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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "Identification and quantification of particulate tracers of exhaust and non-exhaust vehicle emissions" *by* Aurélie Charron et al.

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–GENERAL COMMENTS– Charron et al present chemical speciation of particulate matter collected from chassis dynamometer experiments as well as near-road and urban background sites. Such measurements are important for understanding both exhaust and non-exhaust emissions and their variability across changing and variable vehicle ïňĆeets as well as locations with different trafïňĄc conditions and meteorology. The wide range of measured species (which are effectively contextualized within other measurements in the literature) strengthens the dataset, but also presents challenges for clear communication. A number of editorial comments are given in order to clarify



ambiguous or unclear meaning as well as to correct grammatical errors. Improving the clarity of ïňĄgures would also strengthen the manuscript. RESPONSE: I thank the referee on behalf of all co-authors for the proposed very accurate amendments and the time spent on this paper.

–SPECIFIC COMMENTS– SECTION 2.1.1 and SECTION 3.2.3: (1) Please provide the sample ïňĆowrates, dilution ratios, and sampling time duration for each vehicle tested (perhaps in supplemental section I). RESPONSE: A table is added in the SI I (Table I-2).

(2) The authors note that differences in dilution ratios could affect the distribution of n-alkanes due to differences in phase partitioning among species with different vapor pressures. Differences in ïňĄlter face velocity could also lead to differences in vapour adsorption (positive artifacts) and particle evaporation (negative artifacts), resulting in different degrees of over-estimation of particle-phase organic material across different sampling conditions (and thus different vehicle types). For chassis dynamometer experiments, ïňĄlter face velocity differs by up to a factor of 1.67 for molecularly speciated measurements and up to a factor of 6 for EC and OC measurements. Would quartz ïňĄlter sampling artifacts due to differences in sample ïňĆowrates (ie. face velocity, pressure drop) affect the authors' conclusions about distribution of n-alkanes as well as OC/EC values? (In particular, how would quartz ïňĄlter artifacts affect the authors' conclusions about the impact of the particulate ïňĄlter retroïňĄt on OC and EC emissions?) REFERENCE Solomon, P. A., et al., Evaluation of PM2.5 chemical speciation samplers for use in the U.S. EPA national PM2.5 chemical speciation network, EPA Rep. EPA-454/R-01-005, Off. of Air Qual. Plann. and Stand., Research Triangle Park, N. C., 2000. REFERENCE McDow, S. R., and J. J. Huntzicker, Vapor adsorption artifact in the sampling of organic aerosol: face velocity effects, Atmos. Environ., Part A, 24, 2563 – 2571, 1990. RESPONSE: This is an interesting question from the reviewer. Quality sampling of exhaust PM is not straightforward and we attempted to make the best choices in order to have repeatable analyses of PM collected from the CVS of

the chassis dynamometer while considering the constraints associated with such sampling conditions. Filter face velocities were similar to, or not too far from, the one of atmospheric near-road measurements (47 cm/s) for chassis dynamometer samplings of 50 l/min (48 cm/s) and 40 l/min (38 cm/s). Then we can expect that this parameter will not significantly modify the partition of n-alkanes in comparison to near-road measurements since PM samplings for organic speciation are made at 40 and 50 l/min. Conversely, very low sample flow rates (5 and 10 l/min, corresponding to filter velocities of about 5 and 10 cm/s respectively) are used for PM samplings dedicated to EC and OC measurements in the exhaust of diesel vehicles non-retrofitted with PF (Euro 3 and Euro 4 diesel vehicles). Indeed, these very low filter velocities may possibly be responsible for enhanced adsorption of organic vapours by the quartz filters, leading to positive artefact for OC (McDow and Huntzicker, 1990; Turpin et al., 2000; Vecchi et al., 2009), while EC would not be affected by filter face velocity (Vecchi et al., 2009). However, the magnitude of such potential artefact is difficult to estimate (Viana et al., 2006) and especially for such conditions that are very different from those in the atmosphere (in particular the very high concentrations of organic gases and OC that are also likely to influence the adsorption equilibrium of the filter with the incoming gas-phase concentrations). If we admit that the positive artefact is more important for these samples, this means that the real OC/EC ratios would be even lower for non-retrofitted diesel vehicles. Therefore, this does not change the conclusion regarding the impact of PF equipment on OC and EC emissions. Therefore, we included the following comment in part 2.1.2 (Exhaust sampling), lines 20-27 (new version of manuscript): "Conditions of vehicle tests are detailed in the supplemental section (Table I-2). Filter face velocities for chassis dynamometer samplings dedicated to organic speciation were similar or close to the one of atmospheric near-road measurements, while, because of very high concentration levels, lower sample flow rates are used for PM samplings dedicated to EC and OC measurements in the exhaust of diesel vehicles non-retrofitted with PF (Euro 3 and Euro 4 diesel vehicles). These very low filter velocities may influence the adsorption of organic vapours by the Quartz filter (McDow and Huntzicker, 1990; Turpin



et al., 2000 ; Vecchi et al., 2009), while EC would not be affected by filter face velocity (Vecchi et al., 2009)." The new references are added.

PAGE 5, LINE 9: Please specify which analysis method (GCMS or LCMS) is used for which organic molecules. RESPONSE: The information is added page 5 lines 21-22. “The chemical speciation of organic particles are performed by Gas Chromatography–Mass Spectrometry (GC-MS), except PAHs that were measured by liquid chromatography (HPLC) using a fluorescence detector”

SECTION2.4: Which type of MLR analysis was used in this work? (ie. Which algorithm was used to calculate the MLR relationships with HD and LD trafïňĄc?) RESPONSE: A standard least square regression method is used since the influence of the two independent variables (light duty and heavy-duty traffic) was expected and in this case, no exploratory procedure (e.g. hierarchical or setwise regressions) was necessary. The sentence is modified as follows: (page 6, line 20-21)” Standard Multiple Linear Regression analyses (SPSS software) are performed. . ..”

PAGE 9, LINE 17-18: Which constants have high p values? Those in Table 3 all have low (signiïňĄcant) values. In addition, the second half of the sentence implies that the authors are comparing the urban background and remote site? Please clarify. RESPONSE: The constants of all regressions have high p-values. As indicated (caption and in table 3), Table 3 does not present any constants (weak interest since they are all not significant), but only the coefficients of the regressions. All coefficients are significant. The authors compare the near-traffic site and the urban background site. In order to be better understood, I propose the following modification: I have transferred the sentence page 9 line 17-18 in the main part that presents the method (2.4 data analysis part) and I modified the text of this part. “The coefficients of the regressions represent average EFs for local heavy-duty and light duty traffics (Table 3). The constants represent the parts not related to local traffic. They are all not significant (p-values above 0.4 for metals and organics, p-value of 0.061 for EC) confirming the above assumption that mostly local traffic contributes to local increments in concentration.”

PAGE 10, LINE 5: What do the authors mean by “smoker vehicles”? RESPONSE: Now “High emitting vehicles” replaces “smoker vehicles”. (now line 15)

PAGE 11 LINES 25-29: 1) Which “unquantiïňĄed compounds”? How is this rough estimate calculated if these compounds are not quantiïňĄed? 2) I suggest also including the measured particulate EF’s for exhaust and non-exhaust emissions to compare both exhaust and non-exhaust EF’s with the standard. RESPONSE: 1) As already indicated in the text, the average brake profile data of Hulskotte et al. (2014) are used to estimate the average emission factor for brake wear assuming that the total proportion of metals is kept, and that 70% of the wear arise from the disc (as suggested by their research). The sentence with “unquantified compounds” is now replaced by (page 11- 12 lines 38-1): “So by adding to the sum of traffic-fleet EFs for metals related to brake wear the portion that corresponds to the elements and compounds not quantified in this study (C, S, Zn, Al, Si, Zr, Mo, V, Ni, Bi, W, P, Pb, Co), the rough estimation of 9.2 mg/km for emissions related to brake wear is got for the RN87 highway traffic.” 2) The emission standards shown in the text correspond to the most recent vehicles (only 7% of Euro 5 in the traffic fleet during the campaign and virtually no Euro 6). This comparison is to show that in the near future, the contribution of non-exhaust emissions would have taken over the one at the exhaust. I propose this modification: “. . .the particle emission standards for the exhausts of the most recent vehicles (Euro 5 and Euro 6 vehicles, 5 mg/km).” The measured particulate EF’s for exhaust are presented in Table 4 and traffic-fleet EFs (exhaust + non-exhaust) are presented in tables 2 and 3.

PAGE 16 LINES 3-4: Please be more speciïňĄc about which divergences were observed. RESPONSE: Now it is specified in the text that the divergence concerns the ratios hopanes to OC (line 18-19). “However the quantification of ratios hopanes to OC showed divergences with other studies that require a better understanding.”

–COMMENTS ON TABLES AND FIGURES– TABLE 1A: 1) 10th column’s title should be “R with EC”. 2) Why are parts of the table highlighted? Please include this in the caption. TABLE 1B: Why are parts of the table highlighted? Please include this in



the caption. RESPONSE: 1) that is right, thank you. 2) and Table 1b) These parts correspond to species significantly correlated with traffic indicators and for which local traffic contributions are above 50%. It was indicated page 7 lines 1-4. I propose in the new version of manuscript to include it in the caption and remove it from the text. In the captions: “Species significantly correlated with traffic indicators and for which local traffic contributions are above 50% are highlighted.”

TABLE 3: Perhaps this would be addressed in the type-setting process, but please ensure that the units column is sufiïňĄciently wide, center the column titles, and use heavier borders to separate the HDV and LDV sections. RESPONSE: Table 3 is now improved.

TABLE III-1: The title should be for a ïňĄgure, not a table. Also, please indicate both data series in the legend (currently only harmonic mean speed is included). RESPONSE: That is right, it is corrected. Only harmonic mean speed is included since it is what best represent the traffic speed. Individual vehicles have different speeds, the magnitude of which depends on the traffic flow.

FIGURE2: Please indicate in the ïňĄgure or caption why there are missing data points in Figure 2B (or leave these categories out of the plot). Suggestions to increase readability: Consider combining EC and OC into one plot. Instead of repeating vehicle type for each set of three conditions (UC, UH, R), consider grouping them with a bracket and labeling them together with the vehicle type. RESPONSE: The reasons why there are missing data points in Figure 2b are now indicated in the caption as follows: “The emission factor for OC for the LD traffic fleet could not be determined and no data available for the hot driving conditions for the Euro 4 diesel vehicles.” Combining EC and OC into one plot would not increase readability, I prefer to keep two plots. The objective is to show how the traffic emission factor corresponds to the respective emissions of the three conditions.

SUPPLEMENTAL VII-1 and VII-2: Please use different colors for different species (ie.

use a single color for Cu and not for any other species). Please also increase the text size of axes titles and tick mark labels. RESPONSE: Different colours are used for different species and single colours for Cu, EC, Pyrene. The text size is increased.

SUPPLEMENTAL VIII: Please increase the text size of axes titles, tick mark labels, and other text. RESPONSE: The text size is increased.

SUPPLEMENTAL IX: Given the attention paid to ratios in this study, I would suggest adding rows for the most relevant ratios (at the least, Cu/Fn, Cu/Mn, and Cu/Sn) where data is available. RESPONSE: The most relevant ratios (Cu/Fe, Cu/Sb, Cu/Sn, Cu/Mn) are now in the table.

–EDITORIAL COMMENTS– PAGE1, LINE 13: grammar: add comma: “vehicular emissions, a large comprehensive dataset” RESPONSE: Now amended.

PAGE 1, LINE 20: ambiguous, replace “Most of the ïňĄrst ones” with “Light-duty trafiňĄc emission factors” and move “in absence of signiïňĄcant non-combustion emissions” to be beginning of the sentence (since it applies to the trafiňĄc emission factors, not the chassis dynamometer measurements) RESPONSE: The referee is right, it is corrected.

PAGE 1, LINE 21: suggested change to correct grammar and increase clarity: “Since recent measurements in Europe including those from this study are consistent, ratios involving copper (Cu/Fe and Cu/Sn) could be used as brake-wear emissions tracers as long as brakes with Cu remain in use.” RESPONSE: the referee’s proposal is accepted.

PAGE 1, LINE 23: The sentence regarding OC/EC ratio does not seem relevant or necessary to the abstract. In addition, the language implies that the OC/EC ratio is always 0.44 in France, which is likely not the intention of the authors. RESPONSE: The referee is right, the OC/EC ratio is not always 0.44 in France since it depends on the traffic fleet and other influential sources. The sentence is modified in the following way: “Near the Grenoble ring road, where the traffic was largely dominated by diesel



vehicles in 2011 (70 %), the OC/EC ratio estimated for traffic emissions was around 0.4.”

PAGE 1, LINE 26: grammar: change “markers; while, their” to “markers, since” RESPONSE: “since” modifies what we attempted to mean, “but” will replace “while”.

PAGE 1, LINE 28: grammar: “environments” (should be plural as written) RESPONSE: Modified

PAGE 1, LINE 30: grammar: “ïňĄlters have been progressively introduced” RESPONSE: Modified

PAGE 1, LINE 36: soften tone: delete “It is obvious that” RESPONSE: Modified

PAGE 2, LINE 1: grammar: “Also, knowledge of the deleterious impacts of PM on human health” RESPONSE: Modified

PAGE 2, LINE 2: grammar: “PM is responsible” RESPONSE: Modified

PAGE 2, LINE 11: grammar: “They also do not represent the variability” RESPONSE: Modified

PAGE 2, LINE 19: clarity / word choice: replace “chemistry of PM” with “chemical composition of exhaust and non-exhaust particulate emissions” RESPONSE: That is a good proposal, it is modified.

PAGE 4, LINE 26: clarity: replace “below installation of” with “below this threshold for” RESPONSE: Modified

PAGE 4, LINE 28: grammar: “30% and 36% respectively” RESPONSE: the first “respectively” is removed.

PAGE 4, LINE 33: “(see SI section IV)” RESPONSE: “section IV” is added.

PAGE 5, LINE 12: grammar: replace “sampler” with “samples” RESPONSE: Modified

PAGE 5, LINE 13: ambiguity, makes it sound like there are two background and two

urban sites: delete “two” RESPONSE: Modified

PAGE 6, LINE 11: I am not sure if perhaps the authors intended “residual” instead of “residues”? RESPONSE: The authors mean “residues”, it is amended.

PAGE 6, LINE 33: Is the discussion of the additional Fe and Mn source in the subsequent paragraph? I do not see it in Section 3.2 as indicated in the text. RESPONSE: This sentence is removed and the discussion on the additional source is page 7, lines 13-22.

PAGE 7, LINE 1: clarity / ambiguity: “are more scattered possibly due to differences between light-duty and heavy-duty emissions factors” RESPONSE: In this part, there is no conclusion on emission factors, but only on the strengths of relationships between datasets. The sentence is modified in order to be better understood (now page 7 lines 11-12). “Here, Cu, Fe and Sn are the metals that are the most closely related (Pearson r2 $\geq$ 0.8), while relationships with Mn and Sb are more scattered (Pearson r2 < 0.5) and more closely related to the heavy-duty traffic (Table 1a).”

PAGE 7, LINE 12: precision / clarity: replace “relationships” with “correlations” RESPONSE: Modified

PAGE 7, LINES 33-34: Do the authors intend that the n-alkanes and hopanes are correlated to each (trafïňĄc, NOx, EC)? If so, change to “NOx, and EC”. RESPONSE: No, we do not. The sentence is slightly modified as follows in order to avoid any ambiguity. “However, they are significantly correlated with NOx and EC and some of them with heavy-duty traffic.” (page 8 lines 4-5)

PAGE 8, LINE 25: grammar: concentrations should be singular: “one for Sr concentration” RESPONSE: Modified

PAGE 8, LINE 36: grammar: “All of these suggest” RESPONSE: Modified

PAGE 9, LINES 8-9: To increase clarity, consider moving this sentence to the end of the ïňĄrst paragraph of this subsection (3.1.2). RESPONSE: Modified



PAGE 9, LINE 18: grammar: “contributes” RESPONSE: Corrected. The sentence is in part 2.4.

PAGE 9, LINE 27: change “technics” to “techniques” for more common spelling RESPONSE: Modified

PAGE 9, LINE 37: grammar: “larger than could be expected” RESPONSE: Modified

PAGE 10, LINE 2: grammar: “as ours, and the EF for exhaust OC” RESPONSE: Modified

PAGE 10, LINE 5: grammar: “contribution of smoker vehicles; and rapid formation” RESPONSE: Modified

PAGE 10 LINE 11-12: grammar: non-retroïňĄtted is less clear than “without” (see comment on PAGE 15 LINE 6 as well): “test diesel vehicles without particle ïňĮlters” RESPONSE: Modified

PAGE 10 LINE 26: grammar: “third highest trafïňĄc emission rate” RESPONSE: Modified

PAGE 11 LINE 28: grammar: “EF” RESPONSE: Modified

PAGE 11, LINE 30 – PAGE 12, LINE 8: The second sentence of this paragraph (regarding Cu and Sb brake wear emissions) confused me because it suggested that the Cu/Sb ratio would be a good candidate as a tracer, which is not the case (as communicated later in the paragraph). I suggest being more direct with the conclusion earlier in the paragraph to avoid confusion. RESPONSE: The second sentence is modified as follows in order to avoid any confusion. “[. . .] Cu/Sb ratio was often considered as a candidate to trace brake wear emissions”

PAGE 11 LINE 35: tone: suggestion to avoid the word “obviously.” Also, please qualify the sentence by adding “in this study.” RESPONSE: The statement is on the basis of national and European inventories. The first sentence is modified to be better under-

stood. “According to inventories atmospheric copper is largely from brake wear.” (p12, line 5)

PAGE 11 LINE 31: Add citation for CITEPA in references RESPONSE: the citation is added in references. CITEPA, édition mars 2018. Inventaire des émissions de polluants atmosphériques en France métropolitaine, format CEE-NU, https://www.citepa.org/images/III-1_Rapports_Inventaires/CEE-NU/UNECE_France_mars2018.pdf

PAGE 11 LINE 35: grammar: “depend” RESPONSE: modified

PAGE 12 LINE 6: replace “Then” with “Thus” RESPONSE: modified

PAGE 12 LINE 23: replace “spent” with “used” RESPONSE: modified

PAGE 12 LINE 31: precision / clarity: “Cu/Sn would be the strongest candidate RESPONSE: modified

PAGE 14 LINE 12: grammar / clarity: “The normalized abundance of 17$\alpha$,21$\beta$norhopane (246 $\mu$g per g of OC) ...” RESPONSE: modified

PAGE 14 LINE 17: replace “data” with “emissions factors and compositions” RESPONSE: “data” is replaced by “EFs and normalized abundances” (p14, lines 31-32).

PAGE 15 LINE 2: grammar: “This study determined ...identiïňĄed ...quantiïňĄed” or “This study attempted to determine...identify...quantify” RESPONSE: Modified

PAGE 15 LINE 6: see comment on PAGE 10 LINES 11-12 for similar issue: “passenger diesel cars without particle ïňĄlters” RESPONSE: Modified

PAGE 15, LINE 5: I am not sure what the authors are communicating with this ïňĄrst sentence (“The trafïňĄc shows the larger emission factor...”). Please rephrase. RESPONSE: Now rephrased (p15 line 20): “EC has the highest traffic emission factors and is strongly. . .”



PAGE 15 LINE 19: As written, implies that different sites in Europe were sampled in this study. Instead: “Cu/Fe ratios consistent with literature values from other sites suggest similar brake composition for these elements throughout Europe (as long as Cu-free brakes do not increase in use).” RESPONSE: The modification is accepted.

PAGE 15 LINES 21-23: Ambiguous as written as to whether these ratios are good or bad tracers. Instead: “Our measurements do not support the use of Cu/Mn and Cu/Sb as tracers of brake wear emissions possibly due to additional sources of Mn as well as the introduction of Sb-free brake pads.” RESPONSE: Since the use of Cu/Mn and Cu/Sb cannot be strongly rejected by this study, I really prefer to replace the 2 sentences by: “Our measurements support more the use of Cu/Sn than that of Cu/Mn and Cu/Sb as tracers of brake wear emissions possibly due to additional sources of Mn and the introduction of Sb-free brake pads.” (page 15-16 lines 38-1)

PAGE 15 LINE 36: clarity: “agreement between chassis dynamometer and near-road measurements” RESPONSE: To be as accurate as possible, the following is added: “between chassis dynamometer and near-road measurements and between this study and other recent studies.” (page 16, lines 12-13)

PAGE 15 LINE 36: delete “the change of the” RESPONSE: Modified

PAGE 16 LINES 5-6: I suggest a more speciïňĄc concluding sentence. Perhaps replace “delivered valuable information” with “describes exhaust and non-exhaust emissions measurements” RESPONSE: Taking into account the comments of both referees, I propose the following amendment (in the new manuscript, page 16, lines 20-21): “This study determines many quantitative data of traffic exhaust and non-exhaust emissions that could help in a better definition of traffic emissions in source apportionment studies.”

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-816/acp-2018-816-AC1-

supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-816, 2018.



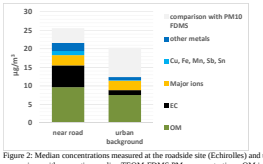


Figure 2: Median concentrations measured at the roadside site (Echirolles) and urban background site (Les Frênes) and comparison with respective median TEOM-FDMS $PM_{10}$ concentrations. OM is computed using the factor 1.8 estimated for Grenoble city (Favez et al., 2010).

**Fig. 1.**

| | Unit | $r^2$ | HDV | | | | | LDV | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Coeff. | SD | *p* | conf.inter. 95% | | Coeff. | SD | *p* | conf.inter. 95% | |
| EC | mg.veh$^{-1}$.km$^{-1}$ | 0.92 | 148.4 | 22.7 | 0.000 | 102.9 | 193.9 | 30.2 | 1.9 | 0.000 | 26.4 | 34.0 |
| Cu | µg.veh$^{-1}$.km$^{-1}$ | 0.73 | 3371 | 990 | 0.003 | 1312 | 5430 | 258 | 104 | 0.021 | 42 | 474 |
| Fe | mg.veh$^{-1}$.km$^{-1}$ | 0.81 | 48.0 | 19.1 | 0.023 | 7.5 | 88.5 | 6.3 | 1.7 | 0.002 | 2.7 | 9.8 |
| Sb | µg.veh$^{-1}$.km$^{-1}$ | 0.77 | 246 | 72 | 0.003 | 96 | 395 | 20.1 | 6.9 | 0.006 | 5.6 | 34.5 |
| Sn | µg.veh$^{-1}$.km$^{-1}$ | 0.82 | 512 | 149 | 0.003 | 198 | 825 | 54 | 15 | 0.002 | 23 | 85 |
| Pyr | µg.veh$^{-1}$.km$^{-1}$ | 0.60 | 28.4 | 6.3 | 0.000 | 15.6 | 41.1 | 1.459 | 0.658 | 0.034 | 0.121 | 2.798 |
| An | µg.veh$^{-1}$.km$^{-1}$ | 0.55 | 0.435 | 0.128 | 0.002 | 0.174 | 0.697 | 0.0352 | 0.0131 | 0.011 | 0.0086 | 0.0618 |
| Fla | µg.veh$^{-1}$.km$^{-1}$ | 0.58 | 7.38 | 3.38 | 0.037 | 0.49 | 14.27 | 1.254 | 0.305 | 0.000 | 0.632 | 1.875 |
| C23 | µg.veh$^{-1}$.km$^{-1}$ | 0.66 | 277.8 | 70.6 | 0.000 | 133.8 | 421.7 | 23.9 | 6.3 | 0.001 | 11.1 | 36.8 |
| C24 | µg.veh$^{-1}$.km$^{-1}$ | 0.62 | 163.9 | 54.0 | 0.005 | 53.7 | 274.1 | 19.2 | 4.8 | 0.000 | 9.3 | 29.0 |

Table 3: Results of the Multiple Linear Regressions with the heavy-duty traffic (HDV) and the light duty traffic (LDV): square correlation coefficients, unstandardized coefficients with standard deviations for HDV and LDV, p-values and confidence intervals at 95%.

**Fig. 2.**