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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Sources and geographical origins of fine aerosols in Paris (France)" *by* M. Bressi et al.

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The anonymous Referee 1 is thanked for his extensive comments on our manuscript. Please find below the answers of the authors.

R.1.1. (stands for Referee 1, 1st comment) "This MS presents a source apportionment analysis using PMF of a 1-year dataset of chemical speciation data. The authors describe the need for this work based on the lack of detailed source apportionment studies for Paris in the literature, and I concur with them. However, despite it being necessary, the work is not novel regarding the approach or the methods used, nor regarding the results. The study is certainly interesting, but it is also certainly not innovative."

A.1.1. (stands for Answer to Referee 1, 1st comment) Regarding the approach and the methods, the authors agree with the reviewer that the PMF model used here has been widely reported in the literature. However, the authors also believe that the way PMF was applied here is innovative in some extent: using the bootstrap technique to determine the appropriate number of factors – which represents a major question in PMF studies – has not been reported elsewhere to our knowledge (see also the acknowledgement of Referee 2 in his comment R.2.11. on this subject). Regarding the results, the authors agree with the reviewer that the nature of the sources found in our study have also been reported elsewhere (although a thorough investigation of their chemical profiles was conducted in our case). However, the conclusions reached from our study are according to us novel and unexpected, such as for instance stating that on average, more than half of PM2.5 mass measured in the city of Paris is due to mid- or long-range transport of secondary aerosols stemming from continental Europe, whereas local sources only contribute a quarter of the annual averaged mass. The contribution of PM wood burning which is equal (on a yearly basis) to PM related to traffic was also quiet unexpected for a megacity and in particular for Paris which is strongly affected by diesel emissions (2/3 of the fleet). A robust database and source apportionment – as presented here - was needed to validate the few (time limited) studies which have highlighted this point before. Finally, the results of this study had strong implications on regional air quality strategic plans, which point is often raised as an objective of many papers dealing with PM pollution in urban areas. The results obtained in this paper have a large societal impact since local authorities have decided beginning of 2013 - for the first time in France - to forbid the use of open fire place in Paris city. This measure is currently undertaken by many other French cities. For these reasons (and those exposed in the paper), we believe that this paper does present original (and robust) conclusions that are worth being published.

R.1.2. "In general, some results are difficult to interpret, such as the nature of the metallic source or the too low traffic contribution. The main limitation of the work is the lack of mineral tracers (and thus mineral dust contributions)."

A.1.2.The limitations stated by the Referee 1 regarding the metallic, traffic and mineral dust sources will be discussed in the comments A.1.22., A.1.3 and A.1.4., respectively.

R.1.3."A number of issues to be addressed are described below: - Traffic contribution: the contribution from this emission source seems really low (14% of PM2.5) considering that the study location is Paris, a megacity (11 million inhabitants) and the second megacity in Europe (stated by the authors). If the model is unable to provide a more realistic estimate, then the authors should describe the limitations of the model, given that I find it very unlikely that the contribution is so low. I believe this could be related to another of the limitations of the study, which is the absence of a mineral dust source. The database used lacks teh major mineral matter tracers, and as a result no mineral dust source is resolved by the model. This could also be impacting the traffic source, whih should probably have a larger road dust component which might then increase its contribution to >20% of PM2.5, which would probably be more realistic. This would change their conclusions, as more mitigation strategies should then be local (and fewer of them external to the city)."

A.1.3. The limitations abovementioned regarding a mineral dust source will be discussed in the comment A.1.4., a focus will be made on the traffic source only in the current comment A.1.3. We agree with the reviewer that the traffic contribution seems at the first glance relatively low considering that the study location is Paris. First, let us recall that the location of our sampling site (roof platform) represents urban background conditions (i.e. not close to traffic and re-suspended dust). Second, this PMF road traffic factor represents primary emissions of vehicles only as stated in the manuscript (p 33258, l6-7; p 33259, l2) and as suggested by the absence of secondary inorganic species in its factor profile as well as its low OC to EC ratio of 1.2 (see p33258, l4-6, 20). As stated p33258, l26-27: “the secondary nature of road traffic related aerosols will be found in other factors” (e.g. the A.N. rich factor). The overall contribution of road traffic emissions to PM2.5 mass including primary and secondary aerosols might thus be slightly higher (although ammonium nitrate is mostly imported in the region of

Paris as suggested by the homogeneity of its levels at different sampling sites across the region, Bressi et al., 2013). Third, only fairly good agreement is observed between modelled and measured EC levels (r2=0.56, see Table S1 and p33252, l4-5), which might lead to higher uncertainty on the road traffic source given the predominance of EC in this factor. However, several evidences support the relevance of the contribution of the road traffic source estimated from PMF here. Comparisons with external compounds that are presumably primarily emitted by road traffic sources have been investigated. As discussed in details in the comment A.3.2., NOx has been monitored by the regional air quality agency (Aiparif) at the same urban background site (AIRPARIF and LSCE, 2012). According to emission inventories (see p33263, l21-29), NOx are primarily emitted by road traffic although other sources (e.g. biomass burning) might also contribute to its concentrations. In addition, black carbon (BC) has been measured with an Aethalometer (AE-31, e.g. see Sciare et al., 2011 for a description of the instrument) at a similar urban background site of Paris (see Favez, 2008 for a description of the site) from 11 September 2009 to 10 September 2010. BC has been apportioned to a fossil fuel (BCff) and a wood burning (BCwb) fraction, following the methodology introduced by Weingartner et al. (2003) and described by Favez et al. (2010) for instance. BCff is often regarded as a tracer of primary traffic emissions (e.g. see Crippa et al., 2013). Results of these comparisons are shown in Fig. A.1.3.a. and A.1.3.b., which can be found in the supplementary material of this comment. Fairly good correlation is observed between NOx and the road traffic source (r=0.50, n=329) although discrepancies are observed during wintertime, which might be related to wood burning emissions of NOx during this period (see comment A.3.2. for further interpretation). Interestingly, correlations between Road traffic and BCff are fairly good all along the year (r=0.50, n=327) including wintertime, while no correlation is found between BCff and the other sources (r typically equals to 0.2, see Table A.3.2.). These fairly good correlations with external tracers give further confidence on the relevance of the contribution of the road traffic factor. The relatively low contribution found here might also be due to the specific flat topography of the Paris region, which likely favours the dispersion of local emissions due to road traffic. Elemental Carbon levels - that mostly come from traffic emissions - are indeed lower in Paris than in other cities at urban background sites: Paris (1.3 μg/m3, Bressi et al., 2013), Barcelona (1.7 μg/m3, Reche et al., 2011), London (1.9 μg/m3, Reche et al., 2011), Istanbul (2.9 μg/m3, Theodosi et al., 2010) or Beijing (8.2 μg/m3, Yang et al., 2011). (Note: this comparison presents some limitations as for some studies i) black carbon and not elemental carbon was measured and ii) PM10 and not PM2.5 was sampled, although EC should mostly be in the fine mode.) In addition, although the average relative contribution of our road traffic source (14%) is lower than the median contribution (20%) found by Belis et al. (2013) in his review on SA studies for urban background sites, it remains in the 11-32% inter-quartile range. Regarding the last part of your comment, stating that "This would change their conclusions, as more mitigation strategies should then be local (and fewer of them external to the city)", the authors do believe that our conclusions remain robust in spite of the abovementioned limitations. Other independent studies indeed support the importance of mid- long- range transport of PM in the city of Paris. First, Airparif estimated the proportion of local versus imported PM2.5 mass based on Lenshow's methodology (Lenschow et al., 2001) at the sampling site described in our study for the same period (see AIRPARIF and LSCE, 2012 for the full report). They concluded that 32% of PM2.5 measured at the urban site are produced by the agglomeration of Paris, whereas 68% are imported from outside the Ile-de-France region (see for instance p3 of the press release, Airparif, 2011). Second, from the one-year chemical characterization of PM2.5 determined at the urban site and with the use of chemical transport models, Petetin et al. (2013) conclude that: "pollution reduction measures at the Paris scale alone are inadequate to prevent most exceedances of PM standards, thus underlying the necessity of integrated AQ management at the regional/continental scale". Third, from a one-month sampling campaign conducted in summer in the region of Paris, Freutel et al. (2013) conclude that: "the influence of the Paris emission plume onto its surroundings (...) [is] rather small". Fourth, from a one-month campaign conducted in winter in the region of Paris, Crippa et al. (2013) reports that: "The similarities in aerosol composition, total mass and temporal variation between the three sites [used in this study] suggest that particulate pollution in Paris is dominated by regional factors, and that the emissions from Paris itself have a relatively low impact on its surroundings." These studies therefore strongly support our conclusions.

R.1.4."- Mineral dust source: as the reader works through the paper this issue arises, given that few mineral tracers are considered in the database (Ca, Mg and K, but only as the water-soluble fraction) and then most of them are excluded from the PMF analysis (e.g., Al, Ca, Ti, because they are weak variables). It seems very likely that a "city dust" source should be resolved in the analysis, but it cannot be due to the lack of tracers. The authors only acknowledge this limitation far into the MS (page 33266), and then they state that this source would represent at most 3% of PM2.5 and that it is therefore negligible. Firstly, I find it hard to believe that in a megacity such as Paris the city dust would have such a low contribution. Perhaps the low mineral dust levels obtained in Bressi (2013) could be related to the analythical methods (digestion wth microwave), which does not use HF and which would then lose a large proportion of the minerals because it is unable to dissolve them? Secondly, even if the contribution from the mineral dust source per se were small, the authors are missing the contribution from mineral dust to the traffic source (road dust), which as stated above would increase the traffic contribution to levels more representative of this type of city."

A.1.4. The authors agree with the reviewer it seems likely that a city dust source should be resolved in the analysis but it cannot be due to the lack of tracers (as stated p33266, l15-20). Limitations related to the analytical technique used have been more clearly stated in the manuscript as follow: P33243, l3: "Note that some minerals (e.g. Al, Ti, etc.) might be underestimated due to the acid microwave digestion procedure used here (with HNO3), which might not be able to dissolve entirely these compounds (see e.g. Robache et al., 2000)." In addition, as discussed in the comment A.2.5. the specific location of our sampling site (20 m a.g.l.) might prevent from being highly affected by a road dust source. The following comment has been added accordingly:

P33242, l9: “It should however be highlighted that this [sampling] site is at 20m a.g.l. which might prevent near ground sources (e.g. road dust) to be considered in our study.” Limitations related to the absence of a clearly identified road dust source have been reported in the manuscript as follow: P33258, l10: “Note that the lack of mineral tracers mentioned in Sect. 2.1.2 might prevent us from identifying a road dust fraction in this factor.” P33274, l5: “As mentioned in Sect. 4.1.2, the absence of a road dust fraction might partly explain the relatively low contribution of our road traffic source.” P33266, l25: “Further research should be conducted to better characterize mineral dust contribution to fine aerosols in the region of Paris.” To the best of our knowledge, only three studies have focused on mineral dust in fine aerosols in the region of Paris (Bressi et al., 2013; Favez, 2008; Guinot et al., 2007). Due to the abundance of calcium in mineral dust (e.g. see Putaud et al., 2004), these studies have used a non-sea-salt calcium (nss-Ca) to dust conversion factor (CF) to estimate the contribution of this source. In the region of Paris, Guinot et al. (2007) experimentally determined a nss-Ca to dust CF of ca. 6.5 based on mass closure exercises. Applying this CF, Favez (2008) found an average mineral dust contribution of 6% to fine aerosol mass from a 2 year sampling campaign performed at an urban background site of the city of Paris. Applying this CF, Bressi et al. (2013) report a mineral dust contribution of 3-4% depending on the site studied from a one-year campaign performed at five different sampling sites of the region of Paris. Note that Putaud et al. (2004) suggest using a CF of 5.6 at their sampling site during non-Saharan dust episodes; applying this conversion factor would thus lead to comparable mineral dust estimation in the region of Paris. The thorough chemical mass closure reported in Bressi et al. (2013) strongly suggest that a noticeable contribution of a mineral source in Paris is not found (since PM obtained from chemistry cannot be above PM obtained from gravimetric methods). The authors thus believe that the contribution from mineral dust to fine aerosols in Paris is per se small. The authors also believe the conclusions of the manuscript remain robust in spite of the lack of a mineral dust source (see second paragraph of the comment R.1.3.).

R.1.5. "page 33239, line 9, USEPA 2011 b and a should be interchanged."

A.1.5. This has been modified accordingly.

R.1.6. "same page, line 23: "possible exceedances...", with an annual mean of 14 ug/m3 the city doesn’t exceed any EU limit values, correct? "

A.1.6. Given the comment of the reviewer “, or to possible exceedances of E.U. limit values” has been deleted from the manuscript.

R.1.7. "page 33240, line 2: please enumerate briefly some of the measures, or at least the sources that were targeted"

A.1.7. The sources that are targeted have been mentioned in the manuscript as follow: P33240, l1: “At the present times, such strategies seem to be rather insufficient in this city. Despite the abatement policies implemented (e.g. prefectoral order nâŮę 2011-00832 of the 27 October 2011 targeting sources such as wood burning, agricultural fertilizers, industrial emissions, etc.), PM2.5 annual levels in Paris have remained rather stable during the last ten years (AIRPARIF, 2012).”

R.1.8. "page 33241, line 1: "questions", I’d rephrase this, it doesn’t question it: it is evident that 19 days are not representative of a longer time series."

A.1.8. This sentence has been rephrased accordingly, taken also into account the comment R.3.5: p33240, l28-29, p33241, l1-2: “Nevertheless, the results reported by Sciare et al. (2010) and Freutel et al. (2013) on fine aerosols were based on few weeks periods (19 and 30 days, respectively) occurring during late spring/summer and thus suffer from a lack of representativeness on a longer time scale.”

R.1.9. "page 33242, Sampling: from the text it is not possible to learn whether sampling artefacts for OC were taken into account. With the use of low-vol samplers, if the artefacts were not taken into account then the OC mass may have been overestimated, and therefore the biomass burning source may have been overestimated too."

A.1.9. First, sampling artefacts may be positive and/or negative. According to the authors, there is no scientific reasons suggesting sampling artefacts should be only positive and thus lead to an overestimation of OC mass. As mentioned p33242, l18-20 the reader is directed to the study of Bressi et al. (2013) for a thorough description of the chemical analyses. Briefly, to minimize sampling artefacts, before being sampled quartz filters (QMA, Whatman, 47 mm diameter) were baked at 480°C for 48h. Field blanks were taken every week for the whole duration of the campaign. Once sampled, filters were stored at -20°C in a freezer prior to chemical analyses. OC was detected in field blanks with an average value of 1.1μgC.cm-2, which represents ca. 15% of sampled filters OC concentrations. Blank corrections have been performed by subtracting the blank average to the sampled filter values. As discussed in Sect. 3.4. of the aforementioned study, filter sampling OC concentrations were compared for a period of 70 days (6 January–15 March 2010) with semi-continuous hourly measurements of VOC denuded OC concentrations in PM2.5, obtained using an OCEC Sunset field instrument (Sunset Laboratory, Forest Grove, OR, USA; Bae et al., 2004). The default thermal program (National Institute for Occupational Safety and Health, NIOSH; Birch and Cary, 1996) was used in this instrument (whereas the EUSAARII protocol, Cavalli et al., 2010 was used for filter analyses). Measurement uncertainty given by the OCEC Sunset field instrument is poorly described in the literature and an estimate of 20% was considered following Peltier et al. (2007). Comparisons between filter sampling and semi-continuous OC measurements are exhibited in Fig. 4b of Bressi et al. (2013) and show good agreements (r2 of 0.84) with a slope of 1.20 and a y-intercept of +0.17 μgm$-$3. Slope difference may partly originate from the different thermal programs used, having a nearly 200 C difference for the last temperature plateau under Helium (Cavalli et al., 2010).

R.1.10. "page 33244: the theory of PMF is well-known, and therefore this page and the next could be summarised using references. In general, the paper is very long and should be summarized (by around 20% would be my suggestion)."

A.1.10. Section 2.2.1 has been shortened by using literature references accordingly. In particular, the text from p33243, l14 to p33245, l19 has been put in the supplementary

material, and has been replaced by: P33243, l14: “A description of SA methods and receptor models can be found in the supplementary material (Sect. S1).

2.2.1. Positive Matrix Factorization (PMF)

The PMF model (Paatero and Tapper, 1994; Paatero, 1997) is used here (see Sect. S1). PMF is a receptor model that assumes mass conservation and uses a mass balance analysis to identify and apportion sources of PM; it aims at resolving the following equation: [please see Eq 3 in the manuscript p33244, l21] (1) where xij is the measured concentration of the jth species in the ith sample, gik is the contribution of the kth source to the ith sample, fkj is the concentration of the jth chemical species in the material emitted by the kth source and eij represents the residual element, or the PMF model error, for the species j measured in the sample i. Equation 1 is solved by minimising a Q function defined as: [please see Eq 4 in the manuscript p33245, l2] (2) where σij is the uncertainty associated to the jth species in the ith sample. Different Q functions can be defined: Qtrue calculated including all data and Qrobust calculated excluding outliers i.e. data for which the scaled residual (eij/σij) is greater than 4. (Note that Qtheoretical will not be studied here as explained in Sect. S1.) A standalone version of PMF using the second version of the multi-linear engine algorithm (ME-2; Paatero, 2000; Norris et al., 2009) has been developed by the United States Environmental Protection Agency (US-EPA) and is used in our study. This version will be named EPA PMF3.0 in the following and can be downloaded at http://www.epa.gov/heasd/products/pmf/pmf.html.”

R.1.11. "page 33243, line 6: Linuma should have a capital “L”"

A.1.11. The first author of the publication is Iinuma, with a capital “i”.

R.1.12. "page 33248, lines 9-11: repetition from the previous page"

A.1.12. Although the parameters chosen for the calculation of backtrajectories are the same for CPF and PSCF, the model versions used are different; these two lines are thus according to the authors necessary (see also comment R.2.10 on this subject).

R.1.13. page 33250, line 20: if Qrobust=Qtheoretical+model error, values of the Qrobust/Qtheoretical ratio <1 should not be valid outcomes of fthemodel, correct? As far as I understand it, Qrobust should be >Qtheoretical, otherwise it suggests that the run should be refined. This is the case for the 7 and 8 factor solutions (.9 and 0.7 according to the authors). Please comment on this.

A.1.13. "Please see comment R.2.7. given to the Referee 2 on this subject. Qtheoretical is not reported in the manuscript anymore."

R.1.14. page 33251, line 22: here the issue of the Q seems to be corrected, as Qrobust and Qtheo are 6403 and 5569, according to the authors. If these data are correct, please correct the previous. Then the 7 factor solution is more robust.

A.1.14. "As mentioned in the comment A.1.13. Qtheoretical is not reported in the manuscript anymore."

R.1.15. page 33252, line 23: "biogenic source", the same is true for the mineral dust source, please make explicit reference to this.

A.1.15. Explicit reference to the mineral dust source has been reported: P33252, l23: “It could also be related to the absence of clearly identified biogenic and mineral dust sources in our study”

R.1.16. "page 33253: these 2 sections are a bit repetitive and only introduce what will be presented in section 4. They could be summarised."

A.1.16. The titles of the sub-sections 3.3.1 and 3.3.2 have been deleted (i.e. only the section 3.3 remains). The text has been shortened as follow: P332523, l5: “On the other hand” has been removed P33253, l9: “the 5th, 25th, 50th, 75th and 95th” have been replaced by “different” Please precise if further changes are necessary (and if yes please precise which ones).

R.1.17. "page 33256, lines 19 and 23, what is "2005 in Puxbaum et al 2007"? Please clarify."

A.1.17. The work of Schmidl (2005) has been written in German and is unfortunately not understandable by the authors. It has however been cited by Puxbaum et al. (2007). For clarification, we would suggest using the Harvard style reference (e.g. accessible at http://www.bournemouth.ac.uk/library/local-assets/how-to/docs/citing-references.pdf , see p5) and referencing the work of Schmidl (2005) as: “Schmidl (2005 cited by Puxbaum et al., 2007)”. If the referee still considers this type of reference unclear “Schmidl (2005)” can be used.

R.1.18." same page, line 26: "10.3 and 10.8", the use of values closer to 13-15 was recommended in the conclusions of the recent Ghent workshop on biomass burning (2-3 December, 2013) by Maenhaut and other authors."

A.1.18. The values of 10.3 and 10.8 are taken from the literature and cannot be modified (note also that the value of 10.3 has been determined in the region of Paris). The values of 13-15 recommended in the conclusions of the Ghent workshop on biomass burning could be reported in our study as well if the referee provides more detailed references (e.g. title and authors of an oral presentation).

R.1.19. "page 33258, line 6: "local origin", the paper Amato, F., Viana, M., Richard, A., Furger, M., Prévôt, A. S. H., Nava, S., Lucarelli, F., Bukowiecki, N., Alastuey, A., Reche, C., Moreno, T., Pandolfi, M., Pey, J., and Querol, X.: Size and time-resolved roadside enrichment of atmospheric particulate pollutants, Atmospheric Chemistry & Physics, 11, 2917-2931, 2011. reports that NO3- from traffic may be formes within the city scale, and therefore it is surprising that no NO3- is found in this source in Paris. It could be related to the lower photochemical activity in Paris (lower oxidation rates), but still some NO3- should be expected in the traffic source. The same is true for mineral dust, as stated above."

A.1.19. We do agree with the reviewer that nitrate from traffic might be formed within the city scale as reported by Amato et al. (2011) in Barcelona (Spain). Although the topography of Paris is substantially different from Barcelona (flat region favouring the dispersion of pollutant in the former case versus complex topography and architecture favouring "the accumulation and resuspension of particulate matter deposited at ground", Amato et al., 2011), we still believe that a fraction of nitrate is formed within the city scale of Paris. This fraction is estimated to be approximately 0.2-0.7 μg.m-3 which corresponds to 3-5% of PM2.5 mass (from a comparison between our urban site and 3 rural sites located from 50 to 65 km away, see Bressi et al., 2013). As stated p33256, l26-27, we believe that secondary nitrate stemming from traffic is found in the Ammoniun Nitrate rich factor in our study. As stated p33264, l8-11, we believe that the Ammonium Nitrate rich factor "stems from a large variety of sources, likely mainly being road and non-road transport, industrial activity, agriculture, and biomass burning". The absence of nitrate in our road traffic factor suggests that this factor is primary, which is in agreement with its low OC to EC ratio of 1.2 (as well as the absence of ammonium and sulphate).

R.1.20. "page 33259, line 2: "carbonaceous", please add "carbonaceous and metallic" "

A.1.20. "metallic" has been added accordingly.

R.1.21. "page 33259, line 24: the explanation that Cu and K may come from shipping seems far-fetched, althouh I don't have a better one. If Cu and K have ever been linked to shipping emissions, please provide the reference."

A.1.21. We agree with the reviewer that the explanation that Cu and K may come from shipping is questionable. The text has been modified as follow: P33259, l24: "Shipping is a possible source of EC and Ni, because (. . .)" P33260, l1: "(. . .) due to inland emissions (of e.g. EC, Ni, K, Cu) from combustion processes. "

R.1.22. "page 33262, line 23: "mesoscale", if this source is mesoscale then it should also have a secondary aerosol component, and not only primary (metals), correct? How do the authors explain this?"

A.1.22. As mentioned by the reviewer, since this source presumably reflects a mesoscale background aerosol, one should expect the presence of secondary aerosol components. Although this factor has been identified thanks to metals (Cd, Pb, Cu, Fig. 1), this does not mean that secondary aerosol component are not present. It is actually clearly shown in Fig. 2 that most of the mass of this factor is due to nitrate, sulphate and OM (for which a noticeable proportion could be secondary given the OC to EC ratio of 1.8 found in this factor). The high contribution of these secondary components to the factor mass is stated p33262, l18-19.

R.1.23. "page 3266, lines 14 to end: indeed, only here is the missing mineral source acknowledged." A.1.23. Please see the additional acknowledgements mentioned in comments R.1.4 and R.1.15.

R.1.24. "page 33271, line 7: 14% for traffic in a megacity such as Paris seems really low. Please describe the limitations of the model."

A.1.24. Please see the extensive answer to Comment R.1.3.

R.1.25. "page 33273: the comparison with Dunkirk doesn't seem valid, given that it is a large harbour area and the authors stated above that this source has almost no (or very little) influence from shipping."

A.1.25. We agree with the reviewer that the comparison with Dunkirk has some limitations. We however consider this comparison relevant given the geographical origin of our heavy oil combustion source (mainly "north of France although a local contribution is not excluded", see p33268, l3-20). Dunkirk is not only influenced by shipping emissions but also by a wide variety of industries. As stated p33273, l16-19: "industry-related sources identified in Dunkirk (such as metallurgical sintering plant, metallurgical coke plant, etc.) (. . .) represent 37% of PM10 mass". These emissions could plausibly influence levels measured in Paris as discussed in Sect. 4.2. In addition, regarding the possible influence of shipping emissions in our heavy oil combustion source, please see our answer A.1.28.

R.1.26. "page 33274, line 7: the data from Canada (5.6 million inhabitants) are hardly comparable with the data from Paris (11 million). The traffic contribution in Paris must be larger."

A.1.26. Once again, we do agree with the reviewer that comparing Toronto and Paris has some inevitable limitations. We however consider the results of Lee et al. (2003) worth to be reported, given their relatively low estimation of 18% of their road traffic source to PM2.5 mass in a 5.6 million inhabitants city.

R.1.27. "page 33275, line 25:"high absolutely concs. along the year", this doesn't seem to make sense: oxidation of SO2 to sulphate is enhanced in summer, therefore absolute and relative values of AS should be lower in winter."

A.1.27. We agree with the reviewer that the oxidation of SO2 to sulphate is enhanced in summer although photochemistry cannot be considered as the only factor driving ammonium sulphate concentrations. Seasonal variations of SO2 show their highest values in winter (Airparif, 2014). Low boundary layer height observable in winter will also enhance the absolute concentration of every species, sulphate included. In the city of Paris, air mass origins will also play a significant (if not the main) role in the levels of sulphate measured. A comparison of the levels of sulphate measured during one year at 5 sites (urban, suburban and rural) in the region of Paris is reported in Bressi et al. (2013, Figs. 10 and 11); sulphate absolute concentrations are high during winter as well as during summer. Please also note that Crippa et al. (2013) report higher sulphate levels in PM1 from AMS measurements performed at 3 sampling sites in winter 2010 (see their Fig. 1), than what is reported by Freutel et al. (2013) in the region of Paris during summer 2009 (see their Fig. 4).

R.1.28. "page 33276, line 17: "vessel activities", again, in the descriptionof the source it was ststed that the influence of ships in this source is minor. The authors should revisit the interpretation ofthis source, is it industrial emissions or ships? Please clarify."

A.1.28. As stated p33260, l15-19: “Vanadium and nickel are primarily emitted by heavy oil combustion, whose sources are industrial boilers (e.g. used in refineries), electricity generation boilers (e.g. oil power stations), large shipping ports, etc. (Jang et al., 2007; Moreno et al., 2010; Pacyna et al., 2007). It is difficult to distinguish between these sources, and “heavy oil combustion” seems to be the most suitable label for this factor.” We agree with the reviewer that from the V to Ni ratio of the heavy oil combustion factor, we concluded that it mainly stems from industrial instead of shipping emissions (p33261 l16-18). However, its geographical origin “suggests that maritime transport clearly affects the contribution of this factor. The low V to Ni ratio reported in our study (Sect. 4.1.4) might thus not be the best proxy to distinguish between industrial and maritime heavy oil combustion” (p33268, l13-15). The authors believe that both industrial emissions and maritime transport affect this factor. Given the comment of the referee, this interpretation has been more clearly stated in the manuscript and the paragraph p 33261, l6-24 has been replaced by the following: P33261, l-6: “The V/Ni ratio might give insights on the sources associated with oil combustion as suggested by Pandolfi et al. (2010) and Moreno et al. (2010). Pandolfi et al. (2010) managed to discriminate between shipping and industrial emissions in a study conducted in the vicinity of a port in southern Spain (Algeciras), and showed that the former source exhibit higher vanadium to nickel ratio (ca. 3.0, range 2.1–3.1) than the later (range 0.9–1.9 for a stainless steel plant). The same conclusions are reached by Moreno et al. (2010). In our study, the V/Ni ratio in the heavy oil combustion factor is 1.4 on average, suggesting that industrial emissions (e.g. oil power station, petrochemical complex, boilers and furnaces) are prevalent. However, the geographical origin of this factor (Sect. 4.2) indicates that shipping emissions cannot be neglected either.”

R.1.29. "page 33277, 1st paragraph:the contribution in winter is very low compared to the rest of the year, and this is unlikely. If the aithors explain the higher AS contributions in winter as resulting from anticyclonic episodes, shouldn't the same occur for the traffic source? Please explain."

A.1.29. As suggested by the referee 3 (last comment) the low PMtraffic contribution could be partly due to an overestimation of EC content in the biomass burning factor and an underestimation in the road traffic one, given that EC is only fairly well modelled by PMF (r2=0.56, n=337 when comparing measured versus modelled EC concentrations, Table 1). However, as discussed in the comment A.1.3 and shown in Fig. A.1.3, BCff (determined from an independent method at another urban background sampling site of Paris) also exhibits lower levels during winter, suggesting that this pattern is real, although it is not fully explained. The higher contribution of the A.S. source is mostly due to the advection of air masses from continental Europe (ammonium sulphate is almost exclusively imported in the region of Paris, Bressi et al., 2013) although anticyclonic conditions will naturally enhance its contribution. The following comment has been added in the manuscript: P33277, l1-3: “The road traffic source exhibits rather stable concentrations all along the year (annual average of 2.1±2.1 μg.m$-$3). Smaller levels are however observed during winter (1.3±1.4 μgm$-$3) and are not fully explained by the authors. From a mathematical standpoint, (. . .)”

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