***The authors would like to thank the reviewer for their careful review. We have attached answers to their specific concerns here and have also uploaded a merged document showing tracked changes we have make within the manuscript in response to their concerns.***

Discussions
Interactive comment on "Direct measurements of near-highway emissions in a high diesel environment" by H. L. DeWitt et al.
Anonymous Referee #1
Received and published: 2 December 2014
Overall Comments –
This paper describes an experimental study of near-highway (~15-20 m away) air pollution concentrations in a diesel dominated environment. They measured ambient concentrations using a suite of high resolution instruments (HR-AMS, SMPS, and PTR-MS). They also collected filter samples for offline analysis (OC/EC, sulfate, organic molecular markers). They performed what is now relatively routine PMF analysis of the AMS data, presenting a 6 factor solution. They performed some analysis of the PTR-MS data, focusing on nitrogen containing fragments. They analyzed aerosol nitrate using approach of Farmer. They compared the results to other previous field studies (they largely agree). They present results from fossil/modern carbon analysis– as expected for this sort of site two-thirds or more of the carbon is fossil.

The paper is well written and very comprehensive (16 figures and 2 tables!). The experiments seem to be well executed. There is nothing fundamentally wrong with the paper, but I found it relatively uninteresting. It breaks little new ground, rather it presents results that are basically consistent with the current AMS world view. The points made are largely those that have been made by previous studies. The most potentially interesting result was that almost none of the oxidized organic aerosol appears to be fossil. The paper could be improved by streamlining (cut the number of figure in half) and focus on the more novel aspects of the results relegating the rest to online supplement.

***Due to comments by both reviewers, we have removed a number of graphs and discussions and moved these to the supplementary information. Specifically, we have moved detailed discussion of the NO and NO2 (gas) and NOA factor, discussion of the spectral differences between LO-OA and MO-OA, and particle-size to the supplementary information section. We also have expanded the section on the fossil vs. modern carbon. The paper now includes only 9 graphs.***

Specific comments:
The paper frequently references BC concentrations. It was not clear how they were measured. The paper does discuss thermal-optical analysis of quartz filters to determine EC concentrations. Did they just switch terminology? EC and BC are

different quantities. If they were using the thermal-optical analysis then I would recommend that they refer to it as EC. Figure 3 suggests they were running an Aethalometer or PAX.

***In fact, both BC (via MAAP) and EC (using a Sunset Laboratories OC/EC measurement system) were measured. The MAAP instrument had a greater time resolution than the EC instrument and thus was used for the time series graphs and the comparison of BC to AMS factors. EC values from the thermo-optical analyzer were used to perform this calculation, and have now been correctly labeled as such (we thank the reviewers for pointing out this error!), and a comparison between the measurements has been included in section 3.3.1. We also now include a figure in the supplementary information showing the comparison between BC and EC concentrations. The two instruments agree fairly well, and as the reviewer suggested, the slope of the MAAP BC and thermo-optical EC data was 1.5 (higher BC than EC). This answers the reviewers concerns below (that perhaps the optical measurement from the MAAP was overestimating the EC/BC concentrations).***

I found the discussion of the fossil/modern carbon data (Figure 16) to be the most interesting part of the paper. The figure suggests that very little of the oxidized organic aerosol (i.e. SOA) is fossil (I assume fossil SOA would be the bright green part of bar, but was not entirely clear to me when I read the text). This seems surprising (e.g. see Zotter et al. JGR 2014). A key detail here may be how they determined BC concentrations.

Is this a true carbon measurement (i.e. thermal optical) or was it inferred from an optical measurement? If it was inferred from the optical measurement what mass absorption cross section was used to convert the absorption data to carbon? This is a critical detail because as an optical measurement often overestimate the true elemental carbon concentration (many intercomparison studies have been published that show this) – potentially by as much as a factor of 2. This detail could change the interpretation of this figure substantially.

***A new section with significantly more detail about this calculation has been added to the paper and a range of potential fossil-OOA has been calculated taking into account various potential errors in our calculation assumption. Additionally, the figure has been redone and relabeled to hopefully make the meanings of the values presented more clear.***

***We used EC data for the fossil/modern carbon calculation, and have now correctly labeled the value EC (versus the BC we used for its higher time resolution in other parts of the paper). We also include a range of possible 'fossil-ooa' assuming some modern carbon contribution to HOA/EC from biofuels and biomass burning. Here is the expanded section 3.3.1:***

> ***A source of uncertainty in the global particulate emissions of vehicles is the formation of SOA from gas-phase emissions and the aging of POA. To discriminate between the relative concentration of modern and fossil carbon, and thus potentially discriminate between OOA from vehicular sources and from modern sources, daily filter samples were collected at the sampling site and 14C radiocarbon measurements were performed. From these measurements, the percentage of modern carbon from TC (OC+EC) was***

*calculated. Modern carbon varied from 15-36% of the total aerosol carbon, a significant portion of the measured carbon considering the close proximity of the measurements to fossil carbon sources. In France, the contribution of biofuel was about 7% and 5% for diesel and gasoline fuel, respectively, in 2011 (UFIP, Union Française des Industries Petrolières, 2011) and cannot explain this relative high proportion of modern carbon observed in the particulate matter. This is similar to findings shown in Hodzic et al. (2010), Minguillon et al. (2011), and El Haddad et al. (2013), which indicate that modern carbon is often more significant than fossil carbon in the carbonaceous fraction of PM, even in cities with high vehicular emissions (e.g., Mexico City, Barcelona or Marseille).*

*As radiocarbon measurements have been performed through a thermal approach (combustion of the samples at 850°C), we consider in the following section EC measured by the thermo-optical method. As shown in figure S12, EC and BC do not differ significantly at low mass loadings, but have a wider scatter in the data at higher mass loadings. The calculation of BC (measured by the MAAP) using an absorption cross-section is imprecise and, at high loadings of BC, may under or overestimates this mass loading. Figure S12 shows a comparison between the MAAP (BC) and thermal measurement (EC) data, with a 1:1 line. As the thermal-optical analysis of EC is a more direct analysis, EC was chosen to be used in this calculation.*

*Assuming that the majority of EC was traffic-related, and thus from fossil origin, the concentration of modern organic carbon and fossil organic carbon was then calculated. While evidence for the presence of biomass burning aerosol was measured at the field site, the main source of EC was likely diesel exhaust. Figure 8 shows the fraction of EC and OC, HOA, and a partitioning between fossil and modern carbon. In Figure 8A, a rough calculation was performed to determine the concentration of non-primary fossil organic carbon. For a first estimate, all EC was assumed to be fossil in origin. Additionally, the HOA aerosol was also assumed to be vehicular, and thus fossil, in origin. The HOA factor concentration has been divided by its OM: OC ratio to remove any non-carbon mass (HOA C, calculated from the elemental formulas of the PMF factor mass spectra, Aiken et al. (2008)). Both EC and HOA C had high ($R^2$=0.89 and 0.85 respectively, n=10) correlations with the fossil C mass, which supported a largely fossil source for these two species. The remaining fossil organic carbon mass after subtraction was then assumed to be from non-primary sources (in blue).*

*This calculation provided a lower estimate of the amount of fossil carbon contributing to SOA mass, and involves several assumptions and potential sources of error. Sources of error in this calculation include error in the PMF resolution of primary (HOA) organic aerosol spectra and error in the calculated OM:OC ratio of this factor species, biodiesel vehicular emissions contributing modern carbon to measured HOA, and biomass burning aerosol contributing modern carbon to measured EC.*

*As the measured HOA:EC ratio was in-line with previous measurements in*

***high diesel environments, HOA concentrations did not appear to be significantly over or under estimated. Up to 7% of fuel use in France was biodiesel, thus, part of the HOA concentration could be from modern sources. While research has shown that the use of biodiesel fuels reduces the overall primary particulate matter emissions (Cheung et al, 2010), biodiesel could still be a modern carbon contributor to OC and EC mass. Additionally, although the concentration of BBOA was generally low (a campaign average of 0.34 ± 0.23 μg $m^{-3}$) and the ratio of BBOA:EC has been found to be on the order of 3-4 in other areas of France (Crippa et al., 2013), some contribution to EC from biomass burning may have been present at the measurement site. In Figure 8B, a range of fossil non-primary organic carbon, normalized to total measured organic carbon, is presented. For the upper limit of this range, HOA C and EC were considered to be 95% fossil and 5% modern (7% biodiesel fuel use and an estimated 25% reduction in particulate emissions from biodiesel fuel). Also for this upper limit, the calculated concentration of BBOA was divided by 3 and used to calculate possible modern EC from biomass burning (Crippa et al., 2013).***

Figure 15 – I assume that the light/bright green is the defined as the difference between the other quantities? This needs to be clarified. ***The reviewer is correct; we have now clarified this point. Line 437 (769 in merged revised document): The remaining fossil organic carbon mass after subtraction was then assumed to be from non-primary sources (in light green originally, now in light blue in the redone graph).***

Figure S1 compares filter and AMS data. The AMS data in this figure are uncorrected? If so that should be noted in the caption. What does the comparison of organic carbon
look like? They mention using a TEOM but never discuss the data. How was the mass closure between the speciated and the mass based measurement? If there is poor mass closure then what does that mean for the results?

***Yes, this is uncorrected data, included in the caption as per the reviewer's suggestion. Figure S3 shows a comparison of AMS data and TEOM data. The general time trends are good but the quantitative comparison of AMS+BC and TEOM data is not perfect, as the TEOM and AMS have different size cut-offs (1 micron and 2.5 microns, respectively) and measure different species (the AMS cannot measure refractory species, and road dust, particularly in supermicrometer sizes, may play a large role in the differences in mass between the TEOM and AMS+BC measurements during high traffic periods). On line 255 (line 392 in the marked merged document), to include TEOM data within the main paper body, we now include the statement "PM2.5 had a somewhat higher mass variation than the AMS + BC measured mass (Figure S3), likely due to the smaller measurement size cutoff for AMS (1 μm) and the presence of road dust in the local environment, a large portion of which may be non-refractory and those unable to be measured by the AMS."***

The two papers from Hellebust seemed interesting, but neither is published. Not clear it is appropriate to reference.
***The paper will be submitted to ACPD within the next few days, or we can remove this reference.***