

We thank the reviewers for their helpful comments. They have improved the manuscript. We provide extensive point-by-point responses below, including excerpts of the modified text. Please note the color scheme below.

Color scheme:

1. Reviewer comments are written in this color. Each comment is designated by reviewer number and comment number (e.g., first comment from reviewer 1 is R1.1).
2. Our responses to reviewer comments are written in this color.
3. Text that has been added to the manuscript in response to a reviewer comment is written in this color.

R1.1

My main concern with the manuscript is related to the difficulty in separating the influence of any of the after-treatment technologies on the emissions and SOA formation characteristics from the variability caused by using different vehicles with different engines and histories. The authors have not really emphasis this point enough in the manuscript and should do so in the revised manuscript. How much of the observed differences are due to the after-treatment technologies employed and how much is due to the variability of emissions and composition among the chosen vehicles.

It was not possible to run experiments in which each vehicle could be tested with and without its aftertreatment device. While we understand the reviewer’s concern regarding this limitation, there is a very dramatic difference between the emissions (PM, NMOG, etc.) of the vehicles with and without aftertreatment. For example, the NMOG emissions from the catalyzed DPF-equipped diesels were two orders of magnitude lower than the non aftertreatment diesels. The result was that the concentration of the NMOG emissions in the CVS was lower than the concentrations in the background air. It is highly unlikely that these sorts of differences could be achieved without aftertreatment (if they could then engine manufacturers would not be adding DPFs to meet the latest regulations). In other words, the differences due to the effects of aftertreatment are larger than the variability of emissions without aftertreatment, which mitigate the concern raised by the reviewer. This hypothesis supported by comparisons of our data with the literature. May et al. AE 2014 compares our data with literature data. The data for our vehicles are consistent with literature data. In addition, there is no overlap in emissions between the DPF-equipped vehicles and the non-DPF equipped vehicles. These two types of vehicles are in totally different emissions regimes. Therefore the main points of this paper are not significantly affected by not testing the same vehicle with and without aftertreatment. We recap the major findings below and explain why they are insensitive to the issue the reviewer raises.

- (1) During normal operation, vehicles with a catalyzed DPF emitted very little primary particulate matter (PM) and non-methane organic gases. Furthermore, photo-oxidation of dilute emissions from these vehicles produced essentially no SOA.
 - a. Fig. 3 shows the PM emissions from 3 different vehicles with DPFs (“2001”, “D1” and “D2”). While the experiments did not include data from these vehicles with/without DPFs, the tests do show that the DPF-equipped vehicles emit/produce essentially zero SOA, POA and BC. These results stand in marked

contrast to every other vehicle without a DPF. We imply that it is likely that DPFs eliminate SOA (which is supported by the dramatic reduction in NMOG emissions), but we do not state this conclusively.

- (2) Significant primary PM emissions and SOA production were measured during active DPF regeneration.
 - a. True control experiments were run in support of this conclusion. Numerous experiments with D1 and D2 were run without regeneration and then a regeneration experiment was performed with each vehicle. The data in Fig. 5 clearly show that regeneration results in measureable quantities of all PM species.
- (3) Under reasonable assumptions about DPF regeneration frequency, the contribution of regeneration emissions to the total vehicle emissions is negligible, reducing PM trapping efficiency by less than 2%.
 - a. This is a simple mathematical calculation that depends on estimates of regeneration frequency provided by a senior industry scientist (as cited in the MS). Regeneration frequency cannot be found in the literature; it is proprietary information. The estimate provided by T. V. Johnson, is the best available estimate.
- (4) For both MDDVs and HDDVs without aftertreatment substantial SOA formed in the smog chamber.
 - a. This conclusion does not depend on testing the same vehicle with and without aftertreatment.
- (5) Less than half of the measured SOA could be explained by traditional (speciated) SOA precursors. The remainder presumably originates from the large fraction (~30%) of the non-methane organic gas emissions that could not be speciated; we estimate that the effective SOA yield was $9\pm 6\%$ if both speciated SOA precursors and unspeciated organics are included.
 - a. This conclusion does not depend on testing the same vehicle with and without aftertreatment.
- (6) SOA production from creep+idle operation was 3-4 times larger than SOA production from the same vehicle operated over the Urban Dynamometer Driving Schedule (UDDS).
 - a. True control experiments were run in support of this conclusion. The same HDDV (D3) was run over the UDDS cycle multiple times and then over the creep+idle cycle. The particle- and gas-phase effects of the driving cycle shown in Figs. 3-4 clearly support the conclusion that driving cycle can profoundly affect emissions/production.
- (7) Fuel properties had little or no effect on primary PM emissions or SOA formation.
 - a. True control experiments were run in support of this conclusion. The same HDDV (D3) was run with low, medium and high aromaticity ULSD (including duplicate experiments with the different fuels), and Fig. 4a shows that the fuel made no difference in POA, SOA or NMOG mass. Furthermore, the NMOG fractions (i.e., speciated SOA precursors, speciated non-SOA precursors and unspeciated) were very similar in experiments with D3 using the three different fuels.

Having said this, we do agree with the reviewer that it is important to include a disclaimer in the MS regarding the possible variability resulting from the lack of true control experiments in certain cases. We now include the following statement in the conclusions:

While these experiments did not test the same vehicle with and without a DPF, there is strong evidence that our conclusions are not limited by this apparent source of uncertainty. There is a truly dramatic difference between the emissions (PM, NMOG, etc.) from those vehicles with a DPF and those without a DPF. For example, the NMOG emissions from the catalyzed DPF-equipped diesels were two orders of magnitude lower than vehicles without aftertreatment. It is highly unlikely that these reductions could be achieved without aftertreatment, for if this were possible, engine manufacturers would not be adding DPFs to meet current regulations. In other words, DPF- and non-DPF-equipped vehicles operate in totally distinct emissions regimes. This hypothesis is supported by comparisons of our primary emissions data with the broader literature (May et al., in press, 2014)

R1.2

Page 24231, lines 12-14: Was the dilution air used for the first stage of dilution also filtered for gaseous impurities (i.e. VOCs)? It seems that an activated charcoal filter was not used for this stage of dilution. If so, what effect did this have on your experimental results?

Yes, the dilution air used for the first stage of dilution was filtered for gaseous impurities. The dilution air preparation consists of a layer of coarse furnace pre-filters followed by activated carbon filters followed by HEPA filters. There is no applied temperature or humidity control for the current system. The dilution air filter housing is part of the Constant Volume Sampling System supplied by Horiba Instruments. Typical particle counts for tunnel blank operation of the CVS are ~300/cc using a 2.5nm cutpoint CPC. The carbon filters are Vari-Pure Lite 50/50 Blend Part#1509725 VARL-05 24x24x12 50/50 BL (Note these filters are loaded with potassium permanganate in addition to the activated coconut shell charcoal) <http://catalog.tfsi1.com/Documents%5CVARI-PURE.pdf> The HEPA filters are 99.97% efficiency by Microguard 2000 by Airguard, Model# MC2000-501 / H2424B00 – OAG00000F, Item# 2970315.

In the revised text we now state that the first stage dilution air was activated charcoal filtered.

R1.3

Page 24231, line 25: more details of on the UV lights should be provided: what was the overall intensity of the used lights? what was there spectral characteristics including JNO2 and JO1D values?

We now include the JNO2 and the wavelength at maximum output, and cite another paper where the spectral characteristics are described further. We have not quantified the intensity or the JO1D. The lights were model F40BL UVA from General Electric. The following text has been added:

The NO₂ photolysis rate in the chamber during the MDDV experiments was approximately 0.16 min⁻¹, and the spectral characteristics of the UV lamps (maximum output was at ~350 nm) are described elsewhere (Presto et al., 2005a).

R1.4

Page 24231, line 25: It is mentioned that up to 4ppm of propene was used to adjust the VOC:NO_x ratios in the experiments. A comment on the possible effect of including this large amount of propene on the results of the experiments should be added (also page 24233, lines 1-5)

Propene (as opposed to some other species) was added because it is reactive and does not generate SOA. Propene is commonly added as an accelerant to support oxidation in chamber experiments. The principal effect is to re-balance the direct sinks of OH radicals in favor of organics vs. NO₂. With disproportionately high NO_x levels (especially NO₂), the NO₂ + OH reaction essentially shuts down oxidation chemistry in the chamber. Propene also increases the steady-state level of peroxy radicals. The following statement has been added on p. 24231, line 25:

Propene is commonly added in chamber experiments to support oxidation by re-balancing the direct sinks of OH radicals in favor of organics rather than NO₂. Propene also increases the steady-state level of peroxy radicals.

R1.5

Page 24231, lines 25-26: No rationale or comments were made on why UV lights were used for the MDDV experiments while sun light was used for the HDDV ones? Was this determined by availability of space or was it motivated by a different factor? Was the intensity of light characterised in the HDDV experiments?

The HDDV and MDDV experiments were performed at two different facilities in different locations (as noted on p. 24230, lines 6-7). It was not feasible to use natural light during the MDDV experiments because the test facility was located inside of a large building which required that the chamber be located indoors. During the HDDV experiments the chamber was conducted in a small building which required locating the chamber outdoors, so sunlight was used. The light intensity during the outdoor experiments was not characterized.

R1.6

Page 24232, line 13: Was this variability in T and RH within each experiment or was it between different experiments? Please clarify.

These variations were between different experiments. The higher temperatures and humidities were recorded during certain HDDV experiments performed outside during the summer. The lower temperature and humidities occurred during the MDDV experiments, which took place in an air conditioned, indoor space. The manuscript now states:

The quoted temperature and humidity ranges describe the variability between different experiments.

R1.7

Page 24233, line 14: This assumes complete combustion of the fuel. The authors made a statement that this is a robust assumption without verifying their claim. Do the CO and CO₂ data verify this assumption?

Yes, the CO and CO₂ (and NMOG and OC) data are what we used to make this statement. CO/CO₂ ratios for MDDV and HDDV were less than 0.005. In most cases, the ratios were several orders of magnitude smaller than that.

The following text has been added:

CO/CO₂ ratios for MDDV and HDDV were less than 0.005.

R1.8

Page 24233, line 19-20: How high were the OH levels at the start of the experiments?

The following text has been added:

2-3x10⁷ molecules cm⁻³.

R1.9

Page 24234, line 16-20 (and supplementary material): The discrepancy between the SMPS and AMS mass measurements was attributed to the AMS. No quantitative discussion was provided for the assumptions about particle shape and density made for the SMPS mass calculation. Scaling the AMS mass data to the SMPS surely introduces an error in the mass estimation that should be discussed as it has an impact on the results presented in the main manuscript.

The following text is included in the SI.

We assume that particles are spherical with average density of 1 g/cm³. However, fractal-like particles will cause the SMPS to overestimate the spherical equivalent diameter and therefore overestimate particle mass. While commonly made, the unit density [80] and sphericity [81-82] assumptions have both been shown to not always be valid for aerosol with high EC (e.g., diesel emissions). After SOA production begins the sphericity assumption improves as the organics coat the primary particles, making them more spherical [62].

R1.10

Page 24235, line 7: what is meant by highly uncertain? Is this due to lack of measurements of the different VOCs or is it due to their wall loss characterisation? Matsunaga and Ziemann (2010) showed that this could be significant for larger VOCs. The authors should clarify their statement in this regard?

The uncertainty is primarily due to the fact that we did not exhaustively characterize the gas-phase compounds in the chamber or their wall loss rates. This is an area of active research and we are not aware of other groups that are making these sorts of corrections to chamber data. We do not know what further clarification we could add to the MS, so we have not changed it due to this comment.

R1.11

Page 24235, line 12: It could also be caused by the lack of activated charcoal filtration of the CVS air. See related comment above.

No. The CVS dilution air is filtered with activated carbon. We now include this information in the revised MS.

R1.12

Page 24237, line 11: Are there any diagnostics or reference measurements that could be used to determine the state of the DOC during the experiments (whether it was malfunctioning or not)? On the other hand, the comparison between D4.1 and D5.3 should not be expected to tell us anything conclusive about the role of DOC in reducing the emissions of VOCs given that the two cars are of different age and engine characteristics. Could the analysis of the gas phase samples from the CVS help identify any potential differences in composition? This is partly included in Figure 4b but not discussed in this part of the manuscript.

No, we do not have any data that could be used to determine the state of the DOC.

The sum of the masses of all the speciated compounds for D4.1 is greater than the total NMOG measured by FID, suggesting a faulty measurement or a reporting error from the GC-MS. Thus, this is an additional possible explanation for the unexpected behavior (i.e., that the DOC-equipped vehicle's NMOG is greater than the vehicle without a DOC) that we note in the text. Given this uncertainty about the gas-phase data from D4.1 we do not feel confident in comparing it with D5.3.

We now note in the text:

A faulty measurement or a reporting error from either the GC-MS or the FID occurred during the D4.1 experiment because the sum of the masses of all the speciated compounds for D4.1 is greater than the total NMOG measured by FID. This technical difficulty is another likely explanation for why the DOC-equipped vehicle's (D4's) NMOG is greater than the NMOG from the vehicle without a DOC (D5).

R1.13

Minor corrections:

Page 24237, line 12: change "due differences" to "due to differences"

Done.

R3.1

Gordon et al. report chamber studies on SOA formation from photo-oxidation of vehicle exhaust from medium- and heavy duty diesel vehicles running with 3 different ultra-low sulphur fuel. Also the effect of different after-treatment devices on emissions and SOA formation are studied. The study is scientifically relevant and the paper is quite well written. The paper could be published in ACP after the following comments have been taken into account by the authors.

R3.2

Experimental section:

- more details of on the UV lights should be provided (intensity, wave length)

We have included additional details on the UV lights in response to the first reviewer's comments (R1.3) above.

R3.3

- Why some of the experiments were performed by using UV lights and some by sunlight. Could this affect the results? This should be discussed in the manuscript.

See our response to R1.5 above. The HDDV and MDDV experiments were performed at two different facilities in different locations (as noted on p. 24230, lines 6-7). It was not feasible to use natural light during the MDDV experiments because the chamber was located indoors. We now state in the MS:

While the different light sources in the MDDV and HDDV experiments could introduce some uncertainty, this is not expected to significantly impact our conclusions for at least two reasons. First, as pointed out by Platt et al. (Platt et al., 2013), the emission fingerprint of the UV lamps as a function of wavelength and temperature overlaps with the absorption cross section for the photolysis of OH, O₃, and HONO (Carter et al., 1995). Therefore, despite differences in emission intensity between UV lights and sunlight, UV lights are a good sunlight surrogate. Second, the primary conclusions of this paper are based on the HDDV experiments; thus, any variability in SOA production due to the different light sources for the MDDV experiments should not alter the main findings. Finally similar SOA production rates were measured for the non-DPF equipped vehicles some of which were tested with natural and others with artificial light.

R3.4

- Page 24232, line 13: Authors mention that there was a pig variability in temperature and RH conditions during the experiments. How much T and RH varied between the different experiments? This could have an effect on measured SOA productions and should be discussed more detailed.

See our response to R1.6 above.

R3.5

- What was the OH concentration in the beginning of the experiments? Was it the same in all of the experiments?

See our response to R1.8 above. The OH concentration was not exactly the same in all experiments. The following text has been added:

2-3x10⁷ molecules cm⁻³.

R3.6

- Authors mention the wall losses of vapors and refer e.g. to the paper of Matzunaga & Ziemann (2010). As shown by them and also recently by Kokkola et al (2013) wall losses may truly be important and their effect on results should be discussed more thoroughly.

The third paragraph of the conclusions has been changed substantially to discuss the potential importance of vapors lost to the chamber walls. The paragraph now reads:

Substantial SOA was formed when emissions from MDDVs and HDDVs not-equipped with DPFs were photo-oxidized in the smog chamber for three hours—with the emissions from some vehicles generating twice as much SOA as POA. Although SOA production from diesel- and biodiesel-fueled vehicles without a DPF was significant on an absolute basis, after three hours of photo-oxidation the net PM (primary+secondary) levels in the chamber were still dominated by the primary emissions because of the high levels of BC. However, BC's dominant role in PM emissions/production from diesel vehicles could be due in part to the conservative approach we have taken in estimating SOA production. As previously discussed, our SOA estimates do not include the loss of organic vapors to the chamber walls. Kokkola et al. suggest that ambient SOA mass production may be underpredicted in chamber experiments by a factor of four due to the loss of low volatility vapors to the walls (Kokkola et al., 2013). Furthermore, Matsunaga and Ziemann show that for a range of gas-phase compounds relevant to our study the OC in the chamber will reside overwhelmingly in the chamber walls (Matsunaga and Ziemann, 2010). Absorption of vapors by the chamber walls would imply that the effective SOA yields in Fig. 6 are lower limits on the yields expected in the ambient atmosphere and that SOA may constitute a larger fraction of total PM.

R3.7

Results

- I guess that the mass concentration of different compounds (SO₄, SOA, POA) are from AMS? This should be mentioned in the text. When DPF was used, were the concentrations high enough for AMS? If you use the SMPS data to estimate the SOA production, are the results comparable to those presented in figs 2-3?

Yes, these components were quantified with the AMS. This is stated in the Experimental Setup section:

Non-refractory submicron aerosol mass and chemical composition were measured with a quadrupole Aerosol Mass Spectrometer (AMS, Aerodyne, Inc.).

As shown in Figs 3-5, the DPF eliminates essentially everything (primary PM, SOA, and NMOG) from the emissions. The exhaust from these vehicles (during the UDDS driving cycle) is cleaner than the ambient L.A. air. Regarding the use of SMPS data rather than AMS, see our response to R3.11 below.

R3.8

- SMPS data: Number concentrations for different cases should be presented and the SMPS concentrations should be compared to the AMS results (See the comment below).

Please see our response to R3.11 below.

R3.9

- Page 24236 lines 10-15. I don't understand why SOA production doesn't decrease during the experiments. If HONO is added only in the beginning of the experiments, the OH concentration should go down during the experiments hence also the SOA production should go down.

This sentence was poorly worded. What we were trying to say is that the SOA production appeared limited by oxidant concentrations and not SOA precursors. Therefore, when the OH levels in the chamber fell (due to photolysis of the HONO), the SOA also production fell. We have reworded the sentence.

R3.10

- The gas phase results (including VOCs) should be investigated more detailed. Do you see changes in the gas phase when you compare e.g. DOC cases? What about in the case of different fuels?

The reviewer's first question is unclear: changes in the gas phase when you compare DOC cases...with what? If the reviewer is asking how the VOC emissions compare for different experiments with the DOC (only)-equipped vehicle, D4, we cannot provide any further information. As we state in the caption of Fig. 4, we do not have any speciated gas-phase data for D4.2, and this is the only experiment other than D4.1 that we could compare. All other vehicles either have a DOC+DPF or no aftertreatment. Furthermore, as we stated in our response above (R1.12), a faulty measurement or a reporting error from either the GC-MS or the FID appears to have occurred during the D4.1 experiment because the sum of the masses of all the speciated compounds for D4.1 is greater than the total NMOG measured by FID. Unfortunately, this means that we do not have any VOC data for the DOC-equipped vehicle that we can compare with the no aftertreatment vehicles.

Regarding differences in the VOCs due different fuels, the MS states:

Although the aromatic content of the fuel and the emissions were positively correlated (see Figure S.4), Figure 4a-b indicates no systematic effect of fuel aromaticity on POA emissions or SOA production. EC emissions from the five experiments with D3 were also tightly grouped with no distinguishable trend based on fuel type (average \pm 1 σ shown in Figure 3; individual values not shown). Furthermore, the relative amounts of NMOG (Figure 4b) in the different broad categories (speciated SOA precursor, speciated non-SOA-precursor and unspeciated) are also identical for the D3 experiments (UDDS cycle) regardless of fuel type.

R3.11

- SOA mass closure: the SMPS volume increase should be compared to the SOA masses analysed from AMS. Based on supplemental material there is a clear difference in the results. Is the difference similar in all cases? What if you estimate the SOA yield from SMPS results, are the conclusions still the same?

None of the main conclusions of the paper comparing PM from vehicles with and without aftertreatment (conclusions (1)-(4) in the list below) change if SMPS measurements are used instead of AMS data. In fact, these conclusions are strengthened in all cases if the SMPS data are used. This is due to the fact that the SMPS-derived estimates of SOA are approximately a factor of 3 higher than the AMS-derived SOA estimates for the non-DPF equipped vehicles but remain zero for the DPF equipped vehicles whether calculated from AMS or SMPS data.

If SMPS measurements are used instead of AMS data, conclusion (5) would change; the yields would increase by about a factor of 3.

If SMPS measurements are used instead of AMS data, conclusion (6) would change; in this case the distinction between creep+idle is more pronounced; the ratio of SOA_{creep+idle}/SOA_{UDDS} is ~10 instead of a factor of 3 to 4.

If SMPS measurements are used instead of AMS data, conclusion (7) would not change.

- (1) During normal operation, vehicles with a catalyzed DPF emitted very little primary particulate matter (PM). Furthermore, photo-oxidation of dilute emissions from these vehicles produced essentially no SOA.
- (2) Significant primary PM emissions and SOA production were measured during active DPF regeneration.
- (3) Under reasonable assumptions about DPF regeneration frequency, the contribution of regeneration emissions to the total vehicle emissions is negligible, reducing PM trapping efficiency by less than 2%.
- (4) For both MDDVs and HDDVs without aftertreatment substantial SOA formed in the smog chamber.
- (5) Less than half of the measured SOA could be explained by traditional (speciated) SOA precursors. The remainder presumably originates from the large fraction (~30%) of the non-methane organic gas emissions that could not be speciated; we estimate that the effective SOA yield was $9 \pm 6\%$ if both speciated SOA precursors and unspeciated organics are included.
- (6) SOA production from creep+idle operation was 3-4 times larger than SOA production from the same vehicle operated over the Urban Dynamometer Driving Schedule (UDDS).
- (7) Fuel properties had little or no effect on primary PM emissions or SOA formation.

We have added the following text to the conclusions to explain the impact of using SMPS measurements rather than AMS:

Throughout this paper reported SOA production was based on AMS measurements. If SMPS-derived estimates were used instead, the clear distinction between vehicles with and without aftertreatment becomes even more pronounced. This is due to the fact that the SMPS-derived estimates of SOA are approximately a factor of 3 higher than AMS-derived SOA estimates for the non-DPF equipped vehicles but remain zero for the DPF equipped vehicles whether calculated from AMS or SMPS data. In addition, SOA yields would

increase by a similar amount to a median of ~27%, and the ratio of $SOA_{creep+idle}/SOA_{UDDS}$ would be ~10 rather than 3-4. Using SMPS data rather than AMS data does not change the conclusion that fuel chemistry has little or no effect on primary PM emissions or SOA formation.

R3.12

- I don't quite understand why the yield would be too sensitive for the seed particle concentrations- If the seed concentration is lower shouldn't particles just grow more (in size) compared to the higher seed concentration case? This should be explained more detailed. The yield might be sensitive to the seed size if the size range is small (Kelvin effect).

We do not understand the reviewer's question. We never claim that our yield estimates are sensitive to seed particle concentration.