Author responses to comments from RC1 are given below in blue font. The original referee comments are provided in *black italicized font.*

This paper describes high resolution mass spectrometry (HRMS) and NMR analysis of water soluble organic compounds (WSOC) in four samples selected to represent fresh and aged aerosol particles as well as fresh and aged fog droplets. Results of this work generally support the importance of aqueous processing of organic aerosols. The data set is definitively interesting and worth publishing. The paper can be improved by addressing several issues described below. In addition, for the amount of new information presented in this paper it is too long. I would recommend shortening it and making it more focused on new findings.

My main criticism of this paper is its reliance on just one sample of each type (fresh aerosol, aged aerosol, fresh fog, and aged fog) to draw far reaching conclusions about chemical processes that are responsible for aging of WSOC. Furthermore, samples come from completely different dates making it quite difficult to faithfully compare them. This is much less satisfying and convincing than the approach taken by the authors in Gilardoni et al. (2016) that looked at the fog dissipation events. The authors rely on aerosol mass spectrometry (AMS) analysis, specifically on the f44-f60 correlation plots, to classify the samples. To prove to the readers that this classification works as expected the authors should compare at least two HRMS data sets from different filters that are supposed to be identical based on the f44-f60 AMS classification. Why not take a couple of samples (as opposed to a single sample) corresponding to closely spaced points in Figure 1 and compare their HRMS data? I am willing to bet that the authors would find very different molecular composition for these supposedly similar samples. If this is the case, the comparison of the HRMS data between different conditions becomes more difficult and potentially not even possible.

We thank the referee for their appreciation of the manuscript content and helpful comments. We understand the main criticism raised by the referee about the limited number of analyzed samples, in fact we are working on the analysis of a larger database collected during a more recent field experiment, specifically designed to investigate aqueous phase processing. Nevertheless, the complexity of ultrahigh resolution FT-ICR MS database generated from a single aerosol or fog water sample set some limitations on the number of samples that could be analyzed within a reasonable amount of time. One of the goals of this study is to analyze extremely different samples of aerosol and fog water in term of ageing of organic content and impact of wood burning emissions, to fully deploy the potential of ultrahigh resolution MS and identify the subset of information relevant for a larger database analysis. In addition, the low time resolution of ultrahigh resolution MS and ^{1}H-NMR analysis (hours or days) compared to HR-ToF-AMS analysis (minutes) requires a different approach in the data analysis compared to what was done in Gilardoni et al. (2016), where we were able to follow the formation and dissipation of single fog events. For this reason, we rely on the high time resolution of HR-ToF-AMS analysis to identify aerosol samples for further analysis with ultrahigh resolution MS and ^{1}H-NMR techniques as described in the text.

The selection of aerosol samples was based on a detailed characterization of the field experiment data reported in a previous publication (Gilardoni et al., 2016), and is not the subject of the present manuscript. Instead, for the selection of fog water samples, we used the approach commonly employed by HR-ToF-AMS users for organic aerosol, investigating the f_{44} and f_{60} space, since it is recognized that f_{44} is a marker of ageing organic content and f_{60} is a proxy for wood burning organic molecules (Cubison et al., 2011). We are aware that this representation is an oversimplification of the complexity of organic fog water content, thus this approach is here employed exclusively to spot marked differences in term of different sources and atmospheric history of organic content. The following was added to section 3.1 on p. 7, line 5-8 to clarify this: “The f_{44} vs. f_{60} space was previously proposed to represent biomass burning vs. atmospheric aerosol aging (Cubison et al., 2011) and was extended here to fog samples. This representation is an oversimplification of the complexity of organic molecules in fog water, employed here exclusively to note the major differences in terms of emission sources and atmospheric history.”

As mentioned above the goal of this work was to study very different samples. Even with these selections, we still observe many of the same molecular formulas across samples as indicated in the van Krevelen diagram Fig. 5. Thus, it is unlikely that similar samples as defined in Fig. 1 would yield “*very different molecular composition”*. However, the day to day composition of aerosol and fog and its evolution with respect to the local meteorology is the focus of a future publication.

Overall, this study provides evidence of the potential of combining high-field spectroscopic techniques (Hertkorn et al., 2007) to trace chemical changes in ambient aerosol in specific environmental conditions. We performed a screening of the possible organic compositions using HR-ToF-AMS and a simple functional group analysis by ^{1}H-NMR, and clearly chose extreme conditions in the chemical space (Fig. 1) for further in-depth chemical analyses. This is a progressive with respect to previous explorative approaches employing combined ^{1}H-NMR and FT-ICR MS methods for aerosol analysis (Schmitt-Kopplin et al., 2010) which provided little information on the actual environmental conditions affecting the composition of the aerosol.

SPECIFIC COMMENTS

Abstract: To avoid confusing the readers I recommend removing the prefix “high resolution” in front of Tof-AMS in the abstract and in the text. I understand that this how this instrument was called when it was designed but it is a stretch to call it a high resolution instrument especially in a paper that relies on FT-ICR as the main method. Using simple “ToF-AMS” should be sufficient.

We agree that the terms high resolution and ultrahigh resolution are similar. However, the term “high resolution” refers specifically to the subclass of mass spectrometers that use the time of flight (ToF) to derive the measured mass. There are ToF instruments without high resolution. For this reason, we consistently refer to the instruments as HR-ToF-AMS and ultrahigh resolution FT-ICR MS (or simply FT-ICR MS).

P1L21: particles containing organosulfates might activate more easily accounting for the higher fraction of organosulfates in fog droplets compared to aerosol particles.

This sentence (now on p. 1 line 18-19) was changed to reflect the intended observational nature of the statement: “Higher numbers of organonitrates were observed in aerosol, and higher numbers of organosulfates were observed in fog water.” While we agree that organosulfate compounds in aerosol may be more hygroscopic and aid in droplet activation, it is well documented that organosulfate compounds form in the aqueous phase of cloud/fog and wet aerosol particles (Darer et al., 2011; Ervens et al., 2011; Schindelka et al., 2013; Herrmann et al., 2015; McNeill, 2015); therefore, pre-existing organosulfates in aerosol may only indicate multiple cycles of fog formation and evaporation. We have added a statement about organosulfates in the fog from nucleation scavenging on p. 12 line 5-6: “…and nucleation scavenging from the preceding fog nuclei composition likely plays a significant role as well…”

P1L25: it would be useful to also add ranges for O:C and H:C for the "fresh" samples so that one can compare

This sentence (now p.1 line 21-23) was edited to compare the values of both the "fresh" and "aged" samples in O:C and H:C values, and the actual range of these values was added to compare more easily: "The average O:C and H:C values from FT-ICR MS were higher in the samples with an "aged" influence (O:C = 0.50-0.58 and H:C = 1.31-1.37) compared to those with "fresh" influence (O:C = 0.43-0.48 and H:C = 1.13-1.30)."

P5L26: it should also be pointed out that valence of 3 is used for N, so the extra double bond in the nitrooxy compounds is not counted

A sentence (p. 6 line 8-9) was added to clarify that the calculated DBE values do not include double bonds formed by pentavalent nitrogen, and tetravalent or hexavalent sulfur: "Note that S and O are divalent in equation (3); additional unsaturated bonds associated with pentavalent nitrogen, and tetravalent or hexavalent sulfur are not included in this DBE calculation."

P5L29: the authors should warn the readers that OS developed by Kroll et al. (2011) only works for CHO compounds, and that it also fails for peroxides. This formula cannot be used for CHOS and CHON compounds. The authors should check their text so that they do not over interpret results from this formula

We thank the referee for this reminder. We modified the OS_C calculation as described in Kroll et al. (2011) to more accurately calculate OS_C for formulas containing nitrogen and sulfur. However, this requires the assumption that when N is present it represents a nitrate functional group and when S is present it represents a sulfate functional group. This assumption is reasonable considering we analyzed the samples using negative ion electrospray, however, it is still an assumption. Furthermore, we assume that unstable peroxide species would not survive sample storage and sample preparation for analysis by FT ICR. This modified calculation is now included in the text (p. 6 line 9-12) along with the necessary assumption: "The average oxidation state of carbon (OS_C) in the molecular formulas was estimated using equation (4), based on the approximation described in Kroll et al. (2011); note that the inclusion of nitrogen and sulfur affects the oxidation state of carbon, and equation (4) assumes both are fully oxidized."

P12L20: the fact that these compounds show in a single daylight sample does not constitute proof that these compounds are related to photochemical properties. This is one example of several statements made by the authors for which they do not have sufficient data. To claim something like this, they would need to demonstrate presence of these compounds in many daylight samples (not one!) and absence in many nighttime samples.

In our discussion of the results, we suggest that these molecular formulas may have been formed from photolysis reactions, because of the ~8.6 hours of daylight in sample collection. Furthermore, this was the major difference between the two aerosol samples. Thus, it would not have been appropriate to ignore such a major difference. We agree that photochemistry is not directly responsible for the N_2 and N_3 formulas, as there is a trend between the presence of these formulas and NO_X concentration during sample collection for all samples. We have modified this statement (now p. 13 line 27-28) describing them as such: "Compared to the other samples, BO0213D was collected during relatively high NO_X

conditions, as well as high humidity and aerosol liquid water content compared to the other aerosol sample."

P13L15: another example where a conclusion is made (about sulfite radical involvement) without having needed data to prove it

Here we related our observation of organosulfates in these samples to literature sources as a suggestion for their origin. We agree that the involvement of sulfite radical is unlikely since most of the samples were collected at night. This statement (now p. 14 line 21-23) was revised to the following: "CHOS and CHNOS formulas were detected with high frequencies in samples with high water content during collection (all samples except BO0204N). This provided some evidence of the production of S-containing SOA species by reactions in the aqueous phase."

Figure 5: What message is conveyed by this figure that cannot be more easily conveyed with average O:C values? I do not see how it helps interpret the data. Two versions of this figure exist, one in the text and one in the SI section. I would just keep it in the SI section or remove altogether.

The van Krevelen space is useful for visualizing both oxidation (O:C) and saturation (H:C). In this work, we have identified thousands of individual molecular formulas. We observed both highly oxidized species and highly saturated species in the same samples, and this plot is able to show these differences. Furthermore, some of these formulas are observed in all of the samples, and some are unique to the individual samples. The van Krevelen plots in Fig. S2 includes all of these formulas, where the symbols in Fig. 5 are differentiated to indicate unique or common molecular formulas. The unique formulas in each sample help to further illustrate the differences between samples (outlined in multiple sections), hence we included two versions of the plot.

Figure 7: it would help explain how the spectra were normalized before the subtraction. The result of the subtraction obviously would depend on the choices made in the normalization.

The normalization procedure and its importance has been expanded upon in the supplemental text (p. S2): "The total ion abundance of the identified monoisotopic molecular formulas reported for each sample was determined by their summation. Then, these values were used to normalize the individual ion abundances within each sample using a ratio of the individual ion intensity to this total ion abundance. Then, the values were rescaled using a normalization constant (10,000). This normalization procedure was done to remove analytical biases introduced by trace contaminants with high electrospray efficiency."

Table 3 and Table S1: it would be useful to specify peak abundance (such as very high, high, medium, minor or something similar). Also, I would point out in the caption that the "identities" specified in one of the columns are for reference only – the fact that formulas match does not mean that this where these compounds came from.

We thank the reviewer for this helpful insight. Table 3 was moved into Table S1. We modified the extended Table S1 to indicate the normalized abundance of each formula. We revised the caption for Table S1 to include additional clarification regarding the nature of molecular formulas vs. chemical structures: "Table S1: Summary of the literature structural insights associated with the identified molecular formulas observed in this study. Because the identified molecular formulas may represent a variety of structural isomers, we note that matched molecular formulas do not necessarily correspond to the same molecular structure or atmospheric origin. The normalized abundances are indicated for each sample, where “ND” (not detected), “Low” (≤ 3%), “Med”, (> 3% and ≤ 15%), “High” (> 15% and ≤ 50%) and “Very High” (> 50%). Molecular formulas from the literature are provided with their references.” An additional paragraph was added to section 2.4 (p. 6 line 22-24) to further clarify the difference between molecular formulas and chemical structures: “Furthermore, it is important to note that the individual molecular formulas likely represent a mixture of structural isomers co-existing in atmospheric organic matter, as recently observed for deep-sea organic matter (Zark et al., 2017).” We also removed all references to specific IUPAC style chemical compound names, e.g. “2,4-dinitrophenol” was changed to “dinitrophenol” in the discussion of formulas matched to the previous literature.

S2: it states it there that the assignments were cut off above m/z 500 but assigned peaks in figure S3 go beyond 600

We describe the *de novo* cutoff in greater detail in the supplemental text (p. S2), as it does not perform a hard cut off for formulas of *m/z* > 500: “A de novo cut-off at *m/z* 500 was applied, indicating that no new formula assignments would occur above *m/z* 500, unless the formula was part of an existing CH_2 homologous series that began at a point lower than *m/z* 500. This is necessary because the number of possible molecular formulas increases at higher values.”

S2: please explain the “rule of 13” – this must be some sort of a mass spectrometry jargon

Descriptions of the rule of 13 and the nitrogen rule, were added to the supplemental text (p. S2): “The rule of 13 checks for a reasonable number of heteroatoms in a formula. A base formula (C_nH_{n+r}) can be generated for any measured mass by solving: $\frac{M}{13} = n + \frac{r}{13}$ (Pavia, 2009). Then, the maximum number of "large atoms" (C, O, N, S) in a formula is defined as the mass divided by 13, because substituting for a heteroatom (O, N or S) involves a substitution for at least one carbon. This maximum number is then compared to the actual number of "large atoms" in a formula, and those formulas exceeding the maximum number are rejected. The nitrogen rule removes formulas with odd masses that do not contain an odd number of nitrogen atoms, and even masses that do not contain an even number (or no) nitrogen atoms; this is due to the odd numbered valence of nitrogen (Pavia, 2009).”

EDITORIAL COMMENTS

P1L34: remove “evolving”

This sentence (now p. 1 line 32-p. 2 line 1) now reads: “Atmospheric organic aerosol particles are comprised of a complex mixture of numerous individual organic compounds, produced by direct emissions and secondary processes, of which a significant impact is from transformations in the aqueous phase.”

P2L7: “and more” -> “and other compounds”

This sentence (now p. 2 line 9-11) now reads: “Biomass burning products include simple organic acids, sugars and anhydrosugars, substituted phenols, polycyclic aromatic hydrocarbons, and other compounds, depending on the type of fuel and burn conditions…”

P2L14: this sentence needs a revision (incompatible list items)

This sentence (now p. 2 line 17-19) now reads: “Atmospheric chemistry models are currently unable to replicate several key aspects of SOA, including SOA concentration levels, chemical oxidation states, degree of functionalization, and the occurrence of high molecular weight compounds, such as atmospheric humic-like substances.”

P6L26: “rich of” -> “containing”

This sentence (now p. 7 line 18-20) was changed to use the same consistent descriptor with all portions describing the 3 categories of interest, and now reads: “These categories are: SOA (enriched in acyl groups, H-C-C=O), biomass burning aerosol (enriched in alkoxyls, H-C-O, and aromatics), and marine organic aerosol (enriched in aliphatic groups other than acyls and alkoxyls, mainly amines and sulfoxy groups).”

P10L30: two sets of references need to be joined in one

This paragraph was revised to be easier to understand. The respective set of references have been combined into the new revised paragraph. The paragraph is provided in response to the next comment below.

P10L31: “act” -> “acted”

This entire paragraph was revised for clarity. The revised paragraph (p. 12 line 3-13) now reads: “The unique molecular formulas found in the fresh fog (SPC0106F) were mostly of the O_{5}-$_{13}S$ and NO_{7}-$_{12}S$ subclasses. Organosulfates are known products of aqueous secondary processes, (Darer et al., 2011; Ervens et al., 2011; McNeill, 2015; Schindelka et al., 2013) and nucleation scavenging from the preceding fog nuclei composition likely plays a significant role as well (Darer et al., 2011; Gilardoni et al., 2014; Herckes et al., 2007; Hu et al., 2011). The aromatic organosulfates and nitooxy-organosulfates observed in fresh biomass burning aerosol (Staudt et al., 2014) were not observed here. In general, organosulfates are the products of aqueous-phase SOA reactions which are expected to be enhanced at acidic pH (Ervens et al., 2011; McNeill et al., 2012; Noziere et al., 2010). Because the pH of SPC0106F was only slightly acidic at 5.81, we propose that the formation of these organosulfates may have been promoted by low LWC, and thus relatively high solute concentrations, during the activation of the fog droplets or possibly in the fully formed fog droplets. Organosulfates may also efficiently nucleate droplets, leading to their eventual presence in the fog samples.”

Figure 4: the choice of colors makes it hard to differentiate between them

This Figure was revised from a yellow scale, to a more discerning color palette including yellow, blue and red.

Table 2: “mass” -> “molecular weight (g/mol)”

The term “Mass” was changed in the Table to “Molecular weight (Da)” to include the unit. Though the Da unit is numerically equivalent to g mol^{-1}, Da is used more frequently as a unit in mass spectrometry literature.

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