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Atmospheric
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Discussions

Interactive comment on "Three-dimensional factorization of size-resolved organic aerosol mass spectra from Mexico City" *by* I. M. Ulbrich et al.

Anonymous Referee #3

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This paper presents the first size-resolved factor analysis of AMS organic mass spectra. Factor analysis techniques are used to deconvolve a 3-dimensional matrix (time x composition x size) into a set of static factor mass spectra, their time-dependent intensities, and, depending on the selected model, their static or dynamic size distributions. The work is a logical extension of the 2-dimensional factor analysis techniques that have been applied to AMS data with great success and are now widely used. The content of this paper is therefore of high interest to the atmospheric community. In the course of the analysis, the authors have made some simplifying assumptions that direct them to a particular set of solutions and results. This limits the method utility,

but does not render it invalid. However, the conclusions drawn from the analysis are held to apply generally to the 3-D factorization problem. This is not justified, and leads to a disconnect between the actual analysis and the scope of the conclusions and recommendations for future researchers. This should be rectified before publication.

My principal concern with the analysis is the assumption that any valid 3-D solution should include the 2-D HR-MS factors. There are several reasons why this might not be the case, including evaporation time distributions, representation of aerosol components as linear combinations of multiple factors, signal-to-noise considerations, and general differences in the nature of the correlations required to extract factors from the respective models. These are discussed below in the specific comments. However, the authors make this assumption, then force the 3-D solutions to fulfill it by (1) using it as a criteria for discarding solutions as non-physical and (2) constraining the 3-D factor mass spectra to resemble the 2-D solution. This method does provide useful data, though limits the model's explanatory power. However, by its forced nature it only explores a small subset of the 3-D solution space. Conclusions drawn from such a forced analysis cannot be held to apply to the entire 3-D factorization problem, and the method should certainly not be recommended as a general approach to 3-D AMS factorization; the authors have confronted a different problem (i.e. they have addressed how best to obtain size distributions corresponding to known 2-D HR-MS spectra). I would recommend that the language of the manuscript be adjusted to explicitly reflect the scope of the present analysis as framed above. Alternatively, the authors could extend their analysis to include a more detailed exploration of the 3-D solution space, which critically should include a detailed analysis of the deviations from the 2-D solution and an evaluation of whether they are physically meaningful that does not use similarities to the 2-D solution as the main criteria.

Specific comments

1. Page 4564, lines 15-20: The ToF-AMS is also capable of single particle measurements, and yields quantitative rather than qualitative results. See Cross et al. (ACP 9,

7769-7793, 2009).

2. Page 4571, line 9: Ions of different sizes will have different IToFs. This can (and probably should) be corrected by instrument calibration. Note also that for determining whether IToF has a significant influence on the measured particle size, the relevant quantity is the delta_IToF between two ions of interest compared to the PToF resolution (i.e. measurement time step dictated by the ToF pulser frequency), not IToF vs. PToF.

3. Page 4571, lines 10-13: "The measured PToF and the length of the particle flight region give the particle velocity, which is inversely proportional to the square root of particle vacuum aerodynamic diameter." This statement is inaccurate. Velocity is inversely proportional to the quantity (1+(dva/d0)ˆb), where both d0 and b are empirically determined from instrument calibration.

4. Page 4572, lines 12-14: "As long as an OA component has a constant distribution of evaporation times, its retrieval in 3-D factorizations will not be affected." I am not sure I understand precisely what the authors mean by "retrieval." Is this retrieval of particular factor profile without bias due to evaporation time distributions, or simply the ability to retrieve a (potentially biased) factor from the model? The first of these is incorrect and conflicts with the authors' statement later in the paragraph ("But the mass spectrum of each organic aerosol component sampled in PToF mode can be slightly biased toward the fast-vaporizing species"). I suspect the second interpretation is also not accurate, as a distribution of evaporation times requires multiple factors to accurately represent, meaning less mass per factor (either by distributing mass across multiple factors or transferring it to the residuals), which the authors previously showed to be detrimental to factor retrieval in 2-D factor analysis (Ulbrich et al., 2009).

5. The issue of evaporation time is quite important for factor evaluation and interpretation, so additional discussion by the authors would be welcome. This is an issue not just for species that vaporize on a slower timescale than the PToF cycle, where I agree with the authors' present treatment, but for species with "fast-but-different" evaporation

times. The difficulty is as follows. If a factor consists of components with a distribution of evaporation times, these can only be represented by multiple size distributions (which broaden towards large sizes for slower-evaporating components). However, both 3-D factor models studied here assume that at a given point in time, a single size factor size distribution corresponds to a single factor mass spectrum. Therefore, even if the multiple size distributions needed to describe evaporation remain constant with time, retrieval of the OA components will depend on vaporization. As an example, one could consider a case in which the "true" factor consists of 50% NH4NO3 and 50% (NH4)2SO4. In 2-D (composition and time) factor analysis, this can be represented by a single factor. However, internally mixed NH4NO3 and (NH4)2SO4 will yield different size distributions because of the slower vaporization of (NH4)2SO4. The 3-D factor models require a minimum of 2 factors to accurately represent this, e.g. a small-size factor with enhanced NH4NO3 (representing faster evaporation) and a large-size factor with enhanced (NH4)2SO4 (slower evaporation), or alternatively, separate factors with unique size distributions for NH4NO3 and (NH4)2SO4. In practice, when such a factor is resolved from a complex ambient dataset, it could also appear as a single factor with the differences in evaporation timescales transferred to the residuals. Note, however, that in this case the retrieved factor is likely be biased towards roughly the geometric mean of the mass distribution (where the signal-to-noise is highest), and may therefore contain biases in both composition and size distribution (whether static or time-varying). For ambient OA, a broad range of evaporation timescales is expected and distinguishing between true factors and evaporation-based split factors is potentially quite difficult. The authors touch on this, noting "the mass spectrum of each organic aerosol component sampled in PToF mode can be slightly biased toward the fast-vaporizing species" (page 4572, lines 14-16). This is not quite true; as discussed above the bias is roughly towards the geometric mean of the factor mass distribution, which depending on the precise nature of the factor is not necessarily the fastest-vaporizing species. Further, the size distribution may also be biased. However, the authors' broader point (biases induced in factor spectra and size distributions due to evaporation time distributions) is well taken. As this manuscript appears intended in part as a blueprint for future 3-D AMS factor analysis, some additional discussion on the magnitude of these biases and methods for identifying them is needed.

6. Section 3.3.1: Why are uncertainties in the measured size not included in the error estimation? I realize that it is not possible to account for different evaporation times. However, because the chopper slit is not infinitely small, it introduces uncertainty into the particle sizing measurement. This uncertainty is not constant as a function of size, and so may affect the model results. If IToF is not explicitly corrected for as discussed in Comment 2, then this becomes an additional uncertainty that should be considered.

7. Page 4578, lines 1-3: How sensitive are the model results to the value selected for the "weak" variable SNR threshold?

8. Page 4585, lines 2-8: "We presume that the bulk aerosol has the same composition whether measured in the MS or PToF modes... We therefore hypothesize that we should find the factors identified in the HR-MS analysis in the 3-D analysis, and may identify additional factors." This appears to govern the application of the authors' metrics for evaluation of the model solutions, so "hypothesize" is perhaps too weak a word. For example, taking together Table 3 and the evaluation of the unconstrained vector-matrix model solutions in section S6, it appears that the criteria for a "physically meaningful" solution include the requirement that all 4 factors from the HR-MS analysis be resolved. I do not find this a compelling argument, as there are reasons one could imagine retrieving a meaningful solution without fulfilling this requirement: (1) As discussed in Comment 5, a distribution of vaporization times within an HR-MS factor could lead to a substantial change or non-retrieval for the size-resolved analysis. Note that because of this, "split" factors having similar time series are not necessarily indicative of non-physical solutions. (2) Factors with distinct mass spectra and time series but similar size distributions could be inherently more difficult to distinguish in the vector-matrix model than in the 2-D HR-MS analysis. (3) The decreased signal/noise in PToF data means that the data pretreatment (e.g. smoothing, downweighting) may affect the

resolution of the HR-MS and vector-matrix models differently, making specific factors harder or easier to resolve.

9. Supplement S6, lines 527-533: I do not understand why the authors prefer a single OOA factor to OOA described by a combination of m/z 44- and 43-dominated factors. Such a split is consistent both with (1) evaporation timescales in the AMS and (2) current descriptions of OOA as consisting of components with a range of volatilities, where high-43 OOA is expected to undergo repeated evaporation/condensation with temperature cycles. This could give a high-43 OOA distribution more influenced by the low-volatility particle surface area distribution. For both cases, one would expect a size distribution skewed towards larger sizes for the high-44 OOA, which appears to be the case in Fig. S7 (and perhaps also in Fig. S12).

10. Supplement S6, lines 534-536: An m/z 15-dominated factor is observed to appear repeatedly in the unconstrained 3-vector and vector-matrix solutions. This is taken as evidence of a non-physical solution. It may simply indicate a problematic m/z for which the sources of error have not been completely assessed. The authors should explore removing or downweighting this element if they believe it impedes their ability to retrieve meaningful results.

11. Supplement S6, lines 536-539: The authors observe a factor having a prominent set of m/z's (67, 81, and 95) corresponding to specific hydrocarbon classes, but discard the factor as nonphysical because "the spectra of real compounds contain more than just these three fragments." First, Figure S12 clearly shows that many more fragments are present. In fact, many of the characteristic HOA m/z are present, albeit at reduced intensities and with the absent peaks grouped at low m/z, so this statement is rather misleading. But more importantly, it is not necessary that the factor mass spectra resemble the spectra of an actual molecule or an "aerosol type," to be meaningful. For example, it is possible for factor analysis to represent a complex or variable factor as the linear combination of two other factors; in this case, only the combination of factors need have a spectrum resembling a molecule or aerosol type. The OOA subtypes are

well-known examples of such linear combinations in two-dimensional factor analysis. The OOA spectra are not understood to represent discrete aerosol types, but rather serve as a basis set for describing the dynamic OOA composition. It is possible that the 67/81/95 factor and HOA shown in Fig. S12 form an analogous basis set. Other interpretations of this and other solutions may be possible, and the authors may be able to demonstrate they are correct in considering the factor physically unmeaningful. However, this requires careful consideration and discussion of the factor, which is currently not included. At present, the analysis structure seems overly governed by the authors' expectation that the resolved factors should follow a particular pattern analogous to the HR-MS solutions (see Comment 8), leading to the exclusion of potentially meaningful factors.

12. Page 4590, lines 18-20: "Thus, the vector-matrix model captures the real variability in the size distribution of each factor better than the 3-vector model when using the same spectra." The case for this statement is built on the lower Q/Qexp values observed for the vector-matrix model. However, Q/Qexp was previously dismissed by the authors as a metric for judging a solution's explanatory power for the unconstrained vector-matrix model, which yields solutions with a lower Q/Qexp but is judged physically unmeaningful. The authors indicated that the decreased Q/Qexp for the unconstrained vector-matrix model was due to fitting the noise (Supplement, lines 518-526). Why is Q/Qexp now used in the vector-matrix model to indicate an improved description of real variability? It is more likely that the apparent improvement is again due to fitting the noise via increased degrees of freedom. If the authors wish to make this case, they should be consistent in the usage of their metrics or demonstrate that Q/Qexp is an applicable metric in only the selected case.

13. Page 4595, line 26 to page 4596, line 3 and Fig. 5: Overall, Q/Qexp values show that the best solution of the constrained vector-matrix model fits the data better than the best 3-vector solution, although the differences are small (0.95 vs. 0.97, respectively; Fig. 5)." I do not understand how the 3-vector Q/Qexp values are represented in

this figure. The legend in the top panel denotes the "range of 3-vector solutions" with a horizontal black bar; in the figure, this extends from beta = 0 to beta ∼0.05, at a constant value of ∼0.965. This doesn't seem right; am I misreading the figure or is the 3-vector solution data not included?

14. Page 4599-4600: The authors compare results obtained with the 3D models to estimated size distributions constructed from tracers for the 2D HR-MS factors. Given the similarity of the tracer size distributions to the vector-matrix model, what do the authors see as the advantage of the 3D analysis over the tracers? As presently formulated, the 3D analysis requires the existence of constrained 2D factor mass spectra, from which tracer size distributions could presumably be constructed. In the case of a disagreement between the vector-matrix model and the 2D size distributions, how would the authors demonstrate that the vector-matrix model yielded useful data? Certainly for the mass concentration data, the 2D HR-MS solution has here been treated as superior. Given this, why should vector-matrix size distributions be superior to a high-resolution tracer (e.g. vector-matrix HOA vs. C4H9+-based HOA)?

15. Page 4601, lines 8 to 10: "OOA has... an asymmetric distribution with strong extension to smaller particles... consistent with the condensation of semivolatile gas-phase molecules onto smaller particles." Note that this is also consistent with the description of OOA as a combination of a more volatile (m/z 43-dominated) OOA and a less volatile (m/z 44-dominated) OOA, as discussed in Comment 9.

16. Page 4604, lines 12 to 17, also page 4606, lines 21 to 24: The authors provide some suggestions for future researchers who wish to investigate 3D factorization of size-resolved AMS data. They suggest beginning with 2D factorization of HR-MS data to better understand the dataset, which makes sense. However, the utility of this step is described in terms of diagnosing unsatisfactory solutions and identifying split factors. Unfortunately, this evaluation appears to depend in large part on the unproven assumption that the 3D model should yield essentially the same set of factors as the 2D model. As discussed above (esp. Comments 8-11 and 15), there are many reasons why this

assumption could break down. Discarding 3D model solutions containing significant deviations from the 2D solution as non-physical or erroneous both severely limits the analysis and renders it circular. To summarize, the authors assume that the 3D solution should resemble the 2D HR-MS, discard solutions that do not satisfy this condition as non-physical, and finally conclude that the 2D solution was vital in interpreting the 3D (after constraining the 3D model such that the output spectra closely resemble those of the 2D solution). While the data obtained by this method may indeed prove quite useful in certain cases, it is far from a comprehensive analysis of the 3D solution, and the recommendation for future researchers to follow the same method is not supported by the analysis. To justify such a recommendation would require a much deeper analysis, focused specifically on (1) characterization of the 3D model behavior with respect to factor identification, mixing, splitting, description of dynamic factor composition (e.g. OOA), etc., and (2) development and evaluation of criteria for evaluating non-physical factors on their own merits (i.e. without invoking the 2D solution), and allowing for the possibility of complex and/or dynamic composition to be characterized by linear combinations of factors.

Minor comments

Page 4585, line 5 “MS and PToF modes” should be “MS or PToF modes”

Page 4586, line 9: “solutsions”

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