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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Distinguishing molecular characteristics of aerosol water soluble organic matter from the 2011 trans-North Atlantic US GEOTRACES cruise" *by* A. S. Wozniak et al.

A. S. Wozniak et al.

awozniak@odu.edu

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Anonymous Referee #2 The authors use electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry for characterisation of water soluble OM molecular fraction of 24 aerosol samples collected as part of the 2011 trans-North Atlantic US GEOTRACES cruise campaign. The authors successfully applied PCA for a very large high resolution MS dataset and identified molecular characteristics of aerosols influenced by primary/secondary marine, continental combustion (North America), and continental dust (North Africa/Saharan dust) sources. The experiments of this work were carefully designed and executed. The paper is clearly written and

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Interactive Discussion

Discussion Paper

the subject matter is appropriate for publication in ACP. I recommend the paper be accepted subject to technical corrections.

Technical remarks: 1) The authors used solid phase extraction PPL cartridges to remove salt content from the samples. This step generally results in the loss of compounds containing carboxylic groups. Most of the carboxylic acids are important constituents of the atmospheric aerosols and are characteristic for certain emission sources. Have the authors checked the recoveries of the representative organic compounds that are expected to be abundant in their samples (e.g., fatty acids that are characteristic for the marine emissions)? I realise that this may not be in the scope of the study; however, I would suggest making a short statement addressing the possible limitations associated with the use of this step. 2) The authors externally calibrated their instrument using fatty acids which is an abundant class of marine aerosol; however, I missed any discussions whether they were able to detect these molecules in the analysed samples. I am wondering whether the homologous series corresponding to fatty acids falls in to the cluster of ions corresponding to primary marine sources identified by PCA. The even to odd carbon ratio of these acids can be used to support their findings.

Response: The reviewer brings up an interesting point. We have not attempted to assess carboxylic acid recoveries. However, the WSOM extract is acidified prior to PPL extraction thereby protonating carboxylic groups and enhancing their retention. Unfortunately, we are unable to use fatty acids as valuable source markers for other reasons: 1) Fatty acids respond especially well to electrospray and are unfortunately present in solvent blanks run by ESI FTICR-MS at the COSMIC facility. Peaks found in solvent blanks – including these fatty acids - are eliminated from our peak lists for formula assignment post-calibration. 2) Further, electrospray ionization is a competitive process, and as a result, the instrument response is not quantitative. Relative magnitudes may well still be useful as source determinants for fatty acids (if relative responses are verified as reproducible among the similar class of compounds), but contributions

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from solvent blanks (and resultant peak elimination) make this comparison rather challenging. As a result, we are unable to explore fatty acids as source determinants with confidence in this manuscript. The benefits and limitations of PPL cartridges (and other solid phase extraction techniques) has been discussed elsewhere (Dittmar et al. 2008). In a revised manuscript, we will add the following text (p6434, line16): "Previous work has estimated that ~60% of dissolved OM is retained using this technique (Dittmar et al., 2008)."

3) Fig 7 shows structures of several amino acids; the direct infusion analysis does not allow obtaining the structural (isomeric) information of the molecules. Unless these structures were confirmed by LC/MS analysis or other appropriate techniques I would suggest removing them from the figure. Moreover, I would add a few lines in the text clarifying that these compounds were identified tentatively.

Response: Yes, the author is correct. FTICR MS does not allow for a structural determination of compound identity. The structures drawn in Fig 7 are amino acid containing compounds that have the same molecular formulas as some of the formulas identified in our samples. As noted in the text (p6443, lines 10-11), these structures are simply presented as examples of "potential amino acid containing compounds that correspond to these formulas", consistent with other lines of evidence that these CHON compounds may be biologically derived. Another reviewer also commented on these structures so we will add text that clarifies that these structures are merely some of many possible structures that can be drawn from the assigned molecular formulas: p. 6443, line 11 "It is noted that these structures are tentative and represent only some of many potential isomers that correspond to the assigned molecular formulas. LC/MS or a comparable technique is needed to verify the structures of the compounds corresponding to these formulas, but this is beyond the scope of this particular paper."

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 6427, 2014.