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Interactive comment on “Peak fitting and integration uncertainties for the Aerodyne Aerosol Mass Spectrometer” by J. C. Corbin et al.

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1 General Response (copied to both reviewers)

We consider ourselves fortunate to have received two detailed and careful reviews for our manuscript “Peak fitting and integration uncertainties for the Aerodyne Aerosol Mass Spectrometer”. The review of Referee #1 was thorough and detailed and addressed exactly the issues that our manuscript attempted to focus on, highlighting what we can agree were the most meaningful areas for significant improvement. The review of Referee #2 addressed important issues that we did not intend to address, such as the relevance of peak-integration uncertainties to general AMS data products, and thus

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also led to significant improvements in our opinion. These reviews as well as the comment by M. J. Cubison have spurred a number of changes in the manuscript, which we begin by describing generally in this section.

The most significant changes have been to the section on multiple overlapping peaks. The section has been rethought and rewritten. To justify these changes, two new figures have been inserted in the isolated-peaks section, to illustrate the importance of m/z calibration biases to m/z calibration imprecision and thus peak-fitting imprecision. One figure compares peak-fitting imprecisions estimated via slightly different approaches, and also serves the purpose of responding to some of the reviewers' comments. The other figure plots m/z calibration biases and imprecisions against peak-fitting imprecisions, providing a general reference which would be valid for any instrument. Thus both figures simultaneously address specific referee comments as noted in the detailed response.

The second of the new plots provides a basis from which the Monte Carlo uncertainty estimation described in the manuscript can be extended to any set of overlapping peaks. The only requirement is a conservative estimate of the m/z -calibration precision, where conservative is defined as being significantly greater than the m/z -calibration bias (mass inaccuracy). The latter can be estimated directly from a mass spectrum containing peaks of known composition.

In addition, the comment by M. J. Cubison has led us to avoid reproducing the figures that were similar to those presented in Cubison and Jimenez (AMT 2015). Rather, we have shifted the focus of our manuscript more heavily towards the estimation of multiple-overlapping-peak imprecisions, which was outside the scope of Cubison and Jimenez's work. A number of minor changes to the text result from this, for the sake of flow, which are not detailed here but highlighted in the attached revised version.

Detailed responses to the remaining referee comments follow. Figure numbers refer to the AMTD figure numbers, unless specified as new figures by "new Fig. x".

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2 Specific Responses to Referee #1

2.1 Major Point 1 of Referee #1

In Figure 6 and associated discussion, the authors neatly show that a bias in the m/z calibration for a given, known, peak leads to an error in fitted peak height that scales linearly with height. The data points agree with simulations performed incorporating this bias, thus backing up their statement about the source of the error (as is also well-argued in the discussion surrounding Figs 3 and 4).

They go on to perform similar simulations for a set of known peaks: In Figure 5, they show that the m/z biases for each of their test ions are different, which impacts the distributions shown in Figure 7 (following from the discussion in 3.6 that the biases impact the imprecision). In order to make their generalization that σ_h is a fixed fraction of height for all ions (not just the test case), they are assuming that this error scales similarly with peak height for all ions irrespective of the m/z bias to which they are subjected. The similar slopes in Fig 2. are meant to support this theory (line 25 p3483). The authors ought show the mean simulated lines of “Fit RMSE vs peak height” for all 7 test ions (like the white line in Fig 6., but with different colors for the different ions) to support this statement. In the event that this slope is identical for all ions, perhaps they might discuss why this is the case, as this generalization is an important part of their conclusions, both here and in the final concluding remarks.

The first part of this point, made in paragraph 2, is that a linear relationship between fit RMSE and peak height does not prove a linear relationship between imprecision-in-fitted height, σ_h , and actual peak height, h . We concur with this statement and did not

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intend to make it. On the cited line 25 p3483, the statement was referring to the slope of each peak. That slope would depend on the peak's individual imprecision and bias. We have changed "a constant relative RMSE" to "a constant relative RMSE for each peak" to clarify this.

The second part of this point, to our understanding, is that Fig. 6 (RMSE vs. peak height) should include information on the trends of imprecision with noise. We have followed this suggestion as part of a new figure plotting imprecision vs. peak height (new Fig. 8).

Here the Referee also questions whether our generalization that σ_h is a fixed fraction of height for PIKA-style constrained fits holds for all conditions. To address this, it was suggested that we show more simulations, but we have taken a different approach and expanded the mathematical analysis in Sect. 3.2. We think that this is better than showing more simulations because it is both more general and direct (though, as just mentioned, we have still added more simulated results as new Fig. 8). In any case, we agree that the fractional imprecision for a given ion should be estimated directly via the Monte Carlo method outlined more clearly in the revised manuscript.

Furthermore, at the end of section 3.8 when estimating the magnitude of peak-fitting imprecision σ_h , it seems like the distributions used to derive the 2% value quoted are taken from Fig. 7, which presumably don't include the biases as (line 18 p3488 "mean fitting error (bias) has been subtracted"). If my interpretation of Fig. 6 is correct, the bias leads to the observed slope and the imprecision (broadened by the slope effects mentioned in 3.6) is the spread in light blue around this line. Therefore using Fig 7, which is considering only the imprecision, to i) estimate their magnitude and ii) demonstrate that this magnitude is generally applicable appears false. Surely if there were no bias, the σ_h imprecision distribution would stay constant as in the noise region for low signal and thus not

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scale linearly with h ? It follows that the important parameter determining the magnitude of the linear increase in σ_h with h is the bias and that the imprecision distribution is largely irrelevant.

Here the reviewer challenges the estimation of fitting imprecision from Fig. 7 under the interpretation that Fig. 7 was generated without including μ -prediction biases. This is not correct – to generate Fig. 7, we simulated both μ -prediction biases and imprecisions as given in Table 2. These simulations provided estimates of both h imprecisions and h biases, but only h imprecisions were plotted because biases are not relevant to the discussion and suggest misleadingly larger differences between ions. We have updated the labelling in Table 2 and the legend of Fig. 7 as a result of this ambiguity.

In the second part of this comment, the Referee also proposes a counterargument to our Figs. 6–7 based on her or his interpretation of Fig. 6. In particular, the reviewer suggests that the slope of Fig. 6 arises from bias and not imprecision in μ , assuming that imprecision in μ leads to an imprecision in h that is independent of h . This is incorrect. A small error in μ (the abscissa of Fig. 1) leads to a small excursion along the slope of the peak. Considering a Gaussian peak (Eq. 2) with $h = 1$, this leads to a negative error in the fitted peak height of equal magnitude regardless of whether the μ error was positive or negative. The negative error is controlled by the exponential term but scaled by the prefactor h . So imprecision is not always independent of peak height for a nonlinear equation. We considered illustrating this in Fig. 6 but did not want to mislead the reader into overinterpreting that figure. Since the RMSE of a fitted model does not indicate the uncertainty in one fitted parameter, Fig. 6 is not a good indication of the imprecision in fitted h that results from μ imprecision and bias, and cannot be interpreted as the reviewer has done.

At present, the “~ 4%” quoted on line 6 of p3495 is simply not supported. At the very least the data for all test ions must be presented. A better approach would be to simulate their calibration routine and evaluate the biases for

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every significant ion across the entire mass spectrum. My principal concern is that, since they show some ions have positive and some negative m/z biases, there must presumably be cases where an ion has no bias at all. The application of a linear error term in this instance would be a gross overestimate of the error, as I'd expect to see a zero slope in a similar plot to Fig 6. If this is wrong, the authors must demonstrate it. If this is correct, then the range of biases must be considered when applying the linear error term.

We believe the new manuscript has responded to this point by recommending direct estimation of all fractional σ_h . However, the small range of observed fractional σ_h in this study suggests that a single value for all isolated ions may present a good approximation to this quantity, for isolated peaks, and may be useful during exploratory data simulation. This is made clearer in the revised manuscript.

We do not believe that a better approach is to simulate the calibration routine. The result of this approach would be a best-case estimate of σ_h . That is, it would only reflect known or well-understood issues with m/z calibration. When the calibration deviates from ideality in this way, as is universally observed to some degree (discussed further in Section 6 of the manuscript), simulating the calibration procedure does not allow the estimation of m/z calibration biases.

Regarding the impact of variation in bias between ions, we believe that the new Fig. 10 and its interpretation is a direct response to the reviewer's feedback here.

2.2 Major Point 2 of Referee #1

Major Point 2 of Referee #1 was taken to heart and motivated a significant amount of the new work and changes presented in the new manuscript. Given the significant changes in the manuscript, we believe that these points have been addressed. But

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since much of the discussion that was criticized in this point has now been significantly revised, it would only be confusing to go through each point in detail. However, we would like to emphasize that we now explicitly discuss the estimation of b (although we no longer use this variable, to avoid confusion), we explicitly discuss the estimation of μ -calibration bias and imprecisions as inputs to the Monte Carlo approach, and we significantly simplified the description of that method. We also address the question of whether the approach represents a min/max/best estimate in the new text.

2.3 Major Point 3 of Referee #1

We have chosen to remove the qualitative discussion of two overlapping peaks and simply cite Cubison and Jimenez (ACP 2015).

2.4 Other comments of Referee #1

Minor Point 1. *I am a little unclear as to what is presented here. The data are from fits to the same mass spectrum, so each data point is a different delta-u? The noise presumably arises from the use of real data, would it not be better to use simulated peaks as indeed the authors do elsewhere? Then perhaps the effect of the detector bins mentioned on line 6 p3492 would be easier to assess.*

The Referee has correctly understood our discussion in Section 4.3, and we have moved this to be next to the rest of the empirical analysis section and rewritten its description so as to clarify.

Minor Point 2. Here the reviewer asks why we ignored the effects of counting errors on the basic effects of multiple-peak-fitting errors. As noted above, we have chosen to remove the qualitative discussion of two overlapping peaks and simply cite Cubison and Jimenez (ACP 2015).

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Minor Point 3. *“In 6.3 line 30 p3498 it is noted that the signal intensity of a single ion varied by 20%. Does this impact the shape of the mass spectra utilized in this study and therefore could it play a role like is assumed for the detector bin spacing?”*

We do not believe that the actual signal area of a single ion varied by $\sim 20\%$, but that the result of the single-ion-area determination procedure. This value does not impact the shape of a mass-spectral peak; a single value was applied to the entire data set. Some users apply different values on different days or weeks, which could lead to a step change in the estimated counting imprecision. This would be beyond the scope of the present manuscript.

Minor Point 4. We find the reviewer’s challenge of kHz as an appropriate unit in mass spectrometer to be quite right here and have changed the units to counts / second.

Minor Point 5. The reviewer’s suggestion here to consider the overall μ -prediction imprecision is not necessary in the revised version, where a graphical guide to choosing the μ -prediction imprecision, given an estimate for the unknown μ -prediction biases, is presented.

Minor Point 6. *“On line 18 of p3488 it is mentioned that the “mean fitting error has been subtracted”. This is not clear. One assumes this means the distributions are shifted in x, otherwise the distribution for the ion used in Fig. 6 ought be centered around 5% as the slope of Fig. 6 would suggest. Both distributions (with and without bias) should be plotted in Fig. 7.”*

The distributions are shifted in x, yes. Plotting these with and without bias in Fig. 7 would mean plotting the same curve with and without a shift, the magnitude of which would not be meaningful as it does not influence the internal imprecision of an AMS data set. The h -fitting bias is too small to influence inaccuracies in AMS data products (non-refractory mass, elemental ratios, etc.) – as is now clarified in the introduction – and we intentionally avoid emphasizing or discussing it, to avoid misleading the casual reader. However, running PMF with incorrect peak-integration imprecisions may lead

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to significantly-incorrect mass loading estimates for PMF factors.

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