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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 #2 comments

We thank the Reviewer#2 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#2 are highlighted with the yellow color.

General Comments: The manuscript "Long range and local air pollution: what can we learn from chemical speciation of particulate matter at paired sites?" provides a de-

tailed discussion on the PM chemically speciated data from European paired monitoring sites. Positive Matrix Factorization (PMF) and Lenschow's approach were applied to assign measured PM and source contributions to the different spatial levels. Long-term data allows the analysis on the annual cycle of the contributions to PM from the common sources and those detected only at subsets of paired sites. The experiment design and data analysis presented were well done. The paper is relevant to the field of the journal and presents some potentially interesting results that merit publication. However, the manuscript was not well written and required substantial improvements, especially some careless discussion.

Specific comments: 1) Too many abbreviations appear in this manuscript, making it really hard to follow. For instance, "photochemistry (PHO) and coal combustion (CC)" are not necessary.

It is true that many abbreviations appear in the manuscript. However, these abbreviations are necessary for example, but not only, to make the text shorter. Moreover, these abbreviations are also used in many figures and tables. Certainly, less attention is paid to source such as PHO (abbreviation used 5 times in the main text) or CC (abbreviation used 11 times in the main text) which were detected only in one Country but which are however potentially important. In order to take into account the Reviewer comment, we removed from the text the abbreviations used for those sources detected only in one Country (e.g. LB for Land Biogenic, MB for Marine Biogenic, PHO for Photochemistry, CC for Coal Combustion, etc.).

2) The abstract and conclusions are verbose. More attention should be paid on the new results or insights of the present study, rather that the apparent results.

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.

Introduction:

1) The introduction did not appropriately summarize the previous studies, and most of the related studies were missing. This impedes the reader's understanding to the context.

The relevant bibliography about Lenschow's approach and PMF model has been added to the Introduction section. Moreover, the following text has been added to the Introduction: "The approach proposed and described in this paper aimed at identifying the urban and non urban (R+C) contributions (or a mix of both) to the PM mass measured at urban level and at calculating the urban increments that corresponds to the concentration difference between the city and the regional locations (Lenschow's approach; Lenschow et al., 2001). This method, detailed in Sect. 2.2 and developed by Lenschow et al. (2001), is based on measurements of atmospheric pollutants at sites of different typologies (i.e. rural and urban background) and has been widely used to discriminate the local and non-local increments (e.g. Pope et al., 2018; Petetin et al., 2014; Gianini et al., 2012 among others). The uniqueness of the present work is that we were able to allocate urban and non-urban pollution to major primary sources by activity sector or to main secondary aerosol fractions thanks to the application of Positive Matrix Factorization (PMF) (described in Sect. 2.1) that quantitatively groups species emitted from the same source. The PMF is a widely used receptor model to perform PM source apportionment studies, identifying main sources of pollution and estimating their contributions to PM concentrations in ambient air (e.g. Hopke P.K., 2016; Liao et al., 2015; Amato et al., 2009; Kim and Hopke, 2007; Kim et al., 2003 among others). This information is useful for devising opportune abatement/mitigation strategies to tackle air pollution."

2) It would be helpful that scientific questions related to the topic are mentioned in the Introduction.

We added the following sentence at the end of the Introduction section: "The scientific questions we are tackling here are distributed over two topics. The first one relates to the relative importance of local and remote air pollution sources. This aspect is of

course the most directly connected to the policy expectations, but is also raises a number of scientific challenges that we address in an innovative manner by differentiating primary/secondary particulate matter of different types. The second one is more related to methodological developments. The approach we use here has already been explored for a given city/region. However, for the first time we intend to compare very different European regions, with also different monitoring strategies, which induce specific scientific questions in terms of consistency that were addressed throughout this work."

Methodology:

1) How to perform PMF, is there any boot strapping results for this study?

Yes. The bootstrapping resampling available in the EPA-PMF v5.0 is very useful to demonstrate the robustness of the detected sources. The bootstrapping results for those sites were the multi-site PMF was performed in this work (i.e. ES, FR and CH) were added in the supporting material (new Table S1).

The following sentence was added to the main text: "Bootstrapping resampling results for ES, FR and CH were reported in Table S1"

2) It is not clear to me why the authors apply different methods to construct uncertainty matrix for different sites.

Undoubtedly, the treatment of uncertainties has a significant effect on the outputs of PMF results. The uncertainties calculation depends on the information available for each database and the techniques used for the determination of chemical species concentration. However, there is not just only one rule to estimate the species uncertainties in the PMF. 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 that higher uncertainties are given to species with low concentrations. 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. Some tests can be applied to understand Âąif 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.

3) The authors likely devoted too much space to describe the monitoring site. I also am not certain that it is really a necessity.

Following the Reviewer comment, the description of the monitoring sites has been substantially shortened in the revised version of the manuscript. Given that this point has been also highlighted by the Reviewer#1, the green color is used to highlight the part of the text which was accordingly changed.

Results:

1) The authors stated that “At all sites the SSA source profile (and consequently the SIA source profile in DE) showed relatively high contents of organic carbon (OC), which was attributed to the condensation of semi-volatile compounds on the high specific surface area of ammonium sulfate”. It needs more evidence, otherwise such conclusion makes no senses. Moreover, they also stated that “The chemical profiles of this source (NSA)

were also enriched in OC.” in Line 434.

It is extremely common to see significant amounts of OC associated with secondary sulfate. This association occurs for two reasons: 1) both secondary sulfate and SOA take time to form in the atmosphere and require oxidants like hydroxyl radicals. Thus, they will form concurrently as the air mass travels to the receptor site and thus, covary in a way that places them in the same profile; 2) local primary SVOCs can condense onto the surface of the sulfate that typically represents a large fraction of available surface area of the ambient aerosol. In addition, if the particle is still acidic, it can catalyze the formation of SOA on the particle surface. Thus, beginning with early urban aerosol analyses with PMF such as Kim et al. (J. Air Waste Mange. Assoc. 53:731-739, 2003; Kim and Hopke, J. Geophys. Res. 109: D09204, 2004) up to recent analyses such as Sources and Geographical Origins of PM10 in Metz (France) Using Oxalate as a Marker of Secondary Organic Aerosols by Positive Matrix Factorization Analysis, J.-E. Petit et al. Atmosphere 2019, 10(7), 370; https://doi.org/10.3390/atmos10070370. Thus, it is expected to see OC associated with sulfate. There is common chemistry and appropriate gas-particle partitioning behavior. These references have been added to the main text and bibliography.

2) “Photochemistry (PHO), showed high mass contributions of NH+ 4 and SO2- 4 and WSOC as well as high species contributions of oxalate.” Was this factor corresponding to any indicator of photochemistry? This factor may also be attributed to aqueous processing.

As reported in van Pinxteren et al. (2016), photochemistry factor concentrations (Fig. 4 and S11 in van Pinxteren et al. (2016)) tended to be higher in summer and showed no clear site-dependent trend. In contrast to the general secondary aerosol, the photochemistry factor thus seems to be more related to radiation-driven formation processes.

The above sentence was added to the main text.

3)The author devoted too much space to discuss “The summer to winter ratio” for each

source contribution. However, I think the summer-to-winter ratio did not provide any additional information for most of the source contribution, and thus it is recommended to be shorten or removed.

We agree with the Reviewer and the discussion about the summer-to-winter ratios was removed from the text.

4) “This sulfate represents direct SO3 emissions from the ship that appear as particulate sulfate at the sampling sites.” Any further evidence? Any direct measurements of SO3 emissions?

Yes, there are direct on-board measurements of ship emissions such as Emission Measurements from a Crude Oil Tanker at Sea, H. Agrawal et al., Environ. Sci. Technol. 2008, 42, 7098–7103 and Emissions from main propulsion engine on container ship at sea, H. Agrawal et al., Journal of Geophysical Research, 115, D23205, doi:10.1029/2009JD013346, 2010. In addition there have been measurements of the impact of fuel switching on sulfate in a port as seen in Source Characterization of Ambient Fine Particles at Multiple Sites in the Seattle Area, E. Kim and P.K. Hopke, Atmospheric Environ. 42: 6047-6056, 2008 and Changes in the SO2 Level and PM2.5 Components in Shanghai Driven by Implementing the Ship Emission Control Policy, X. Zhang et al., Environ. Sci. Technol. 2019, 53, 11580−11587. These references have been added to the main text and bibliography.

Minor Comments

1) “Three additional common sources were detected”. I do not think it is appropriate to use “detect” herein. Corrections are required throughout the current manuscript.

The term “detect” has been substituted with “identify”, “find” or “resolve”.

2) “Based on the present analysis, an improvement of air quality in the 5 cities included here could be achieved by further reducing local (urban) emissions of PM, NOx and NH3 (from both traffic and non-traffic sources) but also SO2 and PM (from maritime

ships and ports”. This is not unique for this study.

The sentence “Based on the present work” has been removed from the text. The sentence is now: “An improvement of air quality in the 5 cities included here could be achieved by further reducing local. . .. . .”

3) “There are various modelling approaches to disentangle the local/remote contribution to urban air pollution.” References would be helpful here.

The relevant references were presented from line 116 in the revised version of the manuscript.

Language requires improvement. Here I give some examples:

Line 438: “The Mineral source (MM) source” Line 470: “: : :by exchange with NO3- during transport: : : ” Done

Line 534: “were considered as a natural sources”

Done

Line 764: “because the measurements of methane sulfonic acid” methane sulfonic acid?

The term has been changed with “methanesulfonic acid”.

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