Source apportionment of highly time resolved trace elements during a firework episode from a rural freeway site in Switzerland

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Response to Reviewer #1

We thank Reviewer#1 for the careful revision and comments which helped improving the overall quality of the manuscript. A point-by-point answer (in regular typeset) to the reviewers' remarks (in italic typeset) follows. Changes to the manuscript are indicated in blue font.

In the following page and line references refer to the manuscript version reviewed by anonymous Reviewer#1.

GENERAL COMMENTS

The manuscript describes a study to determine the sources impacting on PM10 in a traffic oriented site using a high resolution elemental dataset and processing data with the SoFi tool based on ME-2 receptor model algorithm. The manuscript is well organized, the language is clear and the English style is appropriate.

According to the authors, the SA study was conducted to characterize the source emissions at a traffic-influenced site. This is confusing because receptor models are normally carried out at the receptor site to characterize the source contributions rather than the source emissions. The authors claim the novelty of the work is due to the limited number of studies for trace element emission sources with high time resolution. However, as the same authors state, many studies were carried out using rotating drum and streakers that, despite being off-line, provide comparable information that can be processed in the same manner as this study.

We agree with reviewer#1 that receptor models characterize the source contributions. Therefore we have replaced "emissions" by "contributions" to make it clear.

The novelty of this work mainly highlights the inclusion of a strong fireworks event in the PMF input data set. Typically such strong, isolated events are excluded from PMF analysis to avoid distortion of the solution. However, here we established that unmixed fireworks can be apportioned by ME-2, without disturbing the model solutions, in contrast to conventional/unconstrained PMF.

We agree with the reviewer that highly time-resolved trace element measurements can be obtained by rotating drum and streaker techniques, and in principle provide similar information as the Xact. However, these samplers require offline analysis, including accessibility and significant beam time availability at accelerator facilities. In practice, this leads to undesirable trade-offs between time resolution and data coverage even for short duration field campaigns, whereas highly time-resolved long-term measurements are impractical. In contrast, the Xact 625 is an online system which has been developed and commercialized for rapid, long-term and semi-continuous detection of the ambient aerosol particle's elemental composition. This is a novel and highly useful analytical capability, and characterization of the instrument's measurement and source apportionment capabilities is therefore of significant interest.

We have rewritten page 3 line 1 as follows:

In practice, the offline samplers lead to undesirable trade-offs between time resolution and data coverage even for short duration field campaigns, whereas highly time-resolved long-term measurements are impractical. A recently introduced online high time resolution instrument can collect samples and perform analysis for elements simultaneously in a near real time scenario for long-term measurements without waiting for laboratory analysis.

SA of the entire PM based only on trace elements representing only a limited fraction of the PM mass (in this case 20%) is very uncertain because a considerable amount of information is missing about the main components of PM: elemental carbon, ions and the organic fraction. The risk is to overestimate the contribution of sources for which the elements are markers and neglect sources where elements are less relevant in particular the secondary organic fraction. In addition, the identification of factors into sources is hindered because the chemical profiles contain few diagnostic species or combination of species.

It is important to know where the inorganic elements / metals come from. Every source apportionment typically focuses on the components that are measured. For example, all the PMF of organic aerosol just does a source apportionment of the organic aerosol. We do not attempt to provide a full source apportionment of the atmospheric aerosol, but rather focus on the inorganic elements / metals. This has been done to a much lesser extent than for the organic aerosol, but it is actually important, and may become more important in the next years, due to the discussion of the possible health effects of metals.

In addition, we have used BC, NO_x and Q-ACSM data to compare the SA results with the time trends of those components. We did not claim to do a SA of PM_{10} just with the elements measured by the Xact. We fully agree with reviewer#1 that it would introduce a lot of uncertainties if we attempted to scale our element SA to the full PM_{10}, however, as mentioned, this is not the case here. We believe that SA of trace elements alone is already interesting. Some elements are directly health-relevant and many are closely related to specific sources. The total SA including elemental carbon, ions, organic fraction and trace elements is quite complicated, requiring blending of data from several instruments. It is also suboptimal for identifying sources of trace elements because it can reduce them to minor factors (in comparison to organics or non-refractory inorganics). In addition, the combined SA would require combining measurements with different size cuts, e.g. Xact with $PM_{10,}$ ACSM with PM_1 and BC with $PM_{2.5}$.

The authors claim MAAP and Q-ACSM were collected in parallel so it is not clear why they didn't use this information to obtain more robust SA results. The impression is that the authors are splitting the study in pieces to make more publications.

As already mentioned above combining different data sets from different instruments into one ME-2 model is challenging due to differences in error propagation. In our opinion, the combination of PM_1 data for Q-ACSM,

$PM_{2.5}$ for MAAP and PM_{10} data for Xact may introduce artefacts in the ME-2 analysis. We have used MAAP and Q-ACSM data sets in the manuscript to compare some of the ME-2 factor time series and diurnal patterns. We are not planning to publish any other paper on the additional data. A major focus was the exploration of the use of the Xact for source apportionment in Europe where the concentrations are considerably lower than in polluted areas in Asia.

We have added in the manuscript as follows on page 3 line 7:

The main focus of this work is the exploration of the use of the Xact for source apportionment in Europe where the concentrations are considerably lower than in polluted areas in Asia.

The study location is not well described. A map is needed to help the reader understanding the characteristics of the site.

We have added a map in the manuscript on page 22.

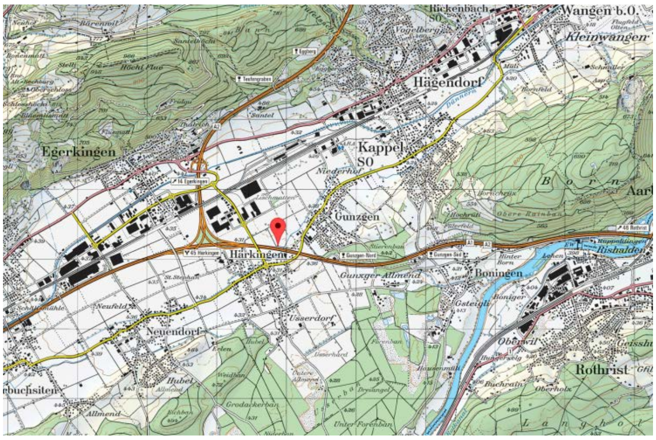

Figure 1: Map of the sampling location (NABEL site in Haerkingen), The site is marked with red google pin. Map reproduced by permission of swisstopo (JA100119).

The Conditional Bivariate Polar Function (CBPF) analysis is an important part of this work, there is a dedicated sub-chapter in the methodology section. However, there are no graphs about the results of this technique in the paper. The supplementary material is supposed to be used to provide information that supports the main findings of the work not to place essential results of the work.

This issue was also raised by reviewer #2. We have modified the graph and moved it into the main text of the revised manuscript.

The conclusion that the study result emphasizes the large influence of highway traffic on the composition of PM10 is trivial considering the study was conducted at a traffic site. In addition, this is not in line with the declared objective of characterizing the emissions.

We have mentioned in the objective that we conducted SA using PMF to characterize the source contributions of highly time-resolved metals during a three-week campaign at a traffic-influenced and otherwise rural site in Härkingen, Switzerland. Therefore, we decided to mention a brief overview of results in the conclusions including the smallest and largest contributions of sources, which is in line with the objective. In fact, the high contribution of traffic is not trivial and not easily accessible with 24-hours sampling. In addition, it is important in the light of the role elements may have concerning health effects. In contrast, the contribution of traffic is minor for organics, also at such a site and also for other components it is not clear how much the rather local source would contribute in comparison to other more regionally influenced components.

In this manuscript there is a contrast between the highly sophisticated data treatment and the limited data input. The model allocates all the PM10 mass on the basis on the predictive capabilities of only 14 elements which do not provide enough information to properly identify all the factors and to allocate the PM10 mass to each of them reliably. This is due to lack of markers to allocate the carbonaceous fraction and part of the secondary inorganic (nitrate). As a consequence there are not well resolved factors (e.g. the two fireworks and the two dust factors and the road dust with the traffic-related factor).

Again, we are not attempting a source apportionment of the full PM_{10}, but rather of the inorganic elements / metals concentrations. For these components, we have been able to retrieve quite well resolved factors, in contrast to the reviewer's opinion. Examples are the strong influence of the fireworks episode and the wind direction dependency. In addition, the high time resolution of the Ca and Si data set make the separation of two dust factors with distinct factor time series possible, while the traffic-related factor shows much stronger diurnal patterns, similar to BC and NO_x as compared to the road dust factor. The BC time series yields a strong correlation with the traffic-related factor (Pearson's $r = 0.86$) while it shows a weak correlation with the road dust factor ($r = 0.34$). The two fireworks factors are resolved due to difference in elemental ratios in the factors as well as based on the residual structure during fireworks days. Fig. 4 in the manuscript shows that we indeed need two fireworks factors to explain the time series of elements related to fireworks.

Source apportionment with receptor models is a routine technique and alone does not represent a scientific novelty. In addition, the application of these models with only trace elements does not fulfill the minimum requirements to obtain robust PM source apportionment because of the absence of important information to allocate the entire PM10 mass.

Some source apportionment applications may be regarded as a routine technique. This is mostly the case for standardized chemical mass balance (CMB) or positive matrix factorization (PMF). The use of partial constraints in ME-2, hybrids of CMB and PMF, is not routine. In addition, it has so far mostly been applied to the organic aerosol, and much less to inorganic elements / metals. And, to reiterate, we did not attempt to allocate the entire mass to sources but rather a sub-fraction like it has been done frequently for the organic aerosol, but in this case mostly for trace elements which are partially specifically toxic.

SPECIFIC COMMENTS

Page 1 line 29: the literature about the health impacts of PM need to be improved.

We have already added several references for health impacts before line 29. We added a line in the manuscript on page 1 line 30 related to health impact of coarse fraction of PM as follows:

In Stockholm, Meister et al. (2012) estimated a 1.7% increase in daily mortality per 10 $\mu g\ m^{-3}$ increase in coarse fraction of PM.

Meister, K., Johansson, C., and Forsberg, B.: Estimated short-term effects of coarse particles on daily mortality in Stockholm, Sweden, Environ. Health Perspect., 120, 431–436, https://doi.org/10.1289/ehp.1103995, 2012.

Page 3 line 6: the study by Park et al was carried out with XACT 620.

We have added in the text some more references in this paragraph as follows: "The Xact 620, 625 and the newer 625i ambient metals monitors (Cooper Environmental Services, Beaverton, Oregon, USA) based on XRF have been developed in recent years and have been used in several field studies (Fang et al., 2015; Cooper et al., 2010; Furger et al., 2017; Park et al., 2014; Phillips-Smith et al., 2017; Tremper et al., 2018; Chang et al., 2018; Liu et al., 2019; Ji et al., 2018). However, only six studies included SA on Xact data (Park et al., 2014; Fang et al., 2015; Phillips-Smith et al., 2017; Chang et al., 2018; Liu et al., 2019; Ji et al., 2018)."

Cooper, J. A., Petterson, K., Geiger, A., Siemers, A., and Rupprecht, B.: Guide for developing a multi-metals, fenceline monitoring plan for fugitive emissions using X-ray based monitors, Cooper Environmental Services, Portland, Oregon, 1–42, 2010.

Fang, T., Guo, H., Verma, V., Peltier, R. E., and Weber, R. J.: $PM_{2.5}$ water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for health studies, Atmos. Chem. Phys., 15, 11667–11682, https://doi.org/10.5194/acp-15-11667-2015, 2015.

Phillips-Smith, C., Jeong, C.-H., Healy, R. M., Dabek-Zlotorzynska, E., Celo, V., Brook, J. R., and Evans, G.: Sources of particulate matter components in the Athabasca oil sands region: investigation through a comparison of trace element measurement methodologies, Atmos. Chem. Phys., 17, 9435–9449, https://doi.org/10.5194/acp-17-9435–2017, 2017.

Liu, Y., Zheng, M., Yu, M., Cai, X., Du, H., Li, J., Zhou, T., Yan, C., Wang, X., Shi, Z., Harrison, R. M., Zhang, Q., and He, K.: High-time-resolution source apportionment of $PM_{2.5}$ in Beijing with multiple models, Atmos. Chem. Phys., 19, 6595–6609, https://doi.org/10.5194/acp-19-6595-2019, 2019.

Ji, D., Cui, Y., Li, L., He, J., Wang, L., Zhang, H., Wang, W., Zhou, L., Maenhaut, W., Wen, T., and Wang, Y.: Characterization and source identification of fine particulate matter in urban Beijing during the 2015 Spring Festival, Sci. Total Environ., 430–440, 628–629, https://doi.org/10.1016/j.scitotenv.2018.01.304, 2018.

Page 6 line 2: is it reasonable to use 10% analytical uncertainty for all the species?

An estimated analytical uncertainty of 10% for all species has been used to derive the uncertainty data set in several previous studies (Kim et al., 2005; Kim and Hopke, 2007; Tian et al., 2016; Ji et al., 2018), which did not impact the interpretability of the PMF results. We also tried metal specific analytical uncertainty from Phillips-Smith et al. (2017) and Jeong et al. (2016) but it did not change the PMF results.

We have modified line 2 on page 6 as follows:

In this study, an estimated analytical uncertainty (p_j) of 10 % was used to derive the error matrix data set (Kim et al., 2005; Kim and Hopke, 2007; Tian et al., 2016; Ji et al., 2018), which did not change the PMF solution. The metal-specific analytical uncertainty was also considered from the previous studies (Jeong et al., 2016; Phillips-Smith et al., 2017), where it was calculated on the basis of high/medium-concentration metal standards laboratory experiments and the additional 5-10% flow rate accuracy, which yielded similar PMF solutions compared to an overall 10 % analytical uncertainty.

Kim, E., Hopke, P. K., and Qin, Y.: Estimation of organic carbon blank values and error structures of the speciation trends network data for source apportionment, J. Air Waste Manage. Assoc., 55, 8, 1190–1199, https://doi.org/10.1080/10473289.2005.10464705, 2005.

Kim, E. and Hopke, P. K.: source identifications of airborne fine particles using positive matrix factorization and U.S. environmental protection agency positive matrix factorization, J. Air Waste Manage. Assoc., 57, 7, 811–819, https://doi.org/10.3155/1047-3289.57.7.811, 2007.

Tian, S. L., Pan, Y. P., and Wang, Y. S.: Size-resolved source apportionment of particulate matter in urban Beijing during haze and non-haze episodes, Atmos. Chem. Phys., 16, 1–19, https://doi.org/10.5194/acp-16-1-2016, 2016.

Jeong, C.-H., Wang, J. M., and Evans, G. J.: Source Apportionment of Urban Particulate Matter using Hourly Resolved Trace Metals, Organics, and Inorganic Aerosol Components, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2016-189, 2016.

Ji, D., Cui, Y., Li, L., He, J., Wang, L., Zhang, H., Wang, W., Zhou, L., Maenhaut, W., Wen, T., and Wang, Y.: Characterization and source identification of fine particulate matter in urban Beijing during the 2015 Spring Festival, Sci. Total Environ., 430–440, 628–629, https://doi.org/10.1016/j.scitotenv.2018.01.304, 2018.

Phillips-Smith, C., Jeong, C.-H., Healy, R. M., Dabek-Zlotorzynska, E., Celo, V., Brook, J. R., and Evans, G.: Sources of particulate matter components in the Athabasca oil sands region: investigation through a comparison of trace element measurement methodologies, Atmos. Chem. Phys., 17, 9435–9449, https://doi.org/10.5194/acp-17-9435–2017, 2017.

Page 7 line 18: how do you know salt is from sea and not road salt?

This point is discussed later in the detailed presentation of the sea salt factor (section 4.2, “sea salt”). As mentioned in the manuscript the observed Mg / Na ratios for sea salt events (0.13 and 0.16) are in line with the expected ratio for marine aerosol (0.135 to 0.185). The measured Cl / K and Cl / Ca ratios (0.27 and 0.33 respectively) from Xact do not lie in the range of road salt snow samples (150±39 and 103±22, respectively) collected near the roadside (≤50 m) in the USA (Williams et al., 2000). The CBPF plot (Fig. 5) and backward trajectories (Fig. S11) also validate the occurrence of the sea salt event. Moreover, during summer (mean temperature 21 ^{0}C), we do not expect de-icing salt on the road.

We have added a line on Page 9 line 17 as follows:

The measured Cl / K and Cl / Ca ratios (0.27 and 0.33 respectively) from Xact do not lie in the range of road salt snow samples (150±39 and 103±22, respectively) collected near the roadside (≤50 m) in USA (Williams et al., 2000), which validates our interpretation as a sea salt factor.

Williams, A. L., Stensland, G. J., Peters, C. R., and Osborne, J.: Atmospheric dispersion study of deicing salt applied to roads: first progress report, Illinois State Water Surv. Contract Report, 2000-05, Champaign, IL, 2000.

Page 7 line 25: the expression factor composition is not clear. Do you mean factor profile?

Yes, the factor composition expression represents the factor profile. The mathematical expression for factor composition is mentioned in line 26 of that page. We replaced "factor composition" with "factor profile" to avoid confusion for readers.

Page 9 line 14: the comparison between the on-line and off-line data is not clear. In the text are mentioned 28th and 30th July but the Mg/Na ratio is similar to marine aerosol also on 31st July.

We apologize for the misunderstanding. Here we discuss the offline measurements of Na and Mg, which were not measured by the Xact, and their ratio in sea salt aerosols. The Mg / Na ratio on 31st July (0.28) does not lie in the range for marine aerosol but it is close to literature values (0.132 – 0.185). The sea salt factor time series as well as the time series of Cl from the Xact have a quite flat pattern on 31st July except for the fireworks peak at 23:00 LT with mostly south-east-north wind directions at low wind speeds (1–4 m s^{-1}) (Fig. S10) which may indicates the background concentration. In contrast, during the sea salt event, wind was mostly dominating from west directions at higher wind speeds (5–8 m s^{-1}).
We modified the text on Page 9 line 11 as follows:
Sea salt also includes Na and Mg, which were not measured by the Xact but analysed by ICP-OES for 24-h offline filters.

Page 9 line 21 and foll.: There is not clear evidence to prove there are two different dust factors. The diurnal profiles are almost overlapping (Figure 3) and in the scatter plot of fig S13 there is only one cloud of points. Also the CBPF plots in figure S8 show overlapping wind speed and directions. Soil dust should be farther from the origin than the more local road dust. Split of sources is a typical problem of using only elements in factor analysis source apportionment. In addition, how do you know that Ca rich is road dust and not other sources? Enriched Ca dust is common in construction works, for instance.

The scatter plot of Si and Ca in Fig. S13 shows quite scattered data points which might be due to influence of more than one source especially during the end of the measurement period. Therefore, there is no strong correlation between Si and Ca elements (Pearson's r^2 0.56). The possible sources for Si and Ca could be the local and regional transport of crustal material partly re-suspended by traffic (south sector) and partly originating from the agricultural area north of the freeway. The factor time series of both factors are not identical except for a few overlapping points. The road dust diurnal pattern shows a maximum traffic rush hour peak similar to NO_x, black carbon (BC), heavy duty vehicle (HDV) count and the traffic-related factor while the background dust factor has no spikes in the diurnals (Fig. 3). Also our interpretation brackets the road dust factor because the road dust resuspension in the road side environment is primarily traffic induced. We have added the modified CBPF plots as well as an explanation about two dust factors in the 2nd referee's general comments section. However we would like to add that the agricultural land immediately to the west and north direction and another freeway (A2) in the northwest direction from the sampling location might be the reason for background dust in the CBPF plot.
We agree that Ca dust is also possible from construction dust. But this hypothesis does not support the Ca rich factor diurnal pattern when we assume that this kind of sources peaked during the day and decreased to almost zero outside of normal working times (08:00 until 17:00 LT). We also found that there is only a weak correlation in the hourly concentrations between Ca and S. If calcium sulfate dihydrate is the main compound in gypsum used

for construction work, Ca and S should show a better correlation. The weak correlation could be possible due to the contribution from different sources for Ca (road dust) and S (ammonium sulfate). During the Ca peaks, ACSM PM_1 sulfate and ammonium did not show high peaks. However, comparing the ACSM PM_1 sulfate with PM_{10} S may not be direct because of the existence of coarse sulfate in the form of calcium sulfate. Pure gypsum typically contains 29.4% Ca and 23.5% S, resulting in an elemental ratio of 1.25 which was not found in our measurements except one data point.

We added the text in the manuscript as follows on page 10 line 1:

Ca has been associated with construction activities in previous studies (Bernardoni et al., 2011; Crilley et al, 2016), which have been found to peak during the day and decreased to almost zero outside of normal working times (08:00 until 17:00 LT). This evidence is not supported by the road/background dust factor diurnal pattern in this study. Further evidence of non-construction activity is found in the Xact elemental ratio of Ca / S (0.62) which is not in the agreement with the pure gypsum Ca / S ratio (1.25) used for construction work (Hassan et al., 2014), where they are the main constituents.

Bernardoni, V., Vecchi, R., Valli, G., Piazzalunga, A., Fermo, P.: PM_{10} source apportionment in Milan (Italy) using time-resolved data, Sci. Total Environ., 409, 4788–4795, https://doi.org/10.1016/j.scitotenv.2011.07.048, 2011.

Crilley, L. R., Lucarelli, F., Bloss, W. J., Harrison, R. M., Beddows, D. C., Calzolai, G., Nava, S., Valli, G., Bernardoni, V., and Vecchi, R.: Source apportionment of fine and coarse particles at a roadside and urban background site in London during the 2012 summer ClearfLo campaign, Environ. Pollut., 220, 766–778, https://doi.org/10.1016/j.envpol.2016.06.002, 2016.

Hassan, A. K., Fares, S., and Abd El-Rahma, M.: Natural radioactivity levels and radiation hazards for gypsum materials used in Egypt, J. Environ. Sci. Technol., 7, 56–66, https://doi.org/10.3923/jest.2014.56.66, 2014.

Page 9 line 25: only the Ca scaled residuals improve not those of Si.

The Si scaled residual was also improved a bit (from 6 to 4). Increasing the number of factors further did not improve the Si scaled residual structure.

Page 10 line 17 and foll.: The chemical composition of this factor indicates brake wear mixed to the re-suspended particles as Fe and Si are components of crustal material. Again there is an overlapping in the chemical composition with the so called road dust profile and these two profiles also have very similar diurnal profiles.

Although Fe and Si are components of crustal material, both can be emitted from anthropogenic sources as well. The diurnal pattern of Fe shows traffic rush hour peaks while Si diurnal cycle is not as prominent as Fe. The sources of Fe are already discussed in the manuscript. We added a sentence for Si in the manuscript. If the road dust factor is attributable mainly to abrasion of the road surface and tires, and the resuspension by traffic vortices, a similar diurnal pattern with the traffic-related factor would be expected.

We have added the following text in the manuscript on page 10 line 24:

Si is one of the brake lining components used as abrasive to increase friction, and as fillers to reduce manufacturing costs, respectively (Thorpe and Harrison, 2008; Grigoratos and Martini, 2015).

Thorpe, A. and Harrison, R. M.: Sources and properties of non-exhaust particulate matter from road traffic: A review, Sci. Total Environ., 400, 270–282, https://doi.org/10.1016/j.scitotenv.2008.06.007, 2008.
Grigoratos, T. and Martini, G.: Brake wear particle emissions: a review, Environ. Sci. Pollut. Res., 22, 2491–2504, https://doi.org/10.1007/s11356-014-3696-8, 2015.

Page 10 line 29: the secondary sulfate does not provide any evidence to allocate the ammonium nitrate (another main secondary inorganic component of PM).

Yes, we agree with reviewer#1 that it does not provide evidence to allocate the ammonium nitrate but this is not what we are attempting in this paper. It is outside the scope of this paper to perform an ACSM PMF analysis.

Page 11 line 8: The characterization of the industrial source is weak. There is no connection to any known industrial process. The fact that other studies in completely different areas found the same profile is not proving the industrial origin of this factor. On the contrary, it is unlikely that the same industrial process is present in many different sites.

This factor time series contains a few spikes which correlate with wind direction, indicating a local point source. Based on this hypothesis, we interpreted this factor as industrial source. The other previous studies are mentioned to represent similar factor profiles from local point sources without a specific industrial emission.
We have modified the text in the manuscript on page 11 line 11:
A similar factor profile was observed in previous source apportionment studies (Crilley et al., 2016; Richard et al., 2011) from local point source emissions without any link to specific industrial activities. Amato et al. (2010) and Dall'Osto et al. (2013) also reported a PMF factor with high concentrations of Zn and Pb and attributed it to emissions from smelters in Barcelona, while Vossler et al. (2016) reported a similar factor profile from coal combustion processes in Ostrava.
Crilley, L. R., Lucarelli, F., Bloss, W. J., Harrison, R. M., Beddows, D. C., Calzolai, G., Nava, S., Valli, G., Bernardoni, V., and Vecchi, R.: Source apportionment of fine and coarse particles at a roadside and urban background site in London during the 2012 summer ClearfLo campaign, Environ. Pollut., 220, 766–778, https://doi.org/10.1016/j.envpol.2016.06.002, 2016.
Richard, A., Gianini, M. F. D., Mohr, C., Furger, M., Bukowiecki, N., Minguillón, M. C., Lienemann, P., Flechsig, U., Appel, K., DeCarlo, P. F., Heringa, M. F., Chirico, R., Baltensperger, U., and Prévôt, A. S. H.: Source apportionment of size and time resolved trace elements and organic aerosols from an urban courtyard site in Switzerland, Atmos. Chem. Phys., 11, 8945–8963, https://doi.org/10.5194/acp-11-8945-2011, 2011.
Amato, F., Nava, S., Lucarelli, F., Querol, X., Alastuey, A., Baldasano, J. M., and Pandolfi, M.: A comprehensive assessment of PM emissions from paved roads: Real-world emission factors and intense street cleaning trials, Sci. Total Environ., 408, 4309–4318, https://doi.org/10.1016/j.scitotenv.2010.06.008, 2010.
Dall'Osto, M., Querol, X., Amato, F., Karanasiou, A., Lucarelli, F., Nava, S., Calzolai, G., and Chiari, M.: Hourly elemental concentrations in $PM_{2.5}$ aerosols sampled simultaneously at urban background and road site during SAPUSS – diurnal variations and PMF receptor modelling, Atmos. Chem. Phys., 13, 4375–4392, https://doi.org/10.5194/acp-13-4375-2013, 2013.

Vossler, T., Černikovský, L., Novák, J., and Williams, R.: Source apportionment with uncertainty estimates of fine particulate matter in Ostrava, Czech Republic using positive matrix factorization, Atmos. Pollut. Res., 7, 503–512, https://doi.org/10.1016/j.apr.2015.12.004, 2016.

Figure 4: Not clear what is the added value of this figure with respect to figure 1. Normalized concentration (should be explained in the caption). Why use different units than the other graphs. The percentile box and whisker and the mean -+SD overlaps making the graph difficult to read. Choose one.

PMF results (Fig. 1) describe potentially complex and time-dependent sources as a single factor (or linear combination of factors). This is a fundamental limitation of the model, and may not accurately describe the behaviour or a complex source (e.g., residuals may be significant). In contrast, Fig. 4 provides an estimate of the overall fireworks composition and temporal variability, complementing the PMF results (which are shown for reference). One can then see both the explanatory power and limitations of the SA model for this source.
We moved Fig. 4 to the supplement and removed ± SD from the figure.
We added in the supplement on page 8 line 6:
Fig. S8 provides an estimate of the overall fireworks composition and temporal variability, complementing the PMF results (which are shown for reference). The figure is constructed in two stages. First, the time series of fireworks contributions to each element is estimated by subtracting the non-fireworks factors (NFF) from the original measurements. Then, the estimated fireworks contribution for each element is normalized by the total fireworks element contribution, and the displayed statistics are calculated. This is represented mathematically below, and the expression has been added to the main text. Note that the variation in fireworks profiles implied by this figure supports the representation of fireworks by 2 fireworks factors.

$$normalized\ concentration_{ij} = \frac{x_{ij} - \left(g_{ik} f_{kj}\right)_{k=NFF}}{\Sigma_j\left(x_{ij} - \left(g_{ik} f_{kj}\right)_{k=NFF}\right)} \qquad \text{(S1)}$$

where X represents the input data matrix for PMF, while G and F represent the factor time series and factor profiles driven by six non-fireworks factors (NFF). Here *i* and *j* denote time series and variables, respectively.

Figure S9: the connection between this data and the days with high "sea salt" is not clear in this figure. It should be better evidenced to allow the reader evaluating if there is a difference between the days with high sea salt and those without it.

We apologise for the misunderstanding. Fig. S9 only shows the Mg / Na ratio for 24-h filter data analysed by ICP-OES along with the literature Mg / Na ratio (0.132 - 0.185) in marine aerosols. In this figure, we presented the existence of sea salt events and non-sea salt events. The sea salt factor time series with high and low concentrations is already shown in Fig.1 and discussed in the manuscript.
We added a line in the caption of Fig. S9 caption on page 9 line 5:
The Mg / Na ratio was 0.13 and 0.16 for 28 July and 30 July, respectively while for the rest of the days it was higher than 0.185.

TECHNICAL CORRECTIONS

Figure S6: not clear why the p25 is a single point while the p75 is a vertical line.

We modified Fig. S6.

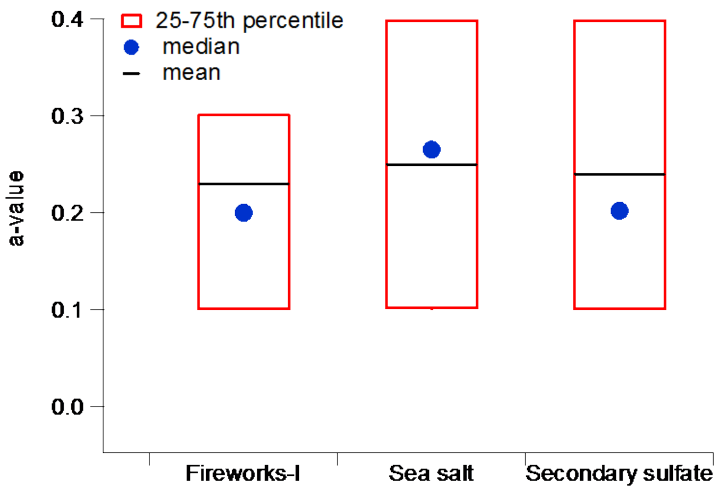

Figure S6: *a*-value statistics of the accepted solutions. *a*-values between 0 to 0.5 were explored during BS analysis. The average *a*-value of the selected solutions was ranging from 0.2 to 0.3 for the constrained factors. The selected *a*-values were homogeneously distributed over that range.