

Interactive comment on “Characterization of the sources and processes of organic and inorganic aerosols in New York City with a high-resolution time-of-flight aerosol mass spectrometer” by Y.-L. Sun et al.

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Response to the comments of referees

We thank the reviewers for their thoughtful comments. The manuscript has been revised accordingly. Listed below are our point-by-point responses to each reviewer's comments, which are repeated in italic.

Response to Referee #1

C12185

This paper discusses observations of the atmospheric aerosol at a location in the city of New York, NY during the summer of 2009. There are a number of components to this paper, but a significant focus is the analysis of the high resolution aerosol mass spectra using PMF and other techniques. The strength's of the paper are in the analysis of the high resolution mass spectra and discussion of diurnal variations of the analyzed components of the organic aerosol. There are also some weaknesses in my view as discussed in the major comments that follow.

Major comments :

1) On page 22677, section 2.3.1 you indicate that you use a CE of 0.5 across the entire dataset. This is a critical assumption that is not justified in the discussion. In one sentence (lines 8-11), the authors suggest that transmission and oven bounce issues are corrected by the simple application of a constant factor of 2. The atmospheric aerosol is composed of a variety of compounds (as you demonstrate) and size distributions. There have been many lab measurements that indicate the CE of pure dry ammonium sulphate is in the area of 0.25, whereas sulphuric acid is close to unity. AMS calibrations are done with pure ammonium nitrate in part because its CE is close to 1.0. Some studies have looked at the CE for pure organics, but organic components are many and varied. As well, evidence is mounting for the presence of organics in crystalline forms in the atmosphere and in general particle phases vary with ambient relative humidity and temperature (e.g. Matthew et al., AST, 2008). Particularly in urban areas, significant particle mass can reside in particles near the transmission limits of the AMS (as the authors demonstrate). Compositions vary with particle size also.

So why should the CE for AMS' be a constant at 0.5?

[Response]: The validity of using CE = 0.5 for this study is supported by inter-comparisons between the measurements from the HR-AMS and those from three different real-time particle instruments, including PILS, TEOM, and a sulfate particle analyzer. These comparisons are shown in Fig. 1 and discussed in detail in Sect.

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3.1 of the paper. The use of CE = 0.5 is also consistent with the conclusion from previous AMS and extensive particle measurement studies at the same site (Drewnick et al., 2003; Drewnick et al., 2004; Hogrefe et al., 2004; Weimer et al., 2006; Bae et al., 2007). The AMS CE value may indeed be dependent on particle composition and phase (Matthew et al., 2008). Specifically, CE values may be significantly larger than 0.5 for particles that are highly acidic (Quinn et al., 2006; Kleinman et al., 2007; Matthew et al., 2008), composed of high fraction of ammonium nitrate (Crosier et al., 2007), or high in liquid water contents (Allan et al., 2004). None of these conditions, however, prevailed during this study. As reported in our manuscript, aerosol particles were overall neutralized (Fig. 14b) and nitrate on average accounted for only ~ 4% of the PM₁ mass (Fig. 2c). We examined the water content of the sampled particles based on the AMS particulate water signal. We very rarely observed AMS PM H₂O mass above 40% of the AMS total dry mass (= SO₄²⁻ + NO₃⁻ + NH₄⁺ + Cl⁻ + Organics), above which CE = 1 was proposed (Sun et al., 2010). In addition, the comparisons between HR-AMS vs. other measurements for this study show no evidence of dependence on RH or particulate nitrate contents (Fig. 1). Given the potential of introducing more uncertainties by applying variable CE values, we use a constant CE = 0.5 for this study. However using the constant CE = 0.5 may introduce an uncertainty of ~ 20-30%. We have revised the manuscript to make these points clear.

You state that the 0.5 value is validated by comparisons with other collocated instruments. In Figure 1 your mean comparisons with sulphate and nitrate indicate that the AMS measured 70-75% of the mass concentrations measured with the PILS. Your comparisons of OM with OC indicate the AMS OM is 2.6 times the OC. You state the average OM/OC is 1.62 based on the high-res analysis, which means that your AMS OC is 1.6 times higher than the Sunset OC. You claim that this is due to volatilization during the carbon analysis, but if your mean CE was 0.8 rather than 0.5 then the AMS and Sunset would agree. A mean CE of 0.8 would result in the sulphate and

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nitrate being about 50% of the PILS values. Certainly a difference in the CE between the inorganic and organic components is reasonable since you indicate that some of your OM is externally mixed and at smaller sizes than sulphate and nitrate. It is also reasonable that in these high emissions areas substantial amounts of the sulphate and nitrate can accumulate in particles larger than the AMS can adequately sample, which leads to another point - the AMS is not a NR-PM1 instrument. The 50% cut size on the upper end is about 700 nm VAD (e.g. Liu et al., AS&T, 2009), which is also suggested from ambient measurements in your region of influence (Fig. 15; Rupakheti et al., AS&T, 2005). A 50% cut at 700 nm VAD means that the AMS measurement is closer to PM_{0.5} than PM₁. The comparison with the TEOM, which can have significant volatilization problems, indicates that the AMS (based on 0.5 CE) is 68% of the total PM_{2.5} on average. This also indicates that there is significant mass above the upper transmission limit of the AMS and 2.5 μm. The fact that your apparent nitrate CE is so low is another indicator that there was significant nitrate mass above the AMS upper transmission limit.

The justification for the use of a constant CE of 0.5 to describe bounce and transmission losses as well as for calling these mass concentrations NR-PM₁ needs significant improvement before the paper can be fully considered.

[Response]: A main reason for the AMS measuring only 70- 75% of the mass concentrations by the PILS is the different size cutoffs of the two instruments, i.e., the AMS measures PM₁ while the PILS measures PM_{2.5}. For the high average ratios of AMS OM to Sunset Lab OC, there are three possible reasons: 1) evaporative losses of semi-volatile species during the carbon analysis, 2) "over-correction" of the OC data using the blank filter values (Bae et al., 2006), and 3) the OA might have a CE value larger than 0.5. While it is true that using CE = 0.8 for organics as the reviewer suggested will lead to better comparisons between Sunset OC and AMS organics mass, there is no justifiable reason for doing so for this study. First of all, the major fraction of the organics appears to be internally mixed with the inorganics, for which

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CE = 0.5 is supported by extensive comparisons to collocated measurements (Fig. 1). Secondly, we did not see clear indication that the CE values should significantly vary as a function of particle size or composition. For example, the correlations of AMS organic mass concentrations vs. the OC concentrations seem to be independent on the mass fraction of the small mode organics or the fraction of hydrocarbon-like OA (Fig. S4).

In response to the reviewer's comments, we expanded the discussions on the reasons we use CE=0.5 for organics in the revised manuscript. The text reads: "Although the HR-AMS organic concentrations show tight correlation with the OC concentrations measured by a Sunset Lab OC/EC Analyzer ($r^2 = 0.79$), the linear regression slope of 2.59 is higher than the average OM/OC ratio of 1.62 determined via elemental analysis of the HRMS (Sect. 3.3). The typical OM/OC ratios observed at urban sites range ~1.6-1.8 (Turpin and Lim, 2001; Takegawa et al., 2005; Zhang et al., 2005b; Bae et al., 2006; Aiken et al., 2008). Weimer et al. (2006) also observed relatively high slopes of 2.06 - 2.72 in winter 2004 at QC comparing Q-AMS vs. Sunset OC measurements. Possible reasons for this discrepancy include: 1) evaporative losses of semi-volatile species during the carbon analysis, which is consistent with the observation that semi-volatile organic species compose a large fraction of OA in NYC (see Sect. 3.5.1), 2) "over-correction" of the OC data using the blank filter values (Bae et al., 2006), and 3) underestimation of the CE value for organics. Note that in a previous AMS study in Pittsburgh, Zhang et al. (2005b) applied a CE value of 0.7 for organics and CE = 0.5 for inorganic species based on the observations that the smaller mode organics appeared to be externally mixed with SO_4^{2-} , NO_3^- and NH_4^+ and that the small mode particles appeared to be primarily sooty combustion particles for which the transmission and detection is close to 1 in the AMS according to laboratory studies (Slowik et al., 2004). Although the chemically resolved size distributions of this study also suggested external mixtures of the small mode organics and the inorganics, we did not see clear indication that the CE values should vary significantly according to particle size or composition. For example, the correlations between AMS OM and

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Sunset Lab OC are independent on the mass fraction of the small mode organics or the fraction of hydrocarbon-like OA (Fig. S4). Given that using CE = 0.5 for inorganic species is supported well by the intercomparisons with other particle measurements (Fig. 1) and that the major fraction of the organics appears to be internally mixed with the inorganics, our decision of using CE = 0.5 for all species seems to be valid and that the organic mass concentrations reported in this study do not seem biased."

2) On pages 22683-22684 you discuss nitrate and its diurnal cycle. Your nitrate peaks occur predominantly during late evening and early morning hours. AMS observations of such nighttime nitrate are common (e.g. Rupakheti et al., 2005) and most likely results from the formation of NO_3 and N_2O_5 , the nighttime analogue of HNO_3 , which is initiated by the reaction of NO_2 with ozone. The process is aided by the increased RH's overnight, presumably because water in the particles enhances the absorption of the N_2O_5 and NH_3 . The apparent correlation of your diurnal cycle of nitrate with your diurnal patterns in HOA+NOA (Fig. 13) is further evidence of this process. You present your diurnal nitrate pattern as being a result of the daytime volatilization of ammonium nitrate. This may be a factor, but you need to discuss the source of the increased nitrate overnight.

[Response]: We agree with the referee that the nighttime nitrate formation mechanism may have contributed to the nighttime increase of nitrate observed during this study. This mechanism is now mentioned in the discussions on the diurnal variation of nitrate in the revised manuscript.

3) In the abstract and the conclusions, you discuss a chemical evolution of SV to LV. But I cannot find where this is explicitly discussed in the text, and it is not clear to me that this evolution proceeds as suggested. Also, there is some evidence that a significant fraction of your SV-OOA may have had biogenic origins; see several of the more detailed comments below. This possibility needs to be discussed.

[Response]: The potential evolution from SV-OOA to LV-OOA is discussed in Section

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3.5.1. SV-OOA might have biogenic contribution as the referee mentioned though there is no clear evidence for this. Following the referee's suggestions, we have expanded the discussions on SV-OOA to mention its possible association with biogenic sources.

Other comments

P 22673, line 20 - Rather than AMS study, perhaps atmospheric aerosol studies using an AMS.

[Response]: The sentence has been revised according to the reviewer's suggestion.

P 22674, lines 10-14 - A bit more detail is needed here about why the advantages of using the HR.

[Response]: More discussions on the advantage of HR-AMS are now given in the revised manuscript.

P 22675, lines 13-14 - are the SP-AMS data used here? What is the point of this sentence?

[Response]: We made reference to the SP-AMS data in this manuscript. The SP-AMS measurements in this campaign provide the size distributions of BC from traffic exhaust plumes and indicate that they are similar to those of m/z 57 from our HR-AMS measurements. The SP-AMS data provide the supporting evidence for the derivation of size distributions of EC using m/z 57 as a surrogate, which was discussed in Sect. 3.4.

P 22676, line 22 and P 22677, lines 21-22; P 22678, line 3 - you need to specify what you mean by elemental compositions/analysis. Are ion fragments elemental compositions, or what are elemental compositions of ion fragments?

[Response]: The elemental composition in this study refers to the nominal composition of carbon (C), hydrogen (H), oxygen (O), and nitrogen (N) for OA. The term of
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"elemental composition" was specified in introduction in the revised manuscript.

P 22678, line 9 - performed ON the HRMS?

[Response]: We have changed the sentence to "performed to the HRMS. . ."

P 22678, lines 14-18 - Does excluding what are effectively zeroes from the PMF analysis bias the differentiation of the OA components?

[Response]: We did not selectively exclude zeros or small negative values from the PMF analysis. Instead, we removed from the HRMS matrix the entire column of an ion if its average S/N ratio is less than 0.2. For ions that have average S/N above 0.2, we kept all the zeros and very small negative values for the PMS analysis. Removing noisy variable is important for optimizing the performance of PMF (Ulbrich et al., 2009). It does not introduce bias in the analysis.

P 22678, line 22 - grammar.

[Response]: The sentence is rephrased.

P 22679, line 4-5 - perhaps say "The 6-factor solution splits the SV-OOA into two components. However, since we cannot offer a physical interpretation of such a split, we choose the 5-factor solution."

[Response]: We have revised the sentence according to the reviewer's suggestion.

P 22680, lines 8-10 Please consider also Buset et al., Atmospheric Environment 40, 2006, S482-S499.

[Response]: Buset et al. (2006) is cited in the revised manuscript.

P 22681, lines 6-9 Your choice of CE could also be the reason. Also, blank correction may be an issue at low concentrations, but I don't see how that can be responsible for your slope?

[Response]: The blank level correction for the OC data was not a constant-value adjustment. Instead, time-dependent blank corrections were applied and would have affected the slope of the linear regression between AMS OM and OC. In addition, the over-correction issue may not manifest as negative OC values since adjustable blank levels were applied.

P 22686, lines 1-2 - C₃H₅O:C₄H₉ was estimated by Liggio et al. (JGR, 2010) at < 0.1 for vehicle emissions, which appears consistent with that shown here for particles less than 100nm (Fig. 7). Liggio et al. also show that C₃H₅O⁺ dominates the m/z 57 in the biogenic aerosol. From your SV-OOA spectrum (Fig. 8), it appears that m/z 57 is mostly C₃H₅O⁺. Could some (or most) of the SV-OOA have come from biogenic sources? There also seems to be pretty good correspondence of your SV-OOA spectrum with that of Shilling et al. (ACP, 2009) for ozonolysis of alpha-pinene.

[Response]: As the reviewer pointed out, C₃H₅O⁺ dominates the m/z 57 in SV-OOA, and the SV-OOA in this study shows overall similar spectral pattern to those of biogenic SOA from chamber experiments (Shilling et al., 2009) and OA with significant impact from biogenic emissions (e.g., Amazon Basin, Chen et al., 2009), which suggest that SV-OOA may have contributions from biogenic sources. However due to the absence of measurements of biogenic volatile organic compounds (e.g., isoprene, monoterpene, and pinene) or its oxidation products (e.g., methyl vinyl ketone (MVK) and methacrolein (MACR)), we are unable to unambiguously identify the biogenic sources to SV-OOA in this study. We have included relevant discussions in the revised manuscript.

P 22686, lines 19-22 - Please consider also Broekhuizen et al., 2005. Atmos. Chem. Physics, 5, 6263-6293, 2005.

[Response]: Broekhuizen et al. (2006) is cited in the revised manuscript.

P 22686, lines 23-25 - Fractionally speaking EC may only be a small compo-

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ment of the accumulation mode particles, but its influence on the particle number concentration may still be significant.

[Response]: We agree. The text has been revised to clarify the point, the sentence now reads: "EC is only a minor mass fraction (< 5%) of particles larger than 200 nm."

P 22688, lines 16-19 - this may depend more on the proximity and types of sulphur and VOC sources influencing the urban site. E.g. such a correlation was not evident in the urban AMS measurements described by Buset et al.

[Response]: Buset et al. (2006) just used three tracer m/z's from the AMS, not the whole spectra analysis performed in this study, and thus their results might be different from ours.

P 22688, lines 20-28 - If SVOA does not correlate well with NH₄NO₃, does this not contradict your argument that both nitrate and SVOA are controlled by volatilization? It may be another argument in favor of a significant contribution from BVOCs to your SV-OOA.

[Response]: The weak correlation between SV-OOA and nitrate was mainly due to the differences in formation mechanisms between NH₄NO₃ and SV-OOA. For instance, the occurrence of several nighttime nitrate plumes (likely from night time formation and hydrolysis of N₂O₅) clearly degrades the correlation. Excluding just one nitrate plume occurred in the night of 22 July improved the correlation coefficient from $r^2 = 0.05$ to $r^2 = 0.17$ (see the third paragraph of Section 3.5.1 in the manuscript for detailed discussions). In addition the component is denoted as "SV-OOA" also because of its correlation with AMS chloride ($r^2 = 0.30$), which is primarily associated with the semi-volatile NH₄Cl. It is also possible as the referee pointed out that the relatively weaker correlations between SV-OOA and chloride/nitrate was due to the contribution of biogenic OA to the SV-OOA.

P 22689, line 2 - define Ox.

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[Response]: O_x ($= O_3 + NO_2$) is defined in the revised manuscript

P 22689, lines 10-14 , The diurnal pattern of the SV-OOA is different from all others, with the exception of the midday increase that appears to correlate with the COA pattern. The absence of a clear connection with the HOA suggests a non-local source - again, perhaps SOA from BOVCs? Is the daytime reduction of SV-OOA related to boundary layer dilution?

[Response]: The midday increase of SV-OOA does not correlate with that of COA (see Fig. 8). We don't understand the reviewer's comment that "the absence of a clear connection with the HOA suggests a non-local source". What "connection" does the reviewer refer to? In addition, we disagree that the decrease of SV-OOA in the afternoon is mainly due to the rising boundary layer. The diurnal profiles of EC and CO_2 (Fig. 3a and 4a) - indicators of atmospheric dilution - are flat between $\sim 1:00$ pm and 17:00 pm. In contrast, the diurnal profile of SV-OOA shows a gradual decrease from $\sim 1:00$ pm to 18:00 pm, which can't be explained only by boundary layer dilution. The partitioning of volatile species back to the gas phase and/or further oxidation to form LV-OOA may play important roles. We have expanded the discussions on SV-OOA in the revised manuscript.

P 22691, lines 24-28 - In contrast, Liggio et al. (2010) found an increase of O/C associated with lower particle loadings. Results such as this can be very strongly location dependent.

[Response]: Our observations do not contradict to those reported in Liggio. et al. (2010). NYC is an urban site, where primary particles are continuously released from various emission sources. The relative importance of POA is higher during low PM loading periods because of less contribution of secondary particles. Particle at rural and remote locations are dominated by secondary species formed over a big region. Low PM loading situations are likely dominated by more aged particles, thus show higher O/C.

C12195

P 22693, lines 5-8 - It is unclear to me how these results suggest this. Can you be a little more explicit?

[Response]: To answer the reviewer's question, we have expanded the discussion on the comparisons of the size distribution of m/z 's during Hi-NOA and other periods in the revised manuscript. It now reads: "In addition, Fig. 14c illustrates a broader size distribution of m/z 58 - the m/z contributed the most by NOA (Fig. 11e) - during Hi-NOA than during Lo-NOA while the size distributions of both m/z 44 and 57 show essentially no difference. Other m/z 's with relatively high contribution of NOA such as m/z 42 ($C_2H_4N^+$) and 30 (CH_4N^+) also show broader size distributions during Hi-NOA. These results together suggest a stronger influence of gas-particle partitioning on the size distribution of NOA, consistent with the hypothesis that NOA is mainly produced via acid-base reactions of amino compounds in the acidic atmosphere (Ge et al., 2010) followed by the condensation onto pre-existing particles"

Figure 15a - your northwesterly trajectory passes over Toronto and Egbert, Ontario that have been sites of a number of (already mentioned) studies using AMS' during late spring and summer. The high organic composition of mostly SV-OOA may indicate a significant biogenic component to that aerosol as shown by Slowik et al., ACP, 2010 at the Egbert site.

[Response]: New York City and Toronto are ~ 700 km apart. There are many industrial, agricultural and biogenic emission sources in between the two cities/regions. It is not scientifically sound to infer the sources of SV-OOA in NYC based on studies in Toronto and Egbert and backtrajectory analysis.

Response to Referee #2

The authors report mass concentration, chemical composition and size distribution information on the aerosol species measured at an urban site in New York City. The majority of the aerosol is composed of organic aerosol and inorganic sulfates. Five

C12196

distinct aerosol organic constituents are observed. In addition, there are several key findings reported in regards to the semi-volatile composition, elemental composition, and organic mass to organic carbon contributions.

The subject matter is relevant and of interest to the larger scientific community. The measurements and correlations add to the existing body of work on atmospheric aerosol composition based on aerosol mass spectrometry measurements. The document is fairly dense and contains large amounts of information. The paper will be a useful reference. The following concerns will clarify minor points in the paper.

MAJOR CONCERNS

The black carbon and elemental carbon measurements presented are somewhat confusing. There are different measurement/estimation techniques used to characterize each and it is not always clear to the reader which are presented at what time. For instance, the DMT single-wavelength Photoacoustic Soot Spectrometers (PASS-1) is an optical measurement, and as such measures BLACK carbon (BC). The filter based Sunset Lab OC/EC Analyzer is a volatility based measurement and hence measures the ELEMENTAL carbon (EC). The authors note (P22682. L10.) "that the EC in this paper refers to optically measured EC with higher time resolution". This is misleading in that the EC in this paper is either optical or thermally measured and interchangeably used (refer to subsequent sentence) and that EC should classically refer to the volatility measurement (even though the R^2 between EC and BC is > 0.8). How does the mass observed in Fig 6 (based on m/z 57) compare to that of the PASS-1? Or the average mass from the Sunset OC/EC Analyzer?

[Response]: In response to the referee's comments, we have clarified the term of "EC" in the revised manuscript, which reads: "Note that the Sunset Lab OC/EC Analyzer also provides an optical measurement of EC, i.e., optical EC by laser transmission in addition to the thermal EC. The optical EC shows tight correlation with thermal EC ($r^2 = 0.86$, slope = 0.93). Here we use the optical EC given its high time resolution (1-min) and hence a better characterization of aerosol evolution. The EC in the text from this study thus refers to the optical EC if there is no special note, while the EC

C12197

from other studies refers to thermal EC."

The integrated EC mass in Fig. 6 is equal to the average concentration of optical EC for the entire study. The size distribution of optical EC is derived from that of m/z 57 (i.e., $C_4H_9^+$) after removing the contribution of $C_3H_5O^+$, and the mass is then normalized to the concentration of optical EC. The optical EC shows good correlation with $C_4H_9^+$ ($r^2 = 0.42$) and better correlation during morning rush hours (5:00 - 9:00 am local time, $r^2 = 0.60$). Also, the optical EC shows very good correlation with the light absorption coefficient (B_{abs} , $r^2 = 0.86$, Chen et al. in preparation) from DMT PASS-1 measurements in this study. These correlation coefficients are now given in the revised manuscript.

How is total OC determined from the Sunset Lab Analyzer data set? (P22680. L28.)

[Response]: OC is determined according to the NIOSH5040 method. The thermal analysis of particulate carbon begin with a two stage ramp first to 600 °C and then to 840 °C in a helium atmosphere to desorb the OC material. The oven is then cooled to around 500 °C prior to the introduction of 2% oxygen in helium mixture for EC analysis. During the EC conversion step the oven is heated up to a final temperature of 850 °C. Continuous monitoring of laser light transmission at 660 nm through the loaded filter is used to determine the split between the EC and OC fractions. Each hourly analysis of EC and OC is calibrated by automatically injecting a fixed volume of an external gas standard consisting of 5% CH_4 in helium through the hot oven.

A detail description of the determination of OC by the same Sunset Lab OC/EC analyzer at the same site was given in Rattigan et al. (2010). This reference is cited at proper places.

P22681. L25. "The decrease in sulfate : : : probably due to ultra low sulfur diesel fuel" justification is a concern of the reviewer. The data presented is a three-week study in the summer months in 2009. Is it statistically relevant to compare the

C12198

average of this data set to the average SO₂ emissions in 2001?

[Response]: We agree that comparing the 3-week of AMS data collected from two different years may not be statistically significant to explain the reason for the decrease of sulfate. However, the reduction of SO₂ emission in NY is statistically significant, drawn from long-term monitoring data (e.g., <http://www.dec.ny.gov/chemical/54358.html>). The implementation of ultra low sulfur diesel fuel starting in 2006 in NYC should have contributed to the reduction of SO₂ emissions and thus the decrease of sulfate, although the magnitude remains to be decided. To make these points clear, we have revised the text and it now reads: "The decrease in sulfate is consistent with the statewide reduction in SO₂ emissions in New York over the years (e.g., by more than a factor of 2 from 2001 to 2009; <http://www.dec.ny.gov/chemical/54358.html>), for which the introduction of ultra low sulfur diesel fuel starting in 2006 is one of the mitigation measures. However, differences in wind patterns between the 2001 and 2009 study periods might have played an important role for the concentration differences as well."

The authors and previously reported works show a distinct smaller mode of particles from primary emissions. This is consistent with already published works of McFiggans et al, 2005 and Asa-Awuku et al., 2009. In short, McFiggans et al., 2005 reported that in 4 urban and polluted locations a smaller, externally-mixed organic mode existed. Asa-Awuku et al., 2009 also observe the POA, (traffic-related species) to be at smaller sizes and compared to the more oxidized SOA species at the larger sizes.

[Response]: Indeed the smaller mode of aerosol particles from primary emissions observed in this study is consistent with those reported in McFiggans et al. (2005) and Asa-Awuku et al. (2009). The two references are now cited in the revised manuscript.

Fig. 6. Is somewhat misleading. The EC distribution is not shown. In fact it is the corrected m/z 57 signal that is used as a surrogate for EC composition. This should be mentioned in the caption.

C12199

[Response]: We have made it clear in the figure caption that the EC distribution was estimated based on the measured size distribution of *m/z* 57 after appropriate corrections.

What is the rationale for determining the mixtures of the species? External versus internal mixture? Please elaborate. This may not be clear to all readers how AMS data (specifically PTOF data) can be used to assume the mixing state of the aerosol.

[Response]: The mixing states of aerosol species can be estimated based on their size distributions. If the aerosol species are internally mixed, they would present similar size distributions with similar shapes. Instead, if they are externally mixed, different size distributions would be expected. These points are illustrated a bit more in the revised manuscript.

What is the size of particles that contain the COA species? That is how does COA component particle number compare to particle mass? If the COA particles are found in the larger particles then they would clearly dominate the mass. However in terms of number, the COA may be negligible. This concern stems from the authors suggestion that "densely populated metropolitan aerosol should focus on controlling both cooking and traffic emissions" (P22691. L20.)

[Response]: In order to determine the size distribution of COA particles, we will have to do factor analysis of the size-resolved mass spectra, which is beyond the scope of this manuscript. However, by examining the mass-based size distributions of organics for selected time periods when COA contributes more than 50% of the OA mass, we found that COA is most abundant in particles in the ~150 - 300 nm size range. Similar analysis for HOA indicates that the mass-based size distribution of traffic-related POA peaks at ~ 100 nm. So, given the similar mass concentrations of HOA and COA observed in this study, the number concentration of COA is estimated at 10 - 15% of that of HOA on average. The fraction of COA may be higher in evening when COA mass loading is substantially higher than HOA (Fig. 13a). So, cooking appears to be a

C12200

significant source of particle number as well.

P22693. L10. What is the correlation between winds from Atlantic Ocean with hi-NOA? Is there a large R^2 value with wind direction?

[Response]: Calculating the R^2 values between NOA concentrations and wind directions recorded in azimuth degrees (i.e., true north is both 0° and 360°) does not give useful information. The correlation between Hi-NOA concentrations and southerly wind (i.e. from the Atlantic Ocean) is shown in Fig. 14a. A wind rose plot of NOA concentration (Fig. S7) is now included in the revised manuscript to demonstrate this point more clearly.

Fig. 9. What is the R^2 correlations with the total OA spectra?

[Response]: Fig. 9 shows the time series correlation coefficients between each OA component and individual fragment ions.

The R^2 for the comparisons of the mass spectra are: 0.25 for HOA vs. OA, 0.70 for COA vs. OA, 0.89 for NOA vs. OA, 0.90 for SV-OOA vs. OA, and 0.87 for LV-OOA vs. OA.

MINOR CONCERNS.

P22676. L11. O.D. not defined.

[Response]: O.D. means outer diameter, it is defined in the revised manuscript.

P22677. L19. Which version of PIKA is used?

[Response]: PIKA v1.06. It is now mentioned in the revised manuscript.

P22678. L28. Insert comma. "the rotational forcing parameter, f_{Peak} "

[Response]: comma is inserted.

P22680. L9. Replace "Pittsburg" with "Pittsburgh"

[Response]: The typo is corrected.

C12201

P22689. L2. What is O_x ? Is it the monoatomic or diatomic oxygen contribution? Or simply the entire elemental oxygen contribution?

[Response]: O_x is the sum of O_3 and NO_2 . It is now defined in the revised manuscript

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