Chemical Evolution of Secondary Organic Aerosol from OH-Initiated Heterogeneous Oxidation

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Supplementary Material

Positive Matrix Factorization (PMF) Analysis

It should first be noted that selection of the number of factors in the Positive Matrix factorization (PMF) analysis is a subjective task and there are no unambiguous diagnostics to choose the appropriate number of PMF factors. Obviously, an increase in the number of factors results invariably to a better fit to the data and to a reduction in the residual error matrix. However, the factors may not be meaningful if too many factors are chosen. The quality of fit parameter Q value (i.e. object function) is the sum of the squares of the residual error matrix normalized to the error in the data matrix (Paatero, 1997). This value can be used to evaluate the degree to which increasing the number of factors improves the fit to the dataset. Ulbrich et al.(2009) gives a further discussion on the determination of the appropriate number of factors for a PMF analysis.

Here, PMF analysis was run on a data set including AMS measurements of SOA1 under a range of OH exposures for up to 6 factors, and the number of factors was chosen to maximize the number of distinct and meaningful PMF profiles. We found from the PMF analysis that the data set was best modeled with a 2-factor solution. Subsequent increase in the number of factors improved the modeling fit to the data to a lesser extent. The Q values were reduced by the greatest amount from the increase in one factor to two factors compared to other solutions with a higher number of factors. Furthermore, solutions with more than two factors produced factors that were not unique, resulting in nearly identical time series or profiles with correlation coefficients of $R \geq 0.9$. Therefore, we found 2-factor PMF solution to be the most reasonable analytical solution for this data set.

Two unique sets of solutions were calculated for the 2-factor solution when the rotational parameter (FPEAK; see Ulbrich et al.(2009) used in the PMF deconvolution model was varied from negative to positive (including 0) values in the FPEAK value range of -1.5 to 1.5. Factor profiles for the two factors calculated under various FPEAK values are shown in Figure A1. For the set of solutions calculated using negative FPEAK values, both factor profiles were qualitatively quite similar to the unreacted SOA1 mass spectrum as shown in Figure A2 but with different relative contributions of m/z 44. For the set of solutions calculated using positive FPEAK values, factor profiles were more in line with Pittsburgh HOA and OOA from principle component analysis of ambient AMS measurements (Zhang et al., 2005) as shown in Figure A3. Because the second set of solutions using an Fpeak = 0 produces factor profiles that are more comparable to PMF or PCA factors deconvolved from organic mass spectra of ambient aerosol particles, we focus on the analysis of FPEAK = 0 solution. In the paper, these PMF factors for FPEAK = 0 are referred to as A1 and A2 for the 2-factor solution. The variability in the fraction of m/z 41 and 55 in the HOA-type factor A1 profiles over the positive FPEAK values compared to FPEAK =

0 are approximately 3 and 4% respectively, whereas the fraction of m/z 44 in the OOA-type A2 profiles is 10%.

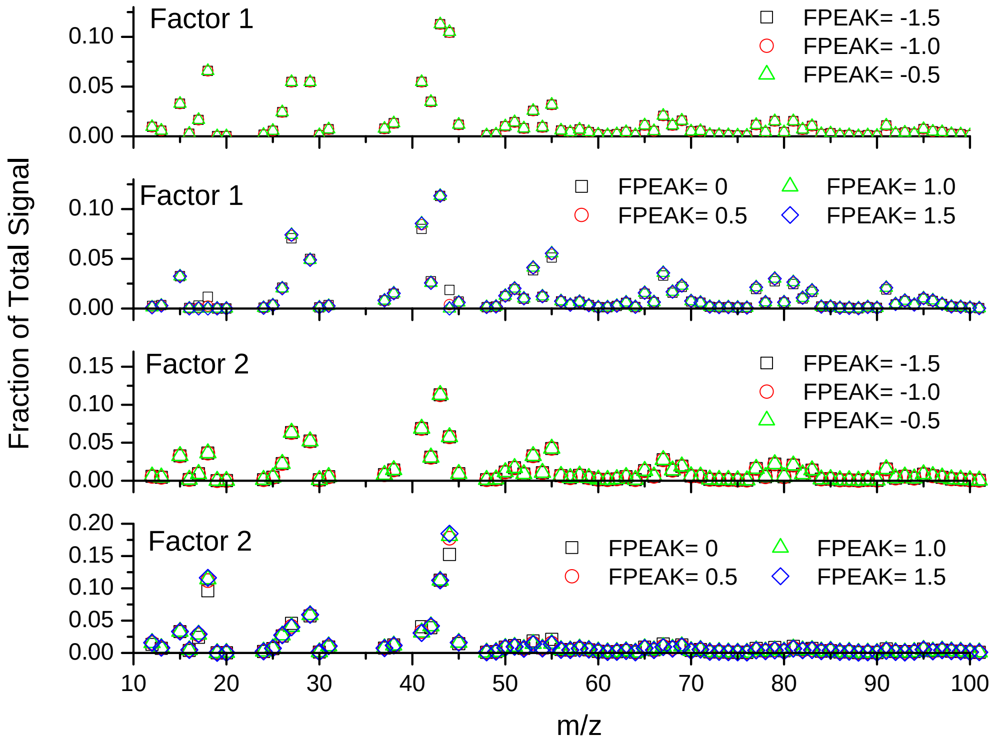

Figure A1. PMF factor profiles for 2-factor solution under variable FPEAK values.

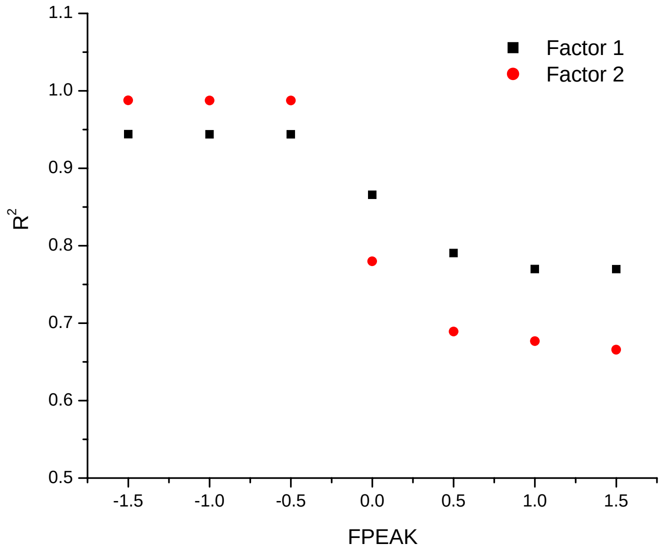

Figure A2. R^2 values between PMF factor profiles in Figure A1 and initial SOA1 mass spectrum normalized to total signal as a function of FPEAK value.

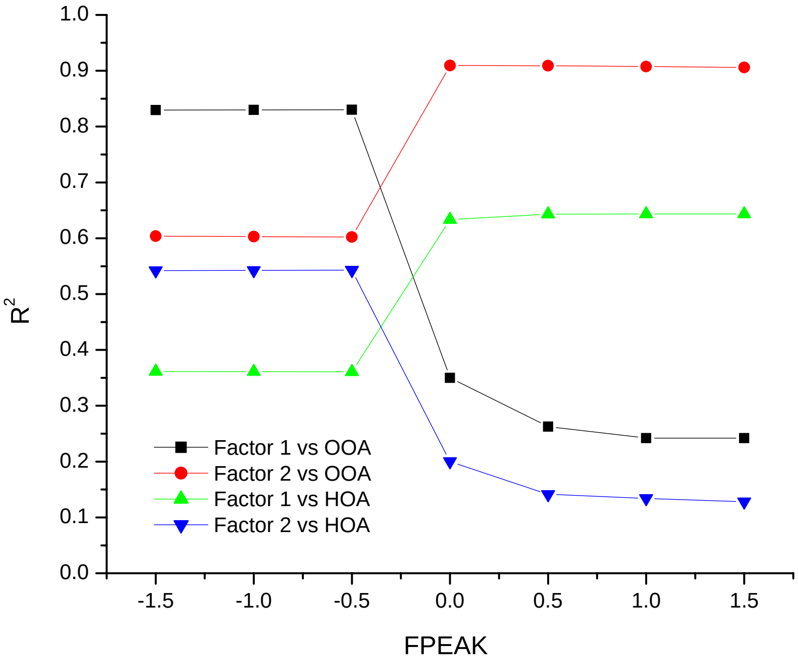

Figure A3. R^2 values of PMF factor profiles in Figure A1 compared to Pittsburgh HOA and OOA factor profiles (Zhang et al., 2005) as a function of FPEAK value.

References

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