

## ***Interactive comment on “Simultaneous factor analysis of organic particle and gas mass spectra: AMS and PTR-MS measurements at an urban site” by J. G. Slowik et al.***

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### **Response to Comments by I. Ulbrich**

We thank I. Ulbrich for the helpful suggestions, which have improved the manuscript. A point-by-point response is presented below. For cross-referencing purposes, comments are numbered by reviewer and comment number, e.g. Comment 1.2 is the second comment in the first posted review. A parallel numbering scheme is used for figures and equations.

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#### **Comment 4.1:**

##### *1. Explanation and Use of CPTR*

*On pg. 6746, lines 11-14, the text states that the error values for the PTR-MS data are multiplied by CPTR; the CPTR values in Fig. 8 are all > 1. These CPTR values would increase the error values, lowering the relative signal to noise ratio (SNR) of the PTR-MS data. It seems that this would downweight the PTR-MS data relative to the AMS, in the same way that increasing the error values can be used to downweight “weak” variables (i.e., low SNR variables) to have less influence on the fit (Paatero and Hopke, 2003). Are the PTR-MS error values instead divided by CPTR? Then the other discussion of the effect of CPTR makes more sense. It would be helpful, however, if the language in this section was parallel to the labels in Fig. 8 (at present the text discusses underweighting but the figure describes overweighting).*

#### **Response:**

We thank the reviewer for correcting this typo. The  $C_{PTR}$  weighting method is now presented in mathematical form, as discussed in response to Comment 1.2. The instrument-weighted uncertainty matrix ( $S_{inst}$ , containing matrix elements  $s_{ij}$ ) is constructed as follows:

$$\begin{aligned} s_{inst,ij} &= s_{ij} && \text{for } j = \text{AMS } m/z \\ s_{inst,ij} &= s_{ij}/C_{PTR} && \text{for } j = \text{PTR-MS } m/z \end{aligned} \quad (1)$$

The language has been synchronized with Fig. 8, and “overweighting” is now used throughout the manuscript.

#### **Comment 4.2:**

*In the discussion of Fig. 8 and balanced solutions (pg. 6755, line 28), you might wish to emphasize the point made in the introduction of CPTR (pg. 6745, line 22-24) that in principle one would expect to have to give extra weight to the smaller PTR-MS dataset (10 m/z's vs. 270 m/z's) by about 27 times, if all m/z's in both instruments have about*

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the same SNR. It may be useful to report the average SNR of both instruments to show that 27 times is too much as presumably the PTR-MS data have somewhat higher SNR than the average AMS m/z for the same averaging time. This would clarify the reason for the need to use CPTR.

**Response:**

In the initial discussion of  $C_{PTR}$ , two points were made regarding the relative weight of the AMS and PTR-MS datasets. First, the PTR-MS dataset is 27 times smaller. Second, for both instruments, the time series of individual m/z are not fully independent (e.g. aromatics in the PTR-MS, alkane or alkene series in the AMS). This second point is dataset-specific and prevents a reasonable a priori estimate of  $C_{PTR}$  from being made. As a hypothetical example, if the 4 aromatic masses presently included in the PTR-MS were replaced with benzene, isoprene, acetonitrile, and methacrolein/methyl vinyl ketone, we would expect a different (probably higher)  $C_{PTR}$  value, independent of the effect on SNR. Because of these issues, we do not feel it is appropriate to include an “expected” value of  $C_{PTR}$ . For clarity, we have revised the initial discussion of  $C_{PTR}$  to emphasize the effects of correlated m/z.

**Comment 4.3:**

*In Figs. 9 and 10, I would suggest that you remove CPTR from the scaled residuals of the PTR-MS elements before summing to the time series. This should make it easier for the reader to compare to the scaled residual time series of the individual instrument cases in Figs. 1 and 4. If you don't wish to do this, I would suggest adding a note in the caption of Figs. 9 and 10 stating that the scaled residuals and  $Q=Q_{exp}$  include the effect of CPTR, even though it is redundant with the text describing the figures. This is also parallel with the removal of CPTR for calculating  $\Delta\bar{e}_{sc}$ . It would also be very useful to plot the time series of scaled residuals for the separate and unified datasets together in the Supp. Info., so that the reader can better appreciate during which periods and*

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*by how much the fitting of the data has changed because of the joint analysis of the datasets.*

**Response:**

The  $Q_{cont,AMS}$  and  $Q_{cont,PTR}$  time series plots in Figs. 9 and 10 are utilized primarily to evaluate (1) the time-dependent relative weight of the AMS and PTR-MS in the unified dataset solution and (2) the changes in the time-dependent contribution to  $Q$  as a function of the number of resolved factors. The first use requires that  $C_{PTR}$  be retained in the calculation of  $Q_{cont}$ . We have added a note to the caption stating that  $C_{PTR}$  is included.

The suggested comparison of the  $Q_{cont}$  time series for the unified and individual datasets has been added to the Supplement. For this plot,  $C_{PTR}$  has been removed from the calculation of  $Q_{cont}$  to facilitate comparison.

**Comment 4.4:**

*Finally, it seems from Fig. 8 that the CPTR=20 solution with 5 factors meets the  $\Delta\bar{e}_{sc}$  criterion better than the reported CPTR=10 solution with 5 factors. In choosing the solution with CPTR=10, the authors are not completely following their own method, and this deviation should be justified. I suggest that some of the discussion of the difficulty with the CPTR=20 solution currently in the Supp. Info. be moved to the main text near pg. 6755, line 20 to support the use of the reported solution.*

**Response:**

As discussed in response to Comment 1.3, implementation of the “pseudo-robust” method of outlier downweighting has caused both the solution to the unified dataset to change ( $C_{PTR} = 10$ , 6 resolved factors). As a result, the discussion of  $C_{PTR} = 10$  vs.  $C_{PTR} = 20$  is no longer applicable, and has been removed from the manuscript. The

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Supplement now includes comparisons of  $C_{PTR} = 10$ , yielding  $\Delta\bar{e}_{sc} = 0.052$ , with the 6-factor solutions yielding  $\Delta\bar{e}_{sc} \sim \pm 0.25$ ,  $\Delta\bar{e}_{sc} \sim \pm 0.50$ , and  $\Delta\bar{e}_{sc} \sim \pm 1.0$ . The factor profiles and time series are overlaid as discussed in response to Comments 1.1, 4.10, and 4.16.

**Comment 4.5:**

*An alternative to the use of CPTR could be to include multiple copies of the PTR-MS data (with the original weights). The number of copies required to achieve a balanced solution might be expected to be similar to the CPTR required for a balanced solution. In this method the robust mode could be used and all of the points would pull with their full weight while limiting the impact of the outliers. It would be helpful to at least mention if this method has been attempted, even (and perhaps especially!) if it has failed. If it has not been tried, I suggest that it is tried and compared with the CPTR method in the revised version of the manuscript.*

**Response:**

The method proposed by the reviewer represents an interesting alternative to the method investigated in the present study. A detailed analysis and comparison of this method is beyond the scope of the present study. However, preliminary results suggest qualitative agreement between the two methods. For clarity of reference, we here refer to the suggested weighting method as the “PTR-redundancy weighting method.” Here the comparison is restricted to 6-factor solutions (i.e. the number selected through analysis of the unified dataset using CPTR).

The instrument weight is balanced ( $\Delta\bar{e}_{sc} = -0.0098$ ) when 50 copies of the PTR-MS data is included ( $n_{PTR}$ ). (A plot of  $\Delta\bar{e}_{sc}$  as a function of  $n_{PTR}$  is included in the Supplement). As shown below and in the Supplement, the PTR-redundancy method increases the number of rows in the residual matrix **E** that contain mostly positive or mostly negative residuals for the PTR-MS. As stated in the review by P. Paatero (Com-

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ment 1.4), a large number of such rows may indicate distortion of the solution due to multiplicative errors affecting entire rows of the individual instrument matrices. As a formal analysis of such distortion has not been published, we are unsure whether this problem is manifested here (not also that the PTR-redundancy method is here analyzed exclusively at  $p = 0$ ,  $f_{peak} = 0.0$ ).

The two methods provide qualitatively similar solutions (see Comments 1.3, 4.9, and 4.14 for a brief description of the differences in solutions caused by implementation of the pseudo-robust outlier treatment method). Differences in the PTR-redundancy method include: (1) the influence of local painting activity appears primarily in the UN-traffic factor rather than UN-Local Point Source; (2) the AMS spectrum for the UN-Local Point Source more closely resembles OOA than HOA (although the AMS mass for this factor may be too low to be reliable in either solution); (3) larger fractions of acetic acid and acetone are apportioned to the UN-Aged SOA and UN-Traffic factors, respectively; (4) 25-50% of the PTR-MS aromatic signal is contained in the residuals.

**Comment 4.6:**

*2. Comparisons of the individual and unified datasets As a reader I would like to examine the comparison of the spectra and time series of the factors and scaled residuals time series from the individual vs. unified datasets more closely. It would be extremely helpful to include (even in the Supp. Info.) plots of the spectra and time series overlaid, perhaps in the style of Fig. 9 of Ulbrich et al. (2008). This presentation should not replace the current Figs. 10 and 11, though, which are needed to see the unified case results clearly.*

**Response:**

As discussed in response to Comment 4.3, a comparison of the individual and unified  $Q_{cont}$  time series has been added to the Supplement. We have added overlaid plots of factor spectra and time series from the individual datasets for cases in which fac-

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tors are sufficiently similar to warrant a direct comparison. Note that to enhance the presentation, we do not directly report either the  $f_{hj}$  or  $g_{ih}$ , but rather the normalized and/or scaled quantities discussed in response to Comment 4.10.

**Comment 4.7:**

*The discussion on pg. 6756, lines 9-11 mentions very large increases in scaled residuals in the unified case compared to the individual cases. It seems that the overall fit of the matrices is much worse in the unified case, though additional information was extracted. If this is not the case, this should be clarified. The increase in the values of  $Q=Q_{exp}$  should also be given in the text, even if the size of the  $Q=Q_{exp}$  insets is increased.*

**Response:**

Implementation of the pseudo-robust mode has altered the unified dataset solution, and the  $Q$ -values of the AMS and unified datasets are now comparable. The  $Q_{true}$  and  $Q_{pseudo}$  values for the AMS component of the unified dataset are now respectively 2.2 and 0.67 times those of the AMS-only dataset.

**Comment 4.8:**

*Taking the assumption that the fit is less good for the unified dataset, it is then surprising that the reconstruction of the total AMS signal and PTR-MS masses in the unified case (Fig. 12) are close to 1 and very similar to the PTR-MS case only (Fig. 7). Perhaps the residuals ( $e_{ij}$ ) of the unified case have much larger positive and negative values that still mostly cancel each other?*

**Response:**

As discussed above in response to Comment 4.7, the implementation of the pseudo-

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robust mode has caused the fit to be of similar quality in the AMS-only and unified datasets. Therefore the issue raised in this comment no longer applies.

**Comment 4.9:**

*At pg. 6748, line 11, please explain how the two OOA factors were mathematically recombined into one factor for presentation of the mass spectrum and time series.*

**Response:** Implementation of the pseudo-robust method for downweighting outliers (see response to Comment 1.3) eliminates the factor splitting. As a result, mathematical recombination of a split OOA factor is no longer necessary.

We now present a 5-factor solution to the AMS dataset that is similar to the 6-factor solution presented in the original manuscript (after the OOA factors are recombined). Splitting of the OOA factor now occurs on moving from  $p = 5$  to  $p = 6$ .

**Comment 4.10:**

*At pg. 6757, lines 12-15, the manuscript states that "Signal intensity is normalized such that each factor mass spectrum of the individual instrument sums to 1." If the spectrum signals are renormalized, the required multiplicative factor must be applied inversely to the time series so that the product of mass spectra and time series still reconstruct the input matrix. Please explain in more detail how the rescaling was applied.*

**Response:**

A related issue was also raised in Comment 1.1, and a portion of the response is reproduced here.

For the unified dataset, it is inconvenient to inspect a single normalized profile containing the mass spectra for both instruments due to the difference in units and scale.

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(Note that the presence of different units in the same  $\mathbf{X}$  matrix does not affect PMF because PMF operates on the (dimensionless) matrix of scaled residuals,  $\mathbf{E}/\mathbf{S}$ ). We feel the PMF solution is easiest to physically interpret if the factor profiles are presented as separate mass spectra for the two instruments. Thus we do not directly report the  $f_{h,j}$ , but rather the quantities  $\frac{f_{h,j,h=n}}{\sum_j^{j=AMS} f_{h,j,h=n}}$  and  $\frac{f_{h,j,h=n}}{\sum_j^{j=PTR} f_{h,j,h=n}}$  for the AMS and PTR-MS, respectively ( $h$  and  $j$  are factor and  $m/z$  indices, respectively, and  $n$  is a single factor in the  $p$ -factor solution). Note that this is identical to the presentation for the individual datasets, except that in these cases the summation constitutes the entire factor profile and the normalization is performed by PMF2.

Likewise, a more meaningful presentation is obtained by plotting the factor time series for the unified dataset in the units of the respective instruments. Similar to the factor profiles, this means we do not directly report the  $g_{ih}$ , but rather  $g_{ih,h=n} \left( \frac{\sum_j^{j=AMS} f_{h,j,h=n}}{\sum_j f_{h,j,h=n}} \right)$  and  $g_{ih,h=n} \left( \frac{\sum_j^{j=PTR} f_{h,j,h=n}}{\sum_j f_{h,j,h=n}} \right)$ , for the AMS and PTR-MS, respectively. The general forms of these expressions are presented here for clarity. However, in our application PMF2 is configured to output factors with  $\sum_j f_{h,j,h=n} = 1$ .

A slightly different reporting scheme is now utilized in the Supplement to overlay solutions to the individual and unified datasets, or to compare unified dataset solutions obtained at different seed,  $f_{peak}$ , or  $C_{PTR}$  (see Comments 1.14, 4.6, and 4.16). The object is to avoid the near-redundancy of separate plots of AMS and PTR-MS time series, which differ only by constant scaling factors, as evident above. We report  $\frac{f_{h,j,h=n}}{\sum_j^{j=AMS} f_{h,j,h=n}}$  and  $\frac{f_{h,j,h=n}}{\sum_j^{j=PTR} f_{h,j,h=n}}$  as above, but the time series are shown as  $g_{ih,h=n}/\overline{g_{ih,h=n}}$  (i.e. normalized to the mean concentration). We report  $\overline{g_{ih,h=n,AMS}}$  and  $\overline{g_{ih,h=n,PTR}}$  for each trace so that the time series may be easily converted to the relevant units and the concentrations readily compared. These means are calculated

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as:

$$\begin{aligned} \overline{g_{ih,h=n,AMS}} &= g_{ih,h=n} \left( \frac{\sum_j^{j=AMS} f_{h,j,h=n}}{\sum_j f_{h,j,h=n}} \right) \\ \overline{g_{ih,h=n,PTR}} &= g_{ih,h=n} \left( \frac{\sum_j^{j=PTR} f_{h,j,h=n}}{\sum_j f_{h,j,h=n}} \right) \end{aligned} \quad (2)$$

Mathematical explanations of these forms of presentation are presented in the revised manuscript.

**Comment 4.11:**

*The text often uses the term "residual" when I think "scaled residual" would be more accurate. It would be helpful to the reader to make this clear distinction.*

**Response:**

The terminology has been clarified. In particular, "scaled residual" is used whenever the quantity  $e_{ij}/s_{ij}$  is described. Where necessary, mathematical symbols are used to clarify the quantity under discussion.

**Comment 4.12:**

*At pg. 6750, line 24 how was it determined that the signal from the factor was concentrated in short spikes, since the modeled data has been averaged to 15 min? It also seems that by averaging to 15 min. the authors are removing some of the temporal contrast that allows PMF to better separate the factors. Were the datasets run in PMF with shorter averaging times, and was there a reason to settle on a time so much larger than the reporting times of the individual instruments?*

**Response:**

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The reviewer is correct that because the PMF was performed on 15 min data, the influence of a particular factor on the raw 1 min data cannot be explicitly determined. However, a number of periods exist where the particulate organic mass is dominated by this factor (i.e.  $> X\%$ ) and the total organic mass is well-represented by PMF (i.e.  $e_{ij}/x_{ij} < X$ ). Under such conditions, the factor signal and the total organic mass can be approximately equated in the 1 min data, and the spikes are evident. This has been clarified in the manuscript.

Preliminary experiments were conducted on datasets with shorter averaging times. In these experiments the resolved factors tended to contain data from either the AMS or PTR-MS, but not both. We speculate that this is caused by the different residence times in the instrument sampling lines, which means that the instrument sampling intervals are, in effect, not perfectly synchronized. The importance of this effect is reduced by a longer averaging interval (because the non-synchronized averaging time is a smaller fraction of the total interval). This is supported by the observation that longer averaging intervals provide consistent results with the 15 min dataset. Comparison of the effect of averaging time with other datasets (e.g. rural locations where the particle/gas composition is less affected by rapidly changing point sources) will provide further insight. A brief discussion of the choice of averaging time has been added to the manuscript.

**Comment 4.13:**

*It would be extremely helpful to present diurnal average plots of all the factors and tracers (from the individual and unified datasets, even if some or all of them are in Supp. Info.), since the text refers to them often and they are considered as a metric used to identify primary emission factors (pg. 6760, lines 7-11).*

**Response:**

The suggested plots have been added to the Supplement.

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**Comment 4.14:**

*Reading the discussion of the factors and making comparisons between Figs. 6-7 and 11-12 would be simpler if all of the factors were assigned names. This would be especially helpful at pg. 6762 line 22, where the text refers to "charbroiling and HOA factors" in the unified dataset, but neither F1UN nor F2UN is clearly identified as HOA at pgs. 6757-8.*

**Response:**

We have assigned the following factor names. As discussed in the original manuscript, several of the PTR-MS factors are ambiguous or mixed-source, and this is reflected in their names. Prefixes indicate the source dataset.

AMS dataset:

F1<sub>AMS</sub>: AMS-OOA-1 (OOA = Oxygenated Organic Aerosol)

F2<sub>AMS</sub>: AMS-HOA (HOA = Hydrocarbon-like Organic Aerosol)

F3<sub>AMS</sub>: AMS-Charbroiling

F4<sub>AMS</sub>: AMS-BBOA (BBOA, Biomass Burning Organic Aerosol), identification tentative

F5<sub>AMS</sub>: AMS-Northern Point Source

PTR-MS dataset:

F1<sub>PTR</sub>: PTR-Traffic

F2<sub>PTR</sub>: PTR-Long-Range Transport+Local Source

F3<sub>PTR</sub>: PTR-Long-Range Transport+Painting

F4<sub>PTR</sub>: PTR-Local SOA (SOA = Secondary Organic Aerosol)

F5<sub>PTR</sub>: PTR-Oxygenates (source unknown)

Unified dataset:

F1<sub>UN</sub>: UN-Charbroiling

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F2<sub>UN</sub>: UN-Traffic  
F3<sub>UN</sub>: UN-Aged SOA  
F4<sub>UN</sub>: UN-Local SOA  
F5<sub>UN</sub>: UN-Oxygenated POA  
F6<sub>UN</sub>: UN-Local Point Source

**Comment 4.15:**

*I support the recommendation by P. Paatero that the rotational freedom of the chosen solutions is explored and suggest that these solutions are included in the Supp. Info. and discussed in the paper.*

**Response:**

The issue of rotational ambiguity was discussed in response to Comment 1.7. For clarity, we repeat the response here.

Solutions for each dataset were obtained at  $f_{peak} = -1.5$  to  $1.5$ . A comparison of solutions obtained at  $f_{peak} = -1.0, 0,$  and  $1.0$  is presented in the Supplement for each dataset. For the AMS and unified datasets, the solutions are very similar independent of  $f_{peak}$ . However, rotational ambiguity is evident in the PTR-MS dataset. Here the solutions at non-zero  $f_{peak}$  are qualitatively consistent with that at  $f_{peak} = 0$  in that factor identification is unaffected. However, quantitative analysis of the factor composition and relative factor concentrations is even more questionable than suggested by analysis of the somewhat ambiguous solution at  $f_{peak} = 0$ . Interestingly, comparison of the individual and unified factor mass spectra as a function of  $f_{peak}$  suggests that PTR-MS rotational ambiguity is significantly decreased in the unified dataset.

**Comment 4.16:**

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*In the Supp. Info., the figure numbers are incorrect in the text. Similar to the suggestion above for overlaying the factors from the unified and individual datasets, better comparison between the factors from different CPTR cases could be made by overlaying the factors here, too. The comparison of the time series in these cases is complicated by the fact that two things are changing at once (the solutions themselves, and the apparent relative weighting applied by normalizing the changing mass spectra of the solutions). If it would be possible to present the results so that direct comparison change of the solutions could be made, the usefulness of these plots would be increased.*

**Response:**

The figure numbers have been corrected. We have added overlaid plots comparing solutions obtained at different  $C_{PTR}$ . Note that to enhance the presentation we do not directly report either the  $f_{hj}$  or  $g_{ih}$ , but rather the normalized and/or scaled quantities discussed in response to Comment 4.10. The Supplement contains comparisons of the 6-factor solutions obtained at  $C_{PTR} = 10$ , yielding  $\Delta\bar{e}_{sc} = 0.052$ , with the 6-factor solutions yielding  $\Delta\bar{e}_{sc} \sim \pm 0.25$ ,  $\Delta\bar{e}_{sc} \sim \pm 0.50$ , and  $\Delta\bar{e}_{sc} \sim \pm 1.0$ . The factor profiles and time series are overlaid as discussed in response to Comments 1.1, 4.10, and 4.16. Results are analyzed as a function of their sensitivity to  $\Delta\bar{e}_{sc}$ . At  $\Delta\bar{e}_{sc} \sim \pm 0.25$  the basic factors are preserved, with the major changes occurring in weakly attached features of a factor (e.g. paint fume contamination in the traffic factor).

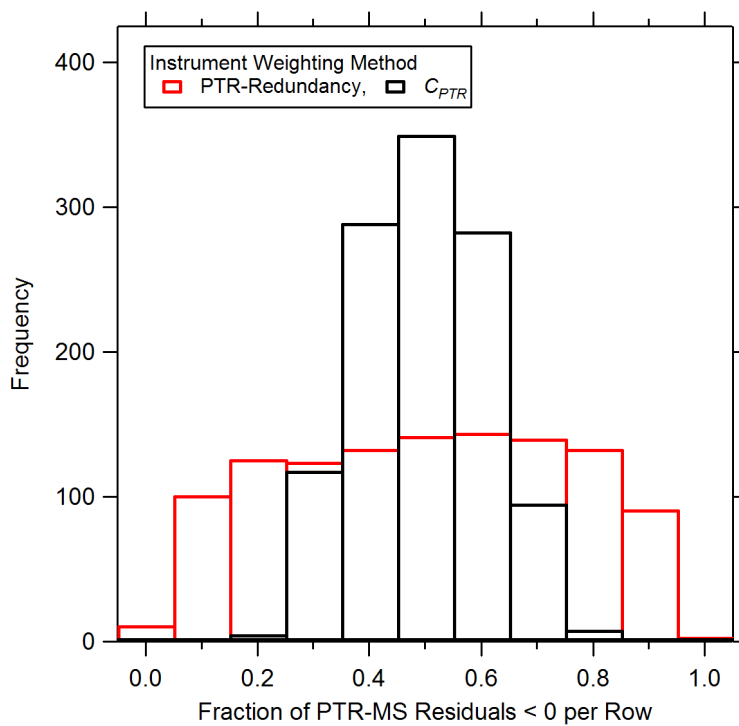
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Ulbrich, I., et al.: Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys. Disc.*, 8, 6729-6791,

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**Fig. 1.** Figure 4.1. Frequency of negative PTR-MS residuals per row (i.e. time point) of residual matrix E. Shown are 6-factor solutions for  $n_{PTR} = 50$  (PTR-redundancy method) and  $C_{PTR} = 10$  (uncertainty-weight)

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