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Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications

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Elemental compositions of organic aerosol (OA) particles provide useful constraints on OA sources, chemical evolution, and effects. The Aerodyne high-resolution timeof-flight aerosol mass spectrometer (HR-ToF-AMS) is widely used to measure OA elemental composition. This study evaluates AMS measurements of atomic oxygen-tocarbon (O:C), hydrogen-to-carbon (H:C), organic mass-to-organic carbon (OM:OC), and carbon oxidation state (OS_C) for a vastly expanded laboratory dataset of multifunctional oxidized OA standards. For the expanded standard dataset, the "Aiken-Explicit" method (Aiken et al., 2008), which uses experimentally measured ion intensities at all ions to determine elemental ratios, reproduces known molecular O: C and H: C ratio values within 20% (average absolute value of relative errors) and 12% respectively. The more commonly used "Aiken-Ambient" method, which uses empirically estimated H₂O⁺ and CO⁺ ion intensities to avoid gas phase air interferences at these ions, reproduces O: C and H: C of multifunctional oxidized species within 28% and 14% of known values. These values are systematically biased low, however, with larger biases observed for alcohols and simple diacids. A detailed examination of the H₂O⁺, CO⁺, and CO₂ fragments in the high-resolution mass spectra of the standard compounds indicates that the Aiken-Ambient method underestimates the CO⁺ and H₂O⁺ produced from many oxidized species. Combined AMS-vacuum ultraviolet (VUV) ionization measurements indicate that these ions are produced by dehydration and decarboxylation on the AMS vaporizer (usually operated at 600 °C). Thermal decomposition is observed to be efficient at vaporizer temperatures down to 200 °C. These results are used together to develop an "Improved-Ambient" elemental analysis method for AMS spectra measured in air. The Improved-Ambient method reduces the systematic biases and reproduces O:C (H:C) ratios of individual oxidized standards within 28% (13%) of the known molecular values. The error in Improved-Ambient O:C and H:C values is smaller (12% and 4% respectively) for synthetic mixtures of the oxidized organic standards, which are more representative of the complex mix of species present in ambient

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OA. For ambient OA, the Improved-Ambient method produces O:C (H:C) values that are 27 % (11 %) larger than previously published Aiken-Ambient values; a corresponding increase of 9 % is observed for OM:OC values. These results imply that ambient OA has a higher relative oxygen content than previously estimated. The \overline{OS}_C values calculated for ambient OA by the two methods agree well, however (average relative difference of 0.06 \overline{OS}_C units). This indicates that \overline{OS}_C is a more robust metric of oxidation than O:C, likely since \overline{OS}_C is not affected by hydration or dehydration, either in the atmosphere or during analysis.

1 Introduction

Organic aerosols (OA) account for a substantial fraction of ambient submicron aerosol mass in urban and rural/remote environments, with important impacts ranging from human health to climate forcing (IPCC, 2007; Pope and Dockery, 2006). In recent years the Aerodyne Aerosol Mass Spectrometers (AMS; Canagaratna et al., 2007) have seen wide use for characterizing the composition, the elemental ratios (H:C,O:C, N:C,S:C,OM:OC) (Aiken et al., 2007, 2008) and the approximate carbon oxidation state (OS_C ≈ 2×O:C-H:C) of OA (Kroll et al., 2011). This information provides key constraints for understanding aerosol sources, processes, impacts, and fate, and for experimentally constraining and developing predictive aerosol models on local, regional, and global scales.

Organic aerosol elemental ratios can be measured with a number of analytical techniques besides the AMS. These include combustion analysis (O'Brien et al., 1975; Krivacsy et al., 2001; Kiss et al., 2002), electrospray ionization coupled to ultrahighresolution mass spectrometry (ESI) (Nguyen and Schug, 2008; Altieri et al., 2009; Bateman et al., 2009; Kroll et al., 2011; Mazzoleni et al., 2010), nuclear magnetic resonance (NMR) spectroscopy (Fuzzi et al., 2001), Fourier transform infrared spectroscopy (FTIR) (Gilardoni et al., 2009; Mysak et al., 2011), and X-ray photoelec-

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tron spectroscopy (XPS) (Mysak et al., 2011). Each of these techniques has its own strengths and weaknesses. AMS measurements of bulk aerosol elemental composition are obtained directly from the average elemental compositions of the individual fragment ions observed in high-resolution AMS spectra. One strength of the AMS approach is that it offers the capability for online, sensitive detection of aerosol elemental composition. A weakness is its use of empirical corrections that can affect the accuracy of the calculated elemental ratios. This manuscript evaluates the accuracy of the AMS elemental analysis approach over a wider range of OA species than has been studied before.

In the AMS, aerosol particles are focused into a beam in a high-vacuum chamber and typically flash-vaporized on a tungsten oven at a temperature of 600°C before constituents are detected with electron ionization (EI) mass spectrometry. Thus, the elemental composition obtained from AMS mass spectra can be potentially biased by two sources: vaporization and ion fragmentation. Organic molecules, particularly oxidized organic species comprising oxidized organic aerosol (OOA), can decompose during the AMS vaporization process to form stable molecules with elemental compositions that differ from the original parent molecule. Carboxylic acids and alcohols, for example, are known to undergo thermally induced dehydration and decarboxylation as follows (Moldoveanu, 2009):

$$RCOOH \xrightarrow{\Delta} CO_2 + H_2O + CO + R'$$
 (R1)

$$\mathsf{RCOH} \ \stackrel{\Delta}{\longrightarrow} \ \mathsf{H}_2\mathsf{O} + R' \tag{R2}$$

The decomposition products are all ionized and detected by the AMS. The loss of neutral CO_2 , CO , and $\mathrm{H}_2\mathrm{O}$ from the parent carboxylic acid and alcohol molecules results in the formation of organic ions in EI (R'^+ and their fragments) that differ significantly from their parents in chemical identity and elemental composition. The accuracy with which the parent elemental ratios are calculated from AMS measurements will depend on the accuracy with which the C , H , and O masses in all of the decomposition fragments are measured or accounted for. Mass spectral interferences from gas and particle species

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further complicate accurate determinations of H₂O⁺ and CO⁺ intensities for OA sampled in air (Aiken et al., 2008).

Previous work by Aiken et al. (2008, 2007) showed that O:C and H:C ratios of laboratory standard molecules can be estimated to within 31% and 10% (average absolute value of the relative error, respectively) with the AMS. The "Aiken-Explicit" (A-E) method averages the elemental composition of all measured fragment ions observed in high-resolution mass spectra and uses H:C and O:C calibration factors derived from laboratory measurements of standard organic molecules. The calibration factors account for differences between the elemental compositions of the detected fragment ions and their parent molecules, e.g. due to the tendency of more electronegative fragments with high O content to end up as neutrals rather than as positive ions during the ion fragmentation process. The "Aiken-Ambient" (A-A) method is similar; however, it uses empirically estimated H_2O^+ and CO^+ intensities for OA sampled in air. The Aiken-Ambient method is used widely for elemental analysis of ambient and chamber OA because the intensities of H_2O^+ and CO^+ originating from OA are difficult to separate from those originating from other background species in air.

In this study we extend the Aiken et al. (2007, 2008) elemental analysis calibrations to a wider range of OA species. The Aiken et al. (2007, 2008) calibration dataset consisted of reduced primary OA (POA)-like organic species and a few OOA surrogates such as dicarboxylic, fulvic, and amino acids. The species chosen for the present study contain multi-functional oxygenated moieties and have high O:C values that are more representative of ambient OOA species. We investigate the extent to which thermal decomposition of these species (cf. Reactions R1 and R2) bias elemental ratio measurements obtained with the AMS. AMS data from the laboratory standard molecules are used to re-evaluate the Aiken-Explicit and Aiken-Ambient methods for calculating elemental ratios. An "Improved-Ambient" (I-A) method (for AMS measurements performed in air) is determined as part of this study; the changes caused by application of the Improved-Ambient method to previously published ambient and chamber data are

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2 Methods

2.1 Aerosol standards

A list of the aerosol standards used in this study is given in Table 1. This list includes alcohols, diacids, polyacids, esters, and other species with multiple functionalities such as keto and hydroxy acids. All of the standards were purchased from Sigma-Aldrich (purity ranges > 96 %) except for three synthesized standards including a racemic mixture of δ-isoprene epoxydiol (IEPOX) diastereomers known to be intermediates in isoprene oxidation chemistry, as well as known isoprene-derived SOA constituents cisand trans-3-methyl-3,4-dihydroxytetrahydrofurans (Lin et al., 2012; Zhang et al., 2012).

Aerosol particles were generated by dissolving small amounts of each standard in about 100 mL of distilled water, followed by atomization. The standards were atomized with argon carrier gas instead of nitrogen, since gaseous nitrogen in air produces a very large peak at m/z 28 that make CO^+ aerosol signals very difficult to separate and quantify (even at high-resolution). Detection of CO^+ is of great interest since this ion is a likely thermal decomposition fragment of acids and potentially other species in OOA. The resulting polydisperse aerosol was then dried (with two silica gel diffusion dryers in series) in order to remove any remaining water from the atomization process and sampled directly into the AMS. The atomization setup was thoroughly cleaned between standards and blank water runs were carried out in between standards to ensure that cleaning between each set of standards was successful.

2.2 AMS operation

The HR-ToF-AMS instrument and its data analysis procedures have been described in detail in previous publications (Canagaratna et al., 2007; DeCarlo et al., 2006). The 19797

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HR-ToF-AMS can be usually operated in two ion optical modes (V or W) with differing spectral resolutions. For these experiments the AMS was operated in the more sensitive V-mode. The resolution of this mode (resolving power of ~ 3000) was high enough to resolve the key isobaric fragments observed from the standards studied here. The higher signal levels observed in the V-mode also allowed for the use of low-concentration samples in the atomizer, thereby minimizing cross-contamination between standards and avoiding signal saturation of the AMS detector or acquisition card. High-resolution ions up to the molecular weight of each standard were fitted in order to account for all of its ion fragments. The AMS data analysis software packages SQUIRREL (version 1.51H) and PIKA (version 1.10H) were used for the analysis of the high-resolution mass spectra.

Data collection occurred over several months and some standards were repeatedly measured at different points in time with the same instrument. Supplement Fig. 1a shows the standard deviations in O:C and H:C values (calculated using Aiken-Ambient method) obtained during these measurements. As can be seen, for most standards O:C and H:C values obtained on a given instrument are reproducible to <5% and <3% respectively. Supplement Fig. 1b and c compare O:C and H:C values obtained for different standards on three AMS instruments. The values compare well across instruments (O:C within 4%, H:C within 7%).

For most of the experiments the AMS vaporizer was operated at a power comparing to 600 °C. The thermocouple readout from the vaporizer is sensitive to its exact placement on the vaporizer and can sometimes differ from instrument to instrument or vary with instrument use. 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. 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. In addition to the standard 600 °C operation, a few experiments were also performed at 200 °C (about the lowest temperature at which the

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AMS vaporizer can be operated continuously) in order to investigate how the amount of thermal decomposition and ion fragmentation changed with temperature. In both of these cases the typical vaporization timescale for particles was measured to be on the order of one hundred microseconds.

5 2.3 VUV ionization

Northway et al. (2007) described the adaptation of an HR-ToF-AMS to the vacuum ultraviolet (VUV) beam at the Advanced Light Source (Lawrence Berkeley Laboratory). We performed a similar adaptation in this study and generated and analyzed selected standards (see Table 1) using the same procedures discussed above. Previous work has shown that, compared to 70 eV EI-AMS spectra, VUV-AMS spectra are typically less complex, with reduced ion fragmentation and increased molecular ion intensity (Canagaratna et al., 2007; Northway et al., 2007). Molecular ions observed in VUV-AMS spectra of unoxidized and slightly oxidized squalane have been successfully used to obtain chemical and mechanistic insight into the squalane oxidation reaction (Smith et al., 2009). Moreover, the tunability of the VUV light can be used to investigate the chemical identity of species by measuring their threshold ionization energy (Leone et al., 2010). The threshold ionization energy of most organic molecules is 10.5 eV and that of H₂O, CO₂, and CO molecules is 12.62 eV, 13.77 eV, and 14.01 eV respectively (NIST Chemistry WebBook: http://webbook.nist.gov/chemistry/). Thus, in this experiment the 8 eV to 14.5 eV VUV range was used.

2.4 Elemental analysis (EA) methods

The procedure for obtaining elemental ratios (O:C, H:C) from AMS spectra was first developed by Aiken et al. (2007, 2008). The atomic O:C and H:C ratios are obtained in terms of the relative mass concentrations of O ($M_{\rm C}$) and C ($M_{\rm C}$) and H ($M_{\rm H}$) as

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$$H: C = \alpha_{H:C} \cdot (M_H/M_C) \cdot (MW_C/MW_H)$$
 (2)

MW_C, MW_O and MW_H are the atomic weights of C, O, and H respectively. Since AMS ion intensities are proportional to the mass of the original molecules present (Jimenez et al., 2003), M_C , M_O , and M_H are obtained as a sum of the appropriate ion intensities across the complete organic spectrum (including H_2O^+ , CO^+ , and CO_2^+) as follows:

$$M_{\rm C} = \sum_{j=m/z_{\rm min}}^{m/z_{\rm max}} I_j F_{\rm C} \tag{3}$$

$$10 \quad M_{\mathcal{O}} = \sum_{j=m/z_{\min}}^{m/z_{\max}} I_j F_{\mathcal{O}}$$
 (4)

$$M_{\rm H} = \sum_{j=m/z_{\rm min}}^{m/z_{\rm max}} I_j F_{\rm H} \tag{5}$$

where I_j is the ion intensity of the jth ion in the spectrum and $F_{\rm C}$, $F_{\rm O}$, $F_{\rm H}$ are the relative carbon, oxygen, and hydrogen mass fractions for that ion. Calibration parameters ($\alpha_{\rm O:C}$ and $\alpha_{\rm H:C}$) account for preferential losses of some atoms to neutral rather than ion fragments during the fragmentation processes. The tendency of hydrocarbon fragments to form positive ions more readily than those containing the more electronegative O atom, for example, can result in such a detection bias. Aiken et al. (2008) obtained slopes of 0.75 and 0.91 (i.e. $\alpha_{\rm O:C} = 1/0.75$ and $\alpha_{\rm H:C} = 1/0.91$), respectively, by comparing measured and known O:C and H:C values for a range of organic standards according to Eqs. (1) and (2).

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In AMS elemental analysis, Eqs. (1) and (2) are applied in two different ways which we refer to here as the Aiken-Explicit and Aiken-Ambient methods (Aiken et al., 2008). The Aiken-Explicit method is used when organic signals at CO⁺ and H₂O⁺ can be directly measured. Laboratory measurements performed in an atmosphere of dry argon, for example, do not contain the interfering H₂O or N₂ species and allow for direct measurement of the organic signals at H₂O⁺ and CO⁺. The organic signals at CO⁺ have also been obtained under ambient conditions from AMS size distributions and by monitoring changes in the m/z 28 intensities (Zhang et al., 2005; Takegawa et al., 2007). Calibrations have also been carried out in laboratory chamber experiments under controlled relative humidity to determine the interference signals and obtain the organic signals at CO⁺ and H₂O⁺ by subtraction (Chen et al., 2011; Nakao et al., 2013).

The Aiken-Ambient method is used for measurements performed in air where the interferences from gaseous N₂ and H₂O are difficult to estimate. Since most field measurements and laboratory chamber measurements are performed under the latter conditions, this method has in practice been the most widely used method of obtaining elemental ratios from AMS measurements. In the Aiken-Ambient method the organic H_2O^+ and CO^+ intensities used in Eqs. (3)–(5) are empirically estimated rather than directly measured. The H_2O^+/CO_2^+ and CO^+/CO_2^+ ratios recommended by Aiken et al. (2008) were empirically estimated from limited ambient OA measurements available at the time to be 0.225 and 1 respectively. The CO⁺ / CO₂ ratio was determined from AMS size distribution measurements where the gas-phase signal from N₂ can be separated from the particle phase CO signal intensities (Zhang et al., 2005; Takegawa et al., 2007). The H₂O⁺ / CO₂⁺ mass ratio was empirically estimated to conserve OA mass concentrations that resulted from the CO⁺ / CO₂ ratio. This H₂O⁺ / CO₂ empirical mass ratio corresponds to a raw ion signal ratio of either 0.225, assuming H₂O⁺ and CO₂⁺ were each formed with a relative ionization efficiencie (RIE) of 1.4 or 0.321, using a recently-determined RIE of 2.0 for the formation of H_2O^+ (Mensah et al., 2011).

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3.1 Evaluation of Aiken-Explicit and Aiken-Ambient methods

We evaluated the performance of both Aiken-Explicit and Aiken-Ambient methods over a large range of species, including those with higher O:C and more multifunctional moieties than originally studied by Aiken et al. (2008). Panels a and b in Fig. 1 show elemental ratios obtained with the Aiken-Explicit method for the laboratory standards studied here. The Aiken-Explicit method results reproduce known molecular O:C and H:C ratios for all the standard molecules with an average absolute value of the relative error (referred to as "error" in the rest of this manuscript) of 20% and 12% respectively. This is consistent with the accuracies reported by Aiken et al. (2008) and confirms that the Aiken-Explicit method can be used for a wide range of OA species.

Figure 1c and d shows Aiken-Ambient results for the laboratory standards. In general the Aiken-Ambient O: C values are biased low for all the standards and observed errors are dependent on the functional groups contained in the different standard molecules. The Aiken-Ambient values for multifunctional standard molecules are biased low by 28% and those for diacids and alcohols are biased low by 46%. The error in Aiken-Ambient H: C values for all standards is smaller, but alcohols and diacids are still biased low compared to multifunctional species.

3.2 Measurements of H₂O⁺, CO⁺ and CO₂⁺ signal intensities with Electron Ionization (EI)

The only difference between the Aiken-Explicit and Aiken-Ambient methods is the measured vs. estimated H_2O^+ and CO^+ ion intensities. Since these ion intensities are estimated based on assumed H_2O^+ and CO^+ ratios to CO_2^+ , we investigate trends in the relative signal intensities of these 3 key ions in the observed standard mass spectra. Figure 2 shows the fractional AMS ion intensities (relative to the total ion signal for each standard) measured for these key thermal decomposition products in the spectra of the

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different laboratory standards. The standards are separated according to functionality, and they are arranged according to increasing molecular O:C. Measurements of the same standard on different instruments are shown as separate bars on the graph. The general agreement between different instruments supports the reproducibility and transferability of the results obtained here to other AMS instruments. The relative intensities of the three ions vary according to specific differences in the decomposition mechanisms including those shown in Reactions (R1) and (R2) above. Spectra from carboxylic acids, esters, polyacids, and multifunctional acids have higher $f_{\text{CO}_2^+}$ (defined as the intensity of CO_2^+ divided by the total ion intensity) and f_{CO^+} than alcohols, indicative of decaboxylation. On the other hand, spectra from alcohols have negligible $f_{\text{CO}_2^+}$ and significant $f_{\text{H}_2\text{O}^+}$, indicative of dehydration (Reaction R2).

Figure 3a shows the $f_{\rm CO^+}$ vs. $f_{\rm CO_2^+}$ scatter plot for all the standards in this study. For most multifunctional systems, the $f_{\rm CO^+}/f_{\rm CO_2^+}$ ratio is relatively consistent with the assumed value of 1 from Aiken et al. (2008). The measured $f_{\rm CO^+}/f_{\rm CO_2^+}$ ratios for alcohols and most diacids are ≥ 2 which likely contributes to the additional underestimation in O : C that is observed for these species with the Aiken-Ambient method. These measurements are generally consistent with previous studies that have shown that most laboratory SOA (thought to contain a mixture of multifunctional species) yield $f_{\rm CO^+}/f_{\rm CO_2^+}$ values around 1 (Chhabra et al., 2010; Chen et al., 2011) with exceptions of SOA produced by isoprene photooxidation (2.63; Chen et al., 2011) and glyoxal uptake under dark, humid conditions (5.0; Chhabra et al., 2010), both of which contain products that are rich in hydroxyl functional groups but poor in carboxyl groups (Hastings et al., 2005; Lin et al., 2012). Ambient estimates are also in the similar range of 0.9–1.3 (Takegawa et al., 2007; Zhang et al., 2005). The $f_{\rm CO^+}/f_{\rm CO_2^+}$ ratios discussed above are summarized in Table 2.

The relationship between $f_{\rm H_2O^+}$ and $f_{\rm CO_2^+}$ for the standard spectra are shown in Fig. 3b and Table 2. The observed signal intensity ratios in the spectra are larger than those calculated from the empirical mass ratios of Aiken et al. (2008). The mea-

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sured $f_{\rm H_2O^+}/f_{\rm CO_2^+}$ ratio of multifunctional species varies from near 0 to over 2, and many diacids are between 1 and 2 (although some are substantially lower than 1). Polyols and alcohol spectra have even higher ratios, mainly due to their lack of CO₂⁺. As shown in Table 2, similar departures from the assumed $f_{\rm H_2O^+}/f_{\rm CO_2^+}$ ratios were originally observed for chamber SOA by Chen et al. (2011) (0.84-3.91) and more recently by Nakao et al. (2013) (0.33–1.23). We note that in mixed ambient aerosols the $f_{\rm H_2O^+}/f_{\rm CO_2^+}$ ratios would be moderated by the presence of species other than alcohols. However, high values for this ratio (1.0) were also reported for ambient measurements from Whistler mountain (Sun et al., 2009). It is clear from Fig. 3 that the biases in the elemental ratios obtained with the Aiken-Ambient method are due to underestimations of the assumed $f_{\rm H_2O^+}/f_{\rm CO_2^+}$ and $f_{\rm CO^+}/f_{\rm CO_2^+}$ values. The $\rm H_2O^+$ and $\rm CO^+$ intensities observed for alcohols, in particular, are severely underestimated in the current assumptions since the estimates are tied to CO₂⁺, an ion that is not produced in any significant intensity in spectra of species that do not contain -C(O)OR moieties (e.g. alcohols).

In the Aiken-Ambient method the intensities of the OH⁺ and O⁺ fragments of H₂O⁺ are estimated according to the ratios measured for gas-phase H2O. Figure S3 in the Supplement shows the scatter plots of measured f_{OH^+} vs. $f_{H_2O^+}$ and f_{O^+} vs. $f_{H_2O^+}$ for all the laboratory standards. The empirical estimate used in the default AMS fragmentation table (Allan et al., 2004) for the OH⁺ / H₂O⁺ ratio is very consistent with the observed relative intensities, indicating that the OH⁺ ion indeed arises from the fragmentation of molecular water from thermal decomposition of the standards. The consistency in these fragmentation patterns also holds for various chamber SOA (Chen et al., 2011). The O⁺ / H₂O⁺ ratio, in contrast, shows substantial scatter, as the dominant source of the O⁺ for our standards appears to be fragmentation of CO₂⁺ rather than H₂O⁺ (Supplement Fig. S3c). Alcohols, which do not produce CO₂⁺, are an exception with O⁺ / H₂O⁺ ratios that are much closer to the empirical estimates. Fragmentation of CO_2^+ to yield O^+ (O^+ / CO_2^+ ~ 6 %) is currently not accounted for in the AMS elemental ratio analysis and will contribute to the underestimation observed in AMS O: C values.

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The H₂O⁺, CO₂⁺, and CO⁺ signals observed in the AMS are produced by dehydration and decarboxylation processes that take place before ionization (i.e. on the vaporizer surface or in the gas-phase after evaporation) and/or after 70 eV electron-impact ionization (i.e. fragmentation of thermally excited ions). VUV-AMS measurements were used to examine the production mechanisms of these ions in more detail. VUV-AMS data were obtained for many standards with the AMS vaporizer set to both 200 °C and 600 °C (see Table 1). All experiments were carried out under an argon atmosphere. A VUV-AMS spectrum of glutaric acid is shown in Fig. 4a as an example. This spectrum was observed with the AMS vaporizer at 200 °C and a VUV photon energy of 10.5 eV. Since VUV is a "softer" ionization method than EI, this spectrum would be expected to contain only the glutaric acid molecular ion if thermal decomposition on the vaporizer was negligible. However, even at this lower vaporizer temperature, the molecular ion of glutaric acid (*m*/*z* 132) has very low intensity and organic ion fragments corresponding to loss of neutral H₂O, CO, and CO₂ from glutaric acid are observed instead. CO₂⁺, CO⁺, and H₂O⁺ are negligible in this spectrum at this VUV photon energy.

Figure 4b shows the CO_2^+ , CO^+ , and H_2O^+ signals observed from glutaric acid as a function of VUV energy. The onsets of CO_2^+ , CO^+ , and CO^+ signals are observed to occur at VUV energies that correspond to the ionization energies of neutral CO_2 , and CO^+ molecules (12.62 eV, 13.77 eV, and 14.01 eV respectively), rather than the 10.5 eV ionization energies of the observed organic ions. This indicates that these ions are formed by VUV ionization of neutral CO_2 , CO_2 , and CO_2 molecules rather than by dissociative ionization of glutaric acid. Neutral CO_2 , CO_2 , and CO_2 fragments formed upon photoionization of glutaric acid could further ionize to give rise to these signals. This process requires the absorption of two photons in the ionization region, however, and is therefore unlikely. Instead, the most likely source of the CO_2^+ , CO_2^+ , and CO_2^+ signals is direct VUV ionization of neutral CO_2^- , CO_2^- , and CO_2^+ , and CO_2^+ molecules formed from thermal decomposition of organic species on the AMS oven. VUV-AMS measurements

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of the other organic standards also show a lack of parent ions and fragments corresponding to loss of CO₂, CO, or H₂O moieties, indicating that a wide range of oxidized organic species undergo dehydration and decarboxylation upon heating to temperatures greater than 200 °C.

3.4 Effect of vaporizer temperature on H₂O⁺, CO⁺ and CO₂⁺

Thermal denuder measurements have shown that ambient OA needs to be heated to a minimum temperature of ~ 225 °C for several seconds in order to insure quantitative vaporization of a significant fraction of ambient oxidized OA (Huffman et al., 2009). Supplement Fig. S3 compares the trends in $f_{H_2O^+}$, f_{CO^+} and f_{CO^+} observed with the AMS (using EI) at vaporizer temperatures of 600 °C and 200 °C. The total CO₂⁺ / CO⁺/H₂O⁺ decomposition fragment intensities observed for both temperatures is remarkably similar across the standards. In most cases, $f_{H_2O^+}$, is slightly higher at 200 °C compared to 600 °C, while f_{CO^+} follows the opposite trend and f_{CO^+} changes little between the two temperatures. This indicates that dehydration is facile for these acids and alcohols even at 200°C, which is also consistent with the VUV results shown in Fig. 4. The extent of thermal decomposition observed in the AMS is likely influenced by its specific vaporization conditions (i.e. porous tungsten hot surface and high-vacuum conditions). For example, Lloyd and Johnston (2009) reported that in laser-desorption-electronionization analysis of SOA, the signal due to CO₂⁺ was much lower than in AMS spectra of the same aerosol type, and attributed the difference to differences in the vaporization conditions. Our measurements suggest that thermally-induced decomposition could affect the interpretation of organic measurements from other aerosol chemistry measurement techniques that utilize thermal desorption on surfaces, even if temperatures of only 200°C are reached. Such techniques include aerosol Gas Chromatography-Mass Spectrometry (GC-MS) and thermal-desorption Chemical Ionization mass Spectrometry (CIMS) (e.g. (Lopez-Hilfiker et al., 2014; Williams et al., 2006; Yatavelli and Thornton, 2010; Holzinger et al., 2013). Proton Transfer Reaction-Mass Spectrometry

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(PTR-MS) measurements of heated ambient filters by Holzinger et al. (2010), for example, show low molecular weight fragments at higher thermal desorption temperatures, consistent with this finding. The specific impact of the surface materials, vaporization temperatures, and pressure conditions on the decomposition reactions of OA should be the focus of future studies.

3.5 Improved-Ambient method

It is clear from Fig. 3 that the relationships among $f_{\text{CO}_2^+}$, $f_{\text{H}_2\text{O}^+}$, and f_{CO^+} are variable and cannot be well prescribed with a single empirical relationship. Furthermore, as discussed in Sects. 3.2 and 3.3, O:C and H:C calculated with the Aiken-Ambient method are biased low because the empirical estimates used in this method often underestimate the intensities of the H_2O^+ and/or CO^+ fragments. Acidic species are observed to be a large source for CO^+ and H_2O^+ fragments while alcohols are a significant source of H_2O^+ fragments.

A correction that is dependent on both acid and alcohol content of the OA is needed to address this composition dependence in the OA fragmentation. Previous AMS measurements have shown that $f_{\mathrm{CO}_2^+}$, can be used as a surrogate for acid content (Duplissy et al., 2011; Takegawa et al., 2007). An AMS surrogate for alcohol moieties has not been identified before, but spectra obtained during this study indicate that f_{CHO^+} (m/z 29) can be used as a surrogate for alcohol content. As shown in Fig. S4, spectra of standard species with no alcohol content have minimal $f_{\mathrm{CHO}^+} < 0.05$ while those with non-zero alcohol content show f_{CHO^+} values ranging from 0.05 to 0.15. High f_{CHO^+} values are found for polyols as well as multifunctional species with non-acid OH groups. Some esters are also observed to yield f_{CHO} similar to species with non-acid OH groups. Previous studies have shown that CHO^+ is also an atmospherically significant ion and a key oxygen-containing ion in many types of ambient and chamber aerosol (Ng et al., 2010a). The $f_{29}(f_{\mathrm{CHO}^+})$ fragment has also been used to monitor photooxidation of glyoxal and related species in the aqueous phase (Lee et al., 2011).

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Based on these results, a composition-dependent correction factor with a linear dependence on $f_{CO_2^+}$ and f_{CHO^+} was examined. While the CHO⁺ fragment is easily resolved from the isobaric C₂H₅⁺ organic fragment in high-resolution AMS spectra, it overlaps with ¹⁵N¹⁴N⁺ fragments from N₂ in air. Thus, a background correction must be used in order to obtain an accurate value of f_{CHO^+} . AMS data acquired while sampling through a particle filter can be used to obtain the information needed for such a background correction (as is already necessary for the accurate determination of $f_{CO_0^+}$).

We performed a multiple linear regression between the known elemental ratios of the OA standards and those determined from Eqs. (1) and (2) to obtain the best-fit constants and coefficients as follows:

O:
$$C_{I-A} = O: C_{A-A} \cdot [1.26 - 0.623 \cdot f_{CO_{A}^{+}} + 2.28 \cdot f_{CHO^{+}}]$$
 (6)

$$H: C_{I-A} = H: C_{A-A} \cdot [1.07 + 1.07 \cdot f_{CHO^+}]$$
 (7)

In the equations above the Improved-Ambient (I-A) elemental ratios are expressed as a product of Aiken-Ambient (A-A) elemental ratios and a composition-dependent correction factor. This allows for simple recalculation of the Improved-Ambient elemental ratios from Aiken-Ambient values without the need for performing a re-analysis of the raw mass spectra and can be easily applied to already published AMS results.

Figure 1e and f shows the O:C and H:C values obtained for the standards after using the Improved-Ambient method in Eqs. (6) and (7). The corrections remove the systematic O:C underestimation seen in Fig. 1c for the multi-functional species. The diacids and alcohols are still biased low in O:C, but the bias has been reduced The errors in the O: C and H: C elemental ratios calculated for the standards with the Improved-Ambient method are 28% and 13% respectively. Smaller errors (8%) are observed for the values of OM: OC using the Improved-Ambient method (see Supplement Fig. S5).

Figure 5a compares the approximate carbon oxidation state values calculated from the Improved-Ambient elemental ratios and the known standard elemental ratios of **ACPD**

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the organic standards. The two sets of values agree with a standard deviation of 0.5 OS_C units. The largest deviations are observed for the laboratory standards whose Improved-Ambient O:C values are biased lower than the known values. Figure 5b shows a comparison between the OS_C values calculated for the standard molecule 5 data using the Aiken-Ambient and Improved-Ambient methods. The error bars on the standard data indicate the estimated uncertainty in the calculated Aiken-Ambient OS_C values (using propagation of O:C (H:C) errors of 28 % (14 %) observed for multifunctional species with Aiken-Ambient method). In general, the agreement between the Aiken-Ambient OS_C values and the Improved-Ambient OS_C values is much better than the propagated errors. This indicates that the oxidation state values derived from AMS data (and potentially from other techniques using thermal desorption MS) are more robust and less variable than measured values of H: C and O: C.

The robustness of the OS_C parameter is largely due to its invariance with respect to dehydration (and hydration) processes (Kroll et al., 2011). The OS_C value that is currently calculated from AMS spectra is not strictly invariant with respect to hydration and dehydration because the AMS fragmentation table neglects small amounts of H⁺ formed from fragmentation of H₂O⁺ ions (Hildebrandt Ruiz, 2014). Other fragments, such as OH⁺, and O⁺ are properly accounted for as discussed above. Figure 5a shows the effect of calculating Improved-Ambient OS_C values with a fragmentation table that includes the H⁺ fragment (see Supplement for details). The Hildebrandt (2014) correction results in slightly smaller OS_C values than obtained with the default AMS fragmentation table due to a small (< 3%) increase in the Improved-Ambient H: C.

Estimated accuracy of the Improved-Ambient method for mixtures

The errors observed in the Improved-Ambient elemental ratios of individual OA standards are expected to be upper limits for the corresponding errors in mixtures, where inaccuracies in individual molecule predictions can compensate for each other. The **ACPD**

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Theoretical standard mixtures were generated by combining equimolar fractions of up to 25 different individual OA standards. Each mixture of individual standards is expressed as $\sum_i n_i C_{xi} H_{yi} O_{zi}$ where n_i is the mole fraction of standard i in the mixture, and xi, yi, and zi are the number of C, H, and O atoms within a molecule of standard i. The O: C ratio for any given mixture is calculated as follows:

$$O: C_{\text{mix}(I-A)} = \sum_{i} (O: C_{i(I-A)} \cdot n_i x_i) / \sum_{i} (n_i x_i)$$
(8)

$$O: C_{\text{mix}(\text{Molecular})} = \sum_{i} (O: C_{i(\text{molecular})} \cdot n_{i} x_{i}) / \sum_{i} (n_{i} x_{i})$$
(9)

H:C ratios are calculated analogously with the appropriate substitutions in Eqs. (8) and (9). For each type of mixture, 1000 different randomly generated versions were examined and the average absolute value of relative errors in the calculated Improved-Ambient elemental ratios over all 1000 variants is calculated for each mixture.

Figure 6a and b shows the error in Improved-Ambient O:C and H:C values as a function of the number of standard molecules in the mixture of interest. It is clear from the figure that the error becomes smaller and plateaus for both of the elemental ratios as the number of OA species in the mixture is increased. For O:C and H:C the errors decrease from 28% to 12% and 13% to 4% respectively as the number of species in the mixture is increased. The plateau in the error is already reached for both elemental ratios by the time that only 10 different standard OA species are added together. Ambient OA is a complex mixture of hundreds of individual species. If the standard molecule mixtures are reasonably representative of ambient OA mixtures, these results indicate that the Improved-Ambient O:C and H:C values calculated for ambient OA and SOA have errors close to $\sim 12\%$ and $\sim 4\%$, respectively.

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Effect of Improved-Ambient method on previous measurements of AMS elemental ratios

Given the large number of AMS datasets that have reported OA elemental ratios calculated with the Aiken-Ambient technique, it is useful to examine the impact that the proposed new corrections will have on existing results and their interpretation.

We focus on several HR-AMS datasets that have been analyzed with the Aiken-Ambient method and for which elemental ratios have been reported in the literature, and/or for which HR spectra are available on the HR-AMS spectral database (http: //cires.colorado.edu/jimenez-group/HRAMSsd/).

For ambient datasets, elemental ratios have been previously reported for total OA as well as OA components (i.e. groups of organic species that represent different OA sources and or processes). Primary OA (POA) species are directly emitted into the atmosphere while secondary OA (SOA) are species formed as a result of atmospheric transformation (Ulbrich et al., 2009; Zhang et al., 2011; Lanz et al., 2007). Several types of POA have been identified, including hydrocarbon-like organic aerosol (HOA), which is associated with fossil fuel combustion and other urban sources, biomass burning OA (BBOA), cooking OA (COA), and other OA from local sources (LOA) (Zhang et al., 2011) and references therein). SOA species, which generally dominate ambient OA mass concentrations, consist of a continuum of oxidized organic aerosol species (OOA) (Ng et al., 2010b; Jimenez et al., 2009). Two broad types of ambient SOA, denoted as LV-OOA (low volatility oxidized organic aerosol) and SV-OOA (semi-volatile oxidized organic aerosol), have been identified at many locations.

Figure 7 shows the average O:C, H:C, OM:OC and OSc values obtained when previously published field and chamber SOA data are analyzed using the Improved-Ambient method. Aiken-Ambient values are shown for all data and Aiken-Explicit values are shown for the chamber SOA. The data for Fig. 7 are available in Table 2 and the detailed values for each field dataset are in Supplement Tables 1 and 2. The Improved-Ambient elemental ratios of chamber SOA are higher than previously reported Aiken**ACPD**

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Ambient values and the relative change varies with the identity of the precursor. For the α -pinene + O₃ and β -caryophyllene + O₃ SOA (Chen et al., 2011), the predicted increase in O:C (H:C) is smaller than that for the isoprene + OH (Chen et al., 2011) and toluene + OH SOA (Hildebrandt Ruiz, 2014). These differences are likely linked to the specific molecular functionalities associated with SOA formed from each precursor. The largest increases are comparable to those observed for the standard molecules with diacid and polyol functionalities while the smaller increases are consistent with those observed for multifunctional standards. The Improved-Ambient elemental ratios of ambient OA (individual components as well as total OA) generally lie at the high error limit of the Aiken-Ambient values. The Improved-Ambient O: C and H: C values of total OA, for example are larger than the corresponding Aiken-Ambient values by approximately 27 % and 11 % on average. These relative differences are similar to those observed for the multifunctional OA standards (Fig. 1c) and smaller than those observed for some of the individual chamber SOA systems or individual SOA standards. Figure 7 shows that chamber SOA elemental ratios calculated with the Improved-

Ambient method agree well with those calculated using the Aiken-Explicit method. This agreement is important since it confirms that the Improved-Ambient method compares well with the Aiken-Explicit method not only for laboratory standards but also for OA mixtures with complex compositions and molecular functionalities that cannot be readily duplicated with commercial standards. Recently, agreement between gas and particle phase elemental ratio measurements of highly oxidized, extremely low-volatility organic species (ELVOC) formed in the α -pinene + O_3 reaction has also been demonstrated (Ehn et al., 2014). This agreement was found when low-volatility oxidized products (ELVOC) were measured as individual molecules in the gas phase using CIMS and as condensed particle phase species using AMS and the Improved-Ambient method. The proposed auto-oxidation mechanism in Ehn et al. (2014) indicates that the ELVOC probably have multiple hydroperoxide moieties. Though hydroperoxides are not represented in the calibration set, the agreement between the individually identified ELVOC

On average, the OM:OC ratios obtained with the Improved-Ambient method for total OA are 9% higher than previously published Aiken-Ambient values. The average Improved-Ambient OM:OC ratio of total OA is 1.84 with variation from 1.3–1.5 for primary OA components to 1.8–2.2 for secondary OA components; chamber SOA Improved-Ambient OM:OC ratios vary with precursor. The OM:OC ratio of the ambient OOA components is consistent with water soluble fraction of aged ambient aerosol, which has been measured by other techniques to be in the range of 2.1 (Turpin and Lim, 2001) to 2.54 (Polidori et al., 2008). A fit of the Improved-Ambient OM:OC data results in the following empirical relationship (see Supplement Fig. S4):

$$OM : OC_{I-A} = 1.28 \cdot O : C_{I-A} + 1.17$$
 (10)

While the changes introduced by the Improved-Ambient method can be significant, they do not change any fundamental conclusions made from previous AMS studies. The relative levels of oxidation for the various OA components do not change with respect to each other. The OOA components still span a continuum of oxidation levels and are still 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. It is important to note, however, that the carbon oxidation state of total OA calculated with the Improved-Ambient method remains relatively unchanged from that determined by the Aiken-Ambient method (Improved Ambient OS_C is higher by only 0.06). The OS_C values from the two methods also agree closely even for the chamber systems that display larger differences in O:C and H:C values (see Fig. 7). This reinforces the conclusion that OS_C is a more robust measure of OA oxidation levels than either O: C or H: C since is not affected by hydration or dehydration processes taking place in the atmosphere or during the measurement process and is thus also not sensitive to other sources of

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The corrected elemental analysis values will have implications for the interpretation of Van Krevelen diagrams (i.e. plots of H:C vs. O:C), which have been used to obtain insights into the chemical transformations of ambient OA. Heald et al. (2010) first showed the utility of this diagram for bulk total OA (including POA and SOA) composition analysis, and demonstrated that for some datasets bulk ambient OA evolved with a slope of -1, suggesting composition changes with aging that are consistent with simultaneous increases in both carbonyl and alcohol moieties. Ng et al. (2011) used the Van Krevelen diagram to follow the oxidative transformations of ambient OOA (as opposed to total OA) from multiple field campaigns and showed that they clustered along a slope of approximately -0.5. This slope was interpreted as being indicative of simple oxidative mechanisms that involve net additions of both C(O)OH and -OH /-OOH functional groups without fragmentation (i.e. C-C bond cleavage), and/or the addition of C(O)OH groups with fragmentation. The Improved-Ambient method yields Van Krevelen slopes that are approximately 20 % shallower than those determined with the Aiken-Ambient method. Details are discussed in Chen et al. (2014). These slopes (-0.8 for total OA, and -0.4 for OOA) suggest that the ambient OA oxidative mechanisms involve different net addition of -OH and/or -OOH functionalities and fragmentation than previously assumed.

Effect of Improved-Ambient method on empirical parameterizations of OA elemental ratios from unit mass resolution data

Empirical methods relating unit mass resolution (UMR) AMS ion tracers with Ambient-Aiken elemental ratios obtained from high-resolution AMS data have been previously reported by Aiken et al. (2008) and Ng et al. (2011). Here we reassess these relationships for elemental ratios calculated with the Improved-Ambient method.

Aiken et al. (2008) presented a parameterization to estimate O: C from measured f_{44} values. High-resolution AMS measurements indicate that the UMR signal at m/z 44 is

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$$_{5}$$
 O: $C_{I-A} = 0.079 + 4.31 \cdot f_{4A}$ (11)

Equation (11) reproduces most of the data points including all the ambient OA components obtained by factor analysis. The O:Cs calculated with Eq. (11) reproduce measured secondary OA component values with an error of 13%. The agreement for primary OA components is not as good, indicating that the accuracy of Eq. (11) is reduced when f_{44} is small (<4% on average). The outliers in Fig. 6a correspond to species with low acid content and high alcohol content (i.e., polyols, and other multifunctional species with OH groups). Thus, the inferred O:C values for some types of marine aerosols that have been shown to contain alcohol functionalities (Hawkins and Russell, 2010) may be somewhat underpredicted by Eq. (11). The chamber data outliers in Fig. 8a also indicate that Eq. (11) may underpredict O: C values substantially in ambient environments dominated by NO_v-free isoprene chemistry and toluene chemistry.

Ng et al. (2011) derived a method for estimating H:C values of OOA components and SOA species from f_{43} . This parameterization was based on ambient OOA components and chamber SOA species with $f_{44} > 0.05$ and $f_{43} > 0.04$. For these species, m/z 43 is typically dominated by C₂H₃O⁺. Only a few of the measured multifunctional standards yield mass spectra which fall within these prescribed valid ranges. Since these few data points do not add enough significant information to derive a new parameterization, we use them together with chamber and field data to evaluate a scaled version of the Ng et al. (2011) relationship. We choose a scaling factor of 1.11 since the Improved-Ambient method increases the H: Cs of ambient OA by 11 % on average. The resulting scaled parameterization is as follows:

SOA H:
$$C_{I-A} = 1.12 + 6.74 \cdot f_{43} + 17.77 \cdot f_{43}^2$$
 (12)

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Figure 8b compares the parameterization from Eq. (12) with the measured Improved-Ambient H: C values. The figure indicates that as in Ng et al. (2011), the measured H: C values for secondary OA components, secondary chamber OA, and several standard molecules are reproduced to within \pm 10 % by Eq. (12).

4 Conclusions

This manuscript evaluates the accuracy of the AMS elemental analysis approach over a wider range of OA species than has been studied before. Thermally-induced dehydration and/or decarboxylation of OA species is observed to be efficient in the AMS not only at the standard vaporizer temperature of 600 °C but also at much lower vaporizer temperature (even 200 °C, the lowest feasible vaporization temperature). These processes likely also play a role in other heated surface vaporization-based aerosol measurement techniques even if they limit heating to $\sim 200\,^{\circ}\text{C}$. The H₂O, CO, and CO₂ molecules produced by these decomposition processes must be taken into account in order to obtain accurate elemental composition information.

The accuracy of elemental ratios obtained with the AMS depends on the exact method that is used. The Aiken-Explicit method reproduces known O:C and H:C ratios to within 20% and 12% respectively. These results validate the use of this methodology for calculating elemental ratios across a range of OA molecular compositions. This method is recommended for laboratory experiments and smog-chamber measurements as well as ambient measurements when sufficient signal is available (e.g. at very polluted sites). Careful control of the sampling conditions and/or calibration experiments that enable unambiguous extraction of the organic signal contributions to measured H_2O^+ and CO^+ ion intensities are recommended for these situations (see for example Chen et al., 2011). The Aiken-Ambient method (used for most measurements of aerosols obtained in air) produces O:C (H:C) ratios for multifunctional species that are within 28% (14%) of known ratios respectively. These values are biased low, however, with larger biases observed for some highly functionalized species (e.g., polyols

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and polycarboxylic acids). Detailed analysis of the AMS spectra indicate that these biases are largely due to the use of empirically estimated intensities for H₂O⁺ and CO⁺ ions that that are lower than the actual measured values for these ions. An Improved-Ambient method for calculating elemental ratios from OA is developed as part of this study and is recommended for measurements obtained in air. This method combines the Aiken-Ambient results together with composition-dependent correction factors that reduce bias and produce O:C (H:C) values for the standard molecules that are within 28% (13%) of the known molecular values. Future work should include comparisons between the OA elemental ratios obtained with the Improved-Ambient technique and other elemental analysis techniques.

Application of the Improved-Ambient elemental analysis to previously published ambient datasets results in an average increase of the O:C and H:C values of total OA by 27% and 11% respectively; The OM:OC ratios of total organic correspondingly increases by 9%. The oxidation state values calculated with the Aiken-Ambient and Improved-Ambient methods, on the other hand, do not differ substantially, since \overline{OS}_C is invariant with respect to hydration and dehydration processes. This indicates that \overline{OS}_C is a more robust parameter for monitoring oxidation of aerosols than either O:C or H:C; comparisons between \overline{OS}_C measurements from the AMS and other elemental analysis techniques are needed to investigate this in more detail.

The Improved-Ambient method indicates that the oxygen content of ambient OA is larger than reported by previous AMS measurements. The chemistry involved in the formation of highly oxidized ambient OOA is still poorly characterized, and chemical pathways that produce high values of O:C are unclear. Thus, more work is required to develop and explore alternative chemical mechanisms and modeling methods for simulating the formation of highly oxidized ambient OA. The Van-Krevelen slope resulting from the Improved-Ambient formulation is also shallower than previously reported (-0.8 for total OA, and -0.4 for OOA). Aging mechanisms of ambient OA that qualitatively involve greater net addition of -COH and -COOH groups relative to -CO groups should be explored.

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Table 1. A list of standards analyzed in this study and their molecular O:C and H:C ratios. Standards are categorized according to their functionality into broad groups. All standards were studied with EI AMS, while standards also studied with VUV-AMS are noted in the last column.

	Name	Formula	O:C	H:C	VUV-AMS
Multifunctional	Cis-Pinonic Acid	C ₁₀ H ₁₄ O ₃	0.3	1.4	Х
	2-Oxooctanoic Acid	C ₈ H ₁₄ O ₃	0.37	1.75	
	Acetylsalicylic Acid	C ₉ H ₈ O ₄	0.44	0.89	X
	Homovanillic Acid	C ₉ H ₁₀ O ₄	0.44	1.11	X
	4-Acetylbutyric Acid	C ₆ H ₁₀ O ₃	0.5	1.67	
	5-Oxoazaleic Acid	C ₉ H ₁₄ O ₅	0.55	1.56	X
	Levulinic Acid	C ₅ H ₈ O ₃	0.6	1.6	
	Gamma Ketopimelic Acid	C ₇ H ₁₀ O ₅	0.71	1.43	X
	3-Hydroxybutyric Acid	C ₄ H ₈ O ₃	0.75	2	,
	2-Ketobutyric Acid	C ₄ H ₆ O ₃	0.75	1.5	
	3-Hydroxy-3-Methylglutaric Acid	C ₆ H ₁₀ O ₅	0.73	1.67	
	1,3-Acetonedicarboxylic Acid		1	1.2	
		C ₅ H ₆ O ₅			V
	α-Ketoglutaric Acid	C ₅ H ₆ O ₅	1	1.2	Χ
	Lactic Acid	C ₃ H ₆ O ₃	1	1.67	
	Pyruvic Acid	C ₃ H ₄ O ₃	1	1.33	
	Citric Acid	$C_6H_8O_7$	1.16	1.33	X
	Diglycolic Acid	C ₄ H ₆ O ₅	1.25	1.5	
	Malic Acid	C ₄ H ₆ O ₅	1.25	1.5	X
	Oxaloacetic Acid	$C_4H_4O_5$	1.25	1	
	Glycolic Acid	$C_2H_4O_3$	1.5	2	
	Tartaric Acid	C ₄ H ₆ O ₆	1.5	1.5	Χ
Alcohols	Cis-3-methyl-3,4-dihydroxytetrahydrofuran Racemic mixture of ?-Isoprene Epoxydiols Trans-3-methyl-3,4-dihydroxytetrahydrofuran Mannitol Mannose Sucrose Xylitol	C ₅ H ₁₀ O ₃ C ₅ H ₁₀ O ₃ C ₅ H ₁₀ O ₃ C ₆ H ₁₄ O ₆ C ₆ H ₁₂ O ₆ C ₁₁ H ₂₃ O ₁₁	0.6 0.6 0.6 1 1	2 2 2.33 2 2.09 2.4	X X X
	•	$C_5H_{12}O_5$			^
Diacids	Sebacic Acid Azalaic Acid Pimelic Acid Adipic Acid Glutaric Acid Malaic Acid Succinic Acid Malonic Acid Oxalic Acid	C ₁₀ H ₁₈ O ₄ C ₉ H ₁₆ O ₄ C ₇ H ₁₂ O ₄ C ₆ H ₁₀ O ₄ C ₅ H ₈ O ₄ C ₄ H ₄ O ₄ C ₄ H ₆ O ₄ C ₃ H ₄ O ₄ C ₂ H ₂ O ₄	0.4 0.44 0.57 0.66 0.8 1 1.33	1.8 1.78 1.71 1.67 1.6 1 1.5 1.33	X X X X X
Polyacids	1,3,5-Cyclohexanetricarboxylic Acid	$C_6H_9O_6$	1	1.5	X
i organius	Tricarballylic Acid	C ₆ H ₈ O ₆	1	1.33	X
	1,2,4,5-Benzenetetracarboxylic Acid	C ₆ H ₆ O ₈	1.33	1	X
_	•				
Esters	Dibutyl Oxalate Gamma Ketopimelic Acid Dilactone Ethyl Pyruvate Dimethyl 1,3-Acetonedicarboxylate	C ₈ H ₁₈ O ₄ C ₆ H ₈ O ₄ C ₅ H ₈ O ₃ C ₇ H ₁₀ O ₅	0.5 0.57 0.6 0.71	2.25 1.14 1.6 1.43	X

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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 default assumptions for the ratio.

	Obs H ₂ O ⁺ / CO ₂ ⁺	Obs CO ⁺ / CO ₂ ⁺	Frag Wave H_2O^+/CO_2^+ RIE $H_2O=1.4$	Frag Wave H_2O^+/CO_2^+ RIE $H_2O=2$	Literature reference
AMS Frag Table					
Default 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	·····o otaay
Polyacids	1	1–2	1	0.7	
Diacids	2	2	2	1.4	
Esters	0.5–1	1	0.5–1	0.35–0.7	
Alcohols	> 10	> 4	> 10	0.35–0.7 > 7	
AICOHOIS	> 10	>4	> 10	>1	
Ambient Aerosol					
Pittsburgh, USA	*	1.3	*	*	Zhang et al. (2005)
Tokyo, Japan	*	1	*	*	Takegawa et al. (2007)
Whistler Mtn, Canada	1	*	1	0.7	Sun et al. (2009)
Chamber SOA					
Isoprene	3.9	1.03-2.6	3.9	2.7	Chhabra et al. (2010),
Photooxidation	0.9	1.05-2.0	0.9	2.1	Chen et al. (2011)
					Offerret al. (2011)
(Low NO _x)	0.3	*	0.3	0.2	Nation of all (0010)
Isoprene	0.3		0.3	0.2	Nakao et al. (2013)
Photooxidation					
(NO _x)					
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), Nakad
					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	1.8	1	1.8	1.3	Hildebrandt et al. (2014)
Photooxidation					, ,
(NO _x)					
Aromatics	0.3-1.3	*	0.3-1.3	0.2-0.9	Nakao et al. (2013)
Photooxidation	3.00		2.00	0.0	
(NO _x , Low NO _x)					
Naphthalene	*	1.2	*	*	Chhabra et al. (2011)
Photooxidation		1.4			Omabia et al. (2011)
(Low NO _x)					

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Table 3. Summary of elemental composition information obtained for chamber and ambient OA.

	Impro	ved-Am	bient		Change (with respect to Aiken-Ambient)			Literature reference	
	O:C	H:C	OM:OC	Osc	O:C (%)	H:C (%)	OM : OC (%)	OSc (Absolute)	
Ambient OA									See Supplement Table S1 for full list
Total OA	0.52	1.65	1.84	-0.60	27	11	9	0.06	
Primary Compon	ents								
HOA	0.13	1.96	1.34	-1.69	27	8	4	-0.09	
BBOA	0.36	1.76	1.64	-1.04	34	11	9	0.01	
COA	0.22	1.81	1.45	-1.37	32	11	6	-0.06	
Secondary Comp	onents								
SV-OOA	0.53	1.62	1.84	-0.57	32	12	11	0.07	
LV-OOA	0.84	1.43	2.25	0.25	25	12	12	0.19	
Total OOA	0.67	1.54	2.03	-0.19	28	12	11	0.13	
Chamber SOA									
Isoprene	0.87	1.94	2.33	-0.19	57	23	24	0.27	Chen et al. (2011)
α -pinene	0.41	1.48	1.67	-0.65	24	9	7	0.04	Chen et al. (2011)
β -caryophyllene	0.47	1.52	1.75	-0.58	29	11	10	0.06	Chen et al. (2011)
Toluene	0.85	1.67	2.28	0.10	50	25	22	0.30	Hildebrandt Ruiz et al. (2014)

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+ Aiken(2007,2008)

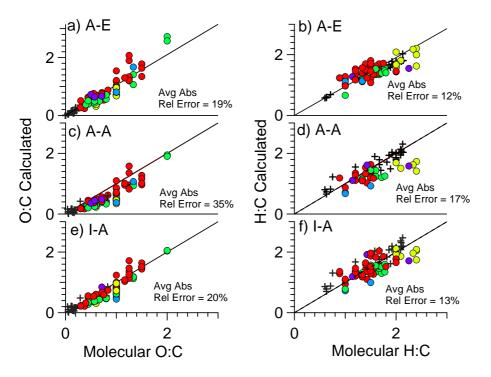


Figure 1. Scatter plots between known molecular elemental ratios and AMS elemental ratios obtained with the Aiken-Explicit (A-E; panels a and b), Aiken-Ambient (A-A; panels c and d), and Improved-Ambient methods (I-A; panels e and f). A 1:1 line is shown for reference in all plots. The standards examined in this study are colored according to their chemical functionality. Also shown are previously published standard molecule data from Aiken et al. (2007).

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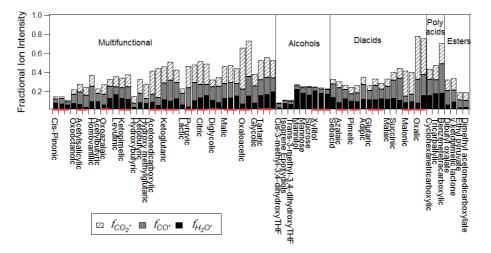


Figure 2. Fractional AMS ion intensities (relative to the total ion signal for each standard) measured for CO_2^+ , CO^+ , and H_2O^+ from each of the laboratory aerosol standards studied here. The standards are classified according to functionality and then arranged according to increasing O:C. Repeat measurements were performed for some of the standards to investigate the consistency of measured mass spectra between different HR-ToF-AMS instruments. Repeat measurements performed for the same standard are arranged together and denoted by red horizontal bars on the bottom axis of the graph.

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<u>Standards</u> <u>Multifunctional, Esters, Polyacids, Alcohols, Diacids</u>

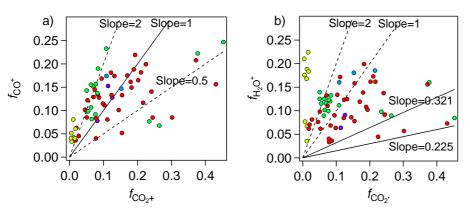


Figure 3. Scatter plots between AMS fractional ion intensities for CO^+ and CO_2^+ (panel **a**) and H_2O^+ and CO_2^+ (panel **b**). The empirical ratios used for each of these relationships in the Aiken-Ambient calculations are shown as solid lines with the appropriate slopes. In panel (**b**) two solid lines are shown to reflect the measured ratios that correspond to possible H_2O RIE values ranging from 1.4 to 2 (see Sect. 2 for more information). Dashed lines on both panels are included for reference to visualize the range of slope values.

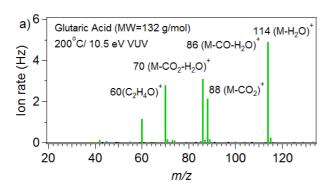
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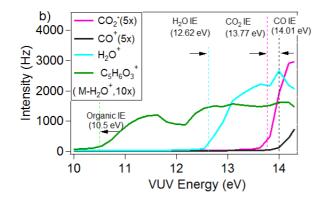


Figure 4. (a) VUV-AMS spectrum of glutaric acid obtained under an argon atmosphere. The spectrum was obtained at a VUV energy of 10.5 eV and a vaporizer temperature of 200 °C. lons corresponding to loss of CO_2 , CO, and H_2O moeities from the parent ion (M^+) are observed. **(b)** Glutaric acid VUV-AMS signals as a function of VUV monochromatic photon energy. The signal intensity of $C_5H_6O_3^+$ which corresponds to the [M-H $_2O$] $^+$ ion, and the signal intensities of CO_2^+ , CO^+ , H_2O^+ are shown. The gas phase ionization energies (IE) for neutral CO_2 , CO, and CO_2^+ on Molecules are shown as colored vertical lines.

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- Hildebrandt Frag Wave
- Aiken et al. (2007,2008)

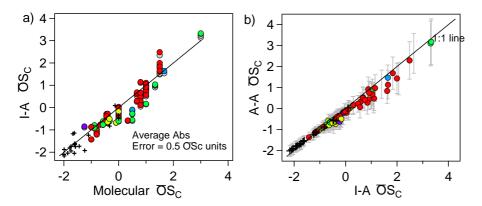


Figure 5. (a) Scatter plot of Improved-Ambient \overline{OS}_C values $(2 \times O:C - H:C)$ of the organic standards vs. their known molecular \overline{OS}_C values. The Improved-Ambient method was applied with the default AMS organic fragmentation wave (colored solid circles) as well as with the Hildebrandt et al. (2014) changes to the organic fragmentation wave. (b) Scatter plot of Aiken-Ambient OS_C values of the organic standards vs. the corresponding Improved-Ambient method values. The error bars denote the propagated uncertainty in the Aiken-Ambient OS_C values due to the uncertainties in the Aiken-Ambient O: C and H: C values. The solid line shows the 1:1 relationship.

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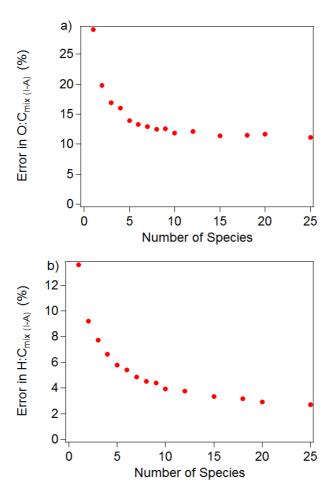


Figure 6. (a) Errors in Improved-Ambient O:C ratio of organic standard molecule mixtures as a function of number of species in the mixture. **(b)** Errors in Improved-Ambient H:C ratio of the organic standard molecule mixtures as a function of number of species in the mixture.

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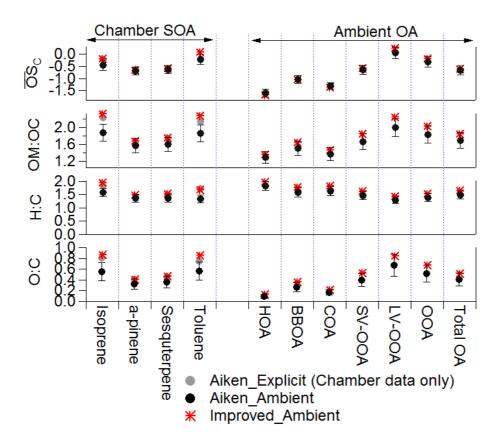


Figure 7. Summary of elemental composition information obtained across chamber and ambient OA measurements. The figure shows values obtained with the Improved-Ambient method as well as the Aiken-Ambient method. Aiken-Ambient elemental ratios are shown with errors from Aiken et al. (2007, 2008) for reference. For the chamber data, Aiken-Explicit values measured by Chen et al. (2011) and Hildebrandt Ruiz et al. (2014) are also shown.

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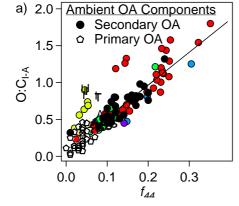
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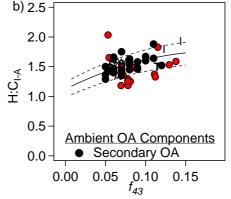


Figure 8. Scatter plot between Improved-Ambient O:C values and f_{44} (fractional ion intensity at m/z 44 from unit mass resolution data). Ambient OA component data from field campaigns are shown as black points. The black line shows the linear fit through the ambient OA (O:C_{I-A} = 0.079 + 4.31 · f_{44}). Chamber SOA and standard OA data are also shown in the figure. **(b)** Scatter plot between Improved-Ambient H:C values and f_{43} for ambient secondary OA components and chamber SOA. OA standard data is shown for the few multifunctional species which fit the criteria for this parameterization ($f_{44} > 0.05$ and $f_{43} > 0.04$). The solid line shows a scaled version of the Ng et al. parameterization (H:C $_{Improved\ Ambient} = 1.12 + 6.74 · <math>f_{43} + 17.77 \cdot f_{43}^2$) and the dotted lines show ± 10 % deviations from the parameterization.

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