

Interactive comment on “Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications” by M. R. Canagaratna et al.

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AUTHOR RESPONSES TO REVIEWER COMMENTS: ANONYMOUS REFEREE #1

R1.1: This is an important paper that provides an authoritative development in the interpretation of data from the Aerodyne AMS. While the instrument has proved to be of much use to the atmospheric community in studying organic aerosols over the last 15 years, it has been confounded by issues surrounding fragmentation of organic molecules and interferences from other peaks in the mass spectrum. There have been

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a number of papers over the years refining the technique and this presents the most significant development since Aiken et al. (2008). By systematically studying authentic standards and SOA analogues using both the standard AMS configuration and the VUV version, the authors find that key metrics, notably O:C and OM:OC, have most likely been underestimated in the past. Overall, this is a very well written paper, dealing with the issues methodically and clearly. The biggest potential issue is that the paper is very close to being of too technical a nature and had it not dealt with implications to previous atmospheric studies, I would have recommended it as more suitable for AMT. However, there is probably just about enough atmospheric science in there for it to qualify, in my opinion. Other than that, my comments and suggestions are very minor and I have no hesitation recommending this be published in ACP subject to these.

A1.1: We thank the reviewer for his/her thoughtful comments. A new section dealing with the implications to previous atmospheric studies has been created (section 3.9) in order to highlight it more and separate it from the technical issues discussed in the paper. The text added in this section is provided in response to comment R2.1 of Reviewer #2.

R1.2: I cannot help feel that the main point of interest to the general AMS community will be the presentation of the new methods for estimating the key metrics (Improved-Ambient). However, the methodology is slightly more complex than the Aiken methods, so I feel that this should be described in more detail in the abstract and conclusions (specifically, that the method uses specific markers to try to predict the signals not correctly accounted for). In addition, this modification will necessitate a change to the algorithm used in the PIKA/APES software routinely used for this. In the interests of traceability, the authors should specifically refer to this software and state the version number that this applies to. While this paper will no doubt prove to be an important milestone in the interpretation of AMS data, the results were previously alluded to in Daumit et al. (Faraday Discuss., 2013, 165, 181 doi: 10.1039/c3fd00045a). Given the prominence of this paper, the authors should comment on whether the parameterisa-

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tions have changed in the intervening time between the works.

A1.2: The following text has been added to the methods section to address the comments related to analysis software information: "The AMS data analysis software package PIKA v.1.10H (Sueper, 2011) was used for the high-resolution analysis. This software allows for ready calculation of elemental ratios from both A-A and A-E methods. The A-A calculation uses the default organic fragmentation wave proposed by Aiken et al. (2008) and the A-E method uses a variant of the default organic fragmentation wave in which the entries for m/z 28,18,17,and 16 are replaced to use measured ion intensities rather than estimated values. The I-A elemental ratios discussed below use A-A values and marker ion relative intensities calculated from normalized organic mass spectra output by the PIKA software."

The following text has been added to address the comment related to the use of marker ions:

In conclusion: This method combines the Aiken-Ambient results together with correction factors that uses specific ion fragments as markers to reduce composition-dependent bias and produce O:C (H:C) values for the standard molecules that are within 28% (13%) of the known molecular values.

In Abstract: These results are used together to develop an "Improved-Ambient" elemental analysis method for AMS spectra measured in air. The Improved-Ambient method uses specific ion fragments as markers to correct for molecular functionality-dependent systematic biases and reproduces known O:C (H:C) ratios of individual oxidized standards within 28% (13%) of the known molecular values.

The authors thank the reviewer for pointing out the fact that the Daumit et al. manuscript had already used a correction based on our work. The correction factors used in Daumit et al. are very similar to those published in this manuscript. The Daumit et al. calculations increased O:C and H:C values by a factor of 1.3 and 1.1 respectively and this manuscript reports that the Improved-Ambient method increases ambient O:C

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and H:C values by a factor of 1.27 and 1.11. This comparison to the Daumit et al. manuscript is now referred to explicitly as follows:

Daumit et al. (2013) have compared the difference in constraints introduced when LV-OOA elemental ratios are calculated using A-A and I-A methods (The I-A elemental ratios in Daumit et al. (2013) were calculated by scaling A-A_O:C and H:C ratios by 1.3 and 1.11, respectively).

R1.3: P19797: Was the humidity after drying measured? Given silica gel's performance at low relative humidities and the long equilibration times reported for some organics, can we be assured that the water was completely removed from the aerosols?

A1.3: The reviewers are correct that it is hard to ensure that all the particulate H₂O in the sampled aerosol is completely eliminated after aerosolization. However, every effort was made to minimize this effect. Two silica gel dryers were utilized in series to maximize drying and fresh silica was utilized every day. The following text has been added to manuscript to directly address the reviewers questions.

"The humidity of the flow after drying was spot checked for several experiments and was found to reproducibly be < 4%. Any H₂O that was not removed from the particles after exposure to these conditions is likely to have been further lost by evaporation when the particles encounter the 2 mbar sampling conditions of the AMS aerodynamic lens. Taken together it is likely that the aerosol H₂O was negligible in these experiments and uncertainties due to the presence of aerosol H₂O should have been small."

Moreover, it is important to note that uncertainties in the measured H₂O intensities will not have any effect on O:C or H:C values calculated using the Aiken-Ambient or Improved-Ambient calculations. These calculations only use H₂O intensities that are empirically estimated according to Aiken et al. (2008). The measured H₂O intensities in these experiments were only used to evaluate and understand whether there were biases in the empirically estimated values of H₂O intensities.

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The measured H₂O intensities were only directly used in the Aiken-Explicit calculations of O:C and H:C. These calculations were performed in order to compare the results from these studies with the original measurements from Aiken et al. (2008) which were performed with a similar aerosol generation and drying process to those used here. Thus, we think that trends observed in these comparisons will not be significantly affected by small uncertainties in the source of the measured H₂O.

R1.4: P19798, L24: The issue of objectively standardising the temperature is of much interest to the community because there is much anecdotal evidence that this is critically important. Therefore, I suggest that the authors provide more details on how this is performed in the supplement.

A1.4: The ACPD manuscript already contained some text to describe the method used to set the oven temperatures. We have added new text (italicized) to clarify the methodology further

“Thus, the measurements were standardized by varying the vaporizer power to minimize the width of a monodisperse 350 nm NaNO₃ aerosol size distribution measured by the AMS. The time-of-flight traces of the NO⁺ ion (m/z 30) from NaNO₃ were monitored as a function of vaporizer ion current. The optimum AMS vaporizer current is obtained by subtracting 0.1 amps from the vaporizer current at which the narrowest NO⁺ ion time-of-flight traces are observed from NaNO₃. Typically this optimum AMS vaporizer current is near 1 amp. In most cases the thermocouple readout at the optimum heater power setting read temperatures in the range 590-600°C, indicating that the thermocouples in these instruments were providing a reasonably accurate measure of the actual heater temperature.”

R1.5: Regarding the effect described on Van Krevelen plots, it would be useful to give an example plot so the reader could get a visual idea of the magnitude of the effect.

A1.5: A figure has been added to supplementary and is referenced in text as follows:

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Van Krevelen plots of ambient and chamber SOA species from Table 3 are shown in Fig. S7.

R1.6: The terms ‘Aiken Explicit’ and ‘Aiken Ambient’ are effectively introduced by this article, however they are referred to in the abstract as if they are established nomenclature. This should be revised for the sake of clarity.

A1.6: The text in abstract has been changed (changes in italics) to reflect the fact that the nomenclature is newly introduced in this manuscript

For the expanded standard dataset, the method introduced by Aiken et al. (2008), which uses experimentally measured ion intensities at all ions to determine elemental ratios (referred to here as "Aiken-Explicit"), reproduces known O:C and H:C ratio values within 20% (average absolute value of relative errors) and 12% respectively. The more commonly used method, which uses empirically estimated H₂O⁺ and CO⁺ ion intensities to avoid gas phase air interferences at these ions (referred to here as "Aiken-Ambient"), reproduces O:C and H:C of multifunctional oxidized species within 28% and 14% of known values.

R1.7: The authors used the term ‘oven’ rather than ‘vaporizer’ on a couple of occasions.

A1.7: The terminology has been standardized throughout the manuscript to ‘vaporizer’

R1.8: P19794, L12: In the interests of being current, more recent references for aerosol impacts should be cited (e.g. the most recent IPCC report).

A1.8: The IPCC report citation has been updated to 2013.

R1.9: P19804, L19: The reference used for the ‘default’ frag tables is given as Allan et al. (2004) here and in table S3, however it is specified as Aiken et al. (2008) in table 2. This should be clarified.

A1.9: The authors agree that this is confusing. The word "Default Assumptions" in Table 2 have been changed to "Aiken Assumptions" in order to clarify that these additions

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to the organic frag table were introduced by Aiken et al. (2008), which was updated from the version originally proposed by Allan et al. (2004).

R1.10: The 'Hildebrandt Ruiz' reference is frequently referred to as 'Hildebrandt'. This should be made consistent.

A1.10: This has been changed as requested. The reference has also been updated to: Hildebrandt Ruiz, L., Paciga, A. L., Cerully, K., Nenes, A., Donahue, N. M., and Pandis, S. N.: Aging of Secondary Organic Aerosol from Small Aromatic VOCs: Changes in Chemical Composition, Mass Yield, Volatility and Hygroscopicity, *Atmospheric Chemistry and Physics Discussions*, 2014.

AUTHOR RESPONSES TO REVIEWER COMMENTS: ANONYMOUS REFEREE #2

R2.1: The manuscript reports the "improved-ambient method" for estimating elemental ratios (O:C and H:C) of organic aerosols (OA) from aerosol mass spectrometer (AMS) measurements. The standard calibration is well performed and covers a wide range of organics with different functionalities. There is no doubt that this work has a significant contribution to improve the accuracy of elemental analysis of ambient AMS dataset, which is largely based on the observations from Aiken et al (2008). In particular, the empirical equations determined in this study allow the AMS users to recalculate O:C, H:C, OM:OC and OSc of their existing dataset directly. Overall, it covers many aspects of elemental ratio determination in great detail. This manuscript is clear and well organized. However, it could be argued that this paper would be more suitable for AMT than for ACP as the main focus of the paper is rather on a technical (method) development.

I recommend this manuscript to be published in ACP if the authors can better highlight the atmospheric implications and address the following comments.

A2.1: The authors thank the reviewer for his/her thoughtful comments. We agree that the atmospheric implications of this work were not highlighted well enough. Thus we have added a new section (3.9) which highlights these implications more clearly as

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follows:

3.9 Atmospheric Implications Aerosol elemental ratios measured with the AMS have been previously used to distinguish between different types of organic aerosol (Jimenez et al., 2009; Ng et al., 2010), examine the degree to which chamber SOA is able to simulate ambient SOA (Chhabra et al., 2010; Ng et al., 2010), and to constrain oxidation mechanisms used in theoretical models (Jimenez et al., 2009; Kroll et al., 2011; Donahue et al., 2011; Daumit et al., 2013; Chen et al., 2014;). Here we show that while the changes introduced by the Improved-Ambient method can be significant, they do not change any fundamental conclusions made from previous AMS studies. As shown in Fig. 7, I-A elemental ratios for ambient OA components have the same trends with respect to each other as previously published A-A elemental ratios. The relative levels of oxidation for the various OA components, for example, do not change with respect to each other. The OOA components still span a continuum of oxidation levels; LV-OOA components remain more oxidized than SV-OOA components and OOA components and more oxidized than the various POA components (Jimenez et al., 2009). In fact, the Improved-Ambient method enhances previous conclusions about the high degree of oxygenation of atmospheric OOA, indicating that ambient OA has a greater oxygen content than suggested by previous AMS studies. Laboratory chamber studies provide the ideal means of simulating ambient aerosol formation and aging processes under controlled and reproducible experimental conditions (i.e. selected reactants, photochemical conditions, and aging times). However, previous work has shown that laboratory chamber studies are unable to generate SOA or photochemically aged OA with the same chemical composition as the LV-OOA species observed in the atmosphere (Chhabra et al., 2010; Ng et al., 2010). The elemental ratios obtained with I-A method reconfirm this difference. Figure 7 shows, for example, that the I-A elemental ratios observed for the SOA from terpene and sesquiterpene precursors are significantly less oxidized than the average ambient LV-OOA component. In fact, the terpene and sesquiterpene chamber SOA generally only reach the O:C and OSc values observed for the less oxidized SV-OOA components. As shown in Table 2, the

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I-A elemental ratios of isoprene and toluene SOA experience large changes compared to their corresponding A-A values. These changes are large enough to bring the O:C and OSc values of these SOA in good agreement with LV-OOA values. However, as shown in Fig. 4a, the oxygen containing functional groups in these SOA still do not reproduce the mass spectral signatures obtained from ambient LV-OOA. Thus, the gap in the AMS chemical compositions measured for chamber and ambient SOA remains even when the I-A method is used. Many studies have used elemental ratios (O:C and H:C) or the oxidation state values derived from them as key constraints to understand how OA chemical composition evolves in the atmosphere. Some two dimensional chemical spaces that directly use these parameters as constraints are: the Van Krevelen space discussed in section 3.7 of this manuscript, OSc vs. carbon number, and OSc vs. saturation vapor concentration (Jimenez et al., 2009; Kroll et al., 2011; Donahue et al., 2011). Daumit et al. (2013) have used a three dimensional space (carbon number, O:C, H:C) to constrain and define the chemically feasible back-reactions that could lead to the oxidized LV-OOA species observed in the atmosphere. In all of these spaces the measured bulk values of O:C, H:C, and OSc provide mechanistic insight by limiting the reaction pathways and intermediates that are potentially possible. Daumit et al. (2013) have compared the difference in constraints introduced when LV-OOA elemental ratios are calculated using A-A and I-A methods (The I-A elemental ratios in Daumit et al. (2013) were calculated by scaling A-A O:C and H:C ratios by 1.3 and 1.11, respectively). For the same LV-OOA volatility, elemental ratios obtained with the I-A method constrain the LV-OOA composition to contain a higher hydroxyl/carbonyl ratio than the elemental ratios obtained with the A-A method. Since hydroxyl groups result in lower volatility than carbonyl groups, this implies that the average LV-OOA carbon number calculated using the I-A constraints is lower than that calculated using A-A constraints. From the standpoint of chemical mechanisms, this also means that the new I-A constraints will result in the need for new reactions that produce more hydroxyl groups relative to carbonyl groups. This is consistent with the general trend noticed in the van Krevelen diagrams (see section 3.7) which indicate that ambient OA

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oxidation increases O:C while maintaining high H:C values. This suggests that models should explore different and or additional mechanisms for adding -OH and/or -OOH functionalities during oxidation of ambient OA.

R2.2: Introduction, second paragraph: Chemical ionization mass spectrometry (CIMS) with aerosol collection interface and high-resolution time-of-flight mass spectrometer has been recently deployed for determination of elemental ratios (i.e. O:C and H:C) of organic aerosols. Please add this information to the introduction with the support of some recent references.

A2.2: The authors agree that this was an oversight. Thus the text suggested by the reviewer and additional text referring GC-MS instruments have been included in the introduction as follows:

Gas chromatography-mass spectrometry (GC-MS) (Williams et al., 2006) and Chemical ionization mass spectrometry (CIMS) with aerosol collection interfaces have also recently been coupled to a high-resolution time-of-flight mass spectrometer to allow for determination of elemental ratios (i.e. O:C and H:C) of organic aerosols (Lopez-Hilfiker et al., 2014; Yatavelli and Thornton, 2010; Williams et al., 2014).

R2.3: Method, Page 19797, line 18-20: A complex mixture of organic aerosols generally retain water even though they are drying under a very low relative humidity condition. Can we ensure that condensed-phase water in organic aerosols cannot be completely removed by silica gel diffusion dryer? What are the potential uncertainties due to this issue?

A2.3: This concern has also been raised by Reviewer #1 and a complete response to this concern can be found in our response R1.3. Briefly, relative humidity measurements were performed for several of the experiments and confirmed low relative humidity operation. While we can't confirm that this completely removed all the condensed-phase water, we want to point out that any uncertainties in the source of the measured water do NOT affect the Aiken-Ambient or Improved-Ambient elemental analysis ratios.

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The measured H₂O intensities are purely compared to the empirical values used in the A-A and I-A calculations to gain insight into sources of discrepancy.

R2.4: Figure 4 is a very good illustration of neutral CO₂, CO, and H₂O production via dehydration and decarboxylation of dicarboxylic acid upon thermal evaporation. It is recommended to add a few more examples (i.e. at least one for each class of organics in the supplement) to demonstrate that the same argument can be applied to different types of organics.

A2.4: A new supplementary figure (S.2.) showing VUV mass spectra of a few more organic standard species has been added.

R2.5: Page 19807, Line 19: How would the presence of aldehydes influence the use of fCHO⁺ as a surrogate for alcohol content?

AR5: The cleavage of aldehydes to give CHO⁺ is not generally observed to be important. This ion is only observed to be dominant for small aldehydes and for species in which the carbon next to the aldehyde contains highly electronegative functional groups. (See McLafferty, F. W., and Turecek, F.: Interpretation of Mass Spectra, 1993). Thus, we do not expect aldehydes to significantly affect the use of CHO⁺ as a surrogate for alcohol functionality.

The following sentence has been added to manuscript: The cleavage of aldehydes to give CHO⁺ is not generally observed to be important (McLafferty and Turecek, 1993).

R2.6: Section 3.6: Please specify the ranges of theoretical O:C and H:C of organic mixtures being investigated. Are they covering the typical ranges observed in ambient aerosols?

A2.6: The following text has been added to the manuscript:

For the 1000 mixtures made of 25 standards, the O:C ratios ranged from 0.3 to 0.83 and the H:C ratios ranged from 1.36 to 1.92. The mixtures made of 10 standards covered a wider range of O:C ratios (0.18 to 1.02) and H:C ratios (1.15-2.02). For comparison,

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the average Improved-Ambient O:C(H:C) values of LV-OOA are 0.84 (1.43) and of SV-OOA are 0.53(1.62). Thus, the elemental ratios of the organic standard mixtures cover the range of ambient observations.

R2.7. Page 19812, line 5-8: Please add appropriate references to support the argument (e.g. isoprene and toluene SOA have a larger content of dicarboxylic acid and polyol functionalities).

A2.7: The following text has been added in this section: Isoprene SOA, for example, is known to produce organic peroxides (Surratt et al., 2006) and polyols (Claeys et al., 2004) while major products of toluene SOA are known to be acids (Fisseha et al., 2004;Claeys et al., 2004;Surratt et al., 2006)

R2.8. Even though the focus of this manuscript is elemental analysis of OA, it is recommended to comment how the improved-ambient method may affect the total OA mass loading if the fragmentation table in Squirrel is modified accordingly.

A2.8: As the reviewer states, this manuscript focused on evaluating AMS elemental analysis methods. The Improved-Ambient method is specifically designed to only correct elemental ratios obtained from the AMS. Thus, this method does not involve explicit changes to the fragmentation table of Squirrel/PIKA that would affect OA mass loading. The only changes involve correction factors that are applied to the A-A elemental ratios alone. However, the increase in O/C and H/C values that result from the Improved-Ambient method also imply an increase in OM/OC ratios of around 9% for total OA. These changes to OM/OC are already discussed in section 3.7.

R2.9.Terminology: Both thermal vaporizer and oven are used. Please use either one in the manuscript.

A2.9: The term vaporizer is now used throughout

R2.10.Page 19806, line 9: Please change "Fig. S3" to "Fig S2".

A2.10: Done

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R2.11. Page 19807, line 9: Please change “3.2 and 3.3” to “3.2”. Section 3.3 only demonstrates the production of CO₂, CO and H₂O fragments upon thermal evaporation.

A2.11: We would prefer to keep these sections separate because they both use different ionization schemes (EI vs. VUV). We think discussion of these two different sets of results is clearer if they are kept in separate sections

R2.12. Page 19808, line 24: The error of O:C shown in the Figure 1e (20%) is different to that reported in the text (28%). Please correct.

A2.12: The number reported in the figure was a mistake and has now been changed to 28%

R2.13. Page 19809, line 17: Please correct the reference to “Hildebrandt et al., 2014”. Please also update the information in the reference list (e.g., add the tentative title of the paper).

A2.13: Done

R2.14. Equation 10 and Figure S4: The empirical relationship is slightly different between the figure (1.29) and the text (1.28)? Please correct.

A2.14: Text is corrected to read 1.29

R2.15. Missing reference: Chen et al. (2014)

A2.15: Reference has been added.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C9283/2014/acpd-14-C9283-2014-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 19791, 2014.

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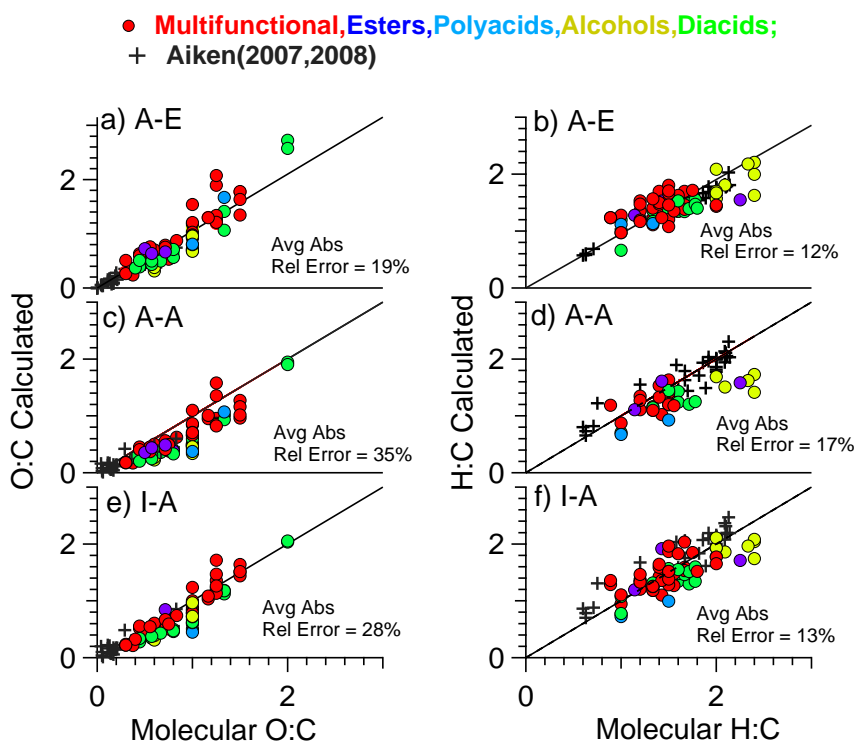


Fig. 1. Figure 1: Scatter plots between known elemental compositions and AMS elemental ratios obtained with the Aiken-Explicit (A-E; panels a and b), Aiken-Ambient (A-A; panels c and d), and Improved-Ambient

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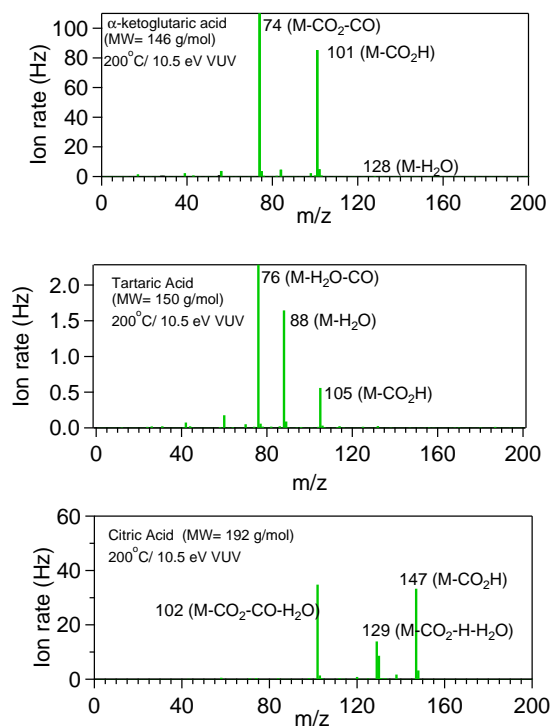


Fig. 2. Figure S2: VUV-AMS spectra of three different organic standards obtained with vaporizer set to 200°C and VUV energy of 10.5 eV. Ketoglutaric acid, tartaric acid, and citric acid correspond to multif

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Table 2. Summary of fragment ion ratios observed for standard molecules, chamber SOA, and ambient SOA. The entry * denotes the use of Aiken assumptions for the ratio in the frag Table.

	Obs H ₂ O ⁺ /CO ₂ ⁺	Obs CO ⁺ /CO ₂ ⁺	Frag Wave H ₂ O ⁺ /CO ₂ ⁺ m/z 102:114	Frag Wave H ₂ O ⁺ /CO ₂ ⁺ m/z 102:112	Literature Reference
AMS Frag Table					
Aiken Assumptions	0.32	1	0.32	0.225	Aiken et al.(2008)
OA Standards					This Study
Multifunctional	0.5-1.5	1-2	0.5-1.5	0.35-1.05	
Polycarboxylic	1	1-2	1	0.7	
Dicarboxylic	2	2	2	1.4	
Esters	0.5-1	1	0.5-1	0.35-0.7	
Alcohols	>10	>4	>10	>7	
Ambient Aerosol					
Pittsburgh, USA	*	1.3	*	*	Zhang et al.(2005)
Tokyo, Japan	*	1	*	*	Takegawa et al. (2007)
Whistler Mtn, Canada	1	*	1	0.7	San et al.(2009)
Chamber SOA					
Bioisoprene Photooxidation (Low NO _x)	3.9	1.03-2.6	3.9	2.7	Chhabra et al. (2010); Chen et al.(2011)
Bioisoprene Photooxidation (NO _x)	0.3	*	0.3	0.2	Nakao et al.(2013)
α-pinene+O ₃	0.8-1	1-1.1	0.8-1	0.6-0.7	Chhabra et al.(2010), Chen et al. (2011), Nakao et al. (2013)
β-caryophyllene+O ₃	0.7-1.3	1.2	0.7-1.3	0.5-0.9	Chen et al.(2011), Nakao et al.(2013)
Toluene Photooxidation (NO _x)	1.8	1	1.8	1.3	Hildebrandt et al.(2014)
Aromatics Photooxidation (NO _x ; Low NO _x)	0.3-1.3	*	0.3-1.3	0.2-0.9	Nakao et al.(2013)
Naphthalene Photooxidation (Low NO _x)	*	1.2	*	*	Chhabra et al.(2011)

Fig. 3. Table 2: Summary of fragment ion ratios observed for standard molecules, chamber SOA, and ambient SOA. The entry * denotes the use of Aiken assumptions for the ratio in the frag Table.

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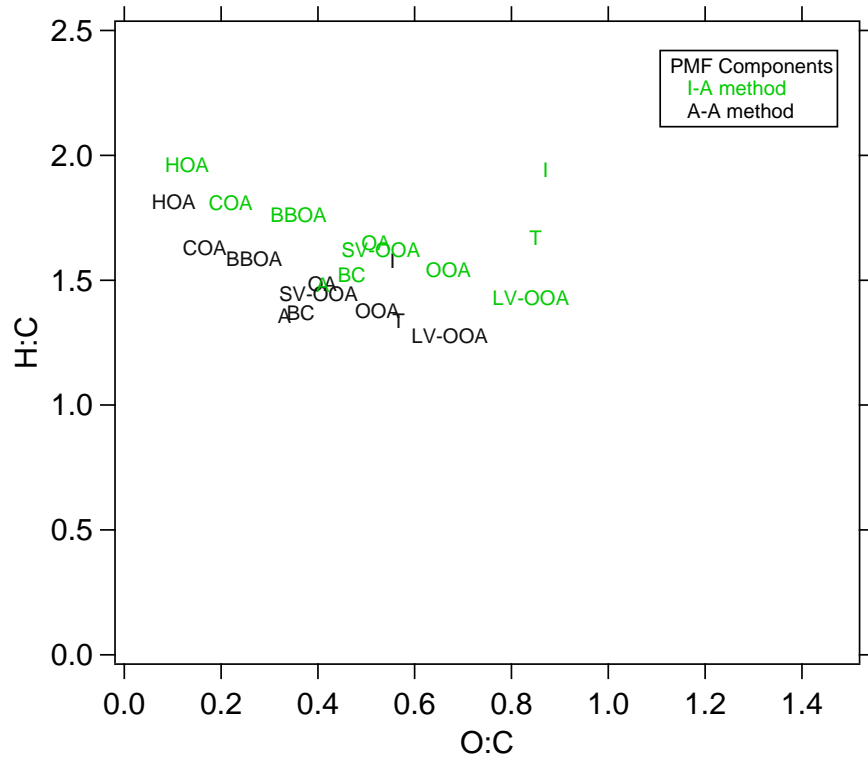


Fig. 4. Figure S7: a) Van Krevelen plots of ambient PMF components (HOA, COA, BBOA, SV-OOA, LV-OOA, OOA) and chamber SOA (α-pinene(A), toluene (T) and isoprene (I)) obtained when the O:C and H:C values are ca