Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-816-AC2, 2019

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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Received and published: 23 January 2019

The study by Charron et al. documents measurements of PM10 samples collected at a roadside in France. Overall, the results appear to be of high quality and are of potential use to further source apportionment work. The authors contextualize the study with the increasing importance of non-exhaust PM to total vehicular emissions, which is an interesting and intuitive concept. RESPONSE: The authors thank the reviewer for supporting their work.

JustiïňĄcation for sampling PM10 should be included in the paper. What is the typical size distribution for vehicular emissions? Exhaust emissions, especially those treated

with a particulate ïňĄlter on board the vehicle are dominated by ultraïňĄne particle emissions, which have vanishingly small mass, especially in comparison to the remainder of PM10. Therefore, does PM10 over-sample the resuspended and non-exhaust emissions? Are aerosol size distributions of non-exhaust emissions known? The size-segregated composition of the PM in this study probably varies strongly, and will have an inïňĆuence on the ïňĄndings. Please discuss this aspect of the study in greater detail. Coarse particles also have fast deposition rates, limiting their inïňĆuence on respiratory exposure compared to PM2.5 (or size classes with smaller upper size limits). RESPONSE: The reviewer is right, we can expect that the proportion of non-exhaust emissions in total traffic emissions is larger for PM10 than for PM2.5 or PM1. In this study, PM10 sampling was done in a deliberate manner to account for the entire breathable fraction of non-exhaust emissions. There are now certainties that PMcoarse have an impact on health (Beelen et al., 2014; Cheng et al., 2015; Malig et al., 2013), and the health of people living near traffic emissions can be strongly impacted. For that reason, we believe that the coarse fraction of particles emitted by traffic also needs consideration. Also PM10 in ambient air is also a quantity that is regulated in Europe and in many European traffic sites the European daily limit value is exceeded more than 10% of time. Note that during the same campaign, PM1 measurements were carried out using on-line instruments, results are published in another paper (DeWitt et al., 2015). The current state of the art of knowledge about the aerosol size distributions of non-exhaust emissions was the purpose of recent reviews (Thorpe and Harrison, 2008, Grigoratos and Martini, 2014), not of this work. But I agree that consideration of the different particle sizes could substantially improve knowledge on particulate traffic emissions. - I propose to first present and explain our choice in the introduction as follows: "(Recently, on the one hand, Shirmohammadi et al. (2017) and Weber et al., (2018) have shown the important role of non-tailpipe emissions to the oxidative potential of particulate matter species identified as tracers of vehicle abrasion; and on the other hand, the health impacts of coarse particles is now better documented (Beelen et al., 2014; Cheng et al., 2015; Malig et al., 2013). Therefore, a better knowledge on vehicular emissions is required to better understand their contribution to urban atmospheric PM10 concentration levels and related health effects. [. . .] This study focuses on PM10 in order to take into account for the entire breathable fraction of non-exhaust particulate emissions, a large part of which are coarse particles (Thorpe and Harrison, 2008; Grigoratos and Martini, 2014)." (p2, line 7-8; lines 25-27 in the new version of the manuscript). - And then, to conclude on the need of research on different particle size fractions of non-exhaust vehicular emissions. "The determination of the particle size distribution of OC could improve knowledge of the organic emissions of traffic." (p 15 lines 28-29, new Ms) "Similarly to OC, the determination of the particle size distribution of metals may possibly improve the discrimination between influential sources in urban areas." (p 16 lines 5-7) Note that the new references are added.

Inclusion of more data visualizations throughout the manuscript, especially related the early sections of results (temporal proïňĄles) is strongly advised. The reviewer's comprehension of the text was heavily improved by opening the SI, which should not be a requirement of reading a paper. This recommendation will likely improve the manuscript by an important margin. Combining metals onto fewer panels may help so that the entirety of SI Section VII does not need to be included as-is (for instance). Please consider this idea for all sections of the manuscript. RESPONSE: A part of the SI VII (temporal variations) is included in the paper as Figure 3 as well as the entire SI VIII (linear relationships) as Figure 4. Unfortunately, combining metals onto fewer panels reduces the readability, so this option has not been kept.

The presentation of the manuscript overall could use some English grammar editing and overall proof reading. A number of small grammatical or usage errors exist throughout the document. RESPONSE: An important correction work of grammatical errors has been done by reviewer 2 and the manuscript has been re-read.

A few salient ones are pointed out in the minor comments below, but this should not be considered an exhaustive list of corrections. Overall opinion: This study should be considered for publication after addressing the comments of this review in a major

revision. Introduction: The study is contextualized well, focused on the importance of nonexhaust emissions from vehicles, which may now be the most important aspect of vehicular emissions. Findings were, however, associated with both exhaust and nonexhaust emissions, which is clear. Methods: Methods were clearly described, with the exception of a lack of deïňĄnition for TEOM-FDMS (a minor comment). RESPONSE: The TEOM-FDMS used during the field campaign are now defined: "PM10 and PM2.5 mass concentrations were also continuously measured using 8500C series TEOM-FDMS (Filter Dynamics Measurement System and Tapered Element Oscillating Microbalance mass sensor housed in a single-cabinet compact enclosure)."

Results: The use of the term 'incremental' is confusing (occurs throughout 'Results'). Referring to the "increment" with a clearer name would greatly clarify the presentation this important quantity. RESPONSE: in order to avoid any confusion, "incremental concentrations" is replaced by "increments in concentration" or "local increments in . . . concentration due to traffic".

Section 3.1.1: It would be helpful to see a graphical representation of the contribution of each component of PM10 to the total mass. RESPONSE: A figure is added as Figure 2 and this graphical representation well highlights the differences between both sites.

Page 6, Line 32: It is becoming clear that the inïňĆuence of particle size may be evident in the data (also see broader comments above). Please include a description or reference to what is known about the size-resolved composition of vehicle emissions from both exhaust and non-exhaust sources. [Such a discussion is not necessarily relevant to insert at this point in the manuscript, however, its importance began to become clear at this point.] RESPONSE: Of course, using another particle size for sampling could help with the separation of traffic metallic emissions and emission from the nearby industrial source, but it was not the purpose of the work. As suggested above, recommendations for further research are included in the conclusions: "Similarly to OC, the determination of the particle size distribution of metals may possibly improve the discrimination between influential sources in urban areas."

Page 7, line 38 – Page 7, line 2: Can a consideration for super-emitting vehicles be included in this part of the discussion? RESPONSE: It is now specified that none of tested vehicles was a high-emitting vehicle.

Page 8, lines 20-22: The measured ‘dominant regional contribution’ to OC may be masking the vehicular primary OC due to differences in the size distribution. Regional, secondary OC may be signiïňĄcantly aged, and therefore larger in size. While this will manifest as an overwhelming signal in a PM10 sample, it may not be so in a PM1 sample, or even a PM0.1 sample. Please discuss the signiïňĄcance of what is known about size-dependent composition of particles associated with vehicle emissions. RESPONSE: I agree with that secondary OC generates an overwhelming signal in PM10, but this is also the case for PM1 samples (see DeWitt et al., 2015). Additionally, the size distribution of traffic OC may possibly be more complex. Secondary OC may be larger in size than OC freshly emitted from the combustion chamber of the vehicles, but other traffic sources of OC (from tyre wear, road wear. . .) may also be larger in size than exhaust OC and possibly larger than secondary OC. While the examination of the size distribution of OC would be very valuable and requires further studies, considering only PM10 does not change the conclusion. I propose to add (p10, lines 17-18, after “Further studies are required to assess the respective importance of these processes.”): “In particular, a better knowledge of particle size distribution of OC emitted by traffic might be useful.”

Page 8, lines 33-38: If Co does not show any correlation with trafïňĄc emissions, how can it be reasonably concluded from the data collected in the present study that Co is a contributor to brake wear? The authors clearly attempt to make a case using the literature. If the contribution of other elements to one another is going to used to explain their similar vehicular sources (Fe, Cu, etc), then the same standard must be held to Co. At best, perhaps there is some other, more consistent, low level source of Co that is ïňĆattening the temporal proïňĄle. A conclusion as written in this passage, however, is dubious. RESPONSE: This is another example of overwhelming signal

from the background or possibly from another local source. Since concentrations of Co are significantly higher at the roadside site, other authors have made the same observation, and Co is measured in brake pads, we cannot totally exclude that Co is not emitted by the traffic. The end of text is changed as follows (page 9 lines 11-13): “All of these suggest that a possible contribution of brake wear to Co concentrations cannot be excluded, despite the lack of correlation with traffic indicators.”

Page 9, lines 11-15: Can the impact of variability within the parts of the vehicle ïňĆeet be incorporated? In such highly controlled emissions from vehicles, a small number of super-emitters may be quite impactful. RESPONSE: Yes, the referee is right, the variability due to the presence of a few high emitting vehicles is now incorporated page 9 line 24. “(This variability reflects the presence of vehicles with various emission levels (diesel/petrol; different standards and engine load; cold start/hot vehicles;) presence of a few high emitting vehicles).”

Page 9, lines 34-35: This is a salient point for air quality management and regulation. RESPONSE: The referee is right. This point is added to the conclusion: “EC emissions from heavy-duty vehicles are estimated to be 5 times higher than those for light duty vehicles”.

Page 10, line 5 (and other instances): Please give a more succinct deïňĄnition to the term “smoker vehicles”. Perhaps the authors could call these super-emitters? (see also comment about Page 9, lines 11-15) RESPONSE: “smoker vehicles” is replaced by “high emitting vehicles”.

Page 11, line 22: The authors use and cite a ïňĄnding that a dominant fraction of brake wear emissions come from the disc and not the brake pad. This seems hard to believe considering the fact that the brake pad is the primarily consumable part, and that brake discs (rotors) do not need to be replaced as often. RESPONSE: That is a judicious remark of the referee. This assumption is based on the work of Hulskotte et al., 2014 and this sensible point is already discussed in Hulkotte’s et al. (2014) that draw on research from Sander et al. (2003) and Varrica et al. (2013), I quote: "it can be concluded that a share of 30%±5% of brake pad wear within total brake wear probably is a realistic value. This in a reasonable agreement with Sander et al. (2003) who reported that at low-metallic brakes (as most frequently used in Europe) about 60% of mass loss has his origin in the brake disc [here we estimated that 70% comes from discs]. While this is a surprisingly result at first, a closer look at a spent brake pad and disc reveals that there can be rather deep wear patterns on the disc and, most important, the surface area of the disc is much larger. So, while the wear in mm from a brake pad might be higher, once this is multiplied with surface area, the wear from the discs appears to be larger. None of the spent brake pad collected was worn so much that the iron base of the brake pad in any way. We assume that in the real world abrasion of the iron base of the brake pad very rarely will occur because obliged periodical roadworthiness tests will prevent this situation. So we may assume that wear of the iron brake pad base will not contribute to emission of iron. Recently Varrica et al. (2013) found that half the concentration of antimony in brake pad residue on wheel rims compared to brake pad linings, suggesting a 50% contribution by brake discs" Since at this state of knowledge the influence of unknown parameters on the high iron emissions observed at different locations cannot be excluded, and new researches are needed anyway, I added in the text (page 11 lines 34-36): "This latter assumption is supported by other researches (Sander et al., 2003; Varrica et al., 2013), even though the generation mechanisms of brake wear particles have not been fully understood yet (Grigoratos and Martini, 2014)."

Page 11, line 35: Please clarify and/or deïňĄne "PM fraction". This term is not used routinely in this manuscript. A change in wording may help in this instance. RESPONSE: "PM fraction" is replaced by "PM size fraction".

Page 11, line 34 - Page 12, line 8: It may help to deïňĄne Cu/Sb in the brake materials themselves. How might consistency in the brake materials themselves drive atmospheric Cu/Sb? Could the act of particle formation (temperature, breaking force,

etc) inïňĆuence the ratio? RESPONSE: These are excellent questions and a field of research to explore which I cannot answer. Not enough is known on the Cu/Sb in the brake materials leading to airborne particles and a few researches are cited in the text. A recent review already exist (Pant and Harrison, 2013) and is already cited in the text. Also, as noted above, little is known on the generation mechanisms of brake wear particles and how the generation mechanisms influence the physicochemical characteristics of atmospheric brake wear particles. Moreover published works show a wide variety of sampling methodologies that lead the results difficult to compare.

Page 15, line 17-19: Has Cu/Fe been reported in any other proportion in the atmosphere? Please illustrate (perhaps in the results section on this topic) that the âĹij4% value is unique to vehicles. RESPONSE: Data measured at the urban background Les Frênes, unpublished data from other French sites and published data at other sites (e.g. Hueglin et al., 2005) show that the Cu/Fe ratios are different in rural and urban background areas (sometimes similar in urban background sites strongly influenced by traffic). This part is modified as follows (page 15, lines 36-39): "Cu/Fe ratios in agreement with literature values for other kerbside sites, while Cu/Fe ratios may be different for urban background or rural sites (e.g. Hueglin et al., 2005; this study: Les Frênes' data), suggest similar brake composition for these elements throughout Europe (as long as Cu-free brakes do not increase in use)."

Page 15, line 24-28: This is a strange placement for an overview paragraph about the signiïňĄcance of redox-active metals, which have only been mentioned as such in the introduction. This paragraph is probably better off at the beginning of the conclusions section, mirroring the structure of the paper itself. RESPONSE: The paragraph is removed and references are added in the introduction (to complete the discussion on the health effect of redox-active metals). "There is now strong evidence that traffic-related PM is responsible for adverse health effects due to the health effect of both carbonaceous material from exhaust emissions and redox-active metals in traffic-generated dust including road, brake and tyre wear (Kukutschová et al., 2009; Cassee et al., 2013; Amato et al., 2014 and references wherein; Pardo et al., 2015; Poprac et al., 2017). Recently, on the one hand, Shirmohammadi et al. (2017) and Weber et al., (2018) have shown the important role of non-tailpipe emissions to the oxidative potential of particulate matter species identified as tracers of vehicle abrasion;[. . .]"

Page 15, line 29: While studies such as this one may be scarce in the literature, the authors have reported agreement with these studies throughout the manuscript – suggesting that the science is highly convergent. Please provide a clear, summary assessment of the novel ïňĄndings of this study. RESPONSE: The paragraph now begins with (page 16 lines 4-6): "Particulate organic emission data for European motor vehicles is scarce. In this study, a few PAHs, n-alkanes and hopanes have been identified as organic molecular markers of fresh diesel traffic emissions and their emission factors have been quantified."

Page 16, lines 5-6: This concluding statement seems to highlight the fact that this is a characterization study with little in the way of entirely new ïňĄndings. (see previous comment) Do the authors believe feel that this is the case? If not, a revised summary statement or declaration of a way forward in light of the present study is in order. RESPONSE: Taking into account the comments of both referees, I propose the following amendment (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." Considering the two comments above, the first paragraph of the conclusion is rewritten in order to better show the most important points and novel findings related to this research (very large dataset including metal, major ions and organic / both in situ and chassis dynamometer measurements / not only identification but also quantification of tracers that could be used in source apportionment studies) (page 15 lines 13-17): "Thanks to a very large comprehensive dataset of particulate species collected from a simultaneous near-road and urban background measurement field campaign and chassis dynamometer experiments of a few in-use passenger cars, this study was able to determine emission factors for many

particulate species from road traffic and to identify and quantify tracers of exhaust and non-exhaust vehicular emissions that could be used in source apportionment studies."

Minor comments: Line 20-21: "Most of the ïňĄrst ones" – please be speciïňĄc, most of the ïňĄrst 'what'? What do you mean by ïňĄrst? I honestly do not know to which prior items this sentence refers. RESPONSE: It is replaced by "In absence of significant non-combustion emissions. . ." (page 1 line 20)

Line 24-26: "On the contrary,..." to what?? RESPONSE: It is replaced by "Although. . ." (line 25)

Page 8, line 9: should refer to "SI Section VII" RESPONSE: It is amended.

Page 9, line 27: change "technics" to "techniques" RESPONSE: it is amended.

Page 10, line 2: deïňĄne DPF, ïňĄrst usage RESPONSE: it is replaced by Diesel Particulate Filter.

Page 10, line 26: change to "third highest" RESPONSE: Now, the sentence is (page 10 line 37): "Fe presents by far the third highest traffic emission rate after those of EC and OC"

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-816/acp-2018-816-AC2-supplement.pdf

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

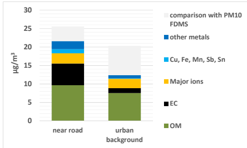

Figure 2: Median concentrations measured at the roadside site (Echirolles) and urban background site (Les Frênes) and comparison with respective median TEOM-FDMS PM_{10} concentrations. OM is computed using the factor 1.8 estimated for Grenoble city (Favez et al., 2010).

Fig. 1.