<u>Answers to referee # 2</u>

General comment

The manuscript reports a standard source apportionment study with a focus on the maritime source. Beyond the original results and the use of a specific receptor site to achieve the goals, the rest of the study presents only the trivial application of well-established source apportionment techniques (PMF-like, CWT, CPF). Another weakness of this study is the "age" of the data, which were collected 10 years ago. However, since the lack of papers focusing on maritime sources, I am in favour of publication. The authors are requested to improve the manuscript by adding more information about the outcomes of the CW-NMF model (in particular about the number of factors extracted).

We would like to thank the referee for his constructive comments that aim at improving the manuscript. We understand the referee's point of view regarding the outcomes of the CW-NMF model and the "overfitting" problem addressed in the following comments. We have checked again the reconstruction of the species added into the model and came to the conclusion that three elements (La, Mn, and Cr) were not as well reconstructed as the other species. For that purpose, we had run again the CW-NMF by removing these elements. In this case, the optimal number of factors obtained was nine, removing by that the "metal-rich" source. The outputs of the CW-NMF model specifically the reconstruction of PM_{10} *as well as the different species and the detailed boostrap analysis that show the robustness of the 9-factor solution will be presented in details in the following comments and will be added in the supplementary information. Amendments in the manuscript especially regarding the outcomes of the CW-NMF model have been done.*

Specific comments

1. Lines 76-79 "Additionally, despite the IMO regulation for global sulfur limit of 0.5% from ship's fuel oil applied starting January 2020, different countries are still adopting higher sulfur limits. It is worth noting that these limits were only set for sulfur content in marine fuels in order to reduce SO2 emissions but no regulations for PM components neither in the sea nor at ports were issued". Not clear why this consideration is reported within the objectives of the study. Is this topic addressed in the current study? Please clarify.

The authors understand the point of view of the referee. This topic is not addressed in the current study. However, it was relevant to include it in this part of the introduction in order to shed the light on the idea that the data is still relevant nowadays since different countries are still adopting sulfur limits higher than 0.5%, which was the case in 2013. Additionally, it was added following the recommendation of the referee #1.

2. Lines 66-80. Please comment on the choice of sampling PM2.5 to quantify the maritime contribution. Combustion emissions are expected to be finer than other sources. On the contrary, other sources in the coastal areas (e.g., sea salt) may emit large particles. Thus, it would be better to analyze PM2.5. Please comment to support your choice.

We agree with the referee regarding the fact that combustion emissions are expected to be in the finer fraction of PM such as $PM_{2.5}$. However, the study was conducted in 2013. Several years before, the EU has placed policies in order to reduce the concentrations of some atmospheric pollutants. The directive 2008/50/EC limits daily PM_{10} concentrations to 50 µg/m^3 with a maximum of 35 days of exceedance per year. This directive is binding and forces countries that do not comply with it to seek solutions for improvement. This was particularly the case of France, which was in a dispute on this subject with the European Union. Several regions in France were thus concerned with high number of exceedance days, especially the Northern region. This is why it was important at the time to identify the sources that contribute to the concentrations of PM_{10} in order to focus on the reduction of emissions of these sources and to quantify the part of maritime contribution.

3. Line 90. “The sampling site is far from major continental pollution sources and can be considered as a background site.” Which background? Rural, urban, suburban? If rural, are you sure the site has the characteristics to be classified in this way? Please comment.

We agree with the comment of the referee regarding the classification of the site as “background”. According to the current Implementing Provisions on Reporting (IPR) 2011/850/EC regarding the type of sampling area and the influence of the immediate surroundings (traffic, industrial or *background), the site cannot be considered as a background site due to its coastal typology with marine anthropogenic emissions (https://www.eionet.europa.eu/aqportal/doc/IPR%20guidance_2.0.1_final.pdf). The term "background" will be removed from the manuscript. As for the definition of a rural site: it corresponds to an area that does not fulfill the criteria of an urban or suburban site with at least 10 km from major sources. The sampling site can be indeed considered as a rural site on the coast.*

4. Section 2.2. The sampling campaign is 1 year long (1st of January to 31st of December 2013) and samples were collected at daily frequency, however only 122 samples were analyzed. Why? How the samples to be analyzed have been selected? Randomly? 1 day over 3? Please explain.

The sampling campaign was conducted between the 1st of January and the 31st of December 2013. A total number of 362 samples were collected at Cape Gris-Nez in 2013. 122 samples were chosen for the chemical analysis. They were not chosen randomly and they represent a sampling of 1 day over 3 in order to ensure that these samples are representative of the whole sampling period.

The information was added in the manuscript:

"Over the sampling period, 362 samples have been collected. 122 samples representing a sampling of one day over three were chosen for the chemical analysis and were presented in this study."

5. Line 100. Was the beta monitor tested against the gravimetric measurement? Which calibration audit? Please add info.

The beta monitor results were not compared to the gravimetric measurement of the filters. However, the LCSQA (Laboratoire central de la surveillance de la qualité de l'air) in France has verified the equivalence of the MP101M-RST measurements using the beta gauge with the *gravimetric reference method in their study conducted in 2011 and published in 2012 (LCSQA, 2012).*

The information will be added in the final version of the manuscript as follows (Line 100): "During the sampling period, PM_{10} concentrations were monitored using a MP101 beta gauge analyzer (Environment SA®). The analyzer was calibrated at the beginning of the campaign and routinely checked by the regional air quality network atmo Hauts-de-France".

6. Line 168 "The yearly-mean PM10 concentration obtained for the set of sampling days was of 24.3 µg/m3". Is this the real yearly average (365 days in a year possibly measured with the beta monitor) or the average over the 122 analyzed samples? It would be great to see both values to understand if the sample selection is consistent with (indicative of, or similar to) the year average.

The PM_{10} concentration of 24.3 $\mu g/m^3$ reported in the manuscript corresponds to the average over the 122 analyzed samples. For the yearly average considering all the samples, the average concentration was 22.8 $\mu g/m^3$. The closeness of the two values is indicative that the sample selection is representative of the whole year.

7. Figure 2. Please report the error bars relative to the bootstrap results. This would clarify some source profiles.

Following the bootstrap results, the percentiles 25th and 75th were added to the contribution of the species by factor and were presented in Figure S2.

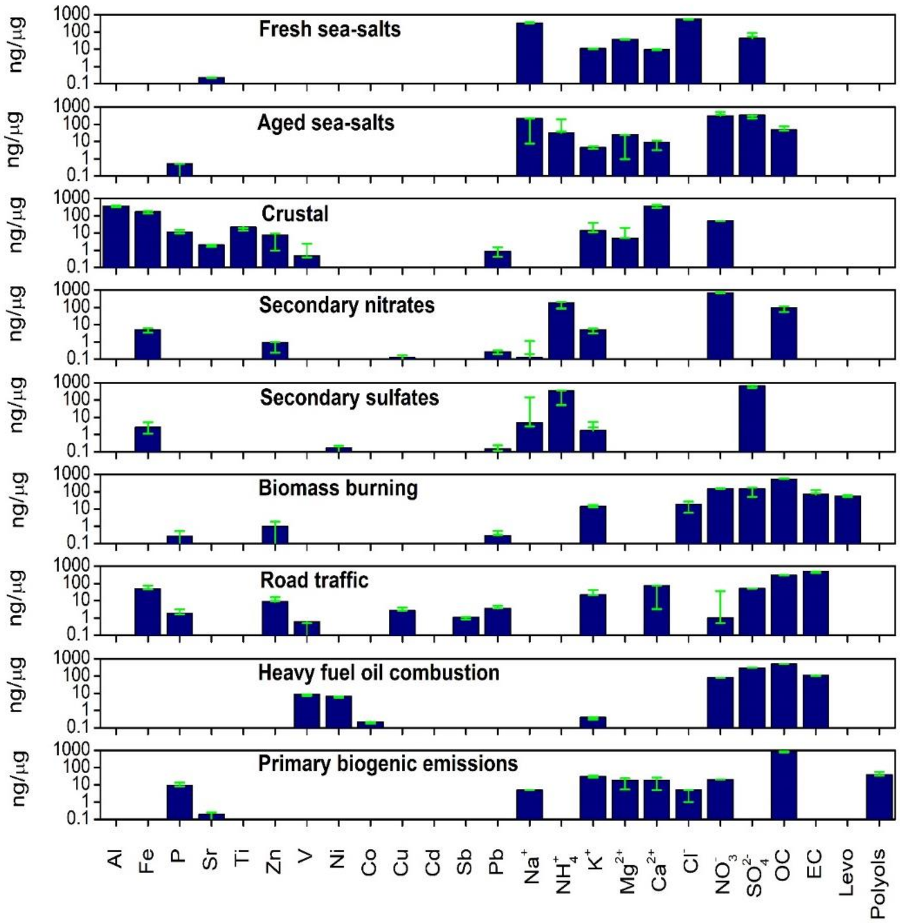


Fig.S2: PM_{10} source profiles at Cape Gris-Nez (CGN) identified using the CW-NMF model along with the percentiles 25^{th} and 75^{th} calculated via the bootstrap analysis.

8. Section 3.2. The description of the model setup lacks many details. In addition, it looks like you pushed the model beyond the limits of what it is capable of**.** It is hard to believe that you can see so many factors with just 122 samples and 28 variables without overfitting the data. For instance, the presence of a "metal-rich" factor may be due to the overfit. Thus, I would ask you to add the scaled residual plots to the SI material file along with all the diagnostics returned by the model. This is to better investigate the goodness of the selected model setup.

As mentioned before, the authors took into consideration the comment of the referee regarding the "overfitting" of the model.

First of all, regarding the number of samples and species, the authors considered a total of 242 samples as input data for the application of CW-NMF model: 122 samples (1 day over three) collected in 2013 + 62 samples collected in 2013 during exceedance days and pollution episodes + 58 samples collected in 2014 at the same site. The contribution of the sources for the 122 samples (1 day over three) in 2013 were extracted from the output data of the model in order to present them in this paper.

Second of all, we have checked again the reconstruction of the species added into the model and came to the conclusion that three elements (La, Mn, and Cr) were not as well reconstructed as the other species. For that purpose, we had run again the CW-NMF by removing these elements. In this case, the optimal number of factors obtained was nine, removing by that the "metal-rich" source. The criteria that help us evaluate the goodness and robustness of the solution are the following:

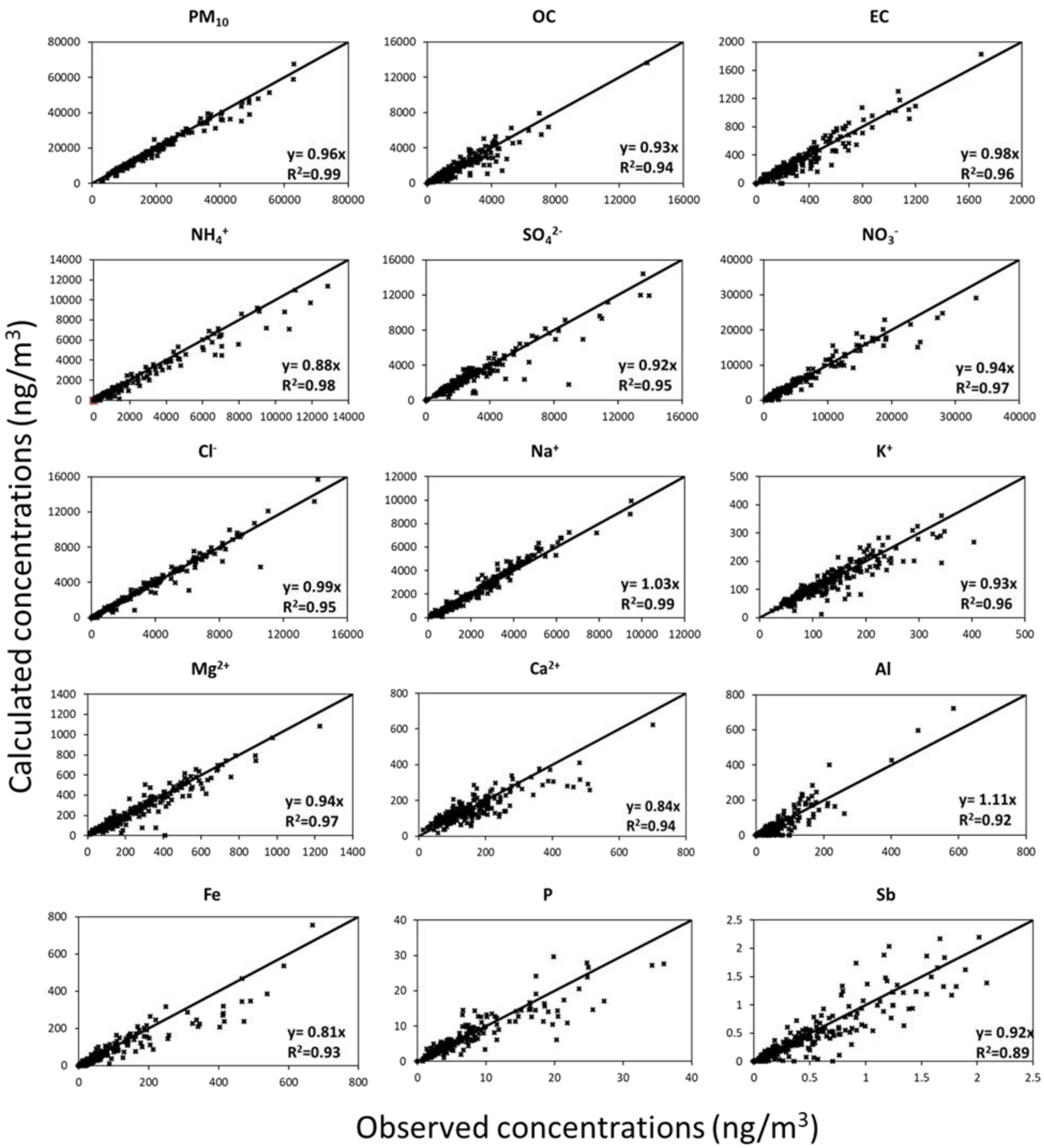
- *The comparison between the source profiles obtained by the model with the source profiles that can be found in the literature and in databases such as SPECIATE or SPECIEUROPE (Pernigotti et al., 2016; Simon et al., 2010) along with the evaluation of the characteristic ratios of the species in the profiles.*

- *The reconstruction of the concentration of PM_{10} and all the species added into the model*

- *The bootstrap analysis that shows the variability of the solution by studying the effects from random errors and partially including the effect of rotational ambiguity. It is used to find if there is a small set of observations that can largely influence the solution. Mapping over 80% of the factors indicates that the BS uncertainties can be interpreted, and the number of factors may be appropriate.*

In the case of the 9-factor solution, the profiles presented in figure 2 were comparable with those of the literature and the details were presented in section 3.2 of the manuscript.

Hereafter, we present the reconstruction of the different species included in the model as well as of PM_{10} (figures will be included in the supplementary information).


PM10
y= 0.96x
R^2=0.99
OC
y= 0.93x
R^2=0.94
EC
y= 0.98x
R^2=0.96
NH_4^+
y= 0.88x
R^2=0.98
SO_4^{2-}
y= 0.92x
R^2=0.95
NO_3^-
y= 0.94x
R^2=0.97
Cl^-
y= 0.99x
R^2=0.95
Na^+
y= 1.03x
R^2=0.99
K^+
y= 0.93x
R^2=0.96
Mg^{2+}
y= 0.94x
R^2=0.97
Ca^{2+}
y= 0.84x
R^2=0.94
Al
y= 1.11x
R^2=0.92
Fe
y= 0.81x
R^2=0.93
P
Sb
y= 0.92x
R^2=0.89
Calculated concentrations (ng/m3)
Observed concentrations (ng/m3)

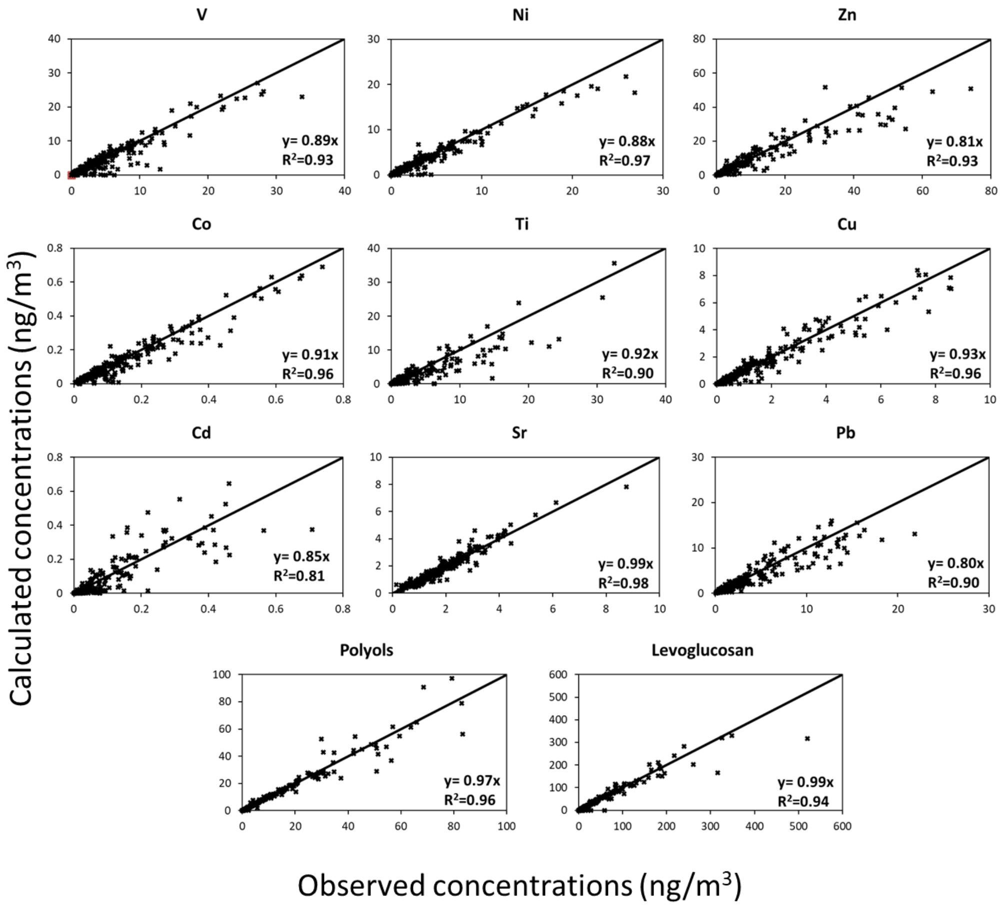


Fig. S3: Calculated species and PM_{10} concentrations using Constrained Weighted - Non-Negative Matrix Factorization versus observed concentrations for all the species considered in the calculation (with the identity line as reference).

As we can see, PM_{10} and all the species were well reconstructed with slopes of the calculated vs observed linear regressions close to 1 (ranging between 0.8 and 1.11) with determination coefficient R^2>0.9 with the exception of Cd (R^2=0.81).

Finally, for the bootstrap analysis, the results (presented in the table below) showed values higher than 80%, indicating a stable solution and a reasonable model fit for the 9-factor solution.

Following all of the above-mentioned arguments, the authors do show that the 9-factor solution is robust and can be presented in the manuscript. For this reason, modifications were done in the manuscript (Section 3.3, 3.4, 3.5 as well as figures 3, 4, and 5 and the supplementary information).

Table S1: Bootstrap mapping results for CW-NMF results at CGN site

Bootstrap mapping ***Min. correlation coefficient r = 0.6***										
	1	2	3	4	5	6	7	8	9	Unmapped
Boot Factor 1 (Fresh sea-salts)	100	0	0	0	0	0	0	0	0	0
Boot Factor 2 (Aged sea-salts)	0	100	0	0	0	0	0	0	0	0
Boot Factor 3 (Crustal)	0	0	99	0	0	0	0	0	0	1
Boot Factor 4 (Secondary nitrates)	0	0	0	100	0	0	0	0	0	0
Boot Factor 5 (Secondary sulfates)	0	0	0	0	100	0	0	0	0	0
Boot Factor 6 (Biomass burning)	0	0	0	0	0	99	0	0	0	1
Boot Factor 7 (Road traffic)	0	0	0	0	0	0	100	0	0	0
Boot Factor 8 (HFO combustion)	0	0	0	0	0	0	0	100	0	0
Boot Factor 9 (Primary biogenic emissions)	0	0	0	0	0	0	0	0	100	0

9. Line 227. "with an average Cl--to-Na+ ratio of 1.8 which is commonly observed for fresh sea salts (Seinfeld and Pandis, 2016)." Is the seawater composition also valid for other fresh sea salt ionic species such as K+, Mg2+, Ca2+, and SO42-?

For the 9-factor solution that is added in the final version of the manuscript, the sea composition is also valid for the other ionic species and are resumed in the following table:

Ratios	*Cl^-/Na^+*	*K^+/Na^+*	*Ca^{2+}/Na^+*	*SO_4^{2-}/Na^+*	*Mg^{2+}/Na^+*
Sea-water composition	*1.8*	*0.037*	*0.038*	*0.251*	*0.12*
Fresh sea-salts profile	*1.7*	*0.033*	*0.027*	*0.15*	*0.11*

10. Line 230. Is the cations/anions ratio balanced in this factor?

The cations/anions ratio in the "aged sea-salts" profile in the 9-factor solution is balanced with a cations/anions ratio of 1.14.

11. Line 240-255. The authors report some literature data in support of their findings. However, most of these studies refer to finer PM (PM2.5 or even PM1). For example, the paper by Khan et al (2021) reports the EC to levoglucosan ratio in PM1. The paper by Salameh et al (2018) refers to the OC-to-EC ratio of PM2.5. It is not reliable that the ratios between different variables (chemical species) remain unchanged on PM10, PM2.5 or PM1. At least, not all. Please comment or change the references.

The authors understand the point of view of the referee. The references were changed in order to reflect the concentration ratios between species in the PM_{10} fraction. The references of Khan et al., (2021) and Salameh et al., (2018) were replaced by others that present concentration ratios in PM_{10} (Amato et al., 2011; Waked et al., 2014; Sonwani et al., 2021).

12. Figure 3. Please provide the uncertainty associated with the results.

We agree with the referee on the importance of having uncertainty values for the sources' contributions. However, the output data of the CW-NMF model, just like the PMF model, does not include uncertainties associated with the contribution of the sources. Instead, the average concentration as well as the standard deviations of each source in ng/m^3 were added in the supplementary information.

Table S2: Average contribution and standard deviation in µg/m^3 and percentages of the factors to PM_{10}

Source	**Contrib. at CGN ($\mu g.m^{-3}$)**	**Standard deviation ($\mu g.m^{-3}$)**	**Contrib. at CGN to PM_{10} (%)**
Fresh sea-salts	4.24	4.57	21.9%
Aged sea-salts	3.0	2.31	15.4%
Crustal	0.18	0.28	0.9%
Secondary nitrates	6.27	9.03	32.3%
Secondary sulfates	1.91	3.24	9.8%
Biomass burning	1.49	3.25	7.7%
Road traffic	0.54	0.61	2.8%
HFO combustion	0.85	1.01	4.5%
Primary biogenic emissions	0.92	1.40	4.7%

13. Section 3.5. It appears that most of the factors come from the same area of origin. This again pinpoints the possible data overfit. However, the results for HFO appear to come from a more "marine" source area than the two secondary factors. It would be better to zoom in on Figure 5 to better visualize the differences. After all, we are not interested in results where the model returns too low a contribution (thus, please cut the more distant areas).

We agree with the referee regarding his comment to figure 5. The figure was changed by replacing the contribution of the sources with the ones determined for the 9-factor solution. Additionally, the CWT representations were zoomed in order to better visualize the differences.

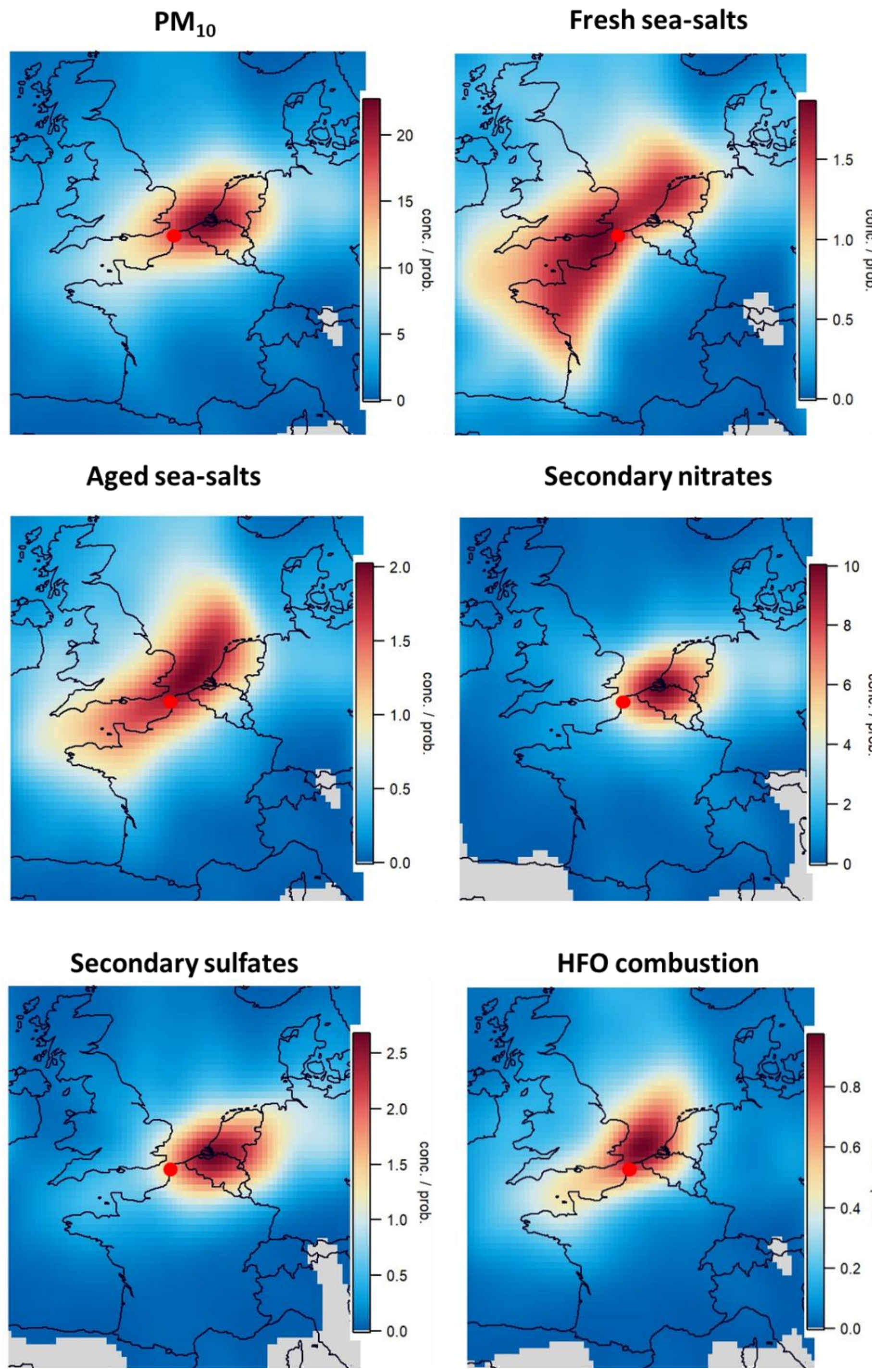


Figure 1: CWT results for PM_{10} and some NMF factors (fresh sea-salts, aged sea-salts, secondary nitrate, secondary sulfate, and HFO combustion). Red colors highlight potential emission zones. Contribution scales are in µg/m^3.

References:

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, Atmos. Chem. Phys., 11, 2917-2931, 10.5194/acp-11-2917-2011, 2011.

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