

Interactive comment on “Aerosol pH Indicator and Organosulfate Detectability from Aerosol Mass Spectrometry Measurements” by Melinda K. Schueneman et al.

Anonymous Referee #1

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Review for Aerosol pH Indicator and Organosulfate Detectability from Aerosol Mass Spectrometry Measurements

Summary:

This paper discusses the challenges of using AMS sulfate ion fragments to distinguish organic sulfates from inorganic sulfates and relates sulfate ion fragment ratios and ammonium balance to aerosol pH calculated from E-AIM. The authors apply previously published methods [Chen et al., 2019 and Song et al., 2019] to several past airborne AMS datasets to test the applicability of these methods for many aerosol compositions. They also determine sulfate ion fragment ratios for mixtures of ammonium sulfate (AS)

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with inorganic and organic species in laboratory experiments. While these methods should be useful in some regions ($\text{pH} > 0$, low ammonium nitrate - AN) based on the laboratory results presented here, the authors have determined that these methods often produce nonsensical values (negative OSf enrichment), suggesting that these methods cannot be used universally across all aerosol compositions. Specifically, high AN and high acidity change the way that sulfate interacts with the AMS vaporizer and prevents use of the Chen method in polluted (high AN) and remote marine regions (high acidity). However, even in the regions that should give good results (low AN, low acidity), the calculated organic sulfate fraction is often negative. The authors also show that sulfate ion fragment ratios correlate to E-AIM-calculated pH under certain conditions ($\text{pH} < 0$, low AN), but correlations of measured ammonium balance with calculated pH are generally better.

General Comments:

As more people apply the methods described in Chen and Song to estimate organic sulfate from sulfate ion fragment ratios in a variety of atmospheric environments, the challenges to those methods highlighted in this paper will arise. The authors show that the Chen and Song methods are not always reliable for all aerosol compositions when applied to large AMS datasets accumulated over several campaigns spanning geographical locations, seasons, altitudes, and chemical regimes. They provide explanations as to how the sulfate ion fragment ratios are affected by high acidity, high AN, and somewhat by high organic aerosol concentrations at the AMS vaporizer through laboratory experiments. This paper is of interest to many AMS users (and data users) as estimating organic sulfate fractions are applied to past and future datasets. Overall, this work is highly important and should be published after addressing the following comments below.

This paper contains important results and discussion of interest to a large audience, but it would benefit from trimming and streamlining the text to improve readability. There is a lot of data and interesting analytical subtleties, but the paper frequently jumps

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around, especially when describing figures. For example, Fig. 1 is complex with a lot of data (lab plus field campaigns). Parts of this figure are described for the first time in disjointed places: Sect 3.1, 3.3 (but not 3.2), and 3.5.1. To help connect the laboratory and field applications of the Chen method, I suggest that the description and discussion of Fig. 1 be presented in its entirety and Section 3.2, which contains explanations for how the AMS responds to various species, could be reduced, moved, or integrated into the discussion of Figure 1.

Specific Comments:

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

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

91. Instead of writing "inorganic" in quotations, be please specific: that these are ions that do not contain carbon and are typically categorized as /associated with inorganic sulfate. However, organic sulfate can also produce these ions.

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

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

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266. Definition of HySO_x: The distinction between its definition in Eq 5 (HySO_x = H₂SO₄ + HSO₃) and Eq 10 (HySO_x = H₂SO₄ + HSO₃ + SO₃) is clear in the text, but it's annoying to have two definitions (and quantities) for the same variable in one paper. The distinction is lost when first introduced (total sulfate signal is defined on Ln 96, but an undefined HySO_x is used on Ln 106).

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

347-364. Consider moving this paragraph from the methods to discussion section

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

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

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

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

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

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

506. Define pH>0 and AN<0.3 as Regime II here in the text. Combine this paragraph with In 526-533.

533. This is a general comment: I’m struggling with the paper setting up the discussion that even though the proposed method does not work for high acidity or high AN as shown in the lab results, it will work for subsets of ambient data that meet the criteria (pH>0; AN<0.3). However, in the end, the method does not work for any subsets of the ambient data as shown in Fig. 1D. This is partially explained by organic aerosol

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moving the AS fragment ratio away from (1,1). Figuring out when/where these methods are applicable seems like an important result from this paper, and Section 3.4 regarding GEOS-Chem assumes that reasonable OSf can be obtained for Regime II. However, the results in Fig 1D and text ln 564-566 indicate that non-negative OSf is not attainable using this method for these past campaigns, even in environments not affected by known interferences on the sulfate fragmentation (i.e. acidity and AN). Perhaps, the recommendation is that if aerosol is in one of the other 3 regimes, more work will be needed to understand the influence of H₂SO₄ or AN, but if the aerosol is in regime II, the method may or may not work, depending on how much OS, AS, and OA are present.

536. Add “estimated” or “calculated” before pH here and for other uses

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

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

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

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

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

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

Technical Corrections:

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

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

79. Missing source of sulfate production?

89. “Recent AMS work.” Reference?

95. “Recent laboratory studies” but only one reference

107. Delete “based on their method”

264. delete “as”

310. Add model numbers of DMA and CPC in SMPS to be consistent with level of detail in previous paragraph.

319. total inorganic nitrate?

318/325. Consolidate sentences. Both describe the same model input.

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

332. Subscript HNO₃

416. Remove paragraph break.

496. Delete D in “Fig. 1D.” Field data is in Fig 1A, C, D.

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533. Change “breaks down” to “is not applicable” or “does not quantify OSf”

570. Change % OS to OSf

Fig 3B. Typo in legend- “Troposphere”

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

632. Remove parentheses around “and potentially in time for a given instrument”

644. Remove parentheses before Guo

682. Redefine CE as collection efficiency for this section.

700. Change “chemical regime I in this work” to “Regime I”

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

1069. Kang et al. Incomplete citation.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2020-339, 2020.

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