Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-388-RC1

Response to comments on "Chemical composition and source apportionment of atmospheric aerosols on the Namibian coast" by Danitza Klopper et al.

The authors would like to thank the two anonymous referees for providing a thoughtful and constructive review on the manuscript. We considered their comments with the highest possible attention.

This concerned in particular the remarks on the PMF analysis. Both Referees #1 and #2 agreed on the fact that the PMF was not bringing sufficiently highlights and additional information with respect to the discussion from the chemical apportionment, and because of that, did not deserve a dedication section of the manuscript. While agreeing on that, we took the advantage of the referee's suggestions to

- Revise our uncertainty analysis on the elemental concentrations by XRF (section 2.1, comment of Referee#2), and therefore revise the input error matrix in PMF (section 3.2);
- Perform sensitivity studies of the PMF including or excluding peak concentrations of As, F-, Na and Cl^- (comment of Referee#1);
- Discarding the separation of the sea salt and non-sea salt components of SO_4^{2-}, Ca^{2+} and K^+ (comment of Referee#1);

Those analyses resulted in a new and more robust PMF solution, which provides additional information with respect to the chemical apportionment analysis. In particular, the obtained new PMF solution provides with the source mass apportionment, distinguishing natural and anthropogenic sources, and furthermore apportions the heavy metals into distinguished sources related to mining and smelting/ship traffic activities. These new results are presented in the abstract and the conclusions of the manuscript (section 5), as well as in section 4.2, which is now called "Variability and apportionment of measured concentrations". Section 4.3 ("Source apportionment") of the original manuscript is now suppressed.

Additional major modifications are

- Elemental/ionic ratios for the *sea salt* and the *mineral dust* PMF components are now shown in Tables 2 and 3
- To improve clarity, a number of tables and figures were added to the supplementary material:
    - Table S1. Correction factor used to scale up the elemental concentrations measured by XRF to account for the X-ray self-attenuation effects in the individual particle grains. A mean diameter of 4.5 μm is chosen to represent the average coarse particle size.
    - Figure S3. PMF mass apportionment for the five component solution.
    - Figure S4. Bivariate polar plots for (a) vanadium and (b) nickel, showing the variability in mean concentrations with changes in wind speed and direction. Wind direction is indicated by the cardinal point in the four quadrants, mean wind speed (m s-1) is indicated by the concentric circles from the centre of the plot and the mean concentrations are measured in ng m-3, and given by the gradient colour scale.
    - Figure S5. Pie charts of the PMF mass apportionment of V and Ni measured at HBAO. Legends provide with the name of the source component and the fraction of the contributed mass elemental concentration.
    - Figure S6. Scatterplot of F- with respect to nssCa2+ for 2016 (blue) and 2017 (orange). Concentrations are expressed in μg m-3. The slope and the Pearson correlation coefficient (R2) are indicated.
    - Figure S7. Same as Figure S5 for F- concentrations.

Additional comments from Referees #1 and 2 are addressed here below (comments by referees in bold and our accompanying responses in plain text), as well as the text revision (in blue) are represented hereafter.

Incorporating the suggestions from both referees has certainly improved the manuscript which we hope is now acceptable for publication in ACP.

Referee #1: specific comments

Line 148. The correlation SO4/S have to take into account the other species containing S (i.e. MSA) even if MSA presents lower concentration than SO4. It seems more correct report the correlation (MSA+SO4)/S, molar ratio will be more correct than weight ratio, even if MSA/S and SO4/S have only slightly different mass ratios.

The aim here was to check the correlation of measurements from ion-chromatography and XRF. We agree with the referee that it would also be correct to report the molar ratio, specifically with the sulphur containing MSA and sulphate species. Subsequently, the molar ratios for MSA+SO_4^{2-}/S were added to the discussion for a more complete representation and the text was updated in lines 154 - 158 as follows, "Mass ratios were 1.3 ± 0.1 (2016) and 1.0 ± 0.1 (2017), 1.3 ± 0.1 (2016) and 0.9 ± 0.1 (2017), and 2.0 ± 0.1 (2016) and 1.7 ± 0.2 (2017) for Cl^-/Cl, Na^+/Na, and Mg^{2+}/Mg, respectively. Conversely, no annual dependence was observed in the slopes of the linear correlations for Ca^{2+}/Ca (~ 0.8 ± 0.1), K^+/K (~ 0.6 ± 0.1) and MSA+SO_4^{2-}/S (~ 2.7 ± 0.4). The molar ratio of (MSA+SO_4^{2-})/S was 8.0 ± 1.2 for 2016 and 7.8 ± 0.9 for 2017". The scatterplot of SO_4^{2-}/S in Figure S1 of the supplementary material was updated to include MSA+SO_4^{2-}/S.

Line 200. The Ca/Na w/w ratio in bulk seawater is 0.04 as correctly reported in table 2 and it is not 0.021.

We thank the referee for noticing this typographic mistake. It has been corrected and all other reported values were double-checked for such errors. No other issues were found.

Table 1. Looking at the values reported in this table I have few considerations:

There are surprising the very high maximum values for few species: Na, Cl and especially F. The STD DEV is not so high; therefore, these high values are occasional. Can be these anomalous high values due to contamination? Is it possible that something go wrong during the sampling? Only considering Na and Cl at their maximum, the sum is 129 ug/m3 that is really a huge PM10 mass value even for a marine windy environment. It is still surprising 25 ug/m^3 of fluoride, it is a huge values, it is difficult to have in open environment such as high concentration of F, this values is more similar to those found in the framework of health in dusty workplace. There are some other anomaly in the sample with the highest values of F, could be a problem of sampling or contamination? I do not believe these high values are reliable so please revise the sentence regarding these high values in the abstract and section 4.2.4. In general, I suggest to e check the data for the sampling showing these se anomalous high values. Could these anomalous high values affect the PMF results?

We have considered in great detail the reliability and uncertainties of the values of highest concentrations of Na, Cl and F which occurred during the sampling period. As the referee does not specify his/her criteria concerning which values should be considered as "very high maximum values ", we explored this issue by qualifying these values as those concentrations exceeding the arithmetic mean plus twice the standard deviation of the population (mean + 2 x STD DEV). The resulting "very high maximum values" are 23.9, 33.7 and 9.8 µg m^{-3} for Na^+, Cl^- and F^- respectively.

Concerning Cl^- and Na^+, 11 samples exceeded this lower limit out of the total 385 values available (Cl^- and Na^+ mass concentrations were above the MQL on all the sampled filters) Dates of those 11 occurrences are provided in Table A1.

Table A1. Start date and time for sampling corresponding to values exceeded the "very high maximum values" of Na^+ and Cl^-, and F^-.

Start date and time (UTC)		
Na^+ and Cl^-	**F^-**	
28-02-2016 7:00	27-02-2016 19:00	29-08-2016 20:00
01-04-2016 19:00	28-02-2016 7:00	25-03-2017 19:00
03-04-2016 8:00	21-03-2016 7:00	06-10-2017 21:00
04-04-2016 8:00	06-04-2016 8:00	15-11-2017 21:00
05-04-2016 8:00	06-04-2016 20:00	16-11-2017 9:00
06-04-2016 8:00	08-04-2016 8:00	16-11-2017 21:00
28-08-2016 8:00	28-08-2016 8:00	17-11-2017 9:00
28-08-2016 20:00	28-08-2016 20:00	17-11-2017 21:00
29-08-2016 8:00	29-08-2016 8:00	
12-10-2016 19:00		
01-11-2017 9:00		

Besides three occasional occurrences, values of Cl^- and Na^+ above the set threshold occurred during two specific periods, from 1 to 6 April 2016 and from 28 to 29 August 2016. The corresponding wind speed for these 11 samples was moderate (arithmetic mean 3.2 ± 0.9 m s^{-1}) and comparable to the average values during the sampling campaign with these 11 values excluded (3.8 ± 1.7 m s^{-1}). Polar plots for Na^+ and Cl^-, shown in Figure A1, indicate that the highest mean concentrations were associated to sea breezes from the SSE and WNW, also characteristic of the year-round mean wind direction. The mean mass ratio of Cl^-/Na^+ for the 11 samples (1.4 ± 0.1) is consistent with the mean mass ratio for the data with these values excluded (1.3 ± 0.1), suggesting no specific analytical issue. For these reasons, we suggest that the 11 samples of Cl^- and Na^+ do not present anomalously high concentrations and can be retained in further analyses.

Regarding F-, and as explicitly stated in the manuscript (section 4.2.4), we agree with Referee#1 that the mass concentration values measured at the site are unexpectedly high and more typical of a polluted work place more than a semi-remote environment. The mean mass ratios of F^-/Na^+ for 2016 and 2017 (0.38 ± 0.24 and 0.32 ± 0.35, respectively) are orders of magnitude higher than expected for marine sea salt. The enrichments were attributed to mining and road construction activities as a consequence of the enrichment of fluoride in the Namibian soils, which is also suggested by the excellent correlation between F^- and nss-Ca^{2+}, which is now shown in the supplementary material (Figure S6). The F6 source apportionment is shown in Figure S7. Section 4.2.4 was partially rewritten as (lines 486-501) "The very good correlation of F- with nss-Ca2+, shown in Figure S6 (R2 equal to 0.76 in 2016 and to 0.84 in 2017), yielded a mean mass ratio of 6.4 and 5.8, respectively, much higher than reported in groundwater, aerosols or precipitation in polluted environments (Feng et al., 2003; Prodi et al., 2009).

The strong relationship to nss-Ca2+ (and a posteriori to Ca2+) drove the PMF apportionment (Figure S7), which attributed approximately the 94% of the F- mass concentrations to the sea salt and mineral dust components (55.1 ± 1.9% and 38.8 ± 1.1%, respectively), and the remaining 6% to fugitive dust (2.3 ± 0.5%) and industry (3.8 ± 1.0%). Possible sources are the emission of fugitive dust during fluorspar mining of carbonatite related fluorospar deposits at the Okorusu Mine (20°3'S, 16°44'E), but very likely also from the periodic surface mining occurring approximately 20 km south of HBAO to provide gravel for the construction of a major road between Swakopmund and Henties Bay which started late in 2015 (A. Namwoonde, pers. corr.). The evaporation of fluoride rich water, leached into groundwater (Wanke et al., 2015, 2017) from fluoride-rich mineral deposits and soils, throughout the region and in the coastal waters (Compton and Bergh, 2016; Mänd et al., 2018), would also increase atmospheric F- concentrations. In an analysis of borehole water in Namibia, roughly 80% of those sites surveyed were deemed unsafe to drink as a direct result of high fluoride concentrations (Christelis and Struckmeier, 2011). “

Furthermore, we have given additional attention to the “very high maximum values”. For F^-, this condition was met by 17 samples (out of 385, Table A1). As for Cl^- and Na^+, the occurrences of extreme values of F^- are not isolated but corresponded to a few-day long periods. The polar plot of F^- mass concentrations with respect to wind direction (Figure A1c) shows that these values corresponded to south-easterly winds exceeding 8 m s^{-1}, which could favour dust resuspension.

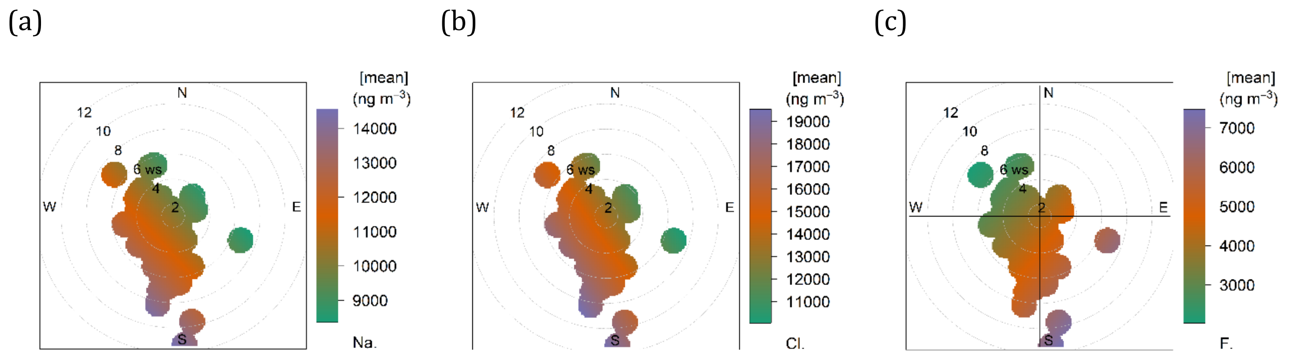


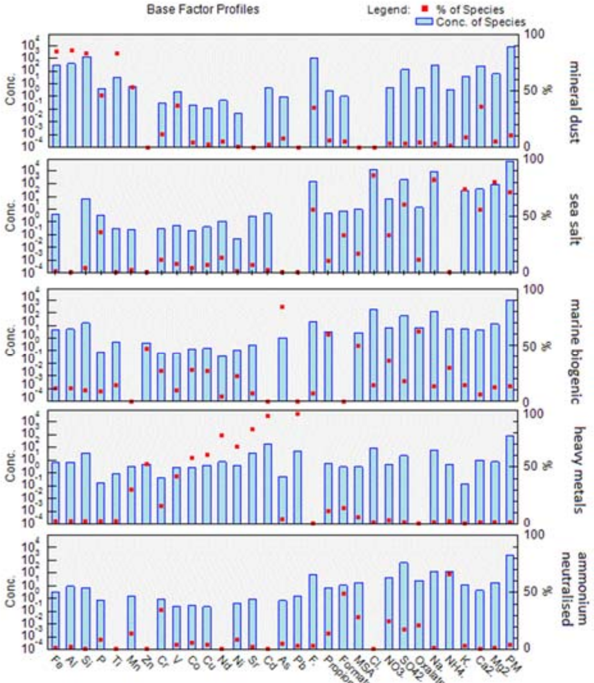
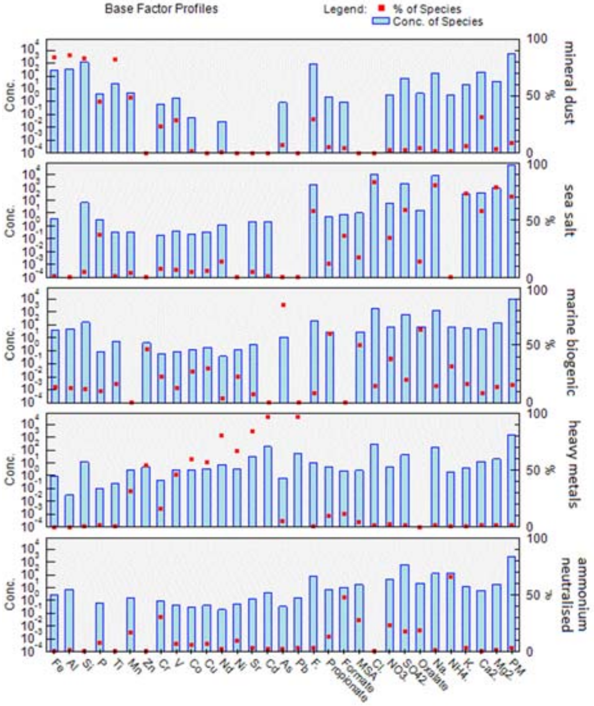
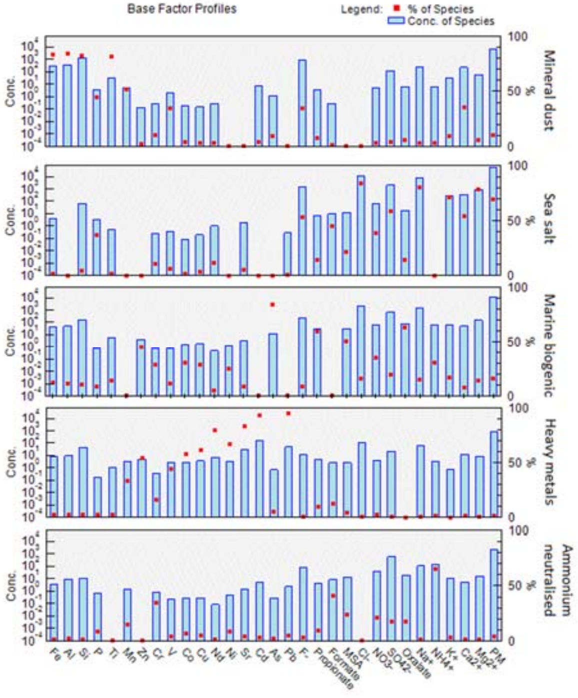
Figure A1. Bivariate polar plots for (a) Na^+, (b) Cl^- and (c) F^- showing the variability in mean concentrations with changes in wind speed and direction. Wind direction is indicated by the cardinal point in the four quadrants, mean wind speed (m s^{-1}) is indicated by the concentric circles from the centre of the plot and the mean concentrations are measured in ng m^{-3}, and given by the gradient scale on the right of plot.

1. **The mean $F^-/nssCa^{2+}$ mass ratio for those occurrences is 6.8± 2.5, close to the annual means, suggesting the validity of these values for further analysis.**

Nevertheless, we agree with Referee#1 that in principle the PMF solution could be biased by those very high concentrations for F^-, Cl^- and Na^+. To explore this possibility, an additional PMF simulation was performed after removing the peak F^- values, and then another after removing the peak Cl^- and Na^+ values. The results of the original PMF with these values included and with them excluded are given in Table A2 below.

The comparison of the two simulations indicates that the inclusion of the F^- "very high maximum values" only marginally modify the results of the PMF simulations but not the identification of the factors which is maintained and prove the robustness of the solutions. The same is true for the PMF solution with the highest Na^+ and Cl^- values removed. The largest change (but marginal) when discarding the highest F^- values is the lowered F^- to the *mineral dust* component and the increased contribution to the *sea salt* and *marine biogenic* components, which entrains a lowered contribution of the *mineral dust* component to the total mass concentration. In the case of Na^+ and Cl^-, changes in the contributions of the different components to these species were smaller than 2% with the biggest differences in *sea salt* and *marine biogenic* components. These differences were not statistically significant and the "very high maximum values" were retained in the dataset.

Table A2. PMF solutions for “very high maximum values” of F^-, Cl^- and Na^+, retained in the dataset, with the original uncertainty file, compared with the solution where “very high maximum values” of F^- were removed from the dataset.

With peak values left in the dataset	With peak F^- values removed from the dataset	With peak Cl^- and Na^+ values removed from the dataset
		

Contribution of the components to the F^- mass concentration		**Contribution of the components to the F^- mass concentration**		
mineral dust	34.2 ± 0.1%	mineral dust	28.1 ± 0.1%	
sea salt	56.2 ± 0.1%	sea salt	58.8 ± 0.1%	
marine biogenic	4.7 ± 0.4%	marine biogenic	7.2 ± 0.4%	
heavy metals	1.3 ± 5.3%	heavy metals	1.3 ± 2.8%	
ammonium neutralised	3.6 ± 1.4%	ammonium neutralised	3.3 ± 0.4%	

Contribution of the components to the mass concentration of Na^+ and Cl^-, respectively						**Contribution of the components to the mass concentration of Na^+ and Cl^-, respectively**		
mineral dust	2.9 ± 0.4%	0 ± 0.3%				mineral dust	2.8 ± 0.5%	0 ± 0.4%
sea salt	81.6 ± 2.5%	85.3 ± 2.3%				sea salt	80.0 ± 2.5%	83.6 ± 2.2%
marine biogenic	13.7 ± 0.2%	14.1 ± 0.1%				marine biogenic	15.3 ± 0.7%	15.6 ± 0.7%
heavy metals	0.5 ± 0.3%	0.6 ± 0.2%				heavy metals	0.7 ± 0.2%	0.8 ± 0.3%
ammonium neutralised	1.2 ± 0.8%	0 ± 0.9%				ammonium neutralised	1.2 ± 0.3%	0 ± 0.3%
Contribution of the components to the total mass concentration								
mineral dust	10.6 ± 0.1%		mineral dust	8.3 ± 0.1%		mineral dust	10.4 ± 0.2%	
sea salt	71.7 ± 0.1%		sea salt	70.6 ± 0.1%		sea salt	69.5 ± 2.0%	
marine biogenic	12.8 ± 0.2%		marine biogenic	15.5 ± 0.2%		marine biogenic	15.4 ± 0.6%	
heavy metals	1.5 ± 1.0%		heavy metals	2.4 ± 0.8%		heavy metals	1.3 ± 0.3%	
ammonium neutralised	3.5 ± 0.4%		ammonium neutralised	3.7 ± 0.2%		ammonium neutralised	3.5 ± 0.3%	

There is another interesting feature of this data set: authors define this area desert coastal, but looking at mean (but also maximum) values of crustal marker the concentration are quite low. For instance, Al present average value of only 478 ng/m3 and its maximum is only 4739 ng/m^3. Therefore, the influence of sea spray aerosol is dominant respect to crustal aerosol, the author explain this by the wind intensity and prevalent direction, that is correct, but this is surprising for this desert and arid region. I think this topic deserve a discussion.

We can see how the term "coastal desert" can be confusing considering the high variability of surface cover in Namibia. The landscape is primarily covered by loose sand in dune fields, but also gravel plains and few clay sources, where aluminosilicates would be sourced from. To clarify, the text (line 357 - 362) was updated as follows, "Our arid sampling site is surrounded by loose sand, gravel plains (Matengu et al., 2019) and the deep Omaruru river valley directly north of the sampling site which is also a recognised source of mineral dust to the offshore waters (Tlhalerwa et al. 2012). While mostly characterised by gravels, some clay-rich deposits are found around the river valley approximately 17 km northeast of HBAO (Matengu et al., 2019). The relatively low aluminium concentrations measured at HBAO suggest that these are not a major local source for the site."

Lines 366 and 370. Please check the year of these references.

The dates for these references were checked and corrected, thank you. All other references were also checked.

Lines 452-458. About the seasonal cycle of MSA, figure 5 shows maxima in austral summer in 2017 (Oct-Nov-Dec) confirming the pattern already find in previous work, but in 2016 the maximum is in autumn (Mar-Apr), the author have an explanation for this maxima? Is this pattern anomalous or it is common to have a late phytoplanktonic bloom? In any case, they have to discuss the pattern that seems anomalous respect to previous results.

The MSA variability and its links to the phytoplankton blooms is certainly an issue that cannot be solved today, because of the lack of direct measurements of the bloom spatial distribution. Unfortunately, satellite images are rare due to the persistent cloud cover. The MSA seasonal cycle was already discussed in Formenti et al. (2019). The text in the manuscript was updated as follows (lines 535-546) "The MSA concentrations measured at the site ranged between 10 and 230 ng m-3 (Table 1). The mean annual concentration was 63 ± 39 ng m-3, three times higher than the mean value of 20 ± 20 ng m-3 (6.2 ± 4.2 ppt) reported by Andreae et al. (1995) over the open ocean along 19°S, and lower than in the southeast Atlantic Ocean (Zhang et al., 2010; Table 4). As already described in Formenti et al. (2019), the MSA concentrations were higher in the austral summer and spring and lower in the austral winter. DMS is more efficiently oxidised in warmer conditions (Ayers et al., 1997; Huang et al., 2017) which explains the the higher daytime mean concentrations of marine biogenic products (MSA and nss-SO42-) and lower means at night and in the winter. Springtime averages for MSA were in the range of that measured by Huang et al. (2018) during a springtime cruise over the South Atlantic and by Prodi et al. (2009) in the Venice Lagoon (Table 4). The mismatch of seasonality with respect to that of the phytoplankton blooms (Louw et al., 2016) is already discussed by Formenti et al. (2019) and attributed to the spread of blooms in the BUS region depending on local conditions."

Equation 1b. As the authors have all the crustal element concentration, they can calculate the crustal content by the sum of the contributions of all the main crustal element oxides (SiO2, Al2O3, Fe2O3, CaO, MgO, K2O, TiO2), following the approach reported in the literature by several authors (e.g. Marcazzan et al., 2001; Nava et al., 2012; Marconi et al., 2014) replacing CaO whit CaCO3 basing on the Ca mineral content in the area. This approach can be more reliable than the use of the only Al and the averaged content of Al in the upper continental crust.

Our choice of the simplified equation with respect to the more complete one (sum of main crustal element oxides as SiO2, Al2O3, Fe2O3, CaCO3, MgO, K2O, TiO2) suggested by Referee#1 is motivated by the fact that the Si/Al ratios measured at HBAO are ~3.6 for both years (see Table 3 in the paper) and close to those expected for the upper continental crust (see Rudnick, R.L. and S. Gao (2003). 3.01 - Composition of the Continental Crust. Treatise on Geochemistry. H. D. Holland and K. K. Turekian. Oxford, Pergamon: 1-64.) than for airborne mineral dust (Table 3 and references therein). This is consistent with the fact that the Namibian soils are characterised by granite and sand banks that dominate over clay deposits (Matengu et al., 2019).

To illustrate the impact of our choice on the evaluation of the estimated dust mass (EDM), Figure A2 illustrates the comparison between the EDM by two approaches, the Referee#1 equation on the y-axis and Equation 1.b in the manuscript on the x-axis.

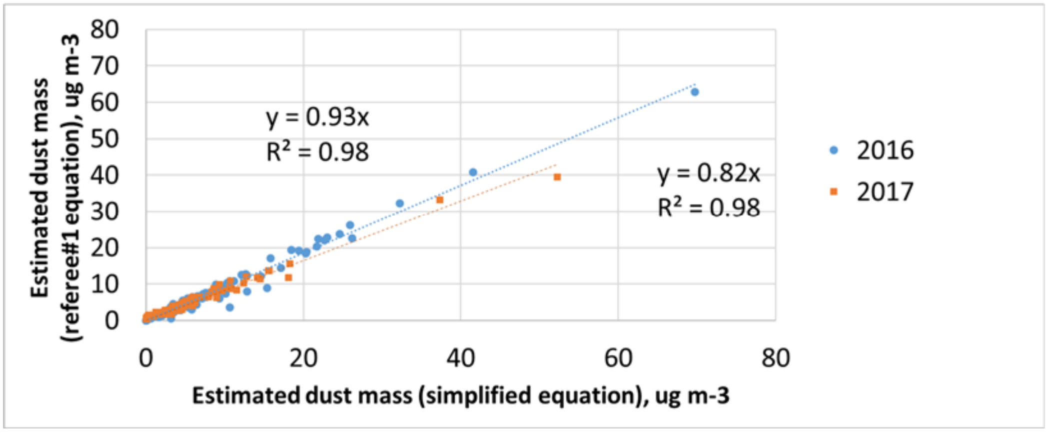


Figure A2. Scatterplot for the estimated dust mass using the Referee#1 equation to that estimated by Equation 1.b in the paper.

The comparison shows that indeed, on average, our simplified equation overestimates the EDM calculated with the Referee#1 equation by 18% in 2016 and 7% in 2017. The underestimation is understandable when comparing the terms of the largest difference which the contribution of aluminosilicate and quartz in the upper continental crust (and accounted for as Al/0.0813) with respect to that obtained through the Referee#1 equation (1.89*Al+2.14*Si), which results in a Si/Al ratio of 1.13. On the other hand, the use of either equation does not induce any temporal bias to the analysis as the linear correlation of the estimated dust masses by the two approaches is excellent (R^2= 0.98). In conclusion, we consider that the estimated dust mass in our approach (Equation 1b) is more adapted as a term of comparison for the PMF analysis applied to the Namibian aerosols.

However, for sake of clarity, in re-organising the manuscript, we have now suppressed those comparisons from the main text.

PMF

Here my main criticism to the paper. The PMF as it is do not add any new finding respect to the simply aerosol component analysis. Besides PMF is not able to distinguish the source of each metals, that are gathered in one factor called heavy metal. In my opinion, the PMF analysis is useless at this level. In the PMF, the author use the following not-independent variable: ss components (K, Ca and SO4) and PM10 mass the latter obtained by the sum of the other aerosol component. For this reason, the ratio between sea spray components and the percentage of sea spray aerosol to the total mass are the same with or without PMF analysis. The sentence at lines 505-511 are obvious. In this context PMF do not add nothing new.

Please see general comments regarding the significance of the PMF results.

The PMF solution with sea salt and non-sea salt fractions of SO_4^{2-}, Ca^{2+} and K^+ already separated (as presented in the paper) was compared with the solution where these values were replaced by independent variables SO_4^{2-}, Ca^{2+} and K^+. Table A3 shows the comparison of the sea salt fractions as evaluated in the two approaches (note that the two simulations yielded a 5 components as the best solution).

Table A*Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.****2.*** The sea salt fractions of SO_4^{2-}, Ca^{2+} and K^+ when estimated by the (i) PMF where the ss and nss components were already separated in the input dataset, (ii) PMF where these components were not separated (i.e. independent values only), and (iii) ratios to unique tracers.

		Sea salt component (%)	
	PMF with ss and nss components separated	PMF with independent values only	Ratios to unique tracers
SO_4^{2-}	61.9	66.6	57.0
Ca^{2+}	49.0	53.0	44.5
K^+	74.6	75.1	89.0

The results for the two PMF solutions are in good agreement (within 5%), and in agreement (within 10%) with the proportions estimated by ratios to unique tracers. A section was added to the text in lines 339 - 340 as follows, "The PMF estimated that sea salt contributed to 53.0 ± 1.6% of the calcium and 75.1 ± 2.4% of the K^+."

We also mentioned the PMF separation of sulphates in line 527, as follows, "The PMF estimated that the *sea salt* component contributed to 66.6 ± 0.4% of the sulphate mass."

The old PMF solution (ss and nss components separated out) attributed some of the nss portions of the SO_4^{2-} and Ca^{2+} to the *sea salt* component and large fractions of the ss portions to components other than the *sea salt* source. This would change the contribution to the total PM10 mass, as noted by the referee, and the separation of the species to the different PMF components as compared to when we use only the independent values. In the interests of keeping the results of the ratios to unique tracers and PMF separate, the referee's suggestion to present the PMF with independent variables was accepted.

The uncertainty file used in the PMF was also updated after consideration of the comments from Referee #2. The text related to the PMF results was updated accordingly to reflect the calculation of the uncertainty file (line 235 - 238) as follows,"In order to weight the concentrations according to their amount, a relative uncertainty of 10%, 20% and 60% was attributed to each value of concentration in the input matrix based on their ratio to their respective MQL (larger than 3.3, comprised between 1.25 and 3.3, and comprised between 1 and 1.25, respectively).." The results were updated throughout the document along with Figure 6 in the paper.

The five component solution obtained by PMF with this new input concentration file (with independent values for SO_4^{2-}, Ca^{2+} and K^+ only) and uncertainty file (with a higher relative uncertainty) was different from that obtained originally. In fact, this new solution addresses the issue as raised by the referee, by separating the heavy metals into two components.

Line 526. Regarding the presence of As in this factor it has to be noticed that As concentration are really high to arise from marine biogenic activity, besides this factor is characterized by secondary species and As, because of it is a metal it is not secondary. Could be As is emitted by smelting activity and transported together with biogenic compounds? May air mass backward trajectory analysis for days with high As concentration clear this process?

The referee is correct in saying that these values for As are high, and that there is no discernible correlation between As and MSA, as discussed in the text. After the inclusion of the new uncertainty file and the removal of the already separated ss and nss components, the PMF solution now associates the As to other heavy metals (Zn, Cu, Ni and Sr) and not to the MSA and other secondary products as in the original PMF solution as reported in the paper. This PMF component is characteristic of smelting operations and oil combustion and was therefore labelled *industry.* The discussion regarding this component can be found in section 4.2.5.

To evaluate the very high As concentrations, the threshold limit was calculated in the same way as for Cl^-, Na^+ and F^-, as the mean + 2 x STD DEV (825 ng m^{-3}).

Measurements made during two sampling weeks (24-31 January and 8-15 February 2017) were classified by these very high As concentrations. In order to better differentiate between the sources of air masses arriving during these two weeks, trajectories and local winds were analysed and are given in Figures A3 and A4. These results suggest primarily marine regions as the source of these air masses, although resolutions are very coarse.

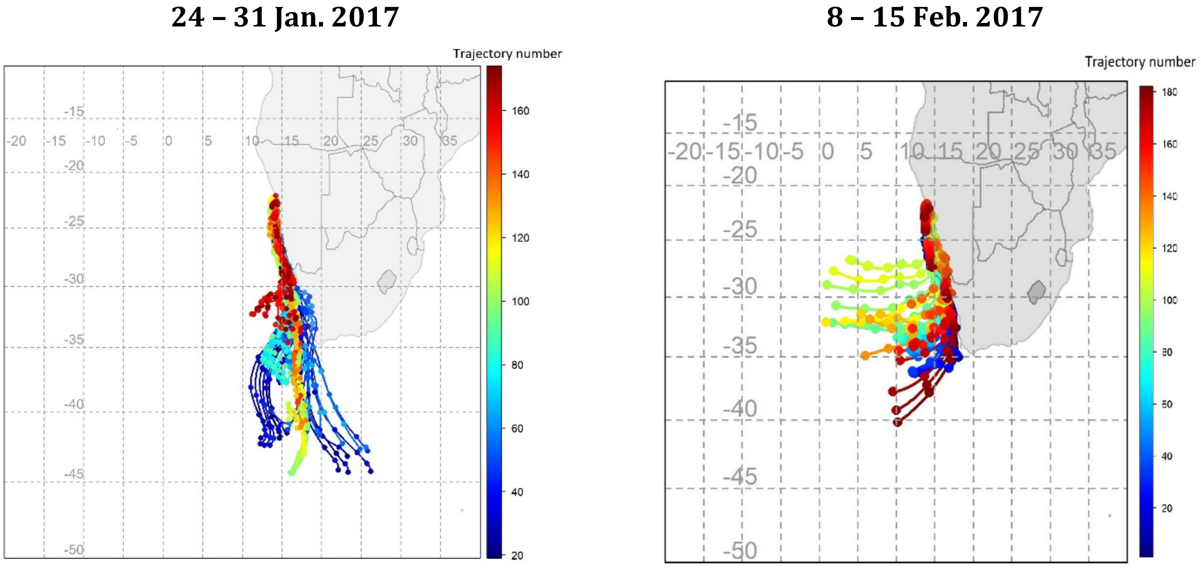

24 – 31 Jan. 2017 **8 – 15 Feb. 2017**

Figure A3. Back-trajectories run for 72 hours (each point representing 6 hours), starting for each sampling period when arsenic concentrations were greater than 2 standard deviations above the mean (825 ng m^{-3}). Each 72-hour back-trajectory is presented by a different colour.

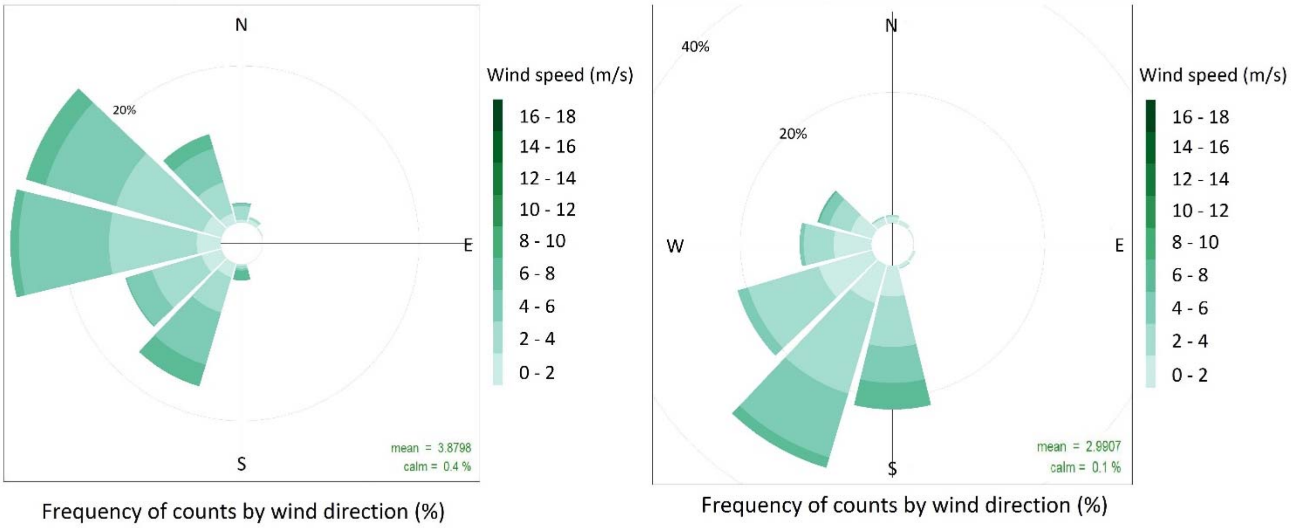


Figure A4. Wind roses of local winds measured at HBAO during sampling where arsenic concentrations were > 825 ng m^{-3}.

Secondary product

This factor can be called NH4 neutralization, as it contain acidic species not necessary arising by the same source, but they are neutralized by ammonia (the latter find in aerosol phase as NH4+ counterbalancing HSO4-, MS-, Formate, oxalate etc.).

This is a great suggestion, thank you. The name was changed to *ammonium neutralised*.

Heavy metals

Unfortunately, metals are gathered in only one factor, preventing the individuation of their source. There are several mining activity in Namibia (as reported in figure 1), therefore the analysis of backward trajectory for days with high concentration of each metals (or particular ratios between them) could be more useful than PMF in constrain metal sources.

Yes, you are correct and the new PMF solution (after consideration of the "main criticism to the paper") now separates the heavy metals into two components, namely *industry* and *fugitive dust*. These results were now incorporated into sections 4.2.,4.2.3. and 4.2.5.

For completeness we also ran back-trajectories corresponding to the sampling times during the week of 6 – 13 October 2016, when the overall highest concentrations of all heavy metals were measured (except for As). Figure A5 shows that primarily marine air masses that were transported southerly within the coastal margin and over, eg. the heavy-oil fuelled power plants or industry, and over a preferential commercial shipping transport pathway (Cape of Good Hope sea route), as mentioned in the paper (lines 106).

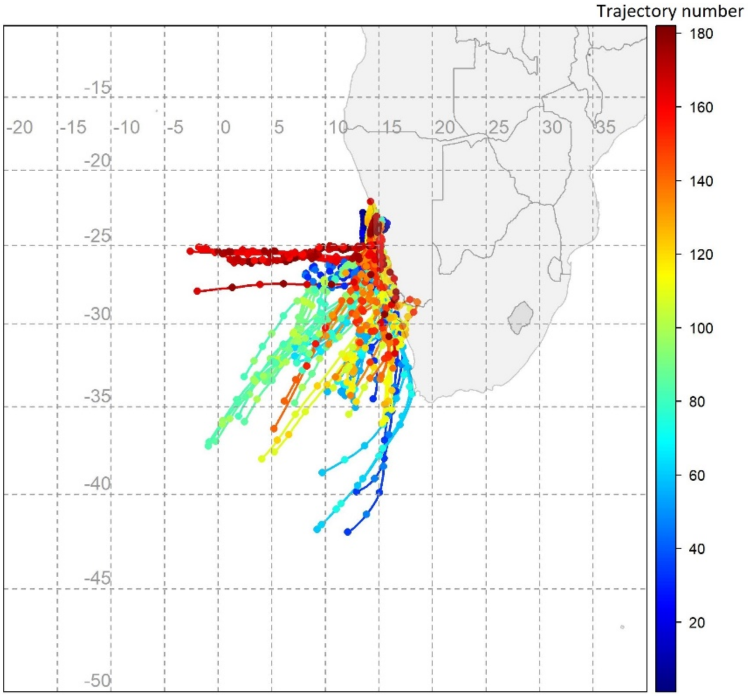


Figure A5. Back-trajectories run for 72 hours (each point representing 6 hours), starting at the same time as the end of the filter sampling during the week of 6 to 13 October 2016. Each 72-hour back-trajectory is presented by a different colour.

Back-trajectories were also run for additional episodes when high V concentrations were measured. These high V concentrations were classified in the same way as for As and F-. These showed the arrival of primarily continental air masses. Due to the well-mixed atmospheric composition and the coarse resolution of trajectory input data, specific heavy metal contributions from sources, such as the multitude of mines to the northeast of HBAO, could not be distinguished from one another on this basis. This is discussed in section 5, lines 615-618, "While the coarse resolution of air mass backtrajectories and the dominance of marine air masses does not allow to distinguish sources at the country scale, the PMF analysis performed in this paper was able to identify the specific and distinct contribution of mining activities, including for road construction for the majority of the heavy metals (ex., V)."

Lines 627-631. This sentence is too general, I think in this upwelling area, nutrient in the ocean arise from sea bed by upwelling of water masses more than deposited from the atmosphere, I can be wrong but these sentences have to be better supported by literature.

Referee#1 is right, the Benguela upwelling region is likely not very sensitive to atmospheric input of macronutrients, which, however, could be important for the productivity of the near-coast waters or, conversely, farther downwind towards the Southern Atlantic where the oceanic upwelling is not active.

To improve its clarity, the sentence was rewritten and updated in line 622 - 630 as follows "The deposition of macronutrients (P, Fe..) from the outflow of mineral dust is not expected to be relevant for the BUS region, one of the most productive marine environments in the world, while it could be important in fertilising waters near the coast (Dansie et al., 2017) and in the Southern Ocean (Okin et al., 2011). On the other hand, the atmospheric deposition of trace metals (Cr, Cu, Ni, Mn, or Zn) in the aerosols, which play a biological role in enzymes and as structural elements in proteins (Morel and Price, 2003), could affect the marine productivity of the BUS and should be explored in future work. The complexity and diversity of sources that might contribute to the mineral dust load at HBAO over a year, as well as the detailed chemical composition including trace metal contamination, deserve certainly further dedicated investigation".

Referee #2: specific comments

Line 120: This is likely true for elements with high concentration. I wonder that trace-elements, often just above the quantification limit, could be detected with negligible statistical uncertainty.

Referee#2 is correct in indicating that, in spite of its importance, the systematic error due to the calibration of the XRF machine does not represent the full analytical uncertainties on the final elemental concentrations. Additional terms contributing to it are

- The uncertainty related to the uniformity of the aerosol deposit on the filters, and the scaling error that can occur due to the fact that the area of the deposit which is analysed is smaller than the area of the aerosol deposit;
- The statistical error on the photon counts, in particular for trace elements whose concentrations are close to their detection limits.
- For the lightest elements (Z < 20), the choice of the correction factor to account for the self-attenuation of the X-ray signal, in particular for particles larger than 1 µm in diameter (Formenti et al., 2010).

These sources of errors have been carefully investigated through the years, and many precautions have been taken at LISA in the construction of a decadal experience in XRF analysis. Former analyses, often unpublished, have supported this experience, and provided with mitigation strategies, while not always resulted into their exact quantification. For example, in order to improve statistics and reduce the statistical error on the photon counts for trace elements, we systematically repeat each analysis three times.
To take all these considerations into account, we have therefore revised our error budget and attributed a 10% uncertainty to all elemental concentrations presented in the paper. The text (lines 121 – 132) was updated as follows

"Elemental concentrations of 24 elements (Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Pb, Nd, Cd, Ba) were obtained at LISA by wavelength-dispersive X-ray fluorescence (WD-XRF) using a PW-2404 spectrometer (Panalytical, Almelo, Netherlands), according to the protocol previously described by Denjean et al. (2016). The relative analytical uncertainty on the measured atmospheric concentrations (expressed in ng m^{-3}) is evaluated as 10%. This represents the upper limit uncertainty, taking into account:

- The uncertainty related to the uniformity of the aerosol deposit on the filters, and the scaling error that can occur due to the fact that the area of the deposit which is analysed is smaller than the area of the aerosol deposit;
- The statistical error on the photon counts, in particular for trace elements whose concentrations are close to their detection limits;
- The percent error on the certified mono- and bi-elemental standard concentrations (Micromatter Inc., Surrey, Canada) used for calibration of the XRF apparatus;
- For the lightest elements (Z < 20, Na to Ca), the choice of the correction factor to account for the self-attenuation of the X-ray signal, in particular for particles larger than 1 µm in diameter (Formenti et al., 2010). Constant correction factors (Table S1) were estimated through the sampling period assuming a mean diameter of 4.5 µm to represent the average coarse particle size."

Line 122 – 123: Such average correction introduces a further term in the uncertainty budget. A quantification should be included in the text.

As shown in Formenti et al. (2010), the self-attenuation correction depends on the individual particle size as well as on its composition. The information on the particle size at HBAO was only partially available during the period of sampling. Particle size was measured by Aerodynamic Particle Sizer (APS) which experienced very high losses for particles larger than 2.5 μm in diameter, therefore could not be used to inform on the full extent of the size distribution of the marine aerosols. The particle size was measured by a GRIMM optical counter during the shorter period of the AEROCLO-sA field campaign (Formenti et al., 2019). Figure A6 illustrates snapshots of these measurements (3-minute averages at different wind speed conditions) and the importance, as expected, of the coarse mode.

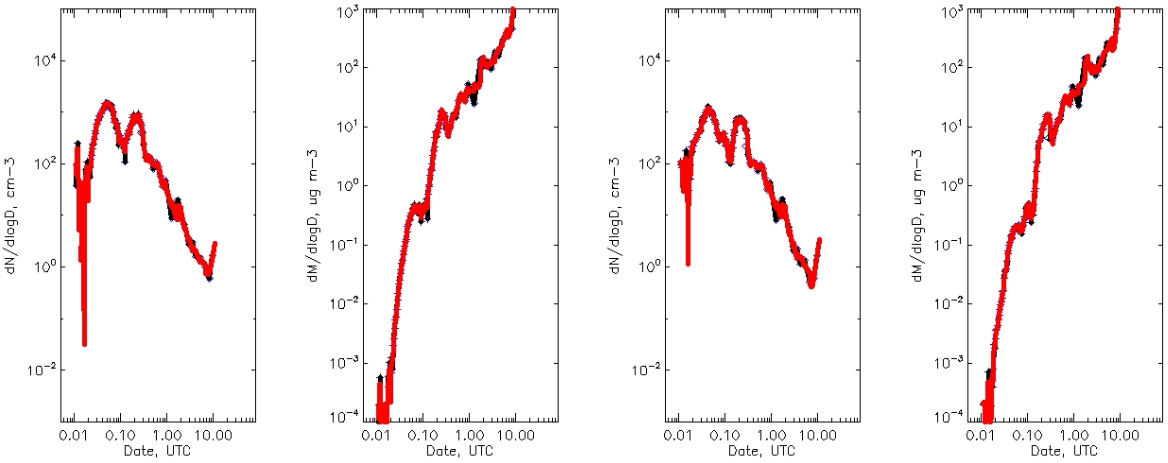


Figure A6. Aerodynamic Particle Sizer measurements (3-minute averages at different wind speed conditions) during the AEROCLO-SA field campaign.

A mean diameter of 4.5 μm was chosen to represent the average coarse particle size to evaluate the self-attenuation correction. For the sake of completeness, Table S1, with the correction factors used to scale up the elemental concentrations measured by XRF, was added to the supplementary material.

Line 146: I see a possible discrepancy for Na only: being this element the most sensitive to self-attenuation effects in the XRF-analysis, a reason for the difference could be related to the mean dimension of the sea-salt particles in the two period.

In principle, Referee#2 is right. However, changes in the Na^+/Na slopes in 2016 occur per batch of analysed data, which points out to some differences in the analyses, and not at a higher frequency, as it would be expected as a result of changes in the particle size distribution during sea spray emission. This is also in accordance with the fact that the Cl-/Cl slope varied in the same way with time (higher in 2016 and lower in 2017). As we said when replying to the previous comment, unfortunately we only have very partial information regarding the aerosol size distribution at HBAO from the measurements of the APS. From those measurements, the aerosol size distribution for particles smaller than 2.5 μm in diameter held rather constant with time.

Line 154: again, this could be due to the self-attenuation effect and to the choice of the corrective factor

Agreed. The sentence was modified at lines 161 - 165 to reflect this as follows "No specific sampling nor analytical problems were found. However, the further comparison of their proportions to those expected for seawater (Seinfeld and Pandis, 2006) as well as the possibility that the choice of a mean, time-independent self-attenuation correction factor, would be erroneous, at least for Na and Mg, suggested to discard the XRF results and only use the values obtained by IC for those three elements."

Line 180: by receptor models (i.e. Positive Matrix Factorization, PMF)

Corrected, thank you.

Line 184: I'd not define sea-salt or resuspension as "emission " sources. I'd also write "source" between quotation marks.

The referee is correct and subsequently we chose to define them as “source types” which offers a more inclusive description. Where applicable “source” or “factor” were replaced with PMF “components” for clarity. Remaining references to “sources” identified by the PMF were put in quotations.

Line 209: Factorization

For consistency with British English throughout the document, the format “factorisation” was kept.

Line 299: actually 10 +/- 4, Line 304: 1.3 +/- 0.1, Line 552: (3.2 +/- 1.0) % - (all factor mass %)

Significant digits were corrected, thank you.

Line 366: actually, there are many other previous papers indicating the V:Ni ratio as tracer of heavy oil combustion

The referee is correct and we have added three references to lines 431 - 434, thank you.

Line 372: The value of the slope of such correlation curve should be given and discussed in comparison with the usual literature figure, i.e. V:Ni ca = 3. This is also related to the discussion from line 380 on

As V and Ni were only poorly correlated, the annual average V/Ni ratios for 2016 and 2017 were preferred to the slope of the correlation curve. These are already reported in the manuscript (lines 430 - 433) and the paragraph was updated to include the PMF results, stating, “The V/Ni ratio for 2016 is 1.7 ± 1.1 and 2017 is 1.3 ± 1.3, and 0.5 ± 0.1 for the PMF *industry* component, lower than reported by Lyyränen et al. (1999) and Corbin et al. (2018) for heavy fuel oil in diesel engines, and by Becagli et al. (2017) and Viana et al. (2009) in the Mediterranean basin ambient air (2.8–2.9 and 4–5, respectively).”

At lines 434 - 435 we included, “…moderate to good correlations of V and Ni with Zn (0.42 and 0.55, respectively), Cu (0.55 and 0.73) and Pb (0.56 and 0.69)…”

We also included “…poor correlation (R^2 around 0.3).” at line 426.

Line 489: I suggest to write the name of the five sources in italic. Furthermore, I do not see appropriate the use of "source" to identify those which appear to be "components" of the PM, not always directly linked with a specific process (e.g. heavy metal, secondary products)

Considering these suggestions and comments from Referee #1, all references to “PMF sources” were changed to “components” and the PMF component names were changed to: *“sea salt, mineral dust, ammonium neutralised, fugitive dust,* and *industry*.”

Line 499: I'd see this discussion better located in section 4.2. with also the quantification of the resulting PM mass

This discussion was merged into one section on source apportionment as suggested, thank you.

Line 552: the "source profile" has nothing to do with the fraction of the PM accounted by a specific source. The word "profile" should be removed here and, as stated before, I'd prefer "component" instead of "source"

Considering outputs of the PMF model as mass fractions of the total, “components” is a better descriptor and has been corrected throughout the document. Thank you.

Line 570: I find not surprising that sea salt is present in all the sources detected in a coastal site.

We agree. This is now added at lines 309-320 “An Fpeak strength of 0.5 was used to retain the best PMF solution whose five components (sea salt, mineral dust, ammonium neutralised, fugitive dust and industry) are shown in Figure 6. The relative contribution of those components to the total estimated mass is shown in Figure S3. Sea salt accounted for the largest fraction of the (mass concentration (: 74.7 ± 1.9%). Mineral dust accounted for (15.7 (± 1.4%,) of the evaluated total mass concentration. The remaining fraction was accounted by three components characterised by secondary species and heavy metals, ammonium neutralised (6.1 ± 0.7%), fugitive dust (2.6 ± 0.2%) and industry (0.9 ± 0.7%). However, the major tracers of the sea salt component, Na+ and Cl-, were ubiquitous in all components, not surprising considering the continuous inflow of marine air to HBAO. As it can be seen in Figure 6, Na+ and Cl- contributed to 35.2 ± 5.8% of their mass to the mineral dust component. to 47.4 (± 1.9%) of the mass of the fugitive dust PMF component 1.3 (± 17.8%) of the mass of the industry component”.

Figure 6: the fits in the bottom panels are misleading: there is no correlation between the plotted variables and the equations (by the way: the uncertainty on slope and bias should be given) have no sense.

You are correct, considering that the axis scales differ, the trend lines appeared misleading. The axes were changed and the trendlines removed from Figure 6 (now Figure 7).

In addition I have a more general comment: in my opinion the importance of the article is in the large and detailed set of data that have been collected. The PMF analysis does not add so-much (and I see that in the conclusions its results poorly commented) since the quantification of the impact (fraction of the PM mass) of each "source" (I do not like the term as it has been used int he text, see comments in the PDF) is not very firm due to the sea salt "contamination "basically in all the detected factors. I’d invite the Authors to add in the text some more comments on the significance of the PMF exercise.

We agree, see general comments.