

***Interactive comment on “Technical note: Emission factors, chemical composition and morphology of particles emitted from Euro 5 diesel and gasoline light duty vehicles during transient cycles” by Evangelia Kostenidou et al.***

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Referee #1:

The manuscript details gas- and particle-phase emissions from 3 diesel vehicles and 4 gasoline light duty vehicles (1 PFI and 3 GDIs) certified to the Euro 5 emission standards. All vehicles were tested on a chassis dynamometer on 2 different driving cycles. Main conclusion from this study is that GDI engines emit more PM and gas-phase PAHs compared to a single PFI engine. The suite of instrument used measurements is com-

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prehensive. The manuscript is well written and the measurements from this study are largely in-line with existing studies. However, given the small vehicle fleet size (and just a single PFI vehicle tested), I expect to see a more detailed discussion of the literature, especially for PFI gas and particle phase emissions. The authors often carefully report measurements of highly resolved instrumentations (e.g., PAHs, TEM XPS measurements) but fail to convey to the reader the main point (and the importance) of conducting these time consuming and expensive analyses. I recommend publication after the authors address these comments (and the below).

We added to the 4th paragraph of the introduction more literature work on cars technology (Wang et al., 2016; di Rattalma and Perotti, 2017; Chan et al., 2014; Short et al., 2015). We also expanded the 4th paragraph of the introduction as: “Despite many studies investigated vehicles’ emissions in the past, non-regulated pollutants are still not well identified and quantified for recent car’s technologies. European databases (as COPERT 5) are still missing information on PM chemical composition preventing a full assessment of car emissions on urban air quality and health. This work provides a detailed description and comparison of PM emissions in terms of chemical composition and emission factors from three diesel and four gasoline (both GDI and PFI) commercial Euro 5 light-duty vehicles tested on a roll bench chassis dynamometer facility. The chemical speciation of particulate matter included BC, organics, sulfate, ammonium, nitrate and PAHs and was accomplished using real time and high-resolution instrumentation, providing real-time emission profiles and information on the impact of after-treatment devices along the cycle. Particles morphology, surface structure and elemental composition were furthermore investigated using offline analysis.” These time consuming and expensive analyses reveal new features of cars pollutants: as the functionalized PAHs and metallic nanoparticles and the potential health related impacts.

Minor comments: Line 24: Odd transition, both PAH and NPAH concentrations were higher in GDIs compared to the PFI engine.

Yes, it is true. We synthesized the sentence as follows: “Both PAHs and nitro-PAHs

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emissions from the GDI technology were more than a factor of 4 higher compared to the vehicles equipped with a PFI system during the cold start cycle”

Line 26: lower detection limit.

We replaced “close to” with “below”.

Line 27: Emissions of Aitken-mode particles (particle with diameter < 30 nm).

Aitken-mode particles are particles with diameters between 20nm and 100nm, so the particles below 30 nm cannot be considered as Aitken-mode particles. In the reality those particles were 15 nm and so we replaced “Emissions of nanoparticles (below 30 nm)” with “Emissions of particles around 15 nm”.

Line 73. Citation needed when citing mentioning that NH3 might enhance NPF.

We added some citations from the following articles: P. Korhonen et al., 1999, Ortega et al., 2008; Pikridas et al., 2012; Kürten, 2019.

Lines 72-73: “Despite all the previous studies for the characterization of the vehicles’ emissions, an integrated and comprehensive analysis for the understanding of these emissions is missing.” Not sure what this means. Either be specific or remove.

As mentioned before, we changed this part as into: “Despite many studies investigated vehicles’ emissions in the past, non-regulated pollutants are still not well identified and quantified for recent car’s technologies. European databases (as COPERT 5) are missing information on PM chemical composition preventing a full assessment of car emissions on urban air quality and health. This work provides a detailed description and comparison of PM emissions in terms of chemical composition and emission factors from three diesel and four gasoline (both GDI and PFI) commercial Euro 5 light-duty vehicles tested on a roll bench chassis dynamometer facility. The chemical speciation of particulate matter included BC, organics, sulfate, ammonium, nitrate and PAHs and was accomplished using real time and high-resolution instrumentation, providing real-time emission profiles and information on the impact of after-treatment devices along

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the cycle. Particles morphology, surface structure and elemental composition were furthermore investigated using offline analysis.”

Table1: Why is the numbering for PFI, GDI, and D vehicles not continuous? This is confusing, I suggest you adjust. There is a single PFI vehicle presented in the manuscript, yet it is numbered PFI4, leaving the reader the impression that the data from at least 4 PFIs were reported. Also, the use of the blue and red colors makes the table harder to read, I suggest keeping all text in black.

The reviewer is right there was a mistake in the numbering, which was based on the whole set of cars measured, but for this paper we selected EURO5 cars only. We changed the numbering as follow:

D1→ D1

D3→ D2

D4→ D3

GDI1→ GDI1

GDI3→ GDI2

PFI4→ PFI

GDI5→ GDI3

We changed the color in Table 1, turning everything in black.

Line 94: add reference for the WLTC cycle. I also think that a brief description of each driving cycle is needed in section 2.1.

The cycles are well known and therefore we refer to literature for their description. We reformulated the sentence as follows: “The emissions of vehicles D3 and GDI3 (D2 and GDI2 with the new numeration) were tested using the Worldwide Harmonized Light Vehicles Cycle (WLTC), (Tutuianu et al., 2015), which is the official cycle for emissions

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legislation of Euro 6 cars, while the vehicles. ...”

Line 98: “The line was heated at 80-120 C..” was this to reduce semi volatile losses?

Yes, the reviewer is right, we had simultaneous measurements of VOCs, IVOCs and SVOCs. We added the sentence: “The line was heated at 80-120o C in order to reduce losses of the semi-volatile compounds (SVOCs) which were analyzed by PTR-MS and GC-MS techniques (Marques et al., in preparation).”

Line 104: (Table 1).

We put the parenthesis before the word Table.

Section 2.2.1: The authors do not discuss the CE of the AMS. Is it 1? 0.5? the choice of CE should be explicit in the manuscript. Also, have the authors compared the AMS non-refractory OM mass to filter OC mass? If OC filters were collected and analyzed the comparison between OC and OM should be provided in the MS or the SI.

The CE selection was discussed in the 2.3.1 section (Organics and PAHs). We used a CE of 1 following previous studies for engine exhaust emissions which used a CE of 1 (Canagaratna et al., 2004; Slowik et al., 2004; Dallmann et al., 2014; Eriksson et al., 2014; Bruns et al., 2015; Herring et al., 2015). Unfortunately, we did not collected filters for total OC measurements so a direct comparison between filters and AMS cannot be done.

Section 2.2.3: This section discusses TEM sampling and not “exhaust gas sampling”. Please adjust.

We changed the title into “Off-line analysis: TEM-EDX and XPS techniques”.

Section 2.3 is named “instrumentation” so is section 2.2. Adjust.

We changed the title into “Methods”.

Line 140: “CO<sub>2</sub> (the signal at m/z 44): : :”

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We put a comma after the word CO<sub>2</sub>, so that the sentence becomes clear. The signal at m/z 44 in AMS could have either gaseous or particulate origin. In our case (fresh vehicle emissions) the vast majority of this signal is deriving from gaseous CO<sub>2</sub> (rather than from particulate oxygenated compounds), thus it was totally removed from the fragmentation table in order to avoid artifacts in the organic mass concentration.

Line 162: “the distance-based EF”.

We added the characterization distance-based before EF.

Line 164: are the concentrations C(t) background corrected?

The concentrations C(t) were indeed corrected subtracting the background concentrations when there was only clean air passed. These concentrations were practically zero. We added in the text that the C(t) concentrations were background corrected.

Line 165: What is DR? dilution ratio?

DR is the external dilution ratio. We updated the manuscript.

Line 170: BC is not measured by AMS. Adjust.

We reformed the sentence into: “Figure 1 shows the particle mass concentration transient profile of the BC recorded by the Aethalometer and those of, organics, sulfate, nitrate and ammonium measured by the HR-ToF-AMS. . .”

Line 173: I was surprised to see that the BC fraction of PM emissions for GDI5 was so high for GDIs (>96%). The authors should provide how often this is seen in the literature.

Indeed, this high BC fraction has been observed in previous studies for GDI Euro 5 vehicles (e.g., Platt et al., 2017; Pieber et al., 2018), who found that the BC emission factors during cold WLTC starts were one order of magnitude higher compared to the organic emissions factors. In these studies, BC was around 80-90% of the BC+OA sum. Later in the manuscript (section 3.3 on emissions factors) we already provide

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a direct comparison between our BC and OA EFs to the corresponding EFs of those papers. We decided to compare directly the EFs rather than the percentages. To our knowledge we did not find many other papers providing both BC and organics EFs for GDI Euro 5 vehicles.

Line 174: 120 mg/m<sup>3</sup> should be for BC and not organics.

The reviewer is right: 120 mg m<sup>-3</sup> refers to BC while and 1600 µg m<sup>-3</sup> to organics. We correct the above sentence.

Line 185: Refer to panels b and c in Fig 2 as Figure 2b and 2c. Right now, “(a) : : (b and c)” is confusing. Adjust also in other instances in the text.

We reformulated the sentence into: “Figure 2 shows the PM emissions of the D1 car (equipped with a CDPF) in terms of chemical composition (Figure 2a) and particle size distribution (Figures 2b and 2c) during a cold urban and three consecutive motorway cycles.”

Lines 190 and 196: The authors claim that the sulfate measured is in ammonium bisulfate form yet offer no justification to why that is. Either justify your assumption or remove.

We claim that the sulfate measured is in the form of ammonium bisulfate, because of the mass ratio of the sulfate/ammonium: the measured mass concentration ratio of the sulfate/ammonium was around 5, which means it is rather ammonium bisulfate, which has a sulfate/ammonium mass ratio equals to 5.33. In case of ammonium sulfate the corresponding ratio would be close to 2.67. We added a clarification that the assumption of ammonium bisulfate is based on the sulfate/ammonium mass concentration ratio: “The identification of ammonium bisulfate was based on the sulfate/ammonium mass concentration ratio.”

Line 207: “Figure 3 shows the HR-AMS mass spectra for the GDI5 and the D3 vehicle during the first (cold start?) and last 2 minutes (hot running exhaust?) of each cycle.”

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We assume that the reviewer means D4 instead of D3 as Figure 3 contains the MS of the GDI5 and D4; with the new numeration these cars correspond to GDI3 and D3. These mass spectra of Figure 3a refer to the two first and two last minutes of each cycle (cold urban, hot urban and motorway) of the GDI car. This means only the 2 first minutes of the cold cycle correspond to a cold start, while all the remaining spectra correspond to hot engine conditions. The engine is “really cold” only during the first cold start of the day, while after that first cycle, the hot urban or the motorway will start with a warm/hot engine (pre-heated). Thus, the beginning of the hot and motorway cycles is characterized by hot engine conditions (this is a very well-known procedure in engine tests). In order to avoid any confusion, we reformulated the sentence as follows: “Figure 3 shows the HR-AMS mass spectra for the GDI3 and the D3 vehicle during the first two and last two minutes of each type of cycle (cold urban, hot urban and motorway).”

Line 228: “Sulfur containing ion fragments were mostly emitted from hot engines (end of urban cycle and motorway cycle) and are tentatively explained by the release of some lubricant oil.” Why would this be the case for the GDI5 vehicle and not for the D3 vehicle as well? It is clear from Figure 3 that only the GDI5 showed trace amounts of sulfur containing organic fragments.

Again, we assume that the reviewer means D4 instead of D3 as Figure 3 contains the MS of the GDI5 and D4; with the new numeration these cars correspond to GDI3 and D3. Figure 3a shows that the higher contribution of sulfur containing fragments are observed at the end of the cold urban, at the end of the hot urban and at both the beginning and the end of the motorway cycle of the GDI5 (GDI3 with the new numeration). This shows that these compounds are emitted when the engine is hot. On the contrary Figure 3b, which refers to the D3 car, shows that the contribution of the sulfur containing fragments was 0% either the engine was cold or hot. Thus, based on the HR mass spectra speciation, D3 car does not emit sulfur containing fragments.

Figure 3: It is worth mentioning in the text that there are no significant differences in

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the non-refractory organic composition of exhaust particle emissions for cold start vs hot start.

At the line 230: we added the following sentence: “Except for the above differences (presence of oil droplets and sulfur containing fragments) no other significant variability was observed between the cold and the hot start HR mass spectra”.

Line 261: The author mention that MPAH are carcinogenic compounds. Looking at Table S3 in the SI, it seems that MPAH emissions during hot start (the large fraction of a trip) are usually larger than during cold starts which can have important implication on public health near emission sources.

The authors suggest to the reviewer to look at Figure 4 instead of Table S4 which presents some of the major PAHs (not all the PAHs). On the other hand, Figure 4 shows all the PAHs families in % and from this figure it is not that clear the increase of MPAHs during hot cycles. This is the case for the PFI car, but it is not the case for the diesel. For the GDI vehicle the corresponding fraction is very alike between the 3 cycles. We do prefer at that stage to avoid a general conclusion. In our future publication on Euro 6 cars, we will discuss more in details PAHs speciation since we could collect many more filters in parallel to AMS analysis and it would be easier to have a more conclusive statement on the trend of MPAHs and NO<sub>2</sub>PAHs vs UnsubPAHs. We will also have the opportunity to analyze NO<sub>2</sub>PAHs collected on filters.

Line 276: replace “the car” with “vehicle tailpipe”.

We make the above replacement.

Line 293: “(below 20 nm)”. Give exact statistics (mean, std). This data is helpful for studies looking at the optical properties of fresh combustion soot particles.

For the cold cycle the gasoline primary particles had a mean diameter of  $24.2 \pm 4.1$  nm and during the hot cycles on mean diameter of  $14.5 \pm 3.4$  nm (these values have been added to the text).

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Line 306: The authors assume that inclusions in soot particles are metals. The authors should provide a reference for this claim.

The paragraph has been revised and literature work added. “Figure 6 (j-l) depicts soot particles from the D3 car tiny sparse dark spots were ubiquitous within the soot particles and were interpreted as metal inclusions. Unfortunately, EDX could not reveal their chemical nature due to the very small amount of material in these inclusions as they were very small (typically less than 0.5 nm) and their spatial density was low. Nevertheless, we suppose that these inclusions were metallic and resulted from the after-treatment device of the FBC-DPF vehicle (D3), which use metallic salts or organometallic additives into the engine combustion chamber. Upon combustion, the additive produces nanoparticles of metal oxides that are mixed with soot particles and get deposited on the DPF walls. The role of these metals is to reduce the DPF regeneration temperature (Ntziachristos et al., 2005; Majewski and Khair, 2006; Song et al., 2006). During DPF regeneration soot oxidation takes place, the DPF filtration efficiency is consequently reduced, (R’мили et al. 2018) allowing for few minutes the emission of the ash particles attached on/or enclosed in soot may occur (Liati et al., 2018)”.

Lines 331-346: it is not clear to me what are the main points the authors are trying to make from that large paragraph.

The point was to describe the nature of the soot surface. Indeed surface defects and bound oxygen may imply higher reactivity and possible health implication of soot particles.

Line 412: replace “should be taken into account”.

We replaced it with “should be considered”.

Figure 1: Change OA in caption to organics.

We replaced “OA” with “Organics”.

Figure 3: make font in panel a same as panel b.

We changed the font in panel a.

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