Authors want to thank sincerely the referees for their contribution. With the help of referee comments, the manuscript has gone through a major revision and has greatly improved.

Anonymous Referee #1

As particulate matter emissions from diesel engines come under progressively better control, the focus will turn to emissions from gasoline engines. Gasoline-direct injection (GDI) engines are becoming increasingly common in the new vehicle fleet, and since they have many operational characteristics in common with diesels, they are a larger source of particulate matter emissions than traditional port injection gasoline engines.

This is an interesting and useful study of emissions from a GDI engine, including an estimate of the secondary organic aerosol which can form from the primary emissions through atmospheric photo-oxidation. The work appears generally sound but there are some issues of presentation and also some clarification is required.

The largest area of uncertainty relates to the measurements of secondary particle formation. These were made using a potential aerosol mass (PAM) chamber installed between primary and secondary dilution units and containing ozone concentrations at the exit of on average 6 ppm. These conditions are far more concentrated for both the exhaust pollutants and the oxidants than occur in the atmosphere and it is far from clear what the results for the secondary formation mean in an atmospheric context.

The sampling setup (PTD + ageing chamber + ejector) without PAM has been used extensively in vehicular exhaust emissions studies for over ten years, and it has been sampling system for dozens of publications of primary (in tailpipe) and delayed primary (seconds after tailpipe) particle emissions. In this study, we adapted the PAM chamber to this existing sampling system. The idea was to measure secondary particles with minimum precursor losses which was the reason for installing the PAM chamber after the primary dilution. We are anyway aiming at measuring the potential secondary aerosol mass, and that’s why minimal precursor losses are an absolute requirement. Otherwise, the oxidation processes of course are very accelerated and different than the actual processes in the atmosphere.

The Oxidant concentrations in the PAM chamber are higher (100-1000 times) than in the atmosphere (Kang et al., 2007, 2011), however the ratios between oxidants are similar to atmosphere. Kang et al. showed that the yields of OA from individual organic precursor gases were similar to those obtained in large environmental chambers and that the extent of OA oxidation appears to be similar to that observed in the atmosphere and greater than that observed in large environmental chambers and laboratory flow tubes. According to results of Tkazik et al., (2013) also the chemical evolution of the organic aerosol inside the PAM reactor appears to be similar to that observed in the atmosphere. They state that: “The mass spectrum of the unoxidized primary organic aerosol closely resembles ambient hydrocarbon-like organic aerosol (HOA). After aging the exhaust equivalent to a few hours of atmospheric oxidation, the organic aerosol most closely resembles semivolatile oxygenated organic aerosol (SV-OOA) and then low-volatility organic aerosol (LV-OOA) at higher OH exposures.” Also Lambe et al., 2015 states that: “This (…) suggests that in the range of available OH exposure overlap for the flow reactor and chambers, SOA elemental composition as measured by an aerosol mass spectrometer is similar whether the precursor is exposed to low OH concentrations over long exposure times or high OH concentrations over short exposure times.” Bruns et al., (2015) compare aerosol in smog chambers and PAM and reach the conclusion that “The chemical composition, as well as the maximum yields and emission factors, of the products in both the a-pinene and wood-combustion systems determined with the PAM and the SC agreed reasonably well."

A more through description of PAM chamber and previous studies using it was added to the manuscript (see chapters: 1. introduction, 2. Material and methods).

Additionally, the secondary pollutants are created in an atmosphere containing the primary pollutants and it is not clear whether they should be determined by difference (i.e. subtracting the primary concentrations) or if this has already been done.

Delayed primary concentrations as well as PM existing in tailpipe for pollutants have been subtracted from the secondary concentrations. This means that delayed primary includes also fraction of the semivolatile compounds that are part of the PM after tailpipe-end mimicking dilution.

Following sentence was modified to: "Fig. 7 shows chemical composition and O:C –ratios of primary and secondary (primary components excluded) exhaust particles for these three sections."

The fact that there are some divergences between results obtained with the PAM chamber and batch chamber studies most probably conducted at more realistic dilutions is attributed to differences in emissions and in wall losses (page 33267, lines 14-16). The presence of different exhaust and oxidant concentrations in comparison to those batch chamber studies may well also be an important explanation which the authors do not discuss.

That is true. All laboratory reactors are imperfect simulations of the atmosphere because they have walls that cause particle loss and can influence e.g. particle growth and composition. PAM chamber was developed to have minimum wall losses and it has been thoroughly compared to other chambers (e.g. Lambe et al., 2011, Kang et al., 2011). Kang et al. showed that the yields of OA from individual organic precursor gases were similar to those obtained in large environmental chambers and that the extent of OA oxidation appears to be similar to that observed in the atmosphere and greater than that observed in large environmental chambers and laboratory flow tubes. The main reason with PAM chamber was chosen to this study is that it has been thoroughly characterized by previous papers and thus we can build on that basis.

The sentence in question was rephrased to "The differences between the studies can be due to the differences in the emissions but also due to the differences in wall losses, exhaust and oxidant concentrations, and photochemical ages."

Most of the other points are relatively minor and including the following:

(a) Page 33259 – the fuel is defined but there is no mention of the sulphur content which is an important determinant of the particulate matter emissions. This should be clarified.

The fuel met the current European fuel standards where sulphur content is at maximum 10 ppm. Text "…with sulphur content of below 10 ppm" was added.

(b) Page 33260, line 26 – a density of 0.619 g dm-3 is described. However, it is not clear what this density relates to (is it the hydrocarbon particles?), but it seems likely to be in error by three orders of magnitude.

Indeed there was an error of three orders of magnitude. The text was corrected to "619 kg m^{-3}".

(c) Page 33263, line 15 should refer to ‘ammonia’ rather than ‘ammonium’.

Text was corrected. “Ammonia …”

(d) Page 33265, line 27 – this refers to the temperature of the catalyst but there has been no earlier description of the position of the catalyst in the pollution control system or the function of the catalyst. Is this an oxidation catalyst?

This is a three-way catalytic converter that is used in gasoline passenger cars, positioned after the exhaust manifold. In experimental section following was added: “… emission level Euro 5 with a three-way catalytic converter”

Anonymous Referee #2

Tailpipe emissions from a Euro 5 gasoline passenger car were either analysed directly, or aged in a PAM chamber prior to analysis. Ageing measurements were time-resolved, contrasting with previous smog chamber studies. The authors observe SOA formation was significantly higher than the primary emission, and that most SOA was formed from the cold start emissions. The authors conclude that legislation to limit SOA precursor emissions is necessary to improve air quality. The time resolved ageing aspect of this work is of interest to the community. This has only partly been investigated before, for example, Gordon et al. (1) examine SOA formation from different phases of a US driving cycle, albeit with a smog chamber, which lacks the resolution of a PAM chamber. For this reason, the ability of the PAM chamber to realistically simulate the ageing of emissions in the atmosphere is of central importance. Unfortunately, a number of details about the PAM and the experiments are missing from the article, but which must have been used in analysing/ interpreting the results presented. This is a serious omission. I also do not believe that experiments on one vehicle with a new and unestablished (and in this work, undescribed) methodology are sufficient to recommend changes to current emission legislation.

Therefore, while this paper is broadly consistent with recent work, I believe major revision is required.

With additional work it might be possible address the problem areas, broken down as follows:

Major issues:

The authors do not describe how background CO2 is corrected for in the AMS. This can be important given the very high CO2 in the exhaust. If CO2 Is highly variable and not accounted for correctly, this would lead to variations in the organic aerosol mass which are merely an artefact.

During all experiments CO_2 concentrations in exhaust emissions was measured in real time. AMS data is corrected for CO_2 using the CO_2 time-series. Following sentence was added to the manuscript: “CO_2 concentrations during the measurement period were significantly higher (up to 1450 ppm) than atmospheric values (400 ppm), thus CO_2 time-series was used to correct the artefact caused by gaseous CO_2.”

In the materials and methods section a single reference is given for a description of the chamber, Lambe et al., which I assume is a general reference for this kind of set up. This is not enough, and a more detailed description should be given, e.g. material, emission spectrum etc. A schematic of the experimental set-up should be shown in the main text.

A more detailed description about the PAM chamber was added to the manuscript. Also, a more comprehensive list of references was added: “(Kang et al., 2007; Kang et al., 2011; Lambe et al., 2011; Lambe et al., 2015; Tkacik et al., 2014)“. Schematic of the measurement setup was added as Figure 1.

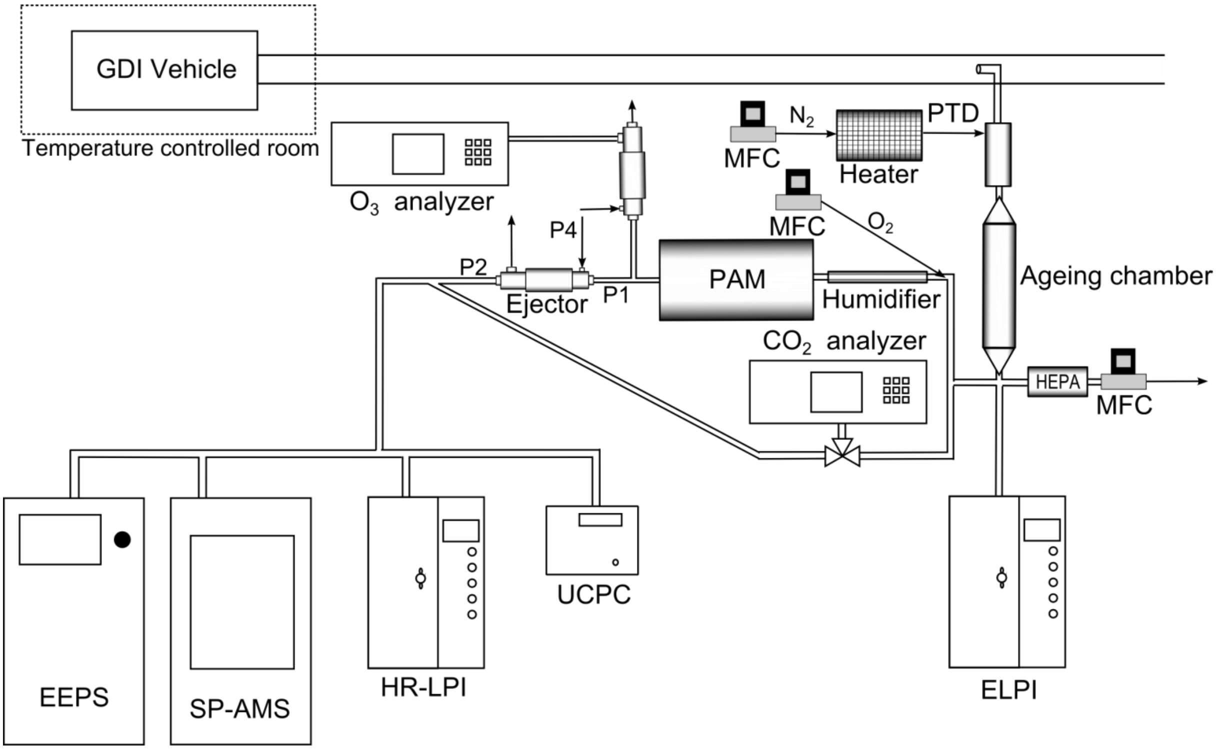

Figure 1. Schematic of the experimental setup (MFC = mass flow controller).

How well do the authors believe the PAM chamber simulates ‘real’ atmospheric chemistry, given the extremely rapid photochemistry? Some of the recent work by the Jimenez group may be of help (2-4) in understanding and discussing PAM chambers. Some of this work should also be referenced in the main text.

A detailed description of PAM chamber and how its results compare to atmosphere based on earlier studies was added to the manuscript.

The H:C vs. O:C graph of the measured SOA (Fig. S3) fits well on the slope given in Heald et al., (2010), as well as within the atmospheric SOA triangle shown in Ng et al., (2010). The authors acknowledge that the chemistry is different when the oxidation is very rapid, but given the similarity of the atomic ratios to atmospheric SOA, the PAM is good enough a tool to start estimating the magnitude of the SOA potential of the exhaust. In general, least SOA was measured when the O:C ratio was the highest indicating that this was due to low precursor emissions instead of low OH exposure, and vice versa the cold start had the highest SOA formation (high VOC emission) while O:C ratio was the lowest.

The graph showing O:C and H:C ratios was added to the supplement (Fig. S3).

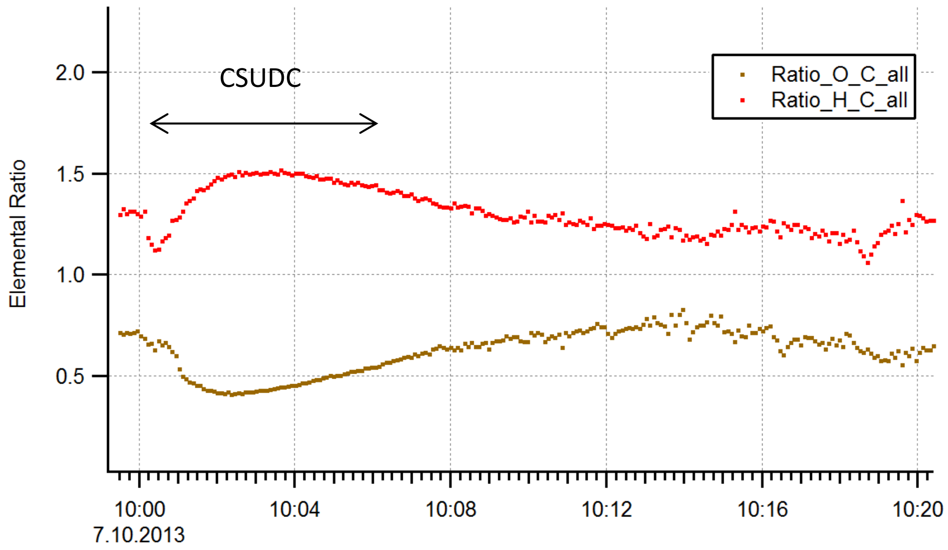

Figure S3. O:C and H:C ratios during the NEDC cycle.

SOA formation depends largely on OH concentrations (or rather, OH exposure, time integrated OH, see also Barmet et al. (5)). Yet, the OH exposure in the chamber is unknown/ unreported. How then, are we to know whether the last part of the driving cycle produces less SOA because there is less OH, or because less precursors are emitted? OH exposure is a function of photon flux, residence time, H2O concentration and OH reactivity (which may depend on VOC concentration). Given that all of these parameters are known, or can be estimated (from typical concentrations and OH reaction rates), it may be possible to estimate the extent to which OH exposure varies during the experiments, even if it cannot be quantified. The author's statement that therelative humidity was 'typically 60%' appears insufficient in this context.

The transient nature of the experiment makes the OH exposure estimation a difficult task, as the precursor (and seed) concentration varies. Based on SO_2 oxidation experiment (as described in Lambe et al., 2011), we estimate to maximum atmospheric equivalent OH exposure to be 1.03E+12 representing approximately 8 days of aging in the atmosphere.

On interactions with the chamber walls. The surface to volume ratio in the PAM chamber is presumably much higher than a traditional smog chamber (though dimensions are not given in the text). It is therefore important to take interactions with the walls into account. Since particle losses to the walls depend exponentially on suspended matter concentrations, some attempt to estimate these losses is required. Are gas phase SOA precursors lost to the walls? This can artificially surpress SOA formation (6). There is strong evidence that at least the 'sticky' gases e.g. ammonia are lost. This is because I note that the ammonium nitrate/ SOA ratio is low compared with both Nordin et al. (7) and Platt et al. (8). To what extent do vapour losses to the walls suppress SOA formation in the PAM chamber? How was the PAM chamber cleaned between tests? A blank test should have been performed/ reported (lights on, and measurement without sampling emissions).

A more thorough description of the PAM chamber, its use and its dimensions were added to the text.

The wall losses do indeed depend on the S/V ratio; however, the total wall loss is also an exponential function of the residence time in a chamber. Reducing the residence time thus also reduces the wall losses in comparison to long-residence time chambers. The gas phase wall losses for the PAM chamber are characterized in Lambe et al., (2011) with CO_2 and SO_2 pulses after a soak-in period, where they found transmission rate of 1.2±0.4, for the stickier SO_2, and somewhat delayed response compared to CO_2.

PAM chamber was cleaned before the test by running pure O_2-N_2 mixture from gas bottles with the same flow as during standard operation. One background aerosol test was even carried out overnight. Without H_2O feed, lights of the blank particle number concentration was 0 but when humidifier was used a ~20 nm GMD particle mode was formed downstream of the PAM which however was not visible in the AMS due to small particle size and small total mass.

The author ran each test twice, once with and once without a PAM, to establish a baseline for SOA formation. However, what was the time interval between the tests? It takes hours for an engine to cool (which is why regulations stipulate a 24h soaking time at ambient temperature before all tests). If insufficient time between tests was given, this can produce very large discrepancies in the emissions, particularly in the cold start period.

Cold-start NEDC tests with and without PAM were performed following the official protocol of the emission regulation in Europe; a preparation NEDC was run in the afternoon and the official run was driven in the following morning. The passenger car was kept in the temperature controlled room about 18 hours after the preparation test.

Only one car was studied, but changes to legislation are recommend by the authors. Such assertions may appear to enhance the importance of this study, but in fact serve to highlight the study's limitations. Furthermore, even if we are to accept that this one vehicle is truly representative of all other gasoline passenger cars, there are many factors to consider e.g. should we worry more about SOA or other pollutants such as NOX? What if reducing SOA could be achieved by increasing NOX e.g. by increasing the fuel air ratio in the engine, would this be helpful? Such considerations are clearly beyond the scope of the paper. Given that the paper could still be published without suggestions for changes in policy I recommend that all such discussions be removed from the text.

Indeed, for sure one vehicle cannot represent the whole gasoline passenger car fleet and this is one boundary limitation of the study. Secondary particle matter (organic or others) is not taken account in any way in the regulations which is not the case with e.g. NO_x and primary PM. However, there is no conclusive evidence that primary PM is more harmful than secondary PM, which currently means that primary PM regulations cannot ensure particle-free air for humans.

As the policy recommendations were not in the scope of this study, the last paragraph of Conclusions and the last sentence of Abstract were deleted.

Minor comments:

One disadvantage with sampling directly at the tailpipe is that while exhaust flow is variable, the sampled flow is constant. A different fraction of the complete exhaust is sampled as the flow rate varies. In theory, this could lead to a sampled composition different from that emitted, if composition and flow rate do not co-vary. As an example Zardini et al., assess this effect in the supplementary material of their article (Fig. S3) (9).

Yes, in this sampling system the inlet flow is constant while the exhaust flow changes. We have the data for exhaust flow rate in 1 second time resolution. This has been used to calculate the emissions as a function of time, taken account the mean delays from engine to instruments in the cases of with and without PAM chamber. In a way that the PAM chamber has averaging effect this is partly problematic, and a challenge also in the future for real-time secondary particle measurements. In the CVS sampling this is taken care of but there the problem is the background precursor levels in the CVS dilution air which is basically filtered ambient indoor air.

Mass spectra from the HR-ToF-AMS can be useful for interpreting the results. I strongly recommend the authors include these, at least in the supplementary section. The very high SOA formation may be related to very high loading in the PAM (which is much above ambient values). This should be discussed/ acknowledged in the text. Did the authors check that the aerosol volume/mass distribuiton was within the size cut-off of the AMS over the course of each experiment?

The mean mass spectra from the HR-ToF-AMS was added as Figure S2. Yes, the particle size distribution was measured with HRLPI and EEPS, and it was in the AMS particle size range.

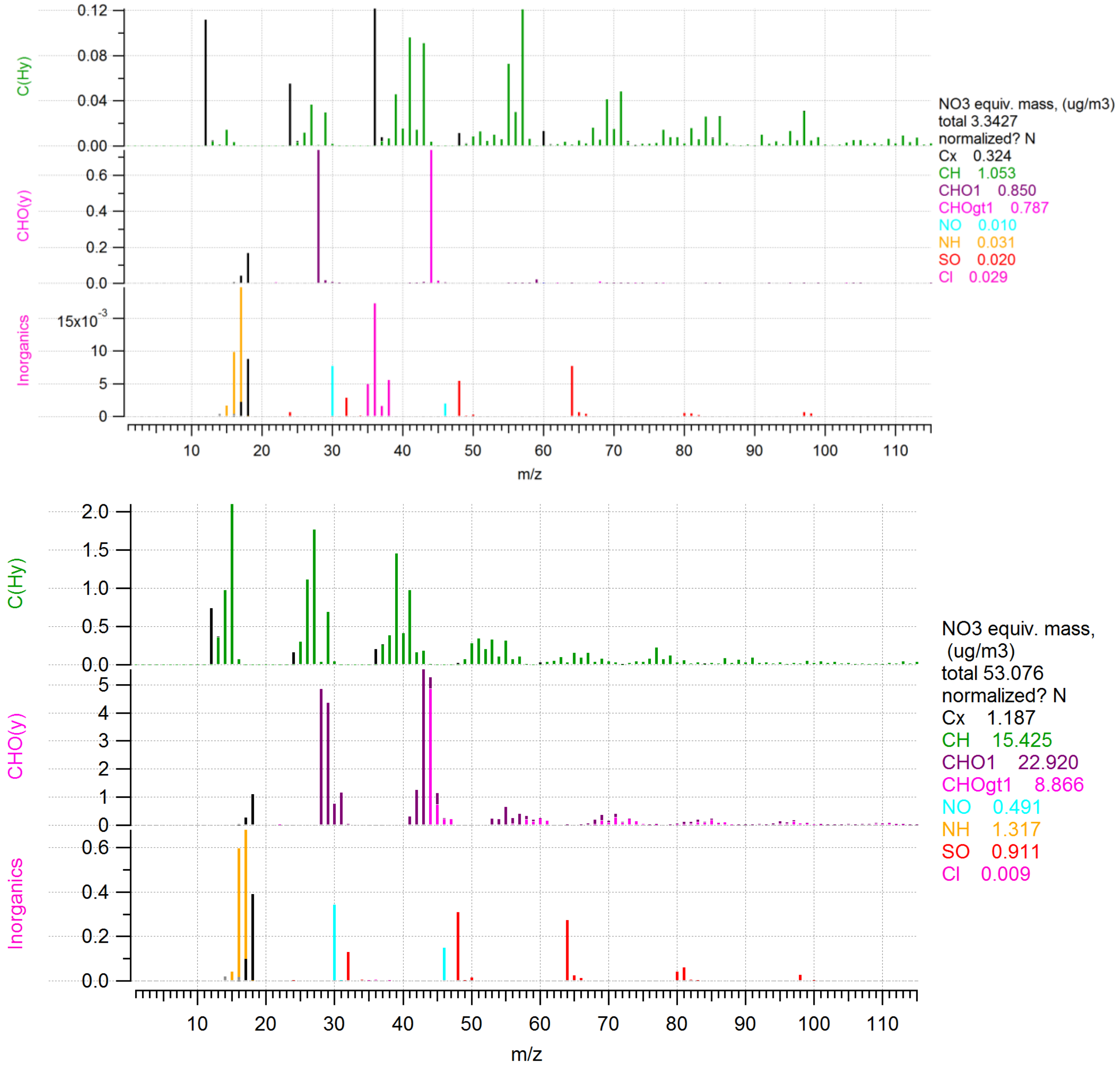

Figure S2. Mass spectra divided to different components (carbon (Cx), hydrocarbons (Ch), oxidized hydrocarbons (CHOx), inorganics) over the NEDC cycle for primary (upper panel) and all (lower panel) particles.

Specific comments:

Pg. 33253: The title should be changed to reflect the fact that secondary particle are not emitted, but formed. Suggest: 'Time-resolved characterization of primary particle emissions and secondary particle formation from a modern gasoline passenger car'

The title was changed as suggested.

Pg. 33255, ln1: 'changes in traffic systems' I understand this as changes to roads and other traffic related infrastructure. . .do the authors mean this? This is not within the scope of the paper in any case, and I would suggest starting with something like 'Changes in vehicle after-treatment technologies have significantly affected traffic related emissions in urban areas'

The starting line was rephrased to: "Changes in vehicle emission reduction technologies significantly affect traffic-related emissions in urban areas."

Pg. 33255, ln5/6: change to 'both primary (direct) particulate emission and secondary particle formation (from gaseous precursors in the exhaust emissions) need to be characterized.

Modified as suggested.

Pg. 33255, ln8: What is modern? State e.g. Euro standard and/ or vehicle age.

Modified to "a Euro 5 level gasoline passenger car".

Pg. 33255 Ln 9: No it doesn't. It is from tailpipe to atmosphere, quite a lot happens before the tailpipe (of course) and this is not investigated. Change to 'from tailpipe to atmosphere'.

Modified as suggested.

Pg. 33255 ln 19: Since this is a study on one vehicle only, 'strongly indicates' changes to any legislation is an overstatement. I suggest deleting this last statement.

This statement was deleted as suggested.

Pg. 33255, ln 27: This is misleading since-though I do not know about regulation everywhere-there are no particle mass (PM) limits for European or Californian gasoline cars. Particle number (PN) is limited only for direct injection gasoline. I suggest being clear here, and stating exactly what is limited for gasoline (since this is the focus of this study) with reference to sources.

Text was rephrased: "In order to reduce the adverse health effects and exposure of people by pollutants, the emission regulation for vehicles with direct injection engines include limits for particulate mass (PM), and in Europe for some vehicle types, particle number (PN) (Dieselnet), of which the PN limit is considered to be stricter." E.g. in Europe, the PM limits are also applicable for GDIs starting from Euro 5.

Pg. 33256 ln 10: Again, PM is not limited for gasoline cars. Therefore, gravimetric sampling is likely not done for type approval of gasoline passenger cars in Europe. The authors can point out that although not directly regulated, SVOCS are likely to be affected by THC/ NMHC limits.

Sentence was added: “Although not directly regulated, low-volatility organics are likely to be affected by gaseous hydrocarbons limits.” As stated in previous answer the PM limits are also applicable for GDIs starting from Euro 5.

Pg. 33257 ln 20: Suarez-Bertoa et al. refers to a Flex-fuel (ethanol) vehicle. The authors may keep this reference (and Nordin et al. should be kept), but Platt et al., 2013 (8) and Gordon et al., 2014 (1) should be included.

Added.

Pg. 33257 ln 21: In Suarez-Bertoa et al., emissions were sampled during a driving cycle, not at constant speed. Furthermore, although the smog chamber part of that study was not time-resolved many measurements e.g. of NOx and various VOCs were in fact time-resolved. The authors may refer to Chirico et al. (10) and Nordin et al. as examples of experiments lacking any time-resolved measurements/ sampling at idling or constant speed.

Changed as suggested.

Pg. 33259 ln 1: The authors should refer to their Figure 1a for the NEDC.

Referred.

Pg. 33259 ln 4: The NEDC has only two test phases (urban and extra urban).

Yes, but here we divided it into three phases to separate urban cold, urban hot and extra urban driving. Expression changed to: “here divided into three test phases”.

Pg. 33259: Please provide a schematic of the experimental set-up

It was provided as new Figure 1.

Pg. 33259 ln 9: What material is the transfer line? Was the transfer line heated?

The material of the thermally insulated and externally heated exhaust transfer line was Stainless steel AISI 316L. The heating mantle temperature was externally set to 100 °C. The actual exhaust temperature was way higher than 100 °C anyway.

The description was modified as follows: “As shown in Fig. 1, particle sampling was conveyed by a partial exhaust sampling system (Ntziachristos et al., 2004) at thermally insulated and externally heated exhaust transfer line (material Stainless steel AISI 316L).”

Pg. 33259 ln 21: The authors provide the typical temperature and relative humidity, but over what range/how much did these in fact vary?

Temperature and RH did not vary much, because the instruments were in a different room away from the vehicle and measurement time was relatively short.

Sentence was rephrased to: “Relative humidity (RH) and temperature were measured prior to the PAM with stable values of 60% and 22 °C, respectively.”

Pg. 33262 ln18: While the AMS community often uses ‘Chl’ for chlorine, this is in fact wrong, and it should be Cl.

All “Chl” references were changed to “Cl”.

Pg. 33262 ln19: It should also read ‘sulfate’ in the figure, not ‘sulphate’

All “sulfur” and “sulfate” references were changed to “sulphur” and “sulphate”.

Pg. 33263 ln21: Missing full stop

Corrected.

Pg. 33263 ln22: Secondary particles are not emitted

Title was changed to: “3.2 Secondary particle formation from a gasoline passenger car”.

Pg. 33265 ln27: How was the catalyst temperature measured?

This was measured from another GDI vehicle (similar size vehicle) with a K-type thermocouple installed close to the catalyst. We expect close to similar temperatures for this vehicle type too.

Pg. 33266 ln 11: Given that exhaust/ catalyst temperature do not seem to have been measured and that only one vehicle was tested, I do not feel that the evidence is strong enough to merit this conclusion.

“This is seemingly caused by high exhaust temperatures linked with high emissions of gaseous nitrogen compounds (see Fig. 3).” was changed to “This is seemingly caused by high emissions of gaseous nitrogen compounds (see Fig. 3).”

Pg. 33266 ln 19: I think this should be calculated and not calculative

We assume this refers to Pg. 33267 ln 19. “calculative” was changed to “calculated”.

Pg. 33267 ln 21: Not enough evidence to suggest an influence on atmospheric pollutant levels, given that only one vehicle was tested

“This highlights the important role primary and secondary emissions during cold start and the effects of emissions during cold start on atmospheric particulate pollutant levels.” was changed to “This highlights the important role of primary and secondary emissions followed by the cold start.”

Pg. 33268 ln 4: Suarez-Bertoa refers to a flexi fuel vehicle. The reference can be kept but Gordon et al 2014/ Platt et al., 2013/ Nordin et al., 2013 should be included in this comparison.

Text was rephrased as follow: “Previous studies for gasoline vehicle reported high O:C –ratios (up to 0.7) for secondary organic exhaust aerosol (Suarez-Bertoa et al., 2015; Platt et al., 2013) but also lower ratios of ~0.4 (Nordin et al., 2013).”

Pg. 33268 ln 6: Secondary particles are not emitted.

"In this study we characterized primary and secondary particulate emission and gaseous compounds emitted by a modern gasoline vehicle." was changed to "In this study we characterized primary particle and gaseous emissions and secondary particle formation from a Euro 5 emission level direct injection gasoline vehicle."

Pg. 33269 ln 22: These conclusions are all too strong given the limited sample size and should be removed.

Answered above under "major issues".

Figure 6: increase the size of the text in the axis labels/ legend. The caption should be written with the letters before the description, and the text clarified e.g. "(a) Chemical composition of primary emission (b) secondary formation. . ."

The figure (now Fig. 7) was updated. Caption was changed to "Figure 6. (a) Chemical composition of primary PM, (b) chemical composition secondary PM, and (c) the O:C –ratios of primary and secondary particulate matter for different parts of the NEDC cycle."

Supplement figure 1: text is rather small, font size should be increased

Font size was increased.

Table S1: Chl should be Cl. Numbers should be in subscript for chemical compounds

Changed as suggested.

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Anonymous Referee #3

This manuscript characterises the primary and secondary particle emissions of a modern gasoline passenger car using a state-of-the-art set of instruments. The concept of the study is very good and attempts to provide a complete picture of the total particle matter produced from a modern gasoline car. However, the manuscript suffers from a number of serious limitations related, mostly, to the methodology of determining secondary particle formation and should not be accepted for publication in its current state.

Main comments:

1. What are implications for the findings of this study of the difference between exposing a given amount of VOCs to very high levels of oxidants in a very short space of time (10s of seconds) to that of exposing the same amount of VOCs to lower, atmospherically realistic levels of oxidants for a longer period of time (~a few days)? In other words, could the results of this study under conditions of fast and high exposure oxidant conditions be used to inform our understanding of what actually happens in the atmosphere? How does this affect the chemistry of the system?, what are the implications for SOA formation and its relevance to the atmosphere given the higher supersaturation in the PAM reactor and its effect on nucleation potential?. The manuscript should include a wider discussion of the effect of OH levels vs OH exposure on the results of this study.

This is related to all research carried out with PAM chambers which are nowadays commonly used as a research method of secondary aerosol. This study is within the context of PAM research which practically means that results are not directly generalized to processes in the atmosphere. The nucleation potential with PAM is not that relevant, instead the PAM method is more focused to total secondary particle mass and composition analysis.

Discussion was added, see other comments, see e.g. other comment 2.

2. The light source (185 and 254 nm) used in the PAM reactor is a very strong UV source, which is not representative of tropospheric solar radiation (mostly >300nm). Given the complex mixture of VOCs generated from combustion sources and the wide range of their chemical structure and that of the early generations of their oxidation products, what are the potential implications of the high energy, sub 300 nm UV radiation on the chemistry of this complex system?. Potential differences caused by using this UV radiation both on the absolute mass as well as the chemical composition of the formed SOA needs to be acknowledged and discussed. Would the reported SOA mass produced under these conditions be relevant to SOA formed from combustion sources in the troposphere?

The maximum molar absorption coefficient of a representative hydrocarbon, benzene is around 200/M/cm, at 250 nm, whereas that of ozone is around 16 times higher (at 260nm). This indeed means that a fraction of the dissociation of the organic compounds may be driven by radiation rather than chemistry, if the hydrocarbon concentration is considerably larger than the ozone concentration. The authors expect the effect of UV dissociation to be mostly bond cleavage, which has similar consequences as the expected primary oxidative mechanism. If the dissociation effects are more aggressive, this is expected to decrease the observed potential mass. Also, Peng et al., 2015 used box model to study relative importance of oxidants (e.g. UV, OH, O_3 etc.) in the PAM chamber. They concluded that for field studies in forested regions and also the urban area of Los Angeles, reactants of atmospheric interest are predominantly consumed by OH. Ortega et al., (2013) and Peng et al., (2015) calculated the loss to photolysis and modelled the importance. In some cases (low RH, high external OH reactivity) photolysis of aromatics are important but in general they are low compared to loss to OH.

3. The manuscript does not contain any discussion of the effect of losses of VOCs and particles to the walls of the PAM reactor and the potential influence of this effect on the reported results. According to Lamb et al., (2011), the elemental ratios and SOA formation potential were strongly affected by reactor design and operating conditions, with wall interactions seemingly having the strongest influence on SOA yield. This is clearly an important factor that should be discussed and clarified in the manuscript given that this it reports absolute mass concentrations of chemical species as well as their emission factors.

The PAM system was specifically designed with lower surface-area-to-volume (SA/V) ratio to minimize wall effects (Lambe et al., 2011). We have measured primary particle losses for a similar PAM chamber (results shown in Fig. S1). In general primary particle losses are small especially in the particle sizes that contains most of the aerosol mass: 25% at 50 nm, 15% at 100 nm and below 10% above 150 nm.

Fig. S1 was added to supplementary material.

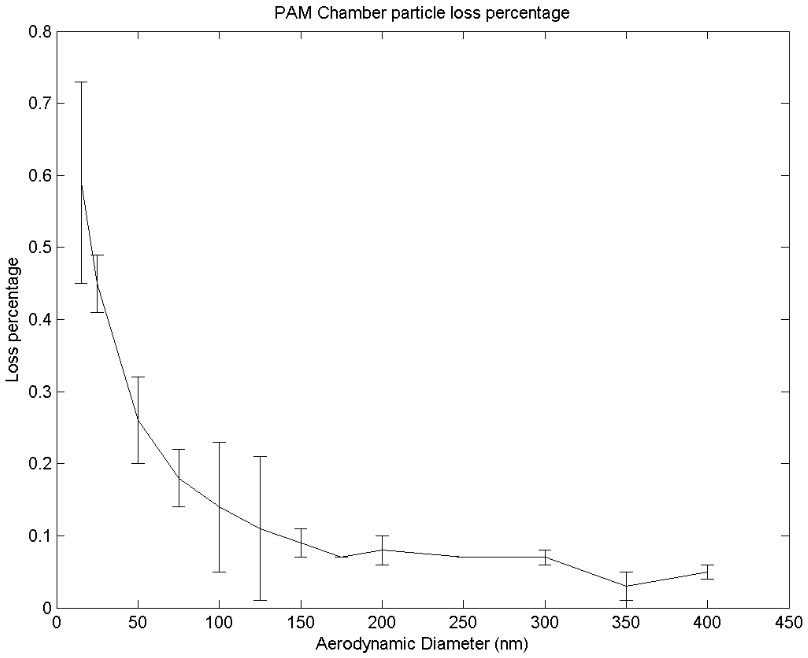

Figure S1. Primary particle losses in a similar PAM chamber that was used in the study.

Other comments:

1. The exhaust sampling conditions need to be explicitly stated in the materials and methods section. For example, what was the dilution ratio of the exhaust during the reported experiments? What was the temperature of the dilution setup?

The dilution ratio for primary dilution was about 12 and for secondary dilution about 8. The primary dilution N_2 was heated to 30 °C. The temperature details is found now in the text.

2. The conditions used in the PAM reactor should be explicitly stated. This should include specifying the PAM type used in this study (i.e. the 185/254nm or the 254nm only), the actual OH levels and the cumulative OH-exposure for these experiments should be mentioned or at least indicated. It is not sufficient to only state that the voltage of the two UV lamps was set at the maximum value of 190V (page 33259). In addition, the variability in OH levels or OH exposure during different stages of the experiment should be discussed given potential changes in PAM conditions as well as changes in the reactivity of the VOC mixture under different engine conditions.

A more thoroughly description of PAM chamber and operating conditions was added to the text. The main wavelengths in the UV lamps were 185 and 254 nm. The amount of oxidants during cycle was likely varying. Especially during the cold start the amount of oxidants was likely too low (due to high amount of emissions consuming the oxidants) and thus the mass during the first part of the cycle can be underestimated. However, during the second and third part of the cycle, the achieved oxidation levels were stable and likely the amount of oxidants was sufficient. With relatively higher SOA concentrations it's also likely that less oxidized material may partition to the particles. This will be the case also in the atmosphere.

Following more thorough description of PAM chamber was added to the manuscript experimental section:

"A potential aerosol mass (PAM) chamber is a small flow through chamber developed to simulate aerosol aging in the atmosphere. The PAM chamber was installed between the ageing chamber and secondary dilution units of sampling system. PAM chamber is thoroughly described by Kang et al., 2007, 2011 and Lambe et al., 2011, 2015. Shortly, PAM chamber is a stainless steel cylinder (length 46 cm, diameter 22 cm, volume ~13 l). In an effort to reduce wall effects the PAM flow reactor was designed with a larger radial/axial dimension ratio and a smaller surface to volume ratio relative to other flow reactors (Lambe et al., 2011, Kang et al., 2011). Two UV-lamps (BHK Ink., Ca) were used to produce oxidants (O_3, OH and HO_2) as well as UV-light (185 nm, 254 nm). The sample flow through the PAM chamber was set to ~9.75 l/min resulting average residence time of 84 s. Voltage of the two UV lamps was at maximum value, 190 V. Relative humidity (RH) and temperature were measured prior to the PAM with stable values of 60% and 22 °C, respectively. Typically ozone concentration after the PAM was on average 6 ppm. The PAM chamber was calibrated using average experiment conditions and following the same procedure described by Lambe et al. (2011). The corresponding OH exposure was calculated to be 1.03E+12, representing approximately 8 days of aging in the atmosphere.

PAM chamber has been used in different ambient environments (Palm et al., 2015; Ortega et al., 2015; Tkazik et al., 2013) and also thoroughly characterized in the laboratory conditions via measurements and modelling (e.g. Lambe et al., 2011, 2015; Peng et al.; 2015, Ortega et al., 2013). The Oxidant concentrations in the PAM chamber are higher (100-1000 times) than in atmosphere (Kang et al., 2007), however the ratios between oxidants are similar to atmosphere. Several studies (e.g. Kang et al., 2007, 2011) have compared PAM results to atmospheric results. Kang et al. (2007, 2011) showed that the yields of OA from individual organic precursor gases were similar to those obtained in large environmental chambers and that the extent of OA oxidation appears to be similar to that observed in the atmosphere and greater than that observed in large environmental chambers and laboratory flow tubes. Also, according to results of Tkazik et al., (2013) the chemical evolution of the organic aerosol in the PAM reactor is similar to that observed in the atmospheric measurements. Also, Tkazik et al., (2013) observed that the mass spectrum of the unoxidized primary organic aerosol closely resembles ambient hydrocarbon-like organic aerosol (HOA) and that aged PM firstly resembles semivolatile oxygenated organic aerosol (SV-OOA) and then low-volatility organic aerosol (LV-OOA) at higher OH exposures. In this study, cycles were firstly run without the PAM chamber to measure primary emissions and secondly with the PAM chamber in order to study the formation of secondary particulate material. Before the experiment, the PAM chamber was cleaned by running pure N_2-O_2 mixture with UV-lights on.

Transmission efficiency of gases (CO and SO_2) in PAM chamber has shown that wall losses in the PAM chamber are very small (Lambe et al., 2011). Primary particle losses for a PAM chamber (results shown in Fig. S1) are in general small especially in the particle sizes that contain most of the aerosol mass: 25% at 50 nm, 15% at 100 nm and below 10% above 150 nm."

Following description and figure was added to the supplementary material:

"High oxidant levels were necessary to ensure the availability of oxidants in chamber during the cycle. AMS O:C, and H:C –ratios and f43, f44 ratios were used to follow the oxidation. After the cold start, high concentrations of gaseous and particulate emissions were observed. Elemental ratios show that right after cold start the O:C ratio dips and H:C ratio increases, and it is possible that temporarily the amount of oxidants is not sufficient to oxidize all compounds to the maximum rate. It is possible that during the cold start and following few minutes the forming secondary aerosol mass is underestimated. However, during five minutes the situation stabilizes and for rest of the cycle the oxidation levels seem to remain stable."

Following addition was made to Results section 3.2.2: "At the beginning of the test cycle, the concentrations of organic compounds in the secondary particulate matter were about 100 times higher than their concentrations in primary particles, while the O:C ratio dipped below 0.5 (see Fig. S2)."

3. The actual O3 levels in the PAM reactor should be mentioned and their effect on suppressing reaction between Nitric Oxide (NO) and organic peroxy radicals (RO2) resulting from the OH oxidation of VOCs and the potential influence of this suppression on SOA formation and composition should be discussed.

Unfortunately Ozone measurement results were not saved during these two driving cycles due to technical issues. The values were followed by the users from the screen.

The exhaust emissions contain a large variety of VOC's and NO_x. Compounds with low number of carbon atoms are less likely to form SOA, whereas aromatic compounds are considered the most important SOA precursors amongst antropogenic hydrocarbons. Also, the SOA yields tend to decrease at high-NO_x conditions. Measurements show that the amount of hydrocarbons and NO_x were elevated during cold start and at the end of cycle during the high-way part. Highest secondary aerosol emissions were observed during these same periods.

4. Have the reported PAM results been corrected for corrected for size-dependent particle transmission efficiency as shown by Lamb et al., (2011)? This should be clarified.

Measured PM concentrations or size distributions are not corrected for size-dependent primary particle losses (Figure S1, measured with a similar PAM chamber) which were relatively low most likely somewhere around ~10% for the total mass. The measured losses were overall smaller than previously reported by Lambe et al., (2011). Actually, the secondary particle size distribution inside the PAM is constantly changing due to nucleation/condensation processes which make the accurate corrections difficult. However, losses for primary particles were measured and included in the supplementary material (Figure S1).

5. SOA produced in this study was reported to be higher or similar to that produced in two previous studies (Suarez-Bertoa et al., 2015; Platt et al., 2013). The authors did not provide sufficient discussion with regards to the conditions under which those two other studies were conducted; in particular, their light sources and oxidant levels assuming they also used reasonably similar gasoline passenger cars.

The chapter was corrected to include more details on previous studies:

"For instance, Suarez-Bertoa et al. (2015) reported 2–4 times higher values for the secondary particle emissions (12m3 smog chamber, 40 UV lights with peak emissions at 350 nm and flexfuel vehicle, fuel E75,E85) when compared to the primary organics and BC. In the diesel exhaust study of Chirico et al. (2010), the secondary and primary particle emissions were at similar level (27 m3 smog chamber, four xenon arc light sources, diesel). However, in the study of Platt et al. (2013) SOA emission (12.5 m3 mobile smog chamber, 40 UV lights, gasoline light duty vehicle) was around 14 times higher than primary organic aerosol (POA) emission when they measured the emissions of gasoline vehicle for the NEDC cycle. All of these studies were conducted using a batch chamber while in our study a flow through chamber was used. The differences between the studies (vehicle, fuel, chamber, dilution setup, etc) can be due to the differences in the emissions but also due to the differences in wall losses and chamber conditions."

6. Does the version of the PIKA code used for the analysis of the HR-AMS data use the old Aiken et al., (2008) calibration method or the more recent updated calibrations by Canagaratna et al., (2015)? This has a direct effect on the reported O:C values and should be stated. Also, on a related note, what AMS collection efficiency value has been used for reporting the AMS mass? How was the corrections for gas phase CO2 applied to the AMS data to ensure that only particulate contribution to this m/z channel is reported.

Old PIKA version (1.16g) was used in data handling, thus all elemental ratios are calculated based on Aiken et al., 2008. However, new PIKA version and Canagaratna et al., 2015 elemental analysis was tested. Results were typically very similar for elemental ratios. However, Canagaratna et al., 2015 elemental analysis was observed to produce unrealistically large values. Canagaratna et al. 2015 method is developed for ambient elemental analysis, which might affect the results in the case of engine emission study. Collection efficiency of 1 was used in this study. CO_2 was measured during measurements. CO_2 time-series was used to correct the data for CO_2.

Following sentences were added to text:

"Elemental analysis (based on Aiken et al., 2008) was performed on the HR-ToF-AMS data to determine the aerosol hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios. CO_2 concentrations during the measurement period were significantly higher (at maximum 1450 ppm) than atmospheric values (400 ppm), thus CO_2 timeseries was used to correct the artifact caused by gaseous CO_2. Collection efficiency of 1 was used in this study."

7. The sulphate profile in Fig 5 appears to anti-correlate with the organic loading. I wonder if this this is a real effect or an artefact with the AMS measurement given the known interferences between organics and sulphate at a number of m/z channels. I realise that this measurement was taken using an HR-AMS, where such effect could be avoided more easily compared to a unit resolution AMS, but I found the temporal trend intriguing!

All results are calculated from high-resolution spectra and sulfate and organics should not interfere each other. Mass defect of sulphate species (SO, SO_2, SO_3 etc.) is negative, whereas mass defect for organics is positive, enabling quite good separation in mass axis terms. Also, a good correlation between individual sulphate ions (SO, SO_2 etc.) was observed, suggesting that they were well separated from isobaric organic ions. In addition, if high organic loadings peaks would interfere sulphate, the influence should be seen as increase in sulphate. The trend in sulphate and organics is in our opinion real.

8. The discussion regarding growth of nanoparticles during deceleration and their contribution to secondary aerosol formation (page 33269 form line 12) is not clear and needs re-writing in order to clarify the point of the authors. Where is the evidence referred to in this discussion about the real atmosphere?

The corresponding text was rephrased to: “These nanoparticles grew in particle size due to the condensation of highly oxidized engine origin compounds; these oxidized compounds were formed in our experiment in the PAM chamber but when forming in the atmosphere likely exhibits similar behaviour and prefer to condense on the nanoparticles. Thus, our results indicate that also nanoparticles can contribute to atmospheric secondary aerosol formation, especially on size distribution of secondary particles.”

Editorial changes:

Page 33255, line 25: change “on” to “to”

Changed.

Page 33260, line 12: should be 600 oC

Was changed to “by normal tungsten vaporizer at 600 °C”.

Page 33264, line 10: shouldn’t this be Fig 4 instead of 3?

Yes that’s right. The figure number was corrected.

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