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Interactive comment on "Evaluating the degree of oxygenation of organic aerosol during foggy and hazy days in Hong Kong using high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS)" *by* Y. J. Li et al.

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We thank the reviewers for their suggestive comments. Here we provide point-by-point responses to those comments. The points from reviewers' comments start with "Comment:", our responses start with "Response:", and changes made to the manuscript start with "Change:".

Reviewer #1

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Comment:

This paper presents an interesting contrast between foggy and hazy periods of various AMS variables indicating degree of OA oxidation or volatility. The results are likely to be of particular interest to the AMS community, but some of the findings are also of general interest to those investigating secondary organic aerosol formation. Although the data is interesting, in my view the author's way over interpret the data. The last line of the abstract and first line of the conclusions are strong statements despite no physical or chemical process actually being measured in this study.

Response:

We agree that these two sentences are strong statements and have removed them. The first sentence of the conclusion section has been changed to (pg3553, L2-4):

Change:

"The present study examines chemical properties of organic aerosols during springtime in Hong Kong, with a focus on two foggy periods and one hazy period."

Comment:

The major premise of this paper is that the observations made at a specific time inform how the aerosol got to its observed chemical state. The authors implicitly assume that all chemical oxidation processes are so fast that this assumption is valid and that the air masses are completely uniform so that no composition variability is due to advection. For example, does particle pH or LWC at a specific time really mean these are the variables that explain the overall fine particle (i.e., bulk) chemical properties, such as SVOA, LVOA, etc? Over a single day, not even considering a particle's lifespan of say a week, it could be exposed to a wide range of pH and LWC. To illustrate, take sulfate, for example, since it's formation is much better known than OA. According to the AMS data presented in Table 1, sulfate concentrations are higher under hazy conditions. Because liquid water concentrations were lower during the hazy period

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(Table 1) does that mean the authors would conclude that a gas-phase oxidation route formed most sulfate observed during the hazy period? To really answer this question one may believe that some more complex analysis is needed, such as for example, a chemical transport model that accounts for the complex history that undoubtedly affects the overall sulfate mass? If one cannot definitively say the sulfate was mainly formed via gas phase oxidation during the hazy period, how can one make detailed predictions on OA partitioning pathways (even though no gases were measured), oxidation routes, etc based solely on particle composition?

Response:

In general, we agree with the reviewer that some of our statements on processes are a bit strong although there are also cases we think that the reviewer has interpreted our statements stronger than what we intended to do. Please see our point by point responses below.

Also, there is a misunderstanding that we have assumed rapid physical and chemical processes leading to our observed chemical states, although we attempted to draw correlations of the various high time-resolution data. Rather, we believe that these periods have prevailing meteorological conditions that led to an overall rather consistent pattern of the measured parameters in each of these three periods. Hence instead of assuming rapid processes, these meteorological conditions afford the use of different measured parameters for an OVERALL discussions and correlations of the properties of the pollutants. It is not our intent to predict the detailed spatial and temporal changes of pollutant compositions, which would require the detailed modeling efforts outlined by the reviewer.

We argue that the assumption of good mixing and uniform concentrations of air pollutants including particles is reasonable in these periods. The air masses during these three periods were relatively stable or well mixed. For the two foggy periods F1 and F2, wind speeds were less than 2 m/s most of the time. That means the air was very stagnant during these two foggy periods, and most of the transport and transformation of air pollutants occurred in a local scale. Without too much advective transport due to low wind speed, the pollutants would very likely accumulate within the stagnant air mass during the foggy periods. For the hazy period, the wind pattern in Lee et al. (2013) showed that “land-sea breeze” circulations (Lo et al., 2006) occurred during this episodic event. In these “land-sea breeze” circulations, air pollutants are transported, trapped, and accumulated in the Pearl River Delta Estuary and a narrow (∼20 km) band along the coastal line (Lo et al., 2006), leading to haze formation. That means, for the hazy period, it is reasonable to expect that the air pollutants become well mixed within the planetary boundary layer (PBL) (Lo et al., 2006).

Sulfate formation is not a main focus of this work. In response to the reviewer’s comments on sulfate formation, we believe that it was a result of prolonged aging during the trapping of air pollutants in the hazy period. Although sulfate concentration was the highest during the hazy period and LWC_fp was low during this period, it cannot be inferred that gas-phase oxidation of SO2 is kinetically more efficient than aqueous-phase oxidation of SO2 in sulfate formation from LWC_fp alone. With reasons provided below, however, we do believe it is indeed a very plausible hypothesis that sulfate formation during the hazy period (H) was mainly contributed by gas-phase oxidation.

First, it is possible that the “land-sea breeze” circulations have brought a much larger amount of gaseous precursors (SO2) from the heavily industrialized Pearl River Delta (PRD) region during the hazy period compared to during the rest of the time of the campaign. The influence of PRD air mass during the hazy period is also supported by the HOA content (a surrogate for POA), which was also higher than the rest of the campaign (see Fig. 2). Even though gas-phase oxidation was not as kinetically efficient as aqueous-phase oxidation (which was possibly occurring during two foggy periods and resulted in moderately high sulfate concentrations), the prolonged trapping and aging during these few days can still result in very high sulfate loading. Moreover, the low RH and low LWC_fp estimated during the hazy period, as well as low cloud cover

(43% on average, Table 1) also suggest that aqueous-phase oxidation of SO2 may not be the major contributor of the high sulfate observed in the hazy period.

In the overview discussion (section 3.1, Table 1, and Figure 2), we focus on the averages of the chosen foggy, hazy, and "other" periods. In the correlation plots (Figures 6 and 7), the uncertainties in pHis and IS are too large (see responses below) for any quantitative relationships. Also, as the reviewer pointed out, it is not valid to attribute the observed degree of oxygenation SOLELY to these parameters. Hence, we did not establish any quantitative relationship in these plots, which simply showed the presence or absence of any dependence of observed degree of oxygenation on these estimated parameters. LWC_fp was not plotted in any of these graphs as a variable since its uncertainty can be up to a factor of 2 at high LWC_fp (at $\sim$80 μg/m3, see below). Instead, we chose to only categorize LWC_fp into low, mid and high as in Fig. 6(b) for qualitative discussions as shown in the original manuscript.

More specific comments.

Comment:

Some statements made in the background that are key to the analysis, which follows, are overly simplistic and should be clarified. This includes:

Pg 3538, L17-18. The statement that OOA is a surrogate of SOA is not strictly true. There are primary sources of oxygenated aerosol (e.g., organic acids, etc), both from mobile sources and biomass burning.

Response:

Although OOA from factor analyses is not strictly equal to SOA, "there is strong evidence that most atmospheric OOA is secondary: increases in OOA are strongly correlated with photochemical activity and other secondary species and OOA levels are consistent with SOA estimates using other methods" (Jimenez et al., 2009).

The reviewer pointed out that there would be some special cases where OOA would be substantially different from SOA, IF the oxygenated organics in aerosols are from primary sources such as mobile sources and biomass burning. For the case of mobile sources, it has been shown that in urban and sub-urban environments in Hong Kong, vehicle exhaust is not a major source of oxygenated organics such as oxalic acid (Huang and Yu, 2007). Furthermore, our site has little traffic. For the case of biomass burning, as we stated in pg 3541 L12-13, we did not observe large contribution from tracer ions such as m/z 60 and 73 (Alfarra et al., 2007). Therefore, we believe that these two types of primary sources contribute little to the OOA factors in our PMF analysis. Nevertheless, a note, as below, on this point is added to the very end of the experimental section (pg 3542 L23):

Change:

“The two OOA factors have been considered as surrogates for SOA (Jimenez et al., 2009) and will be used in the following discussion, along with other indicators including f44 (fraction of m/z 44 in organic mass spectra) (Ng et al., 2010), the elemental ratio of oxygen to carbon (O:C) (Aiken et al., 2008), and the carbon oxidation state (ÂŕOS_c) (Kroll et al., 2011), to evaluate the degree of oxygenation of OA. Note that if primary sources such as vehicle exhaust and biomass burning contribute to oxygenated organics, the usage OOA factors to represent SOA could lead to an over-estimate of SOA. However, it has been shown that vehicle exhaust did not contribute much to oxygenated organics such as oxalic acid in Hong Kong (Huang and Yu, 2007) and we did not observe elevated tracer ions such as m/z 60 and 73 from biomass burning (Alfarra et al., 2007).”

Comment:

2) Pg 3538, L20-22. The link between oxygenation and hygroscopicity is not as strong as the authors imply. See, for example, Atmos. Chem. Phys., 13, 2735–2756, 2013 and references therein.

Response:

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We do not think our statement “The degree of oxygenation was suggested to affect aerosol hygroscopicity” indicates a strong link. There are multiple studies showing some effects of degree of oxygenation on hygroscopicity of aerosol organics, such as Massoli et al. (2010), Wong et al. (2011), and Duplissy et al. (2011). On the other hand, as pointed out by the reviewer, there are also some studies that found no effects, such as the one listed for example by the reviewer: Lathem et al. (2013). It is worth to note that another recent study found that aged (i.e., higher degree of oxygenation) organics from biomass burning did show higher hygroscopicity (Martin et al., 2013). Given these contradictory findings, the second part of our sentence in pg 3538 L20-22 “although the effect is still not well constrained” served as a reminder on the uncertainties. The sentence (pg 3538, L20-22) now reads as below:

Change:

“The degree of oxygenation was suggested to affect aerosol hygroscopicity (Chang et al., 2010; Massoli et al., 2010; Duplissy et al., 2011; Lambe et al., 2011; Wong et al., 2011; Martin et al., 2013), although some other studies (Frosch et al., 2011; Lathem et al., 2013) found opposing results.”

Comment:

How was the quantitative accuracy of the AMS determined? How do uncertainties in key species affect predictions of pH, LWC, etc. Example, pg 3541 L17, how does an inaccurate CE not affect the analysis, be specific. pH is going to be very sensitive to SO4= and NH4+ concentrations. Was the same CE used to calculate both? Which leads to, what are the uncertainties in IS and pH given the typical uncertainties in AMS ion measurements? An uncertainty analysis is needed.

Response:

accuracy of AMS

The overall uncertainty of AMS measurement was estimated to be around 35% (from

30-37% depending on species and instrument performance) (Bahreini et al., 2009). This was based on error propagation by taking into account of uncertainties of the following:

ionization efficiency (IE) uncertainty of 10%. For our case, weekly IE calibrations with ammonium nitrate were performed. The 7 ratios of IE to AB (airbeam, signal of N2) had an average of 6.21e-13 and a standard deviation of 3.5e-14, corresponding to 5.5% as the instrumental fluctuation. A correction factor ioneff_to_ab_rel_ratio is applied to the data to correct for that. Therefore, this part of uncertainty is within 10%.

relative ionization efficiency (RIE) uncertainties (Bahreini et al., 2009) are 10% for ammonium, 15% for sulfate, and 20% for organics based on previous lab studies and computational results (Canagaratna et al., 2007).

collection efficiency (CE) uncertainty is 30% (Bahreini et al., 2009) based on previous lab and field results (Middlebrook et al., 2012).

transmission efficiency (TE) uncertainty is 10% (Bahreini et al., 2009) for particles with a size from 60-600 nm.

flow rate (Q) uncertainty is small with routine calibrations with a Gilibrator (<1%).

The error propagation was done for the concentration calculation equation:

Mass_concentration is proportional to (1/IE_NO3), (1/RIE_species), (1/CE), (1/TE), and (1/Q).

with an error propagation equation:

Err =((Err_IE)ˆ2 + (Err_RIE)ˆ2 + (Err_CE)ˆ2 + (Err_TE)ˆ2 + (Err_Q)ˆ2)ˆ0.5

For example, for the case of organics

Err_org =((Err_IE)ˆ2 + (Err_RIE)ˆ2 + (Err_CE)ˆ2 + (Err_TE)ˆ2 + (Err_Q)ˆ2)ˆ0.5 = Err =((0.055)ˆ2 + (0.2)ˆ2 + (0.3)ˆ2 + (0.1)ˆ2 + (0.01)ˆ2)ˆ0.5=0.37

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collection efficiency

A CE of 0.5 was used throughout the campaign and the reasons were outlined in pg 3541 L5-17. In fact, using component-dependent CE as in Middlebrook et al. (2012) resulted in little difference in mass concentrations because the CEs were still around 0.45-0.5 for most of the data points.

Although CE is the major source of uncertainty, as shown in (a) above, the uncertainty associated with the choice of CE would be relatively small if compared to the sensitivity of estimated LWC_fp to RH (see below). The claim that the choice of CE will not affect further analysis in pg 3541, L17 refers to the parameters (f44, O:C, and ÂŕOS_c etc.) that are used to describe the degree of oxygenation of OA, which are all normalized parameters that have no dependence on CE.

The sentences (pg 3541, L17) are changed to reflect this point:

Change:

“For particles overwhelmingly dominated by sulfate as in this study, a CE of 0.5 might be an overestimate. However, the parameters used to represent the degree of oxygenation of OA will not be affected by the choice of CE.”

uncertainties in LWC, pH, and IS estimations

These are estimated in response to the comment below for relationship between RH and LWC.

Comment:

Pg 3541, L14, define what the measured to predicted NH4+ ratio is? That is, how is it predicted?

Response:

NH4+ mass concentration was “predicted” based on the balancing anion concentrations (SO42-, NO3-, and Cl-) and the assumption that only ammonium ion is available for ion balance, by the equation below:

$$\mathrm{NH4\_predicted} = 18 * (2 *(\mathrm{SO4}/96) + (\mathrm{NO3}/62) + (\mathrm{Chl}/35.5))$$

all in mass concentrations.

This sentence (pg 3541, L13-16) is changed to include the definition of the measured to predicted NH4+ ratio, as below:

Change:

“As for acidity, we observed a measured-to-predicted NH4 ratio (NH4_m/NH4_p, see Eq. 1) of 0.7-0.9, with an average of 0.82, which is higher than the point (0.75) where bouncing starts to reduce and CE starts to increase from 0.45 (Middlebrook et al., 2012).

$$\mathrm{NH4\_m}/\mathrm{NH4\_p} = \mathrm{NH4\_m}/(18 * (2 *(\mathrm{SO4\_m}/96) + (\mathrm{NO3\_m}/62) + (\mathrm{Chl\_m}/35.5))$$

where NH4_m, SO4_m, NO3_m, and Chl_m are the measured mass concentrations of ammonium, sulfate, nitrate, and chloride, respectively, while NH4_p is the predicted mass concentration of ammonium with the assumption that ammonium is the only cation to balance the anions.”

Comment:

What is the uncertainty in RH when RH>95%. RH meters typically have issues with accuracy at high RH. Also, at RH greater than roughly 90% the LWC is highly sensitive to RH. At these RHs the LWC must be highly uncertain. This should be discussed and the uncertainty estimated and included in the analysis and figures.

Response:

The uncertainty of the RH sensor used is 3% for RH >95%, and 2% for 20%<RH<95%. As shown in Figure R1 below, by choosing the highest uncertainty (3%), the estimated

LWC_fp has an uncertainty of -20% to +40% for LWC_fp < 50 μg/m3, while the uncertainty can be -30% to +100% for LWC_fp > 50 μg/m3. Correspondingly, the IS can be -30% to +25% for LWC_fp < 50 μg/m3, and -50% to +43% for LWC_fp > 50 μg/m3. The pH would be different by 0.3 unit at most for a factor of 2 (100% uncertainty) for LWC_fp estimation.

As the reviewer pointed out, the uncertainty in RH measurement may be a major source of estimated LWC_fp, IS, and pHIS, while the mass concentrations of the input species all have relatively small uncertainties compared to the uncertainty caused by RH measurement. However, in all of the later discussion with these three parameters we deliberately did not show any quantitative relationships between degree of oxygenation of OA and these three parameters. What we showed was simply the effects of these three parameters in a relative scale, as in Fig. 6 (b) for low, mid and high LWC_fp. In Fig. 6, we showed the dependence of mass concentrations and fractions of SVOOA and LVOOA on Ox concentrations. In Fig. 7, dependences of degree of oxygenation on IS and pHis were shown but not in a quantitative manner. Figures 8-10 have been removed (see below). For a purpose of qualitative comparison, we believe our conclusion that the causes of the similarly high degree of oxygenation in the two foggy periods are different won't be affected by the uncertainties of RH and other parameters.

A note on the uncertainty estimate is added to pg 3542 L12-14 as below:

Change:

"All these parameters were generated from E-AIM II with the hourly averaged inorganic compositions measured by HR-ToF-AMS. Note that the estimation of LWC_fp is highly sensitive to RH measurement uncertainty, which in our case is 3% for RH > 95% and 2% for RH < 95%. Using the highest uncertainty of 3% for RH measurement, the uncertainty of LWC_fp estimation is -20% to +40% for LWC_fp < 50 μg/m3 and -30% to +100% (a factor of two) for LWC_fp at ~80 μg/m3 (the highest estimated in this study). Correspondingly, the IS estimation has a highest uncertainty of -50% to +40%, while the pHis has a highest uncertainty of ~0.3 unit. Given the high uncertainties in the estimations of particle constituents, all discussions below related to LWC_fp, IS, and pHis are qualitative without attempting to show any quantitative relationships."

Figure R1

Comment:

Section 3.3 comparing LVOOA and SVOOA. It seems highly speculative to discuss partitioning mechanisms bases solely on aerosol composition and LWC data. I don't see any direct evidence to support these types of statements (pg 3548, L2 to 11), all one really can say is that the data are consistent with . . . and note that it is really speculation.

Response:

Agree. Due to the lack of information on gaseous semi-volatile species, the discussion on partitioning (pg 3551 L13 to pg 3552 L24) including Figures 8-10 has been removed.

Comment:

Section 3.4, again I find it somewhat surprising that such definitive statements can be made on partitioning and oxidation processes from a correlation analysis, despite no gas phase measurements. Much of this just seems to be speculation.

Response:

Agree. Due to the lack of information on gaseous semi-volatile species, the discussion on partitioning (pg 3551 L13 to pg 3552 L24) including Figures 8-10 has been removed.

Reviewer #2

Comment:

This study attempted to evaluate the influences of different processes on the oxygenation degree of organic aerosols in Hong Kong using data from an Aerodyne HR-

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ToFAMS. Two foggy periods and one haze episode were analyzed in detail. An aerosol thermodynamic model (EAIM) was applied to estimate the water content, pH, and ionic strength in particles based on the inorganic aerosol speciation observed by the AMS. The EAIM results and the concentrations of Ox were then used to interpret the mechanisms responsible for the changes of the oxygenation degree observed for organic aerosols, mainly based on analyzing correlations among different variables. Understanding the processes of atmospheric organic aerosols is important. The manuscript is quite well written with some insightful discussions. But a main issue is that the AMS results (including the PMF organic factor results), which are the foundation of the work presented here, have not yet been published nor peer-reviewed. It is somewhat difficult to evaluate the results reported in this manuscript without access to some basic information regarding the three OA factors, although it is probably reported in Lee et al., 2013.

Response:

Lee et al. (2013) is currently under revision. A revised manuscript can be sent to the Editor for the review process if needed.

As for PMF analysis, a diagnostic plot as suggested in Zhang et al. (2011) is included in the supporting information and is shown below (Figure R2).

Figure R2

Comment:

It does not seem consistent that while noticeable amounts of nitrate were detected in particles (Avg= 0.63 microgram / m3) aerosols were found generally acidic during this study. HNO3 is volatile and unlikely survives in acidic particles. If there are issues with species quantification, all related discussions should be revised.

Response:

The semi-volatile characteristic of ammonium nitrate does affect the partitioning of nitrate and it has a dependence on particle acidity (Pathak et al., 2003c). However, the equilibrium of ammonium nitrate (with respect to ammonia and nitric acid in gas phase) is affected by many factors such as temperature, RH, and sulfate content (Seinfeld and Pandis, 2006). This is why in the above cited study in Hong Kong (Pathak et al., 2003c), nitrate was still detectable even when the particle acidity was high ([H+] = 40 nmol/m3). In a recent study by Pathak et al. (2009a), it was found that in cities such as Beijing, large amounts of nitrate was detected in particle phase even when the particle acidity was extremely high ([H+] > 200 nmol/m3). The authors attributed this observation to yet another factor in particulate nitrate formation: heterogeneous hydrolysis of N2O5, instead of homogeneous (gas-phase) formation of HNO3 and partitioning.

Nitrate formation in ammonia deficient aerosol has been observed in previous studies (Pathak et al., 2003a; Pathak et al., 2003b; Pathak et al., 2004; Pathak and Chan, 2005; Pathak et al., 2009b; Huang et al., 2011a) and it has been established that nitrate formation via gas-phase homogeneous reaction NH3 (g)+HNO3(g)↔ NH4NO3 becomes evident at [NH4+]/[SO4 2−]=1.5 (Pathak et al., 2003a; Pathak and Chan, 2005; Pathak et al., 2009b).

For most parts of the sampling period, the [NH4+]/[SO4 2−] ratio was in the range of 1.5-2.0, with an overall monthly mean value of 1.75.

Comment:

It is not appropriate to use the Van Krevelen diagram to interpret aerosol processing mechanisms based on the relationship between H/C and O/C observed in total OA. Generally HOA has higher H/C than OOA whereas OOA has substantially higher O/C. HOA accounted for an important fraction of the OA mass during this study (Avg HOA/OA _ 30%) and its contribution varied as a function of time. For these reasons, the observed slope of O/C vs. H/C could be strongly affected by the mixing of different aerosol types. The discussions on chemical processing should be revised.

Response:

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Except for in Ng et al. (2011) where H/C and O/C ratios from OOA factors in many field observations were compiled, a number of studies used the H/C and O/C ratios of the bulk aerosol organics to show relative degree of oxygenation of OA (Heald et al., 2010; Huang et al., 2011b; Sun et al., 2011). It is true that simple mixing with HOA, which has high H/C and low O/C, would complicate the inference to chemical processes and one cannot attribute the changes of slope/intercept to chemical process alone. However, for the periods discussed, the hazy periods (H) had the highest HOA fraction of ∼30%, while the other two had even lower HOA fractions. For the H period, the data points (small red rectangles in Figure 3) are of both high H/C and high O/C compared to the other two periods. The high H/C may be due to relatively higher fraction of H/C, which was not pointed out in our original manuscript, while high O/C is certainly due to the long-time aging process, presumably in gas phase in this period (3 days). The latter point was highlighted in the original manuscript.

Below we evaluate how sensitive the H/C and O/C ratios and the slopes in VK are to the HOA fractions. The average H/C ratios for HOA, SVOOA, and LVOOA for the whole May campaign are 1.71, 1.59, and 1.21, respectively (Table R1). The average O/C ratios of HOA, SVOOA, and LVOOA are 0.15, 0.16, and 0.80, respectively (Table R1). A simple calculation is performed to evaluate the sensitivity of H/C and O/C ratios, as well as the slope in the VK plot, to the changes of the HOA fraction. To calculate the overall H/C and O/C ratios from the individual ratios of HOA, SVOOA and LVOOA, the "molar" fractions of HOA, SVOOA and LVOOA need to be known. Two methods were used to estimate the fractions of the PMF-resolved factors: 1) use mass fractions directly; and 2) use a "molar" fraction on a one-carbon-number basis. Note this "molar" fraction is not the actual molar fraction of individual organic compounds. Instead, it is the molar fraction of the PMF-resolved factors in an empirical formula of C1HH/COO/C. The "molar" mass of such empirical formulae are shown in Table R1. The "reconstructed" H/C and O/C ratios are calculated as below.

H/C = (f_HOA * (H/C)_HOA + f_SVOOA * (H/C)_SVOOA + f_LVOOA * (H/C)_LVOOA)/

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(f_HOA * (C/C)_HOA + f_SVOOA * (C/C)_SVOOA + f_LVOOA * (C/C)_LVOOA)

O/C = (f_HOA * (O/C)_HOA + f_SVOOA * (O/C)_SVOOA + f_LVOOA * (O/C)_LVOOA)/ (f_HOA * (C/C)_HOA + f_SVOOA * (C/C)_SVOOA + f_LVOOA * (C/C)_LVOOA)

For example, the “reconstructed” overall H/C and O/C ratios for the overall campaign (HOA 24%, SVOOA 30%, and LVOOA 46% by mass) based on mass fractions are as below:

(H/C)_mass = (0.24 * 1.71 + 0.30 * 1.59 + 0.46 * 1.21)/(0.24 +0.30 + 0.46) =1.44

(O/C)_mass = (0.24 * 0.15 + 0.30 * 0.16 + 0.46 *0.80)/(0.24 +0.30 + 0.46) =0.45

As shown in the base case in Table R2 below, the H/C and O/C ratios are 1.49 and 0.38, respectively, if “molar” fractions were used to reconstruct the H/C and O/C ratios. The ratios in both mass-fraction-based and “molar”-fraction-based calculations were close to the measured ones (1.36 and 0.40 for H/C and O/C, respectively), suggesting both are reasonable estimates. Since the HOA mass fractions in F1, F2, and H were 29%, 23% and 30% (maximum 7% difference), respectively, two scenarios with -7% and +7% HOA were calculated (Table R2), with the loss and gain of 7% equally shared by SVOOA and LVOOA.

Table R1

Table R2

Figure R3 below shows the positions of the “reconstructed” H/C and O/C ratios in all cases in Table R2 in the VK plot. It can be seen that no matter mass fractions or “molar” fractions were used, the deviation of the positions with HOA mass fraction deviated by +7% and -7% were small. If a fixed intercept is chosen (H/C = 1.75 and O/C = 0, black circle in Figure R3), the slopes for all cases in Table R2 would only vary by 0.02. Compared to the difference of 0.20 between F1/F2 and H, this deviation is relatively small. Therefore, we believe that mixing with HOA cannot explain the difference in trends (i.e., slopes) observed in the foggy and hazy periods.

Figure R2

Nevertheless, the discussion on the Van Krevelen plot has been revised to include an additional note on possible interference of HOA is added in pg 3547 L8-10.

Change:

“This similarity of slopes in our hazy period and the high-oxidation-level period in MILAGRO further suggests that gas-phase oxidation likely have prevailed during the hazy days, similar to the high photochemical aging period in MILAGRO. Note that the presence of HOA would slightly move the data points to high H:C ratio and lower O:C ratio by simple mixing of other OA fractions with HOA and the effects on the slopes by this mixing would be relatively small. Sensitivity analysis shows that changing the HOA percentage contributions to HOA from 17% to 31% would only result in changes of 0.02 in the slope of the VK plot, which is significantly smaller than the difference of the slopes between F1/F2 and H periods of 0.20 (see below).”

Comment:

In addition, since organic aerosol may undergo many changes during its lifetime, its history tends to have a strong impact on its composition and properties. One should be cautious with using in-situ measurements that only represent the instantaneous values in ambient air, to infer aerosol processes.

Response:

We agree with the reviewer that the aerosol composition has a strong dependence on the history of air mass before arriving at the measurement site. For the chosen periods for detailed analysis, we believe that they had prevailing meteorological conditions that led to an overall rather consistent pattern of the measured parameters (see response to similar general comments of reviewer 1). Hence, these meteorological conditions and/or stable air mass allowed us to explore the overall properties of aerosol composition. We did not intend to use instantaneous measured values to interpret aerosol formation processes. Rather, we showed some overall correlations between certain measured or estimated parameters to differentiate these three different periods.

Comment:

It is also unclear how the volatility statuses of the two OOA components were inferred? Are there any correlations between LVOOA and sulfate and between SVOOA and nitrate? It seems too much of a speculation to hypothesize adsorptive partition based on just the correlations between HOA and LVOOA mass concentrations and the total organic concentration (Fig. 8).

Response:

Agree. Due to the lack of information on gaseous semi-volatile species, the discussion on partitioning (pg 3551 L13 to pg 3552 L24) including Figures 8-10 has been removed.

Detailed comments:

Comment:

Fig 1d, the three factors do not add up to 100% of OA, why is it?

Response:

There is a small amount of residuals left in PMF analysis, which represent the signals that cannot be explained by the three factors. In our three-factor solution, the residuals have an average mass concentration of 0.1 μg/m3, or 2.3% of the total organic mass.

Comment:

Line 20- 22, page 3550, how do the authors know that LVOOA is more polar than SVOOA?

Response:

The PMF-resolved LVOOA and SVOOA factors do not directly relate to the polarity of the (many) species in each factor. However, the relatively more oxygenated feature of LVOOA compared to SVOOA (Jimenez et al., 2009; DeCarlo et al., 2010) and the more abundant carboxylic groups (from which the ion of CO2+ is derived) may indicate indirectly that LVOOA would be relatively more polar than SVOOA.

To avoid confusion that the polarity can be derived from our factor analysis, this sentence is changed to:

Change:

“The high ionic strength may favor the dissolution of the more oxygenated fraction of LVOOA in comparison to SVOOA.”

Reference:

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Interactive Discussion

Discussion Paper

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., et al. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmospheric Chemistry and Physics, 10, 4625-4641, 2010.

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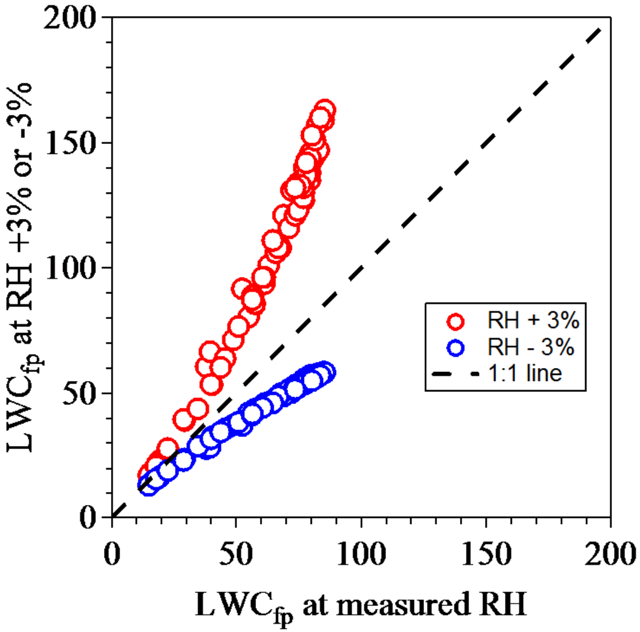

Fig. 1. Figure R1. Uncertainty estimate for LWC_fp estimation during the F1 period. The values in the x axis are calculated (from E-AIM II) with measured RH.

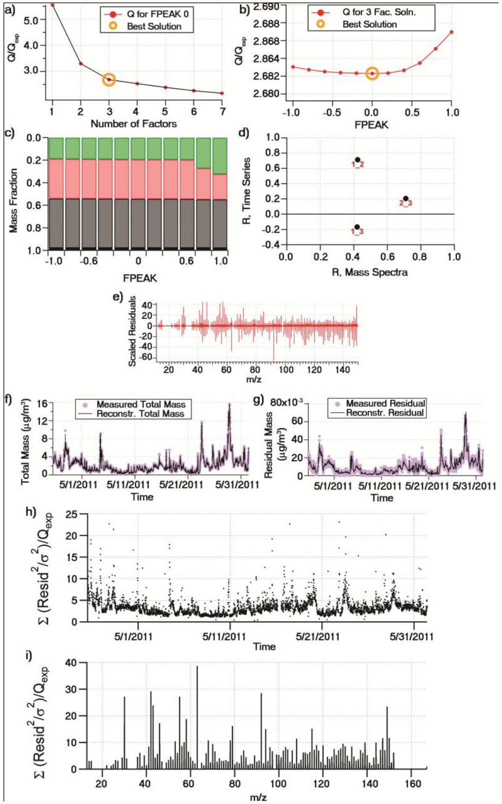

Fig. 2. Figure R2. Summary of key diagnostic plots of the PMF analysis on the V-mode OA spectra.

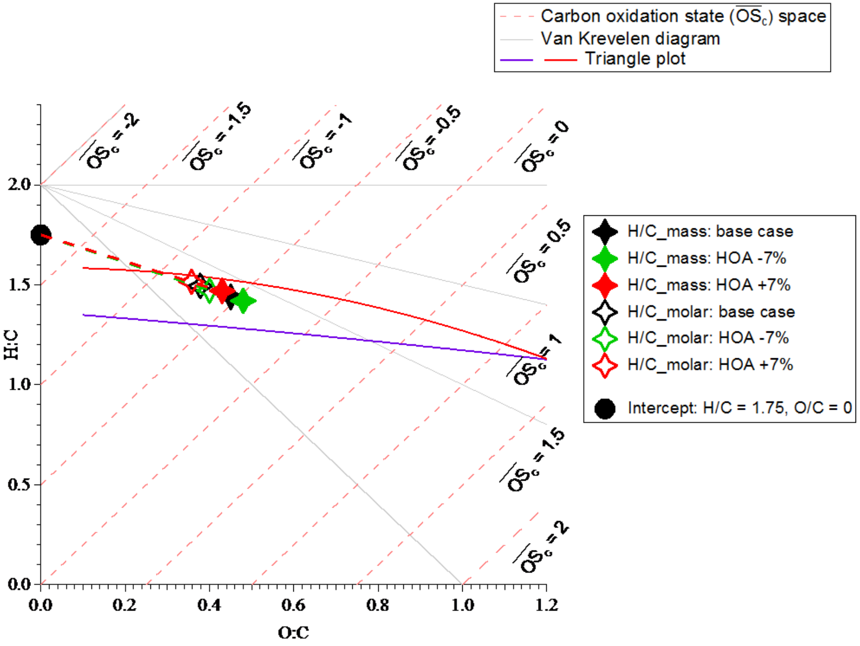

Fig. 3. Figure R3. Sensitivity of H/C and O/C position in VK plot in all scenarios in Table R2.

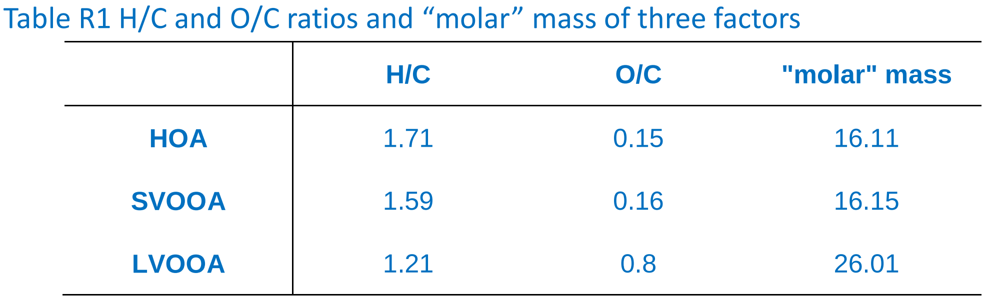

Table R1 H/C and O/C ratios and “molar” mass of three factors

	H/C	O/C	"molar" mass
HOA	1.71	0.15	16.11
SVOOA	1.59	0.16	16.15
LVOOA	1.21	0.8	26.01

Fig. 4. Table R1

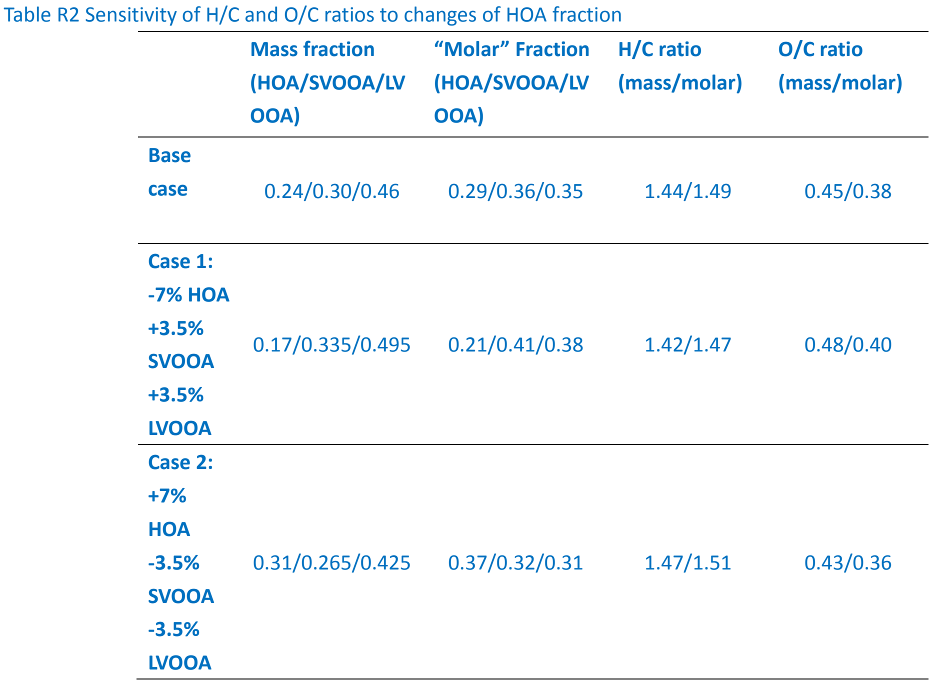

Table R2 Sensitivity of H/C and O/C ratios to changes of HOA fraction

	Mass fraction (HOA/SVOOA/LVOOA)	**“Molar” Fraction (HOA/SVOOA/LVOOA)**	**H/C ratio (mass/molar)**	**O/C ratio (mass/molar)**
Base case	0.24/0.30/0.46	0.29/0.36/0.35	1.44/1.49	0.45/0.38
Case 1: -7% HOA +3.5% SVOOA +3.5% LVOOA	0.17/0.335/0.495	0.21/0.41/0.38	1.42/1.47	0.48/0.40
Case 2: +7% HOA -3.5% SVOOA -3.5% LVOOA	0.31/0.265/0.425	0.37/0.32/0.31	1.47/1.51	0.43/0.36

Fig. 5. Table R2