

***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.**

E. Matta et al.

Received and published: 12 March 2003

We would like to thank the referee #2 for extremely useful and constructive comments. As a consequence of his suggestions there have been several changes in the text. The specific concerns are described below and the following replays are in the same order as in the referee's comments

GENERAL COMMENTS

1. Title. The comment of the reviewer is accepted: the title is changed in "Mass closure on chemical species in size-segregated atmospheric aerosol collected in an urban area of the Po Valley, Italy" "Mass balance" is substituted with "mass closure" also throughout the text.
2. The reviewer criticizes the completeness of the aerosol chemical analysis and argues that only a near complete characterization of the water-soluble fraction is

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

achieved. We do not agree with this, since the characterization of the water-soluble fraction (inorganic salts + WSOC) is actually complete. WSOC analysis is based on a functional group method instead of being performed at the molecular level and this is clearly expressed in the text. The characterization of WSOC by means of this method is complete with respect of the high recovery provided by the HNMR and HPLC techniques, which allowed to achieve a general information on water-soluble organic carbon functional groups instead of on specific compounds.

We have also carried out the determination of the water-insoluble fraction of carbon, even if no speciation was made, and only the "unknown fraction" has not been analyzed.

3. The reviewer states that the measurements reported in the manuscript should not be presented as an accurate representation of the two sampling periods (fall-winter, and spring-summer), due to the low number of samples. It was not our aim to collect a statistically representative fraction of the sampling period, and we have restricted the analysis to samples which can be considered "typical" for the two seasonal periods, on the basis of meteorological data and automated PM10 records (Fig. 2), which were available for the whole year. We think that the limit of this approach (e.g. not accounting for winter rainy days and the missing mid-summer samples) are clearly reported in the text.

4. The reviewer's comments are accepted in part. The size intervals correspondent to the stage numbers are now reported in the tables and in the captions of all figures. For graphical reasons, we have preferred to leave the stage numbers in the figure apart from Fig. 12. The representation of data as $dC/d\log(D_p)$ facilitates the intercomparison of different impactors, but loses information on absolute mass concentration. For the purpose of this study -a "chemical" assessment on an urban Po Valley aerosol, we considered more important to show the absolute concentrations than representing the data on a log scale.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

5. With respect to the comparison of our results from HNMR analysis, with the modeling work of Aumont et al. (2000) some clarifications are needed. We have quoted Aumont et al. (2000) as a suitable reference which reports the theoretical functional group composition of WSOC derived from the oxidation of VOCs. But we have not stated that our results are in contradiction with the conclusions of Aumont and co-authors. On the contrary, the conclusions are exactly the same: measurements are in disagreement with the known mechanism of gas-to-particle conversion, therefore the secondary origin of WSOC can be accounted only by introducing oxidation processes in the deliquescent particles. The novelty of the present work lies in the fact that the comparison between the modeled functional group composition and the observed one (by HNMR) is straightforward, whereas the measurements cited by Aumont et al. (2000) referred to determination of specific di-carboxylic acids contributing to WSOC depend on several assumptions (Saxena and Hildemann, 1996, *J. Atmos. Chem.*, 24, 57-109).

Concerning the possible origin of WSOC by primary sources such as biomass burning, we fully agree with the Reviewer. The sentence "In addition, tracer analysis (levoglucosan) suggests that biomass burning may represent an important primary source of WSOC in the Po Valley environment (Decesari et al., 2001)" is added in the Conclusions to clarify this point.

SPECIFIC COMMENTS

- 1) The paragraph of the WSOC analysis is re-phrased and details of analysis are provided.
- 2) The two values are statistically different at a significance level of 0.05 according to the t test. This means that the two sets of samples actually show different percentages of coarse particles mass on total PM on average. Concerning the rationale for grouping samples, see response to general comment 3.
- 3) References are added to the text.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

4) The different content of neutral compounds in the period October-December compared to January to March is reported in the text. Figure 4 is retained since it shows lumping of winter samples according to PM concentrations, not to chemical composition.

5) The individual compounds were recognized according to chemical shift values determined either by analysis of standards in previous work (Decesari et al., 2001) or found in the literature (Suzuki et al., 2001). The signature of five peaks of levoglucosan (a sixth one is hidden by the signal of water) identifies this compound unambiguously. In contrast, the other compounds were identified according to singlets, and in principle interference by other compounds showing exactly the same chemical shift cannot be ruled out.

6) The C/H ratios of the functional groups were not assumed based on model compounds, but were calculated using a method that we have published previously (Fuzzi et al., 2001): for each functional group C/H ratio are calculated as an average value plus an interval of variation, according to the ratios allowed by stoichiometry (see Fuzzi et al., 2001). In the case of aromatic moieties we did not assume any C/H ratio since its theoretical interval of variation is too high. Conversely, this was estimated by the aromatic H content from HNMR and the C content of the sample after subtracting the aliphatic C calculated by the model. In this case, it turned out that the aromatic C/H ratio is very high, which is typical of highly condensed and/or substituted aromatic rings.

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

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)