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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 #1 Received and published: 22 April 2014 Overview: The presented publication reports molecular characteristics of aerosol water-soluble organic matter (WSOM) collected as part of the 2011 trans-North Atlantic US GEOTRACES cruise. Aboard the ship, a high volume filter sampler was used to collect 24 individual samples Nov 7, 2011 - Dec 9, 2011. The samples were analyzed using ultrahigh resolution FT-ICR MS. Using multivariate statistical analysis the identified molecular formulas were used to separate the 24 samples into 5 key groups associated with the air mass histories. For each of the groups, the molecular characteristics are described

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based on the unique molecular formulas identified using the PCA. Overall, this is an interesting piece of work with very high quality data. The molecular insights to marine organic aerosol from this paper represent a substantial contribution of interest to the readers of ACP.

Specific Comments: Several specific comments are listed here in no particular order.

1) P6428, L26: The following includes a typo, “higher O/C ratios and lower O/C ratios”.

Response: We thank the reviewer for picking up this typo. The revised text will reflect that this has been corrected to read “higher H/C ratios and lower O/C ratios”.

2) P6432, L09: The PCA was done on selected assigned molecular formulas and not on the MS data.

Response: We agree with the reviewer that the precision of this sentence could be better. The PCA was performed on the relative spectral intensities of a subset of the assigned molecular formulas for our samples. Those molecular formulas correspond to peaks at m/z ratios which are derived from the MS data. The revised text will be changed to read “Principal component analysis (PCA) is performed on data derived from the FTICR-MS spectra. . .” as this is a more precise description of what was done.

3) P6434, L14: Please note the addition of HCl may catalyze many oligomerization reactions. Also, methanol has been shown by Bateman et al. ES&T 2008 to contribute to artifacts from acetal reactions.

Response: We are aware of potential artifacts due to the use of methanol as a solvent as documented by McIntire and McRae (2005) and Bateman et al. (2008), and every effort was made to minimize self esterification. McIntire and McRae found self-esterification to be more significant in positive ion mode relative to negative ion mode and to increase with the amount of time the sample remained in methanol. Our samples were run in negative ion mode within 2 h of elution and stored in the dark in a freezer between elution and running. We feel comfortable that this minimized the ex-

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tent of self-esterification and did not affect the conclusions of the manuscript.

To ensure high WSOM recoveries for PPL extractions, WSOM must be acidified, and the addition of HCl in PPL extractions for FTICR MS studies is commonplace (e.g., Dittmar et al., 2008; Gonsior et al., 2009; Stubbins et al., 2010; Kujawinski et al., 2011). The water extracts were acidified to a very dilute concentration (~ 0.005 M) and samples were eluted and run within 2 h of elution as described in the preceding paragraph in an effort to minimize any artifacts. Examination of sample mass spectra do not show evidence for oligomerization reactions, and we are comfortable that any artifacts have been minimized.

4) P6435, L01 – L22: Molecular formula assignments appear to be limited only the elemental ratios, mass accuracy and the number of heteroatoms. Are there additional measures to ensure data quality? The method described by Kujawinski et al., 2009 is more extensive than just the number of heteroatoms. They also advocate using formula extensions because mass accuracy alone is insufficient with the high number of elemental combinations. Furthermore, the limit on the O/C is relatively low for atmospheric aerosol.

Response: Formula assignments were also confirmed using Kendrick mass defect series in a manner similar to Kujawinski et al. (2009). Text has been added to the methods reflecting the use of a formula extension approach.

In spite of what has been reported in recent aerosol OM publications, we have chosen a maximum O/C ratio of 1.2. 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 more than 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

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

5) P6440, L03 – L18: Why are the compounds considered ubiquitous? Perhaps they are strongly associated with biogenic hydrocarbons? A similar statement about “terpene-like” molecular formulas that has been presented in Schmitt-Kopplin et al., 2010 and Mazzoleni et al., 2012. This underlines the significance of biogenic hydrocarbons as sources of atmospheric OA components.

Response: As described in the text, the compounds are considered to be ubiquitous because they are present in the majority of the samples from this study and additional samples collected in terrestrial environments in Virginia and New York, USA. Of course, biogenic sources account for major portions of all types of organic matter including that in the atmosphere (minus that contributed by fossil fuel combustion), but we assume that the reviewer refers specifically to terpene-like biogenic compounds such as secondary organic aerosols from isoprene, alpha-pinene, and other terpene-like precursors. While it is possible, these ‘ubiquitous’ molecular formulas could be derived from terpene-like biogenic compounds – which are undoubtedly important atmospheric OA components – we do not have confirmation that they are indeed terpene-like biogenic compounds. Specific confirmation of a terpene-like source for these ‘ubiquitous’ formulas requires more detailed structural analysis and is beyond the scope of this paper.

6) P6443, L03 -06: How do you explain the amino functional groups in negative ion mode? Typically the H-affinity of amines is so high, that the multifunctional compounds (amino acids) will be zwitterions in the negative ion mode unless there are multiple deprotonations. However, most of the studied OM components have been singly charged.

Several of the tentative structures drawn in Figure 7 do not seem likely to be observed in the negative ion mode as indicated on P6433.

Response: Examination of peptides by our group using peptide standards in the negative ion mode has not observed this issue. Peptide standards are observed as singly charged ions. The structures presented in Figure 7 are intended to demonstrate that the formulas are consistent with peptide-like structures and not meant to identify the specific compounds in our samples. Identifying compounds from molecular formula information alone is not possible. Text has been added to the paper to clarify that these structures are tentative: 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.”

7) P6449, L08– 09: How was the WSOM defined as combustion-influenced? Or, how was the contribution of biogenic SOA removed from the complex mixture to better understand the composition of the combustion influence? How does the fossil fuel combustion composition differ from biomass burning?

Response: The WSOM is defined as combustion-influenced based on it having air mass trajectories from the North American continent which is widely known to have higher combustion-influence (specifically, anthropogenic fossil fuel combustion influence) than the north African continent (the other continental influence in this study). Because combustion processes impact WSOM composition via increased SOA formation, increased inclusion of combustion byproducts (NO_x, SO_x) into SOA and aged POA (e.g., de Gouw et al., 2005), and the direct emission of WSOM, the terminology is accurate. Biogenic SOA were not removed from the complex mixture and likely comprise a portion of the North American influenced WSOM. Text will be added to a revised manuscript that clarifies our definition of WSOM coming from the North American continent as combustion-influenced.

8) P6451, L23 - 27: A lack of condensed aromatic compounds could be a result of other factors. For example, aerosol-aging processes may promote transformation of the compounds over the longer distances. Have condensed aromatic compounds been observed in the remote atmospheres previously?

Response: The reviewer is correct that our explanation for the lack of condensed aromatic compounds as important PCA loadings to the North American samples is insufficient. Yes, condensed aromatic compounds measured as soot or black carbon have been observed in the remote marine atmosphere previously (e.g., Posfai et al., 1999). Drawing on the data from the full FTICR MS dataset tens to hundreds of peaks in the North American samples are assigned formulas that correspond to condensed aromatic or aromatic compounds using Koch and Dittmar's (2006) aromaticity index. It is our contention that these compounds do not ionize efficiently enough to account for an important component of the spectral intensity relative to the more aliphatic sulfated WSOM compounds in these spectra which are known to ionize efficiently. We do recognize that these aromatic and condensed aromatic WSOM compounds could be transformed via photochemical aging, but these processes would impact the North African influenced samples to which the North American influenced are being compared. In the revised manuscript, we will add text that acknowledges explains our argument more clearly while acknowledging alternative hypotheses.

9) Figure 6: A few figure labels are missing or use different fonts.

Response: Figure panels that appear to be missing labels do not contain molecular formulas of a given combination that define these groups of samples. For example, panel C does not have CHONP or CHOSP listed because none of the PCA loadings found to define the North American-influenced sample group contained CHONP or CHOSP. In the revised manuscript, we will clarify the figure labels for the readers.

10) Figure 1: Only 3 of the 5 groups are shown here. Why?

Response: As is described in detail in the text, the air mass trajectories displayed

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on Figure 1 describe the three types of air mass trajectories observed for this set of samples. The five PCA groups discussed in the text are defined from the PCA and are named taking the definitive molecular characteristics and environmental characteristics (e.g., air mass trajectories) into account.

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