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Atmospheric
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Discussions

Interactive comment on "Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data" *by* I. M. Ulbrich et al.

I. M. Ulbrich et al.

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We thank B. Resson for her comments. We agree that determining the absolute concentrations and relative amounts of diesel vs. gasoline vehicle emissions in ambient OA is a topic of high interest, and that analyses along the lines of those suggested may yield information on this or related topics. We would like to make the following points in response:

(1) The types of analyses suggested are outside the scope of the current paper. This paper addresses a specific question: "what components can be separated from PMF-type time series analysis of a whole Q-AMS dataset at an urban background site, when only the AMS data is used in PMF?" Many groups are carrying out this type of anal-

ysis in this manner with promising results, so trying to answer the above question is important. The paper is already long and complex, because in our opinion much detail is needed in to address that question. For this reason we have limited this paper to addressing that question, while we and others will address many interesting related questions in future papers.

If we wanted to expand the current paper, we think that rather than the studies suggested by B. Resson, a more relevant expansion would be to repeat the type of analyses in the paper using other urban background datasets from different cities and seasons, to further explore the generality of our conclusions. However this would add much delay to the publication of what we think is a timely paper, and would also further increase the length of this paper, making it harder to read and therefore less useful to the reader.

(2) When PMF is applied to AMS data as in our paper, separation of sources whose spectra are very similar (such as diesel and gasoline vehicle emissions) is limited by the correlation of their true spectra. This is discussed in our paper, e.g. the abstract states "Components [..] with high correlation (R>0.9) with other components are suspect and should be interpreted with care." See also section 3.2.2, the discussion on p. 6764, and Figures 11, 12, and 13. Perhaps this has not received sufficient emphasis. This means that true factors (e.g., diesel vehicles and gasoline vehicles) with highly correlated time series and/or mass spectra will be difficult so separate accurately. The correlation coefficient (R_{MS}) between several diesel and gasoline vehicle exhaust spectra measured by the AMS is 0.97-0.99, (Mohr et al., *Environ. Sci. Technol.*, submitted, 2008) - too high to be reliably separated from unit-resolution Q-AMS data with PMF. We will try to clarify and emphasize this aspect in the revised version of the manuscript, using the diesel vs. gasoline separation as an example.

(3) As an aside, the paper cited by B. Resson in her comment likely explains the reason for the very high correlation between the diesel and gasoline emission spectra in the Q-AMS. The AMS analyzes all of the organic mass. Fraser et al. note that the most

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common compounds in diesel exhaust are also found in gasoline-powered vehicle exhaust and that unique tracer compounds are present only in small amounts. Sampling these particles with a relatively hard ionization technique in the AMS (electron impact), most of the fragments would be formed from the common compounds (or compounds in the same general families such as linear and branched hydrocarbons, etc. that produce similar fragments), with very little signal from the distinct fragments of the tracer compounds. Overall this will give rise to very similar spectra. This result is unlikely to change, even if rush hour periods were removed from the dataset or analyzed separately with PMF (using only Q-AMS data).

(4) Note that the separation of diesel vs. gasoline emissions from organic molecular markers can be very difficult and has been the subject of controversy and much work for a decade. The cited Fraser et al. paper is part of that body of work addressing that controversy and trying to confirm the differences between the measured molecular tracers using the *known* fractions of diesel/gasoline vehicles vs. time from the video recording.

For example in p. 6749 of our paper, we state that “PMF analysis of molecular markers results in a similar phenomenon in which the composition of gasoline and diesel emissions are too similar and a factor representing the sum is often retrieved (Brinkman et al., 2006).” Much work on this topic has been carried out as part of the same Pittsburgh Supersite study that our work is part of, including the following studies. Shrivastava et al. (2007) report on a PMF analysis of organic molecular markers and conclude that “PMF could not differentiate between gasoline and diesel emissions.” And Subramanian et al. (2006) report (also for the same site) that “variability in the diesel profiles creates uncertainty in the gasoline-diesel split. On an OC basis, one set of scenarios suggests gasoline dominance, while a second set indicates a more even split.” SubuMramanian et al. (2007) report when using CMB that “estimates for the contributions of gasoline-vehicle and cooking emissions can vary by an order of magnitude.”

(5) Although outside of the scope of the current paper, AMS data can be used to

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investigate the diesel vs. gasoline OA apportionment in a variety of ways, e.g.:

(5.1) in tunnel studies like the one in the Fraser et al. paper cited in the comment, or similar studies next to a highway with varying fractions of diesel and gasoline vehicles. We know of one group which is preparing for such a study.

(5.2) using ambient ratios of total organics (or components such as HOA) to tracers such as CO, NOx, EC, or certain PAHs, which have very different emission ratios between gasoline and diesel vehicles, etc. For example Zhang et al. (*Atmos. Chem. Phys.*, 5, 3289-3311, 2005; http://www.atmos-chem-phys.org/acp/5/3289/) notes that small variations in diurnal patterns of the HOA/CO ratio may reflect different activity patterns of primary particle emitters. Also in Dzepina et al. (*Int. J. Mass Spec.*, 263: 152-170, 2007, cited in our paper) we report that PAHs of low and high molecular weight measured with a Q-AMS in Mexico City have different diurnal cycles that are qualitatively consistent with the diurnal cycles of diesel and gasoline vehicle usage, and consistent with the same difference reported in previous studies.

(6) Note that several previous papers have addressed the apportionment of diesel vs. gasoline vehicle emissions in Pittsburgh, e.g.:

- Shrivastava MK, Subramanian R, Rogge WF, et al., Sources of organic aerosol: Positive matrix factorization of molecular marker data and comparison of results from different source apportionment models, *Atmos. Environ.*, 41(40), 9353-9369, 2007.

- Subramanian R, Donahue NM, Bernardo-Bricker A, et al., Contribution of motor vehicle emissions to organic carbon and fine particle mass in Pittsburgh, Pennsylvania: Effects of varying source profiles and seasonal trends in ambient marker concentrations, *Atmos. Environ.*, 40(40), 8002-8019, 2006.

- Martello DV, Pekney NJ, Anderson RR, et al., Apportionment of ambient primary and secondary fine particulate matter at the Pittsburgh National Energy Laboratory particulate matter characterization site using positive matrix factorization and a potential source contributions function analysis, *J. Air & Waste Manage. Assoc.*, 58(3), 357-368, 2008.

- Subramanian R, Donahue NM, Bernardo-Bricker A, et al., Insights into the primary-secondary and regional-local contributions to organic aerosol and PM2.5 mass in Pittsburgh, Pennsylvania, *Atmos. Environ.* , 41(35), 7414-7433, 2007.

- Eatough DJ, Mangelson NF, Anderson RR, et al., Apportionment of ambient primary and secondary fine particulate matter during a 2001 summer intensive study at the CMU supersite and NETL Pittsburgh site, *J. Air & Waste Manage. Assoc.*, 57(10), 1251-1267, 2007.

- Lane TE, Pinder RW, Shrivastava M, et al., Source contributions to primary organic aerosol: Comparison of the results of a source-resolved model and the chemical mass balance approach, *Atmos. Environ.*, 41(18), 3758-3776, 2007.

- Robinson AL, Subramanian R, Donahue NM, et al., Source apportionment of molecular markers and organic aerosols-1. Polycyclic aromatic hydrocarbons and methodology for data visualization, *Environ. Sci. Technol.*, 40(24), 7803-7810, 2006.

- Grieshop AP, Lipsky EM, Pekney NJ, et al., Fine particle emission factors from vehicles in a highway tunnel: Effects of fleet composition and season, *Atmos. Environ.*, 40(Suppl. 2), S287-S298, 2006.

(7) The typographical error at the beginning of Sect. 3.1.1 will be corrected to read, “There is a local minimum at 4 factors and another at 6 factors.”

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6729, 2008.