6th Mars 2022

Object – Answers to the Reviewers for the paper: "Substantial organic impurities at the surface of synthetic ammonium sulfate particles", Ref. amt-2021-327

Dear Editor, dear Reviewers,

We would like to thank the Editorial Board for considering our paper "Substantial organic impurities at the surface of synthetic ammonium sulfate particles" for publication in AMT. We would also like to thank the reviewers for the constructive comments, suggestions and corrections in English writing which clearly help us to improve this article. We have carefully studied the comments, and the original paper has been revised accordingly. In particular, as suggested by the reviewers, more arguments have been added in the introduction to highlight the case of why the amount of organic impurities on AS aerosol particles is so important. We have also completed some details of the experiments to illustrate the thoroughness of the results.

With our best regards,

Dr. Junteng Wu on behalf of all authors

Notice on the answers: 1. Bold text were written by the authors to answer each question.

2. Concerning the modifications, "bold text in red" was removed and "bold text in blue" was added in the revised paper.

Answers to anonymous Referee #1.

Overview.

The authors present a very thorough investigation of the amount and chemical composition of organic impurities on aerosol particles produced from commercially available ammonium sulphate (AS). Atomised AS particles are probably the most used calibration and test particles in aerosol particle measurements. In many applications, organic impurities can bias the calibration results and thus the interpretation of measurements. Hence, this article is highly relevant for the community and should be published in AMT after some minor revisions which are mostly related to the presentation of the work.

Main comments

1) The authors build a very good case of why the amount of organic impurities is so important, e.g., for using AS in calibrations of instruments for hygroscopicity related measurements (HTDMA, CCN-Counter). It will strengthen this paper if they could give an estimation of how much such calibrations could be affected (i.e., be biased) if the used AS has the observed amount of impurities. The calibration of the true super saturation (SS) in a CCN-Counter or the RH in an HTDMA could serve as such an example. So, how much could the SS or RH be "wrong" if the user assumes 100% AS, but in reality, there is 1-4% organic with an average hygroscopicity parameter of, e.g., k=0.1? Such an estimation would be very helpful since it seems impossible to reduce the organic impurity content below 1- 2 % even with the purest AS sample and the purest water.

Answer: This is a very interesting question. To answer it, we have performed some simple calculations using the κ-Köhler equation (Petters and Kreidenweis, 2007), (SI11), and some additional experiments to measure the potential amount of surface-active organic species in the impurities (SI12). We have added the following 2 paragraphs in the section "conclusions and implications" (line 397):

"**From this suggestion, the potential effects of organic impurities on CCN activation of AS aerosols were investigated, to determine the error made on the critical supersaturation if one assumes 100% AS, omitting the presence of organic impurities. This estimation was performed with a simple calculation using the κ-Köhler equation (Petters and Kreidenweis, 2007), see SI11 for details. For the estimation of the critical supersaturation in the presence of organic impurities, two extreme hypotheses were explored. In hypothesis 1, the organic fraction was considered soluble and non-surface-active, whereas in hypothesis 2, it was considered extremely surface-active, using the most powerful surfactant as a proxy. Following each of these hypotheses, the supersaturation was calculated along the droplet activation of an AS particle of 130 nm with and without organic impurities (Figure SI11). The results show that whereas the critical supersaturation of AS aerosols is not significantly impacted by the presence of organic impurities under hypothesis 1, it is highly impacted under hypothesis 2, with a potential error of more than 70%.**

In view of these extreme results, and especially the very important error observed for surface-active compounds, the potential quantity of surface-active species contained in AS solutions (Across 99.5 % diluted in Milli-Q water) was investigated (SI12). The results showed that AS solutions contain extremely low amounts of cationic and non-ionic surfactants and an upper limit of [Org surfactant]/[Sulfate] mass ratio of 1×10^{-5} % was determined. Although this ratio is five orders of

magnitude lower than the total organic fraction detected in AS particles, the potential effect of these surfactants on the surface tension of 130 nm diameter AS particles was investigated. For such particles, the obtained [Org surfactant]/[Sulfate] mass ratio induces a concentration of 6×10^{-7} mol.L^{-1} of surfactants. At this very low concentration, even the most surface-active molecules show a surface tension similar to that of pure water as shown by surface tension isotherms (Ekström et al., 2010; Frossard et al., 2019; Arabadzhieva et al. 2020). It was thus concluded that the CCN activity of AS particles with d_m = 130 nm should not be significantly affected by the presence of the organic impurities. However, caution should be taken to keep their amounts as low as possible."

2) Is it possible to quantify the amount of organic mass in the LC-MS measurements? If so, are the relative fraction of organic impurities ([Org]/[SO4]) comparable to the one determined with AMS? Not every aerosol particle measurement group has access to an AMS to check for the amount of impurities of the AS they use. But it may be possible to send out samples for a LC-MS analysis to an external lab.

Answer: Unfortunately, it is not possible to quantify the amount of organics with LC-MS. The instrument comprises electrospray ionization (ESI) which efficiency highly depends on the structure of each molecule. For calibration, we need standards of the molecules, but as the formal identification could not be done, quantification was impossible by LC-MS. Another option for the measurement of organic impurities is a thermo-optical analysis to quantify the organic carbon (OC) and elemental carbon (EC) levels in synthetic AS particles collected on quartz fiber filters. For the specific measurement of surface-active compounds, a simple method has been developed by (Nozière et al. 2017) as described in the new paragraph added in the conclusion of the manuscript and in the answer to the first question.

3) It is known in the AMS community that inorganic salts like AS or ammonium nitrate can trigger a CO2+ signal (m/z 44) due to reactions on the vaporiser of the AMS instrument ("Pieber effect", Pieber et al. (2016)). This artefact is highly instrument specific and is strongly related to the measurement history of the AMS in question. Although it is mostly relevant for NO3- salts, it can occur for AS as well. Are the authors aware of this effect and have they checked if some of the observed CO2+ signal could be affected by this? It would be good to acknowledge the existence of this effect and point out that the observed organic signals in this study have a different source (i.e., the salt itself).

Answer: Thanks very much to the reviewer for this suggestion. Indeed, the "Pieber effect" was not taken into account in the paper. Pieber et al. (2016) shows a large effect on ammonium nitrate particles, i.e., +3.4 % relative to nitrate. However, the effect on the ammonium sulfate particles is 3-10 times lower. In our study, the CO_2^+ signal represented 20±5 % of the total organic signal. Thus, if all the CO_2^+ fragments came from the interference signal of sulfate, the maximum Pieber effect in this work would be 0.76 % relative to sulfate. It was thus not taken into account. This was added to the new version of the manuscript

Minor and language related comments

1) line 11&16: "from 200 nm to 500 nm": Please indicate which size is used here – aerodynamic or electromobility. As this paper is directed at different parts of the aerosol particle measuring community, you cannot be sure, what the reader will assume here.
Answer: it is aerodynamic here.
Modification: line 11 "from 200 nm to 500 nm" was replaced by **"200 nm to 500 nm aerodynamic diameter"**

2) line 18: The authors have to be more precise when they use the term "density". To my knowledge, the default definition is density = mass/volume. But here, the context suggests that the "surface density" is meant (mass/surface). The authors have to be clearer when they refer to density and when surface density is meant. See also later comment.

Answer: Yes, we agree with the reviewer, surface density was applied in the revised paper.

Modifications: line 18 "on the AS particle surface with a density" was replaced by **"on the AS particle with a surface density"**

line 259 "density" was replaced by **"surface density"**

3) line 37: "it is well acknowledged…": this phrase sounds odd to me. I suggest replacing it with "it is well established…" or "it is well known…"

Answer: Done

Modification: line 37 "it is well acknowledged" was replaced by **"it is well established"**

4) line 42ff: The water solubility of (di)carboxylic acids quickly decreases with carbon chain length towards very low solubility. Succinic acid (C4) is still somewhat soluble in water (58 g/L), but adipic acid (C6) is already barely soluble at room temperature (15 g/L). κ values derived from their HGF values are in the range of <0.006 (Petters and Kreidenweis, 2007 and therein). Please, specify that the authors are referring to small/short carbon chain (di)carboxylic acids in this sentence.

Answer: Done.

Modification: line 42 **"Firstly, for water soluble organic compounds such as (di)carboxylic acids, their effects on AS aerosols are represented by their hygroscopicity and mass fraction suggested by the ZSR assumption"** was replaced by **"Firstly, for water soluble organic compounds such as short carbon chain (di)carboxylic acids, their effects on AS aerosols are represented by their hygroscopicity and mass fraction suggested by the ZSR assumption"**

5) lines 47ff: This sentence over-simplifies the case of organic-inorganic mixtures. It is not simply the incomplete dissolution of the organic fraction that causes non-linear behaviour. Below the deliquescence point of AS, only small amounts of water are present in the particles due to the low hygroscopicity of the organic fraction. Consequently, the formed solution will be very concentrated and thus very much non-ideal. But the assumption of (dilute) ideal solution is used for most of the calculations around predicting hygroscopic growth behaviour (e.g. when calculating κ from HGF values).

Answer: Done.

Modification: line 47 **"Specifically, at RH below the deliquescence point, AS seeded SOA do not follow the ZSR predictions due to the incomplete dissolution."** was replaced by **"Specifically, at RH below the deliquescence point, AS seeded SOA do not follow the ZSR predictions because the solution is highly concentrated and thus non-ideal".**

6) line 52ff: "Thirdly, several studies…" The sentence structure is difficult to follow. The double listing (marine organic compounds and ozonolysis products, a-pinene and monoterpene) is confusing. Is it the products of the reaction of O3 with a-pinene & monoterpenes? Or the products of ozonolysis of a-pinene and the products of ozonolysis of monoterpenes? Also, it should be plural and not singular for monoterpenes.

Answer: Done.

Modification: line 52 **"Thirdly, several studies have observed that marine organics under low concentration and ozonolysis products of α-pinene and monoterpene affect AS's hygroscopicity by lowering the surface tension, thus enhancing their CCN activity (Engelhart et al., 2008; King et al., 2009; Moore et al., 2008; Wex et al., 2009)."** was replaced by **"Thirdly, it was found that organic compounds could affect the hygroscopicity of AS by lowering the surface tension, such as marine organic compounds at low concentrations (Moore et al., 2008), or ozonolysis products of monoterpenes (King et al., 2009; Wex et al., 2009; Engelhart et al., 2008)."**

7) line 52: "marine organics under low concentration". First, it should be "organic compounds" not "organics". Second, it is "at low concentration" not "under".

Answer: Done. Please see question 6)

8) line 53: "AS's hygroscopicity" the "s" genitive form (possessive form) is usually not used for non-living things. Use "the hygroscopicity of AS" instead.

Answer: Done. Please see question 6)

9) lines 52ff: Again, the authors oversimplify a rather complex matter. The conclusion that the presence of small amounts of moderately surface-active organic compounds results in a strong depression of the surface tension of the droplet is based on the interpretation of a specific modelling approach (Ovadnevaite et al., 2017). A recent comparison study for this and other thermodynamic models (Vepsäläinen et al., 2021) showed that the inferred behaviour of the surface tension of a droplet strongly depends on the selected modelling approach (e.g., if the surface tension could vary with droplet growth or how the surface-to-bulk partitioning was handled). I recommend that the authors add a sentence at the end of this paragraph, pointing out that organic compounds can have a very complex impact on the hygroscopic growth and CCN activity of aerosol particles which may go beyond the simple reduction of the value of a single parameter in the Köhler equation.

Answer: We have added 2 sentences in line 59: "More recently, several models have shown that the inferred behavior of the surface tension strongly depends on the selected modelling approach (Prisle et al., 2021; Vepsäläinen et al., 2022). In conclusion, organic compounds can have a very complex impact on the hygroscopic growth and CCN activity of aerosol particles which may go beyond the simple reduction of the value of a single parameter in the Köhler equation, and numerous models are currently under development on this issue."

10) line 65&69: what does "In (the) humidification process" mean in this context? Especially, the sentence in line 69f is difficult to understand. Do you mean that the hygroscopic growth curve displays certain distinct features (like a one or two sharp stepwise increases at the deliquescence points of the individual compounds?

Answer: Both expressions were replaced by "hygroscopic growth".

11) line 69: "internally mixing and/or organic coating". If the particles are internally mixed, it means that the constituents of the particle are truly mixed and not separated into a core and surface layer. Or do you mean that there is a bulk-to-surface partitioning when the aqueous solution is formed with a part of the organic material in solution and another part as a film/monolayer on the surface of the droplet?

Answer: We have replaced the sentence: "In humidification process, small organic/inorganic ratios (< 20 %) lead to internally mixing and/or organic coating on the particle surface (Nandy and Dutcher, 2018; Smith et al., 2013)" by: "During the hygroscopic growth, for small organic/inorganic ratios (< 20 %), there is a bulk-to-surface partitioning with a part of the organic material in solution, and another part as a film coated at the surface of the droplet (Nandy and Dutcher, 2018; Smith et al., 2013)"

12) line 75: "Ammonium cation (NH_{4+}) is in pH-dependent equilibrium with…" should be "Ammonium cations (NH_{4+}) are in a pH-dependent equilibrium with…"

Answer: Done
Modification: line 75 "Ammonium cation (NH_4^+) is in pH dependent equilibrium with dissolved ammonia in the aqueous phase." was replaced by "Ammonium cations (NH_4^+) are in a pH-dependent equilibrium with dissolved ammonia in the aqueous phase."

13) line 80: "… as they impact on both human health and climate.". The use of "impact" as an intransitive verb has been increasingly accepted. However, it still feels unprofessional in such a sentence. Using "… as they affect both human health and climate." or "… as they have an impact on both human health and climate." would be a more elegant phrase in this context.

Answer: Done
Modification: line 80 "These reactions are of particular interest for the atmosphere, as they impact on both health and climate." was replaced by "These reactions are of particular interest for the atmosphere, as they have an impact on both health and climate."

14) line 86ff: This is just a note: Every scientist I know who works with AS (and other inorganic salt) particles for instrument calibration purposes is aware that there is always a chance of contamination with organic compounds and that that will bias the calibration results. Usually, the contamination is blamed on not very clean water (e.g. MiliQ water sitting around in plastic containers for months before using) or an "old" AS supply (i.e., bottles of AS opened years ago and everyone using a potentially contaminated spoon/spatula to get their sample). Scientists will check for signs if this contamination affected their measurements (e.g., considerable water uptake below the deliquescence RH for HTDMA measurements) and simply reject such measurements and try again to obtain a "better" calibration with a cleaner AS solution. However, this procedure is rarely mentioned in publications as it is assume as "getting the

calibrations right". It is commendable that finally a group of scientists decided to thoroughly investigate these contaminations and their true origin. I hope that this study will trigger a more transparent and thorough approach to the reporting of AS based calibration measurements.

Answer: Thank you for the note, this is exactly the aim of the paper!

15) Section 2: There are 3 different particle diameters used in this manuscript (dm, da, and dve). Although these are standard ways of describing the particle size and the authors do introduce them when they first occur in the text, it would be nice to instead introduce them all at the same place and indicate their relation to each other and which instrument/classifier is related to their measurement. The end of section 2.1.1 or 2.1.2 could be a place for this very brief information.

Answer: This is a very good idea.

Modifications: line 125 The following sentence was added to section 2.1.2: "In this work, four different particle diameters were used: the mobility diameter (d_m), the aerodynamic diameter (d_a), and the vacuum aerodynamic diameter (d_{va}) were given by the SMPS, the AAC and the AMS measurements, respectively; while the volume equivalent diameter (d_{ve})was used to determine the surface of AS particle. The relations between these diameters can be found in (DeCarlo et al., 2004)."

line 118 "This setup allowed the characterization of the suspended particles by their mobility, aerodynamic and vacuum aerodynamic sizes, as well as their organic content as a function of particle sizes with respect to the total mass of AS particles selected." was replaced by "This setup allowed the characterization of the aerosol particles by their sizes, as well as their organic content as a function of particle sizes with respect to the total mass of AS particles selected."

16) Introduction to Section 2 and section 2.1: I find these sections displays overall a "sloppy" writing style. In many instances, the authors are not clear enough in the description of their setup and methods. A reader with strong background knowledge about atomisers, DMA, AAC, and AMS will draw the right conclusions. But the vagueness in almost all sentences will make it hard for a novice in this field to understand what exactly was done. The next 13 comments are all concerning section 2.1.1. I recommend that the authors carefully improve section 2.1 to get it to the same high quality that they show in section 2.2.

Answer: more detailed descriptions on the DMA, AAC and AMS were added in the revised paper. See also answers to comments 17)-29).

17) line 100: The term "suspended particles". Why do the authors introduce this new term? It is ambiguous as it could mean particles suspended in air (= aerosol) or suspended in liquid (suspension or emulsion). The term "aerosol particle", on the other hand, is clear and well established. Hence, it should be used throughout the manuscript if indeed aerosol particles are meant.

Answer: Done: the term "aerosol particle" was used in the revised paper.

Modifications: line   100&107&118&123&124&146&151&169&233&360&364&369&385   the term "AS suspended particles" was replaced by "AS aerosol particles"

18) line 101 & 103: "previously employed". It is absolutely unclear what this term is referring to: employed by whom? By the authors? In what study? I can only guess that the authors mean that these are solution concentrations, particle sizes, and aerosol particle concentrations typically used in AS calibration measurements. If that is the case, they have to write it that way.

Answer: Yes, the authors indicate that the concentrations of AS used were similar to those used in the literature.
Modification: line 100 "AS suspended particles were generated by atomization of AS solutions at concentrations ranging from 0.01 to 0.5 M, similar to those previously employed." was changed to "AS aerosol particles were generated by atomization of AS solutions at concentrations ranging from 0.01 to 0.5 M."

19)-26) **Thank you very much for the thorough improvements of the writing: all the suggestions were included in the revised manuscript and the expressions were checked throughout the manuscript when necessary.**

19) line 102: "This procedure allowed to form…". The grammatical structure for the verb allow used in this context must be: "to allow SOMEONE to verb something". "allow" requires a direct object when used in the meaning of enable/make something possible. The authors must correct their usage of "allow to" here and throughout the manuscript to one of the following forms (using a shortened form of the sentence in line 102 as an example):

a. This procedure allowed us to form AS aerosol particles. (adding a direct object)

b. This procedure allowed the formation of AS aerosol particles. (convert verb to noun)

c. This procedure allowed forming AS aerosol particles. (using gerund as direct object)

20) line 102: "monodisperse AS particles". Since you point out later that there was a considerable amount of double charged particles when the DMA was used, the authors should change this to "quasi-monodispers".

Modification: **line 102 "This procedure allowed to form monodisperse AS particles at mass concentrations ranging from 5 to 30 μg m⁻³, similar to those previously employed."** was replaced by **"This procedure allowed us to form quasi-monodisperse AS particles at mass concentrations ranging from 5 to 30 μg m⁻³, concentrations typically used for aerosol generation and/or calibration in the literature."**

21) line 104: "Aqueous solutions of AS were prepared and analysed by a…" The structure of the sentence can be misunderstood as that preparation and analysis were conducted with an LC-MS. The prepared part is not necessary in this sentence and it can be simply "Additionally, aqueous solutions were analysed with a….". Note that also In parallel is not the best choice of phrase here. The authors did not even use the same solution or even the same concentration for aerosol generation and LC-MS measurements.

Modification: **line 104 "In parallel, aqueous solutions of AS were prepared and analyzed by a Liquid Chromatography–tandem Mass Spectrometry (LC-MS) to tentatively identify organic content."** was replaced by **"Additionally, aqueous solutions of AS were analyzed by Liquid Chromatography–tandem Mass Spectrometry (LC-MS) to tentatively identify organic content."**

22) line 104f: The employed method is called mass spectrometry. The employed instrument (LC-MS) is called mass spectrometer. So, it should be spectrometer here.

Modification: **line 14 term "Spectrometry"** was replaced by **"Spectrometer"**

23) line 108: "Aerosol generation and classification" The term "classification" is also used with the meaning of characterisation. It is better to use "size classification" or "size selection" to clarify the content of this section.

Modification: **line 108 "Aerosol generation and classification"** was replaced by **"Aerosol generation and size classification"**

24) line 109: "A scheme of the experimental setup…" should be "The schematic of the experimental setup…"

Modification: **line 109 "A scheme of the experimental setup for quantifying organic content is shown in Figure 1."** was replaced by **"The schematic of the experimental setup for quantifying organic content is shown in Figure 1."**

25) line 113: "…controlling AS concentrations". This is another example of the sloppy writing style in this section. Yes since this is now about the particles, the reader can infer that this is the particle concentration. But why not be precise in the description?

Modification: **line 113 "Dry AS particles then passed through a dilution system aimed at controlling AS concentrations."** was replaced by **"Dry AS particles then passed through a dilution system aimed at controlling AS particle concentrations."**

26) line 114: "it consists in" should be "consists of"

Modification: **line 114 "It consisted in two parallel pathways, one of which was connected to a HEPA filter."** was replaced by **"It consisted of two parallel pathways, one of which was connected to a HEPA filter."**

27) line 115: "an electrostatic classifier combined with a differential mobility analyser" What the authors describe here is a tandem DMA: An electrostatic classifier (=DMA) and a DMA. Someone who has worked with these platforms can guess that they used an TSI 3080 platform as a size selector. But again, without this detailed background knowledge, the sentence is misleading.

Answer: the suggestion of the reviewer is important for readers to better understand the setup.

Modification: **line 115 "An aerodynamic aerosol classifier (AAC, Cambustion) and an electrostatic classifier combined with a differential mobility analyzer (DMA, TSI, 3080) were alternatively used to select monodisperse particles."** was replaced by **"An aerodynamic aerosol classifier (AAC, Cambustion) and an electrostatic classifier (TSI, 3080) combined with a differential mobility analyzer (3081 long DMA) were alternatively used to select monodisperse particles."**

Line 153 "The particles number size distribution was measured with a scanning mobility particle sizer (SMPS) consisting of a Differential Mobility Analyzer (DMA, TSI, 3080) coupled with an Ultrafine

Condensation Particle Counter (CPC, 3776, TSI).” was replaced by **“The particles number size distribution was measured with a scanning mobility particle sizer (SMPS) consisting of a DMA (TSI, 3080) coupled with an Ultrafine Condensation Particle Counter (CPC, 3776, TSI).”**

28) line 116f: “To regulate the flow rate at the exhaust…” What exhaust is meant in this sentence? The only part in Fig 1 labelled with “exhaust” is at the inlet of the dilution system. There is no MFC added there (which is what the sentence implies). Having worked with similar setups, I am very sure that the authors try to describe that they regulated the total sample flow through the classifier by adding a variable additional flow controlled with an MFC. Then the sample flow through (not before) the classifier was $0.4 – 1.4$ L min^{-1}.

Answer: the objective using the MFC is to regulate the flowrate through the classifier.

Modification: **“To regulate the flowrate at the exhaust, a mass flow controller (MFC) was connected to a vacuum pump.”** was changed to **“To regulate the flowrate through the AAC classifier, a mass flow controller (MFC) was connected to a vacuum pump.”**

29) line 116f: follow-up question: was a variable sample flow only used for the AAC or also for the DMA setup? From the results section it seems that this was only done for testing the AAC behaviour. The current sentence implies that both classifiers had variable sample flow.

Answer: the variable flowrate was only applied for the AAC classifier, not for the DMA classifier.

Modification: **“Under this configuration, the sample flow before the classifier varied from 0.4 to 1.4 L min^{-1}.”** was changed to **“Under this configuration, the sample flow through the AAC varied from 0.4 to 1.4 L min^{-1}, while the tests performed with the DMA classifier were only done at one flowrate (0.4 L min^{-1}).”**

30) line 135: which water was used for the recrystallisation?

Answer: Milli-Q water (18.2 MΩ cm, TOC < 2ppb) was used for the recrystallisation. The precision was added in the manuscript.

Modification: **“In EXP P4, AS crystals (99.5 %, for analysis, from ACROS Organics™ Fisher Scientific) were tentatively purified by recrystallization in water:”** was replaced by **“In EXP P4, AS crystals (99.5 %, for analysis, from ACROS Organics™ Fisher Scientific) were tentatively purified by recrystallization in Milli-Q water:”**

31) line 136f and Table 1: How do the 5 d_m sizes selected with the DMA relate to the 4 d_a sizes selected with AAC?

Answer: the 4 sizes (d_a = 200, 300, 400 and 500 nm) selected with the AAC classifier correspond to the mobility size of 130, 201, 269 and 336 nm. These values were chosen to plot figure 5. In this figure, The 5th size (d_m = 375 nm) is an additional point.

Modification: line 149 **“The four sizes (d_a = 200, 300, 400 and 500 nm) selected with the AAC classifier correspond to the mobility sizes (d_m = 130, 201, 269 and 336 nm)” is added at the end of the table 1 title description.**

32) line 141f: “the smaller size, the higher rotational speed and the larger σ_{geo}”. First, it will be easier to understand if the cause (the rotational speed) is put first in this and the effects last (smaller size and larger σ_{geo}). Second, this needs the 145 defined articles (the): “The higher the rotational speed, the smaller the selected size and the larger the σ_{geo}”.

Answer: done

Modifications: line 140 **“Rotational speed has been reported to influence the geometric standard deviation (σ_{geo}) of size distribution, i.e., the smaller size, the higher rotational speed and the larger σ_{geo} (Johnson et al., 2018).”** was replaced by **“Rotational speed has been reported to influence the geometric standard deviation (σ_{geo}) of size distribution, i.e., the higher the rotational speed, the smaller the size and the larger the σ_{geo} (Johnson et al., 2018).”**

Table 1 **“(sample flow = 0.5,1.0, 1.4 L.min^{-1})”** was replace by **“(sample flow = 0.5, 1.0, 1.4 L.min^{-1}, corresponding to rotation speed of 190, 285 and 369 rad/s)”**

33) line 155f: Please add which vaporiser was used in the AMS – normal or capture.

Answer: The HR-ToF-AMS uses a standard vaporizer (SV)

Modification: line 155 **“The instrument was used under standard conditions (vaporizer at 600 – 650 °C and electron ionization at 70 eV) in V-mode and in p-ToF mode.”** was replaced by **“The instrument was used under standard conditions (standard vaporizer at 600 – 650 °C and electron ionization at 70 eV) in V-mode and in p-ToF mode.”**

34) line 162: "The data treatment has been performed by AMS Analysis toolkit…" It is not the toolkit that performs the data analysis, it is the user. Change "by" to "with" to clarify this.

Answer: done

Modification: line 162 "The data treatment has been performed by AMS Analysis Toolkit 1.63 and PIKA 1.23 under the software Igor Pro 6.37." was replaced by "The data treatment has been performed with AMS Analysis Toolkit 1.63 and PIKA 1.23 under the software Igor Pro 6.37."**

35) line 164ff: The authors make it sound as if the presence of air ions was unexpected or exceptional. The detection of the named ions are the normal behaviour of any AMS. Their absence or lower abundance than the ions stemming from the aerosol sample would indicate instrumental issues or require special treatment (e.g., for the air beam correction to account for sensitivity variations).

Answer: The presence of air ions is evident in the AMS, and the correction of the air beam was applied for all experiments. Signals of NH_x and SO_x are extremely high with the presence of the ammonium sulfate particles. Consequently, fragments located at the tail of these main peaks such as CH_3^+, CH_4^+, CH_2N^+ and $C_2H_4^+$… were excluded from the calculation of total organic content.

Modifications: line 163 "The measured mass spectra were dominated by NH_x and SO_x fragments, but air fragments such as N^+, O^+, HO^+, H_2O^+, N_2^+, $^{15}NN^+$, O_2^+, $^{18}OO^+$, Ar^+, CO_2^+ showed also large ion signals. To avoid any over-estimation of the organic fraction, only CHO^+ and CO_2^+ were apportioned to organics using $C_2H_3O^+$ following the procedure of Aiken et al., (2007) and Canagaratna et al., (2015)." was replaced by "To avoid any over-estimation of the organic fraction, CHO^+ and CO_2^+ fragments (at m/z 29 and 44) were corrected from the remaining gas phase in the AMS (Aiken et al., 2007 and Canagaratna et al., 2015)."

line 167 The following sentence was added to the manuscript: "In addition, due to the very high signals of the fragments NH_x and SO_x, other fragments located at the tail of these main peaks (such as CH_3^+, CH_4^+, CH_2N^+ and $C_2H_4^+$…) were excluded from the calculation of the total organic content, to avoid any over-estimation of the organic fraction"**

36) line 166f: As an experienced AMS user, I am confused by this sentence. They calculated the organic mass from CHO^+ and CO_2^+ only? That would be very strange. OR are there referring to the correction of gas-phase contributions to signal of these two ions and using the established fragmentation table (Frag Table) approach? If so, the method is to adjust the amount of subtracted gas-phase CO_2^+ signal to reach a signal of 0 of the particle-phase CO_2^+ for $C_2H_3O^+$ signals of 0 (i.e., when no particles are present in the sample air). The standard setting for the Frag Table approach is to set the CO^+ signal (which cannot be determined next to N_2^+) to the same value as CO_2^+. If this was done, the estimated CO^+ also contributes to the calculated organic mass. If indeed these things were done in this way (which is the standard procedure for AMS data analysis), these confusing sentences starting with "The measured mass spectra…" should be changed to something like:

"CHO^+ and CO_2^+ ions were corrected for the influence of the remaining gas phase in the AMS (Aiken, Canagaratna). Other air ions which also might have small contributions from particulate organic matter were omitted to avoid any over-estimation of the organic fraction."

As a final note on this matter: Since a HR-AMS was used, the only problematic ions for organic mass calculation are CO^+ (masked by N_2^+), CHO^+ (masked by $^{15}NN^+$) and CO_2^+ (gas-phase contribution). The other air ions do not overlap with any strong organic signals. The calculation of particulate water is a whole other matter but not relevant for this study.

Answer: The suggested sentence was modified in the revised paper. See the modified sentence in our answer to question 35)

37) line 169: "In parallel…" If the LCMS measurements were not truly in parallel, it should be "In addition…"

Answer: see our answer to remark 38)

38) line 172: Same as Comment 22: The instruments are a Liquid Chromatograph and a Mass Spectrometer.

Modification: line 169 "In parallel with the characterization of suspended AS particles, organic traces were investigated directly in AS aqueous solutions by Liquid Chromatography–tandem Mass Spectrometry (LC-MS) for tentative molecular identification." was replaced by "The characterization of organic traces on AS aerosol particles were also investigated directly in AS aqueous solutions using a Liquid Chromatography–tandem Mass Spectrometer (LC-MS) for tentative molecular identification."**

39) line 173: "…the mobile phase consisted in two eluents" should be "consisted of"

Answer: done
Modification: line 173 "the mobile phase consisted **in** two eluents:" was replaced by **"the mobile phase consisted of two eluents:"**

40) line 205: "…three extraction cycles were operated." "conducted" is a better word than "operated" in this context.
Answer: done
Modification: line 202 "For these extractions, an Accelerated Solvent Extractor (ASE 300, Dionex) system was used under the following conditions: acetonitrile was the extraction solvent, the oven was set at 100 °C under 100 bars, the heat up time and static time were 5 min each, three extraction cycles were operated"** was replaced by **"For these extractions, an Accelerated Solvent Extractor (ASE 300, Dionex) system was used under the following conditions: acetonitrile was the extraction solvent, the oven was set at 100 °C under 100 bars, the heat up time and static time were 5 min each, three extraction cycles were conducted"**

41) line 213ff & Figure 2: How were these background experiments conducted? Was the pure water atomised in the same way as the solutions? Is this still size selected or was the polydisperse sample used. The issue with spraying pure water on its own is that even if contaminations are present, their total amount is probably low and the formed particles are typical much smaller than the AMS inlet cutoff (~60nm Dva with standard PM1 inlet). Hence, these impurities are potentially "invisible" to the AMS. With AS (or any other salt) solutions, the AS will form large particles. Any contaminations of the water itself will then be on these larger particles and thus be detectable with the AMS.
Answer: the pure water was atomized in the same way as AS solutions. Both size selected and polydisperse samples were used. In Figure 2, backgrounds show size selected particles with d_m = 200 nm. Although the impurities in pure water nebulization are potentially invisible to the AMS (due to the size cutoff), it is important to note the background for quality check. Furthermore, our LC-MS measurements clearly show that water contamination was not the reason for the organic content of AS solutions (as mentioned in section 3.4).

42) line 216: "quantity of organic" should be "quantity of organic compounds"

Answer: done
Modifications: line 161&214&216&219&222&299&305 term **"organic"** was replaced by **"organic compounds"**

43) line 220f: "The same observations were made…"
Modification: line 220 **"The same observations were made"** was replaced by **"The same observations were obtained"**

44) line 222: "the presence of organic" should be "the presence of organic compounds"
Answer: done, please see our answer to remark 42)

45) line 222f: "respectively" is used incorrectly here. In this context, it needs to follow the items it is referring to and be separated with a comma: "Reference A and reference B, respectively". However, it would be easier for the reader to understand which study had the higher/lower values if this sentence was restructured.
Modification: line 221 **"Overall, it was observed that [Org]/[Sulfate] varied from 1.5 % to 3.8 %, slightly higher (respectively lower) than in the two previous studies mentioning the presence of organic in laboratory experiments on AS particles (respectively Badger et al., 2006 and Trainic et al., 2011)."** was replaced by **"Overall, it was observed that [Org]/[Sulfate] varied from 1.5 % to 3.8 %, in the range of the values reported by studies mentioning the presence of organic compounds in laboratory experiments on AS particles (0.8 wt % of C in Badger et al., 2006 and up to 8% in Trainic et al., 2011)"**

46) Figure 2: "two pure waters in different qualities". This just feels wrong. It should be: "two types of water with different purity"
Answer: done
Modification: line 227 **"Background signal obtained with pure water in EXP P1 and P2 is also shown for quality check and for comparison between the two pure waters in different qualities."** was replaced by **"Background signal obtained with pure water in EXP P1 and P2 is also shown for quality check and for comparison between the two types of water with different purity."**

47) line 230: "Unit-mass HR-ToF-AMS spectrum" It should be "unit-mass resolution spectrum". However, it would be even better to explain that these were not UMR measurements but rather that the HR data was converted to UMR to enhance readability of the mass spectrum.

Answer: done in the text.

Modifications: line 230 "Figure 4 shows the Unit-mass HR-ToF-AMS spectrum of AS aerosols selected by the AAC at d_a = 200 nm." was replaced by "Figure 3 shows the Unit-mass resolution spectrum of AS aerosols selected by the AAC at d_a = 200 nm."

line 233 "Unit-mass spectra (averaged over 12 measurement runs) of AS suspended particles (d_a = 200 nm) in EXP P1, performed at AS concentration of 0.5 M." was changed to "Unit-mass resolution spectra (averaged over 12 measurements, converted from the high-resolution data) of AS aerosol particles (d_a = 200 nm) in EXP P1, performed at AS concentration of 0.5 M."

48) Caption of Figure 3: What are 12 measurement runs? The term "run" is not defined anywhere.

Answer: The term "run" was deleted in the revised paper. Each measurement point was averaged for MS cycle of 1 min and p-ToF cycle of 30 s (given in section 2.1.3).

49) Caption of Figure 3: "Unit-mass spectra" should be "unit- mass resolution spectrum"

Answer: done, see our answer to comment 47)

50) line 235: "…SO_x^+ and NH_x^+ are the major fragments." The term SO_x^+ or NH_x^+ fragments is not commonly in the context of AMS data. Instead, related ions (e.g., with only C and H atoms; or with only S, H, and O atoms) are grouped into "families" (e.g., the C_xH_y family, representative of hydrocarbons, or the SO_x family, representative of sulphate or sulphuric acid). The names of these families are spelled without the "$^+$". Carefully check each instance in the manuscript to clarify when these families are meant and use the correct terms to differentiate them from the cases when individual ions ("fragments") are meant. E.g., in line 304, the term clearly refers to the families and not individual ions. One of the reasons not to use the term "fragment" in this context is that some of the ions in the families can indeed be the "parent ion" of a compound. This is especially the case for inorganic salt ions, e.g. the SO_x family which includes: SO_4^+, HSO_4^+, $H_2SO_4^+$. The corresponding compounds are sulphates, bisulphate, and sulphuric acid.

Answer: Thanks for the detailed explanation on the difference between the term fragment and the term family.

Modifications: line 235 "Representing sulfate and ammonium respectively, SO_x^+ and NH_x^+ are the major fragments." was replaced by "SO_x and NH_x families represent sulfate and ammonium, respectively."

line 304 "From the HR-ToF-AMS mass spectra, the three main organic fragments present in AS particles were C_xH_y $C_xH_yO_{(1-2)}$ and $C_xH_yNO_{(0-2)}$." was replaced by "From the HR-ToF-AMS mass spectra, the three main families present in AS particles were C_xH_y, $C_xH_yO_{(1-2)}$ and $C_xH_yNO_{(0-2)}$."

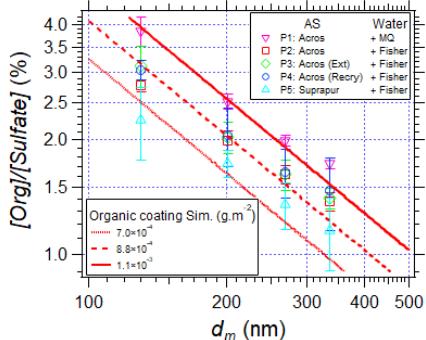
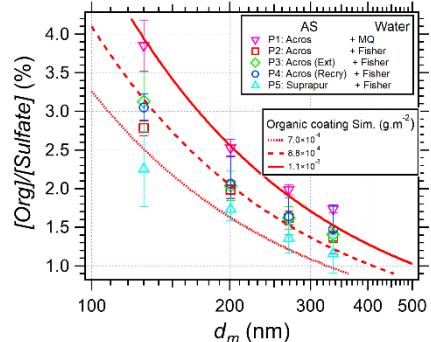
51) line 236: I do not understand the comment about the low signal inhibiting the calculation of inorganic/organic nitrate contribution? The first Figure in SI3 shows that NO_+ could be fitted nicely. What was the problem? The authors should at least provide an estimation of the upper limit of organic nitrates assuming that all detected NO_+ and NO_{2+} stem from organic compounds. Also, what is the upper limit of inorganic nitrate mass calculated from these values assuming that all of the signal stems from an inorganic compound? Inorganic nitrate also constitutes a contamination of the AS which potentially alters its properties.

Answer: the authors agree, the sentence was not clear

Modification: line 236 "The low signal detected for the NO^+ and NO_2^+ fragments at m/z 30 and 46, inhibits the distinction between inorganic and organic nitrate." was replaced by "The sum of the signals of NO_2^+ and NO^+ fragments represent 30% of the total organic signal (Figure SI4-2). To figure out the source of this non-negligible nitrate signal, the AMS signal NO_2^+/NO^+ ratio was investigated and showed significantly lower values in AS aerosol (0.46 in EXP1) compared to ammonium nitrate particles used for calibration (1.18) – Figure SI4-1. It is thus suggested that the observed nitrate signal in AS aerosol is due to the presence of organic nitrates (Kiendler-Scharr et al., 2016)."

52) Figure 4: The y-axis in this figure seems to be logarithmic which is not easily visible at first glance since the axis range is from 1.5 to 4 and the ticks on the right-hand side are equidistant. Why was a logarithmic scale chosen for such a small range? It makes it harder to interpret the spread of points.

Answer: A comparison of figure 9 using both logarithmic and linear scales is shown below. The comparison clearly shows that the data points are better separated for large sizes using the logarithmic scale than using the

linear scale. So the authors would like to keep the logarithmic scale for all figures concerning *[Org]/[Sulfate]* v.s. *dₘ* in this work, i.e. Figures 4, 5 and 9.

| **Figure 9 with y-axis in log scale** | **Figure 9 with y-axis in linear scale** |

53) Figure 4: The unit in the legend is m³ for both density types. Also, the abbreviations are not very helpful since they were not introduced elsewhere. The legend would be more readable if the authors introduced the surface density properly in the text and used a single symbol throughout.
Answer: m³ has been changed to m² for surface density in the legend of Figure 4.

54) line 255: What does "multi-characterisation" mean?
Answer: It means the characterization on the size of aerosol particles using d_m, d_a, d_{va} and d_{ve}.
Modification: line 254 "To achieve this calculation, a thorough study of the morphology of AS particles was needed which was obtained from multi-characterization of particle size." was replaced by **"To achieve this calculation, a thorough study of the morphology of AS particles was performed using the various sizes measurements (Appendix A)."**

55) line 258: This sentence is broken. Should it read: "The calculations of the organic-inorganic ratio using each of these two hypotheses are detailed hereafter."?
Answer: Yes.
Modification: "The calculations performed under each of the two hypothesizes on the organic-inorganic mixing are detailed hereafter:" was changed to **"The calculations of the organic-sulfate ratio using each of these two hypothesizes are detailed hereafter:"**

56) line 261: The relation of da and dve is not described in Appendix A. Appendix A introduces the shape factor and explains the relation between mobility and vacuum aerodynamic diameter. The relation between da and dva is missing. This is even more confusing since Appendix A uses only equations with dva and then provides values calculated from ACC data while explicitly stating that instruments selects by da.
Answer: Appendix A describes how the shape factor of AS aerosol particles is calculated. The relation of da and d_{ve} is given in Eq.1. By knowing the shape factor χ and d_a (given by the AAC), we can calculate d_{ve} for each size. All this confusion could be avoided by properly introducing all used diameter types together as early as possible and clearly stating which instrument provides which diameter type and how they are related. A logical point for this would be a section in the methods part after all instruments were introduced.
Answer: see our answer to comment 15)
Modification: line 261 "According to DeCarlo et al., (2004), the relation between volume equivalent diameter (d_{ve}) and d_a is determined in Appendix A." was replaced by **"According to DeCarlo et al., (2004), the relation between volume equivalent diameter (d_{ve}) and d_a is described as Eq. 1:"**

57) line 259: "size-independent density". I assume this is supposed the same as "surface density" in the rest of the text?
Answer: yes, please see our answer to comment 2).

58) line 265: Which diameter type is used in the calculation of the Knudsen number?
Answer: in Eq.1, both d_a and d_{ve} are required to calculate K_n and further to get C_c.

59) line 268 f: "Therefore,…" It is not clear how Eq. 3 is connected to the Eq. 1 and 2 or the content of Appendix A. Also, MSO4 and MAS are not introduced.

Answer: The definition of M_{SO4} and M_{AS} has been added in the revised manuscript. One sentence has been added in the revised paper to clarify that the surface of AS particle is determined based on d_{ve}.
Modifications: line 265 "In this work, normal temperature and pressure (293.15 K at 1 atm) were applied for the calculation of the shape factor of AS aerosols. In this work, morphological properties of AS particles are shown in Appendix A: Morphological properties of AS aerosols." was replaced by "In this work, d_a was given by the AAC; χ was determined by dm and d_{va} (Appendix A). Normal temperature and pressure (293.15 K at 1 atm) were applied for the calculation of d_{ve}. The surface of AS particles was estimated from the value of d_{ve}."
**   line 269 "Where S_{ve} and V_{ve} are respectively the surface and volume of the volume equivalent AS particle." was replaced by "Where S_{ve} and V_{ve} are the surface and volume of the volume equivalent AS particle, respectively. M_{SO4} and M_{AS} are molar mass of SO_4^{2-} and $(NH_4)_2SO_4^-$, respectively."**

60) Eq. 4: what is $\rho_{N,intern}$?
Answer: This was a mistake. Eq 4 has been rewritten as follows:

$$\frac{[Org]}{[Sulfate]} = \frac{V\rho_{org,V}}{V\rho_{AS}\frac{M_{SO_4}}{M_{AS}}} = \frac{\rho_{org,V}}{\rho_{AS}\frac{M_{SO_4}}{M_{AS}}} \times 100\%$$

61) line 275: "…independent to particle size." should be "… independent of the particle size."
Answer: done
Modification: line 275 "Where V is the total volume of studied aerosol particle. In this case, the ratio [Org]/[Sulfate] is independent to particle size." was replaced by "Where V is the total volume of studied aerosol particle. In this case, the ratio [Org]/[Sulfate] is independent of the particle size."

62) line 279f: Did the authors expect that the Nafion drier should be efficient in removing the organic compounds? Usually, only semi-volatile compounds or very polar ones are assumed to be lost significantly in Nafion driers.
Answer: Here, we would like to highlight that organic compounds in AS aerosol particles are not semi-volatile compounds.

63) line 287: "… the DMA selects particles bearing a given electrical mobility size…" This should be "… the DMA selects particles by their electromobility." Or "...due to their mobility in an electrical field."
Answer: done
Modification: line 286 "While the AAC selects particles using centrifugal force, the DMA selects particles bearing a given electrical mobility size, providing size distributions that are not perfectly monodisperse but with double or triple modes, due to multi-charging effects. DMA has been widely used so corrections of these effects have been successfully applied in aerosol studies (Petters, 2018; Wiedensohler et al., 2012). In this work, we compared [Org]/[Sulfate] in AS particles selected by the DMA and by the AAC respectively (Figure 5)." was replaced by "While the AAC selects particles using centrifugal force, the DMA selects particles by their electromobility. In the latter, the selected distribution is thus not exclusively monodispersed as it contains double- and triple-charged particles at the corresponding sizes. Corrections of the multi-charge effect were successfully applied following the and is routine in aerosol size distribution determination (Petters, 2018; Wiedensohler et al., 2012). However, Figure 4 shows that the larger particle the lower content of the organic compounds. In this case, the multi-charged particles affect the organic quantification using the DMA and the AMS, so that corrections are needed to do. In this work, we compared [Org]/[Sulfate] in AS particles selected by the DMA and by the AAC, respectively (Figure 5)."

64) line 287f: The rest of this sentence is also not strictly correct and should be split into a separate sentence to enhance readability "Thus, the selected distribution is not truly monodisperse but also contains double- and triple-charged particles at the corresponding sizes."
Answer: done, please see modification to remark 63)

65) line 290: The authors should clearly state, why the presence of multi-charged particles of larger sizes is an issue in their analysis. For an SMPS (same selection method and size resolved measurement), the correction for multi-charged particles is routine and no issue at all. The problem arises from using the "bulk" mass concentrations measured by the AMS over all sizes because typically the pToF mode (size resolved measurement) is not sensitive enough to reliably detect the small amounts that this study is investigating.
Answer: please see modification to remark 63)

66) Figure 5: The logarithmic y-axis makes it difficult to correctly judge the differences between the black and white markers and the red line. This would be much easier with a linear scale.

Answer: see our answer to comment 52). We would like to keep the logarithmic scale for y-axis for Figures 4, 5 and 9.

67) Figure 5: What are the y-direction error bars? Standard deviation over from averaging multiple measurements? Or are they an estimation of the true uncertainty?

Answer: the y-direction error bars of AAC selection (red solid dots) and DMA selection (black solid dots) data points are standard deviations from averaging multiple measurements. The error bars of DMA corrected (black hollow dots) data come from the standard deviation of DMA selection data and standard deviation of size distribution obtained by the SMPS.

68) line 297: SI5 is not very helpful for understanding what was done here. Too many steps are skipped or not well described. How were Eq. 5.1 and 5.2 combined to obtain 5.3? What diameter type is "d" in these equations?

Answer: SI7 (SI5 before the modification) describes the procedure to estimate the corrected [Org]/[Sulfate]. In Eq. SI7.1 and Eq. SI7.2, $\rho_{org,S}$ is unknown and the corrected [Org]/[Sulfate] is what the authors would like to estimate. The combination of Eq. SI7.1 and Eq. SI7.2 removes the term $\rho_{org,S}$ and build the relation between corrected [Org]/[Sulfate] and experimental [Org]/[Sulfate].

69) line 297ff: From how I understand the corrections lined in SI5, [Org]/[Sulphate]*corr* is not the total amount of organic compounds and sulphate but rather only the amount attributed to the first mode. The reason that this value is higher is that there is a size dependence with smaller values for larger particle sizes. Thus by removing the contribution of the larger multi-charged mode, the corrected values are higher.

Answer: Correct. $\dfrac{[Org]}{[Sulfate]_{clac}}$ was replaced by $\dfrac{[Org]}{[Sulfate]_{corr}}$.

70) line 299: "From the result, using the DMA selection…" delete "from the result"

Answer: done
Modification: line 299 "From the results, using the DMA selection after correction," was replaced by "Using the DMA selection after correction,"

71) line 302: "…selection by ACC leads to lower uncertainties…" What are the errors/uncertainties in x direction? I.e., what are the uncertainties for the size selection in the DMA and ACC? Only if this information is given can such a statement be made.

Answer: In this work, no errors are considered in x direction.
Modification: line 302 "… and it also shows that the selection by AAC leads to lower uncertainties and therefore more accurate results." was changed to "… and it also shows that the selection by AAC leads to lower uncertainties on the y axis and therefore more accurate results."

72) line 313: "Further identification was investigated LC-MS on liquid AS solutions." Should be "Further identification was conducted by LC-MS with liquid AS solutions."

Answer: done
Modification: line 313 "Further identification was investigated LC-MS on liquid AS solutions." was replaced by "Further identification was conducted by LC-MS with liquid AS solutions."

73) line 325f: This sentence is broken. Probably needs to be split in two.

Answer: The sentence was split in three: "The mass error was always well below 5 ppm and no raw formula with sodium adduct was suggested. Some of the m/z showed two different retention times, implying potentially the presence of isomers. For example, at m/z 226.1918, two peaks were detected, one at 2.89 minutes and the other at 3.11 minutes as described in detail in SI8 for the most intense ions. In the negative ESI mode, the signal was overwritten by the sulfate ion (detected at [M+H]⁻: 96.9596, HSO₄⁻) along the whole chromatogram, due to the high ammonium sulfate concentrations used."

74) line 336: " …molecules marked as *…" Should be "…molecules marked with *…"

Answer: done

Modification: line 335 "In the negative mode, the signal was systematically much lower (ion current intensity < 10³ counts per second) and only molecules marked as * in Fig. 7 were detected." was replaced by "In the negative mode, the signal was systematically much lower (ion current intensity < 10³ counts per second) and only molecules marked with * in Fig. 7 were detected."

76) line 345f: C5H9+ is a typical CH type ion in AMS mass spectra data which occurs in many samples of organic aerosol. It can have many different parent molecules. Hence, the co-occurrence in LC-MA and AMS spectra should not be over interpreted.

Answer: The authors do agree with the reviewer about the co-occurrence in LC-MS and AMS spectra.
Modification: line 345 "… as well as the fragment ion at m/z 69.072 corresponding to C₅H₉ which was also a fragment observed in the spectra from the HR-ToF-AMS." was shortened to "… as well as the fragment ion at m/z 69.072 corresponding to C₅H₉ which was also a fragment observed in the spectra from the HR-ToF-AMS with high intensity."

77) Figure 9: It is impossible to see the red squares for most sizes which makes it hard to follow the discussion in the text. The authors could think about changing the marker shape to try make the P2 data more visible. Another option is to apply a small offset to the true d_m values for each set of data points (eg., plot the dark blue ones at 245nm, the green one at 250nm, and the red ones at 255nm. Then add a note to the Figure caption that markers were spread around the true d_m value to enhance visibility).

Answer: Different marker shapes were applied to Figure 9 as shown below

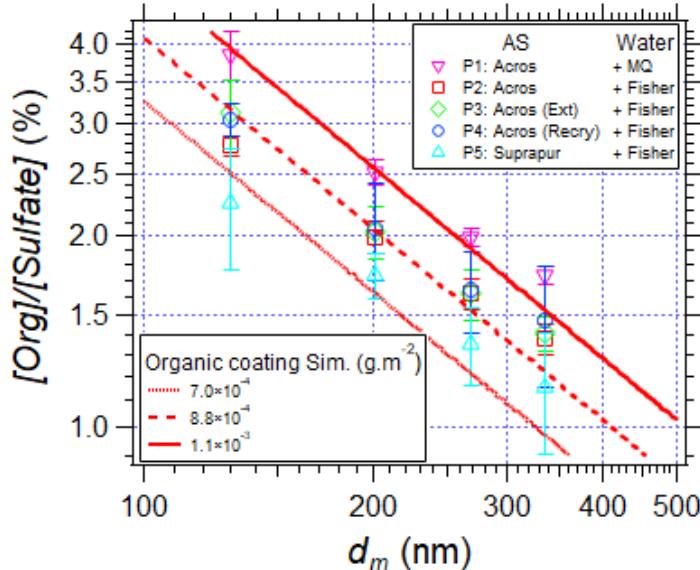



Figure 9 in the revised manuscript

78) line 383f: "… a wide range of commercial AS products…" The study contained 3 different AS products. I would not call that a "wide range".
Modification: line 383 "a wide range" was replaced by "widely used"

79) Line 389: "Regarding to the particle size…" Should be "Regarding the particle size…"
Answer: done
Modification: line 389 "Regarding to the particle size selection system, the comparison between AAC and DMA showed consistent [Org]/[Sulfate] ratio, thus highlighting that the observed particle size effects were not due to instrumentational artifacts." was replaced by "Regarding the particle size selection system, the comparison between AAC and DMA showed consistent [Org]/[Sulfate] ratios, thus highlighting that the observed particle size effects were not due to instrumental artifacts."

80) line 391: "that their structures are independent to the particle size" First, it is "independent of". Second, the conducted MS measurements did not reveal any structural information – only the "raw formulas" were determined. Thus, structure is the wrong term here. Third, the only comparison of composition data between particle sizes was

Figure 6. Frankly, that is not convincing to support such a statement. LC-MS suggests highly functionalised molecules with nitrate, amin, and/or sulphate groups. These are compounds which show strong fragmentation with mostly loss of the functional group. Thus, the AMS may not be sensitive to changes in composition between these compounds.

Answer: to illustrate what is suggested by Figure 6, the sentence "The chemical analysis of the organic content showed that their structures are independent to the particle size." was modified to "The chemical analysis of the organic content showed stable highly functionalized organic compounds which composition seemed independent of the particle size."

81) line 394: "…confirming their low volatility." Deriving volatility from sum formulas is not as straight forward as it may seem. The presence of O and N in a molecule may mean that there is 1 NO_2 or NO_3 group. Depending on the size of the carbon backbone, this may lead to anything between intermediate and extremely low volatility. Since no volatility measurements were conducted, it may be better to speak of "… suggesting low volatility".

Answer: done

Modification: line 392 "Theses formulas include mostly C_{12} compounds with mono- or poly-functional groups with at least two heteroatoms (N and O were always present, and S was found in 10 molecules) confirming their low volatility." was replaced by "These formulas include mostly C_{12} compounds with mono- or poly-functional groups with at least two heteroatoms (N and O were always present, and S was found in 10 molecules) suggesting low volatility."

82) line 394f: "As these molecules…" This sentence is broken.

Modification: line 394 "As these molecules were largely detected in the positive mode by LC-MS, all carrying at least one nitrogen atom. Based on the observation that they are coated at the surface of the suspended AS particles. It can be suggested that they are cationic surfactants such as quaternary ammonium salts remaining from the manufacturing processes." was changed to "These nitrogenous molecules were abundantly detected by LC-MS in AS solutions in the positive ESI mode, and in the nebulized solutions, they were observed to be coated on the surface of AS aerosol particles. Thus, it could be suggested that they might be cationic surfactants such as quaternary ammonium salts remaining from the manufacturing processes."

83) SI has different formatting for section headings than main manuscript. Some of the table have a different font. This is sloppy. The authors must ensure that the style of the SI meets the standard of the main manuscript text.

Answer: This was fixed in the new version of the SI

84) SI3: The quality of the figures in SI3 is not acceptable. These are literally low-quality screenshots of the HR fitting panel in PIKA with blurry y-axis labels, no legends, the residual y-axis is cut off, no Figure numbers, no caption.
I do not see the point of adding these Figures. They only show that some $C_xH_yN_x$ ions could be separated from other potentially overlapping ions. The main message I can derive from these figures as an AMS user is that the majority of organic compounds containing also N are detected as NO_+&NO_{2+} (NO_+ signal is one order of magnitude larger than $C_3H_8N_+$ and $C_4H_{10}N_+$). No inorganic nitrate should be present in the sample. Hence, a method using the NO_+ and NO_{2+} signals should be used to determine an upper limit for the contribution of "organic nitrate" mass.

Answer: These figures illustrate the identification of CHN compounds. Their quality was improved in the new version

85) SI4: The first 3 sentences in SI4 are identical to the main manuscript text in 2.1.2. This repetition does not seem to serve any purpose. The one additional piece of information (the exact speeds) could be added to the main text in section 2.1.2 and the exact values of the result (average +/- stdev) stated in section 3.3 with a reference to the Figure in the SI. Note that "CN/sulfate" is not introduced anywhere. The name of the family is $C_xH_yN_x$ in the main text.

Answer: The first 3 sentences were removed from SI6 (SI4 before the modification). The rotation speeds were added in Table 1. In SI6 (SI4 before the modification), "CN/sulfate" was changed to "CxHyNx /sulfate".

86) I do not understand why Appendix A and SI5 are split. Things will be easier to follow if these two parts are joined (either as Appendix or as SI section). However, more information is still needed (about the skipped steps in the equation development, see comments above) to make this part usable.

Answer: Appendix A shows the morphological information of AS aerosol particles in this work and the relation between different diameters which are important for the calculation of the model predicting [Org]/[Sulfate] ratios. SI7 (SI5 before the modification) shows the procedure of the multi-charge correction which is often used in the literature. The authors would like to keep them separated.

Answers to anonymous Referee #2.

Overview.

This paper describes a series of experiments looking at the amount of organic impurities in ammonium sulfate solutions and also across different particle sizes when those solutions have been aerosolised. The authors present a convincing argument for a significant size dependence on the ratio of [Org]/[sulfate] and have suggested the results indicate that the organic is concentrated at the surface of the particles rather than forming an internally mixed particle. This is a highly relevant and interesting result, which has important implications for laboratory simulations and measurements of physiochemical properties. I recommend publication after some minor corrections.

Comments

Line 82: Organosulfates can be formed via a range of routes, not only by isoprene epoxides. I would suggest adding a few more examples and references
Modification: line 81 "In addition, SO_4^{2-} is not inert in atmospheric water. Aqueous phase reactions with isoprene-derived epoxides to form organo-sulfates have been reported (Darer et al., 2011; Liggio et al., 2005). Epoxides, which are formed by the ozonolysis of a carbon-carbon double bond, undergo an acid-catalyzed nucleophilic attack by sulfate anions. In addition, tertiary organic nitrates, formed by nighttime $NO_3 \cdot$ reaction with isoprene or other terpenes, undergo nucleophilic substitution in the presence of sulfates forming organo-sulfates (Surratt et al., 2008)." was replaced by "Sulfate anions can react with $\cdot$OH radicals forming sulfate radicals ($SO_4 \cdot^-$), an important atmospheric oxidant (Herrmann, 2003). Besides, sulfate radicals contribute to the formation of organosulfates (Nozière et al., 2010; Brü et al., 2020; Wach et al., 2018; Szmigielski, 2016). Organosulfates are ubiquitous compounds in SOA with important implications in their physicochemical properties (Shakya and Peltier, 2015). Other chemical pathways that lead to the formation of organosulfates might involve directly sulfate anions, i.e., their nucleophilic substitution to epoxides or tertiary nitrates (Hu et al., 2011; Darer et al., 2011), and the acid-catalyzed esterification of alcohol groups (Surratt et al., 2008; Iinuma et al., 2007)."

Line 88: It would be helpful for the reader to know a bit more about how ammonium sulfate is manufactured. This would allow some indication of the potential sources of organic contaminants.
Answer: We have added the sentence in the SI2: "Most of the ammonium sulfate particles used in the laboratory are commercial. About 90% of ammonium sulfate is produced by 3 different processes: (1) as a byproduct caprolactam production, (2) from synthetic manufacture by combining anhydrous ammonia and sulfuric acid, and (3) as a coke oven byproduct by reacting the ammonia recovered from coke oven offgas with sulfuric acid. No detailed information is given about the potential organic compounds during these manufacture processes."

Line 90: is the 0.8 % in the ammonium sulfate without humic acid? Its is a bit confusing what is meant here.
Answer: No, the 0.8 wt % of C was observed in ammonium sulfate solution without humic acid.
Modification: line 90 "For example, 0.8 wt % of C was observed in ammonium sulfate solutions in the study of phase transitions of AS and humic acid mixtures (Badger et al., 2006)." was replaced by "For example, 0.8 wt % of C was observed in solutions where only ammonium sulfate was present as solute in the study of phase transitions of AS (Badger et al., 2006)"

Line 115: I would like some more details about the air/N2 difference. Zeroi air is also likely to contain organics and it is important to determine whether the air is also a source of absorbing material.
Answer: One additional experiment (P8) using pure N2 has been added in the manuscript. Globally, no significant difference was observed compared to EXP P1.
Modification: two rows were added in Table 1:

Effect of gas supplier (pure N2 instead of compressed air)			
P8	99.5 [1]	Milli-Q [5] 0.5	d_a = 200, 300, 400, 500

Line 221 one sentence was added "It was checked in EXP P8 that replacing compressed air by pure N2 (Linde Gas, 99.999 %), no significant differences were observed from EXP P1 under the same conditions (SI3)."

Line 159: Need to explain that the second two are relative to the NO3.
Modification: line 236 "**The low signal detected for the NO$^+$ and NO$_2^+$ fragments at m/z 30 and 46, inhibits the distinction between inorganic and organic nitrate.**" was replaced by "**The sum of the signals of NO$_2^+$ and NO$^+$ fragments represent 30% of the total organic signal (Figure SI4-2). To figure out the source of this non-negligible nitrate signal, the AMS signal NO$_2^+$/NO$^+$ ratio was investigated and showed significantly lower values in AS aerosol (0.46 in EXP1) compared to ammonium nitrate particles used for calibration (1.18) – Figure SI4-1. It is thus suggested that the observed nitrate signal in AS aerosol is due to the presence of organic nitrates (Kiendler-Scharr et al., 2016).**"

Line 200: What is the difference in the chromatograms using the two different eluents – you say its been optimised but I don't see any discussion about why one set was used over another. Also, why is only +ve mode used for optimisation? This may result in you discounting negative mode as unimportant, when it hasn't actually been optimized specifically.
Answer: The acetonitrile and methanol eluents showed similar results for the separation.
Modifications: Table 2 "**No (direct injection)**" was replaced by "**None**"; "**ESI$^+$-MS**" was replaced by "**ESI+-MS/ ESI$^-$-MS**"

line 199 "**In EXP C1 and C2, aqueous solutions of AS were directly injected into the LC-MS, and two elution solvents were tested to optimize the chromatographic separation, the signal was only monitored in ESI+.**" was replaced by "**In EXP C1 and C2, aqueous solutions of AS were injected into the LC-MS, and two elution solvents were tested to optimize the chromatographic separation.**"

Line 315 one sentence was added: "**The acetonitrile and methanol eluents showed similar results for compound separation.**"

Line 221: "slightly higher (respectively lower)" – this is unclear and I don't follow the meaning.
Modification: line 221 "**Overall, it was observed that [Org]/[Sulfate] varied from 1.5 % to 3.8 %, slightly higher (respectively lower) than in the two previous studies mentioning the presence of organic in laboratory experiments on AS particles (respectively Badger et al., 2006 and Trainic et al., 2011).**" was replaced by "**Overall, it was observed that [Org]/[Sulfate] varied from 1.5 % to 3.8 %, in the range of the values reported by studies mentioning the presence of organic compounds in laboratory experiments on AS particles (0.8 wt % of C in Badger et al., 2006 and up to 8% in Trainic et al., 2011)**".

Line 237: what is the source of the nitrate ions?
Answer: They are organic nitrates rather than inorganic nitrates according to the ratio NO$_2^+$/NO$^+$. See our answer to remark for line 159.

Line 240: "large organic molecules"? The AMS doesn't provide justification for this statement. The LC-MS may, but I don't think this statement is justified here. Also, what does "large" mean?
Answer: "large" was removed from the sentence in the revised manuscript.

Figure 4: While not outside your uncertainties, there certainly seems to be a pattern in the effect of concentration on the ratio. Can this data be included in the SI?
Answer: No pattern was found in the effect of concentrations on the ratio

Line 255: what does "multi-characterization" mean here?
Answer: It means the characterization on the size of aerosol particles using d_m, d_a, d_{va} and d_{ve}.
Modification: line 254 "**To achieve this calculation, a thorough study of the morphology of AS particles was needed which was obtained from multi-characterization of particle size.**" was replaced by "**To achieve this calculation, a thorough study of the morphology of AS particles was performed using the various sizes measurements (Appendix A)**".

Figure 6: I would change the colour scheme here – I got confused with the standard AMS colour scheme i.e. red = sulfate.

Answer: the color in the figure 6 was changed.

Modification: line 311 one sentence was added in the figure caption: "**The error bars represent the standard deviation from averaging multiple measurements.**"

Line 322: Give the DBE for the neutral masses not the ions.

Answer: done

Modification: line 322 "**The double bond equivalence varies from 1.5 to 5.5 showing that the molecules are unsaturated and potentially cyclic.**" was replaced by "**The double bond equivalence (DBE) varies from 1 to 5 showing that the molecules are unsaturated and potentially cyclic.**"

SI8(SI6 before the modification) one column was added to show the DBE of major ions.

Line 325 – 327: This sentence doesn't make sense. Needs reworded.

Answer: the sentence was split in three: "The mass error was always well below 5 ppm and no raw formula with sodium adduct was suggested. Some of the m/z showed two different retention times, implying potentially the presence of isomers. For example, at m/z 226.1918, two peaks were detected, one at 2.89 minutes and the other at 3.11 minutes as described in details in SI8 for the most intense ions. In the negative ESI mode, the signal was overwritten by the sulfate ion (detected at [M+H]⁻: 96.9596, HSO₄⁻) along the whole chromatogram, due to the high ammonium sulfate concentrations used."

Figure 7: Is this the TIC or base peak chromatogram? I assume the later due to the quality of the chromatogram.

Answer: This figure is the base peak chromatogram. The precision was added in the figure caption.

Line 334 and earlier – To me direct injection means injection of a solution directly into the MS source without prior chromatography. This needs to clarified.

Answer: "direct" was removed from these sentences.

Modification: line 314 "**In EXP C1 and C2, an aqueous solution of ammonium sulfate (99.5 %) at 1.5 M was directly injected and was analyzed in the positive mode.**" was replaced by "**In EXP C1 and C2, an aqueous solution of ammonium sulfate (99.5 %) at 1.5 M was injected and analyzed in the positive mode.**"

line 333 "**In the positive mode, more than 60 % of the molecules identified by direct injection were also detected.**" was replaced by "**In the positive mode, more than 60 % of the molecules identified without the extraction step were also detected.**"

Line 340: I think "mark" should be "make"

Answer: "mark" was replaced by "brand" in the revised paper.

Line 339: no data is presented to back up the "factor or 20 lower" – can you include a chromatogram in the SI?

Answer: a chromatogram (SI9) was added in the SI.

Line 355: Is the mass accuracy really good enough to assign a C24 peak?

Answer: Yes, it is, combined with the isotope prediction algorithm, and the defined atomic ranges.

Line 379 – add the particle size to this final statement.

Answer: size range was added in the revised paper.

Modification: line 379 "**In this case, the organic traces are lower than 2.5 % on the AS particles.**" was replaced by "**In this case, the organic traces are lower than 2.5 % on the AS particles with d_m = 130 to 336 nm (corresponding to d_a = 200 to 500 nm).**"

Line 394-396: This needs to be reworded – it seems like one sentence split into 3

Modification: line 394 "**As these molecules were largely detected in the positive mode by LC-MS, all carrying at least one nitrogen atom. Based on the observation that they are coated at the surface of the suspended AS**

particles. It can be suggested that they are cationic surfactants such as quaternary ammonium salts remaining from the manufacturing processes.” was changed to**: “These nitrogenous molecules were abundantly detected by LC-MS in AS solutions in the positive ESI mode, and in the nebulized solutions, they were observed to be coated on the surface of AS aerosol particles. Thus, it could be suggested that they might be cationic surfactants such as quaternary ammonium salts remaining from the manufacturing processes.”**

Several other modifications were made throughout the text to improve the manuscript