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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.

Anonymous Referee #1

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The authors present an application of H-NMR techniques for the identification and quantification of organic functional groups in atmospheric aerosol collected in the Amazon basin. Chemical derivatization of carboxylic acid functional group allows the quantification of this class of compounds by H NMR, extending the potentiality of H NMR for the investigation of atmospheric aerosol properties. Organic carbon content is deduced from the H NMR measurement and compared to TOC determination; poor agreement is achieved but further investigations will be performed. In summary, this manuscript reports data collected with a creative and novel approach to a very important and timely problem - this would make it an ideal candidate for publication in ACP. However, the

quality of the analysis and presentation of the data are, in its present form, likely to lead to significant misconceptions. I recommend fixing the existing gaps in (1) quantifying errors and (2) comparing to literature.

(1) The manuscript has not done a good job of quantifying the many errors they cite in their technique, so much so that I was confused about whether they were only presenting qualitative results. Some specific problems in the text are found at: 9465, l.13-27: all three explanations are likely, and it is the burden of the authors to quantify - as best they can using literature and other sources - each of these contributions to the "missing" carbon. Also, the carbon is not necessarily missing, it is just not measured by this method; i.e. it is an error. ALTERNATIVELY, it is quite possible that the TOC method has consistent positive artifacts resulting in an overestimate. I note that the values of OC are very high for the fine fraction, and so the TOC accuracy also needs to be evaluated.

(2) While I agree that this approach is novel, the authors repeatedly overstate the way in which it is novel (and fail to cite precedents in the literature) and they seem to use this as a reason to not compare their results to the literature (except for the results of their own group with the same method). There is an obligation for a new method to compare with existing data - from other regions and other methods. Such a comparison would also lend credibility (hopefully) to the stated ad hoc assumption about C:H ratios (which the authors fear may result in their missing carbon). Some specific problems in the text are: 9451, l.5-15: using derivatization for organic aerosol was pioneered by the Cass group in the 80s, and these works need to be referenced. Equally important, those studies discussed the artifacts associated with derivatization and the associated increases in blanks, detection limits, and errors. In some cases - the errors simply outweigh the information gained. The present authors need to provide sufficient uncertainty analysis to show that their samples are sufficiently large to avoid these problems. 9466, l. 1-4 and 9469, l.16-18: The statement about closure is also false, e.g. Maria et al. 2003 (cited above by the authors) showed agreement with TOC

ACPD

5, S4167–S4169, 2005

within 10%. 9462, l.13–this statement is untrue; similar derivatization was carried out by Hildemann et al. on atmospheric aerosol p.9449, l.20: approach is not conceptually new; authors have failed to review the literature comprehensively

Other notes to improve the presentation: - Define the Berner impactor substrate in the first part of the sampling paragraph and specify that Tedlar substrate corresponds to polyvinilfluoride. Explain why extraction of Tedlar WSOC has been performed using deionized water and not ultrapure MQ water, like in the case of fiber-quartz filters. - 9459, l. 26. One sample has been identified as FNS25/09N. FNS25/09N doesn't correspond to any of the conventions used for filter identification mentioned in the experimental section. - Specify detection limit for hydrogen concentration determined by the employed experimental procedure and detection limit for TOC analyzer. It will help to understand the discussion about hydrogen/carbon ratio on page 9458 and the comparison between deduced and measured organic carbon content in the "Discussion" section. - Page 9466, line 16. IC measurements have been performed only on one sample. Even though a "clear difference appears" among the three classes of SWOC, the observation on one single filter cannot be generalized. Reminding that the observation derived from the study of one filter would be enough to make the statement less conclusive. - Two different kinds of filters have been used to separate the extract in water from the solid residue, during the sample preparation. No further mention to the filter materials have been done during the discussion. It would be interesting to know if the use of one kind of filter could affect in a more incisive way the difference between calculated and measured organic carbon content. - Table 3 and 7. Add standard deviations or ranges of variation to the average values. It will help to observe differences among aerosol types. - 9452 l. 2 loadings not loads - 9453 N-methyl-N-nitrosop-toluensUlfonamide - 9463, l. 29 - "1 carbon IN 9 up to 1 carbon IN 6"

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