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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.

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Anonymous Referee #3 The chemical composition of WSOM is essential for tracking their sources and transformations in the atmosphere as well as assessing their environmental outcomes. In this manuscript, the authors employed a state-of-art ultrahigh resolution mass spectrometer for molecular level characterization of WSOM samples collected during the research cruise from North America to North Africa. Both the samples and data are valuable and rare, as considering the fact that recently there are only few studies on the detailed chemical composition of WSOM on marine aerosols. The authors also successfully applied the statistic method (PCA) on classifying and distin-

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Interactive Discussion

Discussion Paper

guishing the sources of WSOM based on the identified molecular formulas. The results and interpretations are reasonable. I recommend the publication of this manuscript after the authors addressing the following questions:

1. Page 10, line 1: the authors used naturally occurring fatty acids as the internal standards for calibrating the mass accuracy, which can dramatically increase the number of unambiguously identified formulas within WSOM samples. However, in the paper they cited (S and H, 2008), there is no detailed information about how to perform this calibration. Moreover, the studies of S and H are mainly focused on aquatic NOM samples, which might possess different chemical natures with the aerosol samples. I would encourage the authors providing more detailed information about this internal calibration in the supplementary material. For example, what kind of fatty acids were chosen as the internal calibrator? What are the criteria regulating their naturally occurring? How to re-correct the mass errors of other compounds by using the mass errors of the internal standards? I believe that the detailed description on this re-calibration method is very helpful in improving UHRMS data processing in atmospheric chemistry society and will make this paper highly cited in future.

Response: The detailed calibration procedure is beyond the scope of this particular paper, and in fact, would be redundant to the Sleighter and Hatcher (2008) paper. While there are differences in the organic matter used in that paper and atmospheric organic matter, there is quite a large amount of overlap in the types of organic matter compounds making up these organic matter classes. Our calibration utilizes the internal calibration procedure provided by the Bruker software using the internal linear calibration mode. We have accumulated a list of CHO molecular formulas that frequently occur in natural and atmospheric organic matter operated in the negative ion mode. The list of formulas we use correspond to fully saturated mono and di acids of many carbon chain lengths (C14-48) and homologous series (differing by CH2 groups) of other frequently occurring formulas. The calibration peak list is chosen to cover the mass range examined by the FTICR MS (in this instance, m/z = 200-800), and care is taken to en-

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sure that at least one formula is found every 28 mass units (2 CH2 units). The Bruker software looks for these pre-selected molecular formulas within an operator assigned acceptable error range (0.002 m/z) and creates a linear calibration based on the measured m/z and exact m/z values. Peaks that show high errors (>0.5ppm, measured vs. modeled m/z) are eliminated from the calibration as they may represent incorrectly assigned calibrant peaks and affect the calibration. The remaining measured m/z values in a spectrum are subsequently adjusted to the linear calibration. This procedure gives the m/z peak list that is used for formula assignment and is repeated for each sample.

2. Page 10, line 11: O/C $\leq$ 1.2 as one of the constraints of formula assignments. This may works well in aquatic NOM. However, in recent years, atmospheric scientists focusing on chamber studies of secondary organic aerosols do find some organic compounds with O/C greater than 1.2. Will the authors' dataset be changed if this constraint is extended to a larger value (e.g. O/C $\leq$ 3.0)?

Response: Reviewer #1 made a similar comment regarding the O/C ratios. Our reply is the same: In spite of what has been reported in recent aerosol OM publications, we have chosen a maximum O/C ratio of 1.2 and believe this to be the best O/C limit for our FTICR MS data. In a study testing appropriate limits for molecular formula assignments, Kind and Fiehn (2007) examined more than 68,000 formulas reported in Wiley and DNP databases and found that 99.7% of formulas were assigned correctly using an O/C limit of 1.2. Increasing that limit to 3.0, only increased the percentage of correctly assigned formulas by 0.2%. Using an O/C maximum of 1.2 allows us to assign >90% of OM peaks in our mass spectra (excluding salts and 13C peaks). It is likely that the chance for incorrectly assigning a formula with O/C between 1.2 and 3.0 is higher than identifying a correct formula. We do acknowledge that compounds having molecular formulas with O/C greater than 1.2 do exist. These may include short carbon length compounds with nitrate and/or sulfate groups including nitrooxyorganosulfates that have been reported in other atmospheric work but that are below the m/z range in our study (m/z<200). As a result, we are very comfortable using the O/C limit we

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have chosen and suggest that molecular formulas with higher O/C limits be viewed with caution.

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