Response to A. Aiken's comment

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

The main issues are dealing with the July 27 data, detailing how the different periods were defined and the significance in those definitions, and in making sure to not over-generalize the implications of the measurements in the abstract and conclusion sections. The data does not need further justification beyond what is presented here, detailing near highway emissions with size-resolved chemical composition. However, if the statements discussed below in comment #3 (and in comment 3 from Reviewer #1) are to be kept, an increased connection between the measurements and the implications stated would be necessary.

[Response]: Following the two reviewers above and A. Aiken's comments, we revised our manuscript accordingly. The July 27 data with the interferences from generator exhaust was removed from the text and figures. The definitions of different periods were further clarified in the revised manuscript, the discussion on exposure assessment was removed from the abstract and the implications of our measurements were significantly revised in the "Conclusion and Implications" section. More details are given in our responses to the comments of Review #2.

General Comments

1. In agreement with reviewer number 1, the comparison of AMS and FMPS data should be elaborated upon. In particular, it would be nice to see the AMS and FMPS data on a mass-averaged plot as the two measurements expand the size range of measured particles in addition to comparing the data from two different measurement techniques.

[Response]: Following the reviewer's suggestions, we expanded our discussions on the comparison of AMS and FMPS data in Section 3.2 in the revised manuscript. The comparison plot of volume-weighted size distribution from FMPS and mass-weighted size distribution from AMS are presented in the supplementary. Also see our reply to the general comment #1 of reviewer #1.

2. As both previous reviewers have mentioned, based on Figure 1, it does not seem clear how highway vs bus emissions could be distinguished since they are both north of the sampling site (discussed around L274). Please look into these details and explain them further. I would also recommend improving the labels used in Figure 1 and throughout the text as it would be much simpler to name the locations LIE, QC, DEC, and bus stop rather than the letters and parking lots, which could be included in the text, but do not help the reader readily assess which site is being discussed. In addition, I suggest using wind rose directions rather than up and downwind for easier interpretation by the reader.

[Response]: Given that the meteorology data at the roadside site was not available, we used the met data measured at the DEC building as a reference. The sampling heights at the two sites are different, thus, there's possibility that the meteorology data, especially wind direction and wind speed was different. We included more explanations and discussions in the revised manuscript.

We thank A. Aiken's suggestion, i.e., using the name of locations rather than letters. Considering that the name of locations, i.e., LIE, can refer to both the roadside site and the highway, we kept the name of the sites, but reduced the use of letters for easy reading in the revised manuscript. Also, we also be more specific in discussions of wind directions and reduced the use of "upwind" and "downwind".

3. In agreement with Reviewer #1's general comment #3 and Reviewer #2's specific comment #11, I also think the authors have put the motivation and applications of this manuscript in too broad of a context. I fail to see how the results relate to individual exposure rates which are much more complex than a set sampling location as is used here. The paper is important and stands on it's own as a chemical and physical characterization of aerosols sampled near a highway. The research can be justified with these motivations alone. The sentences about the oxidation or photochemical reactions of the aerosols are not addressed and it should not be implied that they are, and any implications of seasonal variability of roadside aerosols are also not addressed in with this short sample period, and it should not be implied that anything is known about that from the data discussed here. I suggest that these sentences (i.e. L51-54, L448-454) be less generalized and or removed without providing further substantiation. Also, (L447) the conclusions about morning and evening periods should be stated in a way that is more descriptive of the measurements made here and less generalized since this sample size and time period is very small, and with one evening period it seems there is not enough information to make generalizations about morning/evening differences based on this data alone, and that the conclusions should be more centered on this specific dataset and only have the potential to suggest such assumptions for other locations and time periods.

[Response]: In response to the reviewer's comments, we removed the over-stated implications as the reviewer mentioned and focused on the conclusions from the data itself in the revised manuscript.

4. The July 27th data needs to be either fully included or excluded. I recommend mentioning it, but moving it's analysis and discussion to the supplementary information. The way it is presented now, included in all the plots, but disregarded in the text is not desirable and just adds confusion for the reader. I tend to agree with Reviewer #2 in that it should be excluded from the plots. I realize that this is not desirable since then there is only one PM period, but only one PM period is fully analyzed currently. The analysis could be moved into the supplemental information for completeness, but the way it is currently it does not add to the discussion, but actually detracts since it is disregarded in the text. I am not against fully analyzing it and adding it to the text, but if this is to be done, also in agreement with Reviewer #2, the PMF factor needs to be included in Figure

7 for completeness. Clearly, exclusion of this day requires toning down the generalizations about the PM analysis, but this is recommended anyway since the data is for such a short sampling period.

[Response]: We have removed the July 27 data from the text and figures. Yet, we kept it in the HR PMF analysis in the revised manuscript. See our response to the specific comments #4 and #5 of reviewer #2 above.

5. Please address how the delineation between LT and MT periods was determined. As the text (L266) is not clear if they were determined by external factors (observations?, measurements?, etc.) to the AMS data or if they were based on differences in the profiles of the mass concentration time series of AMS species. Line 280 implies they were based on external observations of traffic flow, but this is not clear.

[Response]: The definition of LT and MT is mainly based on aerosol composition, especially HOA, and external primary tracers including BC and NO_x. We clarified it in the revised manuscript, i.e., "The separation of LT and MT is mainly based on the variations of primary HOA, BC, and NO_x."

6. Are morning and evening the most accurate titles for the different sampling periods? One of the "evening" periods starts at 2:50pm. If this sample is included (July 27), I recommend naming the periods something less specific, such as AM and PM.

[Response]: Because the July 27 data was removed, we kept the title of morning and evening in the revised manuscript.

Specific Comments

1. L92 – The sentence implies a causal relationship. Is this intended?

[Response]: This sentence was revised as "The number distributions rapidly evolved to larger sizes within 30-90 m downwind of freeways due to condensation and coagulation."

2. L102 – PM0.18? Is this a common unit? If not, please define, as it was unclear to me.

[Response]: PM0.18 was changed to "PM with aerodynamic diameter smaller than 0.18 μm" in the revised manuscript.

3. L125 – move DeCarlo et al. to after < 100 in the previous line

[Response]: corrected

4. L127 – suggest citing Ulbrich et al. 2008

[Response]: cited

5. L167 – suggest describing the inlet or adding a citation that references such information

[Response]: Sun et al. (2011) was cited to reference the sampling information

6. L168 – suggest adding something like mass-sensitive to imply what V-mode is sensitive to

[Response]: It was specified as "mass-sensitive" following the reviewer's suggestion.

7. L220 – should this not say "internal tracer method" to make it clear that there is not a tracer external to the AMS measurements being used for the size distributions.

[Response]: "tracer based method" was revised as "tracer *m/z*-based method" for clarification.

8. L231 – I am not quite clear on how the HOA size distribution was derived. I suggest adding a few more details to let the reader know whether the average fraction of $C_4H_9^+$/m/z 57 is used or whether this value uses the fraction present in each sample.

[Response]: Following the reviewer's suggestions, we expanded the descriptions on how to derive the HOA size distribution. The size distribution of HOA of *m/z* 57 was derived by subtracting the corresponding fraction of $C_3H_5O^+$ at *m/z* 57 for each sample since the fraction varied sample by sample. Now the descriptions read: "Thus the size distribution of HOA was derived using that of *m/z* 57 by subtracting the contribution of $C_3H_5O^+$, the size distribution of which is assumed to be the same as *m/z* 44 - an AMS spectral tracer for OOA (Zhang et al., 2005). The subtracted signals between 30-1500 nm were then normalized to the corresponding HOA concentrations.

9. L252 – What does the LV-OOA mass concentration time series look like from the QC/Lot 6? Does it support the interpretation mentioned here?

[Response]: Considering the simultaneous HR-AMS measurements were not available at the two sites, the direct comparison of time series of LV-OOA was not possible. However, as shown in Fig. S2, the trends of sulfate, which often correlates well with LV-OOA and mainly driven by regional production, at the two sites are very similar and are both relatively flat, supporting our interpretations here.

10. L256 – SV-OOA also appears to increase quickly around 6:30am on July 28th. Why is this not mentioned?

[Response]: The SV-OOA showed an increase from ~6 μg m^{-3} to ~9 μg m^{-3} at around 5:30 am on 28 July. Such increase co-varied with those of inorganic species (sulfate,

nitrate, and ammonium), which is likely due to a small change of the air mass. We mentioned it in the revised manuscript.

11. L257 – The organics still appear to have sharp changes. Do the inorganic species co-vary with them? Could R^2 values be used to justify this qualitative statement?

[Response] A few organic spikes, likely due to the influences of traffic emissions on 1 Aug. did not correspond to synchronous variations of inorganic species. However, this didn't affect the overall co-variations of aerosol species with the correlation coefficient r^2 = 0.49 – 0.57.

12. L265 – suggest adding the range of organic percentages sampled, possibly divided into AM and PM periods if statistically different.

[Response]: The organic percentage of 55-74% was added.

13. L274 – suggest using a wind rose direction rather than the term upwind here and in all subsequent references in order to be clear to the reader.

[Response]: "upwind" was changed to "south" for clarification. The use of "upwind and downwind" in the text was either more specified or revised following the reviewer's suggestion.

14. L294 – could this hypothesis be supported by bus schedule times if not recorded observations? If not, please state what the assumption is based on.

[Response]: Indeed, the conclusion is consistent with the bus schedules. When the MTA bus stopped at the sampling site, we often observed synchronous organic spikes from the screen of AMS DAQ software.

15. L299 – Should SOA not be OOA? A sentence could be added to clarify the relationship if deemed necessary, but all other statements use the AMS factors, i.e. HOA and OOA, and not the broader terms POA and SOA.

[Response]: "SOA" was revised as "OOA"

16. L303 – July 27th also appears to have a bimodal size distribution, yet this is not discussed.

[Response]: Given that July 27 data has interferences from the generator exhaust, we didn't discuss the size distributions in the text. In addition, the July 27 data was removed in the revised manuscript to avoid confusion.

17. L309 – Could a plot of this be added or at least R^2 values to qualify the statement?

[Response]: The correlation coefficient between 30-200 nm organics and HOA were added to support the statement, e.g., r^2 = 0.69 and 0.59, respectively on 28 July and 30 July for the correlations between organics in the size range of 30 – 200 nm and HOA.

18. L331 – I suggest softening the language about the internal mixtures to saying that this implied, unless it can be further supported.

[Response]: revised following the reviewer's suggestion.

19. L345 – suggest deleting the sentence about exposure estimates as per the reasons mentioned above in the general comments

[Response]: deleted

20. L392 – suggest adding this plot

[Response]: The discussions on this plot were removed from the revised manuscript given that such conclusion could be over-stated just based on one evening's measurement.

21. L401 – why was the background calculated using the MT period? If this was calculated with the LT period, how would it compare?

[Response]: Actually, the background was calculated using the whole sampling period. We also checked the CO_2 background calculated from the LT and MT periods separately. They are 409 and 408 ppm, respectively, consistent with 410 ppm used in the text.

22. L406 – I suggest adding the range of ER values from Canagaratna et al., 2004.

[Response]: The ER range from Canagaratna et al. (2004) was added in the revised manuscript.

23. L414 – How does this EI compare to other published values? Could some of those be added here and discussed for comparison? It also could be beneficial to have a little more detail about how the emission ratio is converted to an EI if it could be simply stated as a quick reference for the reader.

[Response]: In the revised manuscript, we compared our results with those determined from the "chase" study on 28 July, 2009 by an Aerodyne Mobile Laboratory in the same campaign (Massoli et al., 2012). The EI of BC is 0.04 and 0.46 g/kg under the traffic conditions being dominated by light-duty vehicles and heavy-duty vehicles, respectively, which is overall consistent with our results. In addition, the equation for the conversion of emission ratio to EI was added in the revised manuscript.

Figure Comments

1. F2 – Add the detail in the text that the MET data is from a different site than the other measurements.

[Response]: The description of the meteorology data was added in the figure caption.

2. F4 – Add the detail in the text about the red/MT and yellow/LT data points. Update the textbox in the figure as it is confusing that it is only in the Organics (a).

[Response]: The figure was revised according to the reviewer's suggestions.

3. F5 – What are the black and grey lines in a? L725 change (a) to (b). L726 light grey lines are not visible.

[Response]: The black and grey lines represent the average size distribution of organics during MT and LT, respectively, which is described in the legend. The light grey lines were removed and only smoothed lines were kept for clarity in the revised manuscript.

4. F9 – Why is there data missing in a (July 27) and b (July 27 and 28)?

[Response]: Some collocated data were missing due to the malfunction of instruments or non-operating because of limited power supply.

Technical Comments

1. L38 – change "mush" to "much". Also consider replacing smoother with smaller.

2. L47 – define FMPS

3. L59 – change "of" to "in"

4. L64 – is there a quantification or reference that could be included here?

5. L66 – Define COPD

[Response]: The technical comments were all addressed following the reviewer's suggestion.

References:

Canagaratna, M. R., Jayne, J. T., Ghertner, D. A., Herndon, S., Shi, Q., Jimenez, J. L., Silva, P. J., Williams, P., Lanni, T., Drewnick, F., Demerjian, K. L., Kolb, C. E., and Worsnop, D. R.: Chase studies of particulate emissions from in-use New York City vehicles, Aerosol Sci. Tech., 38, 555-573, 2004.

Massoli, P., Fortner, E. C., Canagaratna, M. R., Williams, L. R., Zhang, Q., Sun, Y., Schwab, J. J., Onasch, T. B., Demerjian, K. L., Worsnop, D. R., Kolb, C. E., and Jayne, J. T.: Pollution gradients and chemical characterization of particulate

matter from vehicular traffic near major roadways: results from the 2009 Queens College Air Quality study in NYC, Aerosol Science & Technology (submitted), 2012.

Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., and Jimenez, J. L.: Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, Environ. Sci. Technol., 39, 4938-4952, doi:4910.1021/es048568l, 2005.