

1 Response to reviewers for the paper:

2 **Aerosol pH Indicator and Organosulfate Detectability from Aerosol Mass Spectrometry**
3 **Measurements**

4 Schueneman et al., *AMTD*, 2020

5 We thank the reviewers for their useful comments on our paper and for their time spent
6 reviewing it. To guide the review process we have copied the reviewer comments in black text.
7 Our responses are in regular blue font. We have responded to all the referee comments and made
8 alterations to our paper (in bold text). *Changes to text in figure captions are shown in bold*
9 *italic text.*

10 **Anonymous Referee #1**

11 Summary:

12 This paper discusses the challenges of using AMS sulfate ion fragments to distinguish organic
13 sulfates from inorganic sulfates and relates sulfate ion fragment ratios and ammonium balance to
14 aerosol pH calculated from E-AIM. The authors apply previously published methods [Chen et
15 al., 2019 and Song et al., 2019] to several past airborne AMS datasets to test the applicability of
16 these methods for many aerosol compositions. They also determine sulfate ion fragment ratios
17 for mixtures of ammonium sulfate (AS) C with inorganic and organic species in laboratory
18 experiments. While these methods should be useful in some regions (pH>0, low ammonium
19 nitrate - AN) based on the laboratory results presented here, the authors have determined that
20 these methods often produce nonsensical values (negative OSf enrichment), suggesting that these
21 methods cannot be used universally across all aerosol compositions. Specifically, high AN and
22 high acidity change the way that sulfate interacts with the AMS vaporizer and prevents use of the
23 Chen method in polluted (high AN) and remote marine regions (high acidity). However, even in
24 the regions that should give good results (low AN, low acidity), the calculated organic sulfate
25 fraction is often negative. The authors also show that sulfate ion fragments ratios correlate to
26 E-AIM-calculated pH under certain conditions (pH<0, low AN), but correlations of measured
27 ammonium balance with calculated pH are generally better.

28 General Comments:

29 As more people apply the methods described in Chen and Song to estimate organic sulfate from
30 sulfate ion fragment ratios in a variety of atmospheric environments, the challenges to those
31 methods highlighted in this paper will arise. The authors show that the Chen and Song methods
32 are not always reliable for all aerosol compositions when applied to large AMS datasets
33 accumulated over several campaigns spanning geographical locations, seasons, altitudes, and
34 chemical regimes. They provide explanations as to how the sulfate ion fragment ratios are
35 affected by high acidity, high AN, and somewhat by high organic aerosol concentrations at the

36 AMS vaporizer through laboratory experiments. This paper is of interest to many AMS users
37 (and data users) as estimating organic sulfate fractions are applied to past and future datasets.
38 Overall, this work is highly important and should be published after addressing the following
39 comments below.

40 R1.1, This paper contains important results and discussion of interest to a large audience, but it
41 would benefit from trimming and streamlining the text to improve readability. There is a lot of
42 data and interesting analytical subtleties, but the paper frequently jumps around, especially when
43 describing figures. For example, Fig. 1 is complex with a lot of data (lab plus field campaigns).
44 Parts of this figure are described for the first time in disjointed places: Sect 3.1, 3.3 (but not 3.2),
45 and 3.5.1. To help connect the laboratory and field applications of the Chen method, I suggest
46 that the description and discussion of Fig. 1 be presented in its entirety and Section 3.2, which
47 contains explanations for how the AMS responds to various species, could be reduced, moved, or
48 integrated into the discussion of Figure 1.

49 We have revised the paper and streamlined the text where possible. We have kept what was Sect.
50 3.2 in the AMTD version (interpretation of sulfate fragmentation) and moved it to be Sect. 3.3
51 (after the section about applying the triangle method to field data). Regarding that topic and also
52 Fig.1, we discussed internally before submission whether to break up Figure 1 into several
53 figures, and went through several iterations and ordering of the sections. At the end we found
54 that alternative configurations also had their own problems, given that the topics are quite
55 complex and interrelated. Therefore we prefer to keep Fig. 1 as it is, which has the important
56 advantage of allowing easy comparison of all the data in one place.

57 The new section 3.3 (3.2 in AMTD) contains very useful details for AMS / ACSM users who
58 wish to understand the trends, and with the new organization (3.1: laboratory data, 3.2: aircraft
59 data, and 3.3: interpretation) we believe it does not need to be trimmed. However, it does contain
60 too much detail for others that are not very familiar with AMS details and may only be interested
61 in using data provided by others. To clarify this and guide the flow of the paper for different
62 readers, we have added the following text at the start of section 3.3:

63 **“We note that this section (3.3) should be of most interest for AMS/ACSM users, and can**
64 **probably be skipped by others.”**

65 Specific Comments:

66 R1.2, In 58. Can you/ did you apply these methods to ACSM data? It seems that assumptions
67 about hydrocarbon contributions at unit mass resolution, especially at m/z 81 (HSO_3^+ , C_6H_9^+ ,
68 $\text{C}_5\text{H}_5\text{O}^+$), would further increase uncertainty in this quantification. Just an interesting thought,
69 since the ACSM was brought up here.

70 No, we did not apply these methods to ACSM data. We have added the following text to address
71 this point:

72 **“We have not explored the application of these methods to ACSM data. ACSM data are**
73 **unit-mass resolution, and the interferences between species at a given unit mass are**
74 **estimated using a fragmentation table approach (Allan et al., 2004). This approach**
75 **introduces more uncertainties, as exemplified by Hu et al. (2015) for similar**
76 **fragment-based methods.”**

77 R1.3, ln 76. Please check that these are the intended citations. I don't see organic sulfate
78 fractions in Riva 2019a “Evaluating the performance of five different chemical ionization
79 techniques for detecting gaseous oxygenated organic species,” so perhaps that is not the correct
80 reference.

81 You are correct, we mistakenly cited the wrong Riva et al. (2019). It has been corrected in the
82 text and bibliography:

83 **“Until recently, most studies have shown that the OS molar fraction ($OS_f = OS / (AS + OS)$,**
84 **calculated using only the sulfate moiety of the molecules) typically makes a small (~1-10%)**
85 **contribution to total sulfate in PM₁ (e.g. (Tolocka and Turpin, 2012; Hu et al., 2015; Liao et**
86 **al., 2015; Riva et al., 2016, 2019)).”**

87 **Citation:“Riva, M., Chen, Y., Zhang, Y., Lei, Z., Olson, N. E., Boyer, H. C., Narayan, S.,**
88 **Yee, L. D., Green, H. S., Cui, T., Zhang, Z., Baumann, K., Fort, M., Edgerton, E.,**
89 **Budisulistiorini, S. H., Rose, C. A., Ribeiro, I. O., E Oliveira, R. L., Dos Santos, E. O.,**
90 **Machado, C. M. D., Szopa, S., Zhao, Y., Alves, E. G., de Sá, S. S., Hu, W., Knipping, E. M.,**
91 **Shaw, S. L., Duvoisin Junior, S., de Souza, R. A. F., Palm, B. B., Jimenez, J.-L., Glasius, M.,**
92 **Goldstein, A. H., Pye, H. O. T., Gold, A., Turpin, B. J., Vizuete, W., Martin, S. T., Thornton,**
93 **J. A., Dutcher, C. S., Ault, A. P. and Surratt, J. D.: Increasing Isoprene**
94 **Epoxydiol-to-Inorganic Sulfate Aerosol Ratio Results in Extensive Conversion of Inorganic**
95 **Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties,**
96 **Environ. Sci. Technol., 53(15), 8682–8694, doi:10.1021/acs.est.9b01019, 2019.”**

97 R1.4, ln 91. Instead of writing “inorganic” in quotations, be please specific: that these are ions
98 that do not contain carbon and are typically categorized as /associated with inorganic sulfate.
99 However, organic sulfate can also produce these ions.

100 We have revised the text to state:

101 **“The vaporization and ionization of AS and OS in the AMS produce similar ion fragments**
 102 **that do not contain a carbon atom, the major ones quantified being SO^+ , SO_2^+ , SO_3^+ , HSO_3^+ ,**
 103 **and H_2SO_4^+ . These ions were attributed primarily to inorganic sulfate in earlier AMS**
 104 **analyses (e.g. Jimenez et al. (2003)), but have been known to have a contribution from**
 105 **organosulfates since Farmer et al. (2010).”**

106 R1.5, ln 93. Decomposition or evaporation + ionization rather than ionization/decomposition?
 107 Section 3.2 and Fig 2C does a nice job of explicitly showing which species evaporate or
 108 thermally dissociate (and ionize) to form which ions, so perhaps use the same ideas and
 109 consistent language here and move parts or all of Fig 3 to the introduction.

110 See response to R1.1.

111 R1.6, Table 1. Be consistent. i.e. DC3: Summer 2012. ATom-1: Boreal Summer/ Austral Winter
 112 [sampling covered both northern and southern hemispheres at the same time but in different
 113 seasons, correct?

114 The table has been updated to read:

Campaign	Location	Season/Year	References	Reference Label
DC3: Deep Convective Clouds and Chemistry	Mid-Latitude Continental United States	Spring/Summer 2012	Barth et al., (2015)	A
SEAC ⁴ RS: Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys	Continental United States	Summer 2013	Wagner et al., (2015); Toon et al., (2016)	A, F, C
WINTER: Wintertime Investigation of Transport, Emissions, and Reactivity	Eastern United States, continental and marine	Winter 2015	Jaeglé et al., (2018); Schroder et al., (2018)	A, F, C
KORUS-AQ: Korean United States Air Quality	South Korean Peninsula and Yellow Sea	Spring 2016	Nault et al., (2018)	A, F, C
ATom-1: Atmospheric Tomography Mission 1	Remote Pacific and Atlantic Basins	Boreal Summer/ Austral Winter	Brock (2019); Hodshire et al., (2019); Hodzic	A, F, C

		2016	et al., (2020)	
ATom-2: Atmospheric Tomography Mission 2	Remote Pacific and Atlantic Basins	Austral Summer/Boreal Winter 2017	Hodzic et al., (2020)	A, F, C

115 R1.7, ln 266. Definition of HySOx: The distinction between its definition in Eq 5 ($\text{HySOx} =$
116 $\text{H}_2\text{SO}_4 + \text{HSO}_3$) and Eq 10 ($\text{HySOx} = \text{H}_2\text{SO}_4 + \text{HSO}_3 + \text{SO}_3$) is clear in the text, but it's
117 annoying to have two definitions (and quantities) for the same variable in one paper. The
118 distinction is lost when first introduced (total sulfate signal is defined on ln 96, but an undefined
119 HySOx is used on ln 106).

120 We apologize for the confusing notation. This mistake occurred because Song et al. ((2019) and
121 Chen et al. (2019) were defining the term H_ySO_x^+ differently. We have changed the notation
122 when we describe the Song et al. method, as $\text{H}_y\text{SO}_x^{+,*}$ as shown here:

123 **$\text{H}_y\text{SO}_x^{+,*}$ (which differs from the notation used in Song's paper, but is necessary to**
124 **differentiate H_ySO_x^+ between the Chen and Song papers) is defined in Song et al. (2019) as**
125 **$(\text{SO}_3^+ + \text{HSO}_3^+ + \text{H}_2\text{SO}_4^+)$.**

126 R1.8, ln 352. What altitude is this? This reference to the DC-8 seems out of context. Does this
127 paragraph only address marine amines at minimum altitudes during ATom only?

128 The ATom campaigns took place on board the NASA DC-8, which is why it is mentioned here.
129 Upon further inspection of Sorooshian et al. (2009), cited in that section, we have revised the text
130 to say:

131 **“Another study found that amine mass concentration dropped off quickly with altitude to**
132 **concentrations less than 25 ng m^{-3} at an altitude between 200 and 300 m, which is the**
133 **approximate minimum altitude flown on the DC-8 during the ATom campaigns**
134 **(Sorooshian et al., 2009).”**

135 R1.9, ln 347-364. Consider moving this paragraph from the methods to discussion section

136 We originally had this section in the discussion but feel it is important to bring this topic up in
137 the methods as it gives credence to the pH results we get from E-AIM. Also, several colleagues
138 have asked us about the impact of amines on our pH calculations, which is another reason to
139 discuss it in the methods to support the validity of the estimation. We also cannot find a location
140 in the discussion section where this text would not be a distraction in the flow of the manuscript.

141 R1.10, ln 387. The thing that strikes me about Figure 1 is that even though “data are expected to
142 lie inside the triangular region,” few of the lab or field averages do! The AS lab cases that should
143 show have fragment ratios of pure AS, do not, and this is explored. The field campaign averages
144 also do not have fragment ratios consistent with calibration AS, and this is partially explored.
145 Stating this discrepancy up front would improve readability of the discussion section.

146 We agree and have added another sentence to the end of that paragraph commenting on this
147 observation (which we explore further in the following sections):

148 **“From applying this method, it is clear that none of the campaign averages or laboratory**
149 **data falls between the [0,0] and [1,1] points, suggesting that there may be additional factors**
150 **(other than sulfate composition) impacting the location of data in this triangular region.”**

151 R1.11, ln 395. I think this example is unnecessary. If I’m understanding correctly, even if 50:50
152 OS:AS gives a non-negative OS_f in the AN_f= 0.95 case, the method would indicate there is no
153 OS which is also not correct. Another way to say this is that as the endpoint for AS with high AN
154 moves away from pure AS due to the interference from AN, the method estimates OS_f with
155 increasing inaccuracy so that it would predict OS_f= 0%, when OS_f is really 50% in this extreme
156 case. So, even though the result (OS_f = 0) is a “reasonable” non-negative OS_f, it is still
157 completely incorrect.

158 We have modified the explanation to follow the structure in the reviewer’s comment, to enhance
159 the readability of this section and provide increased clarity as to why the OS_f method can be
160 incorrect even in the situation where it provides a value > 0. We have changed the text as:

161 **“When AN_f is increased past 0.50, there is an increase in both $nfH_ySO_x^+$ ions, even when all**
162 **of the particulate sulfate is inorganic. As the particle AN_f increases up to AN_f=0.95, the OS_f**
163 **estimation becomes increasingly inaccurate. The method may estimate OS_f=0% in the**
164 **latter situation, when OS_f is actually 50%. While OS_f=0% may be reasonable in some parts**
165 **of the atmosphere, and one may be inclined to accept this result as it is non-negative, it is**
166 **actually incorrect due to the effect of particulate AN.”**

167 R1.12, ln 399. Figure 2b does not effectively show the information in this paragraph since the
168 points overlap on a small region of the plot. What is the ratio of OA/AS when OA > 100 ug/m³?
169 All other experiments are in relative terms, so 100 ug/m³ does not have any context here. How
170 does OA/AS ratio compare to that of the campaign averages? The regime II averages?

171 We assume the reviewer is referring to Figure 1b, not 2b. We agree that all of the details of the
172 OA_f trend discussed in that paragraph may not be fully discernable in Fig. 1a. We have revised
173 the text to also refer the reader to the specific panels in Figure S6 earlier and throughout this

discussion. Those figures clearly show all of the trends described for each dataset separately. However, we consider it informative to include the summary of that data as Fig. 1b for direct comparison to the other effects in the other panels, with all graphs on the same scale. The fact that for all experiments at modest OA concentrations $nfH_ySO_x^+$ ratios are only slightly altered is the most important observation for ambient data considerations. We have also listed the average OA_f values for the two average $OA > 100 \mu g/m^3$ points on the Fig. 1 caption and stated the maximum OA values that are beyond the colorbar scale for the two terpene datasets in Figs. S6 a,c (in caption). Additionally we added a description of the 2014 terpene SOA trends which were not previously discussed.

The revised text for that paragraph and the figure captions now read:

R1.12a: Revised text (Sect. 3.1):

“The effect of OA internally mixed with AS on the sulfate fragmentation pattern was also explored with toluene, alkanol, and monoterpene SOA (Fig. 1B and Fig. S6). For the alkanol SOA experiments we found that the presence of even a small coating of alkanol SOA (which is thought to be liquid (Liu et al., 2019)) shifts the normalized AS [1,1] point to $\sim[1.08,1.08]$, but increases in the fraction of OA (OA_f) from 0.1 to 0.3 lead to no further changes in $nfH_ySO_x^+$ (Fig. 1B). This means that for a sample containing a mixture of AS and alkanol SOA, the calculated OS_f would be -15% (Chen). In contrast, toluene SOA, which spans $0 < OA_f < 0.5$, shows no clear change in the $nfH_ySO_x^+$ ions, indicating that OA_f would not bias the Chen method for this example. The monoterpene SOA, from two different experimental datasets (2014 and 2015) using different AMSs, show more varied results than the previous two studies. Overall, the 2014 data shows a very small increase in the “pure” AS value in the OA_f range 0-0.50, whereas the 2015 monoterpene data shows a consistent and constant 10-20% increase in $nfH_ySO_x^+$ compared to the pure AS calibration point (similarly to the alkanol SOA). However, when OA_f is in the range of $0.50 < OA_f < 0.70$, 30-40% increases are observed for the 2014 and 2015 data. This result is only applicable to a few of the experiments (see Fig. S6), potentially due to very high SOA loadings (up to $300 \mu g m^{-3}$). These high OA concentrations could potentially lead to a change of the particle phase due to condensation of more volatile and liquid species, potentially altering the interactions of the particles and the vaporizer surfaces. These experiments collectively suggest that a “pure” AS calibration point of $[1.15,1.15]$ may be more appropriate when applying the Chen et al. method to some mixed aerosol at typical OA concentrations observed in the atmosphere; this is discussed further in Sect. 3.2.”

R1.12b: Figure 1 caption:

“Fig. 1. Laboratory and field data for sulfate fragmentation shown in the triangle diagram proposed by Chen et al. (2019). (A) Data split into 10 quantiles of AN_f value for the full

210 *KORUS-AQ campaign, as well as for different laboratory internal mixtures of AS and AN.*
 211 *(B) Data from two chamber experiments, split into 5 quantiles of OA_f . Data with very high OA*
 212 *($>100 \mu\text{g m}^{-3}$) are shown as grey triangles. The average of OA_f for the very high OA data in*
 213 *2014 and 2015 is 0.8. Two separate datasets of monoterpene SOA chamber experiments are*
 214 *labelled as “2014” and “2015”. (C) Data split into 10 quantiles by calculated pH for ATom-1*
 215 *and 2, colored by calculated pH from E-AIM. (D) Averages for 5 aircraft campaigns for the*
 216 *full campaign and a subset of each campaign where $\text{pH}<0$ and $AN_f<0.3$.”*

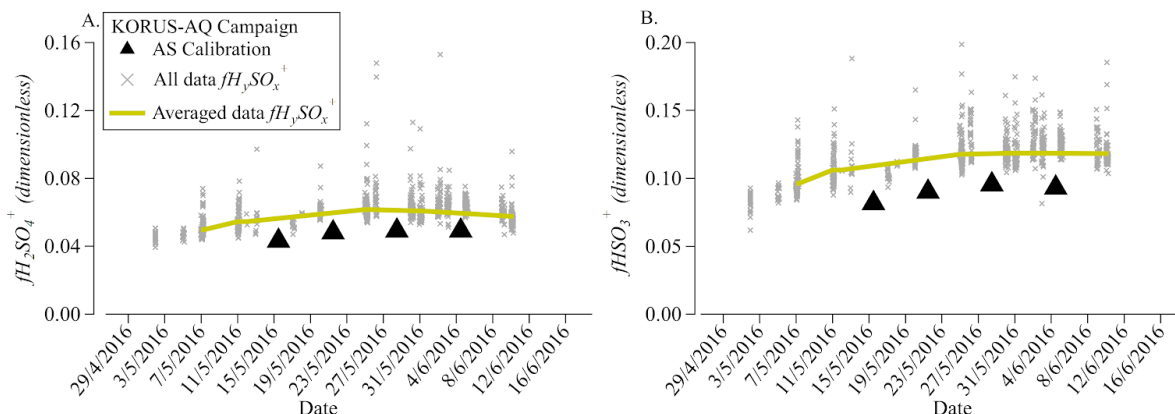
217 R1.12c: Figure S6 caption:

218 *“Fig. S6. $fH_ySO_x^+$ ions vs. OA_f colored by total OA concentration (left and bottom right) and*
 219 *top right colored by experiment index. All data are from chamber experiments where SOA was*
 220 *formed on ammonium sulfate seed aerosol from (A, B, C, D) nitrate radical reaction with*
 221 *monoterpenes (where 2014, 2015 represent different series of experiments done in different*
 222 *years and different instruments), and photooxidation of (E) alkanols and (F) toluene. The*
 223 *maximum [OA] concentrations observed in (A) and (C) are 204 and $206 \mu\text{g m}^{-3}$, respectively.*
 224 *The $fH_ySO_x^+$ ratios have been normalized to the average ratios for the ammonium sulfate seed*
 225 *for each experimental dataset.”*

226 R1.12d: We also added another paragraph and figure (Fig. S7) to Sect. 3.2 and the SI, with text
 227 stated as such:

228 *“The effect of OA (shown in Fig. 1B for laboratory data) on sulfate fragmentation in*
 229 *ambient data is less clear due to the lack of data that has a lower AN_f , higher pH, and*
 230 *little/no OS (see Table S1 for average campaign OA_f). In the presence of any one of those*
 231 *factors, the sulfate fragmentation will be affected. It is especially challenging to confirm the*
 232 *absence of OS, due to the lack of direct total OS measurements available. In Fig. S7, we*
 233 *isolate a subset of the KORUS-AQ dataset (where $AN_f<0.3$ and $\text{pH}>0$, defined as “regime*
 234 *II” and discussed in detail in Sect. 3.4) to see if there is an offset in the AS under these*
 235 *chemical conditions as observed in the laboratory data shown in Fig. 1B. Similarly to the*
 236 *lab data, there appears to be a $\sim 10\%$ offset between the pure AS $fH_ySO_x^+$ values from*
 237 *calibrations, and the KORUS-AQ data that occupies regime II (average $OA_f\sim 43\%$). This*
 238 *offset is smaller than some of the offsets observed in from the laboratory data (Fig. 1B and*
 239 *S6), but may hinder the ability of the Chen OS_f quantification method to estimate [OS]*
 240 *even in conditions where the $\text{pH}>0$ and the $AN_f<0.3$.”*

241 R1.12e: SI Figure S7 and caption:



242 ***“Fig. S7. $fH_2SO_4^+$ ions (not normalized) vs. time for AS calibrations and ambient sampling for***
 243 ***the KORUS-AQ campaign. (A) shows $fH_2SO_4^+$ and (B) shows $fHSO_3^+$. The yellow line shows***
 244 ***smoothed, average data for the campaign, and the grey points show the non-averaged ambient***
 245 ***data. Black triangles show the average $fH_2SO_4^+$ values for four pure AS calibrations done***
 246 ***during KORUS-AQ.”***

247 R1.13, ln 415. The hypothesis here is that you can change the relative HxSOy fragments due to
 248 different residence times on the vaporizer for OA-coated particles (i.e. less bounce, more thermal
 249 decomposition)? Update: I see this gets discussed more in Section 3.2, so perhaps it would be
 250 better to introduce these ideas within Section 3.1.

251 See response to R1.1.

252 We have modified the text to make an explicit reference to section 3.2 (now 3.3) for interested
 253 readers:

254 ***“These high OA concentrations could potentially lead to a change of the particle phase due***
 255 ***to condensation of more volatile and liquid species, potentially altering the interactions of***
 256 ***the particles and the vaporizer surfaces (see section 3.3).”***

257 R1.14, ln 425. I suggest putting Section 3.2 somewhere else. Before 3.1? After 3.3? Figure in the
 258 SI with the key points in the discussion of Fig 1? Moving the generalize fragment discussion (Fig
 259 3C) to the intro? Figure 1 includes both lab and field data, and it seems odd that the discussion of
 260 a single figure is broken up like this without any indication that the discussion will be picked up
 261 again. I got to the end of Section 3.1 wondering about Fig 1D and why all the campaign averages
 262 are out still of the “Chen triangle.” It seems to me that Section 3.2 contains the analytical crux of
 263 why this method isn’t universally applicable, so this is an important section. It just seems in a
 264 weird place. This discussion of the AMS response is applicable for both the lab and field data, so
 265 I think it makes sense to describe Figure 1 in it’s entirety, and then, as a discussion, talk about the

266 fragmentation for these different conditions (in context of both the lab experiments and the
267 complex mixtures in the ambient data).

268 See the responses to R.1.1. After having tried alternative ordering of the material, we agree that
269 the order suggested by the reviewer would be less confusing. We now describe all of Fig. 1 in
270 Sect. 3.1 and Sect. 3.2, and then describe Fig. 2 in Sect. 3.3.

271 R1.15, ln 458. Based on this explanation, that particles with longer contact time with the
272 vaporizer experience higher temperatures and thus more thermal decomposition, I would expect
273 the sulfate ion fragment ratios to depend on the vaporizer temperature. Has sensitivity to
274 vaporizer temperature been tested?

275 This is a good point. Relevant data were included in a previous study, and we have added the
276 following text to refer to them here:

277 **“Consistent with this interpretation, it was shown that the $\text{H}_2\text{SO}_4^+/\text{SO}^+$ fragment ratio**
278 **increased as the vaporizer temperature was reduced while sampling ambient air, while the**
279 **$\text{SO}_2^+/\text{SO}^+$ ratio did not change (Docherty et al. (2015), their figure S5).”**

280 R1.16, ln 506. Define $\text{pH}>0$ and $\text{AN}<0.3$ as Regime II here in the text. Combine this paragraph
281 with ln 526-533.

282 We do not agree that line 506 and the paragraph in lines 526-533 should be combined, as this
283 could potentially create confusion. In this text we first introduce Fig. 1D and say what we
284 observe, then go through it by discussing ATom and KORUS-AQ campaigns, and finally
285 explaining the additional points from the SEAC⁴RS and WINTER campaigns. We did change the
286 text to specify regime I:

287 **“In Fig. 1D, average values for each campaign in regime I, defined as $\text{AN}_f < 0.3$ and**
288 **calculated $\text{pH} > 0$, are shown.”**

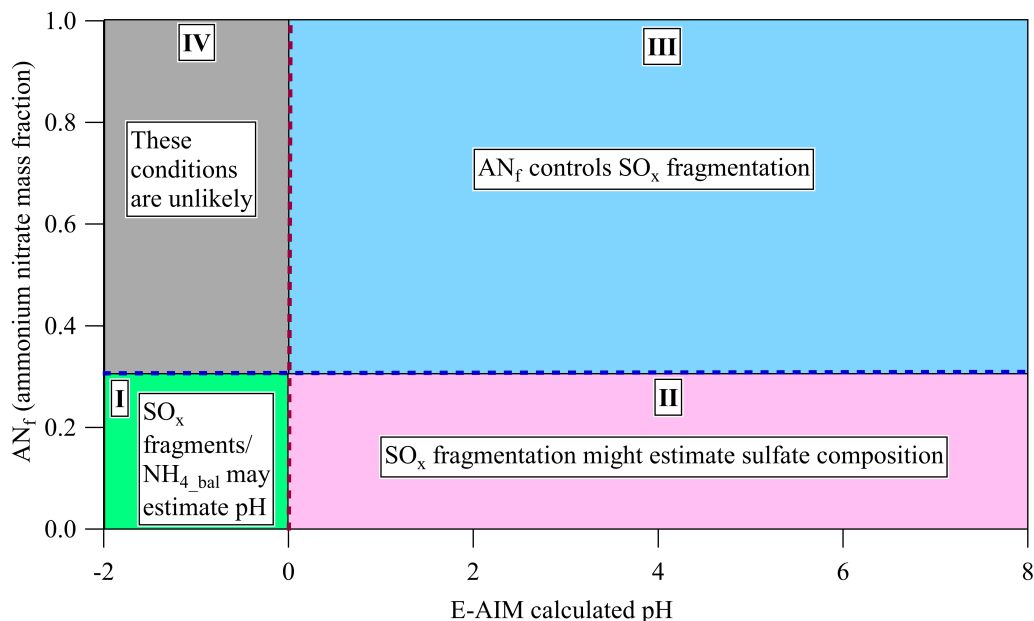
289 R1.17, ln 533. This is a general comment: I’m struggling with the paper setting up the discussion
290 that even though the proposed method does not work for high acidity or high AN as shown in the
291 lab results, it will work for subsets of ambient data that meet the criteria ($\text{pH}>0$; $\text{AN}<0.3$).
292 However, in the end, the method does not work for any subsets of the ambient data as shown in
293 Fig. 1D. This is partially explained by organic aerosol moving the AS fragment ratio away from
294 (1,1). Figuring out when/where these methods are applicable seems like an important result from
295 this paper, and Section 3.4 regarding GEOS-Chem assumes that reasonable OSf can be obtained
296 for Regime II. However, the results in Fig 1D and text ln 564-566 indicate that non-negative OSf
297 is not attainable using this method for these past campaigns, even in environments not affected

298 by known interferences on the sulfate fragmentation (i.e. acidity and AN). Perhaps, the
299 recommendation is that if aerosol is in one of the other 3 regimes, more work will be needed to
300 understand the influence of H₂SO₄ or AN, but if the aerosol is in regime II, the method may or
301 may not work, depending on how much OS, AS, and OA are present.

302 We have revised the text to make clearer that even when considering only the data in regime II,
303 that appears unaffected by AN_f and pH, the OS_f method still failed for most of our campaigns.
304 The only way to truly know if the OS estimation method works is to have a completely
305 independent measurement of total OS. An approximation to total OS was only available to us for
306 ATom-1 and -2, and we comment on this on the revised text. We have altered the wording of
307 Sect. 3.4, in reference to regime II, to make it clear that this method did not work for our
308 datasets:

309 **“Regime II (lower right) involves less acidic conditions (calculated pH > 0) and lower AN_f**
310 **(< 0.3). In this region sulfate fragmentation in the AMS is not strongly impacted by either**
311 **AN_f or acidity. In principle, in this regime the recently proposed sulfate deconvolution**
312 **methods could be applicable. The geographical regions studied in Chen et al. (2019) and**
313 **Song et al. (2019) generally fall in this regime, and this might explain the lack of large**
314 **negative OS_f values in those studies, in contrast to our observations for other regions.**
315 **About half of our campaign data is located in this regime, more so for the continental**
316 **campaigns and much less so for the remote campaigns. Specifically, 65% of KORUS-AQ,**
317 **60% of DC3, 87% of SEAC⁴RS, 11% of ATom-1 and 20% of ATom-2 fall in this regime. We**
318 **have applied the 1D version of the Chen method to each field campaign after filtering it by**
319 **the AN_f and calculated pH constraints for regime II. OS_f is nominally slightly greater than**
320 **zero for ATom-1, OS_f ~ 3%, of the order of the 0.3% estimate in regime II from PALMS**
321 **(for ATom-1 and ATom-2, estimated by only considering the sulfate moiety from the**
322 **IEPOX or glycolic acid sulfate (GAS) OS, neither of which was detected in the supermicron**
323 **aerosol (Froyd et al., 2009, 2019; Liao et al., 2015)(see Fig. S7). However, OS_f is much less**
324 **than zero for ATom-2 (OS_f ~ -23%) and KORUS-AQ (OS_f ~ -26%). These unreasonable**
325 **results may be due to the effect of OA on sulfate fragmentation in the AMS (discussed in**
326 **Sect. 3.2). For this reason, strong caution is advised in applying OS_f estimation methods to**
327 **ambient data, even in regime II. In addition, estimating OS with sulfate ions may be**
328 **susceptible to errors due to inaccuracies in AS calibrations, noise present in the ambient**
329 **data, or other factors.”**

330 New abstract figure:



331 R1.18, ln 536. Add “estimated” or “calculated” before pH here and for other uses

332 We have clarified this in the methods section with the text below as (and modified the paper
333 accordingly):

334 **“We have added the modifier “calculated” before pH for all situations where we are**
335 **describing the E-AIM pH, and “estimated” when we refer to pH from the empirical**
336 **estimation methods from AMS measurements, introduced in this study.”**

337 R1.19, ln 550-566. Like the previous comment, this paragraph sets it up like this method will
338 work for specific conditions (Regime II), but its conclusion is that it still gives large negative
339 OSf values for Regime II, but for errors in calibrations, noise and “other factors.”

340 See the response to comment R1.17.

341 R1.20, ln 620. This is either inconsistent with the definition of fH₂SO₄ in Eqns 1 and 3 or it is
342 written in a misleading way. Please correct and be specific.

343 We accidentally wrote our new variable, H_ySO_x⁺/SO_x⁺ instead of the fH_ySO_x values. This has
344 been corrected:

345 “Fig. 1C shows that $fH_2SO_4^+$ and $fHSO_3^+$, i.e. the amount of sulfate fragments retaining one
346 or two hydrogens ($H_2SO_4^+$ and HSO_3^+) relative to the total sulfate fragments ($H_2SO_4^+$,
347 HSO_3^+ , SO_3^+ , SO_2^+ , and SO^+) increases as calculated pH decreases.”

348 R1.21, ln 633. The pH estimation shows good correlation under certain conditions (pH estimated
349 from E-AIM <0), so I’m thinking the real-time estimate of pH from ammonium balance and
350 HySOx/SOx is useful only if you already know that you are in a highly acidic environment
351 through an independent estimation, as indicated here. Is there an alternative filter than E-AIM
352 pH<0 for the relevant conditions?

353 This is not correct for the better method (ammonium balance), as the method itself allows you to
354 know whether you are in a part of the atmosphere when the method works, i.e. where ammonium
355 balance < 0.65. Another rule of thumb is to look at data that is exclusively outside of the
356 boundary layer. This is mentioned already in the conclusions. We have also added a brief
357 statement to Sect. 3.5.2:

358 “As shown in Fig. 6, NH_{4_bal} and calculated pH for the aircraft studies show a strong and
359 consistent relationship in regime I (calculated pH < 0), providing another potential method
360 for estimating pH (all one needs to use this method is the ammonium balance, and if it is <
361 0.65, the method should be applicable).”

362 The reviewer is correct for the fragment-based pH estimation method, but in any case that
363 method is clearly noisier and less desirable.

364 R1.22, Fig 5. Is just Regime I data shown and used for the ATom fit? (i.e. E-AIM pH<0 only for
365 ATom)

366 Figure 5 shows ATom and KORUS-AQ data, but only the data where pH<0 is fit. When pH<0,
367 the AN partitions out of the particle phase, so this is exclusively regime I data being fit. We
368 added the following text to the Fig. 5 caption:

369 “*when calculated pH<0*”

370 R1.23, Fig 7. pH estimated by nHySOx/SOx is missing for a large portion of this time series, but
371 there seems to be more data points in Fig 7D. Is this a data gap in the sampling, or an issue with
372 the application the pH estimation method?

373 You are correct, for Fig. 7B some of the data is missing for $nH_ySO_x^+/SO_x^+$ estimated pH. This is
374 because of slow evaporation of sulfate in the AMS in the second half of the transect, leading to
375 altered fragmentation. The Fig. 7 caption has been altered to mention this point as:

376 *“(B) Time series of sulfate and pH for a large power plant plume sampled during WINTER,*
377 *only a few data points are shown for pH estimated from $\text{nH}_y\text{SO}_x^+/\text{SO}_x^+$ because sulfate in the*
378 *AMS evaporated slowly during the second half of the plume transect, leading to altered sulfate*
379 *fragmentation, and this effect cannot be corrected for, due to infrequent backgrounds in*
380 *aircraft fast acquisition mode.”*

381 In Fig. 7D, we do not show the $\text{nH}_y\text{SO}_x^+/\text{SO}_x^+$ estimated pH results for the SO_2 plume during
382 WINTER because there are only a few data points.

383 R1.24, ln 707. How does one to assess whether the results for OSf are accurate for “Regime II”
384 aerosol, even if they are non-negative, given all the interferences/complexity shown here?

385 See response to R1.17.

386 A recent paper in ES&T titled “Overestimation of monoterpene organosulfate abundance in
387 aerosol particles by sampling in presence of SO_2 ” also mentions that even other OS
388 measurements in past literature may have substantial associated positive biases (Brüggemann et
389 al., 2020).

390 We have added this sentence to the introduction:

391 **“It should be noted that a recent study reports that OS filter-based measurements in past**
392 **scientific studies may have substantial associated positive biases, leading to an overestimate**
393 **for [OS] (Brüggemann et al., 2020).”**

394 We have added this sentence to the conclusions to further emphasize this point:

395 **“For the ambient data analyzed here, even in regime II the OS_f estimation produced**
396 **nonsensical results. Extreme caution is recommended to anyone who chooses to apply the**
397 **OS_f estimation methods.”**

398 Technical Corrections:

399 R1.25, Organosulfate vs organic sulfate vs organic sulfur. Pick one or make distinctions clear
400 (like it was done for MSA – that this is organosulfur, but not an organosulfate).

401 We do not see anywhere where we used the term “organic sulfur” but we have changed any
402 mention of “organic sulfate” to “**organosulfate**”, for consistency.

403 R1.26, Define “Regime” I-IV the first time that they are mentioned with both pH and ANf and if
404 they are redefined/reminding the pH and ANf, use consistent descriptions (e.g. Regime II: pH>0;
405 ANf<0.3)

406 See R1.16 for regime I definition (added to the text at the first place regime I was mentioned).

407 We also define Regime II in R1.12d.

408 Sect. 3.4 defines all of the regimes in detail. We tried adding this to the abstract, and it did not fit
409 or flow well.

410 R1.27, ln 79. Missing source of sulfate production?

411 We modified this text to read:

412 **“Another important recent subject of debate is the missing sources of sulfate production in**
413 **haze events in China...”**

414 R1.28, ln 89. “Recent AMS work.” Reference?

415 We added two references: Chen et al. (2019) and Song et al. (2019).

416 R1.29, ln 95. “Recent laboratory studies” but only one reference

417 It is only one reference, Chen et al. (2019), where they conducted multiple laboratory studies.

418 Text was changed for clarity:

419 **“However, a recent laboratory study with many OS standards found reproducible**
420 **differences in the fragmentation of AS vs OS (Chen et al., 2019).”**

421 R1.30, ln 107. Delete “based on their method”

422 The text now states:

423 **“These authors reported OS_f~17%±7% (which corresponds to [OS] ~5-10 µg m⁻³) during**
424 **winter haze episodes in China.”**

425 R1.31, ln 264. delete “as”

426 We deleted “as”.

427 R1.32, ln 310. Add model numbers of DMA and CPC in SMPS to be consistent with level of
428 detail in previous paragraph.

429 The text now states:

430 **“Aerosol composition was monitored by AMS and size distributions were monitored with a**
431 **scanning mobility particle sizer (SMPS: DMA was TSI Model 3081, electrostatic classifier**
432 **was Model 3080, and the CPC was Model 3775).”**

433 R1.33, ln 319. total inorganic nitrate?

434 It is total nitrate (organic+inorganic) which was shown in Nault et al. (2020) to not impact the
435 calculated pH or ammonium balance. The text was modified to include this:

436 **“Total nitrate (inorganic+organic) was input, as Nault et al. (2021) found that removing**
437 **estimated organic nitrate does not significantly impact the pH calculation.”**

438 R1.34, ln 318/325. Consolidate sentences. Both describe the same model input.

439 We consolidated the sentence mentioned by the reviewer, and the paragraph now states:

440 **“Aerosol pH was estimated using the Extended Aerosol Inorganic Model (E-AIM) Model**
441 **IV (Clegg et al., 1998; Massucci et al., 1999; Wexler and Clegg, 2002). We input into the**
442 **model (ran in “forward mode”), the total nitrate (gas-phase HNO_3 plus particle-phase total**
443 **NO_3^-), sulfate, ammonium, relative humidity (calculated according to the parameterization**
444 **of Murphy and Koop (2005), which is critical for upper tropospheric conditions), and**
445 **temperature. Total nitrate (inorganic+organic) was input, as Nault et al. (2021) found that**
446 **removing estimated organic nitrate does not impact the pH calculation (Nault et al., 2021).**
447 **This was done to calculate aerosol liquid water and aerosol pH. Model IV was not run with**
448 **chloride ions, as their concentrations were very low, and including chloride limits the**
449 **model to temperatures ≥ 263 K (Friese and Ebel, 2010), which would greatly limit the**
450 **analysis of calculated pH for WINTER, ATom-1, and ATom-2. We have added the modifier**
451 **“calculated” before pH for all situations where we are describing the E-AIM pH, and**
452 **“estimated” when we refer to pH from the empirical estimation methods from AMS**
453 **measurements, introduced in this study. Also, including chloride precludes running the**
454 **model under supersaturated solution conditions, which is a closer approximation of**
455 **ambient aerosol (Pye et al., 2019). All aerosol mass concentrations were from the CU AMS.**
456 **$\text{HNO}_3(\text{g})$ was measured by the California Institute of Technology chemical ionization mass**
457 **spectrometer (CIT-CIMS) (Crounse et al., 2006), which was flown in all of these missions**

458 (excluding WINTER, where the UW-CIMS was used for the HNO₃ measurements) (Lee et
459 al., 2014, 2018).”

460 R1.35, ln 320. To keep consistent tense in model description, change “is” to “was”.

461 See R1.34.

462 R1.36, ln 332. Subscript HNO₃

463 This has been done.

464 R1.37, ln 416. Remove paragraph break.

465 This has been done.

466 R1.38, ln 496. Delete D in “Fig. 1D.” Field data is in Fig 1A, C, D.

467 Fixed to say:

468 “The results of applying the Chen et al. (2019) method to five aircraft campaigns are shown
469 in Fig. 1.”

470 R1.39, ln 533. Change “breaks down” to “is not applicable” or “does not quantify OSf”

471 This text was changed to:

472 “It is observed that every single campaign average falls outside of the triangle (for the full
473 campaign and non-acidic, low AN_f averages), indicating that the Chen et al. (2019) method,
474 as proposed, is not applicable to many regions of the atmosphere.”

475 R1.40, ln 570. Change % OS to OSf

476 Fixed to say:

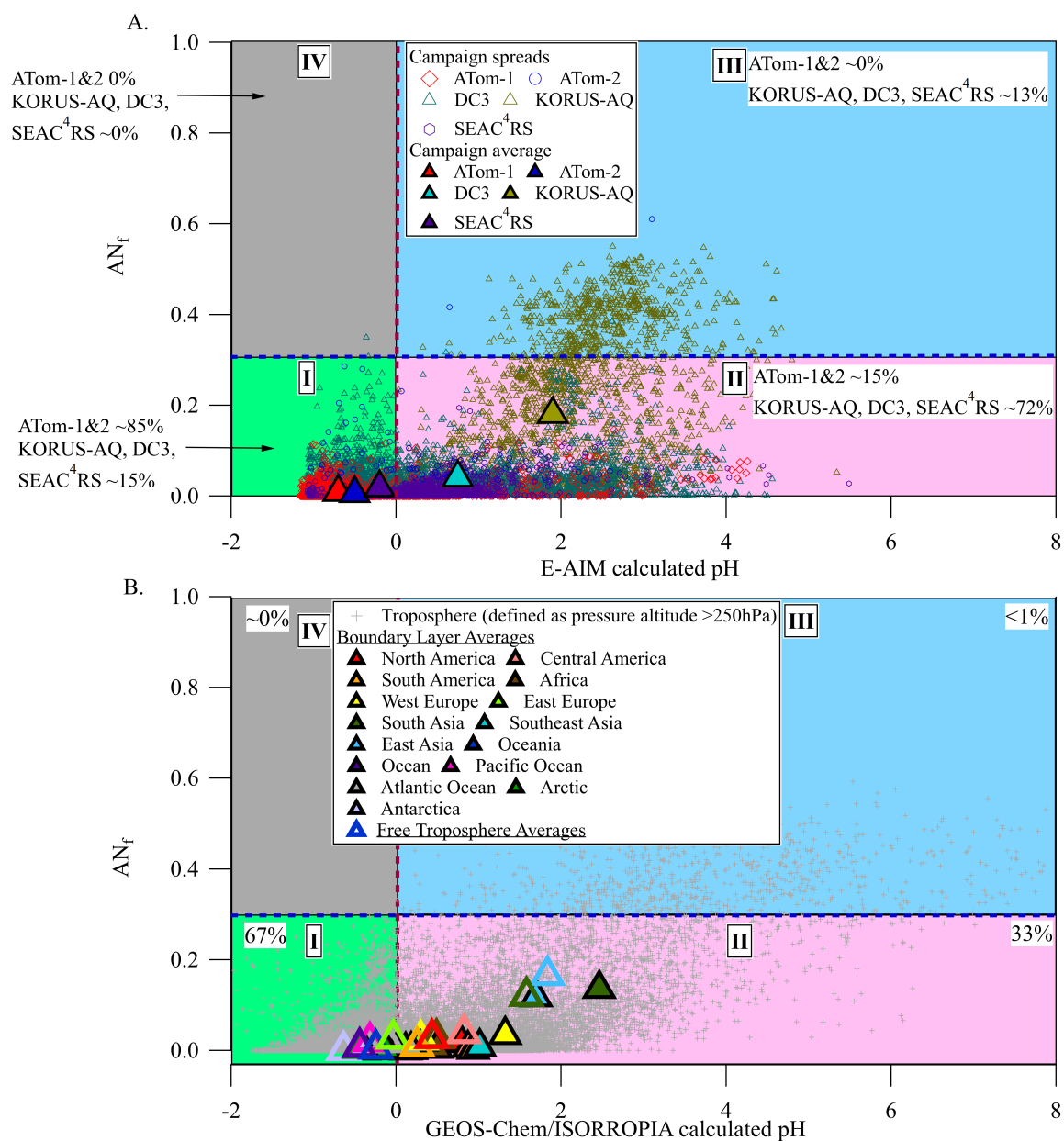
477 “For the entire atmosphere, shown in Fig. S10, the distribution for OS_f looks similar to Fig.
478 S9.”

479 R1.41, Fig 3B. Typo in legend- “Troposphere”

480 This typo was fixed.

481 R1.42, Figure 3A. Points are very hard to distinguish from the background, particularly teal on
482 gray, yellow on pink, yellow on blue, teal on green. I see these colors are used in Figure 4, so I
483 understand the temptation to use them as background colors here, but the data points are almost
484 impossible to see. Try dropping the background colors or find background/data colors with
485 higher contrast.

486 We explored different options, and we decided to darken the points in (A) for KORUS-AQ and
487 DC3 and in (B) we increased the thickness of the markers. This was the best option to make
488 them easier to see, while maintaining consistency of the color scheme across the manuscript.



489 R1.43, ln 632. Remove parentheses around “and potentially in time for a given instrument”

490 The parentheses have been removed.

491 R1.44, ln 644. Remove parentheses before Guo

492 The text says:

493 “e.g., Guo et al., (2015), (2016); Hennigan et al., (2015); Weber et al., (2016)…”

494 R1.45, ln 682. Redefine CE as collection efficiency for this section.

495 The text now states:

496 “3.6 Possibility of Estimating Collection Efficiency (CE) from Sulfate Fragmentation”

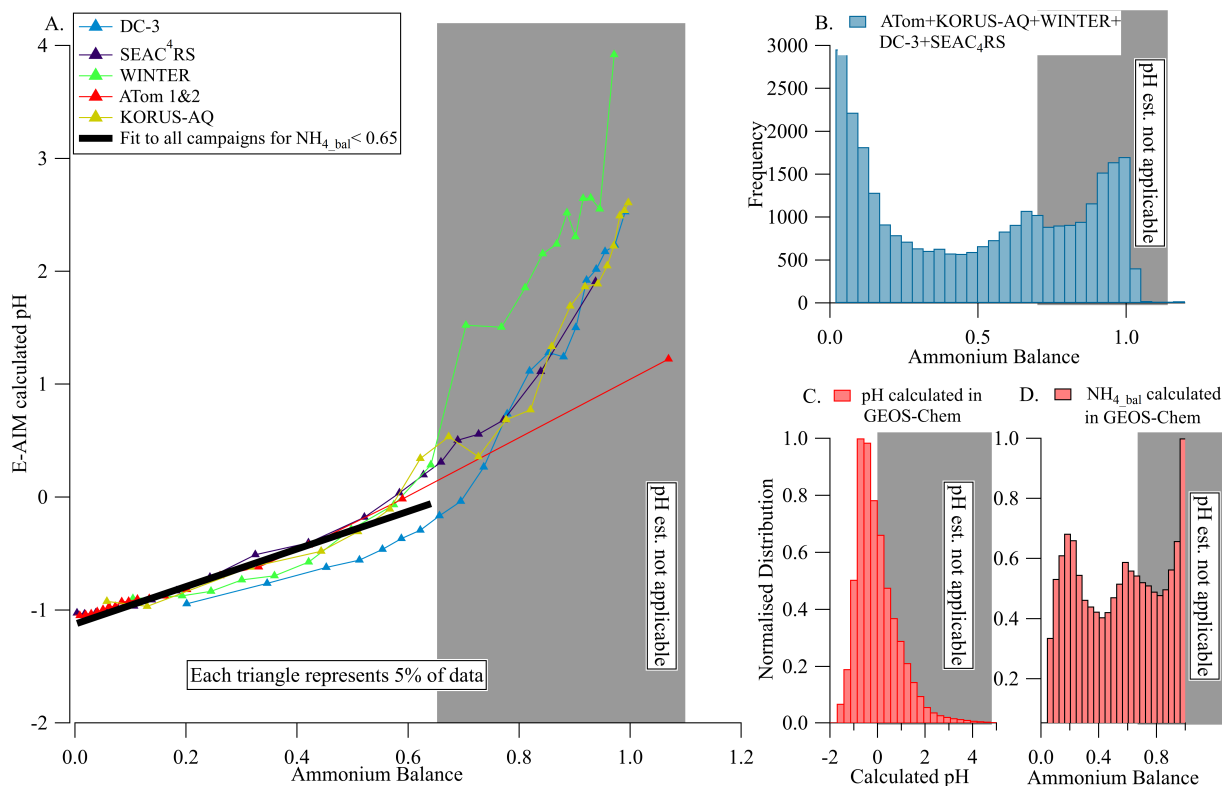
497 R1.46, ln 700. Change “chemical regime I in this work” to “Regime I”

498 The text now states:

499 “We show using both laboratory and field data that both high acidity (regime I) and high
500 AN_f (regime III) result in major changes in sulfate fragmentation, which often lead to
501 nonsensical results for the OS_f methods.”

502 R1.47, Fig 6. Remove histogram from legend in 6A. Label B, C, D in descriptive terms. I.e. in C,
503 Model -> GEOS-Chem

504 This was fixed. The revised figure is shown below.



505 R1.48, ln 1069. Kang et al. Incomplete citation.

506 Kang et al., (2016) has been fixed to say:

507 “Kang, H., Day, D. A., Krechmer, J. E., Ayres, B. R., Keehan, N. I., Thompson, S. L., Hu,
508 W., Campuzano-Jost, P., Schroder, J. C., Stark, H., Ranney, A., Ziemann, P., Zarzana, K.
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510 organic aerosol mass yields from the dark NO₃ oxidation of α -pinene and-carene: effect of
511 RO₂ radical fate, in American Geophysical Union Fall Meeting., San Francisco, CA, USA,
512 12-16 December 2016.”

513 **Anonymous Referee #2**

514 R2.0. Summary: This study examines the performance and validity of recently published OS
515 estimation methods through analyzing the AMS spectral data of sulfate-related ions in ambient
516 and lab-generated PM. This work reveals that the published OS estimation methods have major
517 limitations and may produce erroneous results on OS concentration although could work under
518 certain PM chemical composition regimes. In addition, this study explores the feasibility of
519 estimating pH based on AMS spectral data and postulates the physical processes associated with
520 sulfate fragmentation in the AMS. This exercise provides useful insights into why sulfate
521 fragmentation changes in response to changes in aerosol chemical composition. This is a solid
522 work that addresses an important topic related to atmospheric aerosol chemistry. This study is
523 timely and significant. The manuscript is well written and fits nicely within the scope of AMT. I
524 thus fully support the publication of this work on AMT after the following comments are
525 addressed.

526 R2.1, It is mentioned that the fragment pattern of sulfate ions may vary from instrument to
527 instrument or even for the same instrument after it is tuned. What’s the range of variations in the
528 fragmentation pattern of sulfate-related ions for inorganic sulfate?

529 This was already shown in the AMTD version (Fig. S3). The range in fH_2SO_4^+ for pure
530 ammonium sulfate is ~0.03-0.08, and fHSO_3^+ is ~0.04-0.16. These are the average values for
531 pure AS calibrations during five campaigns.

532 This was already in our manuscript published in AMTD, discussed in Sect. 2.4, quoted below
533 for clarity:

534 “All variables were normalized to the values of the same variables for pure AS calibrations
535 (conducted during each field experiment) in order to eliminate some of the spread in the sulfate
536 ions that is likely due to instrument-to-instrument or instrument-in-time variability (Fry et al.,
537 2013; Chen et al., 2019) (Fig. S3).”

538 R2.2, It would be helpful to give a more clear definition of organosulfate (OS) here. The paper as
539 it reads seems to refer OS to all organic compounds that can produce SO_x ions. It is useful to
540 note that not just the ROSO₃ types of compounds generate SO_x ions in the AMS, compounds
541 with sulfone, sulfoxide, and sulfonate functional groups may do so as well.

542 We have added the following text to the introduction to clarify this point:

543 **“In contrast to nitrates, deconvolving inorganic vs. organosulfates (OS, which includes**
544 **sulfonic acids, when present) is thought to be more difficult. The fragmentation pattern for**
545 **one atmospherically relevant OS was similar to those of inorganic sulfates (mainly**
546 **ammonium-sulfate salts, AS) in an early study, with minimal C-S-containing fragments**
547 **(Farmer et al., 2010).”**

548 R2.3, For the PM data analyzed in this study, are there measurements other than the AMS that
549 can be used to validate the quantification of OS concentration?

550 There are no measurements from these campaigns that fully quantify OS concentrations. The
551 PALMS instrument can see major OS species (like glycolic acid sulfate and IEPOX-sulfate), see
552 Fig. S7 for a visual comparison, as well as our discussion in Sect. 3.4.

553 R2.4, Consider to increase font size in the figures to make the texts more readable.

554 The font size in Fig. 3 (see R1.41) and Fig. 6 (see R1.47) were increased by one point. We think
555 the current font size is sufficient in other figures and that it matches the 12 point font of the paper
556 well. We will pay attention to the proofs of the final paper, as the sizing of the figures in that
557 version can lead to problems as well.

558 Specific Comments:

559 R2.5, In 41, fraction of what mass? Please clarify.

560 We have updated this text to read:

561 **“In regions with lower acidity (pH>0) and ammonium nitrate (fraction of total mass<0.3),**
562 **the proposed OS methods might be more reliable, although application of these methods**
563 **often produced nonsensical results.”**

564 R2.6, ln 46 – 47, this sentence is vague, what values of measured ammonium balance or
565 HySO_x/SO_x ratio that are indicative of pH < 0?

566 The text now states:

567 **“Under highly acidic conditions (when calculated pH<0 and ammonium balance<0.65),**
568 **sulfate fragment ratios show a clear relationship with acidity.”**

569 R2.7, ln 102, spell out SOAS

570 The text now states:

571 **“From this method, an average OS mass concentration (C_{OS}) of 0.12 µg m⁻³ was estimated**
572 **for the Southern Oxidant and Aerosol Study (SOAS) ground campaign in rural Alabama**
573 **(Carlton et al., 2018), with OS_f ~ 4% (Chen et al., 2019).”**

574 R2.8, ln 147, what “sticky” means here, in what sense or towards what substrate?

575 The text has been modified for clarity as:

576 **“Many field studies do not include measurements of NH₃ or HNO₃, two species that are**
577 **difficult to measure due to inlet delays caused by strong interactions with surfaces. Both**
578 **species are typically present at low concentrations and not routinely measured, limiting the**
579 **ability to calculate aerosol pH (Hennigan et al., 2015).”**

580 R2.9, ln 221-222, please elaborate a bit more on the “alternative methods” mentioned here

581 We apologize that the original sentence was confusing as written. What we meant to say is that if
582 someone could come up with an alternative CE estimation method, that would be of interest. So
583 we explore that (briefly) in Sect. 3.6. We added the text below for additional clarification:

584 **“Alternative methods to estimate ambient CE for ambient particles are of interest, we**
585 **explore a potential alternative method here.”**

586 R2.10, ln 264, remove “as”.

587 We fixed it to say:

588 **“We also define a new AMS sulfate ion ratio, $H_ySO_x^+/SO_x^+$, and create the normalized**
589 **$nH_ySO_x^+/SO_x^+$ to reduce the influence of instrument-to-instrument or instrument-in-time**
590 **variability:”**

591 R2.11, Eq 6, stay consistent with the nomenclature, add square parenthesis to denote
592 concentrations

593 In Eq. 5 we define $H_ySO_x^+/SO_x^+$ without using brackets, so that is why we do not use brackets on
594 the left or right side of Eq. 6. We are only using the concentration brackets when we are
595 denoting a value directly measured by the instrument.

596 R2.12, Eq. 8, is it inorganic NO₃ or total NO₃? was the contribution of organic nitrate signals
597 removed?

598 The equation shown in the AMTD article states inorganic nitrate. We removed the estimated
599 contribution of organic nitrate.

600 R2.13, ln 507, “in the absence of acidity” does not make sense.

601 We changed this to say:

602 **“For less acidic aerosols/conditions and in the absence of OS or AN_f effects, it is expected**
603 **that the data would fall on top of the [1,1] pure AS point in the 1D triangle plot, but this is**
604 **not observed.”**

605 R2.14, ln 716, it would be interesting that the authors explain what “careful instrument
606 calibration” involves, through analysis of pure inorganic sulfate particles?

607 A paper on this topic is being worked on by our group that will discuss calibrations in more
608 detail.

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