Simultaneous factor analysis of organic particle and gas mass spectra: AMS and PTR-MS measurements at an urban site

J. G. Slowik[1,3], A. Vlasenko[1,3], M. McGuire[2,3], G. J. Evans[2,3], and J. P. D. Abbatt[1,3]

[1]{Department of Chemistry, University of Toronto, Toronto, Canada}

[2]{Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Canada}

[3]{Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Toronto, Canada}

Correspondence to: J. P. D. Abbatt (jabbatt@chem.utoronto.ca)

SI-1: Unified dataset: Comparison of solutions at C_{PTR} = 5, 10, and 20

As discussed in the main manuscript, the 5-factor solution at C_{PTR} = 10 was selected as optimal. To further explore the solution space in terms of instrument weighting, we compare this selected solution to the 5-factor solutions obtained at C_{PTR} = 5 and C_{PTR} = 20, which are the adjacent points in Fig. 8. The mass spectra and time series of the C_{PTR} = 10 solution are compared to that at C_{PTR} = 5 in Figs. S5 and S6, respectively, and to C_{PTR} = 20 in Figs. S7 and S8. In Fig. S9, we plot the fraction of signal apportioned to each factor for the AMS and at each PTR-MS *m/z*. The difference between the stacked *m/z*'s and 1 is due to signal contained in the residuals. The solutions are mostly similar, however the major differences are discussed below.

The most prominent change in the time series shown in Figs. S6 and S8 occurs in factor $F3_{UN}$. As shown in Fig. S9, the AMS signal apportioned to $F3_{UN}$ decreases by approximately a factor of 3 between C_{PTR} = 10 and C_{PTR} = 20. From Fig. S8, it is evident that the signal decreases both during the two discrete events on 30 January and during the extended 31 January to 2 February period. Proportionally, the 30 January event is decreased less than the extended period. As shown in Fig. S9, the decrease in the AMS fraction at $F3_{UN}$ corresponds with an increase in $F1_{UN}$, which is mostly due to increased signal during the 31 January to 2 February period. The AMS $F1_{UN}$ mass spectrum is also affected, with the oxygenated marker *m/z* 44 increasing from 1.6% of the spectrum at C_{PTR} = 10 to 4.1% at C_{PTR} = 20. Although this specific change is unique to the C_{PTR} = 20 solutions, it is representative of a general trend of increased similarity in AMS factor mass spectra with increasing C_{PTR}.

Changes in the PTR-MS factors are mostly due to reapportionment of acetone (*m/z* 59) and acetic acid (*m/z* 61) among the factors. Acetone and acetic acid apportionment is consistent between C_{PTR} = 10 and C_{PTR} = 5. In contrast, at C_{PTR} = 20, there is proportionally more acetone apportioned to $F2_{UN}$ and more acetic acid to $F3_{UN}$. This is consistent with the emergence of factors dominated by acetone and acetic acid (i.e. factors $F3_{PTR}$ and $F2_{PTR}$) as the PTR-MS weighting increases. A corresponding change in the AMS mass spectra of $F2_{UN}$ is observed, moving from hydrocarbon-like

(C_{PTR} = 5 and 10) to oxygenated (C_{PTR} = 20). The oxygenated AMS spectrum is not consistent with the time series, which correlates with primary emission tracers such as NO_x (see Fig. 11). This lack of self-consistency suggests that the AMS data is underweighted and therefore not reliable at C_{PTR} = 20. Because of this, the AMS data does not carry sufficient weight to enable the apportionment of acetone and acetic acid into primary and secondary sources, as was discussed in detail in the main manuscript.

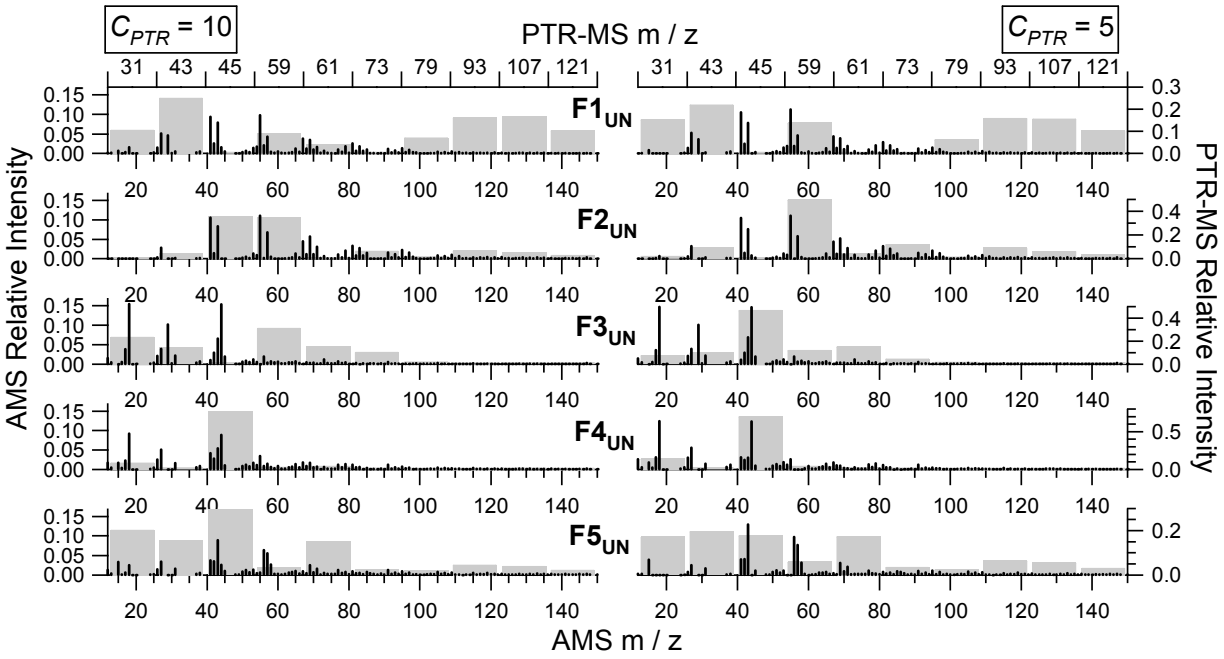

Figure S1. Factor mass spectra for the solutions to the unified dataset at C_{PTR} = 10 (left column) and C_{PTR} = 5 (right column). AMS mass spectra are shown as black traces (left and bottom axes); PTR-MS mass spectra are shown as grey bars (right and top axes).

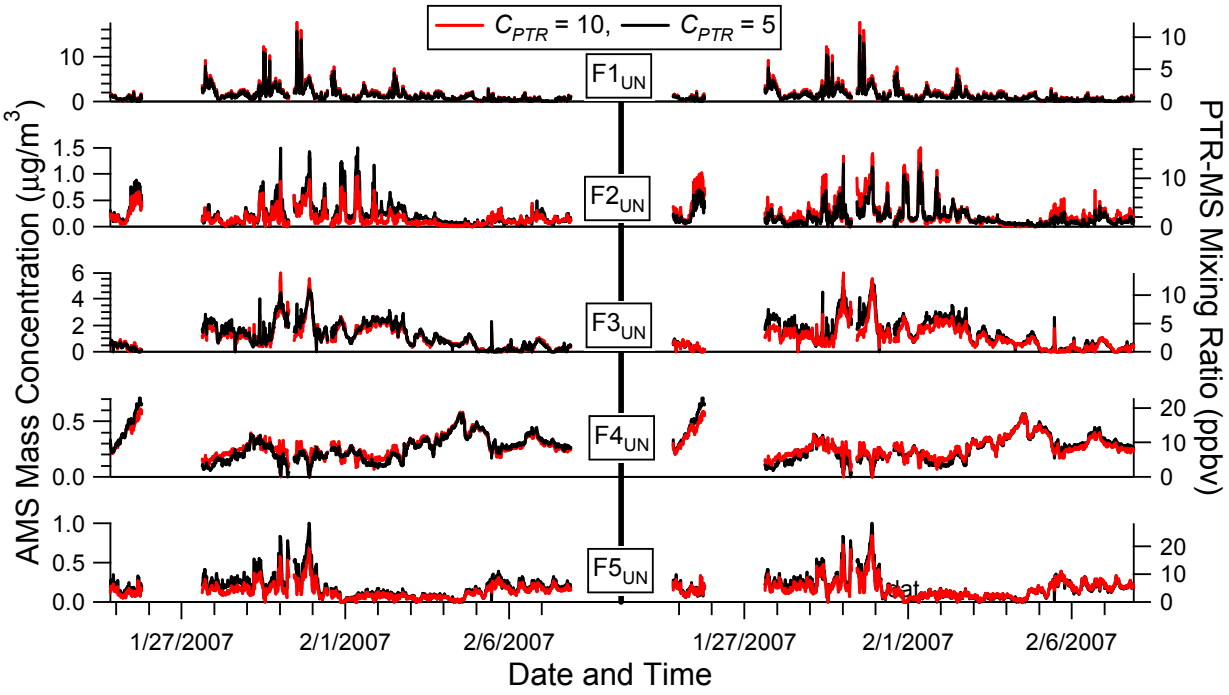

Figure S2. Factor time series for the solutions to the unified dataset at C_{PTR} = 5 (black) and C_{PTR} = 10 (red). AMS and PTR-MS time series are shown on the left and right axes, respectively.

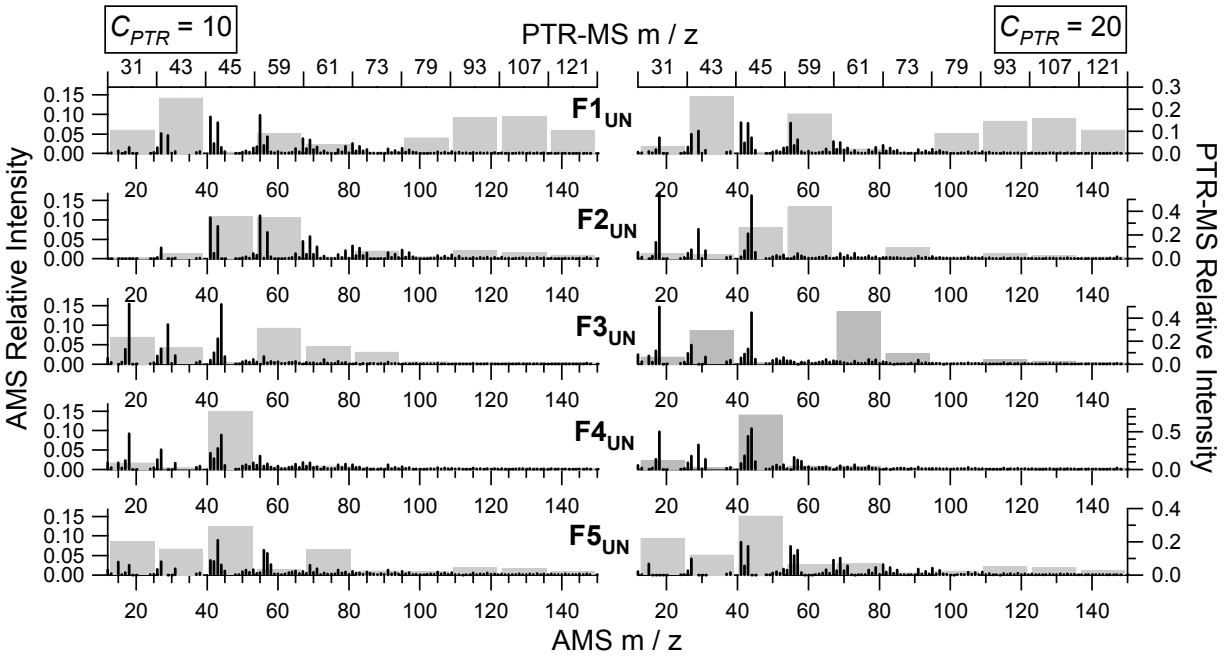

Figure S3. Factor mass spectra for the solutions to the unified dataset at C_{PTR} = 10 (left column) and C_{PTR} = 20 (right column). AMS mass spectra are shown as black traces (left and bottom axes); PTR-MS mass spectra are shown as grey bars (right and top axes).

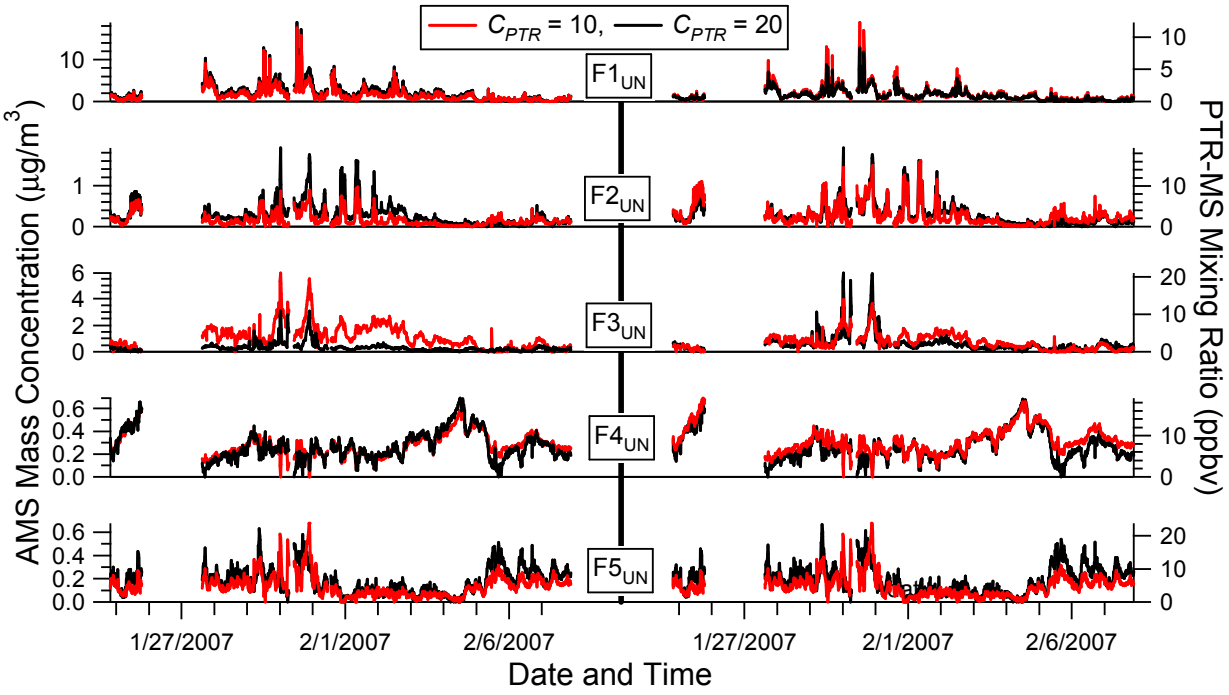

Figure S4. Factor time series for the unified dataset solutions at C_{PTR} = 20 (black) and C_{PTR} = 10 (red). AMS and PTR-MS time series are shown on the left and right axes, respectively.

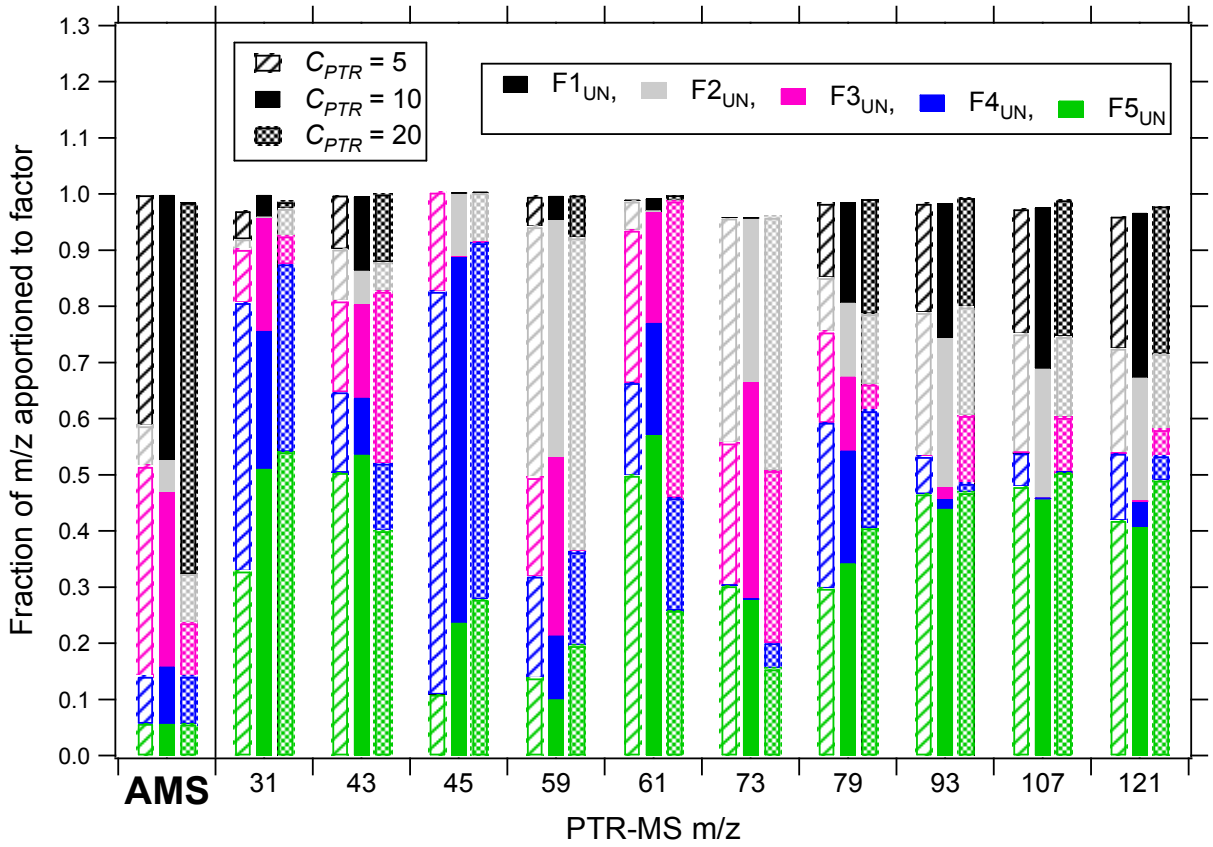

Figure S5. Mass spectra for the unified dataset solutions at C_{PTR} = 5, 10, and 20 represented as the fraction of signal in the AMS and at each PTR-MS *m/z* assigned to the specified factor. Differences between the stacked total and 1 are due to signal contained in the residuals.