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Interactive comment on "Functional group analysis by H NMR/chemical derivatization for the characterization of organic aerosol from the SMOCC field campaign" *by* E. Tagliavini et al.

E. Tagliavini et al.

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We acknowledge the Referee for his thorough review of our paper. Here, we provide answers to the specific comments of the Referee. We have also prepared a revised version of the manuscript for publication on ACP, where we have addressed all the issues risen by both Reviewers, particularly with respect of the uncertainty analysis.

(1) The first point put forward by this referee (S4168 line 4) is related to the sources of the imbalance between the organic carbon accounted for by the NMR functional groups and the measured TOC (page 9465, l.13-27 of the original manuscript). We have estimated the uncertainty associated with the functional groups quantification

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in spectra with low signal-to-noise ratio, and concluded that this cannot be the major source of underestimation of the organic carbon. We have therefore removed this point from the discussion section, while the presentation of the other two hypotheses was kept. We must emphasize that the lack of knowledge of the structure of the compounds actually present in WSOC prevents the estimation of the relative importance of the two remaining sources of uncertainty, although it is unlikely that the H/C ratios used for the aliphatic groups are significantly overestimated. Finally, the uncertainty in the TOC analysis is around 5% over the entire concentration range, therefore it can only be responsible for a minor contribution of the carbon imbalance.

(2) The second point regards the incomplete survey of the literature related to our paper. We believe the citations to the works by Cass and Hildemann are not pertinent. Those papers contain applications of derivatization methodologies to chromatographic analyses of aerosol samples. Indeed, derivatization is a very common procedure in chemistry to modify specific properties of organic molecules: organic synthesis, analytical chemistry, radical chemistry, photochemistry, etc. amply rely on it. We want to stress that the novelty of our work is the application of functional group derivatization for NMR investigation of ambient aerosol. We have further specified this aspect by correcting the sentence on p. 9462, l. 11. The past studies on atmospheric aerosols employed methylation of carboxylic acids to improve elution on GC columns, whereas here we introduced methylation to “add hydrogens” to the carboxylic acids allowing their detection by H-NMR analysis. The two methods (GC and H-NMR) have definitely different scopes (analysis of specific compounds and functional groups, respectively), applicability and interferences, therefore cannot be compared. In conclusion, we believe that our approach is conceptually new for application to atmospheric aerosols. Concerning the fact that the methylation procedure introduces an additional source of errors due to the increased blank levels, we are aware of that and we have repeatedly stressed this in the paper. As a matter of fact, however, in the spectral region of interest (3.3 - 4.4 ppm of chemical shift), the contribution from blank to the signals of the methylesters of the carboxylic is acids is 30% for the less concentrated samples of the

wet period, but is below 20% for the samples collected in the other periods of the campaign.. The overall discussion about blanks and about method validation was improved in the text of the revised manuscript. About our statement on carbon mass closure on page 9466, l. 1, we agree with the Referee and we have dropped that sentence from the revised version of the paper.

(3) We have corrected the revised version according to the specific comments related to the Berner impactor and the naming of some samples.

(4) We agree with the Referee that the discussion about the functional groups composition of the IC fractions must be done with more caution since this is based on data collected on a single sample. The text of sections 3.3 and 4 was changed accordingly. However, the observations are in agreement with preliminary analyses performed on biomass burning samples collected during the 1999 EUSTACH campaign (unpublished results). Interestingly, the data obtained for the SMOCC and EUSTACH biomass burning samples qualitatively agree with the functional groups distributions of the IC classes in samples from other continental polluted areas (Decesari et al., 2000, 2001; Fuzzi et al., 2001).

(5) We have switched from MCE to PTFE filters because the latter afford much better blank levels. Unfortunately, we could not replicate the analysis for some of the samples treated with the MCE filters. In these cases, the peaks due to MCE contaminations were carefully subtracted by each spectrum By such procedure, beside the difference in blank levels, we could not find any other effect of the filter type on the results of the analysis, and specifically no correlation was found with the “unrecovered” carbon.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 9447, 2005.