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Interactive comment on "Long range and local air pollution: what can we learn from chemical speciation of particulate matter at paired sites?" *by* Marco Pandolfi et al.

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Reply to Anonymous Referee #1 comments

We thank the Reviewer#1 for her/his valuable comments that greatly contributed to the improvement and readability of the present manuscript. In the revised version of the manuscript the replies to the comments from Reviewer#1 are highlighted with the green color.

General Comments:

This manuscript deals with the evaluation of the relative contribution of rural and ur-

ban sources for the urban aerosol measured in 5 countries of Europe, by using PMF source apportionment of aerosol samples collected in parallel in rural and urban areas. The evaluation methodology and the results are interesting and the results merit to be published.

Unhappily the manuscript is not well written. It is too long and with several sections too descriptive, making the paper difficult to follow and repeating the reasoning and conclusions in various sections. The data has the problem of being taken from several research initiatives with methodologies of sampling, analysis and data treatment that are different, which makes more difficult to intercompare the results between the various European regions. For some of the sites and data the source apportionment results have already been published and it is not worthwhile to repeat the simple source apportionment results and discussion. There is also an important fraction of the text that mostly repeats the information that already is given in figures and tables.

Thanks to the comments raised by the Reviewers the text has been considerably shortened compared to the original version. Comment #2 below addresses the Reviewer question about the comparability of the results despite the use of different methodologies for uncertainties calculation.

In my opinion the present manuscript should concentrate and put most of the effort in the spatial increments using the Lenschow's approach to evaluate in each country the incremented contributions of urban areas in relation to regional contributions, of the aerosol mass and aerosol source groups. Sections such as Section 3.3 should be reduced and if possible integrated in the spatial increments approach sections.

We agree with the Reviewer that the Section 3.3 was too long. Consequently, this Section was considerably shortened in the revised version of this manuscript. We shortened the text and removed Figures 3, 4, and S7 (annual cycle of source contributions). Following the Reviewer's comment #9 below, we moved from the Supporting material to this Section Figures S8 and S9 in order to better follow the discussion about primary

emissions of sulfate from ships.

Specific Comments:

1) Line 28- Abstract- the Abstract is too long and too descriptive of results- reduce and concentrate in the more prominent outcomes from spatial increment conclusions.

We have attempted to reduce and consolidate it. This paper is multifaceted and provides much information. We need to provide the reader with a sufficient amount of information that they can make an informed decision about reading it.

2) Line133 and following- Quite different methodologies were used for calculating uncertainties in the data base used for PMF in each country. Which is the influence of these variable approaches in the uncertainty of the final results? This subject should be discussed in the manuscript. How were estimated the uncertainties for EC, OC and sugars?

The treatment of uncertainties has a significant effect on the outputs of PMF results. For this reason, it is important to perform some tests which help understanding if the uncertainties are properly estimated. These tests can be performed for example studying if the scaled residuals are within the range of -3 and $+3$ of the standard deviation and if the bootstrap results can be mapped for all the factors. However, there is not just only one rule to estimate the species uncertainties in the PMF. In fact, the uncertainties calculation depends on the information available for each database and the techniques used for the determination of chemical species concentration. For this reason, different formulas are reported in literature (and in the present manuscript) and considered equally valid. What is important is that the applied formulas allow weighting the uncertainties as function of the specie concentrations. So higher uncertainties are given to species with low concentrations and the data with more information content has a greater weight in determining the results. In the present manuscript, the different methodologies we used for uncertainties calculation were based on sensitivity studies performed by the data providers (and published in previous publications). For example,

the uncertainties used here for the French database were based on sensitivity studies performed by Waked et al. (2014). Based on this sensitivity study, Waked et al. (2014) selected the uncertainties providing the best and stable PMF solution. Similarly, the uncertainties used in the Spanish database were based on the sensitivity studies performed by Amato et al. (2009) and Escrig et al. (2009). These different schemes used for uncertainties calculation led to stable PMF results and can be considered as equally valid. Thus, we assume that the influence on the final results of the variable approaches applied here for uncertainties estimation is minimal because the formulas we applied were tested and were demonstrated to provide stable and robust PMF outputs. Also, as long as the uncertainties err on the side of being too large (greater downweighting), there is little probability of serious errors in the analysis. Downweighting rarely perturbs the solution. The bigger issue is having too small uncertainties. That is generally easily observed through seeing a variable be placed in many profiles, often where it would not be expected to be present in order to provide the fit to the specified level of precision. For EC and OC, expanded relative uncertainties were calculated to account for the uncertainty in the split point position of the thermo-optical technique used to determine the concentrations of OC and EC. For the French, Spanish and Swiss databases 10%-15% for OC and EC (Cavalli et al., 2010) were added (e.g. Waked et al., 2014). Moreover, a 15% uncertainty was added for monosaccharide sugars (French database) such as levoglucosan, arabitol, sorbitol and mannitol (e.g. Piot et al., 2012; Waked et al., 2014). Again such downweighting is not going to undermine the quality of the results.

The following sentence was added to the Section 2.1: "For EC and OC, expanded relative uncertainties were calculated to take into account for the uncertainty in the split point position of the thermo-optical technique used to determine the concentrations of OC and EC. For the French, Spanish and Swiss databases 10%-15% for OC and EC (Cavalli et al., 2010) were added (e.g. Waked et al., 2014). Moreover, a 15% uncertainty was added for monosaccharide sugars (French database) such as levoglucosan, arabitol, sorbitol and mannitol (e.g. Piot et al., 2012; Waked et al., 2014). The different

schemes used here for uncertainties calculation were tested by data providers and their robustness demonstrated in previous publications. Thus, despite the different methodologies, the presented final PMF results were stable and their robustness estimated using bootstrapping resampling and studying the distribution of the scaled residuals for each variable (e.g. Paatero et al., 2002)."

3) Line 281 and following- The description of sampling sites characteristics is too long. Try to reduce the length of the text referring to other publications where these descriptions have already been done.

Following the Reviewer comment, the Section 2.3 was considerably reduced.

4) Line 413 and following- Most of the discussion presented here is repeated in the following sections.

Following the Reviewer comment the Section 3.1 (PMF sources) was shortened in order to avoid repetitions in the text.

5) Line 456- WISC (water insoluble carbon; sum of EC and WISC). ??- The second WISC shouldn't be WIOC (water insoluble organic carbon)?

This was a mistake. The sentence was changed, as presented in van Pinxteren et al. (2016), as follows: "....high mass contributions of WISC (water insoluble carbon; i.e. EC + hydrophobic organics)"

6) Line 491 and following- this subsection is difficult to follow because it is the result of previous studies and possibly not all information is provided here. For example "Cooking" can't be characterised only by WISC and WSOC.

We agree with the reviewer that the sentence is difficult to follow as it is. Consequently, we changed the text presenting only the list (with a very short description were necessary) of the six additional sources found in DE and providing the reference to the original paper were these sources were better described (i.e. van Pinxteren et al. (2016)). In this way we further reduce the length of the text. Moreover, these sources

were grouped together in the following of the manuscript and a detailed description is not needed here. Accordingly, the sentence was changed as follows: "Six additional sources were detected only in DE, namely: sea salt/road salt (SSRS; an SS source with influence of road salt for de-icing), Coal combustion (CC) and Local coal combustion (this latter contributing mostly at the EIB site, which was removed from this analysis), Photochemistry (PHO; with high mass contributions of NH_4+ and SO_42- and WSOC), Cooking, and Fungal spores. A detailed description of these additional sources can be found in van Pinxteren et al. (2016)."

7) Line 543- Table 1- Why in Spain the "Sea Salt" source is not considered "Aged Sea Salt"? Even in Barcelona more than 50% of the CL- has already been evaporated and substituted by SO4/NO3-.

We agree with the reviewer that a better definition of sea salt source in Spain is "Aged sea salt". The text and Table1 were accordingly changed. Moreover, in order to further shorten the text and following the Reviewer's comments #9 AND 10 (below), we moved the Table 1 to the Supporting Material leaving more room in the main text to discuss the theme of ship emissions of sulphur and primary sulphate. The Section 3.2 "Feasibility of the multi-site PMF" was accordingly changed.

8) Lines 589-590- Did not understood the objective of this sentence. Following some Reviewer comments, i.e. avoiding repetitions and shortening the text and especially Section 3.3, the sentence has been removed from the text.

9 AND 10) Line 592- Here the theme of ship emissions of sulphur and primary sulphate is initiated. This interesting theme is discussed in various parts of the paper which makes difficult to fully understand the relative importance of the emission source. If Ship emissions are so relevant in Europe why PMF could not separate a ship emission source, at least for coastal areas?

10) Line 699 and following – Here and throughout the text Figures and Tables in the Annex Section are used in the discussion of results. In my opinion Figures and Tables

in the Annex should exist only as complementary information. If these figures and Tables need to be used to follow a discussion and to demonstrate a statement in the text they have to be added to the main part of the paper.

Maritime shipping can potentially be an important source of pollutant especially in port towns. As explained in the present manuscript (cf. Section 3.3 and Conclusion section), the fundamental tracers of ship emissions, i.e. V and Ni, must be measured (especially the V) to properly detect this source thorough application of PMF. In the present work, both V and Ni were available in Spain and The Netherlands (where the shipping source was detected), whereas only V was available in Switzerland (where the shipping source was not detected). In France and Germany the concentrations of V were not available thus preventing the detection of the maritime shipping source. The concentrations of V in the Zurich (Switzerland) were about one order of magnitude lower compared to the V concentrations measured in Barcelona, mostly because the distance of Zurich from shipping emissions (coastline and major ports) or other sources of residual oil combustion. For this reason, the shipping source was not detected in Switzerland. For example in Gianini et al. (2012), the Ni was excluded from PMF analysis because of its very low signal-to-noise ratio, demonstrating the small effect of residual oil combustion sources (such as shipping) at the Swiss sites.

To address the Reviewer's comment, we moved Figures S8 and S9 in supporting material to the main text. Moreover, Table 1 (feasibility of multi-site PMF) was moved to supporting material.

11) Line 729- "showed" instead of "slowed"?

Is "slowed". We meant that for the four additional sites included in this work (where more recent (2013-2014) data were available) the primary SSA produced for every 1 ïА∎g/m3 of residual oil was lower compared to 2007-2008.

12) Line 782 and following- Some information should be provided about the precision/ accuracy of urban and regional estimations of aerosol mass and source classes.

Estimating the accuracy of urban and regional estimations from application of the Lenschow's approach is extremely difficult if not even unmanageable. There are important sources of errors such as meteorology on a daily base that are difficult to manage. For this reason, we selected chemically speciated PM datasets covering at least one year and presented average values to reduce all possible sources of error. The comparability of the calculated estimations among the selected countries and the agreement with previous studies is used here to prove the robustness of the analysis. In order to further demonstrate the feasibility of the of the present work, we report in supporting material the results of the bootstrapping resampling from PMF which is used to prove the robustness of the detected sources.

13) Line 815 and following.- In the paper the word "increment" is used both for urban and regional/continental contributions to the aerosol. The use of the term for R+C is somehow confusing (increment in relation to what?). Substitute by contribution? The main motivation to prefer the term "increment" to "contribution" is that "contribution" implies a univocal link to a given source. Referring to the increased concentration levels over the city as "urban contribution", implies that the city sources only contribute to air pollutant concentrations over the city, whereas they also contribute to background levels outside of the city, because of advection/diffusion referred to as "City Spread" in Thunis (Atmospheric Environment 173 (2018) 210–222). Similarly, R+C is an increment compared to a clean background, we considered that referring to an R+C contribution, would ignore the fact that regional background also contributes to urban levels.

14) Lines 950-960- SSA does not need the NH3 in order to be high! NH3 merely neutralices the already formed sulphuric acid.

The sentence: "...and the high concentrations of NH3 measured in the city." Was removed from the text.

Please also note the supplement to this comment:

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