Reply to Referee Comments

Characterization of particulate matter emissions from on-road gasoline and diesel vehicles using a soot particle aerosol mass spectrometer

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Referee #1

Note: Authors' reply included here in *italic* text following each referee comment.

p. 4009, lines 1-21
The abstract could be improved by mentioning conclusions three and four (cited above in my general comments): emissions from gasoline vehicles is dominated by lubricating oil and the similarity in gas/diesel OA spectra will make apportionment difficult. In addition, it is worth mentioning the sample size (n=293 for SP-AMS and n=145 for the mass spec analysis) since it informally establishes the statistical power of the results. I would also consider mentioning the diesel truck BC "fingerprint" idea in the abstract.
Response: We have revised the abstract to include sample size for the HD truck plume analysis and to emphasize the conclusions listed by the referee:
"Particulate matter (PM) emissions were measured in July 2010 from on-road motor vehicles driving through a highway tunnel in the San Francisco Bay area. A soot particle aerosol mass spectrometer (SP-AMS) was used to measure the chemical composition of PM emitted by gasoline and diesel vehicles at high time resolution. Organic aerosol (OA) and black carbon (BC) concentrations were measured during various time periods that had different levels of diesel influence, as well as directly in the exhaust plumes of individual heavy-duty (HD) diesel trucks. BC emission factor distributions for HD trucks were more skewed than OA distributions (N=293), with the highest 10% of trucks accounting for 56 and 42% of total measured BC and OA emissions, respectively. OA mass spectra measured for HD truck exhaust plumes show cycloalkanes are predominate in exhaust OA emissions relative to saturated alkanes (i.e., normal and iso-paraffins), suggesting that lubricating oil rather than fuel is the dominant source of primary organic aerosol (POA) emissions in diesel vehicle exhaust. This finding is supported by the detection of trace elements such as zinc and phosphorus in the exhaust plumes of individual trucks. Trace elements were emitted relative to total OA at levels that are consistent with typical weight fractions of commonly used additives present in lubricating oil. A comparison of measured OA and BC mass spectra across various sampling periods revealed a high degree of similarity in OA and BC emitted by gasoline and diesel engines. This finding indicates a large fraction of OA in gasoline exhaust is lubricant-derived as well. The similarity in OA and BC mass spectra for gasoline and diesel engine exhaust is likely to confound ambient source apportionment efforts to determine contributions to air pollution from these two important sources."

p. 4011, lines 1-4
Engine age and condition are also important factors. Add reference(s).
Response: We agree with the referee that engine age and condition are important factors in determining the relative contributions of fuel and lubricating oil to OA emissions from diesel trucks. We have changed the sentence in question to include these factors.

p. 4011, line 8
Add Worton et al., 2014 reference.
Response: We have added this reference at the specified text location.

p. 4011, line 14
"Kittelson," not "Kittleson"
Response: This misspelling has been corrected.

p. 4012 lines 11-13
Why have the authors chosen to define MD and HD diesels like this? It would be more logical to use one of the standard definitions from CARB or the US EPA. Dieselnet provides the following discussion: "Heavy-duty vehicles are defined as vehicles of GVWR (gross vehicle weight rating) of above 8,500 lbs in the federal jurisdiction and above 14,000 lbs in California (model year 1995 and later)" (https://www.dieselnet.com/standards/us/hd.php). Or if they choose to retain their classification scheme, please briefly outline how it contrasts with the widely held definitions and why this choice was made. In making broad conclusions about vehicle classes (HD, MD, LD), it will be helpful if researchers from different groups are using a common language.
Response: The vehicle classification system used for this study was selected to maintain consistency with previous vehicle emission measurement campaigns conducted at the Caldecott tunnel (e.g. in the years 1997 and 2006). A lengthier description of this system, including examples of specific vehicle types included in each of the vehicle categories, is provided in a companion publication (Dallmann, T. R.; Kirchstetter, T. W.; DeMartini, S. J.; Harley, R. A. Quantifying on-road emissions from gasoline-powered motor vehicles: Accounting for the presence of medium and heavy-duty diesel trucks. Environ. Sci. Technol. ***2013****, 47, 13873-13881, DOI:10.1021/es402875u). We have added a sentence to the manuscript to refer readers to this publication: "Further information on the vehicle classification system used here can be found in Dallmann et al. (2013)."*

p. 4019, lines 7-9
Please add a one sentence explanation for why the negative artifact is expected to be low relative to adsorption.
Response: The sentence in question has been revised to state that the negative sampling artifact is expected to be small relative to the positive artifact based on previous investigations of sampling artifacts in motor vehicle emissions studies: "Volatilization of collected OA from the front quartz filter may result in a negative sampling artifact, though this effect has been found to be small relative to the adsorption of organic vapors for emissions from gasoline and diesel engines (Schauer et al., 2002; Shah et al., 2004; Lipsky and Robinson, 2006; May et al., 2013)."

p. 4019, lines 14-17
Why choose OA=1.25xOC? Provide references and/or quantitative explanation.
Response: The OA/OC ratio of 1.25 was calculated based on SP-AMS measurements using established mass spectral analysis methods. The sentence in question has been changed as follows to more clearly explain the provenance of the OA/OC ratio: "Organic carbon mass loadings determined from the quartz filters were converted to equivalent OA mass by multiplying by a factor of 1.25. This factor represents the organic aerosol to organic carbon mass ratio (OA/OC) and accounts for additional mass, mainly hydrogen, associated with organic carbon present in the particle phase. The OA/OC ratio for PM in the Caldecott tunnel was calculated using SP-AMS data following methods developed by Aiken et al. (2007, 2008)."

p. 4019, lines 26-28 and Fig. 2
Why include the OA from QBT? It confuses the graph and makes it harder to see that the quartz filter samples accounted for 87% of the Teflon PM mass. This figure needs a little work. First, too small and crowded; please widen it. Provide more space between the different sampling periods; right now it is difficult to see at a glance (if you don't look carefully at the x-axis labels) that the data should be viewed in three bar groups. Please add labels for weekday and weekend.
Response: In response to the referee's comments, we have increased the spacing between each sampling period in Figure 5 and have added a label to the figure to distinguish weekend from weekday sampling periods. We have decided to keep the unshaded bars representing the organic concentration measured on quartz-behind-teflon (QBT) filters in order to give readers an indication of the gas-particle partitioning of motor vehicle OA measured in the tunnel.

p. 4027, line 28
Please compare your emission factors with recent results from Gordon, T. D., A. A. Presto, et al. (2013). "Secondary Organic Aerosol Production from Diesel Vehicle Exhaust: Impact of Aftertreatment, Fuel Chemistry and Driving Cycle." Atmos. Chem. Phys. Discuss. 13: 24223-24262.
Response: The following text has been added to subsection 3.3: "HD truck BC and OA emission factors presented here are approximately three times the values measured during a recent dynamometer test of an uncontrolled HD diesel truck operating on an urban dynamometer driving cycle, though similar OC/BC ratios were measured in both studies (May et al., 2014)." This reference (May et al., 2014) presents results from primary emission measurements for HD trucks conducted during the measurement campaign described in the reference listed by the referee.

p. 4029, lines 6-10
Do the authors consider their estimates of the mixing ratios of trace elements to be accurate enough to provide a range for the fraction of the PM due to fuel vs. oil? Is there any way to make more quantitative conclusions from the data in Table 1, recognizing the greater uncertainty in the Ca and Mg emission factor?
Response: Given the uncertainties involved in calculating emission factors for trace elements from individual HD trucks, it is not possible to provide quantitative results as the referee has requested. Instead we refer interested readers to the paper by Worton et al. (ES&T 2014) where we do reach quantitative answers of the kind the reviewer is requesting, based on detailed analyses of the chemical composition of the organic aerosol present in tunnel samples.

Please add a figure showing a simple cartoon of your experimental set-up. It will help readers see at a glance what was done and the instruments that were used.
Response: A figure showing details of the experimental set-up has been included in the Supplemental Information.

Fig. 5
Enlarge figure in x and y. Enlarge legend. Split legend so that OA and BC goes with the bottom subplot and the other entries stay with the top subplot.
Response: We have enlarged Figure 5 and the Figure 5 legend, and have split the legend to show BC and OA on the bottom panel of the figure.

Fig. 6
Unclear what m/z ion signal is chosen as the point of comparison (y-value of 1). Should it be m/z 12? Identify your chosen reference m/z in caption.
Response: Refer to the caption of Figure 6, which states that "Ion signals for each carbon ion (C_x^+) are normalized to total carbon ion signal."

Fig. 7
Enlarge figure in x and y. Put Zn and P on separate subplots, thereby changing this into a four panel plot instead of two.
Response: We appreciate the referee's comments on Figure 7, but have decided to leave the figure in the form originally submitted. We believe that showing data for trace elements (Zn and phosphorus/phosphate) on the same plot as data for carbonaceous species (OA and BC) is an effective visual demonstration of: (1) the orders of magnitude difference in emission factors for the two species types and (2) the similar log-normal shapes of the trace element and OA distributions. We believe that the clarity of these two points of emphasis would be reduced if the figure were to be split into four panels.

Referee #2

Specific Comments
pg 4009 - line 19: Why does the presence of trace elements in particular raise a concern about ash deposits? This specific link is not made in the text.
Response: The following sentence was added to the introduction to more clearly explain why lubricant-derived trace elements are of concern for diesel particle filters: "Lubricant-derived trace elements are not effectively removed during normal filter regeneration processes and thus have a tendency to form incombustible ash deposits on particle filters, which may degrade performance of these new control technologies (Sappok and Wong, 2011; Cross et al., 2012)."

4014 - 19: What is the actual duty cycle of the SP-AMS? That is, how much of that 1 s is spent with the beam open and collecting ambient data?
Response: Instrument background measurements were conducted for 20 seconds of every 120 second sampling cycle. The following sentence has been added to the text to better explain this point: "Instrument background measurements (i.e. particle beam blocked) were conducted for 20 seconds of every 120 second sampling cycle."

4015 - 1: What was the inner diameter of the copper tubing? The inner diameter is more relevant than the outer diameter.
Response: The inner diameter of the copper tubing used in this study was 1.4 cm. The text has been changed to include the inner, rather than outer diameter.

4015 - 7: What "experimental measurements and theoretical calculations" were done to quantify particle transmission efficiency in the sampling line? Because you quote absolute numbers later in the paper and are comparing to a gas-phase instrument (a CO2 instrument), sampling artifacts should be more carefully considered. If this is answered in the previous paper, it should be cited here.
Response: A section explaining the particle transmission efficiency testing conducted for this study has been added to the Supplemental information.

4015 - 18: It might be helpful to talk more about potential evaporation or condensation in the sampling line that could affect chemical composition of the particles. You assume that these processes are not happening, but why is that a good assumption? How does the temperature of the sampling line change from 50 m inside the tunnel to outside the tunnel to inside the mobile lab? Is the ventilation duct drawing air into or out of the tunnel? Are there any references for what the volatilities are for typical engine exhaust?
Response: We collected temperature information from instruments inside the tunnel and inside the Aerodyne Mobile Laboratory during this study. The average temperatures during the IOP's were 19±1^{o}C inside the tunnel and 22±2^{o}C inside the Mobile Laboratory. From Figure 8 in Huffman et al. 2009, HOA is one of the most volatile components of ambient particles, with an approximate ~1% decrease in HOA PM / 1^{o}C increase in temperature under room temperature conditions. Using our temperature measurements and these estimated volatilities, we estimate that the sampled OA may have lost ~5% of their mass from within the tunnel to sampling in the mobile laboratory. (Huffman, J. a. et al. Chemically-resolved aerosol volatility measurements from two megacity field studies. Atmos. Chem. Phys. ***9****, 7161–7182 (2009).)*

4016 - 19: Tied in with the comment below about page 4019 - line 24, I am a little confused about exactly what is at play in determining the calibration of the SP-AMS. This is probably all discussed in the previous SP-AMS literature, but I think there is room for a few more sentences of explanation in this paper so that readers aren't required to read the previous literature in order to understand this work. Considering just the species vaporized by the laser, i.e. black carbon and some of the lubricant derived trace species, black carbon is the only species with an RIEs not equal to 1. Despite this large correction for the ionization efficiency, there is still another large correction for collection efficiency, which I assume is really vaporization efficiency of black carbon. Does this collection efficiency factor back into the calibration of RIEBC in any way? Basically, my cause for concern is that you apply two large correction factors to the black carbon mass measured by the SP-AMS in order make the measurements align with a MAAP instrument, and yet other species that are assumed to be vaporized in the same manner as BC in the SP-AMS are not corrected in the same way (because data and calibrations specific to these species do not exist). Then, ratios of these species to each other are used to conclude that the source of aerosol is dominated by lubricating oil rather than diesel fuel. Because the treatment of the individual species signals in the SP-AMS plays such a critical role in the final conclusions of the paper, I would like a little more detail throughout this section of the paper, particularly with regards to the assumptions made regarding the calibrations.

Response: Thank you for drawing attention to the issue of trace element quantification (here and in the comment below for pages "4019-24", both of which will be addressed here), as it is an important part of our analysis and results. However, we will point out that while the measurements of the trace elements from individual truck plumes, especially zinc and phosphorous, support our other observations that OA is likely dominated by lube oil, they are not the most important of these observations from which we have drawn our conclusions. Specifically, we feel our strongest observations include the high degree of similarity between OA spectra measured at different times and the evidence for unsaturation (cyclic alkanes) in the POA emissions measured by SP-AMS. Both of these observations agree quite well with related results published in Worton et al. (2014).We feel that our current wording accurately represents the interpretation that our trace element observations are consistent with our other lines of evidence that point to the dominance of lube oil source, but are not 'critical' to our arguments.

Likely, the cause of uncertainty here comes from our original interpretation that the trace elements we were measuring were all coming from the laser vaporizer. What we have subsequently learned is that the two most important of these trace elements, zinc and phosphorous, likely derive ion signals in the SP-AMS from both the laser and the heated tungsten vaporizers. We attempted to address our changing understanding in the submitted manuscript, but apparently did not do a fully satisfactory job. We will address these further concerns here. The following discussion starts by addressing the issue of the RIE_BC = 0.2, compared with ~1 for other species, and continues into our analysis of the trace elements zinc and phosphorous and how we quantified these species. Finally, we will address the trace elements calcium and magnesium.

As pointed out by the reviewer here, the laser vaporizer measurements for BC (which is not detected from the heated tungsten vaporizer) need to account for (1) an apparently low RIE_BC value of 0.2 (compared with ~1 for other species) and (2) a low CE of 0.27. We agree that the apparently low RIE_BC value requires further examination and we are investigating this in related, but not yet completed work. As shown in equation (1), which has been modified to include CE explicitly, the important term is the combined CE_s * RIE_s *for a given species, s. Since we are using the MAAP absorption values to derive the mass concentration of BC (*C_s *in equation 1), that is to calibrate the SP-AMS laser vaporizer measurements, the right hand side must equal these "known" values. Therefore, if the value of 0.2 for RIE_BC is in fact lower than it should be, in our current application this would only increase RIE_BC and lower CE_BC (below our estimated 0.27), keeping* CE_s * RIE_s *constant. Thus, our determined best estimate CE of 0.27 can be considered an upper limit on the CE for particle detection from the laser vaporizer.*

These results indicate that only a fraction (≤0.27) of the sampled BC-containing particles are vaporized by the laser vaporizer. By analogy, we assume that 0.27 of all trace element containing particles pass through the laser. Further, we assume that all trace elements are located on BC-containing particles and thus could be vaporized in the laser (without this assumption, the fraction of particles containing trace elements that pass through the laser and vaporize would be less than the 0.27 fraction). Therefore, if the trace elements were only vaporized in the laser vaporizer, we would need to apply a CE = 0.27. However, as we point out in the manuscript, it is likely that both zinc (boiling point = 907^{o}C) and phosphorous *(represented by phosphoric acid which decomposes at 158^{o}C) vaporize, at least partially, from the 600^{o}C tungsten vaporizer. Thus, we are also getting ion signals for these two trace elements from the fraction (≥0.73) of particles that do not pass through the laser, but strike the heated tungsten vaporizer. Assuming that the two vaporizers generate similar ion signals for a given mass of material (i.e., RIE is constant) and that the CE for particles vaporizing on the tungsten vaporizer is unity (1), as reported in the literature, it is likely that a significant fraction of the ions detected for zinc and phosphorous comes from the heated tungsten vaporizer, as opposed to the laser vaporizer. Therefore, if we correct all of zinc and phosphorous ion signals for the 0.27 laser vaporizer CE, we will overestimate the measured mass for these trace elements. Without further information about the fraction of zinc and phosphorous ion signals from the laser and tungsten vaporizers, we feel that the best approach is to use our best estimates of the RIEs for these species (see next paragraph) and a CE = 1, assuming that the largest fraction of ion signals for these materials likely are generated from the heated tungsten vaporizer. Thus, our estimates represent lower limits for the mass concentrations of these elements.*

For the trace elements, since we do not know their RIE values from laboratory measurements, we follow past conventions in the AMS community (e.g. Jimenez et al. 2003) for estimating RIE values based on previous measurements of the electron impact ionization cross-sections and find that the RIE values are 1±0.3 for the trace elements we have identified in the SP-AMS mass spectra (i.e., zinc, phosphorous, calcium, and magnesium).

Finally, we address the question of the calcium and magnesium. As we point out in the current manuscript, these trace elements have much higher boiling points, such that they likely only vaporizer from heated rBC-containing particles inside the laser vaporizer. Thus, it would make sense to apply the 0.27 CE for these species. However, these two trace elements are alkaline earth metals that may undergo surface ionization (or thermal ionization) from heated surfaces, such as the tungsten vaporizer and/or the laser heated rBC particles. Therefore, these two trace elements have two potential ionization mechanisms, making the quantification of these elements much more uncertain than for species that are ionized via electron ionization only.
Given these uncertainties, we have decided to exclude these species from the quantitative analysis of diesel truck plume emission factors presented in Section 3.3 of the manuscript. Emission factors for calcium and magnesium have been removed from Table 1, though we have kept discussion of these trace elements in Section 3.2 which focuses on ion signals (rather than mass concentrations) of chemical species measured in individual diesel truck plumes.

To help improve the clarity of the presentation of the SP-AMS calibration details and mass concentration calculation (Eq. 1) we have made the following changes to the manuscript: (1) explicitly included collection efficiency (CE) in Equation 1, (2) moved discussion of the CE values used for non-refractive species and trace elements from Section 3.1 to Section 2.3 (Data Analysis) following the discussion of RIE values, (3) revised text of Section 2.3 to more clearly state our current understanding of the SP-AMS instrument and factors influencing the conversion of ion signals to mass concentrations.

4017 - 5: Everything after "assuming" is confusing and I'm not sure what you are trying to convey. What you have before that might be enough – you are saying that calcium and magnesium ions may be generated inside the SP-AMS and therefore may have higher than expected ion signals which means an overestimation of the mass of those species.
Response: This sentence has been changed according to the referee's suggestion: "Calcium and magnesium ions may also be generated through thermal ionization mechanisms, which would result in higher than expected ion signals for these species and an overestimate of their sampled mass."

4018 - 25: Does the fact that Massoli et al., 2012 reports a factor of 9 and this study reports a factor of 4 difference in SP-AMS BC and MAAP BC indicate that alignment of the particle beam and laser were better in this study than the previous study?
Response: Yes, this is the likely implication of these two results. However, other issues that may also affect the particle beam – laser beam overlap include the dispersion of the rBC particle beam due to sampled particle size and shape. There is still much to do with respect to fully understanding the quantification of the SP-AMS technique. Therefore, in all current studies, including this study, we make the effort to directly correlate the SP-AMS rBC measurements with other co-located measurements. Here, we explicitly show that the SP-AMS rBC is highly correlated with the MAAP and PAS derived BC mass concentrations and derive a collection efficiency from these direct comparisons.

4019 - 6: Was the SP-AMS ever run in laser-only mode during this campaign? Is there any way of knowing if there were significant coatings on the BC particles?
Response: Due to the emphasis on quantifying OA emission factors for individual diesel trucks in this study, the SP-AMS was not run in laser-only mode. Thus, it is difficult to assess the level of coating on BC particles, though this would be an interesting topic to investigate in future SP-AMS studies.

4019 - 24: It seems like a bit of a stretch to assume that all lubricant-derived trace species have a CE of 1. I can understand this being the case for non-refractory species (mainly because of previous literature), but for the refractory species which are vaporized in the same way that black carbon is, why wouldn't the CE be much lower than 1 and closer to the CE of black carbon? Also, you are assuming that calcium and magnesium are heated by the BC particles vaporizing, which means you are assuming that calcium and magnesium are attached to the black carbon. So if only 27% of the black carbon particle mass is being vaporized, why can you assume that 100% of the BC coating mass is vaporized? Even if the calcium and magnesium were separate particles from the BC particles but were primarily vaporized by the laser, they would still suffer from the same beam alignment issue you discuss on pg 4018 - line 25. I think justification for this assumed CE needs to be stronger in this section. Also, what is the uncertainty of the black carbon CE?
Response: These concerns are directly addressed in the response to the comment on pages "4016-19" above.

4020 - 15: Is "equivalent OA mass" the same as OM/OC ratio discussed by Hallar et al., 2013? It would be worthwhile to discuss your correction factor in context with others present in the literature. Hallar, A. G., D. H. Lowenthal, S. L. Clegg, V. Samburova, N. F. Taylor, L. R.

Mazzoleni, B. K. Zielinska, T. B. Kristensen, G. Chirokova, I. B. McCubbin, C. Dodson, and D. R. Collins (2013) Chemical and hygroscopic properties of aerosol organics at Storm Peak Laboratory, . Geophys. Res. Atmos., 118(10), 4767–4779, doi:10.1002/jgrd.50373.
Response: The factor of 1.25 (OA/OC ratio) used to convert filter based OC measurements to OA is equivalent to OM/OC ratios reported in previous studies that applied similar techniques to convert between OC and organic aerosol mass. Please see response to Referee #1 comment p. 4019, lines 14-17 for an explanation of changes made to clarify the meaning of the OA/OC ratio and how it was determined in this study.

4020 - 17: What specifically was evaluated using the SP-AMS? How might this evaluation be affected by the higher OA concentrations measured with the SP-AMS versus the filters?
Response: Please see response to Referee #1 comment p. 4019, lines 14-17 for an explanation of changes made to clarify the meaning of the OA/OC ratio and how it was determined in this study. The SP-AMS instrument provided the first real-time, chemically-speciated (i.e., rBC, Org, SO4, NO3, NH4, Chl, and trace contaminants such as zinc, phosphorous/phosphate, calcium, and magnesium) measurements for a large collection of individual truck plumes. These results provided the emission factor distributions in Figure 7, the chemical information on the nature of the Organic PM in Figure 8 (i.e., highly correlated with lubricating oil) and the observations of trace contaminants similar to that observed from lubricating oils in the laboratory (Cross et al. 2012) as shown in Figures 4, 5, and 7. If the SP-AMS technique overestimated Organic PM, then the emission factor distributions (and averages) will be overestimated.

4021 - 24: Is this a heavy-duty truck?
Response: Yes. This has been clarified in the text: "The concentration time-series response of the SP-AMS to a passing HD truck is shown in Figure 4 for BC, OA, and several elements."

4022 - 12: Is the tunnel background mass spectra subtracted out from the exhaust plume mass spectra?
Response: Yes, the background spectra measured immediately prior to each truck's passage is subtracted from the plume spectra. This point has been clarified in the text: "Tunnel background subtracted mass spectra for each truck were normalized to the total ion signal and then averaged to obtain the results shown in Figure 5."

4023 - 8: What does the average tunnel background BC mass spectrum look like?
Response: The tunnel background BC spectrum is very similar to the average spectrum measured in HD diesel truck plumes. This point is discussed in Section 3.4, where we compare plume spectra with IOP spectra, which are representative of the tunnel background.

4023 - 16: The discussion here now switches back to Figure 5 - consider reorganizing this section slightly so that discussion of Figure 6 comes after all of the discussion of Figure 5.
Response: The paragraph relating to Figure 6 has been moved to the end of subsection 3.2, following the discussion of Figure 5.

4024 - 19: What does the word "slightly" mean here? Are these quantifiably unsaturated compounds?
Response: We agree the use of "slightly" here is ambiguous and have removed it from the text.

4025 - 6: Aren't these literature results opposite your findings? These results suggest ratios less than 1 when you report ratios greater than 1 on line 3. This also calls into question your conclusion on lines 13-14.
Response: The cited reference (Sakurai et al., 2003) found that for mixtures of varying ratios of diesel fuel and lubricating oil, a mixture of at least 95% oil was required to match the mass spectrum measured for diesel exhaust particles, where the ratio of ion signals m/z = 69 to 71 and m/z = 83 to 85 were greater than one. For mixtures containing a smaller relative volume of oil (e.g. 20% fuel, 80% oil and 10% fuel, 90% oil), ratios of these ion signals were less than one and more similar to the spectra for pure fuel. From this evidence, the authors conclude diesel exhaust particles are composed of at least 95% unburned oil. In our study, we similarly measured ion ratios for these m/z ranges greater than one and cite the line of evidence presented in the Sakurai et al. study to support the conclusion that lubricating oil is the primary source of OA measured in truck exhaust plumes at the Caldecott tunnel. The paragraph describing these results has been revised to improve clarity.

4026 - 5: Can you define "ash" and how it relates to your measurements?
Response: See response to Referee #2 comment pg 4009 - line 19. We have changed the sentence in question to link more explicitly the emissions of trace elements to the formation of ash deposits on diesel particle filters: "While these trace elements typically account for a small fraction of the total PM mass emitted by diesel engines, trace element emissions may accumulate over time and negatively affect the performance of diesel particle filters, as ash deposits related to these species are not readily removed from exhaust filters by oxidative regeneration schemes that are used to remove accumulated BC and OA (Maricq, 2007; Sappok and Wong, 2011)."

4030 - 5: What is the uncertainty on the 2.6 value?
Response: We have added an uncertainty estimate (2.6±0.8) to the text.

4030 - 21: Assuming that the background tunnel mass spectra are not subtracted from these mass spectra in Figure 8, what effect might that have on this correlation? It is probably impossible to do this subtraction for the IOPs, but it should be able to be done for the single gasoline and diesel vehicle events to ensure that the correlation is still strong. My concern is that this correlation is dominated by the background tunnel signals and any actual differences are masked by that background signal.
Response: As addressed in the response to Referee #2 comment 4022 – 12, we have subtracted tunnel background spectra from all HD diesel truck plumes and the gasoline plume event. For IOP periods, there may be a contribution to the spectra from ambient OA. However, because ambient OA concentrations were typically an order of magnitude lower than tunnel concentrations this contribution is expected to be minor.

4031 - 1: Did the gas vehicle event show BC signals above background levels?
Response: Yes, there was a discernible BC signal in the gasoline vehicle plume event, though, as shown in Figure 8, OA emissions were much higher than BC emissions for this vehicle (OA:BC ~ 19).

4031 - 4: To be clear, the conclusion is that the carbon fragments in the SP-AMS the same way on the weekdays as it does on Sunday, which may or may not say something about how the carbon was emitted in the first place.
Response: Our argument in this paragraph is that BC spectra measured during time periods when gasoline vehicles were the predominant source of BC in the tunnel are very similar to BC spectra measured in diesel exhaust plumes. Thus, our conclusion that carbon ion distributions, as measured with the SP-AMS, are similar for gasoline and diesel vehicles and that this similarity will complicate BC source apportionment efforts using this instrument.

4031 - 8-9: This finding just says that all OA fragments in the same way in the SP-AMS regardless of the number of diesel trucks. If the OA is vaporized primarily by the heater and not the laser, and the presence of diesel trucks is more pronounced in the BC signal - which is vaporized by the laser - then this finding isn't necessarily surprising.
Response: We are emphasizing the similarity between gasoline and diesel vehicle OA mass spectra in this paragraph.

4031 - 28: For the single gas vehicle event shown in Figure 8, were the lubricant derived ions above background like they are in the diesel vehicle events?
Response: Yes, there is a discernable signal above background for zinc and phosphorus/phosphate during the gasoline plume event. This point was not included in the manuscript, as our goal in this section was to emphasize similarities in the OA and BC spectra of the gasoline plume event with those measured in diesel truck plumes and IOP sampling periods.

page 4043: What does it mean that absorbed vapors are as much as the real OA for some of these sample periods?
*Response: As noted in the response to Referee #1, comment p. 4019, lines 26-28 and Fig. 2, the unshaded green bars representing the concentration of adsorbed organics on QBT filters are included in Fig. 2 to give readers an indication of the gas-particle partitioning of motor vehicle exhaust OA emissions. Because of the semivolatile nature of motor vehicle exhaust OA, dilution and cooling of exhaust upon emission will change the relative amounts of organic material in the condensed and gas phases. Generally, dilution lowers the concentration of condensed organic material, which, following absorptive partitioning theory, tends to promote evaporation of semivolatile organics. Thus, for the dilution conditions present at the Caldecott tunnel, it is not surprising to see a significant amount of adsorbed organics on the QBT filter. For comparison, a recent dynamometer study of HD truck OA emissions applied a similar filter sampling set-up to that employed here and found positive sampling artifacts due to adsorbed organic vapors accounted for 10-95% of organic carbon measured on front quartz filters (May, A. A.; Presto, A. A.; Hennigan, C. J.; Nguyen, N. T.; Gordon, T. D.; Robinson, A. L. Gas-particle partitioning of primary organic aerosol emissions: (2) Diesel vehicles. Environ. Sci. Technol. **2013**, 47, 8288-8296.)*

Technical corrections
4013 - line 18: "operational" should be "operating"
4014 - 4: "impact on..." should be "will impact on..."
4014 - 28: It would be more clear if "prior to" is replaced with "from" or "inside".
4017 - 25: It might be helpful if the notation were "EFS" rather than "EFP " because "S" is clearly defined as species.
4025 - 4: "mixtures" should be "ratios"
4025 - 5: "and" should be "to"
4026 - 26: "in" should be "between"
4028 - 1: "Note that ..." sounds better than just "Note ..."
4028 - 7: "Note that ..." sounds better than just "Note ..."
4030 22: Remove the comma in this sentence, assuming that you mean that all BC mass spectra are highly correlated with that single spectrum from a diesel truck.
4031 - 27: "omitted" should be "emitted"
4033 - 4: Should "abd" be "and"?
Response: We have made the corrections suggested by the referee.

4022 - 24: The sentence beginning with "In the average diesel PM mass spectrum..." is found in the figure caption and doesn't need to appear in the text.
Response: We decided to keep the sentence in question in the text as well.

4026 - 16: Technically, BC has the highest correlation with OA as presented in the figure.
Response: This sentence has been changed to clarify only trace element correlations are being discussed: "For trace elements, the highest correlation with OA was observed for lubricant-derived species, including phosphorus containing ions (phosphorus/phosphate), zinc, and magnesium."

4028 - 6-7: This sentence is a repeat of page 4027 - line 21.
Response: The text has been edited to remove this duplication.

4031 - 21: Consider making a Conclusions section starting here.
Response: We appreciate the referee's suggestion, however we have decided not to include a conclusion section here for the sake of brevity.

page 4043: In the legend, isn't "OA (QBT)" really absorbed vapors and not organic aerosol?
Response: We agree with the referee that it is probably not correct to refer to organic compounds measured on QBT filters as "organic aerosol". In response, we have changed the corresponding legend entry from "OA" to "Organics" and have made similar adjustments to the text and Figure 2 caption.

page 4044: The legend for the red circle and blue triangle is incomplete. Also, the "IOP2212" notation is confusing in the context of this figure - this text box could just be stated in the figure caption.
Response: The textbox in question has been removed from the figure and the following sentence was added to the caption for Figure 3: "Boxed points at the right of the figure were excluded

from the regression analysis due to an anomalous street sweeping event that occurred during the IOP2212 sampling period."

page 4046: The sentence beginning with "Only trucks with ..." is found in the text of the paper and doesn't need to be repeated in both location. Either remove from the text or remove from this caption. Also, in the figure, it is hard to see a difference between the bars and error bars. Might it be better to have a third panel with the error bars plotted on that? Or come up with some other way that more clearly shows where the relative ion signal is such that it isn't masked by the error bars.

page 4047 : See the comment about the bars and errors bars for page 4046

Response to both of the above comments: The sentence in question has been removed from the caption for Figure 5. The width of the bars in Figures 5 and 6 have been widened to differentiate more clearly between the bar height and error bars.