Full length article

Aerosol source apportionment uncertainty linked to the choice of input chemical components

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ABSTRACT

For a Positive Matrix Factorization (PMF) aerosol source apportionment (SA) studies there is no standard procedure to select the most appropriate chemical components to be included in the input dataset for a given site typology, nor specific recommendations in this direction. However, these choices are crucial for the final SA outputs not only in terms of number of sources identified but also, and consequently, in the source contributions estimates. In fact, PMF tends to reproduce most of PM mass measured independently and introduced as a total variable in the input data, regardless of the percentage of PM mass which has been chemically characterized, so that the lack of some specific source tracers (e.g. levoglucosan) can potentially affect the results of the whole source apportionment study. The present study elaborates further on the same concept, evaluating quantitatively the impact of lacking specific sources' tracers on the whole source apportionment, both in terms of identified sources and source contributions. This work aims to provide first recommendations on the most suitable and critical components to be included in PMF analyses in order to reduce PMF output uncertainty as much as possible, and better represent the most commons PM sources observed in many sites in Western countries. To this aim, we performed three sensitivity analyses on three different datasets across EU, including extended sets of organic tracers, in order to cover different types of urban conditions (Mediterranean, Continental, and Alpine), source types, and PM fractions. Our findings reveal that the vehicle exhaust source resulted to be less sensitive to the choice of analytes, although source contributions estimates can deviate significantly up to 44 %. On the other hand, for the detection of the non-exhaust one is clearly necessary to analyze specific inorganic elements. The choice of not analysing non-polar organics likely causes the loss of separation of exhaust and non-exhaust factors, thus obtaining a unique road traffic source, which provokes a significant bias of total contribution. Levoglucosan was, in most cases, crucial to identify biomass burning contributions in Milan and in Barcelona, in spite of the presence of PAHs in Barcelona, while for the case of Grenoble, even discarding levoglucosan, the presence of PAHs allowed identifying the BB factor. Modifying the rest of analytes provoke a systematic underestimation of biomass burning source contributions. SIA factors resulted to be generally overestimated with respect to the base case analysis, also in the case that ions were not included in the PMF analysis. Trace elements were crucial to identify shipping emissions (V and Ni) and industrial sources (Pb, Ni, Br, Zn, Mn, Cd and As). When changing the rest of input variables, the uncertainty was narrow for shipping but large for industrial processes. Major and trace elements were also crucial to identify the mineral/soil factor at all cities. Biogenic SOA and Anthropogenic SOA factors were sensitive to the presence of their molecular tracers, since the availability of OC alone is unable to separate a SOA factor. Arabitol and sorbitol were crucial to detecting fungal spores while odd number of higher alkanes (C27 to C31) for plant debris.

1. Introduction

Source apportionment (SA) is a common modelling exercise aimed at identifying sources of pollutants, both for VOC and particulate matter (PM), and estimate their contributions to concentration levels in ambient air. When achieved through the analysis of PM chemical and/or physical properties measured at specific sampling sites, such an exercise is known as receptor model (RM). Among the diverse RM techniques, Positive Matrix Factorization (PMF) is the most widely used model. It is based on the time-series concentrations (and their uncertainties) of multiple PM components to identify the main factors/sources responsible for their variations. Given that the different factors/sources are identified by means of their chemical profiles, it is of crucial importance that a proper choice of chemical analyses is performed prior to the PMF analysis. A large body of literature aimed, during the last decades, to identify the most appropriate tracers for the specific sources potentially important at the site of the study, considering its typology. For example, the inorganic elements Cu, Sb, Sn, Ba, Fe, among others, have been linked to brake wear emissions, Zn to tyre wear emissions, Pb, Mn, Zn and Cd to metallurgy, or V and Ni to shipping emissions (or more generally heavy fuel oil combustion). For the organic fraction, PAHs are associated mostly to primary combustion products, alkanes to plant debris, levoglucosan and isomers to biomass combustion, and many other organic molecular markers for biogenic and secondary aerosols.

The choice of chemical analyses of PM samples depends on many different factors beside their suitability as tracers, such as available laboratory instrumentation and standards, budget limitation, or sample mass limitation. In addition, there is no standard procedure to select the most appropriate chemical components to be included in a PMF study for a given site typology, nor specific recommendations in this direction. However, these choices are crucial for the final SA outputs not only in terms of number of sources identified but also, and consequently, in the source contributions estimates. In fact, PMF tends to reproduce most of PM mass measured independently and introduced as a total variable in the input data, regardless of the percentage of PM mass which has been chemically characterized, so that the lack of some specific source tracers (e.g. levoglucosan) can potentially affect the results of the whole source apportionment study. Sensitivity tests on this topic of the influence of the input data on the final results are limited in the literature (Belis et al., 2020; Borlaza et al., 2021). An example is that of a study by Cesari et al. (2016), with a few tests of comparison on complete datasets (using the full range of available chemical species) and incomplete datasets (with reduced number of chemical species) for SA studies on 3 sites in Europe. This study shows that the profiles and the contributions of the different sources calculated with PMF were comparable within the estimated uncertainties, indicating a good stability and robustness of PMF results. However, it was performed only on inorganic PM speciation datasets, and the choice of excluded components was aleatory.

The present study elaborates further on the same concept, evaluating quantitatively the impact of lacking specific sources' tracers on the whole source apportionment, both in terms of identified sources and source contributions. This work aims to provide first recommendations on the most suitable and critical components to be included in PMF analyses in order to reduce PMF output uncertainty as much as possible, and better represent the most commons PM sources observed in many sites in Western countries. To this aim, we performed three sensitivity analyses on three different datasets across EU, including extended sets of organic tracers, in order to cover different types of urban conditions (Mediterranean, Continental, and Alpine), source types, and PM fractions.

2. Methodology

In the framework of the RI-URBANS (Research Infrastructures Services Reinforcing Air Quality Monitoring Capacities in European Urban & Industrial AreaS) project (H2020-GD, 101036245) we compiled existing European PM speciation datasets at urban background locations and selected 3 of them for the purpose of this study (Table 1). The main selection criteria were: i) at least 1 year of measurements; ii) at least 120 samples; iii) presence of both organic and inorganic components. The three data sets were from:

- Barcelona (Spain), including an urban background air quality station (Palau Reial, 41°23′14.5″N 2°06′55.6″E; 68 m a.s.l.) and a traffic site (Eixample). The city of Barcelona lies along the western coast of the Mediterranean Basin, and it is delimited by two river basins (Besòs in the North and Llobregat in the South) and a forest mountain range in the West. The city is densely populated (15.880 inhabitants/km^2) counting 1.6 million inhabitants which doubles when the whole metropolitan area is considered (36 municipalities). The city suffers poor air quality in terms of particulate matter and NO$_2$, mostly due to road traffic emissions, although other significant contributions to PM levels are originated from industries, harbour and urban works (Amato et al., 2016). No significant impact of residential heating has been historically observed. The urban background sampling site is located in the University Campus area, 250 m away from one of the main roads in the city, while the traffic site is located on a busy road uphill with an average traffic volume of 80,000 vehicles/day. PM10 and PM1 samples were collected on quartz filters during 3 different campaigns in September-October 2010, July-December 2019 and April-May 2021, collecting a total of 440 samples. Merging samples obtained in distant periods in the PMF analysis may produce bias due to the possible variation in chemical profile of PM sources. However, based on a sensitivity analysis we observed no significant change in chemical profile with and without 2010 samples. In addition, given that the 2010 campaign consisted of > 100 samples separated between day and night we decided to include them in the analysis as it is known that samples with high contrast of source contributions improve significantly the PMF results (Norris et al., 2014). A fraction of each filter was acid digested (5 mL HF, 2.5 mL HNO$_3$, 2.5 mL HClO$_4$) for the determination of major and trace elements (Querol et al., 2001) (Table 1); another fraction was leached for the determination of water-soluble ions by ionic chromatography (IC), using 20 mL of MilliQ water (with an ultrasonic bath for 30 min); another fraction was used for determination of organic carbon (OC) and elemental carbon (EC) by thermal–optical analysis with the EUSAAR2 temperature program (Cavalli et al., 2010) by means of Sunset analysers. Organic components, namely, polycyclic aromatic hydrocarbons (PAHs), sugars, anhydro-sugars, hopanes, acids, and polyols were analysed by means of GC–MS (Alier et al., 2013; Fontal et al., 2015).

- Grenoble (France), urban background air quality station (Les Frênes, 45°09′41″ N, 5°44′07″ E). The city, surrounded by three mountain ranges, is considered the most densely populated area (160,000 inhabitants) of the French Alps. In addition to the urbanized area, forests, including both deciduous and coniferous species, and agriculture areas (pastures) dominate the land cover around Grenoble. This region experiences frequent severe PM pollution events in the winter due to the formation of thermal inversion layers that may promote pollutant accumulation (Bessagnet et al., 2020; Tomaz et al., 2016). Previous PMF studies have shown that residential heating, mainly biomass burning, accounts for a major fraction of PM in the winter, but that many other sources are also important for the composition of PM (Favez et al., 2010; Srivastava et al., 2018; Weber et al., 2019; Borlaza et al., 2021). Traffic and industrial activities contribute significantly to the observed PM concentration levels in Grenoble (Polo Rehn et al., 2014), and primary and secondary biogenic organic aerosol are also largely present in the PM10 (Samake et al., 2019). The current study focuses on the PM10 samples (Tissu-quartz, Pallflex, Ø = 150 mm) collected every three days for one year (2013) using high volume samplers (DA-80, Digitel; sampling duration of 24 h at 30 m^{3}h^{-1}). Overall, approximately 194

Table 1
Description of the input data used for three PMF base solutions, and classification into strong and weak variables based on S/N ratio.

			Stations	Strong components	Weak components	Seed	Number of runs	Additional uncertainty
Barcelona (Spain)	PM10, PM1	2010, 2019, 2021	Urban background Traffic	PM, Al, Ca, Fe, K, Mg, Na, S, Li, Mn, Ti, V, Cr Co, Ni, Cu, Zn, As, Rb, Sr, Zr, Cd, Sn, Sb, La, Pb, Ba, OC, EC, NO$_3^-$, Cl, NH$_4^+$, succinic acid, glutaric acid, phthalic acid, *cis*-pinonic acid, malic acid, 3-hydrox-yglutaric acid, methylbutanetricarboxylic acid (MBTCA), 2-methylglyceric acid, galactosan, mannosan, levoglucosan, benzanthracene, chrysene,benz (b + j + k)fluoranthene,benzo(e) pyrene,benzo(a) pyrene, benzo[ghi]perylene,	azelaic acid, 2-methylthreitol, 2-methylerythritol,17a (H)21β(H) -29-norhopane,17a(H) 21β(H) -hopane	23	10	10
Milan (Italy)	PM10	2017–2019	Urban background	Al, Si, Cl, K, Ca, Ti, Fe, Cu, Zn, Pb, OC, EC, NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, Levoglucosan	Mn, Ni, Br, PM10	38	20	10
Grenoble (France)	PM10	2013	Urban background	OC, EC, HULIS, Na$^+$, NH$_4^+$, Mg^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Levoglucosan, Arabitol, Sorbitol, Benzo[a]pyrene, Benzo[g,h,i]perylene, In. [1,2,3-cd]pyrene, Coronene, Acenaphthenequinone , 6H-Dibenzo [b,d] Pyran-6-one 1,8-Naphthalic anhydride, 1-Nitropyrene, Ba, Cu, Pb, Sb, Ti, Zn, Cr, V, Al, Ca, Fe, C27, C29, C31, C33, HP6, HP7, Coniferylaldehyde, Vanillic acid, Alpha-methyl glyceric acid, DHOPA, 3-Hydroxyglutaric Acid, Phthalic Acid, 2-Methyl erythritol	PM10, HP5, HP8	55	20	5

species were quantified in each sample. EC/OC was measured using a Sunset lab analyzer using the EUSAAR-2 thermal protocol (Cavalli et al., 2010). HuLiS were analysed following the protocol described by Baduel et al. (2010). Anions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$), cations (NH$_4^+$, Ca^{2+}, Na$^+$, Mg^{2+}, K$^+$), methanesulfonic acid (MSA) and oxalate (C$_2$O$_4^{2-}$) were analysed by ionic chromatography (Jaffrezo et al., 2005). Thirty-four metals and trace elements were quantified by ICP-MS (Alleman et al. 2010). Trace elements were analysed after mineralization, using 5 mL of HNO$_3$ (70 %) and 1.25 mL of H$_2$O$_2$ during 30 min at 180 °C in a microwave oven (microwave MARS 6, CEM). The elemental analysis (Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, K, La, Li, Mg, Mn, Mo, Ni, Pb, Pd, Pt, Rb, Sb, Se, Sn, Sr, Ti, Tl, V, Zn, Zr) was performed on this extract using inductively coupled plasma mass spectroscopy (ICP-MS) (ELAN 6100 DRC II PerkinElmer or NEXION PerkinElmer). Cellulose combustion markers (biomass burning) (levoglucosan, mannosan and galactosan), 3 polyols (ara-bitol, sorbitol and mannitol) and glucose were quantified using HPLC-PAD (Piot et al. 2012). Twenty-one PAHs, 27 oxy-PAHs, and 32 nitro-PAHs were quantified using UPLC/UV-Fluorescence and GC/NICID (Srivastava et al., 2018; Albinet et al., 2006; Albinet et al., 2014; Albinet et al., 2013; Tomaz et al., 2016). Twenty-seven higher alkanes (C13–C39), 10 hopanes, pristane, phytane, 5 sulfur con-taining PAHs, 5 lignin combustion markers (vanillin, co-iferaldehyde …) (Golly et al., 2015) and 11 compounds usually recognized as SOA markers (α-methylglyceric acid, pinic acid, methyl-nitrocatechols…) (Nozière et al., 2015) were analysed by GC/ EI-MS. Note that the quantification of all SOA markers was performed using authentic standards (Albinet et al., 2019).

- Milan (Italy), urban background air quality station (Pascal, 45○28044 N, 9○14007 E). Milan, and the Po Valley in general, ex-periences one of the worst air quality across Europe, due to high anthropogenic emission of primary PM but also of gaseous precursors (mostly NH$_3$) from the agricultural sector, provoking high formation of secondary aerosols. The station is part of the ARPA Lombardia Air Quality Network, and it is one of the Italian supersites. It is located on the eastern side of Milan, the University area called Città Studi, in a playground about 130 m from the road traffic. PM10 and PM2.5

samples were collected during 2017–2019 on Teflon (Pall), mixed cellulose ester (MCE, Advantec) and quartz microfibre (Pall) filters (47 mm diameter), with low-volume US-EPA reference method samplers (TECORA). Metals, EC/OC, ions and anhydro-sugars were analysed by X-ray fluorescence (XRF), thermo-optical analysis and ionic chromatography respectively (Amato et al., 2016).

Positive Matrix Factorization (PMF) is the most common receptor model used for SA and it is based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{jk} + e_{ij} \quad i = 1, 2, \cdots, m \quad j = 1, 2 \cdots . n \tag{1}$$

where x_{ij} is the concentration of the species j in the ith sample, g_{ik} is the contribution of the kth source in the ith sample, f_{jk} is the concentration of the species j in source k and e_{ij} is the residual concentration. PMF can be solved with the Multilinear Engine (ME-2) developed by Paatero (1999) and implemented in version 5 of the US EPA PMF. In this study, the US EPA PMF v5 was applied to the three datasets independently. For each dataset, a different method was used for calculating measurement uncertainties, given that the laboratories were different. For Barcelona and Milan, we used the method published by Amato et al. (2009) and for Grenoble the method published by Srivastava et al. (2018). In the case of Barcelona, all the samples were merged into a unique input matrix, combining PM10 and PM1, urban background and traffic sites. The se-lection of PM components to be used as input for PMF was based on several criteria:

i) The S/N ratio (Paatero and Hopke, 2003)
ii) The percentage of data above the detection limit (Amato et al., 2009)
iii) Additionally, we discarded several components in order to meet a maximum number of chemical species equal of 1/3 of that of samples, as suggested by the US EPA PMF manual.

The list of strong and weak variables (determined with the S/N ratio) used for each dataset is shown in Table 1, together with the additional input parameters (seed number, number of runs and the additional

Table 2
The different PMF solutions in Grenoble varying the number of families of components.

Grenoble	Characterized mass (%)	Reconstructed mass (%)	# of factors	Type of factors (average % of contribution)
Base solution	67	93	9	Mineral (17 %)Sea salt (4 %)Primary Traffic (9 %)Anthropogenic SOA (3 %)Biogenic SOA (13 %)Plant debris (11 %)Fungal spores (4 %)SIA (17 %)Biomass burning (18 %)
Excluding EC/OC	37	93	9	Mineral (16 %)Sea salt (4 %)Primary Traffic (8 %)Anthropogenic SOA (2 %)Biogenic SOA (13 %)Plant debris (10 %)Fungal spores (5 %)SIA (15 %)Biomass burning (19 %)
Excluding ions	41	90	7	Mineral (19 %)Primary Traffic (10 %)Anthropogenic SOA (5 %)Biogenic SOA (14 %)Plant Debris (12 %)Fungal spores (4 %)Biomass burning (26 %)
Excluding elements	62	91	7	Sea salt (5 %)Primary Traffic + Fungal spores (13 %)Anthropogenic SOA (4 %)Biogenic SOA (14 %)Plant Debris (15 %)SIA (20 %)Biomass burning (20 %)
Excluding GC/ EI-MS analytes	67	92	8	Mineral (13 %)Sea salt (2 %)Primary Traffic (5 %)Nitrate (16 %)Anthropogenic SOA (2 %)Fungal spores (7 %)Sulfate (26 %)Biomass burning (20 %)
Excluding PAHs	67	92	8	Mineral (15 %)Sea salt (2 %)Primary Traffic (13 %)Biogenic SOA (14 %)Plant Debris (11 %)Fungal spores (5 %)SIA (19 %)Biomass burning (13 %)
Excluding Levoglucosan, arabitol, sorbitol	65	93	8	Mineral (19 %)Sea salt (5 %)Primary Traffic (10 %)Anthropogenic SOA (3 %)Biogenic SOA (13 %)Plant Debris (9 %)SIA (14 %)Biomass burning (20 %)
Excluding HULIS	64	93	9	Mineral (17 %)Sea salt (4 %)Primary Traffic (9 %)Anthropogenic SOA (3 %)Biogenic SOA (13 %)Plant Debris (10 %)Fungal spores (4 %)SIA (14 %)Biomass burning (18 %)

uncertainty used in order to meet the criterion of $Q_{robust}/Q_{expected} < 2$).

Once the base solution was definitively selected (without any further addition of constraints on these base cases), the sensitivity analysis was based on a "brute force" approach by excluding families of analytes, one at a time. A family of analytes is defined as a group of analytes which are determined by the same laboratory technique (e.g. X-Ray Fluorescence or Ionic Chromatography), in order to mimic choices of input data that would be resulting from the availability of the chemical technique. Therefore, for each dataset, we obtained a number of N solutions where N is the number of families of analytes. N is equal to 8, 7, 5 for Grenoble, Barcelona, and Milan, respectively (Tables 2, 3, 4). Each solution was compared with the base solution to identify the impact of excluding that specific family of analytes on the number/type of factors (f) and on the source contribution (g). The uncertainty related to source contributions was calculated as the standard deviation among the N solutions, divided by the base (reference) value.

3. Results and discussion

In Figs. 1 to 6, the uncertainty intervals due to the choice of input chemical components are plotted for each source versus the reference solution (base case). Such intervals do not include those cases in which that specific source is not identified, which would deliver a null contribution. For Barcelona, the plots are made separately for the urban and the traffic sites and for the PM10 and PM1. The following discussion is organized according to the type of sources of PM.

3.1. Road traffic sources

Primary traffic: This factor was always found in Grenoble, regardless of which family of analytes was excluded, due to the fact that is traced by two families of analytes: EC (with OC/EC ratio lower than 1) and elements such as Ba, Cu, Sb (among others). However, when the elements' family was excluded, this factor was merged with the Fungal spores factor, thus hampering the separation of the two sources contributions. The sensitivity analysis reveals for Primary traffic source contributions a symmetric uncertainties interval in Grenoble (± 28 % compared to the base case solution) when a family of analytes is excluded.

Vehicle exhaust: in Barcelona and Milan the total traffic contribution was separated in 2 main factors: the vehicle exhaust and the vehicle non-exhaust factors. In Milan, the exhaust factor was always found. It was mostly of primary origin as it was traced by Zn and an OC/EC ratio of 1, regardless of the input components chosen. The uncertainty interval of Vehicle exhaust source contributions was also symmetric in Milan (± 15 %) when a family of analytes was excluded, except in the case that elements were excluded, provoking a merging of exhaust and non-exhaust contributions in one factor with also an overestimation of this exhaust + non-exhaust contributions ($13.6 \mu g/m^3$ vs $7.3 \mu g/m^3$) compared to the reference solution. In Barcelona it was traced by several PAHs and hopanes (17a(H)21β(H)-29-norhopane, 17a(H)21β(H)-hopane, benzanthracene, chrysene, benz(b + j + k)fluoranthene, benzo (e)pyrene, benzo(a)pyrene and benzo[ghi]perylene) and EC and an OC/EC ratio of 1.93 indicating the inclusion of some SOA. This factor was always found except when non-polar organics (PAHs) were excluded.

In Barcelona urban PM10, we observed an asymmetric interval with a more likely underestimation (-44 %) of exhaust source contributions when families of analytes were excluded. When non-polar organics were excluded, we observed a merging of exhaust and non-exhaust contributions in one factor but with an underestimation of total contribution ($5.8 \mu g/m^3$ vs $8.8 \mu g/m^3$). For urban PM1, the figure is similar but the underestimation of exhaust + non-exhaust contributions, when non-polar organics were excluded, was even more important ($0.4 \mu g/m^3$ vs $3.9 \mu g/m^3$). In the Barcelona traffic site, we observe a systematic over-estimation (up to 3.5 and 2 0.5 times for PM10 and PM1, respectively) when some analytes were excluded.

Table 3
The different PMF solutions in Barcelona varying the number of families of components.

Barcelona	Characterized mass (%)	Reconstructed mass (%)	# of factors	Type of factors (average % of contribution)
Base solution	47	94	10	Aged biogenic SOA (6 %)Vehicle exhaust (7 %)Biomass burning (1 %)Mineral (13 %)Shipping (9 %)Fresh biogenic SOA (9 %)Aged sea salt (11 %)Metallurgy (3 %)Vehicle non-exhaust (12 %)Regional Sulfate (21 %)
Excluding EC/OC	31	94	10	Aged biogenic SOA (11 %) Vehicle exhaust (3 %)Biomass burning (6 %)Vehicle non-exhaust (10 %)Mineral (12 %)Shipping (8 %) Fresh biogenic SOA + Metallurgy (6 %)Aged sea salt (10 %)Fresh sea salt (7 %)Regional Sulfate (22 %)
Excluding ions	39	94	8	Aged biogenic SOA (9 %)Vehicle exhaust (9 %)Biomass burning (7 %)Mineral (11 %)Shipping (9 %) Fresh biogenic SOA + Metallurgy (5 %)Aged sea salt (14 %)Vehicle non-exhaust (9 %)Regional Sulfate (21 %)
Excluding elements	36	91	6	Aged biogenic SOA (7 %)Traffic (8 %)Biomass burning (11 %) Fresh biogenic SOA + Fresh sea salt (9 %)Secondary nitrate (31 %)Regional Sulfate (24 %)
Excluding polar organics	47	94	9	Vehicle exhaust (11 %)Vehicle non-exhaust (6 %)Hopanes (1 %)Mineral (13 %)Shipping (7 %)Metallurgy (5 %)Aged sea salt

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Table 3 (*continued*)

Barcelona	Characterized mass (%)	Reconstructed mass (%)	# of factors	Type of factors (average % of contribution)
Excluding NH$_4^+$	45	94	10	(16 %)Fresh sea salt (7 %)Regional Sulfate (28 %) Aged biogenic SOA (13 %) Vehicle exhaust (8 %)Vehicle non-exhaust (8 %)Biomass burning (2 %)Mineral (11 %) Shipping (8 %)
Excluding non-polar organics	47	94	9	Fresh biogenic SOA + Metallurgy (6 %)Aged sea salt (14 %)Fresh sea salt (5 %)Regional Sulfate (19 %) Aged biogenic SOA (11 %)Traffic (10 %)Biomass burning (1 %)Mineral (13 %)Shipping (7 %) Fresh biogenic SOA + Metallurgy (9 %)Aged sea salt (14 %)Fresh sea salt (5 %)Regional Sulfate (23 %)

Table 4

The different PMF solutions in Milan varying the number of families of components.

Milan	Characterized mass (%)	Reconstructed mass (%)	# of factors	Type of factors (average % of contribution)
Base solution	69	99	8	Vehicle exhaust (9 %)Vehicle non-exhaust (14 %)Secondary sulfate (23 %)Secondary nitrate (18 %)Mineral (15 %) Biomass burning (8 %)Industrial (8 %)Sea/road salt (4 %)
Excluding EC/OC	42	99	8	Vehicle exhaust (9 %)Vehicle non-exhaust (14 %)Secondary sulfate (22 %)Secondary nitrate (18 %)Mineral (16 %)Biomass burning (9 %)Industrial (7 %)Sea/road salt (4 %)
Excluding ions	39	96	7	Vehicle exhaust (10 %)Vehicle non-exhaust (19 %)Secondary sulfate (31 %)Mineral (13 %)Biomass burning (13 %)Industrial (4 %)Sea/road salt (6 %)
Excluding elements	57	98	4	Traffic (43 %) Secondary sulfate (30 %)Secondary nitrate (19 %)Biomass burning (7 %)
Excluding sugars	68	99	7	Vehicle exhaust (8 %)Vehicle non-exhaust (18 %)Secondary sulfate (23 %)Secondary nitrate (20 %)Mineral (13 %)Industrial (10 %)Sea/road salt (7 %)

Vehicle non-exhaust: The non-exhaust fraction of vehicle emissions was traced in both Barcelona and Milan by heavy metals and metalloids such as Cu, Sb, Sn, Ba, Fe, Cr and EC with an OC/EC ratio of 2.2 in Barcelona and Cu, Fe, Pb and EC with an OC/EC ratio of 2.3 in Milan. In both cities, this factor was found except when elements were excluded from the PMF analysis, yielding to a unique traffic factor, as already mentioned earlier. For Barcelona, removing non-polar organics also provoked the loss of separation between exhaust and non-exhaust source contributions. The uncertainty interval of vehicle non-exhaust source contributions revealed a systematic underestimation in Barcelona for PM10 at the traffic and background sites (down to 50 %) when a family of analytes was excluded, except in the case that ion chromatography was excluded provoking an overestimation (45 %) of non-exhaust contributions. In Milan, instead, we observed a generic overestimation (up to 30 %) of the N solutions excluding families of components.

3.2. Other anthropogenic sources

Biomass burning: We observed very different outcomes from the sensitivity analyses in the three cities. In Milan and Barcelona, levoglucosan was crucial to identify BB contributions in spite of its volatility in summer and the presence of K and PAHs in Barcelona, while for the case of Grenoble, even discarding levoglucosan, the presence of PAHs allowed identifying the BB factor, as confirmed by the high correlation between the two source profiles, mostly for the concentrations of tracers such as EC, OC and PAHs. In Milan and Barcelona, the uncertainty due to the different input components selection was estimated in a generic underestimation (up to a factor 2) of biomass burning source contributions, both in PM10 and PM1 fractions, at both urban background and traffic sites.

Shipping. The shipping emissions were identified only in Barcelona due to the presence of the harbour, and traced by V and Ni (V/Ni ratio of 2). As expected, such contribution was missing when elements were excluded from the PMF analysis. Among the rest of solutions, the uncertainty due to the different input components selection was narrow, and estimated in 8 % in PM10 and 12 % in PM1 with a generic underestimation of 6–20 % in source contributions.
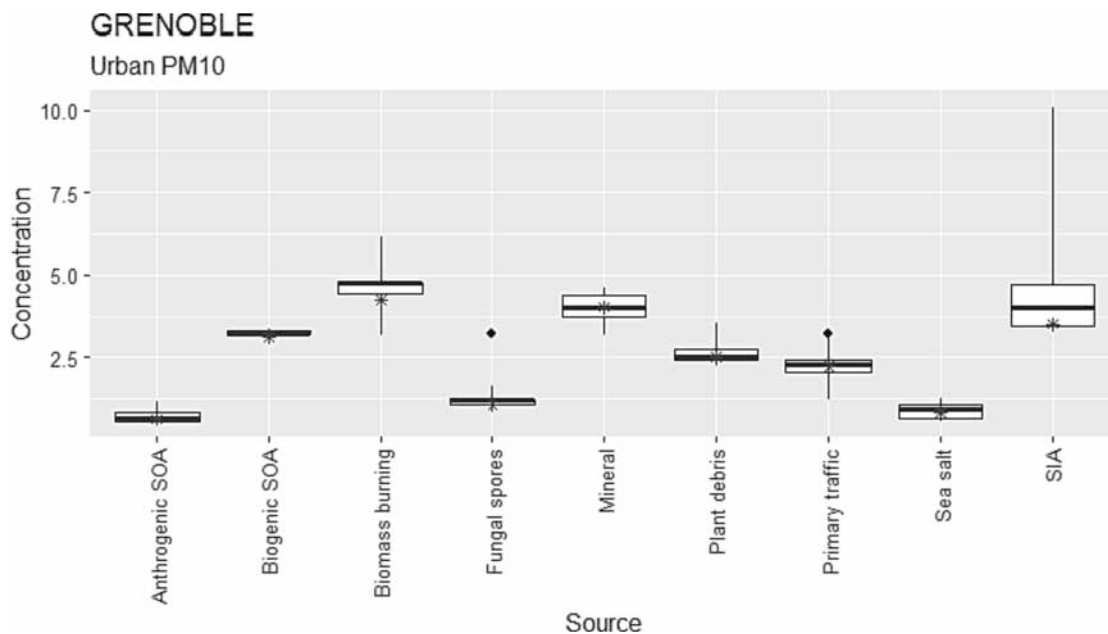
Fig. 1. Uncertainty intervals of PMF source contributions ($\mu g/m^3$) in Grenoble urban PM10 due to the exclusion of different families of analytes. The case(s) in which a factor is not identified is not presented (i.e. null contribution). Stars indicate the base reference solution. Dots indicate fusions of factors.
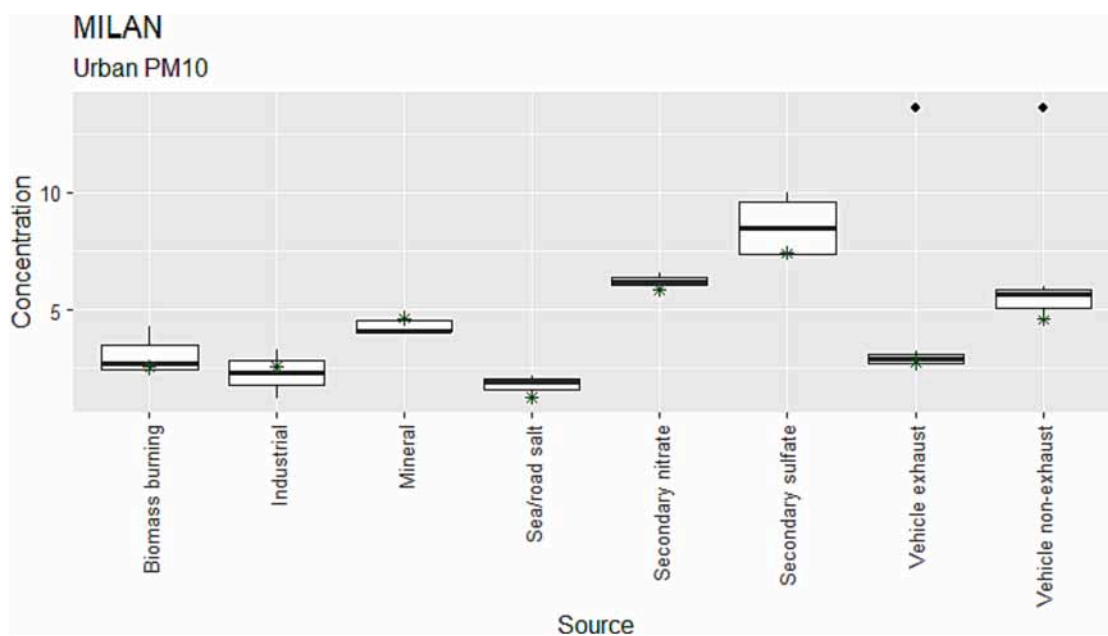

Fig. 2. Uncertainty intervals of PMF source contributions ($\mu g/m^3$) in Milan urban PM10 due to the exclusion of different families of analytes. The case(s) in which a factor is not identified is not presented (i.e. null contribution). Stars indicate the base reference solution. Dots indicate fusions of factors.

Industrial sources. Industrial factors were identified only in Milan and Barcelona and traced by Pb, Ni, Br, Zn and Mn in Milan and Pb, Zn, Mn, Cd and As in Barcelona. This factor has been identified in Grenoble in some other PMF studies (Weber, 2019; Borlaza et al., 2021), but only represent a few % of the PM. While in Milan this industrial factor was sensitive only to the presence of elements, in Barcelona, it was also merged to the fresh biogenic SOA (*cis*-pinonic acid from a-pinene oxidation) in several cases, when excluding ions, non-polar organics, or ammonium. This merging was interpreted as transport-related as both industries and forests are located to the NW sector of the monitoring city site (Amato et al., 2016). In those cases, however, the total source contributions were much smaller than the sum of industrial and fresh biogenic SOA contribution of the base solution. The uncertainty due to

the selections of input components was quite narrow in Milan (40 %), but very large in Barcelona (overestimated up to a factor of 5). The reason of such difference is unclear.

3.3. Secondary aerosols

Secondary Organic Aerosols: In Grenoble the base solution provided two factors related to SOA: Aged Biogenic SOA and Anthropogenic SOA. Both of them were sensitive to their tracers, namely the oxidation products of isoprene (α-methylglyceric acid (α-MGA) and 2-methylery-thritol (2-MT)) and of α-pinene (hydroxyglutaric acid (3-HGA)) (Claeys et al., 2004, 2007; Edney et al., 2005) for biogenic SOA and acenaphthenequinone, 6H–dibenzo[b,d]pyran-6-one, 1,8- naphthalic
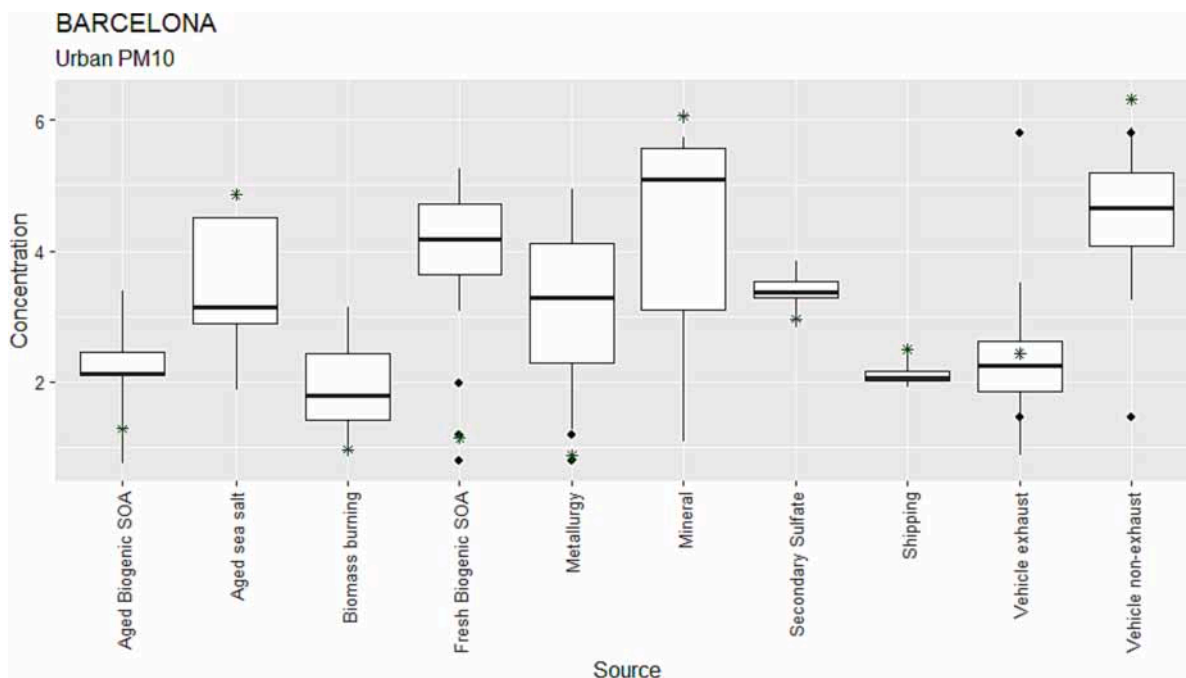
Fig. 3. Uncertainty intervals of PMF source contributions (μg/m³) in Barcelona urban PM10 due to the exclusion of different families of analytes. The case(s) in which a factor is not identified is not presented (i.e. null contribution). Stars indicate the base reference solution. Dots indicate fusions of factors.
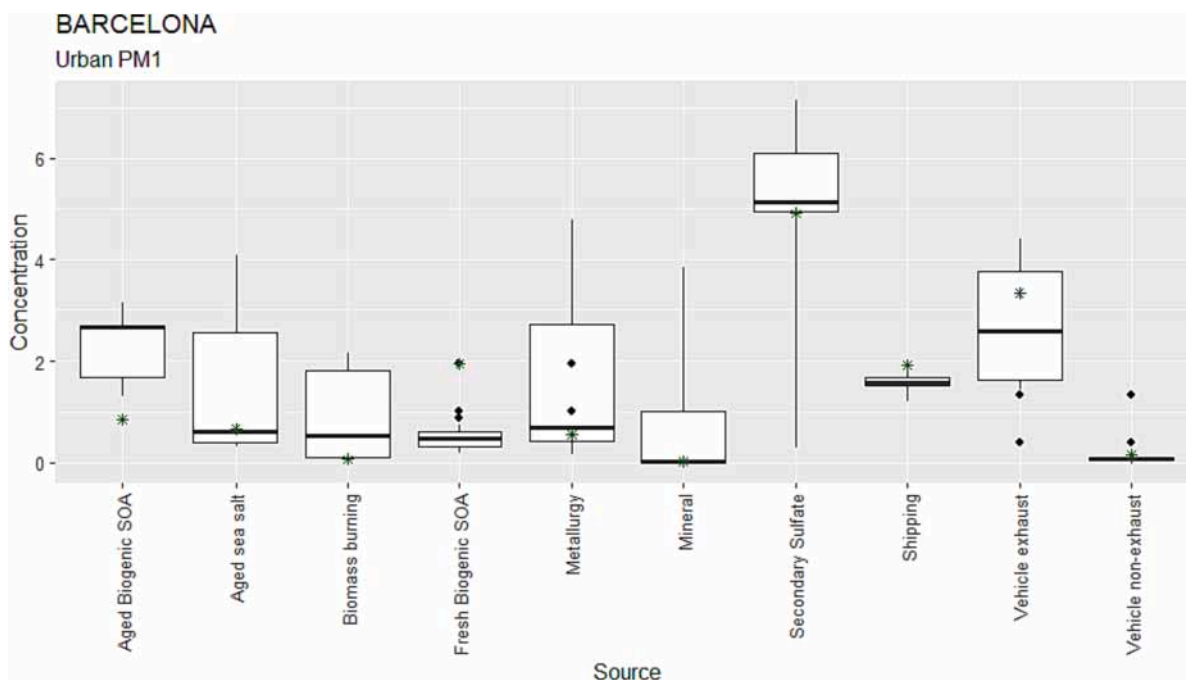

Fig. 4. Uncertainty intervals of PMF source contributions (μg/m³) in Barcelona urban PM1 due to the exclusion of different families of analytes. The case(s) in which a factor is not identified is not presented (i.e. null contribution). Stars indicate the base reference solution. Dots indicate fusions of factors.

anhydride and DHOPA for anthropogenic SOA. In Barcelona, the same is true for the Aged Biogenic SOA factor, traced by malic acid, 3-hydroxy-glutaric acid, methylbutanetricarboxylic acid (3-MBTCA), 2-methylgly-ceric acid, 2-methylthreitol, 2-methylerythritol, and fresh Bio SOA traced by *cis*-pinonic acid. In Milan, no SOA factor was identified due to the lack of tracers. The uncertainty due to the different input compo-nents selections was very narrow for Aged Biogenic SOA (3 %) but very large for Anthropogenic SOA (40 % in Grenoble and 120 % in Barce-lona), resulting in a systematic overestimation (except at the Traffic site

for PM10 in Barcelona) of Anthropogenic SOA due mostly to one large peak, where concentrations can vary up more than 100 %.

Secondary Inorganic Aerosols. In Grenoble, a single SIA factor was identified in the base case solution. The reason is unclear, since other PMF works at this site generally indicate clear separation of sulfate-rich and nitrate-rich factors (Weber et al., 2019; Borlaza et al., 2021). Such SIA factor was identified as long as ions were selected as input infor-mation. If GC / EI-MS analytes were excluded, the SIA factor was split in two factors, Nitrate-rich and Sulfate-rich, but source contributions were
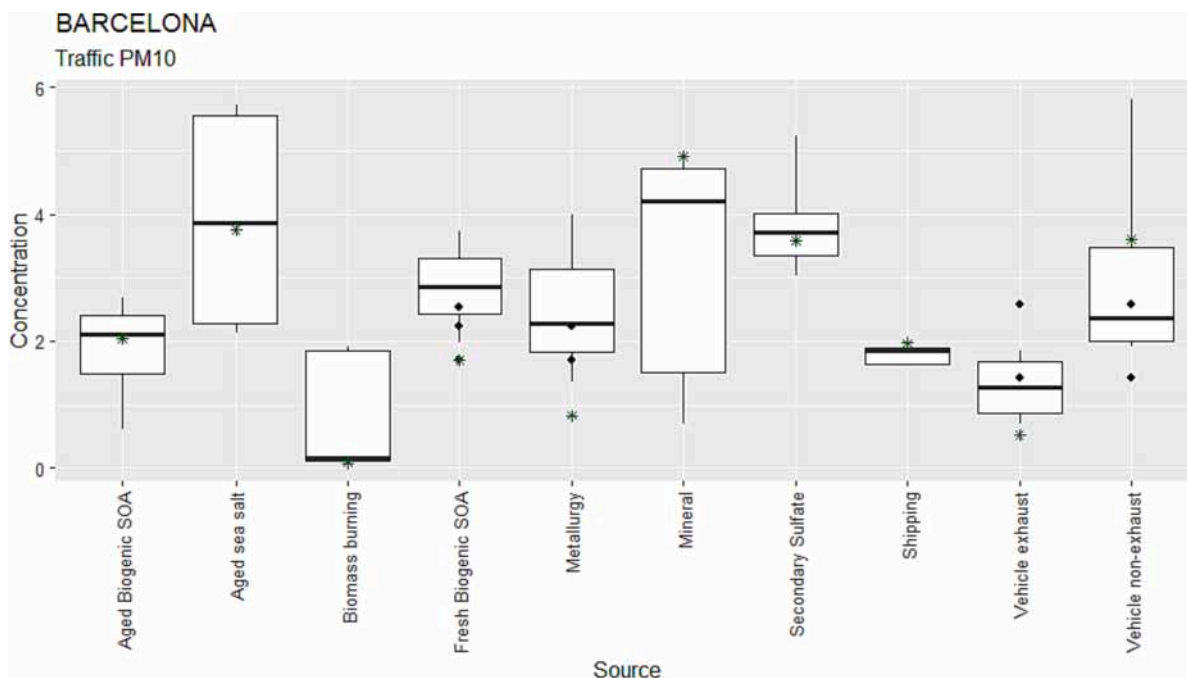
Fig. 5. Uncertainty intervals of PMF source contributions (μg/m³) in Barcelona traffic PM10 due to the exclusion of different families of analytes. The case(s) in which a factor is not identified is not presented (i.e. null contribution). Stars indicate the base reference solution. Dots indicate fusions of factors.
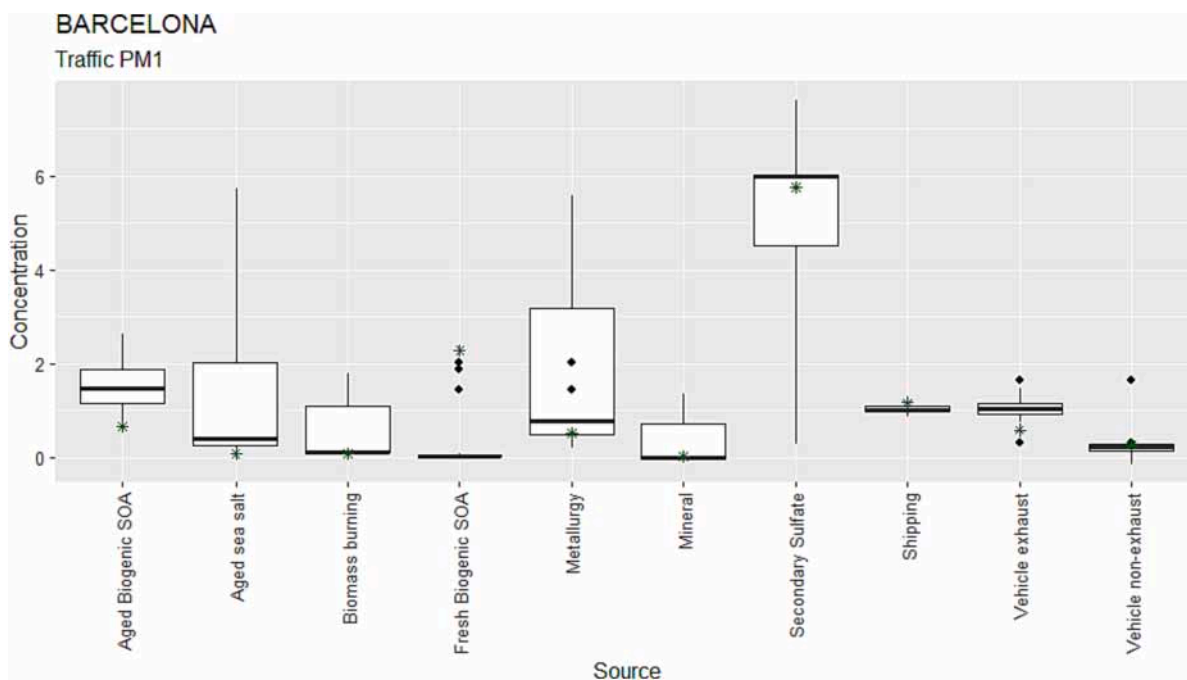

Fig. 6. Uncertainty intervals of PMF source contributions (μg/m³) n Barcelona traffic PM1 due to the exclusion of different families of analytes. The case(s) in which a factor is not identified is not presented (i.e. null contribution). Stars indicate the base reference solution. Dots indicate fusions of factors.

largely overestimated compared to the base case. In Barcelona also a single SIA factor was identified, more related to sulfate than nitrate, probably due to the dominance of warmer months in the sampling campaigns. Such Sulfate factor was always identified since it can be traced either by S and SO_4^{2-}. In Milan, secondary sulfate factor and secondary nitrate factor were separated in all solutions except when ions were not used as input species. In that case, Secondary Sulfate (traced by S) contributions were increased by approximately 50 %, probably due to the higher ammonium content. Among the rest of solutions, the

uncertainty due to the different input components selection was a general overestimation.

3.4. Natural primary aerosols

Dust sources. In all cities, the mineral factor was found in the base case and characterized with enrichment in Ca/Ca²⁺, Si, Al, Ti, Fe, Li, Rb, Sr and V. Consequently, it was sensitive to the presence of these elements among the input species. Among the rest of solutions, the

uncertainty due to the different input components selection was estimated at ± 11 % in Milan and ± 13 % in Grenoble, but large in Barcelona (39 %) with a systematic underestimation.

Sea salt. The identification of sea salt factor is more site-dependent due to several reasons. In Barcelona, it was traced either by ions (Cl-, NO3–, Mg2 +..) and elements (Na, Cl, Mg, S) so that it was always found, and even split in two factors (aged and fresh) when OC/EC or polar organics were not selected as input species. In Grenoble, no elemental Na nor Cl were available, so that the identification of sea salt was sensitive to the ions analysis. In Milan, the sea salt was merged with road salt contributions and sensitive to the elemental analysis. Among the rest of solutions, the uncertainty due to the different input components selection was estimated in the range 33–45 % among the three cities, generally symmetric with respect to the reference value.

Primary biogenic particles. Two factors related to primary biogenic aerosols were identified in Grenoble thanks to the analysis of specific tracers (arabitol and mannitol) of Fungal spores (Bauer et al., 2008; Caseiro et al., 2009; Rogge et al., 2007; Yttri et al., 2011; Samake et al., 2019) and plant debris (odd number higher alkanes:C27 to C31, Rogge et al., 1993). As expected, both factors were sensitive to the presence of their specific tracers, but, in addition, we observed a merging of fungal spores factor with the Primary traffic factor, when elements were excluded from the analysis. This could be related to the resuspension processes for fungal spores (Borlaza et al., 2021). Among the rest of solutions, the symmetric uncertainty due to the different input components selection was estimated in 23 % and 18 % respectively.

4. Conclusions

In conclusion, road traffic sources are generally identified by analysing at least 2 groups of analytes, namely OC/EC and PAHs and/or elements. The exhaust source resulted to be less sensitive to the choice of analytes, although source contributions estimates can deviate significantly up to 44 % (positively or negatively). On the other hand, for the detection of the non-exhaust one is clearly necessary to analyze specific inorganic elements. Still, the exclusion of another group of analytes can provoke a bias of non-exhaust contributions up to 50 %. The choice of not analysing non-polar organics likely causes the loss of separation of exhaust and non-exhaust factors, thus obtaining a unique road traffic source, which provokes a significant bias of total contribution.

Levoglucosan was, in most cases, crucial to identify biomass burning contributions in Milan and in Barcelona, in spite of the presence of PAHs in Barcelona, while for the case of Grenoble, even discarding levoglucosan, the presence of PAHs allowed identifying the BB factor. Modifying the rest of analytes provokes a systematic underestimation of biomass burning source contributions.

SIA factors resulted to be generally overestimated with respect to the base case analysis, also in the case that ions were not included in the PMF analysis.

Trace elements were crucial to identify shipping emissions (V and Ni) and industrial sources (Pb, Ni, Br, Zn, Mn, Cd and As). When changing the rest of input variables, the uncertainty was narrow for shipping but large for industrial processes. Major and trace elements were also crucial to identify the mineral/soil factor at all cities. The modelling error when others analytes were excluded was estimated to be very narrow in Milan and Grenoble (11–13 %) but large in Barcelona (39 %) with a systematic underestimation.

Biogenic SOA and Anthropogenic SOA factors were sensitive to the presence of their molecular tracers, since the availability of OC alone is unable to separate a SOA factor. This is contrary to what was found by Veld et al., (2021), where a SOA-like factor was found when combining urban and rural sites in a single PMF matrix. In addition, while Biogenic SOA contributions were very robust in the sensitivity analysis, the opposite was found for the Anthropogenic SOA.

Sea salt was traced either by ions (Cl^-, NO_3^-, Mg^{2+}…) and elements (Na, Cl, Mg, S) so that it is generally well identified and even splitted into

two factors (aged and fresh) depending on the input matrix. Uncertainty interval ranges within 33–45 %. The lack of Na can provoke a wrong estimate of source contributions since it is known that the other important marker, Cl, can react and disappear. In addition Na can help in separating an aged sea salt from a fresh one.

Arabitol and sorbitol were crucial to detecting fungal spores while odd number of higher alkanes (C27 to C31) for plant debris. When other groups of analytes were excluded the error intervals in source contributions were symmetric and estimated in 23 % and 18 %, respectively.

Based on the above results, the following general recommendations can be drawn for selecting the most appropriate species as input for PMF receptor modelling:

- In order to perform a decent source apportionment with the PMF technique, a data base including at least EC-OC, major ions (using ionic chromatography), trace element (preferably by ICP-MS), and analysis of BB tracers (either by LC-PAD or by GC–MS) should be mandatory. This allows to identify most of the main contributors to PM in Europe, i.e dust, sea-salt (eventually separated into fresh and aged sea salt), traffic emissions (eventually separated between exhaust and non-exhaust), biomass burning aerosols, industrial emissions (possibly separated in different types depending on the knowledge of the emissions at the site), and possibly shipping emissions (characterized with V and Ni). It also leads to the determination of secondary inorganic aerosol factors (commonly separated into nitrate- and sulfate-rich components). However, such an approach does not allow to properly apportion primary biogenic emission, nor the various SOA fractions.
- If IC measurements include MSA and oxalate, it may lead to further determination of the main marine SOA fraction (traced with MSA) and to roughly apportion aged SOA factors originating from various origins (traced with oxalate),
- HPLC-PAD measurements for sugars alcohols (in particular arabitol and mannitol) may lead to the further determination of primary biogenic that can be a substantial PM fraction at some sampling sites, especially from Spring to late Autumn, and in the coarse mode.

A refined PMF analysis, including the determination of further sources, requires additional measurements of specific tracers, such as secondary biogenic emission when including tracers like 3-MBTCA, 2-MT's, etc measured with techniques like GC–MS, LC-MS, and/or IC-MS.

The inclusion of a range of PAH's measurements (or some PAH derivatives) may lead to some improvements in some combustion sources separations, but these results should be studied with caution in terms of chemical profiles, since these species are coming from many various origins. Additionally, the inclusion of species like higher alkanes may also lead to some improvements in organic sources determination, especially plant debris, but results should also be considered with caution.

CRediT authorship contribution statement

F. Amato: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. **B.L. van Drooge:** Investigation, Methodology, Validation, Writing – review & editing. **J.L. Jaffrezo:** Data curation, Funding acquisition, Investigation, Supervision, Validation, Writing – review & editing. **O. Favez:** Data curation, Investigation, Software, Visualization, Writing – review & editing. **C. Colombi:** Data curation, Investigation, Software, Visualization, Writing – review & editing. **E. Cuccia:** Data curation, Investigation, Software, Visualization, Writing – review & editing. **C. Reche:** Data curation, Investigation, Software, Visualization, Writing – review & editing. **F. Ippolito:** Data curation, Investigation, Software, Visualization, Writing – review & editing. **S. Ridolfo:** Data curation, Investigation, Software, Visualization, Writing – review &

editing. **R. Lara:** Visualization, Writing – review & editing. **G. Uzu:** Data curation, Supervision, Validation, Writing – review & editing. **V. Ngoc:** Data curation, Supervision, Validation, Writing – review & editing. **P. Dominutti:** Data curation, Supervision, Validation, Writing – review & editing. **S. Darfeuil:** Data curation, Supervision, Validation, Writing – review & editing. **A. Albinet:** Data curation, Supervision, Validation, Writing – review & editing. **D. Srivastava:** Data curation, Supervision, Validation, Writing – review & editing. **A. Karanasiou:** Data curation, Supervision, Validation, Writing – review & editing. **G. Lanzani:** Funding acquisition, Resources, Supervision, Writing – review & editing. **A. Alastuey:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing. **X. Querol:** Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Xavier Querol reports financial support was provided by European Commission. Fulvio Amato reports financial support was provided by Spain Ministry of Science and Innovation. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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