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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical mass balance of size-segregated atmospheric aerosol in an urban area of the Po Valley, Italy" *by* E. Matta et al.

Anonymous Referee #2

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The subject manuscript describes the measurement of the size resolved chemical composition of atmospheric particulate matter collected with cascade impactors over the course of a year in the Po Valley, Italy. The chemical measurements employ both routine chemical measurements (i.e., mass by gravimetric determination, ions by IC, EC and OC by thermal evolution and combustion) and employ a relatively novel strategy of H-NMR to characterize water soluble organics. Although the authors claim that they have made a "full characterization" of the aerosol samples, this is not completely true since they have made no attempt to characterize water insoluble organic compounds and water insoluble inorganic species. A more appropriate description of the manuscript is a "near complete characterization of the water soluble fraction" of the aerosol that employs a semi-quantitative strategy for water soluble organic compound characterization. The manuscript is well written and describes research that is of great

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interest to the atmospheric chemistry community and the readership of Atmospheric Chemistry and Physics. However, the comments listed below need to be addressed before the manuscript should be accepted for publication. After properly addressing the issues, the manuscript should be accepted for publication.

General Comments

1) The title of the manuscript should be changes since the term "chemical mass balance (CMB)" is a widely used in the atmospheric aerosol community as a source attribution technique that uses source fingerprints and receptor measurements to apportion source contribution from sources. The use of the terms is clear from the following sources: 1) Seinfeld and Pandis, Atmospheric Chemistry and Physics Ű a seminal reference for the atmospheric chemistry field, 2) a search on ICI Web of science, and 3) a web search using search engines such as Yahoo. The authors are attempting to close the mass balance on the chemical composition of the aerosol samples, which is often termed "mass closure on the chemical species" and/or reconstructed mass. 2) As stated above, the manuscript claims in the abstract, introduction, and conclusion that the measurements provide "complete" chemical characterization of the aerosol chemical composition. A more appropriate description of the manuscript is a "near complete characterization of the water soluble fraction" of the aerosol that employs a semi-quantitative strategy for water soluble organic compound characterization. 3) The Authors collected 34 8-hour samples over the course of a year. These sampling periods represent 34 of the potential 1095 sample periods and are missing samples from July and August. In addition, samples collected after rains storms, which represent low aerosol concentrations are not included in the data analysis. The low number of samples and the bias missing samples from the two months and low aerosol concentrations make the measurements a poor statistical representation of the of the fall-winter (FW) and spring-summer (SS) periods. To this end, the comparison of averages, minimums and maximums between the two periods (FW and SS) are not really appropriate. Certainly, these measurements are important and represent typical atmospheric conditions

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but should not be presented as an accurate representation of the two sampling periods. 4) Many of the figure and tables present impactor data as a function of stage number. This presentation is not instructive to the reader who is not familiar with the Berner impactor or uses other impactors. To this end, the data should be presented in more common form, which presents the size range of the impactor stage. In addition, impactor data is more commonly presented dC/d(logDp) and the Authors are encouraged to present data in this form. 5) The comparison of results from the modeling study of Aumont et al. (2000) does not support the conclusions presented in the manuscript. Aumont et al. (2000) state that their modeling study does not agree with measurements and do propose possible explanations. There is considerable uncertainty in the composition of secondary organic aerosols in the atmosphere. To this end, the stated conclusion that "gas-to-particle conversion of anthropogenic VOCs showed that this pathway provides a minor contribution to the organic composition..." In addition, it is unclear how the authors demonstrate that the observed functional groups that are in common with the modeled secondary organic aerosol are not actually emitted from primary sources. It is well known that much of the the organic compounds in wood smoke are water soluble.

Specific Comments

1) Page 4, lines 1-3: This implies that the WSOC analysis was performed without acidification and purging. The details of the analysis should be provided for the reader to help understand the operationally defined WSOC measurement. 2) Page 6, line 3: In context to the General Comment 3, can the comparison of these averages really be used to represent the period averages. Are these values statistically different using a 95% confidence interval? 3) Page 7, lines 26-28: References should be provided that demonstrate the association of water soluble potassium with biomass aerosols. 4) Page 8, lines 5-6: Why not show the difference between the October to December and January to March measurements. This would be more instructive to the reader than Figure 4. 5) Figure 12: How were these compounds identified? Where standards actu-

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ally analyzed? Are there possible interferences? 6) Page 8, lines 37: If the C/H ratios were assumed based on specific model compounds, how can the Authors conclude at the bottom of page 8: "It is noticeable that the aromatic moieties account for only a few percentages of the total hydrogen content, but up to 50% of TOC,..."

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 2167, 2002.