Applying receptor models Unmix and PMF on real data set of elements in PM for sources evaluation

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Abstract

Two advanced receptor modeling techniques Unmix and PMF were applied to a data set of daily measurements of 11 elements in particulate matters (PM) of 252 samples. Samples were collected every sixth day as a 24h sample in the 5 year period (1995 – 2000) in the coastal part of the Herceg-Novi town (Montenegro) of the sea costal side region (Southeast Adriatic Sea). In the vicinity of the sampling site road traffic is a permanent.

The application of the receptor models to find the emission sources in the reverse order, using data set of pollutants concentrations measured on the receptor, is not enough to get satisfactory real solution relying only on the results of the applied models even if used the state-of-the-art models such as Unmix and PMF. In this work we applied Unmix and PMF on dataset which already modeled by PCA and EF in order to show how many solutions could be find and how many errors could be made as well as we harmonized these advanced models to find the most realistic solution. The model Unmix has the ability to suggest the solution by self-modeling while PMF model can be adjusted to calculate the solution for the number of emission sources that we have set. Unmix found thirteen solutions in total for several combinations of species, but four solutions satisfy its criteria: Min $R^2 > 0.8$ and Min $S/N > 2$. The PMF model has given 3 possible solutions and by further analysis the best solution of four sources was selected. F-peak refinement enabled finding a more realistic solution. We noticed that for the species with many missing values but, their presence is not desirable because of its harmfulness such as cadmium in this work the knowledge of emission sources is very important. Due to their limitations Unmix

and PMF is not able to give the solution for such cases. Other simple model applied together with advanced models could help to solve similar problems.

Key words: Modeling, Unmix, PMF, real data set

Introduction

A state-of-the-art multivariate receptor models are applied in the diverse fields of environmentrics, chemometrics, geology and remote sensing. Multivariate receptor modeling is a term applied in the field of air quality for the solution of the general linear mixture problem. For conservative chemical species, i.e. those that do not undergo reactions in the atmosphere, the principle of mass balance is applied. The mass balance for species *i* can be written as:

$$C_{ij} = \sum_{k=1}^{N} a_{ik} S_{kj} \quad i = 1,\ldots,m,\ j = 1,\ldots, n \tag{1}$$

In this equation, C_{ij} is the observed concentration of species *i* in sample *k*, S_{kj} is the total amount of particulate mass from source *k* in sample *j* and a_{ik} it the composition fraction of species *i* from the source *k*. In air quality studies, the units of C_{ij} are usually micrograms per cubic meter. Thus, since a_{ik} is a dimensionless mass fraction, the units of S_k are also micrograms per cubic meter. Eq. (1) is the physical basis of all receptor models. C_{ij} is subject to random error and a_{ik} to random variations (Henry, 2002).

Unmix seeks to solve the general mixture problem where the data is assumed to be a linear combination of an unknown number of sources of unknown composition, which contribute an unknown amount to each sample. Unmix assumes that the data and the compositions of the sources are all strictly positive (because of the effects of errors, small values less than zero are allowed in order to reduce the bias in the results). Unmix further assumes that for each source there are some samples that contain little or no contribution from that source. For a given selection of species, Unmix estimates the number of sources, the source composition, and source contributions to each sample. The usual analytical approach to fitting the model in Eq. (1) is to find the values of a_{ik} and S_{kj} that minimize the weighted mean square error *F* (Henry, 2002) of the model:

$$F = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(w_{ij} C_{ij} - \sum_{k=1}^{N} a_{ik} S_{kj} \right)^2 \ i = 1,\ldots,m,\ j = 1,\ldots, n \tag{2}$$

Unmix diagnostic edges plots are used to show how well-defined one or more edge is by the data. If the edge plots show that all the edges are straight and well defined, then the Unmix results should be more reliable and should be preferred over the PMF results (Henry and Christensen, 2010).

The General Mixture Problem and the special case of multivariate receptor modeling are ill posed problems. There are simply more unknowns than equations and thus there are many wildly different solutions that are all equally good in the least-squares sense. In a statistical way these problems are not identifiable. One approach to ill-posed problems is to impose conditions that add additional equations, which then define more realistic solutions to be closer to unique solution. The non-negativity conditions as additional conditions are imposed by the physical nature of the problem (Henry, 2001). Source composition and contributions must be non-negative but non-negativity conditions alone are not sufficient to give a unique solution. More constraints are needed (Henry, 1987). Under certain, rather mild conditions, the data themselves can provide the needed constrains (Henry 1997). This is how Unmix works.

Based on the multivariate factor analysis and the results in factor profiles and contributions, Paatero and Tapper (Paatero and Tapper, 1993; Paatero and Tapper, 1994; Paatero, 1997) established the advanced factor analysis method - positive matrix factorization (PMF). Several features are incorporated in this model:

- weights data points by their analytical uncertainties,
- constrains factor loadings and factor scores to non-negative values and thereby minimizes the ambiguity caused by rotating the factors,
- uses weighted least-squares fits for data,
- expresses factor loadings in mass units, which allows factors to be used directly as source signatures,
- provides uncertainties for factor loadings and factor scores.

In PMF, the matrix $\boldsymbol{X}$ (n × m) includes measured mass concentrations, and is represented as the sum of the product of $\boldsymbol{G}$ (n × p) and $\boldsymbol{F}$ (p × m) matrices and the residual matrix $\boldsymbol{E}$ (n × m), where **n** is the number of samples, **m** is the number of chemical species, and **p** is the number of independent source types. This model can give a solution that can be displayed in matrix form:

$$X = G \cdot F + E \tag{3}$$

The object function $\boldsymbol{Q}$ that is to be minimized is defined as:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\varepsilon_{ij} / u_{ij}\right)^2 \tag{4}$$

where $\boldsymbol{u_{ij}}$ is the uncertainty of the species $\boldsymbol{j}$ in a sample $\boldsymbol{i}$ and residuals $\boldsymbol{\varepsilon_{ij}}$ i.e. the portion of the measured concentration.

In addition, non-negativity constraints should be fulfilled, meaning that all the elements in $\boldsymbol{G}$ and $\boldsymbol{F}$ are to be non-negative. The main process of the PMF is minimizing the $\boldsymbol{Q}$-value which is defined in the Eq. (4) as the sum of square of the residuals ($\boldsymbol{\varepsilon_{ij}}$) weighted inversely with uncertainty ($\boldsymbol{u_{ij}}$) of the data point (Polissar et al., 1998; Lee and Hopke, 2006).

The solution of Eq. (4) is obtained by iteration until convergence is reached.

Bootstrapping is an advanced analysis that examines the stability of solutions of the tested models. The bootstrap method is essentially based on resampling methods in which "new" data sets that are consistent with the original data are generated. Each "new" data set (which is essentially a subset of the original database), is decomposed into profile and contribution matrices, and the resulting profile and contribution matrices are compared with the base run (Eberly, 2005), giving the distribution for each species to evaluate the stability of the solution.

Numerous studies employing both the PMF and Unmix models have been done in recent years (Pekney et al., 2006; Poirot et al., 2001; Kim et al., 2004; Chen et al., 2007 in: Hegg et al., 2010). Paatero's positive matrix factorization (PMF) approach weights the data by the inverse of the measurement error for each observation. A major advantage of this approach is that the missing data can be included as observations with a large error. However, the minimization of F is still an ill-posed problem, or in other words, the model is not identifiable. Even the inclusion of the non-negative constraints does not provide an identifiable model. Paatero addresses this problem, which he named rotationally indeterminacy, by adding one or more user-selected parameters. Park et al., (2002) have used modern constrained minimization methods on F along with specific conditions, e.g. each source composition must have at least one species absent from that source. Finally, Paatero has generalized F in a natural way to include the estimation of even more unknown parameters associated with spatial variations (Henry, 2002).

Multivariate source apportionment models, Unmix and positive matrix factorization (PMF), often produce nearly the same source apportionment, however some investigations have shown that this is not always the case (Henry and Christensen, 2010). These models do not specify a minimum number of samples, but the stability of their solutions increases with the number of samples (Chen et al., 2007). In this study, we calculated sources composition and sources contributions of elements in PM using real data base.

The main aim of this study is to show that a simple application of the most advanced mathematical models may leads to erroneous conclusions because each of these models can provide a larger number of mathematically correct solutions. Which solutions are really true cannot be known only on the basis of the results obtained by modeling, even using models such as Unmix and PMF. Our goal was to apply these state-of-the-art models, respecting their criteria, on data-base previously submitted to other models; Principal Component Analysis (PCA) and Enrichment Factors (EA) to compare, to be able to finding the most accurate solution relying on Unmix self-modeling and PMF application to adjust and confirm the solutions found by Unmix.

Materials and Methods

The sampling site is situated only 10 meters away from the coast of the Adriatic Sea. Samples of PM were subjected to gravimetric analysis for determination of total mass concentrations and subsequently to elemental analysis for Fe, Mn, Ti, Pb, Cr, Cu, Cd, Co, Ni, Hg and Se. Suspended particles were collected using a high-volume Aerosol Sampler, AQUERO model 400XT sampling system, on boron-silicate fiberglass filters every sixth day as a 24h sample in the period of 1995 - 2000. The sampler was located in the town of Herceg-Novi (Fig. 8) 18^{0}33" N, 42^{0}27", Montenegro (Fig. 1). The meteorological station is part of the MED POL program. The nearest road is located about 100 m north of the meteorological station. There are no significant grassy areas around the meteorological station, and there is no considerable construction work in progress. The terrain surrounding the receptor is rocky with some small areas of soil (Đorđević et al., 2004). Filters were digested with HNO_3 (ultra pure). A Flame Atomic Absorption Spectrometry (F-AAS), Varian AAS–Spectr AA 55 instrument, was used to measure the concentrations of Cd, Co, Cr, Cu, Ni, Pb, Ti, Fe and Mn. The concentrations of Hg and Se were determined by the hydride vapor AAS method (HV-AAS) (Đorđević et al., 2005). The maximum expanded uncertainty of measurements for all elements was about 5%.

The real data set of 11 trace elements in particulate matter (PM) obtained in 252 observations was analyzed by Unmix 6.0 and PMF 3.0. The applied Unmix and PMF models were available on the EPA Internet site (www.epa.gov).

Unmix and PMF used in this study do not limit the number of factors. The following initial operations were subjected to the Unmix model data: *Suggest Exclusion*, *Initial Species*, *Additional Species* including SAFER and Initial Points. PM was chosen for the total and for the normalization. The data was screened using the signal-to-noise ratio (Min S/N ratio) criteria higher than 2, estimated by Unmix. Only the component with S/N value greater than 2 will be used for sources estimation. The agreement between the true and estimated source contribution (Min R^2 greater than 0.8) was considered as well (Henry, 2003, EPA/600/R-07/089).

Applying of PMF model the procedure of Polissar et al. (1998) was used in this study to calculate uncertainties in the species concentrations. Briefly, for the data below detection limit (DL), the concentrations were replaced with the value DL/2 and the uncertainty was set as $\frac{5}{6}DL$. For the missing data, concentrations were replaced by the geometric mean and the respective uncertainty was set at four times of this mean concentration. At the first set up all elements are labeled as Strong, since (the signal/noise ratio) S/N > 2 for all of them. Based on input data statistics, residuals show bimodal distribution in the case of Ni, Mn, and Hg, so their uncertainties are increased labeling them as Weak. Selenium is excluded from the model because of a very small contribution and the correlation factor, while for cadmium more than 50% of samples are below the detection limit. The Q value represents the goodness-of-fit and assesses how the model fits the experimental data. Qtrue is calculated taking into account all data points while Qrobust is calculated accounting for outlier points. Data with scaled residuals above 4 are regarded as outlier points. Evaluation of the validity of a solution is possible by using the G-space scatter plot. Scatter plot of one versus the other factor may indicate the existence of a rotational ambiguity. Namely, if the points on this graph fill the entire solution space evenly then the edges of the Scatter Plot correspond to axes. If this is not a case it is indication that there is rotational ambiguity and should be considered the possible rotation of the solution, using the function Fpeak. The F-peak functions is used to rotate the data set, make fine tuning and improvement of the model in the case of data with high noise (positive values F-peak) or clean data (negative values F-peak). Normally, the default settings give satisfactory results, but in some cases subsequent adjustments are needed. To ensure the robustness of statistics, 300 bootstrap runs were performed, while the default value of the minimum correlation (R-Value) of 0.60 was used.

Results and Discussion

We applied the Unmix and PMF models on dataset from our previous work regarding trace elements in the PM (Đorđević et al., 2005). Fig. 2 shows the comparison of measured and the predicted concentrations of trace elements in PM through time series and Min R^2. Model Unmix did not calculate R^2 values for Cd, Co, Hg and Se and neither satisfactory solution included these elements since these variables contain a large number of missing values and outliers. Min R^2 values are given in table 1.

From statistical parameters displayed for each species, after input data and the following operations: *Suggest exclusion*, *Influential points*, *Initial species*, *Additional species* and *SAFER*, Unmix finds six combinations of species that give any kind of solution (Table 2). Min S/N for each principal component and Min R^2 of all combinations of elements estimated by Unmix was selected as good solutions that are in accordance with the Unmix criteria (Henry, 2003). Thirteen solutions in total were found, but four solutions satisfy the above criteria, signed in bold in Table 2. The standard deviation of variable (sigma) is the criterion for evaluation whether the variable eligible for modeling or not. The sigma-based parameters (Significant/Strong Species in Sources) for each of satisfactory solution are also given in Table 2.

Taking into account the calculated good solutions presented in Table 2, the Edges plots were done for these solutions (Fig. 3). The source profile of the solutions chosen according to the criteria S/N > 2 and R^2 > 2 are given in Fig. 4.

In the first solution (combination of species Mn-Ti-Pb-Cr-Cu, 3 Sources Solution) the second and third source are well defined by many points on the *y*-axis while source 1 has just a few points on the *x*-axis. Pb is strong in the first source and this source can be attributed to traffic. In the second source Cr and Cu are strong and Ti and Mn are significant. This source can be re-suspension of elements previously settled from anthropogenic sources. In the third source neither element is strong or significant.

The second satisfactory solution is for Fe-Mn-Ti-Pb combination of elements it also found 3 sources (Table 2, Fig. 4b) and does not show good accumulation of points on the x and y axes (Fig. 3). This solution has the best values of Min R^2 and Min S/N compared to all combinations. The first and the third source contain Pb which is a tracer for traffic. In the third source Pb is strong, and it is reasonable to associate this source with traffic, while the first source could be local re-suspension. The second source in this combination could be a long range transport of Saharan dust since it contains crustal elements.

The third solution (combination of species Fe-Mn-Ti-Pb-Cr-Cu-Ni, 4 Sources Solution) shows the edges on the *y*-axis defined by many points for the third and the fourth source, but the *x*-axis has just a few points (Fig. 3).

In the fourth solution (combination of species Fe-Mn-Ti-Pb-Cr-Cu, 3 Sources Solution) good accumulation of points are on the y-axis, for sources 2 and 3 while the *x*-axis has just a few points for source 1 (Fig. 3).

In the third and the fourth solution, the sources where Pb is strong can be attributed to traffic; namely, source 3 for Fe-Mn-Ti-Pb-Cr-Cu-Ni combination (Table 2, Fig. 4c) and source 1 for Fe-Mn-Ti-Pb-Cr-Cu combination (Table 2, Fig. 4d). Another source in which Pb is present as significant but not strong could be re-suspension. Source 4 for Fe-Mn-Ti-Pb-Cr-Cu-Ni combination and source 2 for Fe-Mn-Ti-Pb-Cr-Cu combination could be attributed to re-suspennsion, probably from various locations depending on wind directions. Factors containing Cr and Ni indicate the existence of an anthropogenic emission source in the region (Đorđević et al., 2005).

In our previous work (Đorđević et al., 2005) we applied the PCA method on this data set and 4 significant groups of sources contributions were found. The following contribution sources were identified: re-suspension combined with re-suspended Saharan dust that had previously settled (Fe, Mn, Ti) and settled combustion products mostly from traffic, and probably some local stationary source (Cu, Pb). The remaining three factors represent the following combinations F2 by Cr and Ni, F3 by Cd and Se and F4 by Hg and Co.

The EF model revealed that in the region of the investigated receptor, the main contribution source of Fe, Mn and Ti is the process of local re-suspension and that local re-suspension has no influence on the content of Se in the atmospheric aerosol. The re-suspension is the dominant emission source of Cd from the south-southeast direction from the nearby peninsula (Luštica) but this source is not permanent (Đorđević et al., 2005).

The application of positive matrix factorization (PMF) to solve the number and profile of the sources applied to the same database resulted in obtaining possible solutions for 3, 4 and 5 sources. For 6 or more sources the model does not find the convergence of the functions Q, which implies that the model did not find any minima. Varying simulation conditions did not contribute to significant improvement, even when the uncertainty is significantly increased. Therefore possible solution should be sought among three possible cases.

Table 3 shows the categories of elements and the R^2 values for each of the three possible solutions.

Each of the possible solutions obtained by PMF analysis will be considered. Fig. 5 shows *F* peak strengths for 3 sources solution (Fig. 5a), 4 sources solution (Fig. 5b) and 5 sources solution (Fig. 5c).

3 Sources Solution: The relatively good correlation was obtained only for Cr and Pb, while bimodal distribution is still present in the case of Co, Ti and Fe. Also, significant outliers are present in the model. In addition, G-Space plots show considerable rotational ambiguity between the sources 1 and 3.

Rotational ambiguity, which was found between the sources 1 and 3, decreases when the value of Strength factor reaches -1.2 (Fig. 5a). This is mostly reflected in the increase of Ti concentration in the source 2. However, such large values for Fpeak is unlikely because the quality of the fit decreases rapidly. The usually dataset rotations are generally much smaller and they are close to the basic solution.

However, a small degree of correlation between the model and database indicates that the model with three sources is insufficient to adequately describe a number of sources.

In this case, only Co, Ni and Fe show relatively good interquartile range of about 20%, while other species show considerable variation and therefore represent a less stable solution. This is especially pronounced in the case of Hg, Cr and Mn. Also, in some cases (Hg, Ti) base run values are not within the interquartile range in the bootstrapping of results. This is probably a consequence of assuming the model with only three sources. Profiles of sources are given in Fig. 6.

4 Sources Solution: The model with four sources shows a significantly better correlation with measured concentrations of elements. Although the agreement of time series for Ti and Cr is excellent ($R^2 > 0.95$), and for Pb satisfactory ($R^2 = 0.70$), in the case of other elements there are still episodes with very high concentrations that this model cannot fit. It should be noted that Cu shows very good agreement between the predicted and observed concentrations, but the existence of outliers have reduced the correlation to 0.34. A small degree of correlation in the case of Co is the result of a significant number of measurements below the detection limit.

Bimodal distribution is still present in the case of Ni and Hg. G-Space plot shows that there is a rotational ambiguity between sources 1 - 3 2 - 3, 3 – 4.

For a model with four sources, rotational ambiguity disappears when the F-Peak strength reaches -0.8 (Fig. 5b). This rotation is mostly reflected in the increase of Ti content in source 1, and largely in sources 2 and 3. On the other hand, this may just mean that the content of titanium in this solution is divided among several sources. As in the case of a solution with three sources, a significant rotation of the dataset (Fpeak = -0.8) is less likely. It is necessary to consider these results carefully and determine whether there is justification for it to be included in further solving of the composition of the sources.

Interquartile range of solutions obtained by bootstraping in the case of Fe, Pb, Cu and Cr are about 20%, while in the case of other species this range is much higher indicating the instability of the solution. Base run values which are not within the interquartile range in the bootstrapping of the results are, in the case of Cu, Mn, Pb and especially Hg, calculated by the model only in the fourth source.

5 Sources Solution: The model and data from the database show agreement (R^2) over 90% for Cr, Ti, Fe and Pb, while just over 50% for Mn. The model also fits Cu real data very well, and the correlation of 0.47 is caused by significant outliers that are related to individual episodes of Cu emissions. In spite of the increased uncertainty Mn, Ni, Co and Hg show a lack of fit.

G-Space plot only shows some rotational ambiguity in the case of sources: 2 – 5, 3 – 5 and 4 – 5. The F-Peak in the range -2 to 2 (Fig. 5c) showed the most impact on the sources of Cu, especially at higher strength values, while the ambiguity between the sources mentioned above still exist. The Peak F-curve is generally symmetrical in the examined interval.

In the case of five sources there are also unmapped results, suggesting a reduced stability of the solution. In general, the most stable solutions are obtained for those elements that are present in the source with the highest percentage. In these cases, the distribution of solutions obtained by bootstrapping lie in the range of 15% of the concentration calculated in the base run. This is the case for Fe, Pb, Ti. A slightly worse result of the bootstrap analysis is obtained for Cu, Mn, Cr, Co and Ni (bootstrapping distribution of solutions equal or higher than 20%). The least stable solution is for Hg with considerable dispersion in the bootstrap analysis solutions.

When discussing the number and origin of pollution sources, it is preferred to take into account the real situation on the field. In this case the following sources that contribute to the overall PM deposition can clearly be predicted: marine aerosols, traffic, re-suspension from the ground, probably some local stationary source, as a shipyard located in the vicinity. Based on these obvious sources, PMF analysis solution with only three sources is exempt from further consideration.

In the case of PMF solution of five sources it may be noted that source No. 5 (Fig. 8), in which Co, Cu, Ni and Mn are present, can be described rather as a splitting factor than as a separate source. The most realistic solution that is imposed upon a detailed analysis is the solution with four sources (Fig.7).

Identification of sources was carried out and it agrees with the results of the Enrichment Factors analysis well (Đorđević et al., 2005). The F-peak profiles shown in Fig. 7 in rotation of data set for -0.8, increase the contents of Ti, in the case of sources 2 and 4.

Source 1 has been identified as re-suspension in combination with the long-range transport of Saharan dust. The prevailing wind directions are over open sea (Đorđević et al., 2005).

Source 2 is attributed to the re-suspension, indicated in our previous work. Titanium found by F-peak is in better accordance with the EF analysis (Đorđević et al., 2005).

Source 3 corresponds to the composition of the particles that come from some anthropogenic source.

Source 4 with the highest content of Pb, is characteristic for urban traffic. F-peak is increasing the value for Ti which is in better agreement with the traffic profile.

Conclusion

In this work we applied state-of-the-art mathematical models Unmix and PMF on database previously modeled using more simple models (PCA and EF) to be compared. In this study we have shown that only application Unmix and PMF for sources apportionment is not guarantee to obtain the unique realistic solution. Thirteen solutions in total were found, but four solutions satisfy the Unmix criteria: three solutions with three sources and one with four sources. In terms of modeling all four solutions found by Unmix are satisfactory. PMF model has given three possible solutions: one with three sources, one with four sources and one with five sources. By further analysis of the results of PMF model the best solution with four sources was selected. F-peak refinement was enabled to find a more realistic solution. Also we have shown that due to their limitations Unmix and PMF were unable to calculate Cd and Se in used database, due to large number of missing values. For example, although the presence of cadmium in terms of concentration is negligible and there are many missing values the knowledge of emission sources is very important regarding its harmfulness. The simple model of EF applied could help to solve similar problem. For obtaining the best results using Unmix and PMF models our recommendation is to start modeling by Unmix relying on its self-modeling to estimate all possible types of sources and then apply PMF for confirmation. For the species that are important and that cannot be modeled by advanced models like Unmix and PMF should be apply other, even, the simple model.

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Tables

Table 1. R^2 values obtained by Unmix of measured and the predicted concentrations of PM and trace elements in PM

	PM	Fe	Mn	Ti	Pb	Cr	Cu	Ni
R^2	0.46	0.75	0.92	0.66	0.83	0.40	0.99	0.00

Table 2. All combination of elements for solutions obtained by calculation by Unmix

Combination of species	Number of sources	Min R^2	Min S/N	Significant/Strong Species in Sources (sigma-based)
Mn-Ti-Pb-Cr-Cu	**3**	**0.84**	**2.49**	Source 1: *Strong – Pb; Source 2: *Strong - Cr, Cu, **Significant - Ti, Mn; Source 3: *Strong – None, **Significant - None
	4	0.89	1.94	
	5	0.90	1.59	
Cr-Cu-Pb-Ti-Mn-Se-Cd-Co-Fe	3	0.68	2.41	
	4	0.76	2.13	
Cu-Ti-Fe-Mn-Pb-Cr-Hg-Se	2	0.56	2.29	
Fe-Mn-Ti-Pb	**3**	**0.90**	**2.85**	Source 1: *Strong – None, **Significant - PM, Pb, Fe Source 2: *Strong – None **Significant - PM, Fe, Mn; Source 3: *Strong - Pb, Mn, **Significant - Ti, Fe
Fe-Mn-Ti-Pb-Cr-Cu-Ni	3	0.76	2.20	
	4	**0.83**	**2.18**	Source 1: *Strong - Cr, Ni, **Significant – None Source 2: *Strong – None, **Significant – Cu; Source 3: *Strong – Pb, **Significant - PM, Cr, Cu, Ti, Fe, Mn; Source 4: *Strong – Ti, **Significant - PM, Cr, Pb, Fe
	5	0.89	1.67	
Fe-Mn-Ti-Pb-Cr-Cu	**3**	**0.83**	**2.57**	Source 1: *Strong - Pb, **Significant – Cu; Source 2: *Strong – None, **Significant - PM, Cr, Pb, Ti, Fe; Source 3: *Strong – None, **Significant - PM, Cr, Cu, Ti, Fe, Mn
	4	0.88	1.97	
	5	0.90	1.62	

* Source Composition ≥ 1 sigma
**Source Composition ≥ 2 sigma

Table 3. R^2 values obtained by PMF of measured and the predicted concentrations

Species	Category	R^2		
		3 sources	4 sources	5 sources
Cr	Strong	0.617	0.980	0.998
Ti	Strong	0.381	0.962	0.959
Fe	Strong	0.401	0.472	0.942
Pb	Strong	0.695	0.701	0.905
Mn	Weak	0.394	0.340	0.528
Cu	Strong	0.345	0.337	0.473
Ni	Weak	0.027	0.031	0.025
Co	Weak	0.006	0.013	0.018
Hg	Weak	0.002	0.005	0.003

Figure Legends

Fig.1 Sampling site and prevailing wind directions

Fig. 2 Predicted and measured concentrations

Fig. 3 Edge plots for chosen solutions that satisfy the conditions of Min S/N and Min R^2

Fig. 4 Source profiles for selected solutions that are in accordance with the Unmix criteria

Fig. 5 F-peak analysis for three a), four b) and five c) source solutions. The red mark represents the value of F-peak Strength, at which the rotational ambiguity disappears.

Fig. 6 Profiles in the case of three sources solutions. Comparison of base run profile and F-peak run profile with the strength of -1.2 (disappearance of rotational ambiguity).

Fig. 7 Profiles in the case of three sources solutions. Comparison of base run profile and F-peak run profile with the strength of -0.8 (disappearance of rotational ambiguity).

Fig. 8 Profiles in the case of three sources solutions. Comparison of base run profile and F-peak run profile with the strength of -2.0 where it can be seen that F-peak Strength does not affect the existing rotational ambiguity.

C2023 Interactive comment on Atmos. Meas. Tech. Discuss., 6, 4941, 2013.

Answers to the **Reviewers 1 comments**

General Comments: In the present manuscript, Dordevic et al. apply two advanced popular receptor modelling techniques(Unmix and PMF) to a dataset of concentrations of 11 trace metals in PM samples obtained from a coastal site close to the Adriatic Sea. The dataset of metal concentrations is re-used from an earlier study (Dordevic et al., 2005), where two other receptor models have been applied to the data. My major problem with the manuscript is that I do not understand what it is actually aiming at:

- Is it aiming at a better understanding of the sources of trace elements at the receptor site, as the manuscript title would suggest? The major part of the discussion section actually reads like a source apportionment study attributing the different solutions of the models to physical PM/metal sources. However, as the authors indicate several times in the manuscript, all the conclusions regarding the different possible metal sources agree with the results from the previous Dordevic et al., 2005, study. And I have to agree: I do not see any scientific progress in the present data analysis beyond what has already been understood/proposed in the previous study (on exactly the same dataset). In addition, if the goal really was a refined or more detailed source apportionment then AMTD might not be the most suitable journal choice.

We corrected the Manuscript according to reviewers complying. We rewritten the Abstract, Conclusion and we more precisely rewritten the goal and discussion of the Manuscript. In yellow we highlighted our changes.

- Or is the main goal of the manuscript an evaluation of the (more complex) Unmix and PMF models as compared to the (more simple) approaches of the previous study, as is stated in P4948L15-19? Such evaluation would certainly fit better into the journal scopes, but I do not see which part of the manuscript would really critically evaluate the models. To me, the whole study seems to be a sheer application of two (further) re-ceptor models to an existing (and published) dataset, which does not represent enough scientific significance to justify publication in AMT.

The Manuscript's title has changed.

It is known that simple modeling even by state-of-the-art mathematical models is not enough to get satisfactory real solution. Our intention were not to only calculate different possible sources of metals in the PM but to use two state-of-the-art models (Unmix and PMF) on data set which already modeled in order to show how many solutions could be find and how many errors could be made as well as adjust these advanced models to find the most realistic solution. These solutions we compared with our previously work.

We made an effort to adjust our manuscript according to this goal.

If at all, the manuscript can only be considered for publication in AMT after major revisions, which would actually include a complete rewrite of several manuscript sections (abstract, discussion, conclusions).

We have rewritten the abstract, discussion and conclusions.

Specific comments: P4942L2-13: The abstract is poorly written. **The Abstract has rewritten**. It lacks important details on the dataset (location of the sampling site, time of sampling, size of dataset, etc. **It Is corrected in Abstract and Materials and Methods**), it only lists the number of possible solutions of the models without really relating them to each other or concluding on their quality, it does not give the physical meanings for all of the mathematically suggested sources, and is in part even contradictory: "traffic is not a significant anthropogenic source at the sampling site" (L5) vs. "...more realistic solution that includes ... traffic as dominant source contribution" (L11-12).

The contradictory part in the Abstract is corrected.

P4942L17 and L24: I am sceptical, whether these references are really suitable to support the rather general statements/explanations in these two sentences. Be sure to avoid referencing secondary sources.

It is corrected. P4942L15 to L24 removed. References: *Lee, D., Balachandran, S., Pachon, J., Shankaran, R., Lee, S., Mulholland, J. A., and Russell, A. G., 2009. Ensemble-Trained PM2.5 Source Apportionment Approach for Health Studies, Environ. Sci. Technol., 43, 7023-7031* **and** *Lee, J. H., Lim, J. M., Kim, K. H., Chung, Y.S., and Lee, K.Y.,2003. Trace element levels of aerosols at an urban area of Korea by instrumental neutron activation analysis, J. Radioanal. Nucl. Ch., 256, 553–560* **was excluded.**

P4942L15-P4947L19: In the introduction, the Unmix and PMF models are described in much detail. The authors might want to check whether such level of detail is really necessary to understand the results and discussion sections of the manuscript (which actually depends on what the latter sections are aiming at).

P4945L7 to L9 removed
P4946L6 to L10 removed
P4946L13 to L21 removed
P4947L3 to L14 removed

P4945L16-P4946L2: This section would be more appropriately placed in the experimental section

It is moved in experimental section

P4947L4-14: This section seems a bit out of place here.

It is excluded from the Manuscript

P4947L15-19: The main goal of the study has to be more clearly defined (see above).

It is corrected

P4947L20-P4948L17: The Materials and methods section is poorly written. It contains paragraphs which have to be moved to other sections (e.g. the first 7 lines are rather introductory than experimental – **It is corrected**), the information on sampling and analysis is incomplete (I miss details on the time of sampling (in which months/years?- **It is corrected**), the country the site belongs to (Google maps did help here but it might be worth to mention Montenegro in the manuscript **- It is corrected**), and data on the manufacturers of the applied instruments and materials **– in P4948L4 to L6** and **P4948L12 to L17 have given**), and – most importantly – it does not give the experimental details of the two models applied. These are actually spread among the introduction (see above) and results sections, but they should be brought together here in this section **- It is corrected**.

P4948L19-27: These are experimental details, not results

It is moved to Material and Methods part

P4949L3: Why is R2 not available for these elements?

Model Unmix did not calculate R^2 values for Cd, Co, Hg and Se since these variables contain a large number of missing values and outliers. It is corrected in the manuscript.

P4949L12-13: How do the authors distinguish between a "strong" and a "significant" species and what does it actually mean?

Distinguish between a "strong" and a "significant" species have done according to criteria Source Composition > 1*sigma for Strong species and Source Composition > 2*sigma for Significant species. The criterion for evaluation whether the variable eligible for modeling or not is standard deviation of variable (sigma) that Unmix model is calculating among the first criteria for involving the variables in the further calculation.

It is corrected in the Manuscript

P4949L14-15: The authors might want to explain the benefits of "edge plots" in the introduction or experimental section.

It is added in the Introduction

P4950L2-22: Not results, move to experimental and/or introduction

It is moved to Introduction

P4951L3-7: I do not understand this paragraph. Please give more explanations.

It is excluded from the Manuscript

P4951L15: Please explain G-Space plots in introduction/experimental

It is added in the Material and Methods part

Evaluation of the validity of a solution is possible by using the G-space scatter plot. Scatter plot of one versus the other factor may indicate the existence of a rotational ambiguity. Namely, if the points on this graph fill the entire solution space evenly then the edges of the Scatter Plot correspond to axes. If this is not a case it is indication that there is rotational ambiguity and should be considered the possible rotation of the solution, using the function F-peak.

P4951L24 and elsewhere: In my understanding of descriptive statistics, the interquartile range (IQR) is always the 25% trimmed mid-range of a data distribution, i.e. rep-resenting 50% of the data points. How can it be 20% only and why would that be a “relatively good IQR”?

It is corrected.

Interquartile range of solutions obtained by bootstraping in the case of Fe, Pb, Cu and Cr are about 20%, while in the case of other species this range is much higher indicating the instability of the solution.
In these cases, the distribution of solutions obtained by bootstrapping lie in the range of 15% of the concentration calculated in the base run.
(**bootstrapping distribution of solutions equal or higher than 20%)**

P4953L14-4955L24: As stated above, the discussion section does not fit into the scopes of AMT as it is focused too much on the source apportionment aspect of the study and hardly at all on the evaluation of the models.

Now is Results and discussion section. Part P4953L14 to P4954L28 has moved behind results of Unmix in the section Results and discussion to make is easier to follow and to better see why it is important to compare with previously work. The discussion is shortened to necessary level.
P4951L4 to L7 have excluded.

P4955L25-P4956L7: The conclusions are not conclusive. What are the main findings of the study? And why is it important for them to be published?

It is corrected

Figures and Tables: - Fig. 1 is not readable. Way too small font size. –

The Fig. 1 in the corrected Manuscript is Fig 2. This figure is original results from the Unmix model and this is reason of pure quality. We made an effort to improve as much as possible the quality.

Figure Numbering does not correspond to the appearance of the figures in the manuscript (e.g. Fig. 8 is the first one mentioned in the text).

We corrected the numbering of the figures. The Fig. 8 now is Fig. 1. In the text of the corrected Manuscript in the red color is the number of figures.