

Response to Reviewer 1

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.

Justification 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 filter on board the vehicle are dominated by ultrafine 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 influence on the findings. Please discuss this aspect of the study in greater detail. Coarse particles also have fast deposition rates, limiting their influence on respiratory exposure compared to PM_{2.5} (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 PM_{2.5} 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 PM_{coarse} 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 profiles) 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 definition for TEOM-FDMS (a minor comment).

RESPONSE: The TEOM-FDMS used during the field campaign are now defined:

“PM₁₀ and PM_{2.5} 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 influence 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 significantly 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 PM_{0.1} sample. Please discuss the significance 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 traffic 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 be 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 flattening the temporal profile. 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 fleet 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 definition 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 finding 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 Hulskotte’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 is 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 its 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 define “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 define 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) influence 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 ~4% 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 significance 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 therein; 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 findings 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 findings. (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 first ones” – please be specific, most of the first ‘what’? What do you mean by first? 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: define DPF, first 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”

Response to Reviewer 2

–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 fleets as well as locations with different traffic 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 figures 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 flowrates, 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 filter 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, filter 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 filter sampling artifacts due to differences in sample flowrates (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 filter artifacts affect the authors' conclusions about the impact of the particulate filter retrofit on OC and EC emissions?) REFERENCE Solomon, P. A., et al., Evaluation of PM_{2.5} chemical speciation samplers for use in the U.S. EPA national PM_{2.5} 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 traffic?)

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 (significant) 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 "unquantified compounds"? How is this rough estimate calculated if these compounds are not quantified? 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 specific 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 sufficiently 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 figure, 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 figure 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”

Now amended.

PAGE 1, LINE 20: ambiguous, replace “Most of the first ones” with “Light-duty traffic emission factors” and move “in absence of significant non-combustion emissions” to be beginning of the sentence (since it applies to the traffic 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: “filters 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 $r^2 \geq 0.8$), while relationships with Mn and Sb are more scattered (Pearson $r^2 < 0.5$) 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 (traffic, NO_x, EC)? If so, change to “NO_x, 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 NO_x 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 first 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-retrofitted is less clear than “without” (see comment on PAGE 15 LINE 6 as well): “test diesel vehicles without particle filters”

RESPONSE: Modified

PAGE 10 LINE 26: grammar: “third highest traffic 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 understood.

“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 α ,21 β norhopane (246 μ 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 ...identified ...quantified” 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 filters”

RESPONSE: Modified

PAGE 15, LINE 5: I am not sure what the authors are communicating with this first sentence (“The traffic 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 specific 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.”

1 Identification and quantification of particulate tracers of 2 exhaust and non-exhaust vehicle emissions

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12 **Abstract.** In order to identify and quantify key-species associated with non-exhaust emissions and exhaust
13 vehicular emissions, a large comprehensive dataset of particulate species has been obtained thanks to simultaneous
14 near-road and urban background measurements coupled with detailed traffic counts and chassis dynamometer
15 measurements of exhaust emissions of a few in-use vehicles well-represented in the French fleet. Elemental
16 Carbon, brake-wear metals (Cu, Fe, Sb, Sn, Mn), n-alkanes (C19-C26), light molecular weight PAHs (Pyrene,
17 Fluoranthene, Anthracene) and two hopanes (17 α 21 β Norhopane and 17 α 21 β hopane) are strongly associated with
18 the road traffic. Traffic-fleet emission factors have been determined for all of them and are consistent with most
19 recent published equivalent data. When possible, light-duty and heavy-duty duty traffic emission factors are also
20 determined. **In absence of significant non-combustion emissions**, light-duty traffic emissions are in good
21 agreement with emissions from chassis dynamometer measurements. Since recent measurements in Europe
22 including those from this study are consistent, ratios involving copper (Cu/Fe and Cu/Sn) could be used as brake-
23 wear emissions tracers as long as brakes with Cu remain in use. **Near the Grenoble ring road, where the traffic
24 was largely dominated by diesel vehicles in 2011 (70 %), the OC/EC ratio estimated for traffic emissions was
25 around 0.4.** **Although** the use of quantitative data for source apportionment studies is not straightforward for the
26 identified organic molecular markers, their presence seems to well-characterized fresh traffic emissions.

27 1 Introduction

28 Traffic is a major source of particulate matter in urban environments through both exhaust and non-exhaust
29 emissions. Thanks to stringent regulations, vehicles with more efficient catalytic converters and diesel particle
30 filters have been progressively introduced into the European fleet. As a consequence particulate exhaust emissions
31 have strongly decreased and non-exhaust particulate emissions (particles resuspended by moving traffic and those
32 from the wear of brakes, tyres, road surface...) will contribute to the major part of particulate vehicular emissions
33 in the near future (Amato et al., 2014). Current research estimates that non-exhaust emissions already substantially
34 contribute to traffic emissions, with differences between sites due to local meteorology, local emissions, or traffic
35 characteristics (e.g. Omstedt et al., 2005; Thorpe and Harrison, 2007; Bukowiecki et al., 2010; Lawrence et al.,
36 2016). Even with electric vehicles, traffic will continue to be a source of PM through non-exhaust emissions (Pant
37 and Harrison, 2013; Timmers and Achten, 2016).

38 Also, knowledge on the deleterious impacts of PM from vehicular emissions on human health is increasing. There
39 is now strong evidence that traffic-related PM is responsible for adverse health effects due to the health effect of
40 both carbonaceous material from exhaust emissions and redox-active metals in traffic-generated dust including
41 road, brake and tyre wear (Kukutschová et al., 2009; Cassee et al., 2013 ; Amato et al., 2014 and references
42 wherein; Pardo et al., 2015; Poprac et al., 2017). Recently, **on the one hand**, Shirmohammadi et al. (2017) and
43 Weber et al., (2018) have shown the important role of non-tailpipe emissions to the oxidative potential of
44 particulate matter species identified as tracers of vehicle abrasion ; **and on the other hand, the health impacts of
45 coarse particles is now better documented (Beelen et al., 2014; Cheng et al., 2015; Malig et al., 2013).** Therefore,
46 a better knowledge on vehicular emissions is required to better understand their contribution to urban atmospheric
47 **PM₁₀** concentration levels and related health effects.

1 Chassis dynamometer measurements allow the determination of exhaust vehicular emissions under controlled
2 testing conditions but, because of high costs, these tests often include small sets of vehicles that cannot be
3 representative of large variation in engine type, age and maintenance history of vehicles. They also do not represent
4 the variability of driving types in various environments. All of these are parameters that strongly influence real-
5 world vehicular emissions. Additionally, these tests cannot simulate accurately the effect of dilution on particle
6 equilibrium in the road atmosphere (Kim et al., 2016), the possible rapid aging effects (e.g. Platt et al., 2017), and
7 non-tailpipe emissions (e.g. Thorpe and Harrison, 2008). For all these reasons, it is thought that more realistic
8 estimates of vehicle emissions are determined from air quality measurements in the near-road atmosphere (Phuleria
9 et al., 2017), including car-chasing, tunnel or roadside measurements (Pant and Harrison, 2013 and references
10 therein; Jezek et al., 2015).

11 In this study, a large comprehensive dataset on the chemical composition of PM_{10} from exhaust and non-exhaust
12 emissions has been obtained thanks to two complementary campaigns: 1) simultaneous near-road and urban
13 background measurements coupled with detailed traffic counts for the estimation of real-world vehicular emissions
14 including non-exhaust emissions and, 2) chassis dynamometer measurements of exhaust emissions of a few in-use
15 vehicles well-represented in the French fleet for the identification of key species in exhaust emissions. **This study
16 focuses on PM_{10} in order to take into account for the entire breathable fraction of non-exhaust particulate emissions,
17 a large part of which are coarse particles (Thorpe and Harrison, 2008; Grigoratos and Martini, 2014).** Possible
18 particulate tracers of exhaust and non-exhaust vehicle emissions are examined and quantified. Emission factors
19 and when possible, typical ratios, are derived from these data.

20 **2 Methodology**

21 **2.1 Chassis dynamometer measurements**

22 Vehicles were operated on a chassis dynamometer, and exhaust emissions were measured using a sampling train
23 including a Constant Volume Sampling (CVS) system in which emissions are diluted with filtered air and sampled
24 using quartz filters and polyurethane foams (PUF).

25 **2.1.1 Vehicle types and driving cycles**

26 Five vehicles representative of the most frequent vehicle classes in the French fleet in circulation were selected
27 (Euro 3 Diesel, Euro 4 diesel, Euro 4 diesel retrofitted with particle filter, Euro 2 petrol, Euro 4 petrol). They were
28 in-use private cars since rental vehicle may not be representative of the national fleet (low mileage). All vehicles
29 were operated using commercial diesel and petrol fuels. Selection criteria and characteristics of tested vehicles are
30 described in the Supplementary Information (SI).

31 Driving cycles designed to be representative of real driving conditions in Europe are performed in this study
32 (André, 2004). The ARTEMIS urban cycle represents driving conditions in urban areas (repeated acceleration and
33 vehicle speed below 40 km/h), while the ARTEMIS rural-road cycle represents driving conditions on main roads
34 in suburban and rural areas outside cities (flowing traffic conditions). These cycles represent most driving
35 conditions encountered on the RN87/E712 highway, where the road side experiments took place, during congested
36 and flowing traffic conditions, respectively. Since urban journeys include cold vehicles, the influence of the cold
37 start on urban emissions has been systematically tested.

38 **2.1.2 Exhaust sampling**

39 Vehicles were operated on a chassis dynamometer using a CVS system to dilute exhaust emissions with filtered
40 ambient air. The filtration system included four filters and a cartridge in series: a M6-F7-F9, M5, F7 EN-779-2012
41 filters; a HEPA H13 EN1822-2009 filter; and a cylindrical cartridge of charcoal scrubber.

42 Regulated emissions were determined with continuous monitors for CO, CO₂, NO_x, and total hydrocarbons
43 (HORIBA system). Particulate matter (PM) and volatile organic compounds (VOC) were sampled out from the
44 dilution tunnel with a servo-controlled system designed by Serv'Instrument for this study. Two driving cycles in
45 series were performed in order to collect enough matter for molecular speciation (except for the EURO 3 vehicles).
46 PM was collected on quartz filters (TissuquartzTM, diameter 47 mm), at flow rates depending on both emission
47 levels of the vehicles being tested and the types of analyses (from 5 to 50 L.min⁻¹ for EC/OC measurements and
48 from 30 to 50 L.min⁻¹ for organic molecular speciation). Dilution factors ranged from about 15 to 40. Conditions

1 of vehicle tests are detailed in the supplemental section (Table I-2). Filter face velocities for chassis dynamometer
2 samplings dedicated to organic speciation were similar or close to the one of atmospheric near-road measurements,
3 while, because of very high concentration levels, lower sample flow rates are used for PM samplings dedicated to
4 EC and OC measurements in the exhaust of diesel vehicles non-retrofitted with Particulate Filter (Euro 3 and Euro
5 4 diesel vehicles). These very low filter velocities may influence the adsorption of organic vapours by the Quartz
6 filter (McDow and Huntzicker, 1990; Turpin et al., 2000 ; Vecchi et al., 2009), while EC would not be affected by
7 filter face velocity (Vecchi et al., 2009). Quartz filters were pre-baked at 500°C for 8h before being used. Samples
8 were stored at -18°C in aluminum foil and sealed in polyethylene bags until analyses.

9 Analysis of test blank filters (collected following the same procedure as vehicle test filters including driving cycle
10 durations with filtered air) showed contaminations from the CVS system. It was obvious that some organic
11 compounds measured in test blanks result from the desorption of semi-volatile organics deposited into the CVS,
12 that is favoured by cleaner air. Since blank levels decreased in time with passing air dilution through the system,
13 our procedure included such a step maintained for a duration corresponding to at least two driving cycles before
14 each vehicle test. Test blanks are used to correct measurements.

15 **2.2 Near-road and urban background measurements**

16 The joint PM-DRIVE (PM-Direct and Indirect on-road Vehicular Emissions) and MOCOPO (Measuring and
17 mOdelling traffic Congestion and POLLution) field campaign took place from September 9th to 23rd, 2011. It
18 included meteorology and traffic measurements, near-road/urban background PM₁₀ sampling (this study) and near-
19 road on-line measurements (discussed in DeWitt et al., 2015).

20 **2.2.1 Description of traffic and urban background sites**

21 The Grenoble conurbation is a large city with about 700,000 inhabitants. It is located in the southeast of France in
22 the French Alps and is surrounded by three mountain ranges (Vercors, Chartreuse, and Belledune). The traffic site
23 was located (45.150641 N, 5.726028 E) about 15 m away from the southern part of the Grenoble ring road (the
24 RN87/E712 highway with 2×2 lanes) (26 m from the roadway central axis). Total traffic flow for the 4 lanes was
25 on average 95,000 and 65,000 vehicles a day on workday and weekend, respectively, with frequent congestion
26 during extended commuting hours. Stop-and-go traffic in both directions generates large braking activity at that
27 time. This sampling site was highly equipped during the joint PM-DRIVE / MOCOPO field campaign.
28 Simultaneous measurements took place at an urban background site (Les Fresnes) which is located about 2 km
29 away from the traffic site, on the rooftop of a school. This site belongs to the regional air pollution network
30 managed by Atmo Auvergne-Rhône-Alpes (<http://www.atmo-auvergnerhonealpes.fr/>). The locations of both sites
31 are presented on Figure 1.

32 **2.2.2 Aerosol and gas measurements**

33 On both traffic and urban background sites, PM₁₀ HiVol (DA80, 30 m³ h⁻¹) samplers collected PM₁₀ on quartz
34 fibre filters (TissuquartzTM, diameter 150 mm) with a time resolution of 4 hours. Filters were preheated at 500 °C
35 during 3 h. After sampling, filters were individually placed in aluminum foil, sealed in polyethylene bags and
36 stored at -18 °C until analysis. In addition, both sites were equipped with NO_x (NO and NO₂) and CO monitors.
37 PM₁₀ and PM_{2.5} mass concentrations were also continuously measured using 8500C series TEOM-FDMS (Filter
38 Dynamics Measurement System and Tapered Element Oscillating Microbalance mass sensor housed in a single-
39 cabinet compact enclosure).

40 **2.2.3 Traffic measurements**

41 Traffic counters (double electromagnetic loops) were installed in order to identify the passing of all vehicles, the
42 length of their chassis and their speeds, the determination of the 2 vehicle classes used in this study (light-duty
43 and heavy-duty vehicles), and the identification of periods of stop-and-go or flowing traffic. Vehicle mean speeds
44 are computed as the harmonic mean speed of the cars passing over the detector (flow speed i.e. the spatial mean
45 speed) (Hall, 2001).

46 Traffic cameras mounted on a roadway gantry were also used to monitor traffic at the measurement site. They
47 were used to capture the license plate numbers of passing vehicles. Plate numbers were later used to classify

1 vehicular traffic into different categories: EURO standards and fuel type (diesel or petrol). The traffic of the
2 highway is detailed elsewhere (DeWitt et al., 2015; Fallah Shorshani et al., 2015). On weekdays, the average
3 hourly traffic included 2,850 diesel vehicles (including about 200 heavy-duty vehicles) and 1,025 petrol vehicles.
4 The harmonic vehicle mean speed was about 80 km/h and ranged from 52 to 94 km/h (note that the RN87 highway
5 has a speed limit of 90 km/h). A sample is considered affected by congested traffic above a threshold of more
6 22,000 vehicles during the 4-h sampling periods (corresponding to vehicle speed below 70 km/h) (see SI file).
7 However, braking may occur [below this threshold for](#) congestion.

8 The vehicle fleet was close to the national one for the year 2011, with 72% diesel vehicles, and EURO 3 and 4
9 vehicles representing most of the vehicles (30 and 36% respectively). Virtually all heavy-duty vehicles are diesel.

10 **2.2.4 Meteorological measurements**

11 A Young meteorological station was installed at the traffic site to capture wind speed and direction, while relative
12 humidity, and temperature data and rain data are obtained from two stations located in Grenoble conurbation (see
13 SI file section IV).

14 The wind speed was low during the field campaign (on average 0.98 m/s, ranging from 0.50 to 2.5 m/s). The
15 temperature was warm (on average 17.6°C, peaked to 27°C) and was higher before the first rain event (on Sunday
16 17/09/11) with average temperatures of 21°C and 15°C, respectively, before and after the rain event. Two rain
17 events occurred during the campaign, the first one from the morning of 17/09/11 to the night of 18/09/11 night (34
18 mm of rain) and the second one from the night of 18/09 to 19/09/11 afternoon (12.7 mm). They corresponded to
19 summer storms.

20 **2.3 Chemical analyses**

21 The measurements of carbonaceous material (EC and OC) in PM samples were performed using the Thermo-
22 Optical Transmission (TOT) method on a Sunset Lab analyser (Jaffrezo et al., 2005; Aymoz et al., 2006) following
23 the EUSAAR2 temperature protocol (Cavalli et al., 2010). Ionic species were analyzed with Ionic Chromatography
24 (IC) following a well-established method (Jaffrezo et al., 1998; Waked et al., 2014). Metals were analyzed using
25 Inductively Coupled Plasma Spectrometry (ICP-MS) (Waked et al., 2014). The chemical speciation of organic
26 particles are performed by Gas Chromatography–Mass Spectrometry (GC-MS), [except PAHs that were measured](#)
27 [by liquid chromatography \(HPLC\) using a fluorescence detector](#) (Piot, 2011; Golly et al., 2015).

28 Hence, a large number of particulate chemical species have been measured in the filter samples simultaneously
29 collected at the traffic and urban background sites, including EC, OC, 9 major ions (Cl^- , NO_3^- , SO_4^{2-} , oxalate, Na^+ ,
30 NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}), 33 metals and trace elements (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg,
31 Mn, Mo, Na, Ni, Pb, Pd, Pt, Rb, Sb, Sc, Se, Sn, Sr, Ti, Tl, V, Zn, Zr), 3 sugars (galactosan, mannosan,
32 levoglucosan), 15 PAHs (phenanthrene, anthracene, fluoranthene, pyrene, retene, benzo(a)anthracene, chrysene,
33 benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene,
34 dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, coronene), 30 n-alkanes (from C10 to C40), 2 branched alkanes
35 (pristane and phytane) and 10 hopanes (trisnorneohopane, 17 α -trisorneohopane, 17 α ,21 β -norhopane, 17 α 21 β -
36 hopane, 17 α ,21 β ,-22S-homohopane, 17 α ,21 β ,-22R-homohopane, 17 α ,21 β ,-22R-bishomohopane, 17 α ,21 β ,-22S-
37 bishomohopane, 17 α ,21 β ,-22S-trishomohopane, 17 α ,21 β ,-22R-trishomohopane).

38 The same array of chemical species were also quantified in the filter samples from the chassis dynamometer
39 experiments.

40 **2.4 Data analysis**

41 A series of multivariate data analysis tools have been used in order to define which species are related to traffic,
42 to identify influential parameters, and to quantify their respective influences. Thanks to simultaneous
43 measurements at near-traffic and background sites, [local increments in concentration](#) at the traffic site have been
44 calculated as the difference between near-traffic and urban background concentrations. Sign and Rank Signed-
45 Wilcoxon tests have been used to estimate if concentrations measured at the near-traffic site are significantly higher
46 than concentrations measured at the urban background site and can possibly be ascribed to local traffic emissions.
47 As a complementary indication of relation to traffic, Spearman correlations with traffic data (total traffic, light-

1 duty traffic, heavy-duty traffic), with NO_x (as an indicator of traffic emissions) and with EC (as an indicator of
2 diesel traffic emissions) (Morawska and Zhang, 2002; Reche et al., 2011) have also been examined. Results for
3 species for which concentrations are significantly higher at the near-traffic site (then including both positive
4 increments and p-values below 0.05 from Sign and Signed Wilcoxon tests) are presented in Tables 1a and 1b.

5 **Increments in concentrations** for all species strongly associated with traffic are transformed into emissions
6 according to a well-established procedure (e.g. Pant and Harrison, 2013; Charron and Harrison, 2005; details in
7 the SI section V). This method enables the calculation of average emission factors for the mixed traffic fleet of the
8 RN87 highway assuming that (1) **increments in concentration (near-traffic site minus urban traffic site)** are from
9 local traffic, (2) emissions of NO_x are known and estimated from emission inventories (COPCETE that uses
10 emission functions from European COPERT4 averaged for fleet composition and speed) and detailed traffic counts
11 and (3) atmospheric dilution affects similarly all pollutants. Average emission factors (EFs) are expressed in
12 mg.veh⁻¹.km⁻¹ or µg.veh⁻¹.km⁻¹ (Tables 2a,b,c,d). Since it is thought that nearby industrial activities influence the
13 concentrations of Ti, Cr, Fe and Mn in the morning, these data are excluded from the calculations. **Standard**
14 **multiple Linear Regression analyses (SPSS software)** are performed between **computed average** emission data and
15 light-duty and heavy-duty vehicle counts. The coefficients of the regressions represent average EFs for local
16 heavy-duty and light duty traffics (Table 3). The constants represent the parts not related to local traffic. **They are**
17 **all not significant** (p-values above 0.4 for metals and organics, p-value of 0.061 for EC) **confirming the above**
18 **assumption that mostly local traffic contributes to local increments in concentration.** Results from Multiple Linear
19 Regressions are not available for all species strongly related to traffic since its use requires normally-distributed
20 data and the model must be validated through residues analyses.

21 **3 Results**

22 Average concentrations measured at the traffic site are presented in the SI (section II). Four-hour PM₁₀
23 concentrations ranged from 4.9 to 45.1 µg.m⁻³ (on average 24.1 µg.m⁻³) and was strongly dominated by EC (on
24 average 5.9 µg.m⁻³) and OC (on average 5.4 µg.m⁻³). At this site in the vicinity of traffic dominated by diesel
25 vehicles, EC and OC concentrations were of similar magnitude. EC concentrations peaked at commuting time in
26 the early morning and at the end of the afternoon, and follows quite well the evolution of traffic; the temporal
27 evolution of OC is closer to that of sulphate with somewhat stronger variability following those of traffic. The
28 other major constituents of PM₁₀ were sulphate (on average 1.2 µg.m⁻³), iron (on average 1.0 µg.m⁻³) and calcium
29 (on average 0.8 µg.m⁻³). Strong showers during the weekend in the middle of the two-week campaign led to PM₁₀
30 concentrations below 10 µg/m³ during a few hours (see Figure 2 and SI VII for individual particulate species).

31 **3.1 Identification of species related to local on-road traffic**

32 Tables 1a and 1b present species for which concentrations are significantly higher at the near-traffic site and
33 assumed from local emissions. These species could be distributed into two main groups according to both the
34 significance of the contribution of traffic to atmospheric levels and the strength of relations with traffic indicators
35 (traffic counts, NO_x and EC concentrations).

36 **3.1.1 Species strongly associated with local traffic**

37 ~~Species significantly correlated with traffic indicators and for which local traffic contributions are above 50% are~~
38 ~~highlighted in Tables 1a, 1b.~~

39 Cu, Fe, Mn, Sb, Sn have concentrations strongly correlated with traffic indicators (Table 1a). Their **local**
40 **increments in concentration due to traffic** range from 54% to 84%. The concentrations of these species are linearly
41 related to each other with near-zero intercepts (Figure 3) confirming that they come from the same source.
42 Similarly to this study, Amato et al. (2011a) and Harrison et al. (2012) measured strong increments for Fe, Cu, Sb
43 and Sn concentrations at traffic sites with strong correlations between them. Here, Cu, Fe and Sn are the metals
44 that are the most closely related (**Pearson $r^2 \geq 0.8$**), while relationships with Mn and Sb are more scattered (**Pearson**
45 **$r^2 < 0.5$**) and more closely related to the heavy-duty traffic (Table 1a).

46 Cr and Ti are also species significantly correlated to traffic indicators but to a lower extent than Cu, Fe, Mn, Sb
47 and Sn. Cr (Boogaard et al., 2011 ; Amato et al., 2011a) and Ti (Amato et al., 2011a) also showed higher
48 atmospheric concentrations at street locations than at urban background sites in previous studies. Cr and Ti show

1 a behaviour different from that of other elements coming from brake wear. They present sharp peaks in the
2 morning, poorer correlations with copper, and significant correlations with Al (Figure 2 and Table 1a). When the
3 very high morning concentrations are removed (mornings of workdays), their temporal variations are much closer
4 to the ones of metals from brake wear emissions. This suggests that another source influenced Cr and Ti
5 concentrations near the traffic site in the morning, possibly nearby metalworking activities. Similarly, while
6 morning peaks are less obvious in the temporal variations, the exclusion of morning data for Fe and Mn improves
7 their correlations with Cu (Figure 3).

8 Many of these species are metals that are known to arise from brake wear emissions (Thorpe and Harrison, 2008;
9 Pant and Harrison, 2013; Grigoratos and Martini, 2014, 2015). Indeed, Fe could come from the lining (steel or
10 iron powder) in semi-metallic brake, from fibres as steel, or cast iron rotor wear for low metallic brake. Cu is a
11 high-temperature lubricant present in linings and it is also included in fibres as brass to increase braking
12 performance. Sb is an element of brake lining both in filler as antimony sulphate and in lubricant as antimony
13 trisulphide. Chromium oxides are elements of the filler of brake linings used for their thermal properties, and
14 potassium titanate fibers are present as a strengthener in organic linings (Sanders et al., 2003; Grigoratos and
15 Martini, 2014 and references therein). Cr could also come from lubricant oil combustion (Pulles et al., 2012).

16 Only three light molecular weight PAHs (An, Fla, Pyr) are strongly associated with traffic indicators even though
17 only the particulate phase is determined (Table 1b). It is well-established that light molecular weight PAHs are
18 emitted by diesel vehicles, while higher molecular weight PAHs are rather associated with petrol vehicle emissions
19 (Zielinska et al., 2004; Phuleria et al., 2006 and 2007; Pant and Harrison, 2013). Not surprisingly, in this site
20 dominated by diesel vehicles, high molecular weight PAHs (from 5 rings) are more significantly correlated with
21 levoglucosan, suggesting a closest relation to biomass burning emissions than to on-road petrol vehicles.
22 Proportional concentrations of An, Pyr, and Fla suggest that they mainly come from the same source, likely diesel
23 exhaust emissions (Figures 2 and 3). Specifically, Pyr and Fla show high increments in concentration (as an
24 indication of the low contribution of the urban background compared to strong traffic contribution, and/or rapid
25 photochemical degradation) and strong linear relationship without any significant intercept (as an indication of
26 common origin). Concentrations of An have more variability and larger contribution from the urban background.

27 The n-alkanes C19 to C26 and two hopanes ($17\alpha21\beta$ norhopane and $17\alpha21\beta$ hopane) are species that are not
28 significantly, or only weakly, correlated to total traffic. However, they are significantly correlated with NO_x and
29 EC and some of them with heavy-duty traffic. The n-alkanes between C18 and C25 are the predominant ones in
30 vehicle exhaust and correspond to the high boiling point components in diesel fuels (Alves et al., 2016). Hopanes
31 are known to arise from unburnt lubricating oil emissions (Rogge et al. 1993a; Zielinska et al., 2004), and
32 $17\alpha21\text{n}$ Norhopane is considered as a tracer for lubricating oil (Kleeman et al., 2008). While n-alkanes have been
33 measured in the exhaust of test diesel vehicles in our study (Table 4), hopanes and steranes were below the
34 quantification limit for all selected vehicles. It was assumed that the tested vehicles (passenger cars, none of them
35 was a super-emitting vehicle) did not emit enough unburnt oil for the proper quantification of hopanes. At the
36 sampling site, the temporal variations of the concentrations of these species show higher values on the second
37 week of the field campaign than on the first one. This observation can be explained by much larger heavy-duty
38 traffic during this period (almost twice the traffic of the first week).

39 3.1.2 Other species

40 This second group corresponds to species with local increments below 50% and no significant, or only weak,
41 correlations with traffic indicators. It is highly heterogeneous since it includes OC, NO_3^- , Na^+ , Ca^{2+} , Mg^{2+} , Ba, Co,
42 Phenanthrene (Phe), Benzo(a)Anthracene (BaA) and some n-alkanes (C18, and from C27 to C33). Most of species
43 from this group are obviously emitted by the traffic but they seem to be less specific than species from the first
44 group since other sources can largely contribute to their emission levels.

45 Not surprisingly NO_3^- is not significantly related to primary traffic indicators. However its concentrations are
46 significantly higher at the traffic site ($p < 0.001$, and median increment of 28%). Additionally, the temporal pattern
47 of NO_3^- is different from that of indicators of regional origin (for example SO_4^{2-} , SI section VII). Amato et al.
48 (2011a) found similar contributions of traffic to NO_3^- concentrations at two traffic sites in Barcelona (34% and
49 25% respectively). They assumed that NH_4NO_3 is quickly formed in the road plume enriched in NH_3 emitted by
50 vehicles. Indeed, the important introduction of vehicles equipped with DeNOx technology such as 3-way catalysts
51 or selective catalytic reduction systems have led to recent increasing vehicular NH_3 emissions (Kean et al., 2009;

1 Suarez-Bertoa and Astorga, 2016) responsible for significant changes in the chemistry of the atmosphere in
2 roadside areas.

3 OC concentrations are significantly higher at the traffic site ($p < 0.001$; increment of 23%), and are weakly but
4 significantly correlated with traffic indicators. Amato et al., (2011a) found slightly higher increments of 34% and
5 41% for OC at their 2 traffic sites. Deconvolution of sources from simultaneous PM_{10} AMS measurements
6 concluded that about 20% of the total PM_{10} organic mass could be attributed to vehicular emissions (DeWitt et al.,
7 2015). Additionally, the temporal pattern of OC concentrations clearly shows a dominant regional contribution
8 (Figure 2 and SI section VII). All these results agree that in summer time, the majority of OC is of regional origin,
9 despite a clear influence of traffic.

10 Na^+ , Ca^{2+} , Mg^{2+} and Sr concentrations are also significantly higher at the traffic site ($p < 0.05$, increments from 33%
11 to 43%, except for Sr for which urban background concentrations are most of the time below detection limit).
12 When three high concentrations for Mg^{2+} concentrations and one for Sr concentration are excluded (all probably
13 not related to traffic), both present temporal variations close that of calcium (Figure 2). All are at least significantly
14 correlated to the heavy-duty traffic ($p < 0.05$). Since Ca^{2+} , Mg^{2+} and Sr are strongly affected by rain events (assumed
15 to influence the silt loading of the road), their incremental concentrations are believed to be from resuspended
16 dust, as concluded in other studies (e.g. Lough et al., 2005, Amato al., 2011a).

17 Ba and Co concentrations are significantly higher at the traffic site ($p < 0.05$, increments of 37% and 36%
18 respectively). Ba concentrations present a temporal behaviour close to the ones of Cu, Fe, Sn and Mn and,
19 accordingly, is known as an element of the filler of brake linings. Higher Ba atmospheric concentrations at street
20 locations than at urban background sites have also been observed in previous studies (Harrison et al., 2012). On
21 the contrary, Co concentrations do not show any correlation with traffic indicators and are correlated with tracers
22 of regional origin (Table 1a). Co is sometimes measured in brake pads (e.g. Hulskotte et al., 2014); and Amato et
23 al. (2011) found similar increments for Co at their traffic sites (respectively 33% and 47%). All of these suggest
24 that a possible contribution of brake wear to Co concentrations cannot be excluded, despite the lack of correlation
25 with traffic indicators.

26 The concentrations of Phe, BaA, C18 and C27-C33 alkanes are significantly higher at the traffic site and some of
27 them are significantly correlated with NO_x and EC. Accordingly these species were detected in the exhaust
28 emissions of diesel vehicles sampled from our chassis dynamometer experiments. However most of them are also
29 significantly correlated with levoglucosan measured at the traffic site, particularly BaA. Indeed the temporal
30 pattern of BaA shows similarities with both the one of Pyr (strongly related to traffic, see below) and levoglucosan
31 (tracer of biomass burning peaking in the evening) (Figure 2). It is therefore believed that most of them are largely
32 emitted by biomass burning and are not specific of road traffic emissions.

33 3.2 Quantification of traffic fleet emissions for species associated with traffic

34 Average emission factors (EFs) are presented in Tables 2a,b,c,d. Most EFs show large standard deviations. This
35 variability reflects the presence of vehicles with various emission levels (diesel/petrol; different standards and
36 engine load; cold start/hot vehicles; presence of a few high emitting vehicles). It could also be related to the
37 variability of the vehicle fleet (on-average 5% heavy vehicles but ranging from 0.3% to 12%) and to the various
38 traffic conditions (from fluid with speeds up to 90 km/h to congested with stop-and-go traffic).

39 Table 3 presents average EFs for heavy-duty and light duty traffics, their standard deviations and confidence
40 intervals at 95%.

41 3.2.1 EC/OC emissions

42 The traffic-fleet EF for EC determined in this study ($39 \text{ mg.veh}^{-1}.\text{km}^{-1}$) is slightly higher than the ones determined
43 in tunnel studies in Austria, China, California, and near a heavily-trafficked highway in Switzerland (about 21
44 $\text{mg.veh}^{-1}.\text{km}^{-1}$ for Handler et al., 2008; Hueglin et al., 2006; Cui et al., 2016; and 31 $\text{mg.veh}^{-1}.\text{km}^{-1}$ for Gillies et
45 al., 2001), while it is similar to the one of a tunnel study in Portugal ($39 \text{ mg.veh}^{-1}.\text{km}^{-1}$) (Alves et al., 2015).
46 Conversely, the traffic-fleet EFs for OC in Austria and China (about 19 $\text{mg.veh}^{-1}.\text{km}^{-1}$) are similar to ours, while
47 the ones for urban tunnels in Portugal (Alves et al., 2015) and U.S. (Gillies et al., 2001) are higher (39 $\text{mg.veh}^{-1}.\text{km}^{-1}$
48 and 25 $\text{mg.veh}^{-1}.\text{km}^{-1}$ respectively). Different traffic fleet and traffic conditions may explain these small

1 divergences. Part of the differences may also be due to the different measurement techniques used for the
2 distinction between EC and OC.

3 The average light-duty traffic-fleet EF for EC is in excellent agreement with the EFs of Euro 3 and Euro 4 diesel
4 vehicles obtained from chassis dynamometer measurements in our study for which the highest EFs were clearly
5 observed when vehicles are cold (Figure 4a). Indeed, these two types of vehicles represented the largest proportion
6 of passenger's cars on the RN87 freeway in 2011 (Fallah Shorshani et al., 2015), as well as in the French national
7 fleet. Similarly to results for diesel vehicles tested by Fujita et al. (2007) and Lough et al. (2007), EC has the
8 highest emission factor in diesel exhaust. It also could be noted that the heavy-duty traffic-fleet EF for EC is about
9 5-times higher than the one determined for light-duty traffic.

10 The emissions of OC could not be discriminated between light-duty and heavy-duty traffic (coefficients not
11 significantly different from zero). However, it can be observed that the traffic-fleet EF for OC is larger than could
12 be expected from exhaust measurement of test vehicles (Table 4, Figure 4b). Note that traffic-fleet EFs for OC
13 from other studies (Handler et al., 2008; Alves et al., 2015, Cui et al., 2016; He et al., 2008) are at least as high as
14 ours, and the EFs for exhaust OC from Cheung et al. (2010) for Euro 4 diesel vehicles (with and without Diesel
15 Particulate Filter) is similar to ours. There are many likely explanations for the traffic-fleet EF for OC being higher
16 than expected: proportionally larger contribution of the heavy-duty traffic to OC than to the EC; contribution of
17 non-exhaust emissions to the OC (e.g. tyres wear); contribution of high emitting vehicles; and rapid formation of
18 secondary OC in the roadside atmosphere. Further studies are required to assess the respective importance of these
19 processes. In particular, a better knowledge of particle size distribution of OC emitted by traffic might be useful.

20 Average OC/EC ratios on increments in concentrations and emissions are respectively 0.33 and 0.44 (Table 5) that
21 is in excellent agreement with observations in a roadway tunnel in Lisbon and with roadside enrichment of OC/EC
22 in Birmingham, U.K. (Pio et al., 2011; Alves et al., 2016). Pio et al. concluded that OC/EC ratios of 0.3-0.4
23 characterizes vehicle fuel combustion at their sites and similar conclusions could be made for Grenoble. However,
24 the OC/EC ratio is expected to depend on vehicle fleet. Indeed, in the exhaust of test diesel vehicles without particle
25 filters (Table 4), OC/EC ratios are lower than 0.4, while they are respectively 6.1 and 1.7 in the exhaust of Euro 2
26 petrol vehicle (urban cold cycle) and Euro 4 petrol vehicle (road cycle) (no average OC/EC ratios has been
27 determined for petrol vehicles because of many measurements below detection limit). Other recent chassis
28 dynamometer measurements (Lough et al., 2007) showed that most OC/EC ratios are above 2 for petrol vehicles
29 (except for two smoker vehicles) and below 0.5 for diesel vehicles (except idling conditions), with even lower
30 ratios for older and heavier diesel vehicles. Because in 2011, diesel vehicles represented about 70% of total
31 vehicles on the RN87 highway, the OC/EC ratio found in this study is lower than the ones of many other studies.
32 For examples, OC/EC ratios from EFs or increments in concentrations were 0.90 ± 0.21 in a tunnel in Austria
33 (Handler et al., 2008); on average 0.52 for a traffic fleet with 40% diesel vehicles in Spain (Amato et al., 2011a)
34 and 0.5 in Marseille where petrol two-wheelers are much more numerous (El Haddad et al., 2009). However, since
35 the OC/EC ratio in the exhaust of the diesel vehicle equipped with particle filter was higher (0.7) possibly due to
36 the more efficient trapping of EC than OC by the particle filter, one can expect that in the future the OC/EC ratio
37 reflecting vehicle fuel combustion would increase with the progressive introduction of vehicles equipped with PF.

38 3.2.2 Metals from brake wear emissions

39 Fe presents by far the third highest traffic emission rate after those of EC and OC ($6.7 \text{ mg.veh}^{-1}.\text{km}^{-1}$, Tables 2).
40 Cu also shows a high emission factor from traffic ($300 \text{ } \mu\text{g. veh}^{-1}.\text{km}^{-1}$ respectively). Similarly, major contributions
41 of Fe and Cu to PM_{10} vehicular emissions were found in other locations (e.g. Kam et al., 2012; Harrison et al.,
42 2012). The analysis of brake wear debris (Apeageyi et al., 2011 ; Sanders et al., 2003 ; Kukutschová et al., 2009 ;
43 Hulskotte et al., 2014) and brake material (Gigoratos and Martin, 2015; Hulskotte et al., 2014) confirmed that Fe
44 is the major element of brakes and that Cu is another important element. Indeed, maximum contents of 60% by
45 mass for Fe (Gigoratos and Martin, 2015) and of 15% for Cu (Denier van der Gon et al., 2007) have been reported
46 for brake lining materials. Fe, Cu, Zn, Sn would represent about 80-90% of metals presents in brake pads and Fe
47 95% of metals in brake discs (Hulskotte et al., 2014)

48 Our results can be compared with other European traffic EFs determined for PM_{10} species measured in roadside
49 environments or tunnels, and with data derived from average brake wear composition (details in SI, section VIII).
50 Most PM_{10} -EFs are consistent with other roadside traffic fleet emissions (Johansson et al., 2009; Bukowiecki et
51 al., 2009) and with data corresponding to braking emissions of $8 \text{ mg.veh}^{-1}.\text{km}^{-1}$ (Hulskotte et al. 2014), but larger

1 than the estimations aimed to quantify brake wear only (Bukowiecki et al., 2009). Our traffic-fleet EF for Sb is
2 much lower than similar EFs determined in other studies, while Ba emissions show large variability from a study
3 to another. EFs related to brake wear component emissions are lower in tunnel environments (Handler et al., 2008;
4 Alves et al., 2015), except for the oldest study (Gillies et al., 2001). This could be explained by less stop and go
5 traffic in such environments. Indeed, interestingly, many EFs determined by Handler et al. (2008) are about half
6 the ones found in this study. Even though this proportionality is not found for Ba, Sb and Ti, this supports that
7 brake wear metal EFs are strongly related with braking strength. The low Sb emissions of our study may possibly
8 be related to the introduction of Sb-free brake pads (von Uexküll et al., 2005 ; Apeageyi et al., 2011).

9 EFs for brake wear metals (Cu, Fe, Sb and Sn) are 8 to 13 times higher for the heavy-duty traffic than for the light-
10 duty traffic (Table 3). The estimations from Bukowiecki et al. (2009) for brake wear only are much lower than
11 ours but somewhat proportional (factors 4.6 to 6.8 for light-duty EFs and from 4.3 to 8.5 for the heavy-duty traffic
12 – Sb excluded). This consistence between brake profiles suggests that brake compositions would be similar in
13 different European countries. Traffic-fleet light-duty EFs for brake wear metals are much higher than the ones
14 from chassis dynamometer exhaust measurements (this study: Table 4; Cheung et al., 2010), confirming the
15 dominant contribution of braking for these elements.

16 The sum of traffic-fleet EFs for metals related to brake wear (Ba, Cr, Cu, Fe, Mn, Sb, Sn, Ti - Table 2b) leads to a
17 total of 7.3 mg/km that should be lower than the real emission factors for brake wear dusts since it only includes
18 metals, and does not take into account of carbonaceous material and other unquantified compounds of brakes (S,
19 Zn, Al, and Si, for the most important ones). Hulskotte et al. (2014) determined a brake profile from the analysis
20 of 65 brake pads and 15 brake discs from 8 very common car brands in Europe. The consistence between with
21 their data and ours suggests that brakes spent in France are quite similar to the ones spent in The Netherlands.
22 Then, their average brake profile data are used to estimate the average emission factor for brake wear assuming
23 that the total proportion of metals is kept, and, according to Hulskotte et al., that 70% of the wear arise from the
24 disc. *This latter assumption is supported by other researches (Sander et al., 2003; Varrica et al., 2013), even though
25 the generation mechanisms of brake wear particles have not been fully understood yet (Grigoratos and Martini,
26 2014).* Since exhaust emissions (chassis dynamometer measurements or EFs from COPCETE inventory when
27 available) represent less than 5% of total emissions for Cr, Cu, Fe, Mn, Sb, Sn, and Ti, traffic-fleet EFs for these
28 elements are assumed to be entirely due to the emissions of brake wear dusts. *So by adding to the sum of traffic-
29 fleet EFs for metals related to brake wear the portion that corresponds to the elements and compounds not
30 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
31 emissions related to brake wear is got for the RN87 highway traffic.* This estimation includes particles directly
32 emitted during braking and those resuspended, and emissions from light and heavy-duty traffic. It should be
33 highlighted that this EF for brake wear emissions is almost twice the particle emission standards for the exhausts
34 of the *most recent vehicles (Euro 5 and Euro 6 vehicles, 5 mg/km).*

35 According to inventories atmospheric copper is largely from brake wear. Indeed brake wear represents 50-75% of
36 European Cu emissions (Denier Van der Gon et al., 2007) and 64% of French Cu emissions (CITEPA, 2018).
37 Since Sb is another well-known constituent of brake with very few other atmospheric sources, Cu/Sb ratio *was
38 often considered as a candidate* to trace brake wear emissions (Gietl et al., 2010; Pant and Harrison, 2013). Pant
39 and Harrison (2013) reviewed Cu/Sb ratios in brake wear particles and found ratios from 1.3 to 9.1 that strongly
40 depend on the *PM size fraction*. The estimation for the Cu/Sb ratio (11.7 ± 5.1 for incremental PM_{10}) is close to the
41 ones for PM_{10} elemental concentrations in other European locations including London, U.K. (on average 9.1, Gietl
42 et al., 2010), Barcelona, Spain (7.0-7.9, Amato et al., 2011a); Bern and Zurich, Switzerland (respectively 13.2 and
43 8.5, Hueglin et al., 2005) and in road dust below 10 μm collected in Barcelona, Zürich and Girona (respectively
44 6.8 ± 0.9 , 13.5 ± 6.1 , 17.0 ± 8.9 , Amato et al., 2011). However, lower PM_{10} Cu/Sb ratio are found for other European
45 traffic sites, in Sweden (4.6 ± 2.3 , Sternbeck et al., 2002 and 3.8, Johansson et al., 2009); in Portugal (about 2, Alves
46 et al., 2015) and in Vienna, Austria (1.6, Handler et al., 2008). To complicate the matter further, published data
47 from the analysis of brake pads and discs are even more scattered, roughly from 1.3 to 2000 (Adachi et al., 2004;
48 Canepari et al., 2008; Ijima et al., 2007), and often different than the chemical composition of brake wear particles
49 (Grigoratos and Martini, 2015). The poorer relationship between Cu and Sb (Pearson $r^2 = 0.4$) than those observed
50 between Sn, Cu and Fe (Pearson $r^2 > 0.8$) and the lower EF for Sb of this study than observations at other sites may
51 be explained by the introduction of Sb-free brake pads. Thus, while the occurrence of Sb may be largely explained
52 by braking activities, the use of a typical factor for braking activities using Sb seems to be less obvious.

1 The very strong linear relationships found between Fe, Cu, Mn and Sn with no significant intercept (virtually equal
2 to zero) suggests that ratios including these compounds also worth attention. Even though Fe is much less specific
3 of brake wear emissions than Cu or Sb, Hulskotte et al. (2014) observed a stable Cu/Fe ratio of about 4 % in
4 different European kerbside locations (The Netherlands: Boogaard et al., 2011; England: Gietl et al., 2010;
5 Switzerland: Hueglin et al., 2005). They concluded that brake wear is probably the single source of both copper
6 and iron in urban aerosols. The review of other recent studies leads to similar conclusions. Pio et al. (2013)
7 determined an average Fe/Cu ratio of 21 (and then, Cu/Fe = 0.048) from tunnel and busy roads measurements in
8 Portugal. Cu/Fe ratios at two traffic sites in Barcelona ranged from 0.034 to 0.058 (Amato et al., 2011a). Except
9 for the site of Weerdsingel in Utrecht, Cu/Fe ratios calculated from average PM₁₀ elemental concentrations
10 measured at 8 street locations in The Netherlands also ranged from 0.039 to 0.048 (Boogaard et al., 2015). Only
11 Alves et al. (2015) found a much higher Cu/Fe ratio in PM₁₀ collected in a tunnel in Portugal mainly due to a very
12 low EF for Cu compared to other studies. The Cu/Fe ratio determined in our study for light-duty traffic
13 (0.041±0.010) is very similar to the ones found in the majority of these European roadside sites (Table 5), while
14 the ratio determined for the heavy-duty traffic (0.070±0.017) is slightly larger due to proportionally higher
15 emissions of Cu. Again, this suggests that brake materials used in different European countries are very similar
16 and that the Cu/Fe ratio could be used as an indication of brake wear emissions.

17 Ratios with Mn and Sn are more rarely discussed in the literature, and published information is scarce. Cu/Sn ratios
18 of 6.2 and 4.3 can be calculated from data published by Handler et al. (2008) and Johansson et al. (2009),
19 respectively. Amato et al. (2011a) found Cu/Sn ratio that ranged from 4.7 to 4.8 and did not estimate ratios with
20 Mn because of the possible influence of a local steel source. Cu/Mn ratios of 3.7; 4.9 and 3.0 (Bern) and 4.4
21 (Zurich) are respectively calculated from the studies of Handler et al. (2008), Johansson et al. (2009), and Hueglin
22 et al. (2005). All these ratios are close to the ones of this study (Cu/Sn=4.1±1.0; Cu/Mn=3.6±1.6, Table 5), showing
23 that they are possible other candidates to trace brake wear emissions. Cu/Sn would be the strongest candidate since
24 the relation between these 2 elements is closer ($r^2=0.84$ for Cu/Sn vs. $r^2=0.47$ for Cu/Mn, see SI).

25 **3.2.3 Emissions of organic markers of diesel exhaust and lubricating oil**

26 As previously observed (Schauer et al., 2002; Perrone et al., 2014; El Haddad et al., 2009), n-alkanes are abundant
27 organic compounds of total quantified organic compounds emitted by vehicles on road.

28 In agreement with other chassis dynamometer measurements (Rogge et al.; 1993a; Cheung et al., 2010; Perrone et
29 al., 2014; Cui et al., 2017), the most important n-alkanes in diesel exhaust emissions are C19 to C26, while, most
30 emissions were below detection limit for the two petrol vehicles (Table 4). Schauer et al. (2002) showed that n-
31 alkanes are present in particulate exhaust emissions of non-catalyst equipped petrol vehicles, but they are almost
32 absent in the exhaust of catalyst-equipped petrol motor vehicles. In 2011 virtually all petrol vehicles were catalyst-
33 equipped (Fallah Shorshani et al., 2015). C19-C26 n-alkanes are also the most important in roadside increments
34 in concentration and as a further indication of road traffic contribution, the Carbon Preference Index (CPI, for
35 calculation see SI section VI) is very close to unity (0.99) indicating equal distribution between odd and even
36 carbon number typical of anthropogenic emissions (Harrad et al., 2003; Cincinelli et al., 2007 ; Kam et al., 2012;
37 Alves et al., 2016). Light-duty traffic-EFs for C23 and C24 are in agreement with the ones of the Euro 3 diesel
38 vehicle from chassis dynamometer measurements (upper range) and with the ones determined by Perrone et al.
39 (2014) for Euro 3 diesel vehicles (C23: 16.3 µg/km ; C24: 12.7 µg/km). Good agreements are also found for C25
40 and C26. However, the traffic-EFs determined by Perrone et al. for C21 is half the one of this study, the one for
41 C20 is 1/5 of the one of this study. All EFs determined by Perrone et al. for Euro 4 diesel vehicles are larger the
42 ones of the Euro 4 diesel vehicle of this study, but of similar size of magnitude.

43 The relative contributions of the n-alkane series in diesel exhaust show Gaussian-like shapes peaking between C20
44 and C22 (Rogge et al., 1993a; Morawska and Zhang, 2002; El Haddad et al., 2009; Cheung et al., 2010; Fujitani et
45 al., 2012; Perrone et al., 2014; Cui et al., 2017). In this study, the dominant alkanes are C21 in the exhaust of test
46 diesel vehicles and C22 in traffic RN87 emissions (Figure 5). Fujitani et al. (2012) showed that shifts from C20 to
47 C22 and differences between real-atmosphere measurements and exhaust measurements are entirely explained by
48 gas-to-particle partitioning at different dilution ratios (dominant n-alkanes were C20 and C22 at dilution ratios of
49 14 and 238 respectively). Accordingly, in this study, C21 is the dominant n-alkane at diesel exhaust dilution ratios
50 of about 80; and a shift toward a heavier n-alkane has been observed in the roadside atmosphere. N-alkanes
51 normalized by OC (µg/g) (Figure 5) show values for Euro 3 and Euro 4 diesel emissions and RN87 traffic
52 emissions that are about half of the values measured in a tunnel in Marseille (El Haddad et al., 2009). Much higher

1 values are found with the vehicle retrofitted with PF (Figure 5). These high values are due to very low OC
2 emissions by the vehicle equipped with PF and clearly show less effective reduction of n-alkanes than total OC.
3 Because of their semi-volatile nature, n-alkanes may pass the particle filter in their gaseous phase at higher
4 temperatures. While the n-alkanes series from C19 to C26 peaking around C20-C22 seems to be characteristics of
5 diesel emissions, increase of the n-alkane/OC values could be expected for the future.

6 Low molecular weight PAH's (An, Fla, Pyr) are frequently associated with particulate diesel exhaust emissions
7 (e.g. Kleeman et al., 2008; Keyte et al., 2016). Accordingly, both chassis dynamometer and *in-situ* measurements
8 indicate that diesel vehicles is a major source of these chemical species. Indeed, they are almost absent in petrol
9 exhaust emissions and are strongly related to RN87 traffic emissions. EFs for PAHs determined for the heavy-
10 duty traffic are much higher than the ones determined for light-duty traffic: from 6-times higher for Fla, up to 20-
11 times higher for Pyr (Table 3). High emissions of Pyr by heavy-duty vehicles have already been observed anywhere
12 else (Liacos et al., 2012; Cui et al., 2017). While the comparison between EFs determined during different
13 conditions is not straightforward in absence of gas phase measurements due to the high vapour pressure of the
14 lowest molecular weight organics (Fujitani et al., 2012; Polo Rehn, 2013), quite good agreements are found
15 between chassis dynamometer measurements and traffic-EFs; and with data from other studies. Indeed, again the
16 light-duty traffic-EFs for Fla and Pyr are quite consistent with the ones of the diesel Euro 3 measured with chassis
17 dynamometer. The light-duty traffic-EF for An is proportionally lower, somewhere between the ones of test Euro
18 3 and Euro 4 vehicles. The average EF for Pyr for the Euro 3 diesel vehicle of this study (Table 4) is close to the
19 ones of Perrone et al. (2014) for Euro 3 diesel vehicles (740±300 ng/km for passenger cars and 1810±570 ng/km
20 for commercial utility vehicles). Traffic EFs for Fla and Pyr are also in good agreement with average EFs in a
21 tunnel in China (40-50 km.h⁻¹/784-2776 veh.h⁻¹/18.4-35.1% HDV, He et al., 2008). These satisfying agreements
22 suggest that EFs determined in this research may be quite well representative of in-use vehicles. However, gas-
23 particle partitioning and photochemical degradation processes may make difficult the use of quantitative data for
24 these markers, as already observed (Zhang et al., 2005; Phuleria et al., 2007; Katsoyiannis et al., 2011; Tobiszewski
25 and Namieśnik, 2012).

26 In agreement with previous observations (Phuleria et al., 2006 and 2007; He et al., 2008; El Haddad et al., 2009;
27 Alves et al., 2016; Pant et al., 2017), 17 α ,21 β -norhopane and 17 α ,21 β -hopane are the two dominant hopanes
28 associated with traffic emissions. Very few traffic-EFs are available for hopanes in the recent literature and most
29 data available from recent studies are related to fuel consumption (e.g. Phuleria et al., 2006 and 2007). Traffic
30 hopane EFs of this study are much lower than those computed for tunnels in China (He et al. 2008; Cui et al. 2016).
31 In order to compare with European tunnel data, traffic-EFs are normalized by OC emissions. [The normalized
32 abundance of 17 \$\alpha\$,21 \$\beta\$ -norhopane \(246 \$\mu\$ g per g of OC\) is similar to the one for a tunnel in Lisbon \(Alves et al.,
33 2016\) but almost half the ones for tunnels in Marseille and Birmingham \(El Haddad et al., 2009; Pant et al., 2017\).
34 Conversely, the value for 17 \$\alpha\$,21 \$\beta\$ -hopane \(301 \$\mu\$ g per g of OC\) is very close to the ones found in tunnels in
35 Birmingham and Marseille but twice the one for the tunnel in Lisbon. These divergences and the quantification of
36 heavy-duty traffic emissions require further work in order to be able to define specific \[EFs and normalized
37 abundances for hopanes\]\(#\).](#)

38

39 **3.2.4 Other non-exhaust emissions**

40 The average traffic-fleet EFs for Ca²⁺ is the fifth highest traffic-fleet emission factor after EC, OC, Fe and NO₃⁻.
41 While the emissions of Ca²⁺ could not be discriminated between light-duty and heavy-duty traffics
42 (autocorrelation), this much larger emission factor than the ones measured in the exhaust of diesel vehicles is in
43 agreement with its origin. If Ca²⁺ mainly comes from road dust resuspension, it does not only depend on the
44 intensity of traffic but also on the amounts of calcium deposited on the road (silt loading). Bukowiecki et al. (2009)
45 used the mass concentration measured 1-hour earlier in order to empirically account for the observed
46 autocorrelation behaviour in the calcium time series due to the accumulation of resuspended dust. The time series
47 resolution of 4 hours for collected particles in this study does not allow such calculations. Note that contrary to
48 Bukowiecki et al., most other trace elements that could be regressed in this study do not have the same behaviour
49 as Ca²⁺. This could be explained by the removal of road dusts thanks to frequent rain events before and during the
50 sampling period.

51 Since EU tyres contain about 1% zinc oxide (Pant and Harrison, 2013) and Zn is the most abundant metallic
52 element in tyres commercialized in the U.S. (Apeageyi et al., 2011), Zn is often proposed as a key tracer of tyre

1 wear emissions. In this study, similarly to other works (Boogaard et al., 2011; Amato et al., 2011), Zn
2 concentrations did not show any roadside increment. This suggests the prevalence of other sources of Zn in the
3 Grenoble-Alpes conurbation, as well as in other urban environments. Further research are needed to determine
4 proper tracers of tyre wear emissions.

5 4. Conclusions

6 Thanks to a very large comprehensive dataset of particulate species collected from a simultaneous near-road and
7 urban background measurement field campaign and chassis dynamometer experiments of a few in-use passenger
8 cars, this study was able to determine emission factors for many particulate species from road traffic and to identify
9 and quantify tracers of exhaust and non-exhaust vehicular emissions that could be used in source apportionment
10 studies. Near-road measurements are made near a freeway with various driving conditions from free-flowing to
11 stop-and-go traffic, including frequent and severe braking events during periods of congestion (morning and
12 afternoon commuting times of workdays).

13 EC has the highest traffic emission factors and is strongly associated with diesel traffic. The emission factor for
14 EC for the light-duty traffic is similar to the ones of passenger diesel cars without particle filters. EC emissions
15 from heavy-duty vehicles are estimated to be 5 times higher than those for light duty vehicles. The traffic-fleet EF
16 for OC is slightly larger than those deduced from exhaust measurement of test vehicles. This later observation
17 would require further investigations in order to delineate the several possible causes for such observation. The
18 determination of the particle size distribution of OC could improve knowledge of the organic emissions of traffic.
19 In this environment dominated by the diesel traffic, the OC/EC ratio is below 0.4 (increments in concentration or
20 emissions), as it is in diesel exhaust emissions. However, this ratio depends on the traffic fleet and then may change
21 in the future with the progressive introduction of vehicles retrofitted with particle filter.

22 Results showed the important contribution of metals from brake wear to particulate vehicular emissions. In
23 particular, Fe has the third higher traffic emission factor after EC and OC. Total brake wear emissions are estimated
24 for the RN87 highway, they are on average almost twice the particle emission standards for the exhausts of newer
25 vehicles (from Euro 5). We have shown that Cu is another important contributor to PM₁₀ from traffic and it could
26 be an excellent tracer of brake wear emissions in most environments. Even though they are less specific than Cu,
27 other metals such as Fe and Sn may be used to trace brake wear emissions through typical ratios. In particular,
28 ratios Cu/Fe of about 0.041 for light-duty traffic may possibly be the best option for estimating the brake wear
29 emissions due to the traffic of European passenger cars. Cu/Fe ratios consistent with literature values from other
30 kerbside or urban sites, while Cu/Fe ratios may be different for rural sites (e.g. Hueglin et al., 2005), suggest similar
31 brake composition for these elements throughout Europe (as long as Cu-free brakes do not increase in use). Our
32 measurements support more the use of Cu/Sn than that of Cu/Mn and Cu/Sb as tracers of brake wear emissions
33 possibly due to an additional source of Mn and the introduction of Sb-free brake pads. Similarly to OC, the
34 determination of the particle size distribution of metals may possibly improve the discrimination between
35 influential sources in urban areas.

36 Particulate organic emission data for European motor vehicles is scarce. In this study, a few PAHs, n-alkanes and
37 hopanes have been identified as organic molecular markers of fresh diesel traffic emissions and their emission
38 factors have been quantified. In agreement with previous works, low molecular weight PAHs (mainly An, Fla,
39 Pyr) are associated with diesel exhaust emissions. Pyrene and Fluoranthene are the ones the most strongly
40 associated with fresh diesel exhaust emissions. Pyrene is more largely emitted by the heavy-duty traffic. Similarly
41 to PAHs, n-alkanes from C19 to C26 are also associated with diesel vehicles, even though the determination of
42 the concentration of the dominant alkanes (from C20 to C23) strongly depends on measurement conditions. While
43 the comparison with other recent studies can be difficult in the absence of gas quantification for *in situ*
44 measurements, a quite good agreement is found for most organics between chassis dynamometer and near-road
45 measurements and between this study and other recent studies. However, the change of the gas-particle partitioning
46 of low molecular PAHs and n-alkanes according to ambient temperature and dilution factors, and their possible
47 short-term photochemical degradation may compromise their use as quantitative markers of fuel combustion.

48 Hopanes are markers of lubricating oil in the emissions of high-emitting vehicles (Rogge et al. 1993a; Zielinska
49 et al., 2004). In this study two hopanes (17 α ,21 β -norhopane and 17 α ,21 β -hopane) have been clearly associated
50 with the traffic and more closely related to the heavy-duty traffic. However the quantification of ratios hopanes to
51 OC showed divergences with other studies that require a better understanding.

1 This study determines many quantitative data of traffic exhaust and non-exhaust emissions that could help in a
2 better definition of traffic emissions in source apportionment studies.

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