the PNSD and a larger contribution of the super-µm particles in winter.

This long-term analysis between the ACSM and other collocated instruments confirms the robustness of the ACSM and its suitability for long-term measurements. Particle mass closure with the PNSD is strongly recommended to ensure the stability of the ACSM. A near real-time mass closure procedure within the entire ACTRIS-ACSM network certainly represents an optimal way of both warranting the quality assurance of the ACSM measurements as well as identifying possible deviations in one of the two instruments.

1. Introduction

Aerosol particles strongly influence our environment, having especially an impact on the ecosystem and human health. In particular, fine particulate pollution directly affects mortality and morbidity (*e.g.* Gurjar et al., 2010;Ostro et al., 2007). Lelieveld et al. (2015) have estimated that air pollution, mostly < 2.5µm aerosol particles, may lead to 3.5 million premature deaths per year worldwide. Consequently, improving air quality represents a clear challenge, especially in urban areas. Quantifying the impact of the regulations to the air quality and changes on aerosol chemical composition needs to perform continuous and long-term measurements of aerosol particle properties such as e.g. the particle number size distribution (PNSD) and the chemical composition. For this purpose, a European ~~network~~ distributed facility of ground-based Aerosol Chemical Species Monitor (ACSM, Ng et al., 2011) is operated within ~~the European Research Infrastructure~~ ACTRIS (European

Research Infrastructure for the observation of Aerosol, Clouds and Trace Gases, http://www.actris.eu). Complementary, the COST Action CA16109 Chemical On-Line cOmpoSition and Source Apportionment of fine aerosol (COLOSSAL, https://www.costcolossal.eu) is gathering a wide community of European research groups (with even further international inputs, as well as participation of some regional air quality monitoring networks) interested in the fine aerosol fraction. One of the main objectives of ~~this~~ these coordinated ~~ACSM network~~programs is to investigate and understand the spatial variability of aerosol chemical composition~~s~~ on a continental scale, including temporal variability over days, seasons, and years. With such instrumental network, it is essential to keep a strong focus on the data quality as well as to assure that the results provided by each instrument are comparable to each other. Therefore, ACSM intercomparison workshops are regularly conducted within the framework of the European Center for Aerosol Calibration (ECAC, www.actris-ecac.eu) at the Aerosol Chemical Monitor Calibration Center (ACMCC) in France. Data quality is ensured by determining instrumental variability between ACSMs (total mass 9 %, organic 19 %, nitrate 15 %, sulfate 28 %, ammonium 36 %, Crenn et al., 2015;Fröhlich et al., 2015a;Freney et al., 2019).

Although intercomparison exercises provide instrumental variability, a comparison between ACSM and collocated measurements remains a fundamental aspect of in-situ quality control. These intercomparisons are considered in a number of publications (e.g. Fröhlich et al., 2015b;Petit et al., 2015;Parworth et al., 2015 ;Ovadnevaite et al., 2014 ;Ripoll et al., 2015;Minguillon et al., 2015;Poulain et al., 2011b;Poulain et al., 2011a;Huang et al., 2018;Takegawa et al., 2009;Wang et al., 2015 ;Crenn et al., 2015 ;Guo et al., 2015 ;Schlag et al., 2016 ;Sun et al., 2015). Usually, the comparisons between ACSM and collocated measurements were only performed for a few months up to one year. This might be perfectly adequate to ensure ACSM quality in that period. Only a few systematic comparisons with datasets longer than one year have been reported in the literature (e.g. Fröhlich et al., 2015b;Petit et al., 2015;Parworth et al., 2015 ;Sun et al., 2015). Ovadnevaite et al. (2014) have written a rare published work that reports long-term AMS comparisons (3-years). Even though the authors successfully compared it with offline $PM_{2.5}$ filter samples, they did not discuss the variability of the correlation and potential source of uncertainties. However, it might not appear sufficiently long to properly evaluate the performance and stability of an instrument designed for long-term monitoring, *e.g.* covering periods of several years. Therefore, there is really a need for such year-long investigations in order to evaluate the robustness of the instrument independently of calibrations and tuning as well as maintenance activities after technical failures (e.g. such as changing filament, pumps, etc.), seasonal variability, and properly define the limits of such exercises.

A key aspect of such a comparison is the individual upper size cut-off of each instrument. That of an ACSM (as well as the AMS since both are using the same aerodynamic lenses) is considered to be near-PM_1 (vacuum aerodynamic diameter), regarding the approximate 30-40 % transmission efficiency of its aerodynamic lenses at 1 µm (Liu et al., 2007;Takegawa et al., 2009). Recently, a near-$PM_{2.5}$ aerodynamic lens has been developed (Xu et al., 2017). However, this new generation of instruments having a near-$PM_{2.5}$ cut-off are not within the ~~scope~~focus of the present work. Overall, only a limited number of investigations referred to a direct comparison of the ACSM (as well as the AMS) with instruments that have a PM_1 cut-off. From those, multiple external references have been considered in order to compare individual species derived from off~~-~~line filter analysis (*e.g.* Ripoll et al., 2015;Minguillon et al., 2015;Poulain et al., 2011b;Poulain et al., 2011a;Huang et al., 2018), impactors (*e.g.* Takegawa et al., 2009;Wang et al., 2015), PILS (*e.g.* Crenn et al., 2015, Guo et al., 2015), and a MARGA (e.g. Schlag et al., 2016). Particle mass closure analysis has also been reported in the literature. It is achieved by adding equivalent Black Carbon mass concentrations (eBC) measured by an Absorption Photometer to the ACSM/AMS ones to obtain PM_1 mass concentrations and compare them with the ones derived from particle number size distributions (PNSD) measured by a MPSS (Mobility Particle Size Spectrometer). One of the main difficulties of a comparison with the MPSS is volume to mass conversion, which requires the density of each detected species (*e.g.* Bougiatioti et al., 2016;Ortega et al., 2016;Ripoll et al., 2015). To avoid this, some studies have reported a direct comparison of mass concentration vs. volume concentration (*e.g.* Setyan et al., 2012;DeCarlo et al., 2008;Parworth et al., 2015;Huang et al., 2010). Although this second approach might represent an advantage in providing a direct estimation of the aerosol particle density, the absolute value of the resulting density might become difficult to interpret in some cases because of possible discrepancies between the two instruments types (e.g. Parworth et al., 2015). Although the MPSS is certainly the most popular instrument for particle mass closure analysis, the TEOM-FDMS can be used, since it provides the PM mass concentration directly (Petit et al., 2015;Guerrero et al., 2017).

The aim of the present work is to investigate the long-term stability and comparability between ACSM and collocated and well-established techniques over year-long measurements. Specific attention was put on the influence of the upper size cut-off diameter to better understand how it might affect the validation step and the robustness of the data. Finally, recommendations are provided for better on-site quality assurance and quality control of the ACSM results, which would be useful for either long-term monitoring or intensive campaigns.

2. Methodology

2.1 Research observatory Melpitz

The atmospheric aerosol measurements were performed at the TROPOS research station Melpitz (51.54 N, 12.93 E, 86 m a.s.l.), 50 km to the northeast of Leipzig, Germany. The station has been in operation since 1992 to examine the ~~effect~~ impact of atmospheric long-range transport on Central European background air quality (Spindler et al., 2012;Spindler et al., 2013). The site itself is situated on a meadow and is mainly surrounded by agricultural pastures and forests. The Melpitz observatory is part of EMEP (Co-operative Programme for monitoring and evaluation of the long-range transmissions of air pollutants in Europe, Level 3 station, Aas et al., 2012), ACTRIS, ACTRIS-2, GAW (Global Atmosphere Watch of the World Meteorological Organization), and GUAN (German Ultrafine Aerosol Network, Birmili et al., 2015;Birmili et al., 2009;Birmili et al., 2016).

All online instruments are set up in the same laboratory container and connected to the same air inlet. This inlet line consists of a PM_{10} Anderson impactor located approximately 6 m above ground level and directly followed by an automatic aerosol diffusion dryer to actively keep the relative humidity on the sampling line below 40 % (Tuch et al., 2009). The aerosol flow is divided among a set of instruments by an isokinetic splitter (WMO/GAW, 2016) ensuring a representative sampling between the instruments ~~The aerosol flow is divided among a set of instruments~~. These instruments include a Multi-Angle Absorption Photometer (MAAP, model 5012, Thermo-Scientific, Petzold and Schönlinner, 2004) to measure the particle light absorption coefficients and the equivalent black carbon (eBC) mass concentration; a dual Mobility Particle Size Spectrometer (TROPOS-type T-MPSS; Birmili et al., 1999;Wiedensohler et al., 2012) to determine the PNSD from 3 to 800 nm (mobility diameter) alternating at ambient temperatures and behind a thermodenuder operating at 300 °C (Wehner et al., 2002); an Aerodynamic Particle Size Spectrometer (APSS; model TSI-3321) to measure the PNSD from 0.8-10 µm (aerodynamic diameter), and a three wavelengths Integrating Nephelometer (model TSI-3563) for particle light scattering and backscattering coefficients.

For a basic overview of the physical and chemical aerosol characterization methods see e.g. Birmili et al. (2008);Spindler et al. (2012);Spindler et al. (2013);Poulain et al. (2014);Poulain et al. (2011b). Physical and optical aerosol instruments are frequently calibrated within the framework of the ECAC. The MPSS is calibrated at the WCCAP (World Calibration Center for Aerosol Physics), following the recommendations given in Wiedensohler et al. (2018). The PNSD uncertainty determined with the MPSS is approximately 10 %. The uncertainty of an APSS is between 10-30 %, depending on the size range (Pfeifer et al., 2016). The uncertainty of the MAAP is also within 10 % as determined by Müller et al. (2011).

2.2 ACSM

The ACSM (Ng et al., 2011) is connected to the same inlet of the previously described laboratory container. It is based on the same working principle as the widespread Aerodyne Aerosol Mass Spectrometer, AMS (Canagaratna et al., 2007;DeCarlo et al., 2006;Jayne et al., 2000). Compared to the AMS, the ACSM cannot provide size-resolved chemical information. It is equipped with a low-cost residual gas analyzer (RGA) type quadrupole (Pfeiffer Vacuum Prisma plus system) with a unit mass resolution instead of a time-of-flight mass spectrometer. The same aerodynamic lenses as in the AMS are also equipped in the ACSM, with a maximum transmission ranging from 75 to 650 nm, with ca. 30 to 40 % transmission efficiency at 1 µm (Liu et al., 2007). Consequently, the ACSM, like the AMS, provides the chemical composition of non-refractory near-PM_1 aerosol particles (organic, nitrate, sulfate, ammonium, and chloride) with a typical time-resolution of 30 min. The ACSM has been permanently operated at the Melpitz since June 2012. The present work will be, however, limited to the period from June 2012 to November 2017. The instrument was sent to the ACMCC (Aerosol Chemical Monitor Calibration Center) near Paris (France) twice to take part of the ECAC intercomparison workshops (Nov-Dec 2013, Crenn et al., 2015;Fröhlich et al., 2015a; and Mar-May 2016, Freney et al., 2019). Overall, the ACSM data ~~covers~~ capture 80 % of the time the instrument was deployed at Melpitz. Missing days correspond to either instrument failures or maintenance operations.
The ACSM was regularly calibrated according to the manufacturer's recommendations at that time with 350 nm monodispersed ammonium nitrate and ammonium sulfate particles selected by a DMA and using the jump scan approach. It is important to note that since recently, the recommended calibration method has changed to a full scan approach (Freney et al., 2019). The total particle number concentration was systematically set below 800 # cm^{-3} to limit the artefact due to multiple charged

particles. An overview of the ionization efficiency (IE) and relative ionization efficiency (RIE) for ammonium and sulfate can be found in Figure SI-1. On average, all performed calibration provides a mean IE value of 4.93 (±1.45) 10^{-11} (mean ± std. dev.) and mean RIEs for ammonium and sulfate were 6.48±1.26 and 0.68±0.13, respectively. These values are very close to the ones used for the data evaluation as indicated in Figure SI-1. Overall, no clear trend for IE and RIE of sulfate can be observed over the period, while a small decrease in the RIE of ammonium can be reported. The lowest RIE of ammonium was reported just after the replacement of the filament indicated a possible need for degassing and stabilization period. However, it is difficult to conclude if these tendencies could be associated with a possible aging effect of the instrument since it corresponds to a single instrument. Similar observations on various other individual ACSMs would be needed to allow for stating such a conclusion and a more systematic investigation of potential trends should then be performed with a large number of ACSM. The ACSM measurements and data analysis was made with the latest version of the Data Acquisition (DAQ) and Data Analysis (DAS) software's available at that time (Aerodyne, https://sites.google.com/site/ariacsm). The ACSM data was analyzed following the recommendation of manufacturer and applying a ~~chemical time dependent~~ composition dependent collection efficiency (CDCE) correction ~~(CDCE)~~ based on the algorithms proposed by Middlebrook et al. (2012) to correct particle loss due to bouncing off the vaporizer before flash vaporization. It is important to note that the CDCE algorithm includes inorganic species only and did not consider a possible effect of the organics on the collection efficiency estimation.

2.3 Off-line chemical characterization

Parallel to the ACSM, the high-volume samplers DIGITEL DHA-80 (Digitel Elektronic AG, Hegnau, Switzerland) collect particles with sizes ~~cutting~~ selective PM$_{2.5}$ and PM$_{10}$ on preheated quartz fiber filters (105 °C) (Munktell, Type MK360, Sweden) for 24 hours from midnight to midnight. Samples were ~~performed in~~collected on a daily-based regime, whereas PM$_1$ was collected every 6 days. During some specific periods, related to different research projects that took place at the station, PM$_1$ sampling was also performed on a daily basis, as with PM$_{2.5}$ and PM$_{10}$.

After sampling, the filters were conditioned for 48 h at 20±2 °C and 50±5 % RH before being weighted by a microbalance Mettler-Toledo (AT 261). The filters were then extracted with ultrapure water (> 18 MΩcm) and analyzed through ion chromatography (ICS-3000, Dionex, USA) for water-soluble anions (column AS 18, eluent KOH) and cations (column CS 16, eluent methane sulfonic acid). For further descriptions of sampling and analyzing procedures, see Spindler et al. (2013).

For the chemical quantification of organic carbon (OC) and elemental carbon (EC), the sum of which is total Carbon (TC), a thermo-optical method was used. Rectangular punches (1.5 cm^2) of every quartz filter were analyzed for OC and EC using the Lab OC-EC Aerosol Analyzer (Sunset Laboratory Inc. U.S.A.). The standard temperature protocol EUSAAR2 (Cavalli et al., 2010) was applied to distinguish OC and EC, and the transmittance mode was used for the charring correction. In European networks, like EMEP and ACTRIS, this thermos-optical method is the preferred technique for quartz fiber filters (final temperature 850 °C). Because filter samples were collected over 24 h, an artefact due to the evaporation of the most volatile compounds during warm periods, like ammonium nitrate or some organic, cannot be fully excluded (Schaap et al., 2004;Keck and Wittmaack, 2005).

2.4 Air mass trajectory analysis

A trajectory analysis was made based on 96 h backward trajectories for the altitude of 500 m above model ground with the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT-4) model (Draxler and Hess (2004), http://www.ready.noaa.gov/ready/hysplit4.html). The trajectories were then analyzed using Zefir 3.7 (Petit et al., 2017) for the identification of potential aerosol sources using the Potential Source Contribution Function (PSCF). Because the filters were collected over 24 h, a total of 12 trajectories were considered for the analysis per day (i.e. every 2 hours), using the enlarge function of Zefir. Finally, the meteorological conditions as available from the HYSPLIT output for each trajectory calculation were also examined. Although backward trajectories were started at a height of 500 m, the Planetary Boundary Layer at the trajectory starting time could be at a lower altitude making the association between the ground-based measurements and the inflowing air mass difficult. Therefore, only air mass trajectories with a HYSPLIT-estimated PBL height above 500 m were further considered for analysis. ~~Finally, the meteorological conditions as available in HYSPLIT during each trajectory were also examined and only the trajectories ending with a Plenary Boundary Layer height (PBL) above 500 m were further considered for analysis.~~ Moreover, trajectories were cut off if they had a precipitation rate of over 1 mm h^{-1} and an altitude of above 2000 m.

3 Results

To assure the data quality of the ACSM measurements, the results were systematically compared to *i*- daily off-line filter samples (PM_1 and $PM_{2.5}$) of individual species (sulfate, nitrate, ammonium and organic) and *ii*- combined with eBC (MAAP) for mass closure analysis of both off-line filter samplers and on-line MPSS. The accuracy of the comparison and the seasonal variabilities will be discussed in the following. All correlation fits were performed using least the orthogonal fitting approach without forcing it to zero.

3.1 Comparison with off-line chemical composition

A comparison between total PM mass concentrations, sulfate, nitrate, and ammonium over the 5.5 years is plotted in Figure 1 for PM_1 and in Figure SI-~~1~~ 2 for $PM_{2.5}$. The seasonal effect on the fitting's correlation to each species and PM cutting is presented in Figures 2 and SI-~~2~~ 3 for PM_1 and $PM_{2.5}$, respectively. In the following, chloride will not be considered due to its very low concentrations and limited detection as described by Crenn et al. (2015). It is also important to note here that the comparison between ACSM and offline samplers generally consists of comparing dry aerosol online measurements to offline analyses of samples collected at ambient RH. A direct consequence is that the offline results might suffer from a cut-off shift due to aerosol hygroscopic growth when ambient RH is high (Chen et al., 2018). Based on this study, the cut-off shift due to aerosol hygroscopic growth should play a minor role at Melpitz, as this effect was estimated to influence the comparison by 2 % for marine air-mass and 1 % for continental air-mass. For European background stations, such a cut-off shift has been estimated to represent less than 10 % for PM_1 and 20 % for $PM_{2.5}$ particle mass loading, while it is stronger for marine or coastal stations (up to 43 % for PM_1 and 62 % for $PM_{2.5}$). Therefore, such artefact has to be considered when comparison ACSM with offline measurements.

3.1.1 Sulfate

Over the entire period, the regression slope of the sulfate mass concentration comparison ~~seems~~ is suggesting ~~to indicate a systematic~~ overestimation of the ACSM compared to PM_1-filters (slope 1.45, $R^2 = 0.59$, Fig. 2 and Table SI-1). Better regression slopes were obtained in spring (slope = 0.98, $R^2 = 0.74$) and summer (slope = 0.87, $R^2 = 0.77$) than in fall (slope = 1.25, $R^2 = 0.58$) and winter (slope = 1.57, $R^2 = 0.61$). However, the overestimation observed throughout the entire period, seems to be strongly influenced by ~~some out-layer days mainly corresponding to~~ three periods taking place in January 2013, October 2015, and February 2017 (these periods are highlighted in Fig. 1). During these periods, the ACSM sulfate mass concentration strongly overestimates the PM_1 one. The correlations with the $PM_{2.5}$ sulfate mass concentration (Fig. SI-~~1~~2 & SI-~~2~~3) underline the systematic underestimation of the ACSM sulfate concentration throughout the entire period (slope 0.68, $R^2 = 0.85$), similar to the value reported by Petit et al. (2015) over 2 years of measurements in the region of Paris (France). This overestimation could be associated with the size-cutting difference between the two methods and the presence of not detected sulfate species on the coarse mode, such as sodium sulfate. The seasonal impact on the regression coefficients is less pronounced than in the comparison with PM_1, with regression slopes ranging from 0.64 ($R^2 = 0.85$) in spring to 0.94 ($R^2 = 0.85$) in summer. Contrary to the correlation with PM_1, no out-layers were identified here.

The following will focus on the ACSM sulfate's overestimation days. There are several reasons that might explain the sulfate overestimation by the ACSM. The first is a technical aspect, since the ACSM has a mass spectrometer with a unit mass resolution, it cannot distinguish between sulfate and organic fragments with the same m/z (for example, $C_6H_8^+$ and/or $C_5H_4O^+$ at m/z 80 for SO_3^+, or $C_6H_9^+$ and $C_5H_5O^+$ at m/z 81 for HSO_3^+), as already discussed in Budisulistiorini et al. (2014). Therefore, an increase of the organic signal at this m/z might lead to an overestimation of the ACSM sulfate mass concentration. Although our previous measurements using High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) at Melpitz (Poulain et al., 2011b) support the presence of organic fragment on the UMR sulfate signal. The difference between the sulfate mass concentration based on UMR (as for ACSM) and the one obtained on the high-resolution (i.e. excluding the contribution of organic fragments on the sulfate signal) is below 10% indicating a minor impact of the organic to the sulfate signal. The second possible instrumental artefact is associated with the presence of a higher amount of organo-sulfate during these specific events. Indeed, organo-sulfate compounds lead to similar fragments as inorganic sulfate on AMS mass spectra (*e.g.* Farmer et al., 2010), which can contribute to the overestimation of the inorganic sulfate mass concentration. However, no particular change of $SO_3^{\pm}/SO^{\pm}$ and $HSO_3^{\pm}/SO^{\pm}$ ratios was observed when directly comparing their values before and after events, which can support neither the presence of organo-sulfate nor an increase of organic fragments at m/z 80 and 81. The second aspect is linked to sulfate size distribution. As can be seen in Figure SI-~~3~~4, the PM$_1$:PM$_{2.5}$ ratio of the sulfate mass concentration has a pronounced season variability with a mean value of above 0.8 in spring and summer and of 0.6 in winter. The influence of super-µm particles is also supported by the PNSD and PVSD as illustrated in Figure SI-~~4~~ 5 for Feb. 2017, which ~~corresponds~~ coincides with the period with the highest discrepancy between the two methods (Fig. 2). In order to investigate a possible dependency on particle mass size distribution, a sensitivity test analysis was performed by investigating the changes of the fitting parameters parallel to the changes of the PM$_1$:PM$_{2.5}$ ratio on both sulfate and total PM mass concentrations (Fig. 3). In both cases, a clear change in regression slopes as well as intercept values could be observed whenever the PM$_1$~~-~~:PM$_{2.5}$ ratio ~~contribution to PM$_{2.5}$~~ became smaller than 60 %. For days with a PM$_1$:PM$_{2.5}$ > 60 %, the regression slope ranges from 0.82 and 0.97 with a small intercept value ranging from -0.06 to 0.015 µg m^{-3}. As soon as the PM$_1$ sulfate or the PM mass concentration represents less than 60 % of the PM$_{2.5}$, the ACSM overestimates the PM$_1$ sulfate. Therefore, the discrepancy between the ACSM and the PM$_1$ can be attributed to the individual upper size cutting of the two instruments, and it highlights the limits of such a comparison. As already mentioned, a minor effect of the RH to the cut-off shift of the offline samplers can be expected at Melpitz (Chen et al., 2018). Consequently, and for the following discussions on sulfate correlation, only the days with a PM$_1$:PM$_{2.5}$ ratio of above 60 % will be considered, which still covers more than 80 % of sampling days. The table SI-1 shows the fitting parameters obtained with and without considering the discussed size effect. ~~Interestingly, the PM$_1$:PM$_{2.5}$ ratio has a minor influence on nitrate and OC correlation parameters, as will be discussed later on.~~ The resulting correlation parameters show a regression slope of 0.96 (intercept = -0.06 and R² = 0.77, Fig. 2), which supports the results reported by Minguillon et al. (2015) (slope = 1.15) and Ripoll et al. (2015) (slope = 1.12). Seasons do not exercise a significant influence on the correlation between the two instruments, with regression slopes ranging from 0.~~88~~ 85 in summer to 1.~~08~~ 06 in ~~winter~~fall, which supports the results reported by Budisulistiorini et al. (2014) and are better than the ACSM reproducibility uncertainties of 28 % reported by Crenn et al. (2015). The very low intercepts (~~50~~ -14 to ~~4~~ 0 ng m^{-3}) might indicate a minor contribution of organo-sulfate on the ACSM sulfate (Fig. 2 and Table SI-1). As was already mentioned, the transmission efficiency of the aerodynamic lenses of the ACSM is decreasing from ≈ 600 nm (d$_{va}$) to 30-40 % at 1 µm. Consequently, the remaining transmission efficiency of the aerodynamic lenses above 1 µm influences the sulfate correlation with the PM$_1$ samples, leading to the reported overestimation of the ACSM sulfate mass concentration on days with a low PM$_1$:PM$_{2.5}$ ratio.

To investigate a possible origin of super-µm sulfate, trajectory analysis was performed for days that have a difference in sulfate mass concentrations in PM$_1$ and PM$_{2.5}$ that is larger than 1 µg m^{-3} (i.e. Sulfate$_{PM2.5}$ – Sulfate$_{PM1}$ > 1 µg m^{-3}) (Fig.4). The ~~air mass~~ trajectory density indicates that during these days, the air masses were dominated by two sectors (East and West), with the highest probability in a near Eastern area of Melpitz. This confirms the predominantly~~ low level of the~~ shallow Plenary Boundary Layer height (PBL) as calculated by HYSPLIT, which was below 500 m for approx. 90 % of the time (Fig. 4-c), rather indicating local/regional sources than resulting from long-range transport processes. For days that have a connection between calculated trajectories and measurements (e.g. PBL > 500 m), PSCF analysis identified super-µm sulfate located inside a narrow corridor starting from Melpitz and going East, then passing over the South of Poland (Fig. 4-b). Since this area is known to host several coal power plants, super-µm sulfate might be associated to coal emissions originating from this area.

3.1.2 Nitrate

The ACSM nitrate mass concentration tends to slightly overestimate the off-line PM_1 nitrate throughout the entire period (slope = 1.16, R^2 = 0.80; Fig. 1 and 2). This overestimation is very small and within the error margin compared to massive overestimation in ~~Such an overestimation of nitrate mass concentrations by the ACSM has already been shown by~~ Ripoll et al. (2015) with a slope of 1.35 (R^2 = 0.77) and Minguillon et al. (2015) with a slope 2.8 (R^2 = 0.80). A similar conclusion was also drawn by Schlag et al. (2016), during a comparison to MARGA PM_1 measurements. The overall results must be carefully interpreted since a strong seasonal effect has been observed (Fig. 2) with very poor correlation in summer (slope = 6.28, R^2 = 0.29) and a strong overestimation during the colder seasons (slope = 1.29, R^2 = 0.80). On the one hand, ambient temperature strongly influences the nitrate mass concentrations on filter samples. Ammonium nitrate is a semi-volatile compound that evaporates, leading to a loss of ammonium nitrate on the filter sample. In an intercomparison study of different sampling supports, Schaap et al. (2004) demonstrated that a quartz filter ($PM_{2.5}$ and PM_{10}) is a suitable material for sampling nitrate as long as ~~the~~ temperature does not exceed 20 °C. The high-volume samplers are sitting outside and are not temperature controlled. Therefore, the inside temperature of the sampler is influenced by the outside temperature. This temperature artefact is clearly illustrated in Figure 5, when the variation of the ACSM:PM_1 nitrate ratio and the maximum temperature measured during the sampling day are compared. For ambient maximum temperatures above 10 °C, an increase of the ACSM:PM_1 ratio can be observed. Here it is imperative to note that the ambient maximum temperature did not reflect the temperature inside the sampler, solar radiation may also contribute to warm up the sampler. The highest discrepancy between the two methods corresponds to the warmest days, supporting the temperature artefact. Moreover, this also corresponds to the period with the lowest nitrate mass concentration measured by the ACSM (Fig. 5-b), which might also interfere with the absolute value of the ratio. On the other hand, the nitrate quantification by the ACSM is not free of artefacts. The ACSM's nitrate quantification is mainly based on the signals at m/z 30 (NO^+) and m/z 46 (NO_2^+), as well as on a minor contribution of N^+ and HNO_3^+ ions in a similar way as for the AMS (Allan et al., 2003). As with sulfate, interferences due to organic contributions at m/z 30 (CH_2O^+ and/or $C_2H_6^+$) and m/z 46 ($CH_2O_2^+$, $C_2H_6O^+$) also cannot be completely excluded. Because the ACSM is working at a unit mass resolution (UMR), it is not possible to distinguish nitrate from organic signals at these two m/z ratios. The direct consequence is a possible overestimation of the nitrate mass concentration in the UMR during high OA:NO_3 periods as shown by Fry et al. (2018). Another source of uncertainties concerning the ACSM nitrate mass concentration is the contribution of organo-nitrates to the nitrate signal, since the nitrate function of the organo-nitrate compounds fragments in a similar way to inorganic nitrate (Farmer et al., 2010). Therefore, the presence of organo-nitrate compounds artificially increases the ACSM-nitrate concentration. Kiendler-Scharr et al. (2016) have already shown that organo-nitrate compounds contribute to a significant fraction of the default AMS-NO_3 signal, especially in summer. It represents 57 % and 29 % of the default nitrate measured by an AMS at Melpitz in summer and winter, respectively (Kiendler-Scharr et al., 2016). Since the ACSM and the AMS are based on a similar principle, a simple assumption was made to tentatively correct the ACSM nitrate assuming the following: Firstly, the winter nitrate filter-PM_1 mass concentration is free of temperature artefacts, and secondly, the contribution of the organo-nitrate to the ACSM nitrate signal is being constant (29 %) over winter and years as previously reported for winter AMS measurements at the site. The resulting winter nitrate mass concentration has a better correlation to the filter-PM_1 (slope 0.88, $R^2 = 0.77$, Fig. SI-~~5~~6). This indirectly confirming the importance of organo-nitrate contributions to the default ACSM nitrate mass concentration during wintertime. Therefore, one should be careful when comparing the ACSM nitrate with an off-line system because of both temperature and organo-nitrate artefacts. Comparing the ACSM with a PM_1 MARGA for a year, Schlag et al. (2016) have obtained a R^2 of 0.96 throughout the year, without discussing seasonal variability. Consequently, all these results tend to indicate that the ACSM inorganic nitrate should properly correlate with the temperature artefact-free PM_1 nitrate measurements, as can be achieved by a PILS or a MARGA for example. Moreover, calculating the difference of nitrate mass concentrations between the ACSM and an online PM_1 system (e.g. PILS or MARGA) might represent a possible way to estimate the organo-nitrate concentration as reported by Xu et al. (2015) using HR-ToF-AMS vs. PILS or by Schlag et al. (2016) using ACSM and MARGA. Due to the unit mass resolution of the ACSM, direct quantification of particulate organo-nitrate remains a challenging task and more investigations are needed to better understand how organo-nitrate can be detected by the ACSM.

In a first approach, comparisons with the $PM_{2.5}$ nitrate mass concentration provided better correlation coefficients over the entire period (slope = 0.76, $R^2 = 0.77$), as well as in winter (slope = 0.~~73~~74, $R^2 = 0.69$), spring (slope = 0.77, $R^2 = 0.83$), and fall (slope = 0.96, $R^2 = 0.74$), compared to PM_1 (Fig. SI-~~1~~ 2 and SI-~~2~~3). Similar to PM_1, no correlation was found in summer. Here, the temperature effect on the filters as well as on organo-nitrate artefacts seems to have a less pronounced influence. Consequently, the presence of non-volatile nitrate compounds such as sodium nitrate ($NaNO_3$), resulting from the reaction of marine sodium chloride with HNO_3 when marine air masses cross polluted areas (Finlayson-Pitts and Pitts, 1986;Pio and Lopes, 1998), might explain the difference of the correlations between PM_1 and $PM_{2.5}$. This is supported by the absence of significant effects of the PM_1:$PM_{2.5}$ nitrate ratio to the fitting parameters when comparing the ACSM nitrate with the PM_1 (Fig. ~~4~~3). The influence of sodium nitrate at Melpitz has already been discussed in Stieger et al. (2017), comparing PM_{10} MARGA results with ACSM ones throughout the same period. Consequently, comparisons between the ACSM and $PM_{2.5}$ nitrate measurements could be strongly biased by coarse mode sodium nitrate that cannot be detected by the ACSM. This might be an important source of artefact, especially for sites under the influence of processed marine air masses, and might lead to a wrong validation of the ACSM nitrate measurements.

3.1.3 Ammonium

The ammonium mass concentration measured by the ACSM mostly corresponds to ammonium nitrate and ammonium sulfate salts. Before comparing ACSM and offline PM_1 ammonium mass concentration, the neutralization state of the particles was estimated for both datasets assuming a full neutralization by nitrate, sulfate, and chloride as described in e.g. Sun et al. (2010). In both approaches, particles can be considered as fully neutralized during the entire period with no seasonality (Fig. SI-7) in agreement with previous AMS measurements made at the same place (Poulain et al., 2011b). Correlations with offline systems fall somewhere between the two previously discussed ions. During the cold season, the ACSM ammonium mass concentration matches the PM_1 (slope 1.02, $R^2 = 0.83$), which supports the larger fraction of ammonium nitrate in the total PM as well as the size effect of sulfate during wintertime (Fig. 1 and Fig. 2). During the warm season, the evaporation of ammonium nitrate as discussed before will also induce a loss of ammonium on the filter samples compared to the online measurements leading to an under-estimation of the ammonium concentration on the offline sampler as well as a poor correlation ($R^2 = 0.49$). Similar conclusions can also be drawn when comparing it to the $PM_{2.5}$ ammonium mass concentration (Fig. SI-2 & SI-3).

~~The ammonium mass concentration measured by the ACSM mostly corresponds to ammonium nitrate and ammonium sulfate salts. Therefore, correlations with off-line systems are something between the two previously discussed ions. During the cold season, the ACSM ammonium mass concentration matches the PM_1 (slope 1.02, $R^2 = 0.83$), which supports the larger fraction of ammonium nitrate in the total PM as well as the size effect of sulfate during wintertime (Fig. 1 and Fig. 2). Although ammonium sulfate dominates during the warmer season, the temperature artefact of ammonium nitrate influences the correlation leading to an under-estimation of the ammonium concentration on the off-line sampler as well as a poor correlation ($R^2 = 0.49$). Similar conclusions can also be drawn when comparing it to the $PM_{2.5}$ ammonium mass concentration.~~

3.1.4 OM and OC

The ACSM provides organic aerosol (OA) mass concentrations but contrary to the inorganic species no direct comparison with collocated organic mass measurements provided organic mass concentration is possible. Actually, only ACSM or AMS systems are nowadays able to provide such measurements and other methods - primarily based on the thermal and/or optical properties of carbonaceous aerosols - are estimating organic carbon (OC) mass concentration instead of OA. Here, offline OC measurements are available from the thermal-optical analyses of filter punches, allowing for comparing both parameters over the entire period of the study. In the following, the limitations of both methods are discussed. First of all, the organic aerosol mass concentration is defined as the sum of the non-attributed inorganic species fragments from the aerosol mass spectra as defined by Allan et al. (2004). A wrong assignment or correction of the fragmentation table during the data analysis process could be a source of mis-quantification of the organic mass concentration. For example, the fragment CO_2^+ (m/z 44) is the major signal on the organic mass spectra. It can suffer from substantial measurement biases, i.e., the so-called Pieber effect

(Pieber et al., 2016;Freney et al., 2019) associated with interference due to nitrate signal. This artefact can lead to an overestimation of the m/z 44 and consequently directly affects the total organic mass concentration. Unfortunately, a thorough quantification of this effect on the present dataset is not possible, as the relevant method to do so includes regular full scan calibrations which has been proposed only recently, and further works are still needed to define associated correction procedures (Freney et al., 2019). Another main source of uncertainty for OA concentration estimates is linked to the assumption of a constant RIE. Here, it has been set at its 1.4 default value during the whole period of the study while it is known that RIE-organic and/or its CE can be influenced by the chemical composition of the organic (Xu et al., 2018). As already mentioned, organic is not included in the CDCE estimation method from Middlebrook et al. (2012), which might also have a potential impact on the resulting mass concentration. Overall, an uncertainty of 19 % in the ACSM organic mass concentration can be considered based on the ACSM reproducibility analysis made by Crenn et al. (2015).

OC mass concentrations derived from the offline analyses of filter samples are also subject to measurement uncertainties They are obtained according to a specific method (here the EUSAAR2 thermal-optical protocol). Applying another method will directly influence the OC concentration (Cavalli et al., 2010;Zanatta et al., 2016;Chiappini et al., 2014). Moreover, the samplers used for this study were sitting outside and were not temperature controlled. A direct consequence is that the evaporation of the more semi-volatile organic during warm days must be expected, which similarly impacted the measured OC concentration than for ammonium nitrate discussed above.

Keeping in mind all the mentioned uncertainties on each method, the~~, whereas the organic carbon concentrations (OC) were measured in the filters. The~~ OA mass concentration was compared to the off~~-~~line OC mass concentration, which can therefore be considered as a ~~direct~~ fair estimation of the OM:OC ratio (Fig. 6-a). Correlation between OA and OC is not significantly impacted by the PM_1:$PM_{2.5}$ threshold ratio of 0.6 as for inorganics (Table SI-1). This supports the fact that organic ~~are~~ is mainly distributed on the sub-µm size range throughout the year (Fig. SI-~~3~~4). As expected, a lower OM:OC ratio was obtained in winter (slope = 1.29, $R^2 = 0.78$), which corresponds with the period with the largest anthropogenic influence. The highest OM:OC ratio was obtained in summer (slope = 2.74, $R^2 = 0.68$), corresponding with the SOA formation maximum. Although such a seasonal variation is coherent with a priori expectations (notably considering higher SOA contribution at summertime), biases related to instrumental uncertainties should still be considered. In a similar way than for nitrate, ambient temperature affects the OC leading to a systematic extreme OM:OC ratio during summer (Fig. 6-c). Consequently, the summer's slope of 2.74 is certainly overestimated. However, some extreme values are found also for some winter days, which can therefore not be associated with a temperature artefact on the offline samplers. Such wintertime discrepancies might rather be attributed to the above-mentioned ACSM uncertainties related to RIE for organics, CE estimation and/or substantial influence of the so-called Pieber effect.

~~The resulting OM:OC values are larger than usually expected values (e.g.), but such unexpectedly high regression slopes have been observed by (slope of 3.39, $R^2 = 0.91$) and (slope of 4.25, $R^2 = 0.82$). In a similar way, and references therein have also seen high OM:OC ratio when comparing the ACSM or AMS to the $PM_{2.5}$ OC from either online or offline measurements. Based on the large dataset available in this study, the time series of the OM:OC ratio (estimated as ACSM-OA divided by~~

~~PM$_1$-OC) as well as its seasonal variation were also investigated (Fig. 6-b and c). The time series also shows some extreme values that are larger than 3, while seasonal means are closer to the expected OM:OC ratios, ranging from 1.66 in winter to 1.98 in summer. Tentative explanations for these unexpected values might be related to a possible seasonal variability of the relative ionization efficiency (RIE) of organic associated with the change of the aerosol organic composition as demonstrated by .~~

Another way to compare ACSM measurements to OC concentrations could be envisaged based on some previous works using AMS systems. Indeed, the estimation of the OM:OC ratio from AMS measurements is normally not done on a direct comparison of organic particle mass concentrations with collocated OC measurements but rather estimated based on the elemental analysis of the high-resolution organic mass spectra Aiken et al. (2007) and Aiken et al. (2008) or the variability of the f$_{44}$, the contribution of mass m/z 44 (mostly CO_2^+) to the total organic signal when only unit mass resolution mass spectra are available (Aitken et al., 2008, Ng et al., 2010). Both methods were reinvestigated and improved by Canagaratna et al. (2015) providing the following equations to convert the f$_{44}$ signal of an AMS into O:C and OM:OC ratios:

~~An estimation of the OM:OC ratio from AMS measurements is normally not done on a direct comparison of organic particle mass concentrations with collocated OC measurements, but rather estimated based on the variability of the f$_{44}$, the contribution of mass m/z 44 (mostly CO_2^+) to the total organic signal when not directly calculated through high-resolution mass spectra analysis. Aiken et al. (2007) and Aiken et al. (2008) developed an elemental analysis approach to the AMS mass spectra to provide O:C, H:C and OM:OC ratios based f$_{44}$. This method was reinvestigated and improved by Canagaratna et al. (2015) according to the following equations to convert the f$_{44}$ signal of an AMS into O:C and OM:OC ratios:~~

$$O{:}C = 0.079 + 4.31 \times f_{44} \tag{1}$$

$$OM{:}OC = 1.29 \times O{:}C + 1.17 \tag{2}$$

By a systematic comparison of the two approaches, the elemental analysis, and the f$_{44}$, Canagaratna et al. (2015) concluded to an accuracy of 13 % of the f$_{44}$ proxy for SOA traces decreasing for primary OA standards having an f$_{44}$ < 4 % on average. Considering that m/z 44 is systematically the dominate fragment of the organic mass spectra for ambient measurements and that the ACSM is based on similar principle than the AMS, it is relevant to apply the f$_{44}$ approach on the ACSM organic results as a proxy for ambient OC, and compare the results with the well-established offline OC method. Therefore, equations 1 and 2 were applied in the present dataset to estimate OC mass concentrations from the measured ACSM organic mass concentration (OC$_{ACSM}$) and to compare them to the OC-PM$_1$ (for the entire dataset: slope = 0.65, R² = 0.73, Fig. 7-a). As previously shown, a seasonal trend can also be observed here, with a unity regression slope obtained during summer periods (slope = 0.99, R² = 0.64), whereas a lower slope (0.56, R² = 0.82) was obtained in winter (Fig. 7-a~~ and Table SI-1~~). Here, the different instrumental and technical uncertainties have to be considered. Contrary to nitrate, temperature seems to have a less significant impact on the ratio between the OC_{ACSM} and the OC_{PM1}, as can be seen in Figure SI-~~6~~8. However, the extreme OC_{ACSM}:OC_{PM1} ratio values mostly happened during warm days supporting our previous conclusion on the temperature artifact on the OM_{ACSM}:OC_{PM1} ratio. ~~Consequently, the loss of the most volatile organic species during filter sampling on a warm day should not play a significant role here.~~ As was mentioned above, the ~~seasonal~~ extreme ratio values during winter might result from ~~effect might emphasize~~ a possible variability of the organic RIE as well as a possible co-call Pieber effect on the m/z 44 that directly affects the estimation of the OC_{ACSM}~~artefact on the CO_2 signal itself (). Moreover, the parameterizations used on Eq. 1 and 2 are only derived from AMS measurements and were not yet tested for the ACSM. Finally, Canagaratna et al. (2015) estimated the uncertainties of Eq. 1 to be around 13 % for SOA aerosol and to be higher for Primary OA. An uncertainty of 19 % in the ACSM-OA mass concentration can be considered based on the ACSM reproducibility analysis by Crenn et al. (2015). Therefore, the larger discrepancy observed in winter might result from the larger uncertainties of the method due to the increase of anthropogenic emissions on the organic fraction~~. Despite this agreement between ACSMs, Crenn et al. (2015) showed a large variability concerning the f_{44} signal itself during the ACSM intercomparison exercise. This variability was attributed to an instrument-dependent difference ~~of~~ in the vaporization conditions. For this reason, the authors did not recommend to systematically use the f_{44} approach to estimate the O:C ratio, as it can be achieved with the AMS and done here, or to interpret the resulting O:C ratios with caution. Since the OC_{ACMS} results are well supported by the offline analysis, we can conclude that our ACSM provides a relatively realistic value of the f_{44} over the considered timeframe and consequently, a reasonable proxy for the OM:OC ratio. However, we cannot rule out that a similar approach would provide the same results when using another ACSM at Melpitz and/or when applying the present method ~~on~~ in another location. Further systematic comparisons between the ACSM and collocated OC-PM_1 measurements should be performed in order to better investigate and characterize the suspected instrument vaporization dependency and/or a possible matrix effect depending on the dominant type of aerosol chemical composition at the considered sampling site, which might influence both the CO_2^+ signal and the organic RIE.

Comparison of the OC_{ACSM} with the OC $PM_{2.5}$ (Fig. 7~~-~~b) presents a systematic underprediction of the ACSM organic, which can be directly related to the size distribution of organic carbon between PM_1 and $PM_{2.5}$ (Fig. SI-4). Similar seasonality effects can be observed, which matches the quite constant distribution of the OC between PM_1 and $PM_{2.5}$ over the course of a year.

3.2 Mass closure analysis

Before performing a mass closure analysis, the total ACSM particle mass concentration (*i.e.* the sum of organic, nitrate, sulfate, ammonium, and chloride mass concentrations) was completed by adding the eBC PM_1 mass concentration. The eBC (PM_{10}) measured by the MAAP was converted to PM_1 by using a factor 0.9, which was obtained by running two MAAPs at Melpitz side by side with different inlets, see Poulain et al. (2011b). The resulting total PM_1 mass, later referred to as the ACSM-MAAP-derived mass concentration, was then compared to the particle mass concentration obtained by weighting filters (PM_1 and $PM_{2.5}$) as well as to the calculated particle volume and mass concentration from the PNSD of the MPSS.

3.2.1 Mass closure with off-line filters

In a similar way to sulfate, the mass closure between the online ACSM-MAAP-derived mass concentration and the offline PM$_1$ mass concentrations strongly depends on the PM$_1$:PM$_{2.5}$ ratio (Fig. 3). Because nitrate and organic did not present such a dependency to the PM$_1$:PM$_{2.5}$ ratio (Fig. 3), the sulfate size distribution should be the main driver of the total mass correlation. Consequently, the same PM$_1$:PM$_{2.5}$ threshold of 0.6 is applied in the following for the mass closure analysis and its discussion. It leads to a strong consistency between the online and the offline methods (slope = 1.02, R² = 0.90, Fig. 2 and table SI-1). Our results support those of Petit et al. (2015), who use a PM$_1$ TEOM-FDMS for mass closure over a 2 years' timeframe (slope 1.06). However, Guerrero et al. (2017) stated that a regression slope of 0.81 could also be found in the PM$_1$ TEOM-FDMS. ~~However~~Therefore, it is not possible to conclude whether this difference in correlation results between the two studies depends ~~of~~ on the ~~a~~ location ~~effect~~ or the presence of more coarse mode. Moreover, a possible loss of the more volatile compounds during the heated transmission line of the TEOM-FDMS could also occur.

Looking at the different seasons, the regression slopes were always around unit except in fall (slope = 1.31), the overestimation of which will be discussed in the following. Despite a near unity regression slope of 0.96 in summer, the low R² and the high intercept value (-3.59 µg m^{-3}) both suggest a possible bias between the two methods. Chemical analysis performed on the filter samples ~~can usually not explain their entire mass~~ cannot typically account for the entire mass, leading to the so-call residual mass fraction. This residual mass fraction is made out of all the non-water-soluble compounds such as mineral dust, carbonated or metal ones that are not detected. Here, the residual mass fraction was calculated as the difference between the weighted filter mass and the sum of the detected compounds (Fig. SI-9). It is important to note here, that to properly convert the OC into OM and to consider all the different limitations inherent to both online and offline approaches, the seasonal means OM:OC ratio values (Fig. 6-b) were applied~~, applying a constant OM:OC ratio of 1.8 to convert OC into OM (Fig. SI-7)~~. Figure 8 illustrates how this residual mass fraction interferes with the comparison of the ACSM-MAAP-derived mass concentrations. In summer, the residual mass fraction represents a significant part of the PM$_1$ mass concentration (above 60 %), explaining the low correlation coefficient and the large intercept value in this season. Similar conclusions can be drawn for fall. The increase of residual mass fraction in summer and fall could be associated with a larger resuspension of crustal material on dry and warm days and/or with agricultural activities (e.g. plowing) at these times of the year. Since mineral dust is not detectable by the ACSM, the presence of such compounds in the PM$_1$ could significantly influence mass closure results and must, therefore, be considered in such an approach.

A comparison with the PM$_{2.5}$ mass concentration provides a regression slope of 0.69 (R² = 0.77, Fig. SI-~~2~~3), which matches the comparisons from the literature using PM$_{2.5}$ TEOM-FDMS mass concentration (*e.g.* Sun et al., 2015;Sun et al., 2012). A seasonal effect on the correlation can be observed (Fig. SI-~~2~~3). In winter, the discrepancy between on-line and off-line techniques becomes more pronounced (slope = 0.65, R² = 0.88). This supports the seasonal variation of the PM$_1$:PM$_{2.5}$ ratio

~~mass contribution to $PM_{2.5}$~~ (Fig. SI.~~4~~5) as well as the impact of coarse mode sulfate that was previously mentioned. Similar results were also shown by Sun et al. (2015) when performing mass closure with a $PM_{2.5}$ TEOM.

3.2.2 Mass closure with PNSD

The PNSD has been continuously measured in parallel to the aerosol mass spectrometer and can, therefore, be used to perform mass closure analysis between ACSM-MAAP and PNSD (ranging from 10 to 800 nm, mobility diameter). To ensure a robust comparison between the two systems, two approaches are reported in the literature: the first one consists of converting the ACSM-MAAP mass concentration into volume and the PNSD in volume concentration. The second one consists of converting the PNSD into mass concentration. Both approaches are based on the same assumptions of (i) spherical, (ii) fully internally mixed particles, and (iii) an identical chemical composition over the entire size distribution to estimate a chemical time-dependent gravimetric particle density based on the following equation from Salcedo et al. (2006):

$$density = \frac{[Total_{AMS} + eBC]}{\frac{[NO_3^-] + [SO_4^{2-}] + [NH_4^-]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[Org]}{1.2} + \frac{[eBC]}{1.77}} \qquad (1)$$

Here, the density was assumed to be 1.75 g cm^{-3} for ammonium nitrate and ammonium sulfate (Lide, 1991), 1.52 g cm^{-3} for ammonium chloride (Lide, 1991), and 1.2 g cm^{-3} for organic matter (Turpin and Lim, 2001). Finally, a density of 1.77 g cm^{-3} (Park et al., 2004) was applied for eBC. A discussion of eBC density can be found in Poulain et al. (2014).

It is important to note that for the volume concentration approach, both measurements (ACSM-MAAP and MPSS) remain independent between each other, which is not the case when using mass concentration. However, only a few numbers of papers reported a comparison between AMS or ACSM and MPSS in volume concentration (e.g. DeCarlo et al., 2008;Elsasser et al., 2012). Even though the two variables are non-independent on the mass concentration approach, it remains the most commonly used. A possible reason is that the mass concentration unit remains easier to use and interpreted as the volume concentration since atmospheric measurements are usually made in mass concentration.

Here, we investigated comparison results obtained using each of these approaches. Results are summarized in Figure 9-a for the volume concentration approach and Figure 9-b for the mass concentration one. ~~The PNSD is continuously measured parallel to the aerosol mass spectrometer. In order to ensure a comparison between the two systems, the PNSD has to be converted into a volume and mass concentration. Here, the particle mass closure between the ACSM-MAAP and the MPSS (ranging from 10 to 800 nm, mobility diameter) was achieved similarly to what was already done for AMS measurements (e.g. Poulain et al., 2014). First, the conversion of a particle volume concentration into a mass concentration was achieved by assuming spherical particles and a chemical time-dependent gravimetric particle density based on the following equation from Salcedo et al. (2006):~~

~~$density = \frac{[Total_{AMS} + eBC]}{\frac{[NO_3^-] + [SO_4^{2-}] + [NH_4^-]}{1.75} + \frac{[Cl^-]}{1.52} + \frac{[Org]}{1.2} + \frac{[eBC]}{1.77}}$ (1)~~

~~Here, the density was assumed to be 1.75 g cm^{-3} for ammonium nitrate and ammonium sulfate (Lide, 1991), 1.52 g cm^{-3} for ammonium chloride (Lide, 1991), and 1.2 g cm^{-3} for organic matter (Turpin and Lim, 2001). Finally, a density of 1.77 g cm^{-3} (Park et al., 2004) was applied for eBC. A discussion of eBC density can be found in Poulain et al. (2014).~~

Over 5.5 years of measurements, the ACSM-MAAP-derived volume or mass concentration correlates well with the estimated volume or mass concentration of the MPSS with similar slopes of 0.79 and 0.77, respectively ($R^2 = 0.90$, Fig. 9-a and 9-b). This matches similar previous comparisons at the same place with an AMS (Poulain et al., 2014). Therefore, the selected method (volume or mass) did not substantially influence the comparison results. In the conditions of the present study both approaches could be applied for the station of Melpitz. Since comparison in mass concentration is the more commonly used, we will focus on it in the following discussions.”

~~This matches similar previous comparisons at the same place with an AMS (Poulain et al., 2014).Over 5.5 years of measurements, the ACSM-MAAP-derived mass concentration correlates well with the estimated mass concentrations of the MPSS with a slope of 0.77 ($R^2 = 0.90$, Fig. 9).~~ ~~This matches similar previous comparisons at the same place with an AMS (Poulain et al., 2014).~~ However, our results also highlight a non-negligible seasonality effect on mass closure, with a better slope in warmer seasons (summer, slope 0.92, $R^2 = 0.85$) than in cold ones (winter, slope 0.75, $R^2 = 0.91$). A similar seasonality was already reported by Fröhlich et al. (2015b) using a ToF-ACSM at the Jungfraujoch (Switzerland) during 14-month measurements. The median particle number (Fig. 9-b) and volume (Fig. 9-c) size distributions throughout the winter and summer months emphasize two different behaviors. In winter, the fine mode volume distribution peak occurs around 340 nm, while in summer it’s around 250 nm. Moreover, the particle volume size distribution in winter also shows a higher concentration of the largest size bins. This difference corresponds to the higher concentration of super-µm particles in winter as confirmed by the seasonality of the PM_1:$PM_{2.5}$ mass ratio (winter 0.73, summer 0.84, Fig. SI-~~7~~4). The PNSD provided by the MPSS is corrected from multiple-charged particles artefact in the sub-µm size range, and in case of low contributions of super-µm particles, the multiple-charged particles coming from super-µm particles on the PNSD are negligible. However, in case of a large coarse mode concentration, multiple-charged particles from the super-µm size range might also affect sub-µm size distribution, leading to an overestimation of the PNSD. This interference represents a possible source of artefact for the MPSS in such a case (Birmili et al., 2008). This artefact may plausibly explain the seasonality ~~might be an explanation of the seasonality trend~~ of the mass closure. An extended particle number size distribution by merging the MPSS and the APSS is presented in Figure SI-~~4~~5 for February 2017 to illustrate the impact of super-µm particle on size distribution. This period was strongly influenced by coarse mode particles that interfered with the comparison between the ACSM and off~~-~~line sulfate and PM as discussed earlier. On the other hand, and as previously mentioned, the transmission efficiency of the aerodynamic lenses of the ACSM decreases to about 30-40 % from ≈ 650 nm (d_{va}) to 1 µm. Consequently, the ACSM certainly underestimates the particle mass concentration for the larger size bins compared to the MPSS, which might also have a significant effect on particle mass closure with the MPSS in wintertime.

Assuming spherical particles and a constant density of 1.6, the size cutting of the Digitel PM$_1$ corresponds to a volume equivalent diameter of approx. 790 nm, which is quite similar to the MPSS (800 nm). The comparison between the MPSS-derived mass concentration and the PM$_1$ filter one also supports our conclusions (Fig. 10). Whereas the correlation slope of 1.79 ($R^2 = 0.75$) over the entire dataset seems to indicate an overestimation of the offline PM$_1$ compared to the MPSS, the correlation slope is strongly influenced by some winter days. Here, again, the discrepancy between the two methods can be linked directly to the upper size cut of each system. As shown in Figure 10, the discrepancy between the PM$_1$ and the MPSS-derived mass concentration is always associated with days with a low PM$_1$:PM$_{2.5}$ ratio corresponding to a larger contribution of the coarse mode particle compared to the other days. This result confirms the individual size cutting effect as well as supports our conclusions on a non-negligible artefact of super-µm multiple charge particles on the estimated MPSS mass concentration on specific winter days. During summertime, the PM$_1$ filter mass concentrations underestimate those derived from the MPSS, which have to be associated with the already discussed, loss of semi-volatile compounds on the filters.

4 Summary and conclusion

A systematic comparison between the ACSM and collocated measurements (including daily PM$_1$, PM$_{2.5}$, and MPSS) over a period of more than 5 years was performed to investigate the robustness of the ACSM as well as to identify the limits of such an exercise and the possible sources of uncertainties and artefacts. For such an exercise, it is fundamental to ensure isokinetic flow splitting between the different instruments connected to the main sampling line to ensure a homogeneous distribution of the air sample.

The comparison with the offline daily PM$_1$ samples over the entire period highlights a strong artefact due to the presence of super-µm sulfate. This artefact becomes non-negligible as soon as the PM$_1$:PM$_{2.5}$ ratio of the sulfate (and subsequently the total PM mass concentration) is below 60 %. The differences were directly associated with the specific size cutting of each instrument and the effect of the remaining transmission efficiency of the aerodynamic lenses of the ACSM above 1 µm. Moreover, similar conclusions were also drawn for the mass closure between the MPSS and PM$_1$ mass concentrations, confirming individual instrumental upper size cut-off effect. Because this artefact strongly depends on the size distribution of sulfate salts, it certainly depends on the sampling location and the origin of the different aerosol sources. Moreover, this effect should also depend on the aerodynamic lenses itself, which should not all have exactly the same transmission efficiency about 1 µm, leading to a certain instrument dependency. Considering these instrumental limits, the ~~ACMS~~ ACSM sulfate mass concentration strongly correlates with the one measured on the filters without any pronounced seasonal effect (slope: 0.96, $R^2 = 0.77$). This also indicates a minor contribution of organo-sulfates to the ACMS sulfate mass concentration at the measurement's site. Consequently, the SO_4-PM_1 appears to be a crucial parameter to ensure the SO_4-ACSM validation as well as to support the ACSM's sulfate calibration. In contrast, nitrate mass closure suffers from strong sampling artefacts for both instruments. On the one hand, offline measurements are strongly affected by a temperature effect, leading to the evaporation and loss of ammonium nitrate as was observed for maximum day temperatures of above 10 °C. On the other hand, organo-nitrate compounds lead to a systematic over-prediction of nitrate by the ACSM, which was clearly demonstrated in winter. Therefore, more investigations on the quantification of organo-nitrate by the ACSM are required in order to reduce this ~~artefact~~ uncertainty.

The ACSM organic mass concentration correlates with the OC-PM_1 (R^2 = 0.68 to 0.81), supporting the ACSM organic measurements. The regression slopes have a clear seasonal variability that matches the expected change of the oxidation state of organic throughout the year. Despite the large inter-instrumental variability of the f_{44} reported by Crenn et al. (2015), the f_{44} was used to convert the organic mass measured by the ACSM into OC by applying the method proposed by Canagaratna et al. (2015), which was developed for the AMS. The good match between the OC-ACSM and OC-PM_1 (slope ranging from 0.99 in summer to 0.56 in winter with an overall value of 0.65) confirmed that the approach for this instrument and at this sampling place, is also suitable for the ACSM. Nevertheless, the method might be difficult to apply for short time measurements (e.g. a few weeks only), where low/high extreme ratios may be misinterpreted, and results interpreted with cautions, such OA-OC comparison and OC_{ACSM}:$OC_{offline}$ methods shall then preferably be used on long term continuous measurements. Finally, it should also be noted that OC is the only regulated organic aerosol-related variable commonly monitored within current air quality networks (Directive 2008/50/CE, 2008;WMO/GAW, 2016) whereas equivalent methods for a better OA quantification at high-time resolution are still to be standardized, reinforcing the need for much more systematic comparison exercises at various locations. ~~Nevertheless, more systematic comparisons should be performed in a similar way in different environments to validate our results and to better identify f_{44} instrumental variability~~.

Not surprisingly, the comparison to the offline $PM_{2.5}$ first highlights the importance of the size cut-off of the filter samples. This is true for all considered species (PM, nitrate, sulfate, ammonium, and organic). Although such conclusions might appear quite trivial, the ACSM as well as the AMS are often compared to $PM_{2.5}$ filters. This is certainly the case, because $PM_{2.5}$ is the monitoring standard of air quality in several countries like the USA, Canada, and China, contrary to PM_1. Therefore, for such a comparison, the limitations due to the different size cuttings must be considered. Moreover, possible cut-off shift due to ambient relative humidity effect on the offline measurements could represent a non-negligible parameter and has to be considered during such an exercise, especially for marine stations.

The total PM_1 mass balance between online (ACSM and MAAP) and offline PM_1 matches throughout the entire time period (slope: 1.02, R^2 0.90) as well as the different seasons when considering the size effect mentioned before. However, non-water-soluble species like dust, metals and carbonate that were not analyzed in the filter samples in this study, and which are also not detected by the ACSM, influence the correlation especially in summer, leading to a lower correlation coefficient during this period ($R^2 = 0.40$). Mass closure with the PNSD certainly represents the best way for in-situ quality control as well as for tracking a possible drift on the ACSM performance. It can be performed by converting the ACSM-MAAP mass concentration into volume concentration or by converted the MPSS volume concentration into mass concentration both using time-dependent density and assuming spherical and fully internally mixed particles. The volume approach is the most robust since it enables a strictly independent method. Being more interpretable, the mass approach may be used instead of for error quantification as long as it agrees with the volume approach. For the present dataset, the selected method did not substantially influence the comparison results. Compared to off-line samples, comparisons with the MPSS do not only have a quite stable correlation over the years and the seasons, but the mass closure between the ACSM and MPSS also presents the main advantage to be done at a near real-time approach, since no further laboratory analyses are needed. Consequently, near real-time mass closure between the ACSM and MPSS should be considered in the near future as a standard way for in-situ quality control of measurements. Moreover, this approach does not remain free of artefacts related to the instrumental upper size cut-off diameter. This should be considered for sampling places with an important coarse mode fraction, in order to considered artefacts induced by both the remaining aerodynamic lens transmission efficiency of the ACSM and the contribution of multiple-charged particles from coarse mode on the PNSD spectra.

Finally, our results clearly emphasize the different limits of a comparison to collocated instruments and the effects of each individual instrumental upper size cut-off diameter. Consequently, there is a need for a better and systematic characterization of the transmission efficiency of the aerodynamic lenses of the ACSM on the upper size range. This knowledge will also certainly be useful to better understand the instrumental variability. Nevertheless, such near real-time comparisons certainly represent the best way to ensure long-term quality assurances of the ACSM measurements, especially at a station where the ACSM is used for long-term monitoring of particle chemical composition. More systematic comparisons performed in a similar way as in the present work over a long time-period in different environments as well as using different reference methods (e.g. TEOM-FDMS, beta-gauge or a PILS with PM_1 inlet for example) are still needed to better characterize the robustness of the ACSM over a long sampling time.

Data availability: all data is available upon request to the corresponding author and are deposited on the EBAS-NILU database (http://ebas.nilu.no/Default.aspx).

Authors contributions: LP, TT, AG, BS collected the data, LP performed data analysis on the ACSM, GS contributed to the evaluation of the off-line dataset and TT to the MPSS. All co-authors participated to the interpretation of the results. LP lead the writing of the manuscript to which authors contributed.

Competing of interest: the authors declare that they have no conflict of interest.

Acknowledgments

This project has received funding from the European Union's Horizon 2020 research and innovation programme within the infrastructure projects ACTRIS (Aerosols, Clouds, and Trace gases Research InfraStructure Network; EU FP7 grant agreement N°262254) and ACTRIS-2 (Aerosols, Clouds, and Trace gases Research InfraStructure, grant agreement N°654109). This work was also supported by the COST Action COLOSSAL CA16109. The physical measurements were also funded by the German Ultrafine Aerosol Network GUAN, which was jointly established with help of the German Federal Environment Ministry (BMU) grants F&E 370343200 (German title: "Erfassung der Zahl feiner und ultrafeiner Partikel in der Außenluft"), 2008–2010, and F&E 371143232 (German title: "Trendanalysen gesundheitsgefährdender Fein- und Ultrafeinstaubfraktionen unter Nutzung der im German Ultrafine Aerosol Network (GUAN) ermittelten Immissionsdaten durch Fortführung und Interpretation der Messreihen") 2012–2014. We also acknowledge the WCCAP (World Calibration Center for Aerosol Physics) as part of the WMO-GAW program. The WCCAP is base-funded by the German Federal Environmental Agency (Umweltbundesamt), Germany. Support by the European Regional Development Funds (EFRE – Europe funds Saxony) is gratefully acknowledged. The authors also thanks R. Rabe especially for technical support in the field and A. Rödger, A. Dietze, and S.Fuchs for numerous laboratory analyses.

References

Aas, W., Tsyro, S., Bieber, E., Bergström, R., Ceburnis, D., Ellermann, T., Fagerli, H., Frölich, M., Gehrig, R., Makkonen, U., Nemitz, E., Otjes, R., Perez, N., Perrino, C., Prévôt, A. S. H., Putaud, J. P., Simpson, D., Spindler, G., Vana, M., and Yttri, K. E.: Lessons learnt from the first EMEP intensive measurement periods, Atmos. Chem. Phys., 12, 8073-8094, doi 10.5194/acp-12-8073-2012, 2012.

Aiken, A. C., DeCarlo, P. F., and Jimenez, J. L.: Elemental analysis of organic species with electron ionization high-resolution mass spectrometry, Anal. Chem., 79, 8350-8358, doi:10.1021/ac071150w, 2007.

Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, Environ. Sci. Technol., 42, 4478-4485, doi:10.1021/es703009q, 2008.

Allan, J., Delia, A. E., Coe, H., Bower, K. N., Alfarra, R. M., Jimenez, J. L., Middlebrook, A. M., Drewnick, F., Onasch, T. B., Canagaratna, M. R., Jayne, J. T., and Worsnop, D. R.: A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, J. Aerosol Sci., 35, 909 - 922, doi:10.1016/j.jaerosci.2004.02.007, 2004.

Allan, J. D., Alfarra, R. M., Bower, K. N., Williams, P. I., Gallagher, M. W., Jimenez, J. L., McDonald, A. G., Nemitz, E., Canagaratna, M. R., Jayne, J. T., Coe, H., and Worsnop, D. R.: Quantitative sampling using an Aerodyne aerosol mass spectrometer 2. Measurements of fine particulate chemical composition in two U.K. cities, J. Geophys. Res., 108, 4091, doi:10.1029/2002JD002358, 2003.

Birmili, W., Stratmann, F., and Wiedensohler, A.: Design of a DMA-based size spectrometer for a large particle size range and stable operation, J. Aerosol Sci., 30, 549-553, doi 10.1016/S0021-8502(98)00047-0, 1999.

Birmili, W., Schepanski, K., Ansmann, A., Spindler, G., Tegen, I., Wehner, B., Nowak, A., Reimer, E., Mattis, I., Muller, K., Brüggemann, E., Gnauk, T., Herrmann, H., Wiedensohler, A., Althausen, D., Schladitz, A., Tuch, T., and Löschau, G.: A case of extreme particulate matter concentrations over Central Europe caused by dust emitted over the southern Ukraine, Atmos. Chem. Phys., 8, 997-1016, doi:10.5194/acp-8-997-2008, 2008.

Birmili, W., Weinhold, K., Nordmann, S., Wiedensohler, A., Spindler, G., Müller, K., Herrmann, H., Gnauk, T., Pitz, M., Cyrys, J., Flentje, H., Nickel, C., Kuhlbusch, T. A. J., and Löschau, G.: Atmospheric aerosol measurements in the German Ultrafine Aerosol Network (GUAN): Part 1 - soot and particle number size distribution, Gefahrst. Reinh. Luft., 69, 137-145, 2009.

Birmili, W., Sun, J., Weinhold, K., Merkel, M., Rasch, F., Spindler, G., Wiedensohler, A., Bastian, S., Loschau, G., Schladitz, A., Quass, U., Kuhlbusch, T. A. J., Kaminski, H., Cyrys, J., Pitz, M., Gu, J., Peters, A., Flentje, H., Meinhardt, F., Schwerin, A., Bath, O., Ries, L., Gerwig, H., Wirtz, K., and Weber, S.: Atmospheric aerosol measurements in the German Ultrafine Aerosol Network (GUAN) Part 3: Black Carbon mass and particle number concentrations 2009 to 2014, Gefahrst. Reinh. Luft., 75, 479-488, 2015.

Birmili, W., Weinhold, K., Rasch, F., Sonntag, A., Sun, J., Merkel, M., Wiedensohler, A., Bastian, S., Schladitz, A., Loschau, G., Cyrys, J., Pitz, M., Gu, J. W., Kusch, T., Flentje, H., Quass, U., Kaminski, H., Kuhlbusch, T. A. J., Meinhardt, F., Schwerin, A., Bath, O., Ries, L., Wirtz, K., and Fiebig, M.: Long-term observations of tropospheric particle number size distributions and equivalent black carbon mass concentrations in the German Ultrafine Aerosol Network (GUAN), Earth System Science Data, 8, 355-382, 10.5194/essd-8-355-2016, 2016.

Bougiatioti, A., Nikolaou, P., Stavroulas, I., Kouvarakis, G., Weber, R., Nenes, A., Kanakidou, M., and Mihalopoulos, N.: Particle water and pH in the eastern Mediterranean: source variability and implications for nutrient availability, Atmos. Chem. Phys., 16, 4579-4591, 2016.

Budisulistiorini, S. H., Canagaratna, M. R., Croteau, P. L., Baumann, K., Edgerton, E. S., Kollman, M. S., Ng, N. L., Verma, V., Shaw, S. L., Knipping, E. M., Worsnop, D. R., Jayne, J. T., Weber, R. J., and Surratt, J. D.: Intercomparison of an Aerosol Chemical Speciation Monitor (ACSM) with ambient fine aerosol measurements in downtown Atlanta, Georgia, Atmos. Meas. Tech., 7, 1929-1941, 10.5194/amt-7-1929-2014, 2014.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., Decarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the Aerodyne aerosol mass spectrometer, Mass Spectrom. Rev., 26, 185-222, doi 10.1002/mas.20115, 2007.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Ruiz, L. H., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, doi 10.5194/acp-15-253-2015, 2015.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J. P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79-89, DOI 10.5194/amt-3-79-2010, 2010.

Chen, Y., Wild, O., Wang, Y., Ran, L., Teich, M., Gross, J., Wang, L. N., Spindler, G., Herrmann, H., van Pinxteren, D., McFiggans, G., and Wiedensohler, A.: The influence of impactor size cut-off shift caused by hygroscopic growth on particulate matter loading and composition measurements, Atmos. Environ., 195, 141-148, 2018.

Chiappini, L., Verlhac, S., Aujay, R., Maenhaut, W., Putaud, J. P., Sciare, J., Jaffrezo, J. L., Liousse, C., Galy-Lacaux, C., Alleman, L. Y., Panteliadis, P., Leoz, E., and Favez, O.: Clues for a standardised thermal-optical protocol for the assessment of organic and elemental carbon within ambient air particulate matter, Atmos. Meas. Tech., 7, 1649-1661, 10.5194/amt-7-1649-2014, 2014.

Crenn, V., Sciare, J., Croteau, P. L., Verlhac, S., Frohlich, R., Belis, C. A., Aas, W., Auml;ijala, M., Alastuey, A., Artinano, B., Baisnee, D., Bonnaire, N., Bressi, M., Canagaratna, M., Canonaco, F., Carbone, C., Cavalli, F., Coz, E., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Lunder, C., Minguillon, M. C., Mocnik, G., O'Dowd, C. D., Ovadnevaite, J., Petit, J. E., Petralia, E., Poulain, L., Priestman, M., Riffault, V., Ripoll, A., Sarda-Esteve, R., Slowik, J. G., Setyan, A., Wiedensohler, A., Baltensperger, U., Prevot, A. S. H., Jayne, J. T., and Favez, O.: 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, 2015.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, Anal. Chem., 78, 8281-8289, doi 10.1021/ac061249n, 2006.

DeCarlo, P. F., Dunlea, E. J., Kimmel, J. R., Aiken, A. C., Sueper, D., Crounse, J., Wennberg, P. O., Emmons, L., Shinozuka, Y., Clarke, A., Zhou, J., Tomlinson, J., Collins, D. R., Knapp, D., Weinheimer, A. J., Montzka, D. D., Campos, T., and Jimenez, J. L.: Fast airborne aerosol size and chemistry measurements above Mexico City and Central Mexico during the MILAGRO campaign, Atmos. Chem. Phys., 8, 4027-4048, 2008.

Directive 2008/50/CE: Ambient air quality and cleaner air for Europe, OJL 152, 11.6.2008, 2008.

Draxler, R., and Hess, G.: Description of the HYSPLIT4 modeling system, NOAA Technical Memorandum, ERL, ARL-224, 2004.

Elsasser, M., Crippa, M., Orasche, J., DeCarlo, P. F., Oster, M., Pitz, M., Cyrys, J., Gustafson, T. L., Pettersson, J. B. C., Schnelle-Kreis, J., Prevot, A. S. H., and Zimmermann, R.: Organic molecular markers and signature from wood combustion particles in winter ambient aerosols: aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany, Atmos. Chem. Phys., 12, 6113-6128, 10.5194/acp-12-6113-2012, 2012.

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, Proc. Nat. Acad. Sci., 107, 6670-6675, doi 10.1073/pnas.0912340107, 2010.

Finlayson-Pitts, B. J., and Pitts, J. N. J.: Atmospheric chemistry : fundamentals and experimenta techniques, John Wiley & Sons, New York, 1986.

Freney, E., Zhang, Y., Croteau, P., Amodeo, T., Williams, L., Truong, F., Petit, J.-E., Sciare, J., Sarda-Esteve, R., Bonnaire, N., Arumae, T., Aurela, M., Bougiatioti, A., Mihalopoulos, N., Coz, E., Artinano, B., Crenn, V., Elste, T., Heikkinen, L., Poulain, L., Wiedensohler, A., Herrmann, H., Priestman, M., Alastuey, A., Stavroulas, I., Tobler, A., Vasilescu, J., Zanca, N., Canagaratna, M., Carbone, C., Flentje, H., Green, D., Maasikmets, M., Marmureanu, L., Minguillon, M. C., Prevot, A. S. H., Gros, V., Jayne, J., and Favez, O.: The second ACTRIS inter-comparison (2016) for Aerosol Chemical Speciation Monitors (ACSM): Calibration protocols and instrument performance evaluations, Aerosol Sci. Technol., 1-25, 10.1080/02786826.2019.1608901, 2019.

Fröhlich, R., Crenn, V., Setyan, A., Belis, C. A., Canonaco, F., Favez, O., Riffault, V., Slowik, J. G., Aas, W., Aijala, M., Alastuey, A., Artinano, B., Bonnaire, N., Bozzetti, C., Bressi, M., Carbone, C., Coz, E., Croteau, P. L., Cubison, M. J., Esser-Gietl, J. K., Green, D. C., Gros, V., Heikkinen, L., Herrmann, H., Jayne, J. T., Lunder, C. R., Minguillon, M. C., Mocnik, G., O'Dowd, C. D., Ovadnevaite, J., Petralia, E., Poulain, L., Priestman, M., Ripoll, A., Sarda-Esteve, R., Wiedensohler, A., Baltensperger, U., Sciare, J., and Prevot, A. S. H.: ACTRIS ACSM intercomparison - Part 2: Intercomparison of ME-2 organic source apportionment results from 15 individual, co-located aerosol mass spectrometers, Atmos. Meas. Tech., 8, 2555-2576, 2015a.

Fröhlich, R., Cubison, M. J., Slowik, J. G., Bukowiecki, N., Canonaco, F., Croteau, P. L., Gysel, M., Henne, S., Herrmann, E., Jayne, J. T., Steinbacher, M., Worsnop, D. R., Baltensperger, U., and Prevot, A. S. H.: Fourteen months of on-line measurements of the non-refractory submicron aerosol at the Jungfraujoch (3580 m a.s.l.) - chemical composition, origins and organic aerosol sources, Atmos. Chem. Phys., 15, 11373-11398, 10.5194/acp-15-11373-2015, 2015b.

Fry, J. L., Brown, S. S., Middlebrook, A. M., Edwards, P. M., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Allen, H. M., Ryerson, T. B., Pollack, I., Graus, M., Warneke, C., de Gouw, J. A., Brock, C. A., Gilman, J., Lerner, B. M., Dube, W. P., Liao, J., and Welti, A.: Secondary organic aerosol (SOA) yields from NO3 radical + isoprene based on nighttime aircraft power plant plume transects, Atmos. Chem. Phys., 18, 11663-11682, 10.5194/acp-18-11663-2018, 2018.

Guerrero, F., Alvarez-Ospina, H., Retama, A., Lopez-Medina, A., Castro, T., and Salcedo, D.: Seasonal changes in the PM1 chemical composition north of Mexico City, Atmosfera, 30, 243-258, 10.20937/Atm.2017.30.03.05, 2017.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Gurjar, B. R., Jain, A., Sharma, A., Agarwal, A., Gupta, A., Nagpure, A. S., and Lelieveld, J.: Human health risks in megacities due to air pollution, Atmos. Environ., 44, 4606-4613, doi:10.1016/j.atmosenv.2010.08.011, 2010.

Huang, S., Wu, Z., Poulain, L., van Pinxteren, M., Merkel, M., Assmann, D., Herrmann, H., and Wiedensohler, A.: Source apportionment of the organic aerosol over the Atlantic Ocean from 53° N to 53° S: significant contributions from marine emissions and long-range transport, Atmos. Chem. Phys., 18043-18062, doi.org/10.5194/acp-18-18043, 2018.

Huang, X. F., He, L. Y., Hu, M., Canagaratna, M. R., Sun, Y., Zhang, Q., Zhu, T., Xue, L., Zeng, L. W., Liu, X. G., Zhang, Y. H., Jayne, J. T., Ng, N. L., and Worsnop, D. R.: Highly time-resolved chemical characterization of atmospheric submicron particles during 2008 Beijing Olympic Games using an Aerodyne High-Resolution Aerosol Mass Spectrometer, Atmos. Chem. Phys., 10, 8933-8945, 10.5194/acp-10-8933-2010, 2010.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for size and composition analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

Keck, L., and Wittmaack, K.: Effect of filter type and temperature on volatilisation losses from ammonium salts in aerosol matter, Atmos. Environ., 39, 4093-4100, 10.1016/j.atmosenv.2005.03.029, 2005.

Kiendler-Scharr, A., Mensah, A. A., Friese, E., Topping, D., Nemitz, E., Prevot, A. S. H., Aijala, M., Allan, J., Canonaco, F., Canagaratna, M., Carbone, S., Crippa, M., Dall Osto, M., Day, D. A., De Carlo, P., Di Marco, C. F., Elbern, H., Eriksson, A., Freney, E., Hao, L., Herrmann, H., Hildebrandt, L., Hillamo, R., Jimenez, J. L., Laaksonen, A., McFiggans, G., Mohr, C., O'Dowd, C., Otjes, R., Ovadnevaite, J., Pandis, S. N., Poulain, L., Schlag, P., Sellegri, K., Swietlicki, E., Tiitta, P., Vermeulen, A., Wahner, A., Worsnop, D., and Wu, H. C.: Ubiquity of organic nitrates from nighttime chemistry in the European submicron aerosol, Geophys. Res. Lett., 43, 7735-7744, 2016.

Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., and Pozzer, A.: The contribution of outdoor air pollution sources to premature mortality on a global scale, Nature, 525, 367-371, 2015.

Lide, D. R.: CRC Handbook of Chemistry and Physics, CRC Press Inc., USA, 1991.

Liu, P. S. K., Deng, R., Smith, K. A., Williams, L. R., Jayne, J. T., Canagaratna, M. R., Moore, K., Onasch, T. B., Worsnop, D. R., and Deshler, T.: Transmission efficiency of an aerodynamic focussing lens system: Comparison of model calculations and laboratory measurements for the aerodyne aerosol mass spectrometer, Aerosol Sci. Technol., 41, doi10.1080/02786820701422278, 2007.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Sci. Technol., 46, 258-271, doi:10.1080/02786826.2011.620041, 2012.

Minguillon, M. C., Ripoll, A., Perez, N., Prevot, A. S. H., Canonaco, F., Querol, X., and Alastuey, A.: Chemical characterization of submicron regional background aerosols in the western Mediterranean using an Aerosol Chemical Speciation Monitor, Atmos. Chem. Phys., 15, 6379-6391, 10.5194/acp-15-6379-2015, 2015.

Müller, T., Henzing, J. S., de Leeuw, G., Wiedensohler, A., Alastuey, A., Angelov, H., Bizjak, M., Coen, M. C., Engstrom, J. E., Gruening, C., Hillamo, R., Hoffer, A., Imre, K., Ivanow, P., Jennings, G., Sun, J. Y., Kalivitis, N., Karlsson, H., Komppula, M., Laj, P., Li, S. M., Lunder, C., Marinoni, A., dos Santos, S. M., Moerman, M., Nowak, A., Ogren, J. A., Petzold, A., Pichon, J. M., Rodriquez, S., Sharma, S., Sheridan, P. J., Teinila, K., Tuch, T., Viana, M., Virkkula, A., Weingartner, E., Wilhelm, R., and Wang, Y. Q.: Characterization and intercomparison of aerosol absorption photometers: result of two intercomparison workshops, Atmos. Meas. Tech., 4, 245-268, 10.5194/amt-4-245-2011, 2011.

Ng, N. L., Herndon, S. C., Trimborn, A., Canagaratna, M. R., Croteau, P. L., Onasch, T. B., Sueper, D., Worsnop, D. R., Zhang, Q., Sun, Y. L., and Jayne, J. T.: An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, Aerosol Sci. Technol., 45, 780-794, doi 10.1080/02786826.2011.560211, 2011.

Ortega, A. M., Hayes, P. L., Peng, Z., Palm, B. B., Hu, W. W., Day, D. A., Li, R., Cubison, M. J., Brune, W. H., Graus, M., Warneke, C., Gilman, J. B., Kuster, W. C., de Gouw, J., Gutierrez-Montes, C., and Jimenez, J. L.: Real-time measurements of secondary organic aerosol formation and aging from ambient air in an oxidation flow reactor in the Los Angeles area, Atmos. Chem. Phys., 16, 7411-7433, 2016.

Ostro, B., Feng, W. Y., Broadwin, R., Green, S., and Lipsett, M.: The effects of components of fine particulate air pollution on mortality in California: Results from CALFINE, Environ. Health Perspect., 115, 13-19, doi:10.1289/Ehp.9281, 2007.

Ovadnevaite, J., Ceburnis, D., Leinert, S., Dall'Osto, M., Canagaratna, M., O'Doherty, S., Berresheim, H., and O'Dowd, C.: Submicron NE Atlantic marine aerosol chemical composition and abundance: Seasonal trends and air mass categorization, Journal of Geophysical Research-Atmospheres, 119, 11850-11863, 10.1002/2013jd021330, 2014.

Park, K., Kittelson, D. B., Zachariah, M. R., and McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates, J. Nanopart. Res., 6, 267-272, doi:10.1023/B:NANO.0000034657.71309.e6, 2004.

Parworth, C., Fast, J., Mei, F., Shippert, T., Sivaraman, C., Tilp, A., Watson, T., and Zhang, Q.: Long-term measurements of submicrometer aerosol chemistry at the Southern Great Plains (SGP) using an Aerosol Chemical Speciation Monitor (ACSM), Atmos. Environ., 106, 43-55, 10.1016/j.atmosenv.2015.01.060, 2015.

Petit, J. E., Favez, O., Sciare, J., Crenn, V., Sarda-Esteve, R., Bonnaire, N., Mocnik, G., Dupont, J. C., Haeffelin, M., and Leoz-Garziandia, E.: Two years of near real-time chemical composition of submicron aerosols in the region of Paris using an Aerosol Chemical Speciation Monitor (ACSM) and a multi-wavelength Aethalometer, Atmos. Chem. Phys., 15, 2985-3005, 10.5194/acp-15-2985-2015, 2015.

Petit, J. E., Favez, O., Albinet, A., and Canonaco, F.: A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind and trajectory analyses, Environ. Modell. Softw., 88, 183-187, 10.1016/j.envsoft.2016.11.022, 2017.

Petzold, A., and Schönlinner, M.: Multi-angle absorption photometry - a new method for the measurement of aerosol light absorption and atmospheric black carbon, J. Aerosol Sci., 35, 421-441, doi: 10.1016/j.jaerosci.2003.09.005, 2004.

Pfeifer, S., Muller, T., Weinhold, K., Zikova, N., dos Santos, S. M., Marinoni, A., Bischof, O. F., Kykal, C., Ries, L., Meinhardt, F., Aalto, P., Mihalopoulos, N., and Wiedensohler, A.: Intercomparison of 15 aerodynamic particle size spectrometers (APS 3321): uncertainties in particle sizing and number size distribution, Atmos. Meas. Tech., 9, 1545-1551, 10.5194/amt-9-1545-2016, 2016.

Pieber, S. M., El Haddad, I., Slowik, J. G., Canagaratna, M. R., Jayne, J. T., Platt, S. M., Bozzetti, C., Daellenbach, K. R., Frohlich, R., Vlachou, A., Klein, F., Dommen, J., Miljevic, B., Jimenez, J. L., Worsnop, D. R., Baltensperger, U., and Prevot, A. S. H.: Inorganic Salt Interference on CO2+ in Aerodyne AMS and ACSM Organic Aerosol Composition Studies, Environ. Sci. Technol., 50, 10494-10503, 10.1021/acs.est.6b01035, 2016.

Pio, C. A., and Lopes, D. A.: Chlorine loss from marine aerosol in a coastal atmosphere, Journal of Geophysical Research-Atmospheres, 103, 25263-25272, Doi 10.1029/98jd02088, 1998.

Poulain, L., Iinuma, Y., Müller, K., Birmili, W., Weinhold, K., Bruggemann, E., Gnauk, T., Hausmann, A., Löschau, G., Wiedensohler, A., and Herrmann, H.: Diurnal variations of ambient particulate wood burning emissions and their contribution to the concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in Seiffen, Germany, Atmos. Chem. Phys., 11, 12697-12713, doi: 10.5194/acp-11-12697-2011, 2011a.

Poulain, L., Spindler, G., Birmili, W., Plass-Dülmer, C., Wiedensohler, A., and Herrmann, H.: Seasonal and diurnal variations of particulate nitrate and organic matter at the IfT research station Melpitz, Atmos. Chem. Phys., 11, 12579-12599, doi:10.5194/acp-11-12579-2011, 2011b.

Poulain, L., Birmili, W., Canonaco, F., Crippa, M., Wu, Z. J., Nordmann, S., Spindler, G., Prevot, A. S. H., Wiedensohler, A., and Herrmann, H.: Chemical mass balance of 300 degrees C non-volatile particles at the tropospheric research site Melpitz, Germany, Atmos. Chem. Phys., 14, 10145-10162, doi:10.5194/acp-14-10145-2014, 2014.

Ripoll, A., Minguillon, M. C., Pey, J., Jimenez, J. L., Day, D. A., Sosedova, Y., Canonaco, F., Prevot, A. S. H., Querol, X., and Alastuey, A.: Long-term real-time chemical characterization of submicron aerosols at Montsec (southern Pyrenees, 1570 m a.s.l.), Atmos. Chem. Phys., 15, 2935-2951, 10.5194/acp-15-2935-2015, 2015.

Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernabe, R. M., Marquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Lesher, R., Shirley, T., and Jimenez, J. L.: 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, doi:10.5194/acp-6-925-2006, 2006.

Schaap, M., Spindler, G., Schulz, M., Acker, K., Maenhaut, W., Berner, A., Wieprecht, W., Streit, N., Muller, K., Bruggemann, E., Chi, X., Putaud, J. P., Hitzenberger, R., Puxbaum, H., Baltensperger, U., and ten Brink, H.: Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL, Atmos. Environ., 38, 6487-6496, 10.1016/j.atmosenv.2004.08.026, 2004.

Schlag, P., Kiendler-Scharr, A., Blom, M. J., Canonaco, F., Henzing, J. S., Moerman, M., Prevot, A. S. H., and Holzinger, R.: Aerosol source apportionment from 1-year measurements at the CESAR tower in Cabauw, the Netherlands, Atmos. Chem. Phys., 16, 8831-8847, 10.5194/acp-16-8831-2016, 2016.

Setyan, A., Zhang, Q., Merkel, M., Knighton, W. B., Sun, Y., Song, C., Shilling, J. E., Onasch, T. B., Herndon, S. C., Worsnop, D. R., Fast, J. D., Zaveri, R. A., Berg, L. K., Wiedensohler, A., Flowers, B. A., Dubey, M. K., and Subramanian, R.: Characterization of submicron particles influenced by mixed biogenic and anthropogenic emissions using high-resolution aerosol mass spectrometry: results from CARES, Atmos. Chem. Phys., 12, 8131-8156, doi:10.5194/acp-12-8131-2012, 2012.

Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., and Herrmann, H.: Size-segregated characterization of PM_{10} at the EMEP site Melpitz (Germany) using a five-stage impactor: a six year study, J. Atmos. Chem., 69, 127-157, doi:10.1007/s10874-012-9233-6, 2012.

Spindler, G., Grüner, A., Müller, K., Schlimper, S., and Herrmann, H.: Long-term size-segregated particle (PM_{10}, $PM_{2.5}$, PM_1) characterization study at Melpitz - influence of air mass inflow, weather conditions and season, J. Atmos. Chem., 70, 165-195, doi:10.1007/s10874-013-9263-8, 2013.

Stieger, B., Spindler, G., Fahlbusch, B., Müller, K., Grüner, A., Poulain, L., Thöni, L., Seitler, E., Wallasch, M., and Herrmann, H.: Measurements of PM_{10} ions and trace gases with the online system MARGA at the research station Melpitz in Germany – A five-year study, J. Atmos. Chem., 10.1007/s10874-017-9361-0, 2017.

Sun, J. Y., Zhang, Q., Canagaratna, M. R., Zhang, Y. M., Ng, N. L., Sun, Y. L., Jayne, J. T., Zhang, X. C., Zhang, X. Y., and Worsnop, D. R.: Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, Atmos. Environ., 44, 131-140, doi:10.1016/j.atmosenv.2009.03.020, 2010.

Sun, Y. L., Zhang, Q., Schwab, J. J., Yang, T., Ng, N. L., and Demerjian, K. L.: Factor analysis of combined organic and inorganic aerosol mass spectra from high resolution aerosol mass spectrometer measurements, Atmos. Chem. Phys., 12, 8537-8551, 10.5194/acp-12-8537-2012, 2012.

Sun, Y. L., Wang, Z. F., Du, W., Zhang, Q., Wang, Q. Q., Fu, P. Q., Pan, X. L., Li, J., Jayne, J., and Worsnop, D. R.: Long-term real-time measurements of aerosol particle composition in Beijing, China: seasonal variations, meteorological effects, and source analysis, Atmos. Chem. Phys., 15, 10149-10165, 10.5194/acp-15-10149-2015, 2015.

Takegawa, N., Miyakawa, T., Watanabe, M., Kondo, Y., Miyazaki, Y., Han, S., Zhao, Y., van Pinxteren, D., Bruggemann, E., Gnauk, T., Herrmann, H., Xiao, R., Deng, Z., Hu, M., Zhu, T., and Zhang, Y.: Performance of an Aerodyne Aerosol Mass Spectrometer (AMS) during Intensive Campaigns in China in the Summer of 2006, Aerosol Sci. Technol., 43, 189-204, doi:10.1080/02786820802582251, 2009.

Tuch, T. M., Haudek, A., Müller, T., Nowak, A., Wex, H., and Wiedensohler, A.: Design and performance of an automatic regenerating adsorption aerosol dryer for continuous operation at monitoring sites, Atmos. Meas. Tech., 2, 417-422, doi:10.5194/amt-2-417-2009, 2009.

Turpin, B. J., and Lim, H.-J.: Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Sci. Technol., 35, 302-610, doi:10.1080/02786820119445, 2001.

Wang, Q. Q., Sun, Y. L., Jiang, Q., Du, W., Sun, C. Z., Fu, P. Q., and Wang, Z. F.: Chemical composition of aerosol particles and light extinction apportionment before and during the heating season in Beijing, China, Journal of Geophysical Research-Atmospheres, 120, 12708-12722, 10.1002/2015jd023871, 2015.

Wehner, B., Philippin, S., and Wiedensohler, A.: Design and calibration of a thermodenuder with an improved heating unit to measure the size-dependent volatile fraction of aerosol particles, J. Aerosol Sci., 33, 1087-1093, 2002.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjaraa, A. M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J. A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Huglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Gruning, C., Faloon, K., Beddows, D., Harrison, R. M., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H. G., Keck, L., Jiang, J., Scheckman, J., McMurry, P. H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Loschau, G., and Bastian, S.: Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions, Atmos. Meas. Tech., 5, 657-685, doi 10.5194/amt-5-657-2012, 2012.

Wiedensohler, A., Wiesner, A., Weinhold, K., Birmili, W., Hermann, M., Merkel, M., Muller, T., Pfeifer, S., Schmidt, A., Tuch, T., Velarde, F., Quincey, P., Seeger, S., and Nowak, A.: Mobility particle size spectrometers: Calibration procedures and measurement uncertainties, Aerosol Sci. Technol., 52, 146-164, 10.1080/02786826.2017.1387229, 2018.

WMO/GAW: Aerosol Measurement Procedures, Guidelines and Recommendation, 2016.

Xu, L., Guo, H. Y., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S. H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences of the United States of America, 112, 37-42, 10.1073/pnas.1417609112, 2015.

Xu, W., Croteau, P., Williams, L., Canagaratna, M., Onasch, T., Cross, E., Zhang, X., Robinson, W., Worsnop, D., and Jayne, J.: Laboratory characterization of an aerosol chemical speciation monitor with $PM_{2.5}$ measurement capability, Aerosol Sci. Technol., 51, 69-83, 10.1080/02786826.2016.1241859, 2017.

Xu, W., Lambe, A., Silva, P., Hu, W. W., Onasch, T., Williams, L., Croteau, P., Zhang, X., Renbaum-Wolff, L., Fortner, E., Jimenez, J. L., Jayne, J., Worsnop, D., and Canagaratna, M.: Laboratory evaluation of species-dependent relative ionization efficiencies in the Aerodyne Aerosol Mass Spectrometer, Aerosol Sci. Technol., 52, 626-641, 10.1080/02786826.2018.1439570, 2018.

Zanatta, M., Gysel, M., Bukowiecki, N., Muller, T., Weingartner, E., Areskoug, H., Fiebig, M., Yttri, K. E., Mihalopoulos, N., Kouvarakis, G., Beddows, D., Harrison, R. M., Cavalli, F., Putaud, J. P., Spindler, G., Wiedensohler, A., Alastuey, A., Pandolfi, M., Sellegri, K., Swietlicki, E., Jaffrezo, J. L., Baltensperger, U., and Laj, P.: A European aerosol phenomenology-

5: Climatology of black carbon optical properties at 9 regional background sites across Europe, Atmos. Environ., 145, 346-364, 2016.

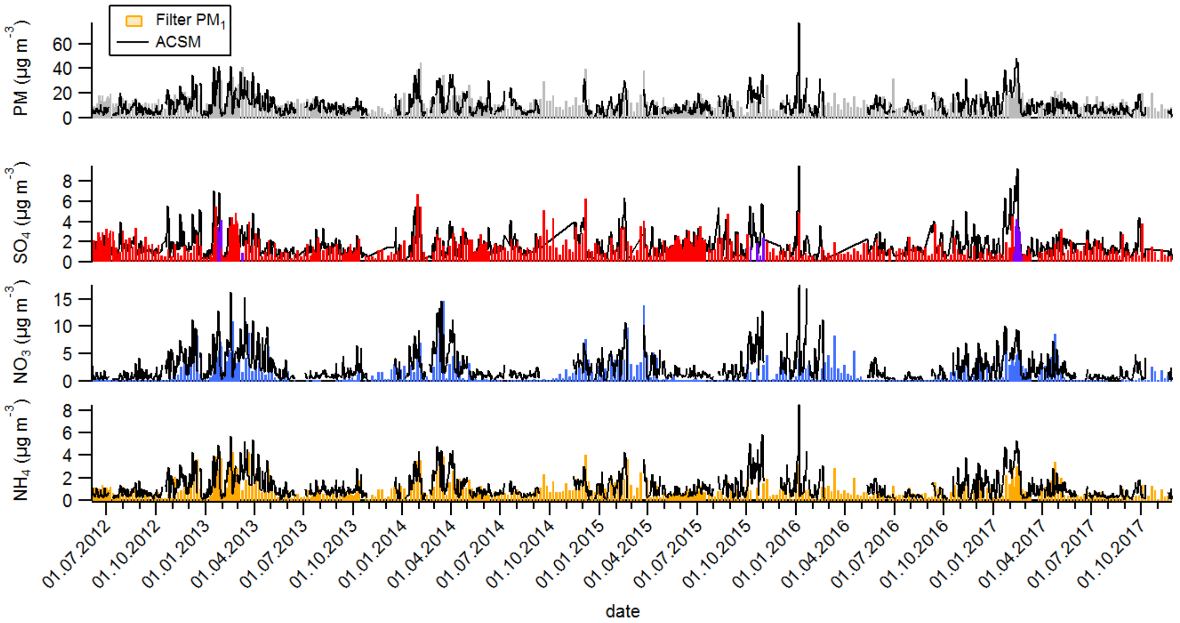


Figure 1: Time series ACSM (daily averaged, black line) and 24 h PM$_1$ filter samples (colored bars) for the total particle mass concentration, the mass concentration of sulfate, nitrate, and ammonium. The particulate matter (PM) corresponds with the sum of ACSM species and eBC$_{PM1}$ for the on-line instrument and the PM$_1$ filter mass for the off-line samples.

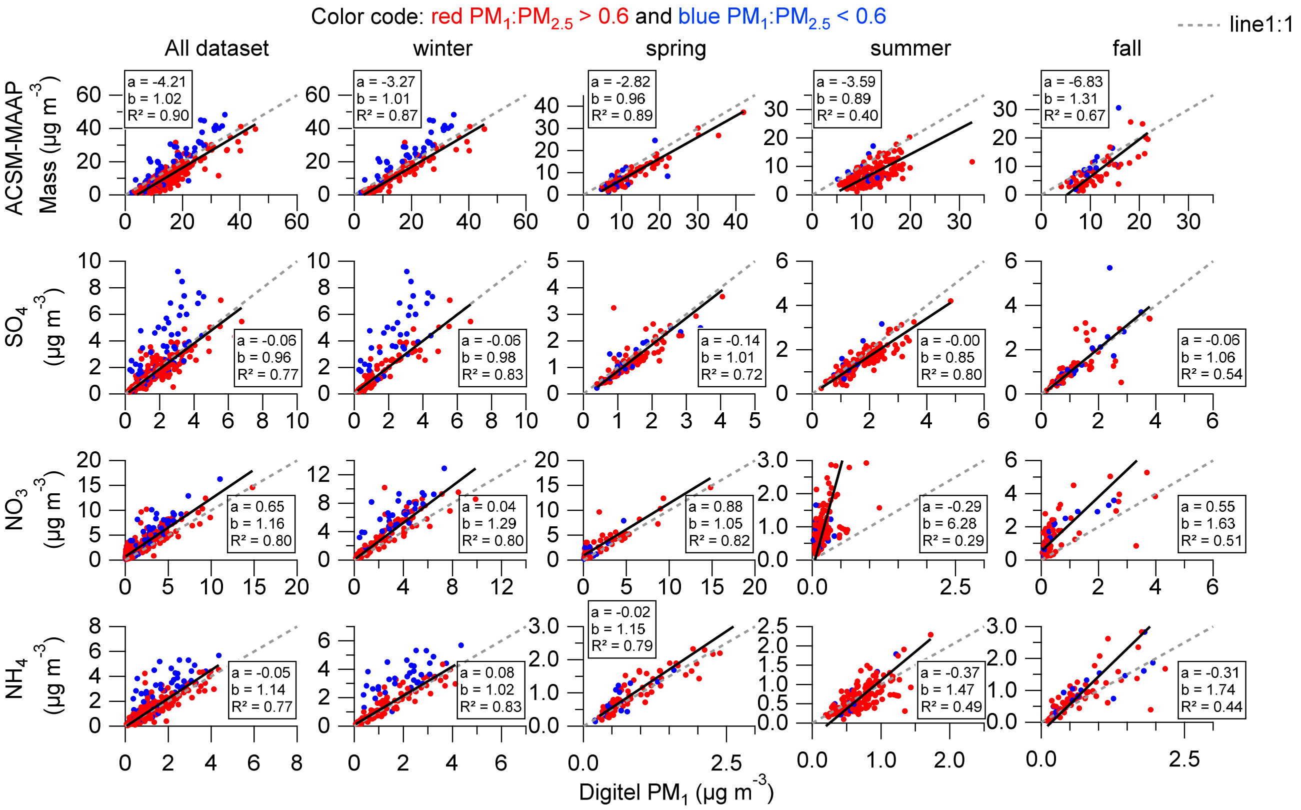


Figure 2: Seasonal variability of the comparison between on-line and off-line PM$_1$ aerosol measurements. The color coding indicates whether the ratio PM$_1$:PM$_{2.5}$ total mass concentration is above (red) or below (blue) the selected threshold value of 0.6 (see discussion in section3.1.1.). Dotted grey lines show the line 1:1 and ~~full~~ solid black lines represent regression fit by least orthogonal distance fit (y = a + bx). Please note the different axis ranges for the same species.

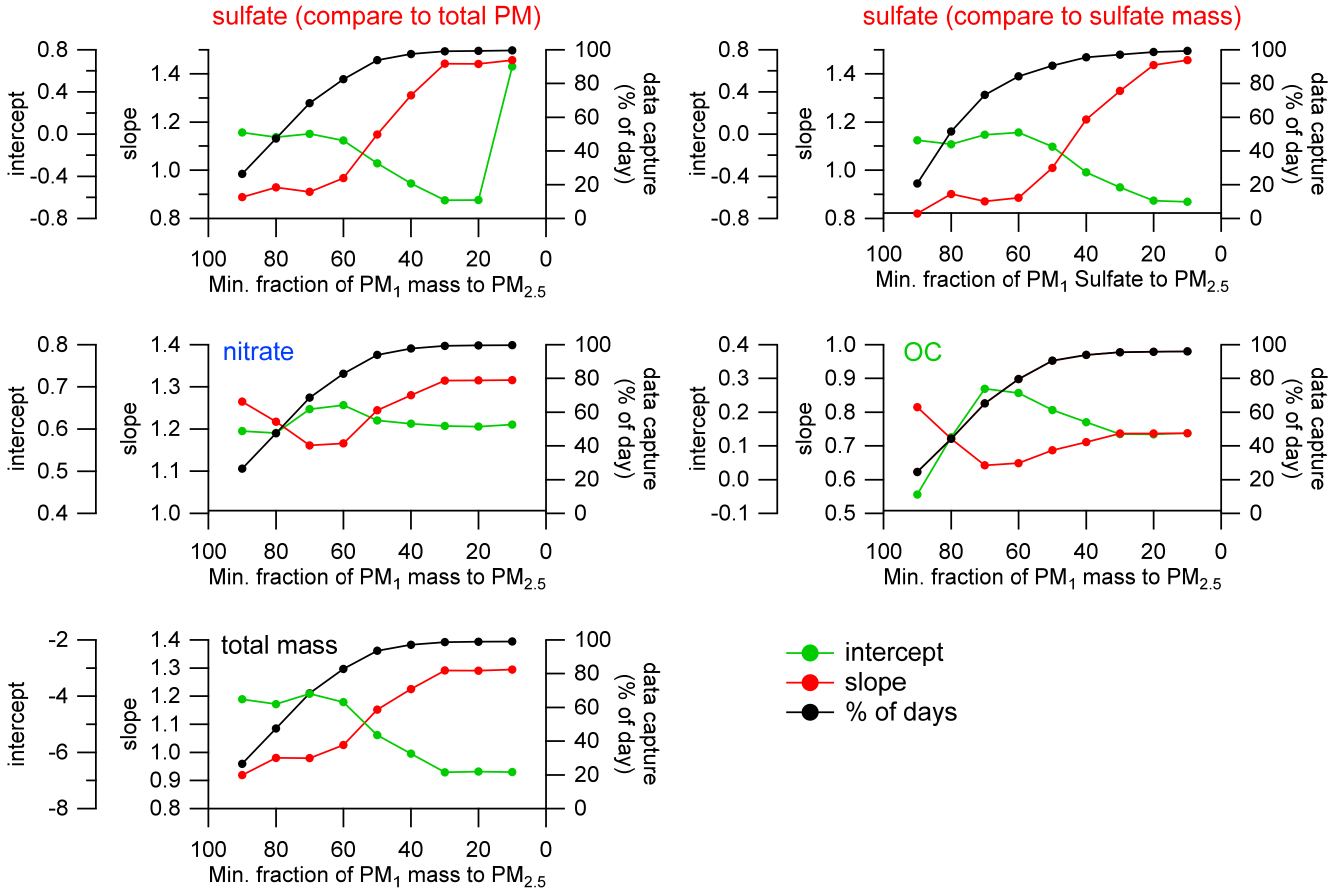


Figure 3: Sensitivity analysis of the correlation between ACSM and PM$_1$ sulfate, nitrate, OC, and total mass concentration depending on the PM$_1$:PM$_{2.5}$ ratio of the total mass concentration in the range 90 – 10 %. The influence of sulfate distribution on PM$_1$ and PM$_{2.5}$ was also investigated (top left).

5

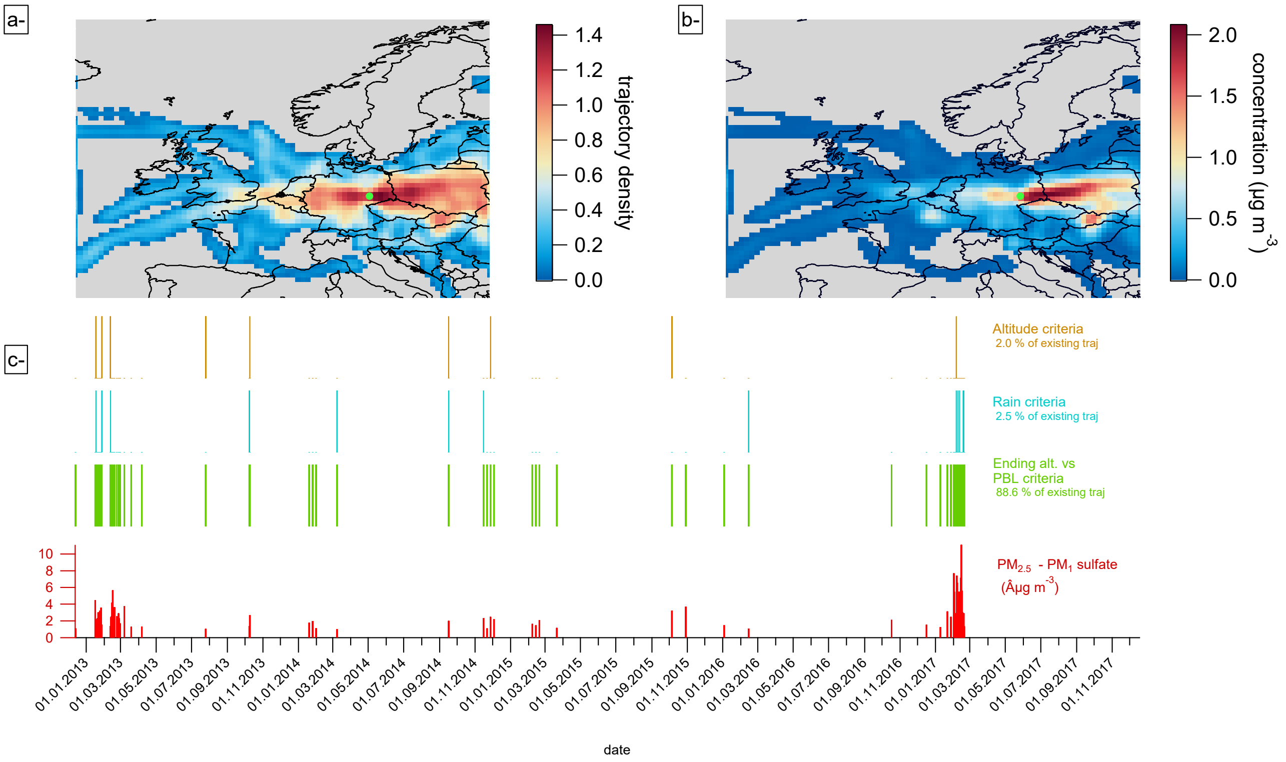


Figure 4: Trajectory analysis for days where sulfate concentration difference between PM$_{2.5}$ and PM$_1$ exceeded 1 µg m^{-3}: (a) overpassing trajectory density; (b) results of the potential source contribution function (PSCF) analysis; (c) time series of sulfate mass concentration difference, trajectory altitude above 2000 m, precipitation events exceeding 1 mm h^{-1} and PBL above the station < 500 m.

~~**Trajectory analysis for days that have a different PM$_{2.5}$ – PM$_1$ sulfate mass concentration above 1 µg m^{-3}. a- Trajectory density, b- potential source maps (PSCF). The panel c- shows the time series of the considered sulfate mass concentration (bottom) and the colored bars show the days when the trajectories did not pass the different trajectory cut-off options: Altitude above 2000 m (top brown), rain > 1 mm h^{-1}(middle blue) and PBL above the station < 500 m (bottom green).**~~

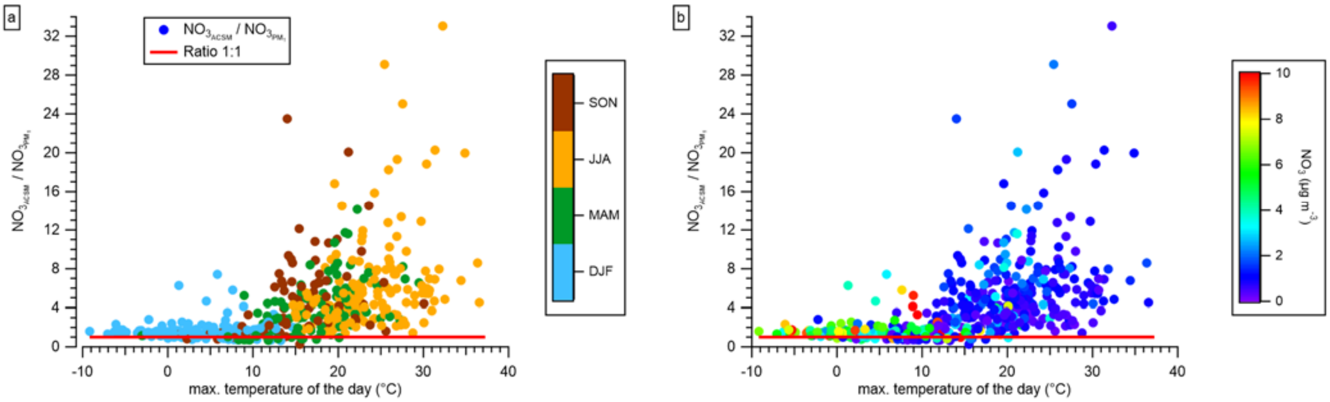
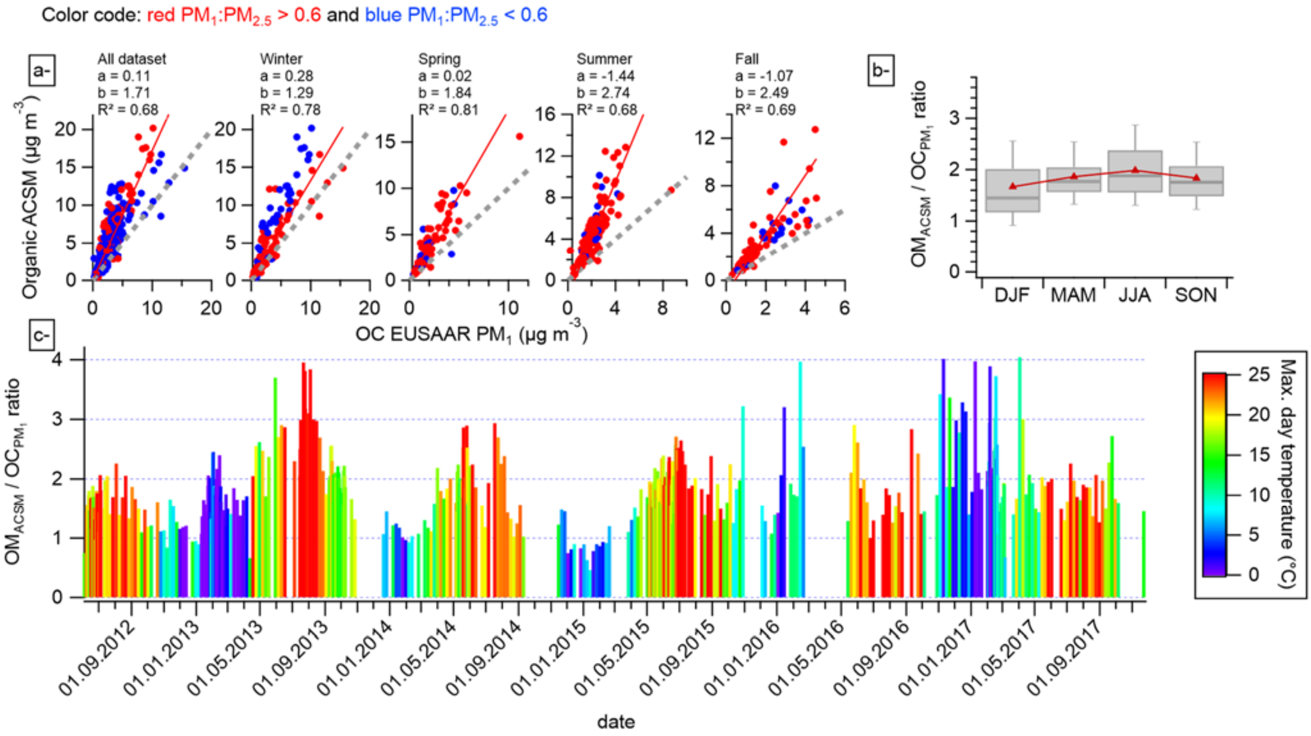


Figure 5: ACSM:PM₁ ratio nitrate mass concentration compared to the maximum temperature of the corresponding sampling day. The color code corresponds to the different seasons (a) and the total nitrate mass concentration of the ACSM (b).



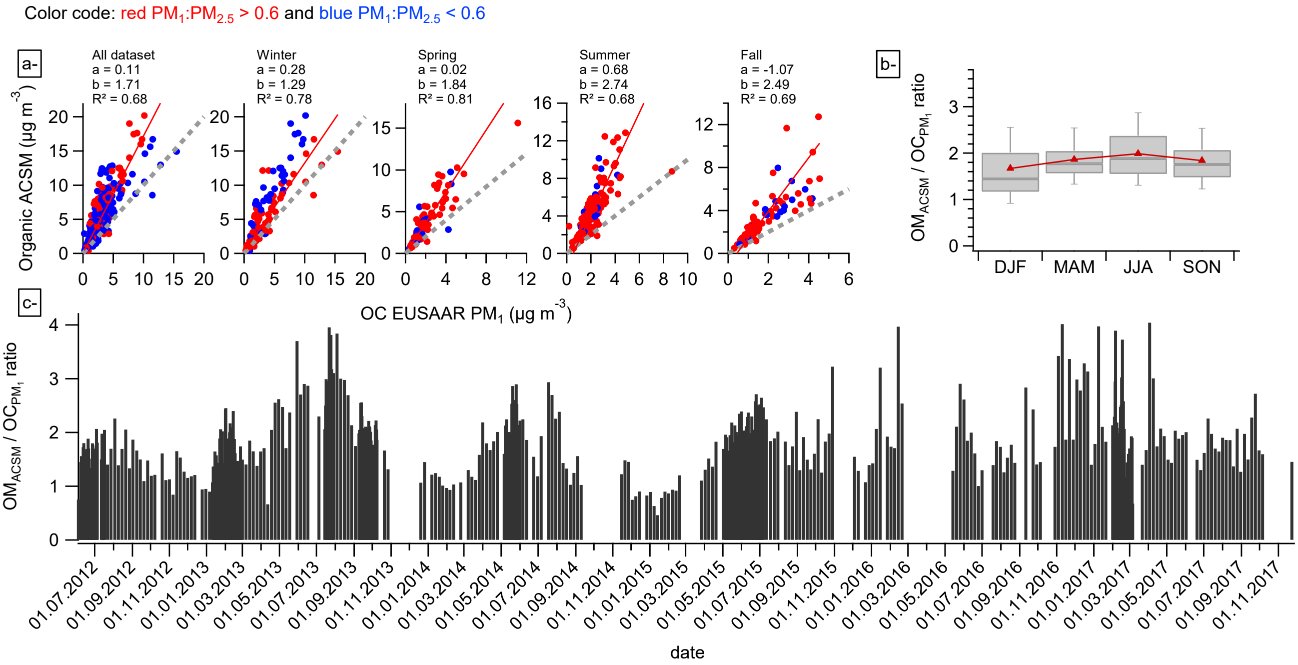


Figure 6: Correlation between ACSM organic mass concentrations and offline OC PM$_1$ (a); seasonal variability of the estimated OM$_{ACSM}$:OC$_{PM1}$ ratio (b), and the entire time series colored by maximum daily temperature (c).

~~Correlation between ACSM organic mass concentrations and off-line OC PM$_1$ (a), seasonal variability of the estimated OM$_{ACSM}$:OC$_{PM1}$ ratio (b), and the entire time series~~

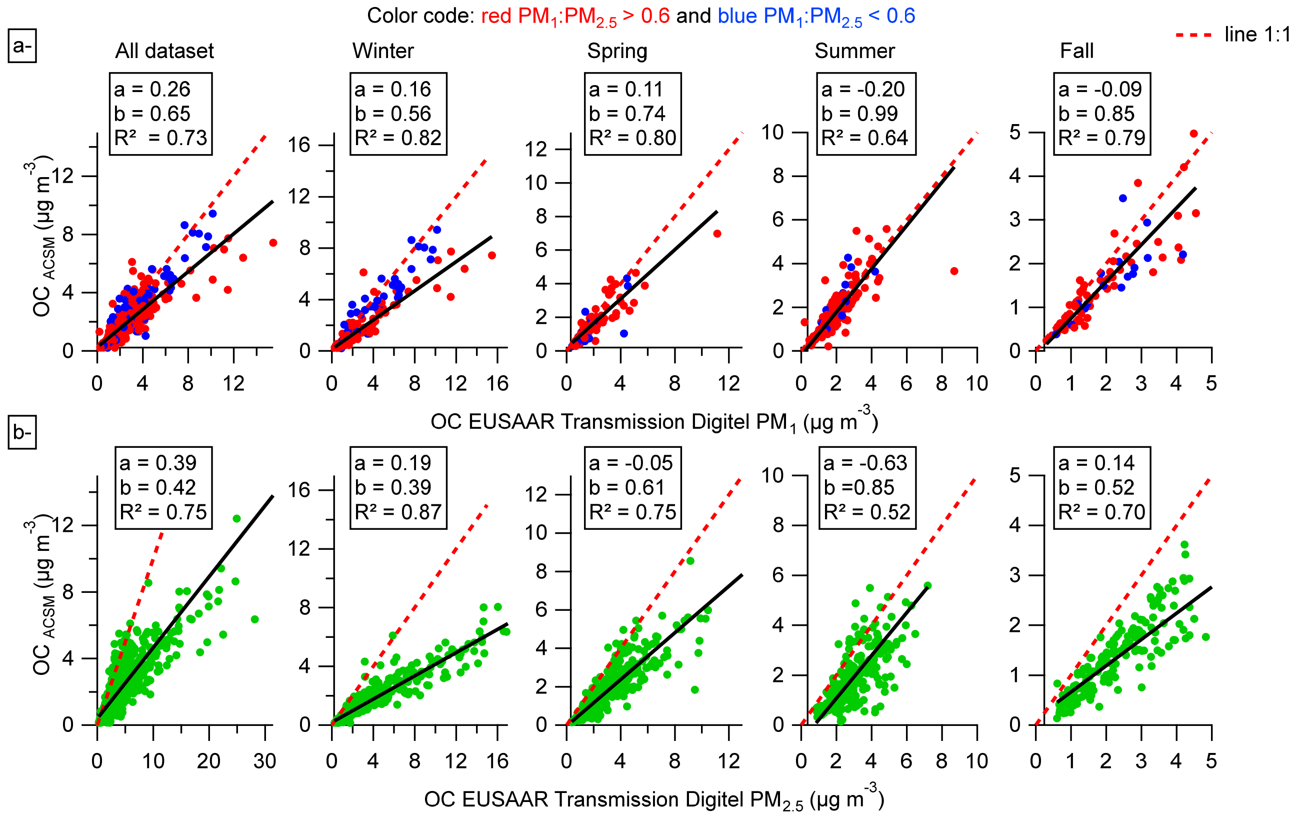
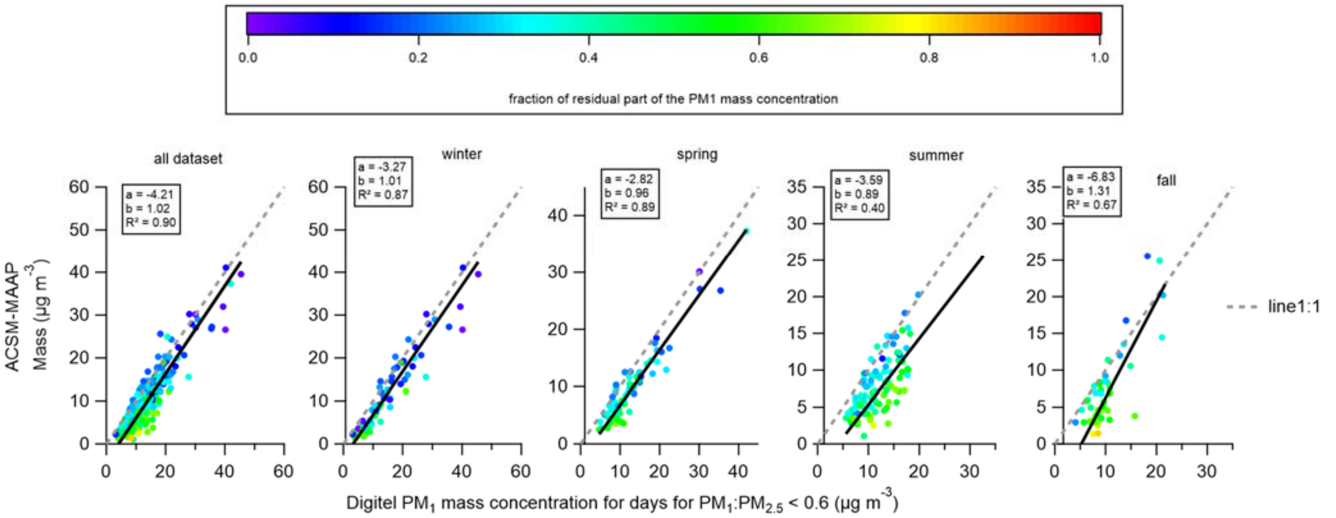


Figure 7: Correlations between the estimated OC_{ACSM} and the offline OC mass concentration over the entire period and seasonality for PM_1 (a), and $PM_{2.5}$ (b). Black lines show the least orthogonal linear fit and the red dotted lines the 1:1 line.

~~Correlations between the estimated OC_{ACSM} mass concentrations and the off-line PM_1 (a) and $PM_{2.5}$ (b) EUSAAR transmission OC mass concentration for the entire period and the different seasons. Black lines show the least orthogonal linear fit and the red dotted lines the line1:1.~~



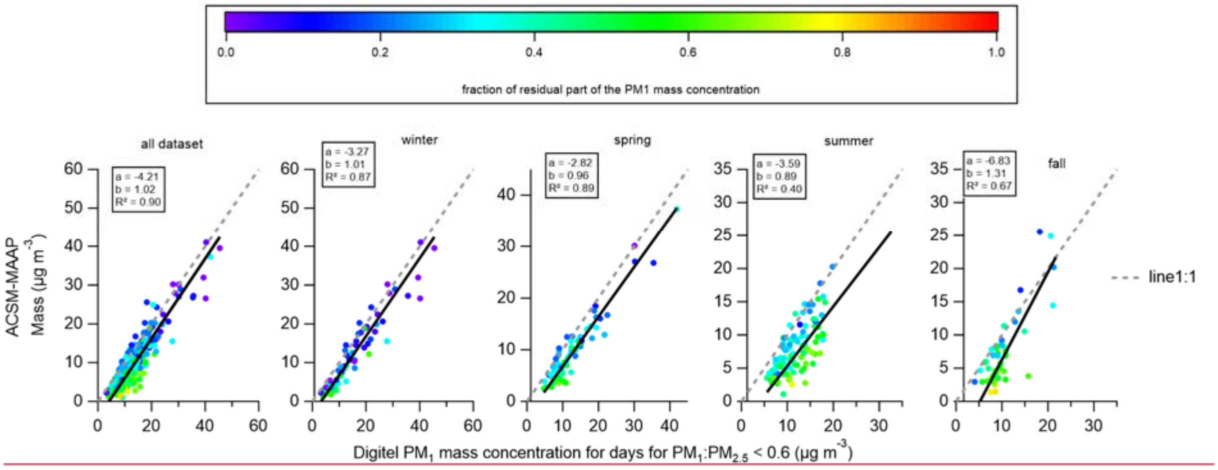
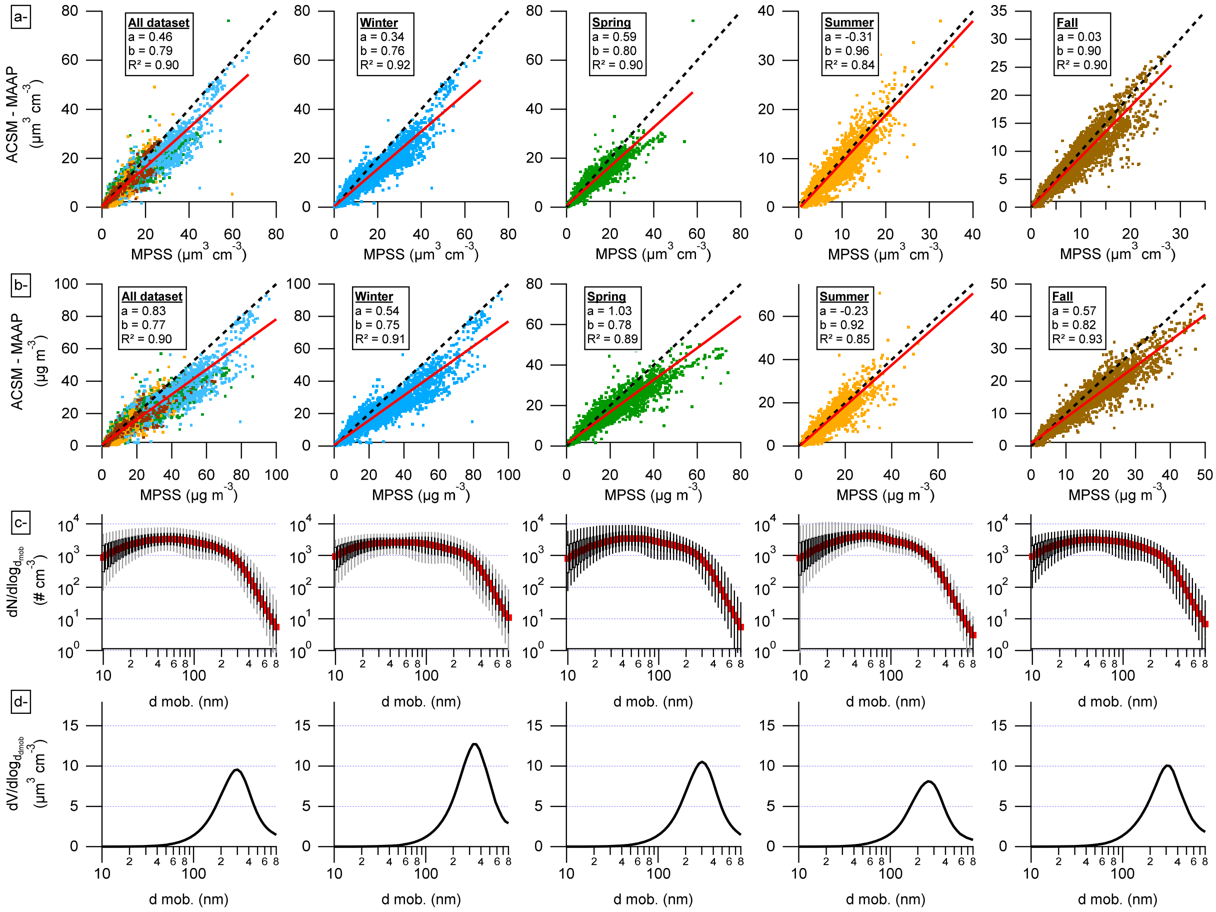


Figure 8: Influence of the residual mass fraction on the PM1 filter to the mass closure with online ACSM-MAAP-derived mass concentration.


a-
ACSM - MAAP ($\mu m^3 cm^{-3}$)
All dataset
a = 0.46
b = 0.79
R² = 0.90
Winter
a = 0.34
b = 0.76
R² = 0.92
Spring
a = 0.59
b = 0.80
R² = 0.90
Summer
a = -0.31
b = 0.96
R² = 0.84
Fall
a = 0.03
b = 0.90
R² = 0.90
MPSS ($\mu m^3 cm^{-3}$)
b-
ACSM - MAAP ($\mu g m^{-3}$)
All dataset
a = 0.83
b = 0.77
R² = 0.90
Winter
a = 0.54
b = 0.75
R² = 0.91
Spring
a = 1.03
b = 0.78
R² = 0.89
Summer
a = -0.23
b = 0.92
R² = 0.85
Fall
a = 0.57
b = 0.82
R² = 0.93
MPSS ($\mu g m^{-3}$)
c-
$dN/dlog_{d_{mob}}$ (# cm^{-3})
10^0
10^1
10^2
10^3
10^4
d mob. (nm)
d-
$dV/dlog_{d_{mob}}$ ($\mu m^3 cm^{-3}$)
0
5
10
15
10
100
d mob. (nm)

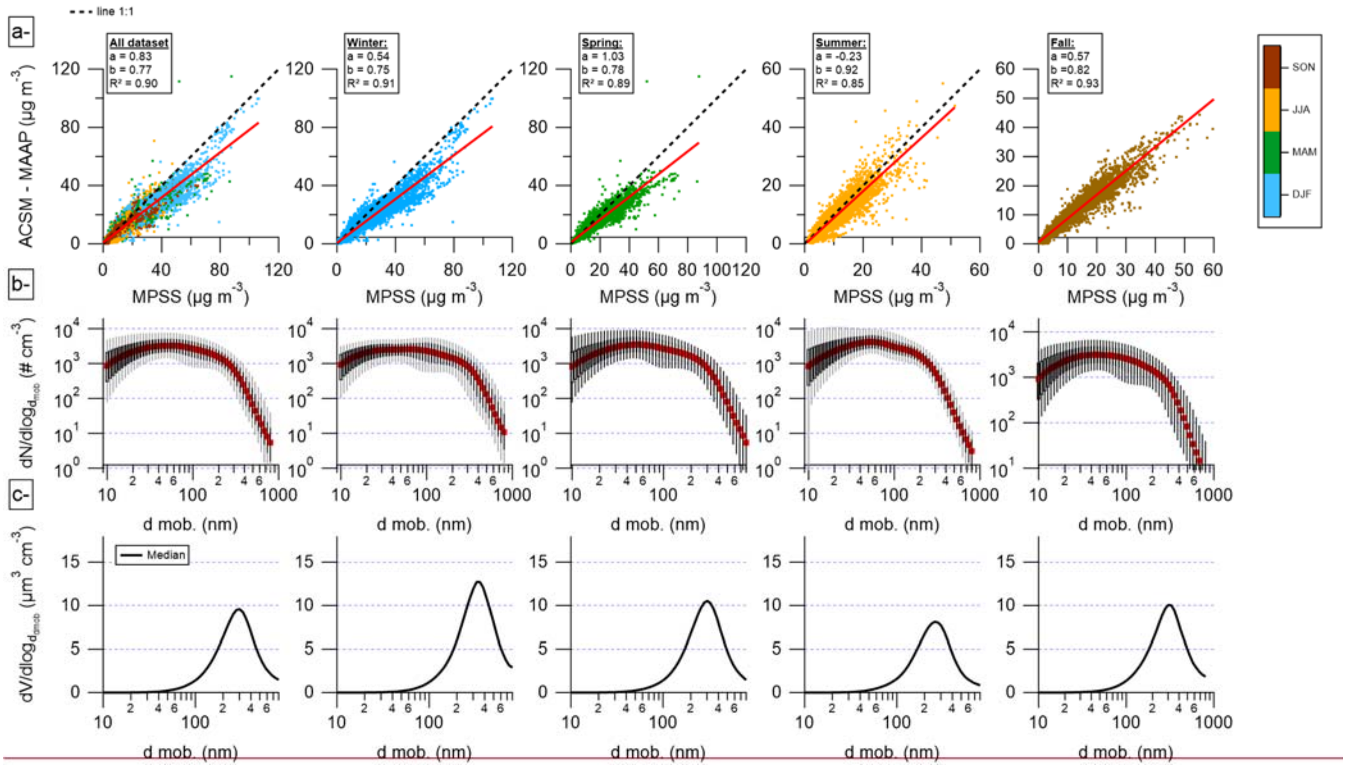


Figure 9: Comparison between measured ACSM-MAAP and MPSS for the entire period and seasonal variability: volume-closure (a), mass-closure (b), median number size distribution (red) with 10-90 (grey line) and 25-75 (black boxes) percentiles (c), median volume size distribution (d). The linear regressions (red lines) were calculated using the least orthogonal distance fit method.

~~**-derived mass concentrations and the MPSS-derived mass concentrations for the entire period and the different seasons (a), median number size distribution (red) with 10-90 (grey lines9 and 25-75 (black boxes) percentiles, (c) median volume size distribution. Red lines represents regression fit by least orthogonal distance fit.**~~

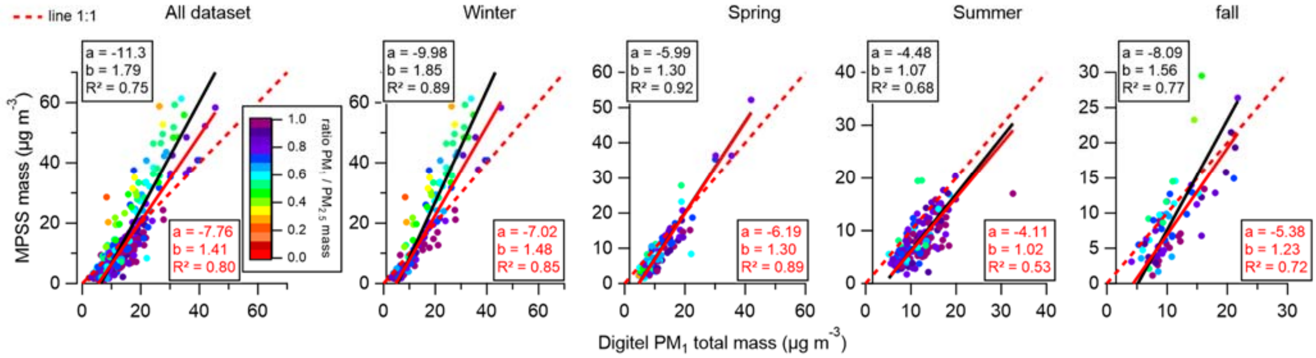


Figure 10: Comparison between filter PM$_1$ total mass concentrations and the MPSS-derived mass concentrations for the entire period (left) and the different seasons. The black lines and boxes correspond to the regression fitting without threshold correction and the red lines to the regression fitting according to a PM$_1$:PM$_{2.5}$ > 0.6.

Supplementary Information

Multi-Year ACSM measurements at the Central European Research Station Melpitz (Germany) part I: Instrument Robustness, Quality Assurance, and Impact of Upper Size Cut-Off Diameter

Laurent Poulain[1], Gerald Spindler[1], Achim Grüner[1], Thomas Tuch[1], Bastian Stieger[1], Dominik van Pinxteren, Jean-Eudes Petit[2,3], Olivier Favez[4,3], Hartmut Herrmann[1], and Alfred Wiedensohler[1]
~~L. Poulain[1], G. Spindler[1], A. Grüner[1], T. Tuch[1], B. Stieger[1], D. van Pinxteren, H. Herrmann[1], and A. Wiedensohler[1]~~

[1] Leibniz Institute for Tropospheric Research (TROPOS), Permoserstr. 15, 04317 Leipzig, Germany
[2] Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS-UVSQ, IPSL, Université Paris-Saclay, 91191 Gif-sur-Yvette, France
[3] Aerosol Chemical Monitor Calibration Centre (ACMCC), Batiment 701 CEA Orme des Merisiers, 91191 Gif-sur-Yvette Cedex, France
[4] Institut national de l'environnement industriel et des risques (INERIS), Parc Technol Alata, BP2, F-60550 Verneuil En Halatte, France

Correspondence to: L. Poulain (poulain@tropos.de)

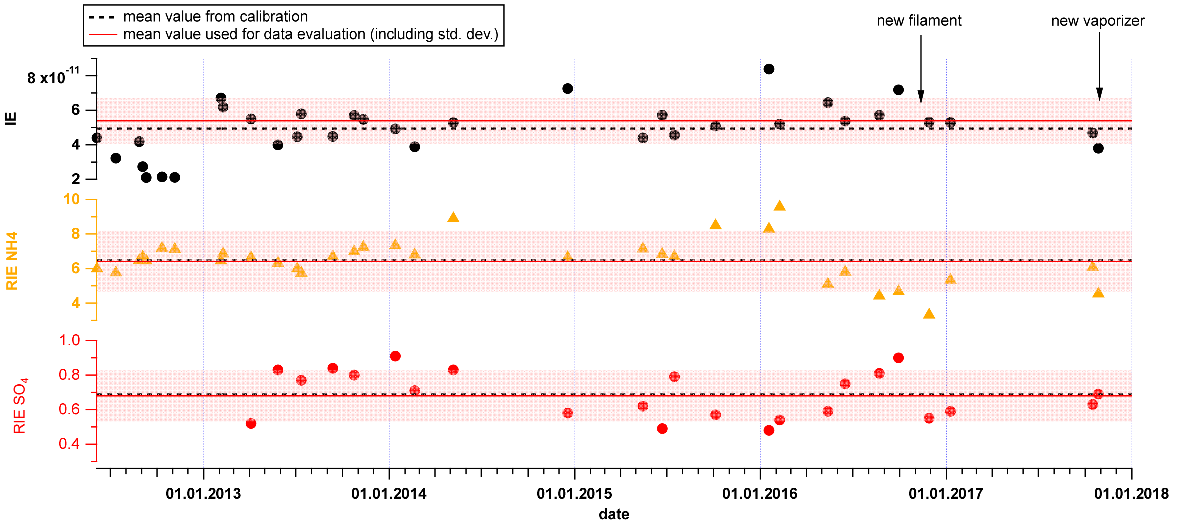


Figure SI-1: Time variation of the IE and RIE for ammonium and sulfate. The single points correspond to calibration, the dashed black line to the mean value from the calibration, and the full red line the mean value from the data analysis (shaded area corresponds to the standard deviation). Major maintenance (change of filament and vaporizer) are including.

Table SI-1: Fitting parameters of the comparison of the mass concentrations measured by the ACSM and offline PM$_1$ considering the identified threshold PM$_1$:PM$_{2.5}$ < 0.6 or the entire PM$_1$ dataset.

		PM$_1$ (threshold PM$_1$:PM$_{2.5}$ < 0.6)			PM$_1$ no threshold		
species	Time period	Slope	Intercept	R^2	Slope	Intercept	R^2
Total mass	All dataset	1.02	-4.21	0.90	1.29	-6.64	0.72
	Winter	1.01	-3.27	0.87	1.3	-5.44	0.77
	Spring	0.96	-2.82	0.89	0.97	-2.85	0.83
	Summer	0.89	-3.59	0.40	0.9	-3.54	0.35
	Fall	1.31	-6.83	0.67	1.55	-8.79	0.58
Sulfate	All dataset	0.96	-0.06	0.77	1.45	-0.63	0.59
	Winter	0.98	-0.06	0.83	1.57	-0.43	0.61
	Spring	1.01	-0.14	0.72	0.98	-0.08	0.74
	Summer	0.85	0.00	0.80	0.87	-0.01	0.77
	Fall	1.06	-0.06	0.54	1.25	-0.29	0.58
Nitrate	All dataset	1.16	0.65	0.80	1.32	0.6	0.79
	Winter	1.29	0.04	0.80	1.49	-0.06	0.74
	Spring	1.05	0.88	0.82	1.09	0.85	0.81
	Summer	6.28	-0.29	0.29	6.47	-0.35	0.27
	Fall	1.63	0.55	0.51	1.9	0.39	0.56
Ammonium	All dataset	1.14	-0.05	0.77	1.40	-0.21	0.71
	Winter	1.02	0.08	0.83	1.36	-0.09	0.65
	Spring	1.15	-0.02	0.79	1.15	-0.01	0.80
	Summer	1.47	-0.37	0.49	1.53	-0.39	0.51
	Fall	1.74	-0.31	0.44	2.01	-0.49	0.46
Organic (OM$_{ACSM}$)	All dataset	1.71	0.11	0.68	1.85	-0.1	0.74
	Winter	1.29	0.28	0.78	1.70	-0.29	0.76
	Spring	1.84	0.02	0.81	1.89	-0.1	0.79
	Summer	2.74	-1.44	0.68	2.83	-1.58	0.66
	Fall	2.49	-1.07	0.69	2.41	-1.06	0.67

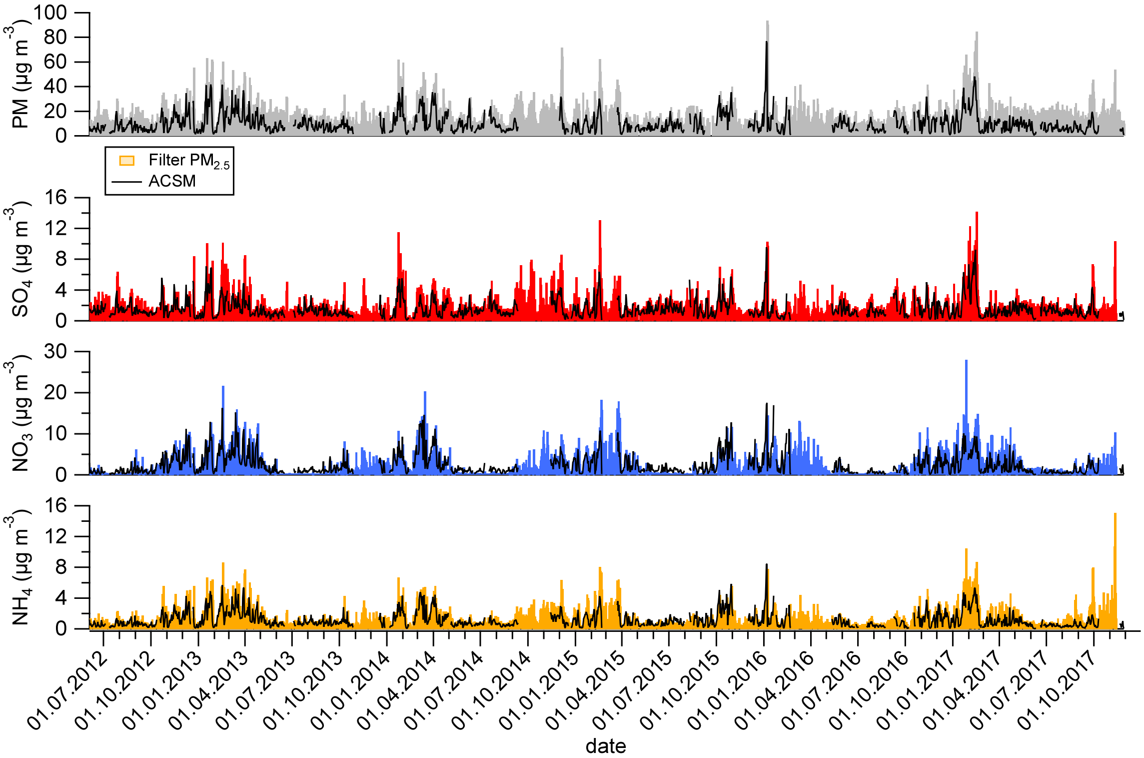


Figure SI-~~1~~2: Time series ACSM (daily average, black line) and daily 24 h PM$_{2.5}$ filter samples (colored bars) for the total mass, sulfate, nitrate, and ammonium. The particulate matter (PM) corresponds to the sum of ACSM species and eBC$_{PM1}$ for the on-line instrument and the filter mass for the off-line samples.

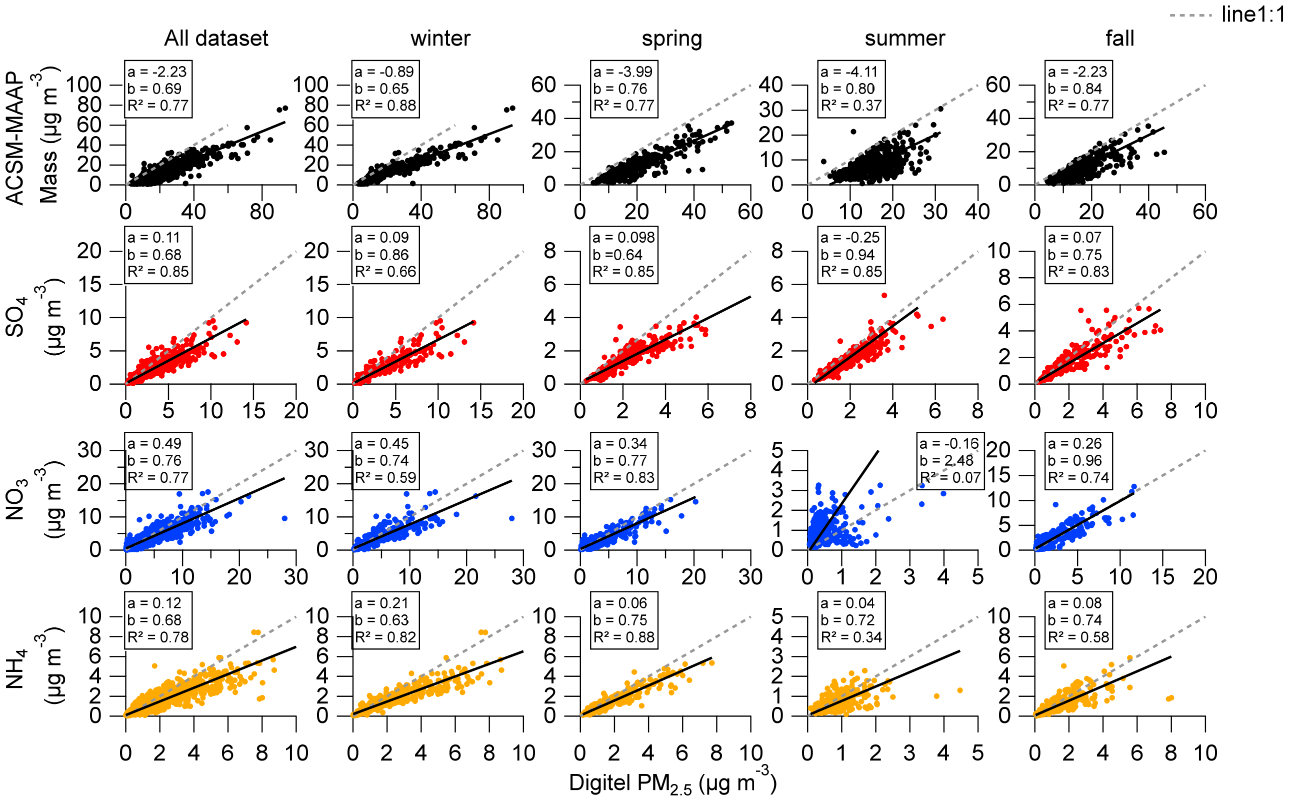


Figure SI-~~2~~3: Scatter plot of the ACSM species mass concentration measurements compared to corresponding daily $PM_{2.5}$ mass concentration over the entire period and seasonality.

~~Scatter plot of the ACSM mass concentration measurements compared to daily mass in $PM_{2.5}$.~~

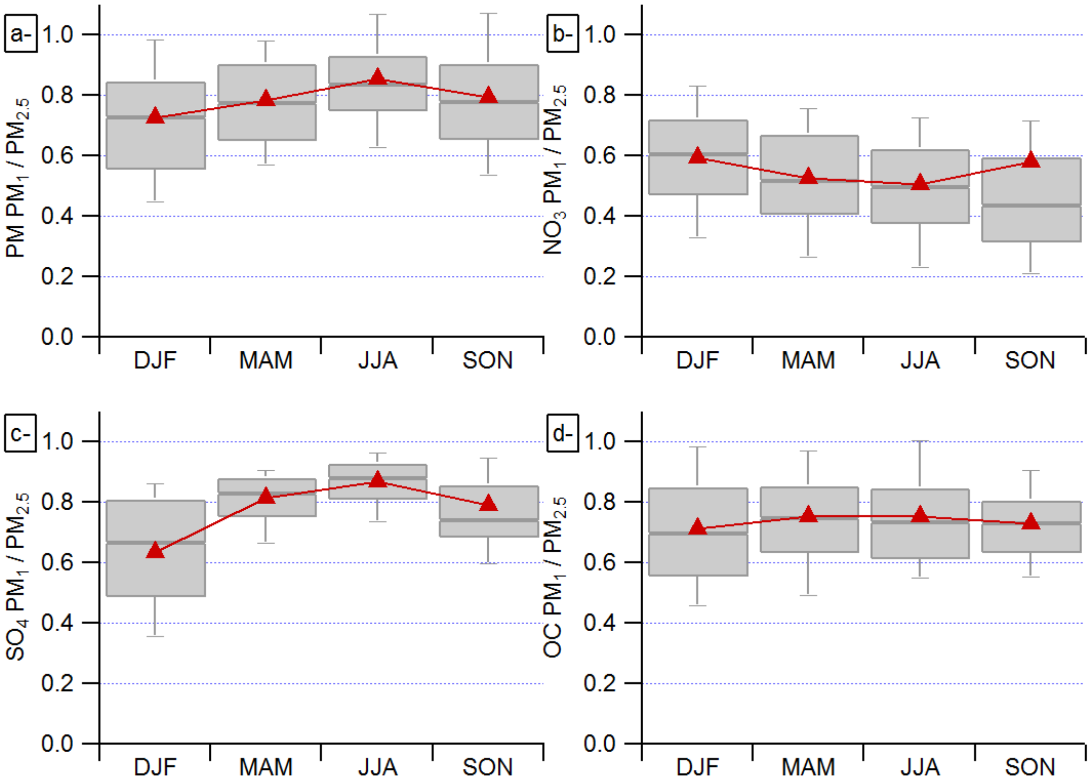


Figure SI-~~3~~4: Seasonal variability of the PM$_1$:PM$_{2.5}$ ratios of total PM (a), nitrate (b), sulfate (c) and OC (d).

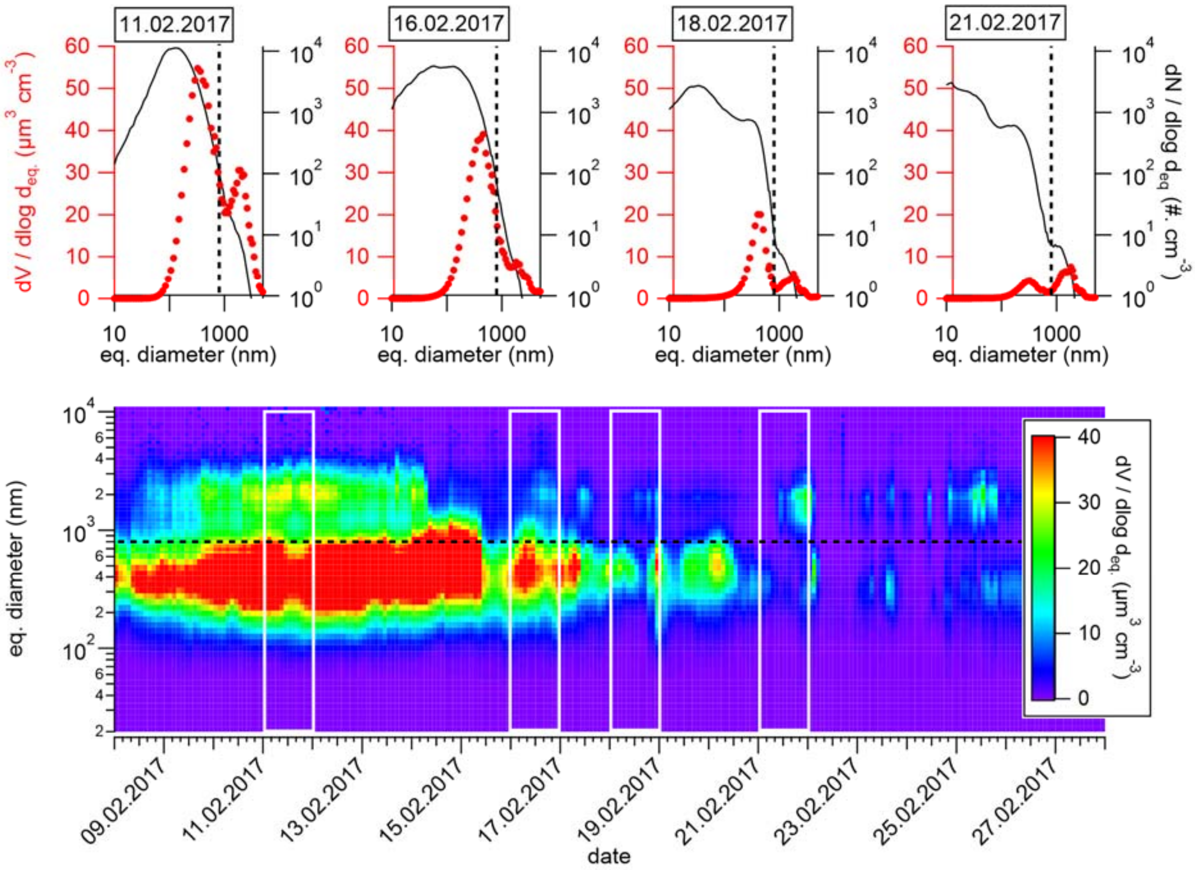


Figure SI-45: Influence of coarse mode particles on particle number and volume size distribution in the range 10 to 5000 nm obtained by merging MPSS and APSS (assuming spherical particle and a constant density of 1.6). The top panels represent the daily median particle number (black full line) and volume (red dots) size distribution for selected days emphasized by the white box on the particle volume size distribution from February 2017. The dashed black lines on the plots indicate the upper size bin of the MPSS.

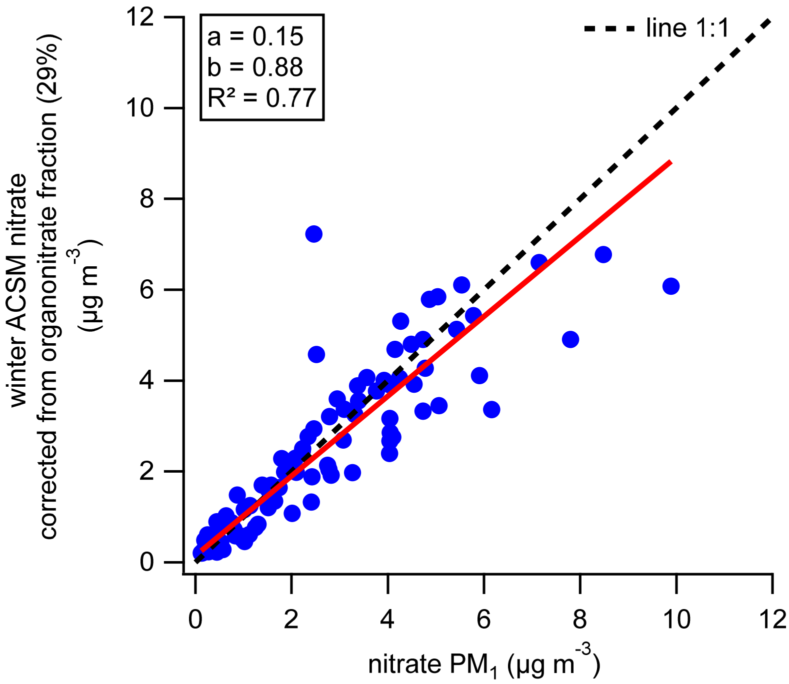


Figure SI-~~5~~6: Scatter plot of the winter (DJF) ACSM nitrate mass concentration corrected for organo-nitrate contribution during days with a $PM_1:PM_{2.5} < 0.6$ compared to PM_1 nitrate mass concentration. The linear regressions (red lines) were calculated using the least orthogonal distance fit method.

~~Scatter plot of the winter (DJF) ACSM nitrate mass concentration corrected from organo-nitrate contribution compared to off-line PM_1 filter samples for days with a $PM_1:PM_{2.5} < 0.6$.~~

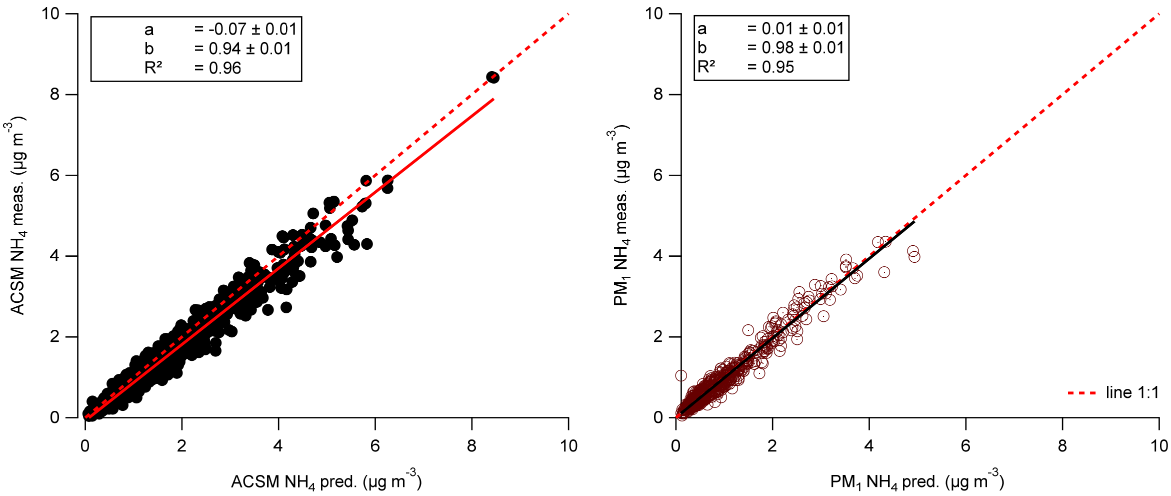


Figure SI-7: Comparison of the measured ammonium with the predicted ammonium mass concentration for the ACSM (left) and offline PM_1 samples assuming a full neutralization by nitrate, sulfate, and chloride. The linear regressions were calculated using the least orthogonal distance fit method (y = a x + b).

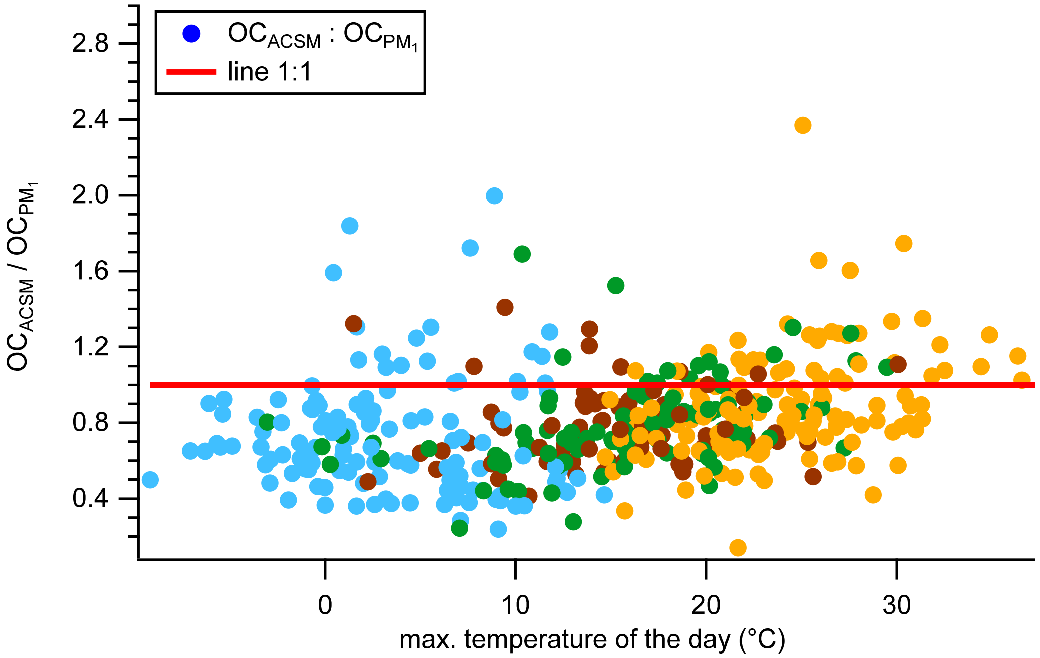
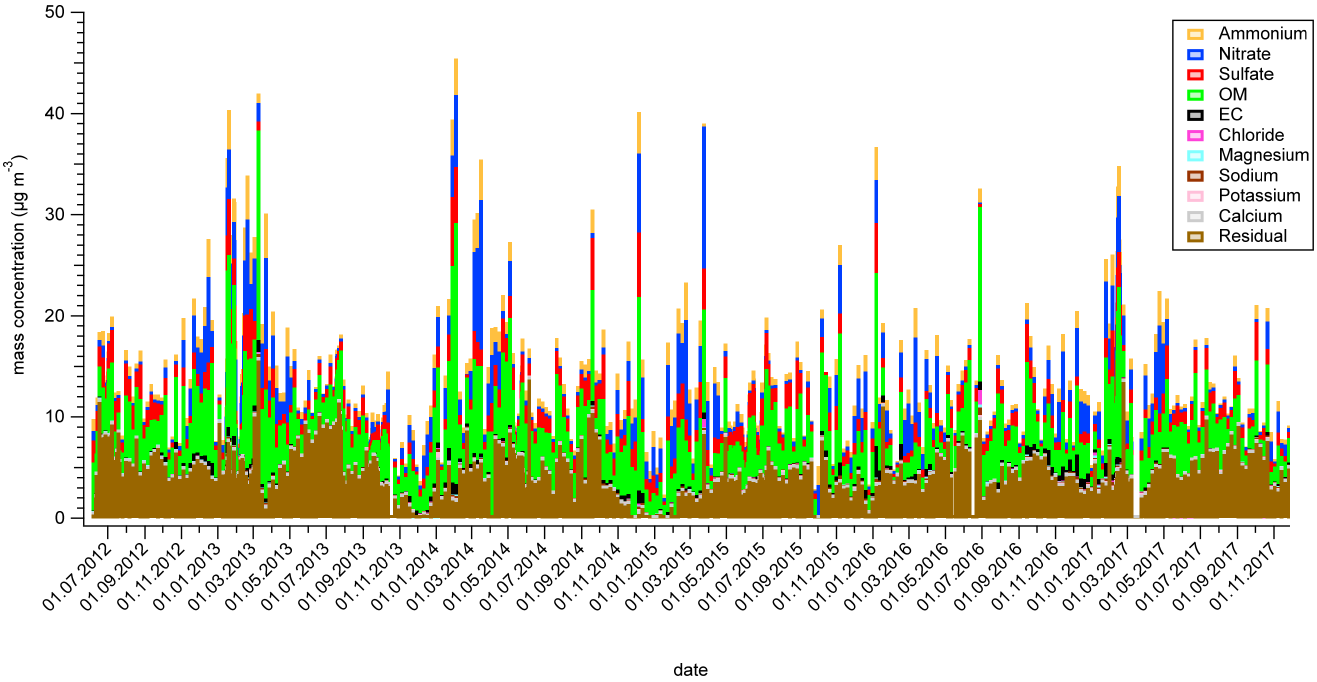


Figure SI-~~6~~8: influence of the maximum day temperature to the OC_{ACSM}:OC_{PM1} ratio.



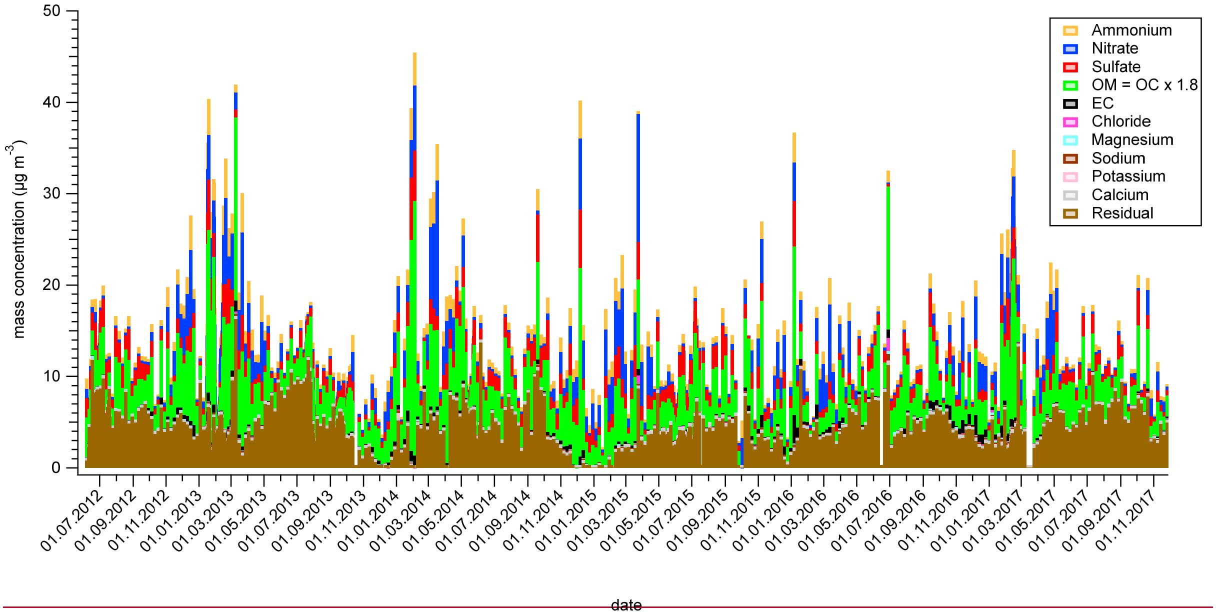


Figure SI-~~7~~9: **Time series of the Digitel PM$_1$ chemical composition.** Conversion of OC into OM was made based on the seasonal OM:OC ratio presented in Figure 6.