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AIRUSE-LIFE+: a harmonized PM speciation and source apportionment in 5 Southern European cities

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The AIRUSE-LIFE+ project aims at characterising similarities and heterogeneities in PM sources and contributions in urban areas from the Southern Europe. Once the main PM_x sources are identified, AIRUSE aims at developing and testing the efficiency of specific and non-specific measures to improve urban air quality. This article reports the results of the source apportionment of PM₁₀ and PM_{2.5} conducted at three urban background sites (Barcelona, Florence and Milan, BCN-UB, FI-UB, MLN-UB) one suburban background site (Athens, ATH-SUB) and one traffic site (Porto, POR-TR). After collecting 1047 PM₁₀ and 1116 PM_{2.5} 24 h samples from January 2013 to February 2014 simultaneously at the 5 cities, these were analysed for the contents of OC, EC, anions, cations, major and trace elements and levoglucosan. The USEPA PMF5 receptor model was applied to these datasets in a harmonised way for each city.

The sum of vehicle exhaust and non-exhaust contributes within 3.9–10.8 $\mu\text{g m}^{-3}$ (16–32 %) to PM₁₀ and 2.3–9.4 $\mu\text{g m}^{-3}$ (15–36 %) to PM_{2.5}, although a fraction of secondary nitrate is also traffic-related but could not be estimated. Important contributions arise from secondary particles (nitrate, sulphate and organics) in PM_{2.5} (37–82 %) but also in PM₁₀ (40–71 %) mostly at background sites, revealing the importance of abating gaseous precursors in designing air quality plans.

Biomass burning (BB) contributions vary widely, from 14–24 % of PM₁₀ in POR-TR, MLN-UB and FI-UB, 7 % in ATH-SUB to < 2 % in BCN-UB. In PM_{2.5}, BB is the second most important source in MLN-UB (21 %) and in POR-TR (18 %), the third one in FI-UB (21 %) and ATH-SUB (11 %), but again negligible (< 2 %) in BCN-UB. This large variability among cities is mostly due to the degree of penetration of biomass for residential heating. In Barcelona natural gas is very well supplied across the city and used as fuel in 96 % of homes, while, in other cities, PM levels increase on an annual basis by 1–9 $\mu\text{g m}^{-3}$ due to this source. Other significant sources are:

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– Local dust, 7–12 % of PM_{10} at SUB and UB sites and 19 % at the TR site, revealing a contribution from road dust resuspension. In $PM_{2.5}$ percentages decrease to 2–7 % at SUB-UB sites and 15 % at the TR site.

– Industries, mainly metallurgy, contributing 4–11 % of PM_{10} (5–12 % in $PM_{2.5}$), but only at BCN-UB, POR-TR and MLN-UB. No clear impact of industrial emissions was found in FI-UB and ATH-SUB.

– Natural contributions from sea salt (13 % of PM_{10} in POR-TR but only 2–7 % in the other cities) and Saharan dust (14 % in ATH-SUB), but less than 4 % in the other cities.

During high pollution days, the largest specific source (i.e. excluding SSO and SNI) of PM_{10} and $PM_{2.5}$ are: VEX+NEX in BCN-UB (27–22 %) and POR-TR (31–33 %), BB in FI-UB (30–33 %) and MLN-UB (35–26 %) and Saharan dust in ATH-SUB (52–45 %). During those days, there are also quite important Industrial contributions in BCN-UB (17–18 %) and Local dust in POR-TR (28–20 %).

1 Introduction

Atmospheric Particulate Matter (PM) concentrations can vary widely across Europe due to different climatic conditions and local features such as anthropogenic source types, emission rates and dispersion patterns. Moreover, natural contributions such as biogenic aerosols, forest fires, sea salt and Saharan dust intrusions impact differently from one region to another (Pey et al., 2013; Manders et al., 2010; Hoyle et al., 2011; Hodzic et al., 2007).

Urban PM_{10} concentrations show significant variability across Europe as reported by routine monitoring networks (EEA, 2013) and research studies (Querol et al., 2004; Putaud et al., 2010; Lianou et al., 2011; Kukkonen et al., 2005; Karanasiou et al., 2014).

For $PM_{2.5}$ the spatial variability across Southern Europe is less known because in most

air quality zones it is not as widely measured as PM_{10} . As a consequence, there is limited information on the geographical variability of the coarse fraction ($PM_{10-2.5}$), which is often linked to local sources and whose evidence of health concern is increasing (Brunekreef and Forsberg, 2005).

Comparability of data is also hampered by the fact that most research studies analyzed PM data from different periods or with different sampling calendars. An example of this is given by the multi-city studies aimed at investigating the short and long-term health effects of exposure to PM_x mass concentrations, NO_x and SO_2 (Eeftens et al., 2012; Medina et al., 2004; Meng et al., 2013; Romieu et al., 2012).

Moreover, the comparison of bulk PM concentrations only, without the necessary chemical characterisation of collected samples and source apportionment analysis, does not allow for an in depth investigation of sources limiting the scope for air quality management purposes.

Recently within the MED-PARTICLES project Karanasiou et al. (2014) studied the concentrations levels of PM_{10} and $PM_{2.5}$ and gaseous pollutants in traffic and urban background sites across southern Europe for the period 2001–2010 but no information on chemical composition of PM was available. PM_{10} and $PM_{2.5}$ mass and particle number were also continuously measured for 18 months in urban background locations across Europe to determine the spatial and temporal variability of particulate matter in Helsinki, Athens, Amsterdam and Birmingham, but no information on PM composition and sources was provided (Lianou et al., 2011). In another study, Querol et al. (2004) compared the PM_{10} and $PM_{2.5}$ levels and chemistry of seven selected EU regions with at least one year of data coverage, at regional, urban background and kerbside sites. However, available datasets were not simultaneous, from 1998 to 2002. Kukkonen et al. (2005) analysed in detail four selected episodes involving substantially high concentrations of PM_{10} that occurred in Oslo, Helsinki, London and Milan but in different periods. The ESCAPE project (Eeftens et al., 2012) investigated the health effects of long-term exposure to ambient air pollution across Europe. $PM_{2.5}$, PM_{10} and particle

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composition were compared at 20 sites across 2008–2011, but measurements were done 3 times for 14 days in different seasons without covering the full year period.

The AIRUSE LIFE+ project generated the first harmonised dataset of Southern European cities for PM₁₀ and PM_{2.5} levels and composition, following the same sampling protocol and 13 months calendar in Barcelona (Spain), Porto (Portugal), Florence and Milan (Italy), and Athens (Greece). The goal is to characterise the similarities and heterogeneities in PM sources and contributions across the Mediterranean region. This chapter describes the source apportionment results for PM₁₀ and PM_{2.5}, highlighting common features and dissimilarities across Southern Europe. Once the main sources of PM₁₀ and PM_{2.5} are identified, the strategic goal of the AIRUSE project is to test and develop specific measures to improve air quality in Southern Europe, targeted to meet air quality standards and to approach as closely as possible the WHO guidelines.

2 Methods

2.1 PM samplings

PM sampling was carried out from January 2013 to February 2014, simultaneously at five urban stations in Barcelona, Porto, Florence, Milan and Athens. PM₁₀ and PM_{2.5} samples were collected simultaneously over 24 h, every third day, on quartz microfiber and/or Teflon filters. Furthermore, in order to evaluate the chemical fingerprint of Saharan dust, additional PM₁₀ and PM_{2.5} sampling was performed at each city under selected Saharan dust intrusions after forecasting the occurrence of this phenomenon. The forecast was based on the interpretation of: (i) air mass back trajectories calculated with the HYSPLIT4 model from NOAA (Draxler and Rolph, 2003), (ii) predictions of dust concentrations by the SKIRON model, University of Athens (<http://forecast.uoa.gr/>) and Barcelona Supercomputing Center (NMMB/BSC-Dust forecasts) prediction models.

The details of each monitoring site and instrumentation used are described below:

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- BCN-UB: Barcelona urban background (Spain). PM₁₀ and PM_{2.5} were collected by means of sequential DIGITEL DH1080 high volume samplers (30 m³ h⁻¹) on 150 mm diameter quartz fiber filters at the Palau Reial station (41°23′14″ N, 2°6′56″ E). This is an urban background (UB) site located within the University Campus (South West part of the city) and part of the local air quality network. The nearest trafficked road (Diagonal Avenue, 90 000 vehicles day⁻¹) is located 200 m away.
- POR-TR: Porto traffic (Portugal). The urban traffic (TR) station is located in Praça Francisco Sá Carneiro (41°09′46.10″ N; 8°35′26.95″ W) and part of the National Air Quality Network, QualAr. It is located in the eastern side of Porto city, next to the Fernão de Magalhães Avenue and at 600 m from the Inner Circular Motorway. Two low volume samplers (TECORA) operating at 2.3 m³ h⁻¹ collected PM₁₀ and PM_{2.5} onto 47 mm diameter Teflon filters. A high volume sampler operating at a flow of 1113 L min⁻¹ with impaction plates from Sierra-Anderson, which enabled the simultaneous collection of PM_{2.5} and PM_{2.5-10} onto quartz fibre filters, was used in parallel.
- FI-UB: Florence urban background (Italy). The urban site Bassi is an air quality UB monitoring station (43°47′8.33″ N, 11°17′13.19″ E) of the Environmental Protection Agency of Tuscany. PM₁₀ and PM_{2.5} samples were collected by means of two low volume (2.3 m³ h⁻¹) CEN equivalent sequential samplers (HYDRA Dual Sampler); each sampler is equipped with two inlets so that aerosol can be simultaneously collected on Teflon and quartz microfibre filters (47 mm diameter, Pall and Aquaria, respectively).
- ATH-SUB: Athens sub urban background (Greece). This station is part of the Global Atmosphere Watch network (GAW-DEM) and is located in NCSR “Demokritos” campus (37°99′50″ N 23°81′60″ E), at the North East corner of the Greater Athens Metropolitan Area and at an altitude of 270 m a.s.l. The sub-urban site is away from direct emission sources in a vegetated area (pine).

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PM₁₀ and PM_{2.5} samples were collected on Teflon filters by means of low volume (2.3 m³ h⁻¹) samplers (Sequential 47/50-CD with Peltier cooler, Sven Leckel GmbH, Tecora Echo PM sampler and Demokritos EN12341 sampler). PM₁₀ and PM_{2.5} samples were also collected on quartz microfiber filters by means of high

- MLN-UB: Milan urban background (Italy). The Milano Pascal urban background station is part of the ARPA Lombardia Air Quality Network, and it is one of the Italian Supersites for the Italian Decree 155/2010 (Italian transposition of 2008/50/CE). It is located in the eastern side of Milan, the University area called “Città Studi” (45°28′44″ N, 9°14′07″ E), in a playground about 130 m from the road traffic. PM₁₀ and PM_{2.5} were collected on Teflon (Pall), Mixed Cellulose Ester (MCE, Advantec) and quartz microfiber (Pall) filters (47 mm diameter), with five low volume US-EPA reference method samplers (TECORA).

2.2 Sample treatment and analysis

Before sampling, quartz or PTFE microfibre filters were dried for 5 h and conditioned for 48 h at 20 °C and 50 % of relative humidity. Weights of blank filters were measured three times every 24 h by means of a microbalance (1 or 10 µg sensitivity). After weighing, ø 47 mm filters were kept in Petri holders, while ø 15cm and large rectangular filters were kept in aluminum foils. After sampling, filters were brought back to the laboratory to be weighed two more times every 24 h of conditioning at the same temperature and relative humidity as the first weighing.

Once the weights of samples were determined, filters were destined for several analytical determinations. These procedures are briefly listed below, according to the different species analysed:

- Major and trace elements were determined:

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- In Teflon filters by different techniques: PIXE (Particle Induced X-Ray Emission), without any pretreatment (Lucarelli et al., 2014); after acid digestion (5 mL HF, 2.5 mL HNO₃, 2.5 mL HClO₄) of 1/2 of each filter, consecutively by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) and ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) (Querol et al., 2001) to assure comparability between the two techniques (only for Porto samples, Fig. S1); by ICP-AES after digestion with HNO₃-H₂O₂ in a microwave oven according to the EU method EN14902:2005 (Traversi et al., 2014), only for Florence samples (Fig. S1); by XRF (X-Ray Fluorescence) with polarized primary X-Ray beam and several secondary targets, after an intercomparison with PIXE (Fig. S2), only for Milan samples (Table S1);
- In quartz filters by ICP-MS and ICP-AES after acid digestion (5 mL HF, 2.5 mL HNO₃, 2.5 mL HClO₄) of 1/4 of each filter (Querol et al., 2001) (Table S1);
- In Teflon and MCE filters by XRF (X-ray Fluorescence), only for Milan samples.
- Water soluble ions by IC (Ion Chromatography), after extraction in 20 mL of MilliQ water (with ultrasonic bath for 30 min) of 1/2 or 1/4 of filter;
- On quartz filters organic carbon (OC) and elemental carbon (EC) by thermal/optical analysis with the EUSAAR2 temperature program by means of Sunset analyzers. Filters from POR-TR were analysed in a thermo-optical transmission system described in detail elsewhere, following a similar protocol of EUSAAR2 (Pio et al., 1998, 2011).
- On the PM₁₀ quartz microfibre filters, Carbonate Carbon (CC), by means of the procedure described by Pio et al. (1994): briefly, the carbonate measurement setup comprises four components: a mass flow meter, a reaction cell, an infrared CO₂ analyser, and a computer terminal for data acquisition. A portion of each filter (9 mm punches) is acidified with orthophosphoric acid (20 %) in a CO₂ free

gas stream to convert the carbonate carbon to CO₂, which is then detected by an infrared analyser.

- On the PM_{2.5} quartz filters, levoglucosan was determined by means of IC after extraction in 10 mL of MilliQ water (with ultrasonic bath for 30 min) on 1.5 cm² punch from quartz filter (Table S1).

2.3 Source apportionment

Source apportionment studies of atmospheric particulate matter are often performed by means of receptor models that are based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^p g_{ik} f_{jk} \quad i = 1, 2, \dots, m \quad j = 1, 2, \dots, n \quad (1)$$

where x_{ij} is the concentration of the species j in the i th sample, g_{ik} is the contribution of the k th source in the i th sample and f_{jk} is the concentration of the species j in source k . Equation (1) can be also expressed in matrix form as $\mathbf{X} = \mathbf{GF}^T$. If f_{jk} are known for all the sources then the Chemical Mass Balance (CMB) can be applied (Watson et al., 1984), as for this model the experimental profiles of all major sources are needed. When both g_{ik} and f_{jk} are unknown, factor analysis (FA) techniques such as Principal Components Analysis (PCA) (Thurston and Spengler, 1967; Henry and Hidy, 1979) and Positive Matrix Factorisation (PMF) (Paatero and Tapper, 1994) are used for solving Eq. (1). PMF can be solved with the Multilinear Engine (ME-2) developed by Paatero (1999) and implemented in the version 5 of the US EPA PMF (<http://www.epa.gov/head/research/pmf.html>).

In this study, the US EPA PMF v5 was applied to the five datasets obtained at BCN-UB, FI-UB, ATH-SUB, MLN-UB and POR-TR. Since PMF is a weighted least-squares method, individual estimates of the uncertainty in each data value are needed. The uncertainty estimates were based on the approaches by Polissar et al. (2008) and Amato

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et al. (2009). Species which retain a significant signal were separated from the ones dominated by noise, following the signal-to-noise (S/N) criterion defined by Paatero and Hopke (2003). Species with $S/N < 0.2$ are generally defined as bad variables and removed from the analysis and species with $0.2 < S/N < 2$ are generally defined as weak variables and down weighted by a factor of 3. Nevertheless, since S/N is very sensitive to sporadic values much higher than the level of noise, the percentage of data above detection limit was used as complementary criterion.

In those cases where the PMF model was not able to resolve a Saharan dust source, the Saharan dust contribution was estimated according to the methodology proposed by SEC (2011).

3 Results and discussion

3.1 PM_{10} and $PM_{2.5}$ levels

As shown in Table 1, the observed mean PM levels during the study period were as follows:

- PM_{10} in the urban background (UB) reached 19–22 $\mu\text{g m}^{-3}$ in FI and BCN, and 39 $\mu\text{g m}^{-3}$ in MLN. In the suburban background (SUB) site in ATH levels reached 20 $\mu\text{g m}^{-3}$, whereas at the traffic (TR) site of POR, concentrations reached 34 $\mu\text{g m}^{-3}$.
- For $PM_{2.5}$, levels reached 13–15 $\mu\text{g m}^{-3}$ at the UB sites of FI and BCN, 31 $\mu\text{g m}^{-3}$ in MLN, 11 $\mu\text{g m}^{-3}$ at the SUB site in Athens, and 27 $\mu\text{g m}^{-3}$ in POR-TR.

All sites met EU legal requirements (2008/50/EC) for the annual limit value of PM_{10} (40 $\mu\text{g m}^{-3}$). However, the legal requirement of not exceeding 50 $\mu\text{g m}^{-3}$ for the 90.4 % of the annual values (daily limit value) was exceeded at MLN-UB (72 $\mu\text{g m}^{-3}$) and POR-TR (53 $\mu\text{g m}^{-3}$). The annual EU target value of $PM_{2.5}$ (25 $\mu\text{g m}^{-3}$, 2008/50/EC) was

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exceeded at POR-TR ($27 \mu\text{g m}^{-3}$) and MLN-UB ($31 \mu\text{g m}^{-3}$). For the UB sites mean levels are similar in the cities with the exception of MLN with relatively higher levels, due to intense local and regional PM source contributions and to the specific meteorology of the Po Valley, with frequent and intensive atmospheric thermal inversions that induce regional accumulation of pollutants.

For $\text{PM}_{2.5}$, similar and relatively lower values (as compared with PM_{10}) were recorded at UB and SUB sites ($11\text{--}15 \mu\text{g m}^{-3}$), with the exception of MLN ($31 \mu\text{g m}^{-3}$). In the case of the TR site, mean level reached $27 \mu\text{g m}^{-3}$. UB and SUB $\text{PM}_{2.5}/\text{PM}_{10}$ ratios were close to 0.7 in the case of FI and BCN, 0.5 for ATH and 0.8 for MLN. At POR-TR site it increased to 0.8. Although at the TR site levels of resuspension of road dust are expected to be higher than at UB sites (causing the $\text{PM}_{2.5}/\text{PM}_{10}$ to decrease), the proximity to the exhaust emissions (dominated by fine PM) causes a shift of the PM load to the fine fraction.

When considering the stricter WHO guidelines, all cities exceeded both the PM_{10} and $\text{PM}_{2.5}$ annual mean thresholds, with the exception of PM_{10} in FI-UB. It is worth noting that the sampling year was particularly rainy in most of the study sites, including Florence. The daily PM_{10} WHO threshold was exceeded only in POR-TR.

As shown by Fig. S3, seasonal trends for PM_{10} at the 5 AIRUSE cities were very different. ATH-SUB was characterised by higher spring-summer and lower autumn-winter PM_{10} levels probably due to higher African dust influence in the warm seasons. A similar but much smoother trend was observed for BCN-UB. For POR-TR, the highest levels were recorded in summer and the lowest in spring. At MLN-UB, lower levels were recorded in spring and summer, when PM_{10} levels reached similar levels to BCN-UB, FI-UB or ATH-SUB; however in autumn and winter levels at MLN-UB were higher by a factor of more than 2 with respect to the other seasons and most of the other cities. This is due to the aforementioned atmospheric stagnation features of the Po Valley that favoured the accumulation of intensive winter PM emissions. At FI-UB a similar trend was observed but with a less pronounced winter increase than that described for MLN-UB. In fact, Florence is also located in a closed basin (the Arno river valley), which

is characterised by stagnant conditions during the cold season. PM_{2.5} levels followed similar seasonal patterns to those described above for PM₁₀ at each city.

3.2 PM speciation

3.2.1 EC, OC and OM

5 EC is a tracer of emissions from road traffic, mainly from diesel vehicles (Querol et al., 2013); it is a carrier of highly health relevant organic species (WHO, 2012). Mean levels of EC reached 1.1 $\mu\text{g m}^{-3}$ in PM₁₀ at the UB sites of BCN and FI and 1.9 $\mu\text{g m}^{-3}$ at the UB site of MLN (Fig. 1). At the SUB site of ATH, EC levels were lower (0.4 $\mu\text{g m}^{-3}$ in PM₁₀, Fig. 1) due to the higher distance from avenues with high traffic load, but also
10 due to the lower proportion of diesel vehicles in the fleet of ATH compared to the other 3 cities. Until 2012, the use of diesel for private cars was not allowed in this city.

As expected, levels of EC at traffic sites were higher than at UB sites by a factor ranging from 3.6 to 4.9. EC levels recorded for PM₁₀ are very close to those of PM_{2.5} (PM_{2.5}/PM₁₀ ratios within 0.9 to 1.0) pointing to the very fine size of the EC-bearing
15 diesel soot particles.

OM was calculated by multiplying OC by a factor accounting for non-C atoms which may change according to location and existing sources (Turpin and Huntzicker, 2005). This factor ranged from 1.2 (in POR-TR site due its proximity to traffic emissions, Pio et al., 2011) to 1.7–1.8 (rest of sites). Mean levels of OM (Fig. 1) reached 5.0 and
20 5.5 $\mu\text{g m}^{-3}$ in PM₁₀ at BCN-UB and ATH-SUB sites, respectively, but increased up to 9.8 and 15.7 $\mu\text{g m}^{-3}$ at FI-UB and MLN-UB. At POR-TR, mean level of OM was 7.5 $\mu\text{g m}^{-3}$. OM has also a fine grain size since PM_{2.5}/PM₁₀ ratios for this component ranged from 0.7 to 1.0. OM/EC ratios for PM₁₀ ranged from 1.6 at POR-TR, reaching values of 4.4 at the UB site of BCN, 8.2 and 8.7 at the UB sites of MLN and FI and 13 at the
25 SUB site of ATH. This ratio indicates the proximity to the emission sources but also the possible influence of biomass burning. Thus, primary diesel soot is characterised by an OM/EC ratio close to 1.0, whereas a higher ratio indicates a major relative abundance

of secondary OM, due to a longer distance from emission hotspots (from TR to UB to SUB) and/or a higher contribution from biomass burning to PM_x levels, since OM/EC from biomass burning is much higher (Puxbaum et al., 2007). Also biogenic emissions can increase the OM/EC ratio.

Levels of OM+EC accounted for around 27–30 % of the PM_{10} load at the UB and SUB sites, with the exception of FI and MLN (45–58 %). At POR-TR this contribution increased to 37 %. In $PM_{2.5}$ the OM+EC load increased as compared with PM_{10} and reached from 37 to 69 % of the $PM_{2.5}$ mass. This is due mainly to the decrease of mineral dust and sea salt in $PM_{2.5}$ when compared with PM_{10} .

The higher levels of OM recorded at MLN, FI, and partially at POR, are probably the result of a high contribution to PM_{10} levels from biomass burning (BB). This is also confirmed by the high OC/EC ratios. Biomass burning PM emissions are characterised by high OM loads but also by a high OC/EC ratio when compared with traffic emissions. In the case of MLN the frequent atmospheric stagnation episodes also favour the formation of secondary OM as is also described later for nitrate. To a lesser extent this also applies for FI, where stagnant conditions are common during winter.

3.2.2 Sea salt

Sea salt was calculated based on the main composition of sea spray (ss) as the sum: $ssNa + Cl + ssMg + ssK + ssCa + ssSO_4^{2-}$, where $ssNa = Na - nssNa$; $nssNa = 0.348 \times Al$; $ssMg = 0.119 \times ssNa$; $ssK = 0.037 \times ssNa$; $ssCa = 0.038 \times ssNa$; $ssSO_4 = 0.253 \times ssNa$. Mean levels of sea salt (Fig. 1) in PM_{10} reached $0.6\text{--}0.7 \mu\text{g m}^{-3}$ at the inland Italian cities (FI and MLN, 2–3 % of the PM_{10} load) and $1.5\text{--}1.6 \mu\text{g m}^{-3}$ (7–8 % of the PM_{10} load) at the Mediterranean coastal sites. However, at the Atlantic site (POR) much higher levels were recorded ($4.6 \mu\text{g m}^{-3}$ in PM_{10} , 13 % of the PM_{10} load at the TR site).

As expected, due to the coarse mass size distribution of sea salt, levels were reduced by 71–86 % in $PM_{2.5}$ with respect to PM_{10} , with the exception of MLN, where levels of sea salt were only reduced by around 38 % in $PM_{2.5}$.

3.2.3 Mineral dust

5 Mineral dust was calculated based on average crust composition as: $1.15 \times (3.79 \times Al + 2.14 \times Si + 1.67 \times Ti)^{-}$. Mineral dust at UB sites reached around $2.2 \mu g m^{-3}$ as annual mean in FI-UB and $3.8\text{--}4.2 \mu g m^{-3}$ at the UB and SUB sites of BCN, MLN and ATH (Fig. 1). These levels account for 18 and 25 % of the PM_{10} mass at BCN and ATH and 12 and 10 % at FI and MLN, respectively. At POR-TR site mineral dust accounts for
10 12 % of the PM_{10} .

As also expected from the coarse mode of occurrence of mineral dust, levels of this PM component were much lower in $PM_{2.5}$, down to 20–49 % of the PM_{10} levels. The contribution of mineral dust reached from 4 to 10 % of $PM_{2.5}$ for all sites.

3.2.4 Sulphate and nitrate

15 There is a marked geographical variability, with increased levels of sulphate from FI-BCN to POR-MLN to ATH ($1.7\text{--}1.9$ to $2.4\text{--}2.9$ to $3.7 \mu g m^{-3}$ in PM_{10} and $1.5\text{--}1.7$ to 1.9 to $2.9 \mu g m^{-3}$ in $PM_{2.5}$, Fig. 1). This is probably due to the influence of the use of coal and petroleum coke/fuel oil for power generation in or/and around the high sulphate regions of this study, but also it may be caused by the influence of SO_2 emissions from petrochemical plants. In the case of POR, when the site is under the influence of
20 NW winds, one of the major sources of sulphate could be the Porto Refinery (10 km away from the sampling site), which began operating in 1970. It is a crude oil industrial processing plant that has an annual installed capacity of 4.5 million tons and produces a wide range of products including fuels, lubricants, aromatics (BTX) for the petrochemical industry, industrial solvents and petroleum waxes. Emissions from shipping in the
25 harbour may represent another possible source. As expected from the fine mode of

occurrence of ammonium sulphate ((NH₄)₂SO₄ or NH₄HSO₄), 76 to 85 % of sulphate in PM₁₀ is present in PM_{2.5}.

Levels of nitrate in PM₁₀ show a less marked spatial variability, with the exception of MLN, with mean annual levels reaching 1.2 (FI-ATH) to 1.9–2.0 (POR-BCN) and 6.0 μg m⁻³ in MLN. This marked difference between MLN and the rest of the other AIRUSE regions is mainly due to the specific meteorological and emission patterns of the Po Valley. In this case, it coincides with a large urban and industrial agglomeration (with the associated road traffic), with the consequent elevated atmospheric emissions and a peculiar meteorology favouring frequent and marked thermal inversions that cause the accumulation of pollutants and the formation of high levels of ammonium nitrate (NH₄NO₃) from the high anthropogenic NO_x and NH₃ emissions. In particular, high NH₃ levels, emitted from agricultural and animal husbandry activities, can be transported from the southern part of the Po Valley to the urbanised northern part, inducing ammonium nitrate formation. On the other hand, it is noticeable the relatively coarse mode of nitrate in all cases, since levels in PM_{2.5} are generally 50–60 % lower than in PM₁₀, with the exception of MLN by 40 % and the ATH-SUB area by 85 %. These large fractions of coarse nitrate are probably due to the high temperatures and dry conditions reached in summer in the study regions. Especially at higher temperatures, NH₄NO₃ dissociate into gaseous HNO₃ and NH₃, and in turn a fraction of this HNO₃ may react with NaCl or CaCO₃ to give coarse NaNO₃ or Ca(NO₃)₂. This accounts for the large differences observed for nitrate in the coarse and fine size fractions at MLN and ATH, with 60 % of nitrate residing in the fine aerosol at the first site and only 15 % at the latter. The hypothesis of a temperature-driven behaviour of nitrate is reinforced by the seasonal trends of the ratios between fine (PM_{2.5}) nitrate and PM₁₀ nitrate: most of the nitrate, i.e. 60–80 % of it, is in PM_{2.5} during fall and winter, while the percentage drastically decreases during spring-summer, down to roughly 15 %. Seasonal trends are less and less pronounced when passing from cities with a continental climate such as FI (and MLN) to coastal ones with a mild climate such as POR and BCN, and are not visible in ATH, with a warmer climate.

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The contribution of sulphate, nitrate and ammonium (secondary inorganic aerosols, SIA) to the PM_{10} load reaches 15–21 % of PM_{10} in BCN-UB, POR-TR and FI-UB, but 30–31 % at MLN-UB and ATH-SUB. In spite of the prevailing fine mode of these PM components, the contribution of SIA to the $PM_{2.5}$ load remains similar to that of PM_{10} , with 13–23 % and 31–37 % for the above groups of sites. The latter two cities (MLN and ATH) are both characterised by similarly high SIA loads, but due to different causes, whereas at MLN SIA is dominated by ammonium nitrate, in ATH ammonium sulphate prevails.

The ion balances between cations and anions of the daily PM_{10} and $PM_{2.5}$ samples collected at the 5 AIRUSE cities are reported in Fig. S4. The results showed that there was a neutralisation of the acidic components of the PM_{10} and $PM_{2.5}$ in all cases with the exception of FI in the $PM_{2.5}$ fraction. Thus, the balances range from Anions = $0.82 \times$ Cations (BCN, $R^2 = 0.72$) to Anions = $1.0 \times$ Cations (POR, $R^2 = 0.96$). A slope lower than 1.0 means that there is a cation load in excess, probably due to the occurrence of Ca and Mg-bearing carbonate minerals (Alastuey et al., 2005). This is expected to occur specially during African dust episodes (see low anion/cation samples present in the balance of BCN in Fig. S4). In the case of FI $PM_{2.5}$ samples, the regression fits with Anions = $1.12 \times$ Cations ($R^2 = 0.95$) which points to a slightly acidic character of the PM samples with a fraction of 12 % of the anionic species being present as acids.

3.2.5 Secondary vs. primary PM

The amount of secondary aerosol was roughly estimated at each site as:

$$\text{Secondary aerosols: } NO_3^- + SO_4^{2-} + NH_4^+ + (OC - (EC \times a)) \times b \quad (2)$$

where a expresses the primary OC/EC ratio (averaged among existing sources, and varying within 0.7–2.2, Pio et al., 2011) and b accounts for the non-C atoms in secondary aerosol mass (varying within 1.6–2.1). Figure 2 shows that for PM_{10} , at the UB

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and SUB sites the secondary fraction dominated the PM₁₀ mass by contributing from 53 % (BCN) to 71 % (MLN), whereas at POR-TR the primary contribution prevailed (60–63 %). For the calculation of the secondary and primary fractions all values are normalised by the sum of reconstructed PM mass. This high load of secondary PM mass is very important to be taken into account in designing air quality plans, since these components are formed in the atmosphere from organic and inorganic gaseous precursors. The organic and inorganic secondary contributions to PM₁₀ are very well balanced (close to 50–50 % in most cases), but not in the case of FI-UB, where 65 % of the secondary PM₁₀ load is from organic aerosols (Fig. 2), indicating probably a relative contribution from biomass burning compared with the other sources. The contributions of secondary aerosols to PM_{2.5} increase when compared with PM₁₀ due to the lower contributions of dust and sea salt to the fine fraction. This secondary contribution then ranged from 66 % (BCN) to 82 % (ATH) in the UB and SUB sites and 37 % at POR-TR (Fig. 2).

3.2.6 Biomass burning tracers

Levels of levoglucosan and K are considered as tracers for biomass burning (Fine et al., 2001; Gonçalves et al., 2010; Nava et al., 2014). In fact, levoglucosan is a sugar emitted into the atmosphere exclusively by breaking cellulose chains during biomass burning. Levoglucosan levels varied by one order of magnitude: 22 (BCN), 37 (ATH), 287 (FI), 303 (MLN) and 413 (POR) ng m⁻³ in PM_{2.5} (Table 1), reflecting a very clear difference of the impact of biomass burning on air quality across southern European cities. The values obtained should be considered as minimum levels because it is well known that levoglucosan may be degraded in highly oxidising environments (Simoneit et al., 1999). This impact is mostly due to differences in using biomass burning for domestic purposes, but also in POR and MLN peak events were detected in summer as a consequence of the impact of the emissions of forest fires and/or agricultural fires. The decreasing impact of biomass burning on PM_{2.5} levels when passing from MLN to FI to POR to ATH and to BCN is clearly demonstrated by the time series of daily

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levels of levoglucosan (Table 1). The lower values for Athens can be also attributed to the suburban character of the site. On the other hand, levels of K in the fine fraction ($PM_{2.5}$) may also increase as a consequence of the influence of inorganic biomass burning ash contributions to the PM load. In this case, the differences are also evident but less marked than for levoglucosan: 89 (BCN), 115 (ATH), 178 (FI), 343 (POR) and 348 (MLN) $ng\ m^{-3}$ in $PM_{2.5}$ (Table 1). This lower differentiation is due to the fact that K may be partially supplied by mineral dust (clay minerals and feldspars) and probably by specific industrial sources.

3.2.7 Trace elements

Levels of Ti, Mn, Sr, Cu, Zn, Sn, Ni, Ba and Pb are higher in MLN, and in some cases in POR (Zn, Ba, Pb, Cd), when compared with the other sites. Most of these elements are usually related to metallurgy and heavy industry emissions.

Levels of As and Se (generally used as tracers of coal combustion) were relatively higher in POR and ATH pointing to a possible local, regional or long range transport influence of emissions from coal combustion sources on air quality. Northern Greece has a number of large coal fired power plants that may partly account for these concentration levels. Transport of emissions from coal fired power plants from the Balkans, Eastern Europe and Turkey may also contribute. In the case of POR, the coal power plant located 15 km southeast of Porto was deactivated in December 2004 and there was no coal combustion activity at the area during the campaign. The closest coal fired power plant is located in Northwestern Spain, at around 300 km from Porto. Is it possible that other industrial sources of As and Se (ceramic, glass, and cement production, among others) may also contribute to increased levels of these elements.

Levels of Cu, Sb, Ba and Sn were relatively higher in POR-TR as compared with UB sites, due to their association with non-exhaust vehicle emissions including brake and tyre wear (Gietl et al., 2010).

Levels of V were 4 to 2 times higher in the cities with a harbour (POR, BCN and ATH) pointing to the fact that, in spite of the possible use of fuel oil or petroleum coke

for power generation or industrial processes, shipping emissions are the main sources of these heavy oil combustion tracers in these AIRUSE cities.

Rare Earth Elements (REEs) are usually occurring in mineral dust and the ratio Ce/La in the Earth's crust is close to 2. The marked decrease of this ratio may be used as a tracer of the influence of emission from La-based oil cracking in petrochemical plants. In this study most of the cities have a ratio Ce/La close to 2.0 with the exception of FI and ATH (1.0 and 1.3), this indicating the possible influence of this type of emissions at both sites, although other sources for La cannot be discounted. In Athens the refinery is located 15 km northwest of city center, while in Florence about 90 km away to the West, in the province of Livorno.

The unaccounted mass of PM is that resulting from the difference of the gravimetric measurements of the filters and the sum of all the components determined by chemical analysis. This unaccounted mass is usually attributed to water molecules contained in potential remaining moisture, and crystallisation and formation water (water molecules in the structure of specific chemical species), as well as heteroatoms contained in the organic species and not analysed. In this study the unaccounted mass was higher at BCN-UB and POR-TR (23 and 31 % for PM₁₀ and PM_{2.5}, respectively) and similarly lower (5–14 %) in all the other sites.

3.2.8 Source apportionment results

For each AIRUSE station, the best PMF solution was found pooling PM₁₀ and PM_{2.5} samples in a single input matrix for PMF. This method is not new, as it was already proven to increase considerably the statistical significance of the analysis, although it assumes that the chemical profiles of sources do not vary between PM_{2.5} and PM₁₀ (Amato et al., 2009). Depending on site, different constraints were added into the PMF model (Paatero and Hopke, 2008), in order to reduce rotational ambiguity and drive the iterations towards a more realistic solution. Table 2 summarises the constraint use in each case, as well as the increment of dQ (Amato et al., 2009). Auxiliary equations were therefore introduced, by means of the USEPA software, and included both

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physical and chemical constraints, which in all cases were accomplished with a total increase in dQ within 3–19 %.

The distribution of residuals, G-space plots, Fpeak values and Q values were explored for solutions with number of factors varying between 6 and 11. Table 2 also lists the factors/source finally identified in each case, which varies within 8 and 10. Five factors were commonly found at all sites: vehicle exhaust (VEX), vehicle non-exhaust (NEX), secondary nitrate (SNI), sea salt (SEA) and mineral dust (MIN). The biomass burning (BB) source was also found at all sites, except for BCN-UB where 96 % of homes are heated by natural gas. The secondary sulphate and organics (SSO) factor was separated from the heavy oil combustion (HOC) only in BCN-UB, FI-UB and ATH-SUB, while in MLN-UB and POR-TR, these two factors were combined in a composite heavy oil and secondary (HOS) factor. In addition the IND source was identified at BCN-UB, POR-TR and MLN-UB, while possible industrial contributions in FI-UB and ATH-SUB would be included in the HOC factor. Finally, in FI-UB two sea salt factors (Aged and Fresh) and two mineral dust factors (Local and Saharan dust) were separated.

The NEX source generally shows a mixed composition (Fig. 3), including crustal species (Fe, Ca, Al, Si among others), carbonaceous compounds (EC generally higher than OC) and trace elements (Cu, Zn, Mn and occasionally Sn, Sb and Ba) from brake wear (see percentage of species in Fig. 5). However, rather dissimilar chemical profiles were found comparing different cities. Although the enrichment in Fe is common to all the cities, the main component of NEX can be either Ca (in BCN-UB), EC (in POR-TR and MLN-UB), OC (in FI-UB), or S (in Athens-SUB). These differences can be due to several factors:

- the proximity to the source: at the traffic site (POR-TR) the NEX source is dominated by the brake wear (EC)
- the climatic conditions: ca is higher in drier regions (BCN-UB and ATH-SUB) due to the enhanced resuspension, when compared to POR-TR and MLN-UB

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- the type of materials used for brakes and road pavement (the higher OC in Florence might be due to higher road wear compared to other cities).
- the “rotational ambiguity” of receptor modelling which may produce false bias.

Other important differences are the absence of OC in POR-TR (again likely due to the dominance of brake wear particles) and in ATH-SUB, the high abundance of NO_3^- in POR-TR and NH_4^+ in Athens. Note that some elements are absent in some cities since they were not used for the source apportionment study (see Table 2).

The VEX source at all cities is almost totally composed by carbonaceous aerosol (Fig. 3), with the sum of OC+EC approximately 90–98 % of the mass. The ratio OC/EC varies widely among different cities. The lowest OC/EC value was found at the traffic site of Porto (POR-TR) due to its proximity to the source and the consequent lower proportion of secondary OC. The value varies within 1.8–3.7 at the UB sites, probably linked to the distance from main roads (BCN-UB, MLN-UB and FI-UB). A much higher value (16.4) is observed in ATH-SUB due to the reduced share of diesel vehicles in the local fleet. Besides EC and OC, other components rarely reach 1 % of the mass: Zn in MLN-UB, S in BCN-UB and POR-TR due to their relatively higher content in diesel fuel and/or to engine oil anti-wear additive ZDDP. Potassium is present in all unleaded fuels (Spencer et al., 2006) and it is also used as an antifreeze inhibitor and as an additive in some oil types.

The annual mean contributions for VEX and NEX sources and associated errors for each city are showed in Fig. 6. The error estimates were calculated based on the standard error of the coefficients of a multiple regression between the daily PM concentration (independent variable) and the source contributions for that day (dependent variables). As result we obtained the symmetric error for each source contribution (Fig. 6).

The sum of VEX and NEX contributions to PM_{10} varies significantly in absolute terms ($3.9\text{--}10.8\ \mu\text{g m}^{-3}$) with the maximum found at POR-TR; the fractional contribution to PM_{10} is within 16–32 %. Similarly in $\text{PM}_{2.5}$ absolute annual contributions vary within

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the range 2.3–9.4 $\mu\text{g m}^{-3}$ but the percentage is quite constant within 15–36 % (Fig. 4). For the total contribution one should add the fraction of secondary nitrate attributable to traffic but the lack of linearity between emissions and concentrations and the uncertainty in emission inventoring do not allow for a robust estimate. Although the importance of NEX source has been increasing during the last decade due to the lack of mitigation measures, VEX contribution is still generally higher than NEX. However the difference (in PM_{10}) between the VEX and NEX contribution is not significant at BCN-UB, FI-UB and ATH-SUB sites, which can be generally interpreted as an equal contribution from the two sub-sources. At the TR site (POR-TR) the VEX contribution is significantly higher (by a factor > 2).

In $\text{PM}_{2.5}$ the share between VEX and NEX varies considerably depending on the site (Fig. 6). At POR-TR, BCN-UB, FI-UB and ATH-SUB the emissions from VEX have higher contribution, while not in MLN-UB. The NEX contribution is significantly lower in $\text{PM}_{2.5}$ due to the coarser size distribution; only in MLN-UB the VEX and NEX contributions in $\text{PM}_{2.5}$ are similar. The daily variation of source contributions at all sites can be seen in Fig. S5.

Individual source contributions were also averaged during only days of exceedances of the PM_{10} daily limit value ($50 \mu\text{g m}^{-3}$), except in BCN-UB where this threshold was never reached and $40 \mu\text{g m}^{-3}$ was used. During exceedance days (or high pollution days), the sum of VEX and NEX contributions changes in PM_{10} and $\text{PM}_{2.5}$ respectively from 25 and 21 % to 27 and 22 % in BCN-UB, from 31 and 31 % to 43 and 32 % in FI-UB, from 16 and 15 % to 19 and 13 % in MLN-UB, from 18 and 20 % to 7 and 10 % in ATH-SUB and from 31 and 37 % to 31 and 33 % in POR-TR (Table 3).

Secondary nitrate (SNI) factor reproduces nearly the totality of the mass of ammonium nitrate formed from NO_x precursors emitted from traffic, biomass burning and industries. The contribution of road traffic to this factor is unknown. The composition of this factor (Fig. 3) is very similar among the different cities, NO_3^- being the main component (28–50 %). Nitrate is usually neutralised by ammonium (5–16 %) or in the case of ATH-SUB by Na (11 %). Another important component is OC representing the

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secondary organics that can condense on the surface of the ammonium nitrate particles. EC is also present in significant concentrations (> 1 %) although not in the case of POR-TR where other primary elements can be observed in this profile (Si, Al, Ca, Fe and K). As previously explained the traffic-related share of secondary nitrate is unknown but in most of sites it is likely to be very important: as an example one should consider that the traffic share of the NO_x emission inventory for the study areas is between 30 and 80 %. However the high uncertainty in emission inventory (mostly for the lack of biomass combustion emissions) does not allow drawing quantitative estimates. The secondary nitrate annual average contributions to PM₁₀ range from 2.2 μg m⁻³ in FI-UB, 3.2 μg m⁻³ in POR-TR, BCN-UB and ATH-SUB, and 10.0 μg m⁻³ in MLN-UB. For PM_{2.5} the annual contributions are in the range between 0.7 μg m⁻³ (ATH-SUB) to 8.5 μg m⁻³ in MLN-UB. As already mentioned these high nitrate levels in the Po Valley are due to several factors: (i) a large urban and industrial agglomeration and associated road traffic, (ii) an intensive use of biomass burning in the basin, (iii) high NH₃ levels, emitted from agricultural and animal husbandry activities, (iv) the peculiar meteorology favouring frequent and marked thermal inversions.

Depending on the geography of each site, sea salt can reach the receptor in a “fresh” or “aged” form, or both. The main chemical difference is the absence of chlorine in the aged sea salt coupled with the presence of the nitrates which means that sodium is in the form of sodium nitrate. Fresh sea salt was identified at POR-TR, FI-UB and ATH-SUB, while aged sea salt was found at MLN-UB, FI-UB and BC-UB. As shown in Fig. 3, the mass fraction of nitrate (μg μg⁻¹) is considerably higher in the aged profiles, by one order of magnitude when compared to the fresh profile. In FI-UB, where both fresh and aged factors were found, nitrate is absent in the fresh sea salt and chlorine is absent in the aged factor, which shows also particularly high level of OC indicating the mixing of the aged sea salt with anthropogenic plumes. In all factors the absence of ammonium indicates clearly the neutralisation of nitrate by sodium. Mean contributions of sea salt (Fig. 5) in PM₁₀ were revealed to be generally higher (by 25 %) than what was found with the chemical speciation (2.5 vs. 1.5 μg m⁻³ in BCN-UB, 5.5 vs. 4.4 μg m⁻³ in POR-

under the influence of NW winds, probably due to the emissions from the Porto Refinery, a plant carrying out crude oil industrial processing for the petrochemical industry.

During exceedance days (or high pollution days), the SSO contribution in PM_{10} – $PM_{2.5}$ always decreases from 26–37 to 19–22 % in BCN-UB, from 10–13 to 5–2 % in POR-TR, from 21–30 to 6–6 % in FI-UB, from 14–19 to 9–11 % in MLN-UB, and from 20–33 to 2–5 % in ATH-SUB (Table 3).

Saharan dust was separated from local dust only at FI-UB, BCN-UB and ATH-SUB (by means of PMF in FI and by the percentile method for BCN and ATH). In MLN-UB and POR-TR the contribution of Saharan dust was estimated as negligible. The chemical profile of Saharan dust (as estimated in FI-UB by PMF) shows a composition very close to the average of the earth's crust, with enrichment factors (EF), calculated with respect to Al using the average continental crust composition reported by (Mason, 1966; Rahn, 1976), that are all close to one: 0.99 (Mg), 0.83 (Si), 1.08 (K), 0.92 (Ca), 1.0 (Ti) and 1.1 (Fe) (Fig. 3). The annual mean Saharan dust contribution during AIRUSE sampling days was estimated as $0.3 \mu\text{g m}^{-3}$ (1 %) in BCN-UB, $0.7 \mu\text{g m}^{-3}$ (4 %) in FI-UB, and $3.0 \mu\text{g m}^{-3}$ (14 %) in ATH-SUB (Fig. 5). This large difference is due to the Southern location of Athens, and the severity of some Saharan dust episodes in the eastern part of the Basin with higher frequency than average, during the period of this study. As mentioned by previous studies, Saharan dust transport occurs in different seasons in western and eastern sides of the Mediterranean (Querol et al., 2009; Pey et al., 2013). Saharan dust inputs in the western side of the Mediterranean are considerably higher between May and October, and in March, when compared to the rest of the year. On the contrary, such inputs are clearly higher between November and May in the eastern part of the Mediterranean. An intermediate outcome is observed for central locations in the Mediterranean, where only slightly higher summer contributions are detected (Pey et al., 2013). For $PM_{2.5}$ the SAH contribution was estimated only at FI-UB ($0.2 \mu\text{g m}^{-3}$) and ATH-SUB ($0.7 \mu\text{g m}^{-3}$), with $PM_{2.5}/PM_{10}$ ratio equal to 0.2 in both cases. Concerning PM exceedances, the relative burden of Saharan dust increases during exceedance days only in ATH-SUB, where it is on average the main

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to Autumn at all cities (Fig. S5). Above the background contributions, sporadic peaks are also found, mostly at POR-TR, probably related to road dust emissions, not well completely included in the NEX factor.

As already mentioned, the contribution of heavy oil combustion was separated only at the cities nearest to the Mediterranean shipping routes (BCN, FI and ATH) in spite of the fact that V and Ni concentrations in POR-TR were twice as high as in FI-UB. In POR-TR and MLN-UB, the HOC source is mixed with the SSO in the combined source HOS. HOC particles are commonly composed by EC, OC and S explaining the high variance of V and Ni. The difference between AIRUSE sites concerns only specific trace elements such as Zn, Sn, Ba (in BCN-UB), Ba and Se (in FI-UB), Sr and Sb (in ATH-SUB), although only a small amount of variance of these elements is explained by HOC (Fig. 6). The annual contribution of HOC is practically the same in BCN-UB, FI-UB and ATH-SUB ($0.9 \mu\text{g m}^{-3}$ in PM_{10} and $0.8 \mu\text{g m}^{-3}$ in $\text{PM}_{2.5}$). The contribution in POR-TR and MLN-UB could not be separated from the composite HOS. The daily variation of HOC contributions, as estimated by PMF is shown in Fig. S5. In FI-UB and BCN-UB higher contributions are observed in summer due to the higher air circulation, which favours their transport and distribution across the regional area, while in ATH-SUB no clear seasonal trend is observed for HOC probably because of the variety of the sources that may contribute to this factor (residential heating and shipping).

During exceedance days (or high pollution days), the HOC contribution in PM_{10} – $\text{PM}_{2.5}$ does not change significantly.

The impact of industrial emissions was identified in only three cities: BCN-UB, POR-TR and MLN-UB. Florence and Athens are in fact the less industrialised cities among the AIRUSE consortium. In the three industrialised cities, OC and Fe are commonly present as main components (Fig. 3). Besides OC and Fe, in BCN-UB and POR-TR the presence of Zn, Pb, S, Cu, Cd, Sb and Mn indicate high temperature metal processing, pointing at the smelters located SW of BCN-UB and East of POR-TR. In MLN-UB the industrial source presents a different chemical profile with NO_3^- , EC, Ca, Cl as main components (together with OC and Fe) and a high variance of Cr, Ni, Cu and Mn

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explained, suggesting a more mixed origin, including metallurgy and also construction activities (Fig. 6). The impact of industrial emissions upon PM_{10} and $PM_{2.5}$ is similarly low at MLN, POR and BCN, ranging within $1.2\text{--}1.7\ \mu\text{g m}^{-3}$ as annual means and with a $PM_{2.5}/PM_{10}$ ratio close to 1. No typical seasonal trend is observable at any site (Fig. S5). The contribution was rather constant throughout the year (around $1\ \mu\text{g m}^{-3}$ daily) in MLN-UB and BCN-UB, while elevated peaks (up to $13\ \mu\text{g m}^{-3}$ as a daily mean) are registered in POR-TR, mostly in the warmer months. During exceedance days (or high pollution days), the IND contribution in $PM_{10}\text{--}PM_{2.5}$ slightly increases from 11–12% to 17–19% in BCN-UB, and decreases from 4–5% to 2–1% in POR-TR, and from 9–5% to 4–3% in MLN-UB (Table 3).

As previously shown, concentrations of levoglucosan varied by over one order of magnitude among the AIRUSE cities, indicating very contrasting scenarios across the Mediterranean for emissions from biomass burning. Similarly, the PMF identified a biomass burning source only in four of the five cities due to the low levels of levoglucosan in BCN-UB ($22\ \text{ng m}^{-3}$ as annual mean). In all other cities, levoglucosan is the main tracer in the chemical profile of the biomass burning source identified by PMF (except in ATH-SUB, where levoglucosan was not used as input species for PMF due to the high S/N ratio). Levoglucosan represents 4–8% of PM mass emitted by biomass burning; OC and EC are the major components in the BB profile (12–65% and 4–14%, respectively). In spite of these quite large ranges (which can be due to the rotational ambiguity of PMF), the OC/EC ratio can be used as a more robust diagnostic of BB composition. The OC/EC ratio in BB aerosols varies from 2.6 (ATH-SUB), 2.9 (POR-TR), 4.6 (MLN-UB) to 6.1 (FI-UB) which may be explained by a higher proportion of secondary organic aerosols in MLN-UB and FI-UB or by different wood types and combustion appliances. Also K (probably the soluble fraction) tracks BB aerosols, representing 2–4% of the mass. Other components can be observed, although more sporadically, such as Cl, S, Zn, Pb, NH_4^+ and NO_3^- (Figs. 3 and 6). BB contributions reproduce quite well the gradients found for levoglucosan among the AIRUSE cities. Although levoglucosan has been detected in some samples from BCN, biomass burning could

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not be assigned as a significant contributor to PM. In the other cities, an annual mean of 1.2–1.4 $\mu\text{g m}^{-3}$ (7–11 %) is estimated in ATH-SUB, 2.9–3.0 $\mu\text{g m}^{-3}$ (15–21 %) in FI-UB, 4.2–4.4 $\mu\text{g m}^{-3}$ (12–17 %) in POR-TR, up to 7.8–5.3 $\mu\text{g m}^{-3}$ (20–18 %) in MLN-UB. Therefore, this reveals quite a contrasting impact of BB emissions across the Mediterranean depending on the type of fuel and combustion device used in each region for residential heating. Differently from other cities, Barcelona is well supplied with natural gas for residential heating; Florence is also well supplied with natural gas but the suburbs on the hill are often provided with chimneys. Even in Milan the use of natural gas for heating is very extensive, however, also due to the current economic crisis, many citizens are equipped with small pellet stoves. In ATH the BB source is also associated with tracers of waste combustion, such as As, Cd, Sb and Pb, with explained variance ranging between 12 and 72 %, as citizens of Athens have turned to alternative heating fuels, such as wood, due to the economic crisis and the increased prices of diesel oil, which has been the regular means of residential heating in Greece. In many cases, treated wood or even combustible wastes are now used as fuel. As previously shown for the traffic source, another factor identified by PMF was secondary nitrate (SNI). Although in urban environments nitrate mainly arises from NO_x from traffic, a substantial fraction can also be derived from biomass burning emissions. Therefore for each city, the corresponding share of NO_x due to biomass burning can be applied also to SNI. Based on this approach, percentages of 16 and 13 were adopted in POR-TR and MLN-UB, respectively, to account for SNI from biomass burning. In FI-UB, on the basis of the emission inventory, about 10 % of NO_x emissions are due to domestic heating, with only 2 % attributable to stoves and chimneys (<http://servizi2.regione.toscana.it/aria/>); it is however suspected that these data underestimate the contribution of domestic heating BB to NO_x . Thus, the total contribution from BB in FI-UB can be appraised as the sum $\text{BB} + 0.02 \times \text{SNI}$, which results in 3.1 and 2.9 $\mu\text{g m}^{-3}$ in PM_{10} (16 %) and $\text{PM}_{2.5}$ (21 %), respectively. In POR-TR, the total contribution from BB was estimated to be 4.7 $\mu\text{g m}^{-3}$ (13 % of PM_{10}) and 4.7 $\mu\text{g m}^{-3}$ (18 % of $\text{PM}_{2.5}$). In MLN-UB, the total

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pollution as main causes of the PM pollution in the city. In $PM_{2.5}$ the mineral dust + sea salt contribution is reduced to 1/6 of the mass, the OM+EC contribution increases to around 2/3 with the remaining part being made by SIA, slightly reduced with respect to PM_{10} because 50 % of nitrate has a coarse mode of occurrence.

- Athens suburban background: for PM_{10} the average composition is similar to that described for BCN, but with slightly higher mineral dust (25 %) + sea salt (9 %) contribution and much higher sulphate load (19 %). This differentiation may arise from the higher African dust influence and the higher coal or S-rich heavy oil combustion emissions in this region of the EU or from the influence of Eastern/Southeastern European countries and Turkey. In $PM_{2.5}$ the influence of ammonium sulphate is very large (sulphate alone is the 26 % of the $PM_{2.5}$ mass) indicating the high influence from coal combustion or other S-bearing fuels. The remaining $PM_{2.5}$ mass is dominated by OM+EC (another 45 %). Levels of SIA are slightly reduced with respect to PM_{10} because 85 % of nitrate has a coarse mode of occurrence.
- Florence urban background: PM_{10} has a predominant OM component (52 %), probably due to a high contribution from biomass burning from the domestic sector, 18 % of SIA and around 15 % of mineral dust (12 %) and sea salt (3 %). The dominant secondary origin of PM_{10} (56 %) is partially favoured by the high emissions, with a relevant contribution from biomass burning, and the specific stagnant conditions and reduced boundary layer depths. The OM contribution is in even higher in $PM_{2.5}$ (OM+EC, 69 %) and the other contributions are relatively reduced with respect to PM_{10} . Again 50 % of the PM_{10} nitrate is not present in $PM_{2.5}$ due to the occurrence of coarse nitrate.
- Milan urban background: PM_{10} is also dominated by OM (around 40 %), but with a very high contribution of ammonium nitrate (22 %) and relatively low mineral dust (10 %) and sea salt (2 %) contributions. The high concentrations of secondary

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components in PM_{10} (71 %) are partially favoured by the high emissions and the specific stagnant conditions and reduced boundary layer depths induced by the typical meteorology of the Po Valley. The composition of $PM_{2.5}$ is similar to PM_{10} but with higher loads of OM+EC (45 %) and ammonium nitrate (23 %), but reduced sea salt and mineral loads (1 and 4 %). In this case most of the nitrate in PM_{10} is present in $PM_{2.5}$ (94 %) pointing to the predominance of fine ammonium nitrate over coarse nitrate as described in the other sites.

- Porto traffic site: OM+EC represents 37 % of PM_{10} (14 % EC), while SIA and dust are about 12–15 % each and sea salt 13 %. High proportion of sea salt, EC and OM are higher are due to the Atlantic location of Porto and to the higher influence of fuel (both fossil and biomass) combustion. In $PM_{2.5}$ the composition is similar but with an increased proportion of OM+EC (29+19 %) and reduced of mineral dust and sea salt (8 and 5 %). SIA levels are slightly reduced with respect to PM_{10} because 40 % of nitrate has a coarse mode of occurrence.

The sum of vehicle exhaust and vehicle non-exhaust emissions is unequivocally the most important source of PM_{10} (18–31 % at all sites, except in MLN-UB where SNI and SSO dominate the mass), while for $PM_{2.5}$ it is clearly the largest source for POR-TR (37 %), the second one at BCN-UB, FI-UB and ATH-SUB after Secondary sulphate and organics (which likely receives significant transboundary contribution). In $PM_{2.5}$ MLN-UB Secondary nitrate is the main contributor although it does not identify one specific source.

Another important “source” of PM_{10} (20–26 %) is secondary sulphate and organics at BCN-UB, FI-UB and ATH-SUB, while this only represents 14 % of PM_{10} in MLN-UB and 10 % of PM_{10} in POR-TR. The relative importance of Secondary sulphate and organics is higher in $PM_{2.5}$ (19–37 % at SUB and UB sites and 13 % in POR-TR). The contributions (in $PM_{2.5}$) progressively increase from POR-TR ($3.4 \mu\text{g m}^{-3}$), ATH-SUB ($3.8 \mu\text{g m}^{-3}$), FI-UB ($4.1 \mu\text{g m}^{-3}$) to MLN-UB and BCN-UB ($5.6 \mu\text{g m}^{-3}$).

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Another important source of PM₁₀ is biomass burning (13% in POR-TR, 16% in FI-UB, and 24% in MLN-UB), although it is only 7% in ATH-SUB and negligible in BCN-UB. In PM_{2.5}, BB is the second most important source in MLN-UB (21%) and in POR-TR (18%), the third in FI-UB (21%) and ATH-SUB (11%), but again negligible (< 2%) in BCN-UB. This large discrepancy among cities is mostly due to the degree of penetration of wood (and its derivatives) as fuel for residential heating. In Barcelona natural gas is very well supplied across the city and used as fuel in 96% of homes, while, in other cities, PM levels increase on an annual basis by 1–6 μg m⁻³ due to this source.

Other significant anthropogenic sources are:

- Local dust, 7–12% of PM₁₀ at SUB and UB sites and 18% at the TR site, revealing a contribution from road dust resuspension. In PM_{2.5} percentages decrease to 2–7% at SUB-UB sites and 15% at the TR site.
- Industries, mainly metallurgy contributing 4–11% of PM₁₀ (5–12% in PM_{2.5}), but only at BCN-UB, POR-TR and MLN-UB. No clear impact of industrial emissions was found in FI-UB and ATH-SUB.
- Natural contributions consist of Sea salt (16% of PM₁₀ in POR-TR but only 2–7% in the other cities) and Saharan dust (14% in ATH-SUB) but less than 4% in the other cities.
- Other sources of non-fossil OC, such as food cooking and enhanced biogenic secondary aerosols could not be separated due to the lack of AMS techniques.

During high pollution days, the largest specific source (i.e. excluding SSO and SNI) of PM₁₀ and PM_{2.5} are: VEX+NEX in BCN-UB (27–22%) and POR-TR (31–33%), BB in FI-UB (30–33%) and MLN-UB (35–26%) and Saharan dust in ATH-SUB (52–45%) During those days, there are also quite important Industrial contributions in BCN-UB (17–18%) and Local dust in POR-TR (28–20%).

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References

Alastuey, A., Querol, X., Castillo, S., Escudero, M., Avila, A., Cuevas, E., Torres, C., Romero, P.-M., Exposito, F., García, O., Diaz, J. P., Van Dingenen, R., and Putaud, J. P.: Characterisation of TSP and PM_{2.5} at Izaña and Sta. Cruz de Tenerife (Canary Islands, Spain) during a Saharan Dust Episode (July 2002), *Atmos. Environ.*, 39, 4715–4728, 2005.

Allan, J. D., Williams, P. I., Morgan, W. T., Martin, C. L., Flynn, M. J., Lee, J., Nemitz, E., Phillips, G. J., Gallagher, M. W., and Coe, H.: Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities, *Atmos. Chem. Phys.*, 10, 647–668, doi:10.5194/acp-10-647-2010, 2010.

Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., and Hopke, P. K.: Quantifying road dust resuspension in urban environment by Multilinear Engine: a comparison with PMF2, *Atmos. Environ.*, 43, 2770–2780, 2009.

Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe OJ L 152, Official Journal of the European Union, 1–44, 11 June 2008.

Crippa, M., DeCarlo, P. F., Slowik, J. G., Mohr, C., Heringa, M. F., Chirico, R., Poulain, L., Freutel, F., Sciare, J., Cozic, J., Di Marco, C. F., Elsasser, M., Nicolas, J. B., Marchand, N., Abidi, E., Wiedensohler, A., Drewnick, F., Schneider, J., Borrmann, S., Nemitz, E., Zimmermann, R., Jaffrezo, J.-L., Prévôt, A. S. H., and Baltensperger, U.: Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris, *Atmos. Chem. Phys.*, 13, 961–981, doi:10.5194/acp-13-961-2013, 2013.

Draxler, R. R. and Rolph, G. D.: HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT_

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info.php, last access: 28 August 2015), NOAA Air Resources Laboratory, Silver Spring, MD, 2003.

Eeftens, M., Beelen, R., De Hoogh, K., Bellander, T., Cesaroni, G., Cirach, M., Declercq, C., Dedele, A., Dons, E., De Nazelle, A., Dimakopoulou, K., Eriksen, K., Falq, G., Fischer, P., Galassi, C., Gražulevičiene, R., Heinrich, J., Hoffmann, B., Jerrett, M., Keidel, D., Korek, M., Lanki, T., Lindley, S., Madsen, C., Mölter, A., Nádor, G., Nieuwenhuijsen, M., Nonnemacher, M., Pedeli, X., Raaschou-Nielsen, O., Patelarou, E., Quass, U., Ranzi, A., Schindler, C., Stempfelet, M., Stephanou, E., Sugiri, D., Tsai, M.-Y., Yli-Tuomi, T., Varró, M. J., Vienneau, D., Klot, S. V., Wolf, K., Brunekreef, B., and Hoek, G.: Development of land use regression models for PM_{2.5}, PM_{2.5} absorbance, PM₁₀ and PM_{coarse} in 20 European study areas. Results of the ESCAPE project, *Environ. Sci. Technol.*, 46, 11195–11205, 2012.

Fine, P. M., Cass, G. R., and Simoneit, B. R. T.: Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States, *Environ. Sci. Technol.*, 35, 13, 2665–2675, 2001.

Gietl, J. K., Lawrence, R., Thorpe, A. J., and Harrison, R. M.: Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road, *Atmos. Environ.*, 44, 141–146, 2010.

Gonçalves, C., Alves, C., Evtugina, M., Mirante, F., Pio, C., Caseiro, A., Schmidl, C., Bauer, H., and Carvalho, F.: Characterisation of PM₁₀ emissions from wood stove combustion of common woods grown in Portugal, *Atmos. Environ.*, 44, 4474–4480, 2010.

Gonçalves, C., Alves, C., and Pio, C.: Inventory of fine particulate organic compound emissions from residential combustion in Portugal, *Atmos. Environ.*, 50, 297–306, 2012.

Henry, R. C., Hidy, G. M. Multivariate analysis of particulate sulphate and other air quality variables by principal components – Part I: Annual data from Los Angeles and New York, *Atmos. Environ.*, 13, 1581–1596, 1979.

Hodzic, A., Madronich, S., Bohn, B., Massie, S., Menut, L., and Wiedinmyer, C.: Wildfire particulate matter in Europe during summer 2003: meso-scale modeling of smoke emissions, transport and radiative effects, *Atmos. Chem. Phys.*, 7, 4043–4064, doi:10.5194/acp-7-4043-2007, 2007.

Hoyle, C. R., Boy, M., Donahue, N. M., Fry, J. L., Glasius, M., Guenther, A., Hallar, A. G., Huff Hartz, K., Petters, M. D., Petäjä, T., Rosenoern, T., and Sullivan, A. P.: A review of the anthropogenic influence on biogenic secondary organic aerosol, *Atmos. Chem. Phys.*, 11, 321–343, doi:10.5194/acp-11-321-2011, 2011.

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Kostenidou, E., Florou, K., Kaltsonoudis, C., Tsiplikiotou, M., Vratolis, S., Eleftheriadis, K., and Pandis, S. N.: Sources and chemical characterization of organic aerosol during the summer in the eastern Mediterranean, *Atmos. Chem. Phys. Discuss.*, 15, 3455–3491, doi:10.5194/acpd-15-3455-2015, 2015.

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.

Kukkonen, J., Pohjola, M., Sokhi, R. S., Luhana, L., Kitwiroon, N., Fragkou, L., Rantamäki, M., Berge, E., Ødegaard, V., Slørdal, L. H., Denby, B., Finardi, S.: Analysis and evaluation of selected local-scale PM₁₀ air pollution episodes in four European cities: Helsinki, London, Milan and Oslo, *Atmos. Environ.*, 39, 2759–2773, 2005.

Lianou, M., Chalbot, M.-C., Kavouras, I. G., Kotronarou, A., Karakatsani, A., Analytis, A., Katsouyanni, K., Puustinen, A., Hameri, K., Vallius, M., Pekkanen, J., Meddings, C., Harrison, R. M., Ayres, J. G., ten Brick, H., Kos, G., Meliefste, K., de Hartog, J., and Hoek, G.: Temporal variations of atmospheric aerosol in four European urban areas, *Environ. Sci. Pollut. R.*, 18, 1202–1212, 2011.

Lucarelli, F., Calzolari, G., Chiari, M., Giannoni, M., Mochi, D., Nava, S., and Carraresi, L.: The upgraded external-beam PIXE/PIGE set-up at LABEC for very fast measurements on aerosol samples, *Nucl. Instrum. Methods Phys. Res. B*, 318, 55–59, 2014.

Manders, A. M. M., Schaap, M., Querol, X., Albert, M. F. M. A., Vercauteren, J., Kuhlbusch, T. A. J., and Hoogerbrugge, R.: Sea salt concentrations across the European continent, *Atmos. Environ.*, 44, 2434–2442, 2010.

Mason, B.: *Principles of Geochemistry*, 3rd edn., Wiley, New York, 1966.

Mohr, C., DeCarlo, P. F., Heringa, M. F., Chirico, R., Slowik, J. G., Richter, R., Reche, C., Alastuey, A., Querol, X., Seco, R., Peñuelas, J., Jiménez, J. L., Crippa, M., Zimmermann, R., Baltensperger, U., and Prévôt, A. S. H.: Identification and quantification of organic aerosol from cooking and other sources in Barcelona using aerosol mass spectrometer data, *Atmos. Chem. Phys.*, 12, 1649–1665, doi:10.5194/acp-12-1649-2012, 2012.

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Paatero, P.: The multilinear engine – a table-driven least squares program for solving multilinear problems, including the n-way parallel factor analysis model, *J. Comput. Graph. Stat.*, 8, 854–888, 1999.

Paatero, P. and Hopke, P. K.: Discarding or downweighting high-noise variables in factor analytic models, *Anal. Chim. Acta*, 490, 277–289, 2003.

Paatero, P. and Hopke, P. K.: Rotational tools for factor analytic models implemented by using the multilinear engine, *Chemometrics*, 23, 91–100, 2008.

Paatero, P. and Tapper, U.: Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, 5, 111–126, 1994.

Pey, J., Querol, X., Alastuey, A., Forastiere, F., and Stafoggia, M.: African dust outbreaks over the Mediterranean Basin during 2001–2011: PM₁₀ concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology, *Atmos. Chem. Phys.*, 13, 1395–1410, doi:10.5194/acp-13-1395-2013, 2013.

Pikridas, M., Tasoglou, A., Florou, K., and Pandis, S. N.: Characterization of the origin of fine particulate matter in a medium size urban area in the Mediterranean, *Atmos. Environ.*, 80, 264–274, 2013.

Pio, C., Cerqueira, M., Harrison, R. M., Nunes, T., Mirante, F., Alves, C., Oliveira, C., Sanchez de la Campa, A., Artiñano, B., and Matos, M.: OC/EC Ratio Observations in Europe: re-thinking the approach for apportionment between primary and secondary organic carbon, *Atmos. Environ.*, 45, 6121–6132, 2011.

Pio, C. A., Castro, L. M., and Ramos, M. O.: Differentiated determination of organic and elemental carbon in atmospheric aerosol particles by a thermal-optical method, in: *Proceedings of the Sixth European Symposium: Physico-Chemical Behaviour of Atmospheric Pollutants*, edited by: Angeletti, G., and Restelli, G., Report EUR 15609/2 EN, European Commission, Luxembourg, 706–711, 1994.

Pio, C. A., Ramos, M. M., and Duarte, A. C.: Atmospheric aerosol and soiling of external surfaces in an urban environment, *Atmos. Environ.*, 32, 1979–1989, 1998.

Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., Sisler, J. F. Atmospheric aerosol over Alaska 2. Elemental composition and sources, *J. Geophys. Res- Atmos*, 103, 19045–19057, 1998.

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- Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., Legrand, M., Preunkert, S., and Pio, C. A.: Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, *J. Geophys. Res.-Atmos.*, 112, D23S05, doi:10.1029/2006JD008114, 2007.
- 5 Querol, X., Alastuey, A., Rodríguez, S., Plana, F., Mantilla, E., and Ruiz, C. R.: Monitoring of PM₁₀ and PM_{2.5} around primary particulate anthropogenic emission sources, *Atmos. Environ.*, 35, 845–858, 2001.
- Querol, X., Alastuey, A., Ruiz, C. R., Artiñano, B., Hansson, H. C., Harrison, R. M., Buringh, E., Ten Brink, H. M., Lutz, M., Bruckmann, P., Straehl, P., and Schneider, J.: Speciation and origin
10 of PM₁₀ and PM_{2.5} in selected European cities, *Atmos. Environ.*, 38, 6547–6555, 2004.
- Querol, X., Pey, J., Pandolfi, M., Alastuey, A., Cusack, M., Moreno, T., Viana, M., Mihalopoulos, N., Kallos, G., and Kleanthous, S.: African dust contributions to mean ambient PM₁₀ levels across the Mediterranean Basin, *Atmos. Environ.*, 43, 4266–4277, 2009.
- 15 Querol, X., Alastuey, A., Viana, M., Moreno, T., Reche, C., Minguillón, M. C., Ripoll, A., Pandolfi, M., Amato, F., Karanasiou, A., Pérez, N., Pey, J., Cusack, M., Vázquez, R., Plana, F., Dall'Osto, M., de la Rosa, J., Sánchez de la Campa, A., Fernández-Camacho, R., Rodríguez, S., Pio, C., Alados-Arboledas, L., Titos, G., Artiñano, B., Salvador, P., García Dos Santos, S., and Fernández Patier, R.: Variability of carbonaceous aerosols in remote, rural, urban and industrial environments in Spain: implications for air quality policy, *Atmos. Chem. Phys.*, 13, 6185–6206, doi:10.5194/acp-13-6185-2013, 2013.
- 20 Rahn, K. A.: Silicon and aluminum in atmospheric aerosols: crust-air fractionation?, *Atmos. Environ.*, 10, 597–601, 1976.
- SEC: 2011.208 final. Secretary-General of the European Commission. Commission Staff Working Paper establishing guidelines for demonstration and subtraction of exceedances attributable to natural sources under the Directive 2008/50/EC on ambient air quality and cleaner air for Europe, European Commission, Brussels, 15 February 2011.
- 25 Simoneit, B. R. T., Schauer, J. J., Nolte, C. G., Oros, D. R., Elias, V. O., Fraser, M. P., Rogge, W. F., and Cass, G. R.: Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, 33, 173–182, 1999.
- 30 Spencer, M. T., Shields, L. G., Sodeman, D. A., Toner, S. M., and Prather, K. A.: Comparison of oil and fuel particle chemical signatures with particle emissions from heavy and light duty vehicles, *Atmos. Environ.*, 40, 5224–5235, 2006.

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- Thurston, G. D. and Spengler, J. D.: A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston, *Atmos. Environ.*, 19, 9–25, 1985.
- Traversi, R., Becagli, S., Calzolari, G., Chiari, M., Giannoni, M., Lucarelli, F., Nava, S., Rugi, F., Severi, M., and Udisti, R.: A comparison between PIXE and ICP-AES measurements of metals in aerosol particulate collected in urban and marine sites in Italy, *Nucl. Instrum. Methods Phys. Res. B*, 318, 130–134, 2014.
- Turpin, B. J. and Huntzicker, J. J.: Identification of secondary organic aerosol episodes and quantisation of primary and secondary organic aerosol concentrations during SCAQS, *Atmos. Environ.*, 29, 3527–3544, 1995.
- US EPA: Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide. EPA/600/R-14/10, <http://www.epa.gov/heads/research/pmf.html> (last access: 28 August 2015), 2014.
- Watson, J. G., Cooper, J. A., and Huntzicker, J. J.: The effective variance weighting for least squares calculations applied to the mass balance receptor model, *Atmos. Environ.*, 18, 1347–1355, 1984.
- WHO: Health effects of black carbon. ISBN: 978 92 890 0265 3, available at: http://www.euro.who.int/__data/assets/pdf_file/0004/162535/e96541.pdf (last access: 28 August 2015), 2012.

Table 1. Mean PM and component concentrations for the study period at the five AIRUSE cities.

ngm ⁻³	PM ₁₀					PM _{2.5}				
	BCN-UB	POR-TR	FI-UB	MLN-UB	ATH-SUB	BCN-UB	POR-TR	FI-UB	MLN-UB	ATH-SUB
PM	22 406	34 533	19 115	38 945	19 676	15 074	26 689	13 459	30 850	11 003
p90.4	33 948	52 630	32 263	72 146	30 389					
OM	5002	7536	9848	15 744	5522	4484	7754	8369	12 146	4631
TC	3908	10 856	6603	10 655	3665	3550	11 291	5693	8246	3048
EC	1129	4793	1132	1908	416	1040	5033	968	1847	324
OC	2779	6083	5471	8747	3248	2509	6258	4719	6307	2724
CO ₂ ⁻	147	35	141	29	38	NA	NA	NA	NA	NA
SO ₄ ²⁻	2413	2398	1716	2902	3653	1676	1926	1527	1894	2888
NO ₃ ⁻	2049	1913	1199	6033	1166	982	1173	677	5668	173
NH ₄ ⁺	610	679	491	3327	1013	714	625	546	2204	943
Levoglucozan	NA	NA	NA	NA	NA	22	413	287	303	37
K	175	426	256	420	249	89	343	178	348	115
S	735	869	770	1142	1250	572	755	690	1064	911
Cl	602	2348	252	366	600	181	696	23	288	41
Na	687	1516	374	190	662	160	440	59	180	112
Mg	152	288	115	113	206	40	80	17	21	35
Al	218	430	191	284	392	68	217	38	150	90
Si	517	884	562	865	974	161	454	124	323	234
Ca	607	333	612	639	767	147	161	102	238	175
Fe	481	828	448	1158	413	151	365	88	324	112
Cu	19.6	31.7	22.7	72.8	6.3	7.1	15.4	4.7	33.6	2.2
Zn	68.1	99.3	18.9	84.2	18.0	46.9	879	10.5	56.8	9.9
Ba	12.1	35.4	15.2	44.2	16.1	4.8	15.4	5.1	30.5	6.9
Sn	4.6	8.1	NA	21.1	1.5	2.2	5.0	NA	18.0	1.0
Sb	2.6	5.2	NA	11.8	0.8	1.1	5.0	NA	10.8	0.5
Ni	1.8	2.8	1.4	6.3	2.6	1.4	2.4	1.0	4.7	1.5
V	4.4	4.5	2.1	1.4	4.0	3.6	3.0	1.7	1.9	2.7
Cr	3.0	4.6	3.3	4.1	2.5	1.4	2.0	0.8	1.8	2.0
Mo	9.4	4.1	1.8	NA	1.8	9.7	1.7	1.5	NA	1.7
Pb	7.6	14.7	4.4	20.4	4.2	5.7	13.2	3.8	15.7	2.7

NA: not available.

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Table 1. Continued.

ngm ⁻³	PM ₁₀					PM _{2.5}				
	BCN-UB	POR-TR	FI-UB	MLN-UB	ATH-SUB	BCN-UB	POR-TR	FI-UB	MLN-UB	ATH-SUB
Cd	0.2	0.5	0.2	NA	0.1	0.1	0.2	0.2	NA	0.1
Co	0.1	0.1	NA	NA	0.1	0.1	0.2	NA	NA	0.1
As	0.4	1.5	0.5	NA	0.6	0.3	0.7	0.4	NA	0.4
Se	0.3	1.0	0.5	NA	0.6	0.2	0.4	0.5	NA	0.3
Ge	0.2	0.1	NA	NA	0.6	0.2	0.1	NA	NA	0.6
W	0.4	0.3	NA	NA	0.6	0.2	0.5	NA	NA	0.6
Bi	0.4	0.3	NA	NA	0.1	0.2	0.2	NA	NA	0.1
Br	NA	11.0	4.4	11.3	5.7	NA	7.6	3.6	10.3	3.4
P	15.7	23.5	9.6	28.0	9.3	6.5	10.8	3.7	NA	6.8
Ti	16.0	25.1	13.6	31.2	24.2	5.0	14.0	3.5	14.5	8.2
Mn	10.2	13.9	7.1	16.7	7.0	4.9	8.6	2.1	8.5	2.2
Rb	0.4	5.6	1.8	1.2	1.7	0.2	2.6	0.7	0.8	0.8
Sr	2.1	3.6	2.1	9.0	3.0	0.6	1.1	0.8	7.5	1.0
Y	0.2	6.2	0.7	NA	0.8	0.2	1.7	0.7	NA	0.7
Zr	6.7	5.8	2.2	NA	1.6	5.5	2.3	0.9	NA	1.1
Li	0.2	0.7	NA	NA	0.3	0.1	0.5	NA	NA	0.1
Nb	0.4	0.5	NA	NA	0.5	0.2	0.5	NA	NA	0.3
Ga	0.1	0.2	NA	NA	0.2	0.1	0.2	NA	NA	0.1
Th	0.1	0.01	NA	NA	0.2	0.1	0.1	NA	NA	0.2
La	0.2	0.3	0.5	NA	0.3	0.1	0.2	0.3	NA	0.2
Ce	0.4	0.8	0.5	NA	0.4	0.2	0.5	0.3	NA	0.3
	BCN-UB	POR-TR	FI-UB	MLN-UB	ATH-SUB	BCN-UB	POR-TR	FI-UB	MLN-UB	ATH-SUB
Secondary inorganic	4605	5005	3437	13 147	5832	3365	3724	2750	9820	4004
Primary	7781	17 339	5614	10 116	6698	3667	11 979	3856	7733	1884
POM+EC	2314	8542	4618	6183	853	2113	8632	3272	5996	663
Secondary	8662	9724	9769	25 832	12 048	6973	8615	9161	18 094	9014
Sea salt	1486	4574	647	733	1633	378	1256	106	455	237
Mineral dust	3981	4266	2244	3790	4155	1176	2091	478	1286	986
Unexplained	6204	7601	7836	7059	1994	4641	6761	638	4982	966
Reconstructed	16 202	26 697	17 276	31 886	17 682	10 433	19 929	12 821	25 868	10 037

NA: not available.

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Table 2. Summary of input species, identified factors and constraints for city-specific PMF analyses.

Station	Input species	Sources/Factors	Constraints
BCN-UB	EC, OC, Al, Ca, Fe, K, Mg, Na, Cl ⁻ , Ti, V, Cr, Mn, Ni, Cu, Zn, Li, Ga, As, Se, Rb, Sr, Cd, Sn, Sb, Ba, La, Ce, Pb, S, Br, NH ₄ ⁺ , NO ₃ ⁻	Vehicle exhaust (VEX), Vehicle non-exhaust (NEX), Secondary nitrate (SNI), Mineral (MIN), Secondary sulphate and organics (SSO), Industrial (IND), Heavy oil combustion (HOC) and Aged sea salt (SEA).	<ul style="list-style-type: none"> – Pulling the difference of source contributions between PM₁₀ and PM_{2.5} to zero. – Pulling the chemical profile (24 species) of the NEX source towards the experimental profile of road dust obtained in Barcelona (Amato et al., 2009). – Pulling the ratios Cl⁻/Na, S/Na, K/Na, Ca/Na, Mg/Na of the SEA profile to the literature values of 1.8, 0.084, 0.037, 0.038, 0.119 respectively.
FI-UB	EC, OC, Levoglucosan, Si, Al, Ca, Fe, K, Mg, Na, Cl, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Se, Rb, Sr, Cd, Ba, Pb, S, Br, NH ₄ ⁺ , NO ₃ ⁻	Aged sea salt (SEA), Saharan dust (SAH), Secondary sulphate and organics (SSO), Vehicle non-exhaust (NEX), Biomass burning (BB), Secondary nitrate (SNI), Vehicle exhaust (VEX), Heavy oil combustion (HOC), Local dust (LDU) and Fresh sea salt (FSS).	<ul style="list-style-type: none"> – Pulling down the EC and OC contributions in the SAH source profile and the NO₃ contribution in the Sea Salt profile. – Pulling down the SAH source contributions during a period (1–22 Jul 2013) when the advection of desert dust can be excluded on the basis of all the used transport models. – Pulling the difference of source contributions between PM₁₀ and PM_{2.5} to zero, only for those days and sources where PM_{2.5} contribution was higher than PM₁₀ contribution in the base run solution (55 days).
ATH-SUB	EC, OC, Si, Al, Ca, Fe, K, Mg, Na, Cl, Ti, V, Mn, Ni, Cu, Zn, As, Sr, Cd, Sb, Pb, S, Br, NH ₄ ⁺ , NO ₃ ⁻	Heavy oil combustion (HOC), Vehicle exhaust (VEX), Secondary nitrate (SNI), Mineral (MIN), Vehicle non-exhaust (NEX), Biomass burning (BB), Secondary sulphate and organics (SSO) and Fresh sea salt (SEA).	<ul style="list-style-type: none"> – For the cases with daily PM_{2.5} contribution significantly higher than PM₁₀ contribution, PM_{2.5} contribution was either set to zero (2 cases) or pulled down maximally (4 cases), depending on the respective PM₁₀ contribution. – OC was pulled up in HOC factor – OC was set to have the original value of the unconstrained solution in the BB factor
POR-TR	EC, OC, Levoglucosan, Si, Al, Ca, Fe, K, Mg, Na, Cl ⁻ , Ti, V, Cr, Mn, Ni, Cu, Zn, Li, As, Rb, Cd, Sn, Sb, La, Ce, Ba, Pb, S, Br, NH ₄ ⁺ , NO ₃ ⁻	Biomass burning (BB), Secondary nitrate (SNI), Heavy oil and secondary sulphate (HOS), Mineral (MIN), Sea salt (SEA), Industrial (IND), Vehicle non-exhaust (NEX), and Vehicle exhaust (VEX).	<ul style="list-style-type: none"> – Pulling the difference of source contributions between PM₁₀ and PM_{2.5} to zero, only for those days and sources where PM_{2.5} contribution was higher than PM₁₀ contribution in the base run solution.
MLN-UB	EC, OC, Levoglucosan, Si, Al, Ca, Fe, K, Mg ²⁺ , Na ⁺ , Cl, Ti, V, Cr, Mn, Ni, Cu, Zn, Rb, Pb, S, Br, NH ₄ ⁺ , NO ₃ ⁻	Vehicle exhaust (VEX), Vehicle non-exhaust (NEX), Mineral dust (MIN), Industrial (IND), Aged sea salt (SEA), Biomass burning (BB), Secondary nitrate (SNI) and Heavy oil combustion and secondary sulphate (HOS).	<ul style="list-style-type: none"> – Setting to zero the presence of levoglucosan in VEX and SEA factors. – Pulling down maximally the presence of Na⁺ in the SNI factor. – In the SEA profile pulling the ratio Cl/Na⁺ to the literature value of 1.8.

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Table 3. Average contribution (%) of PM₁₀ and PM_{2.5} sources during high pollution days (PM₁₀ > 50 µg m⁻³, and > 40 µg m⁻³ in BCN-UB).

	BCN-UB		FI-UB		ATH-SUB		POR-TR		MLN-UB	
	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}	PM ₁₀	PM _{2.5}
Aged sea salt	2	1	< 1	< 1			3	< 1	2	1
Saharan dust	< 1	< 1	< 1	< 1	52	45	< 1	< 1	< 1	< 1
Local dust	4	2	< 1	< 1	1	2	27	22	3	2
Sec. sulphate and organics	19	22	6	6	2	5	5*	2*	9*	11*
Vehicle non-exhaust	14	2	9	1	3	1	6	3	14	8
Vehicle exhaust	13	20	5	5	4	9	25	30	5	5
Heavy oil combustion	4	6	3	3	3	10				
Industrial	17	18			< 1	< 1	2	1	4	3
Secondary nitrate	27	29	36	32	3	4	7	3	28	34
Fresh sea salt			< 1	< 1	7	1				
Biomass burning			30	33	1	2	25	33	35	26
Unaccounted			8	20	24	21		5		10

* Includes heavy oil combustion.

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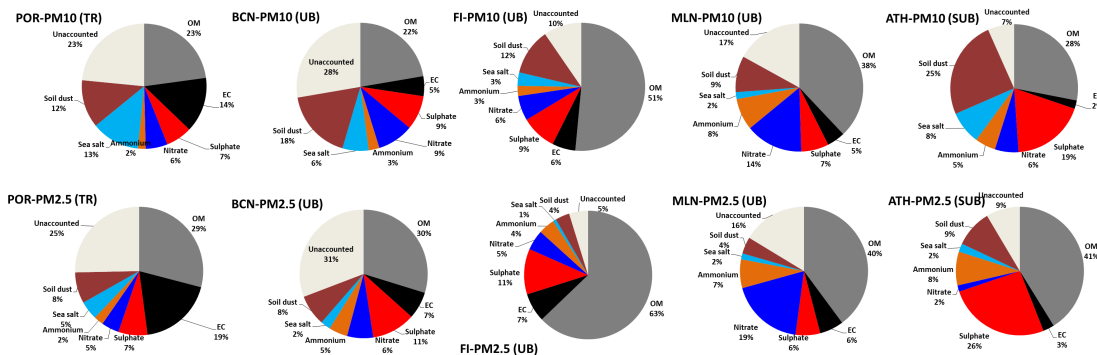


Figure 1. Mass closure of PM₁₀ and PM_{2.5} chemical speciation data for the 5 AIRUSE cities.

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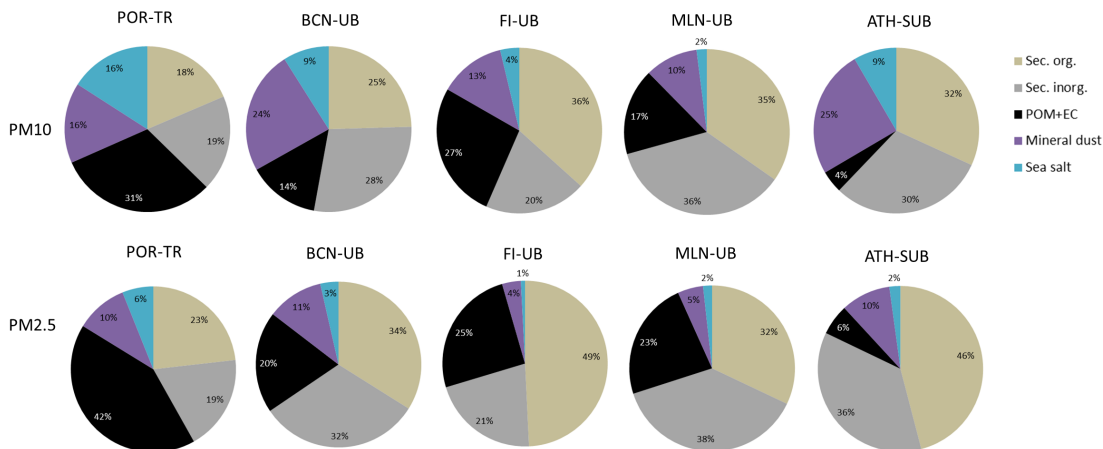


Figure 2. Secondary and primary PM components to the mean PM₁₀ and PM_{2.5} levels at the 5 AIRUSE cities.

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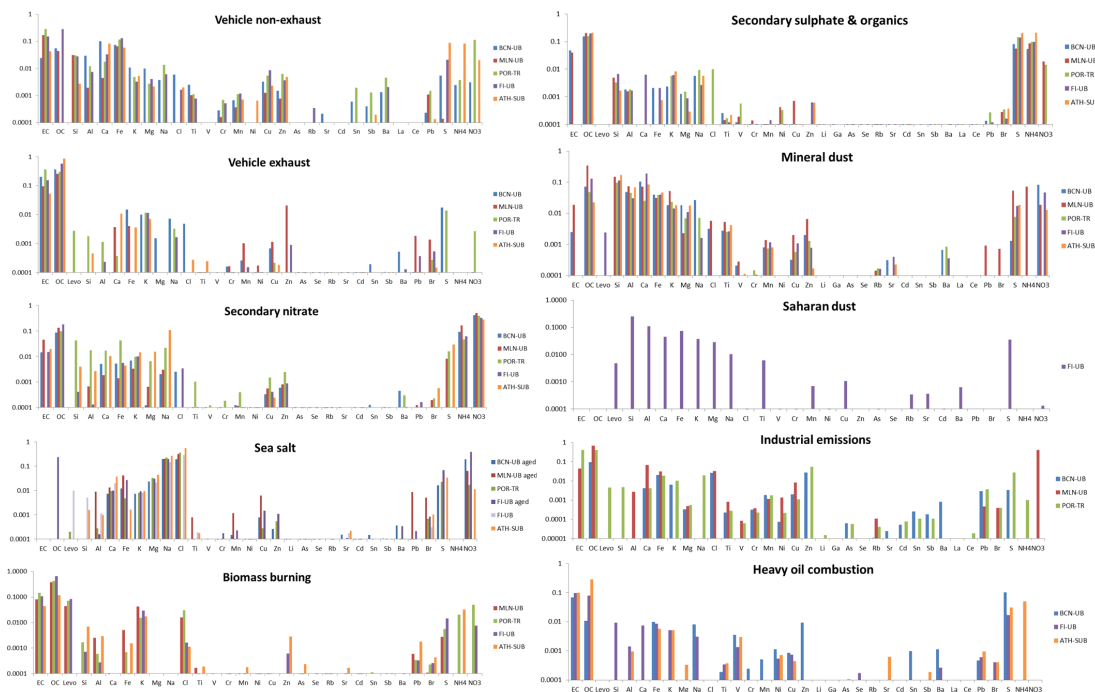


Figure 3. PMF factor profiles ($\mu\text{g}\mu\text{g}^{-1}$) for each monitoring site. Some null concentrations are due to species not used for PMF. See details in Table 2.

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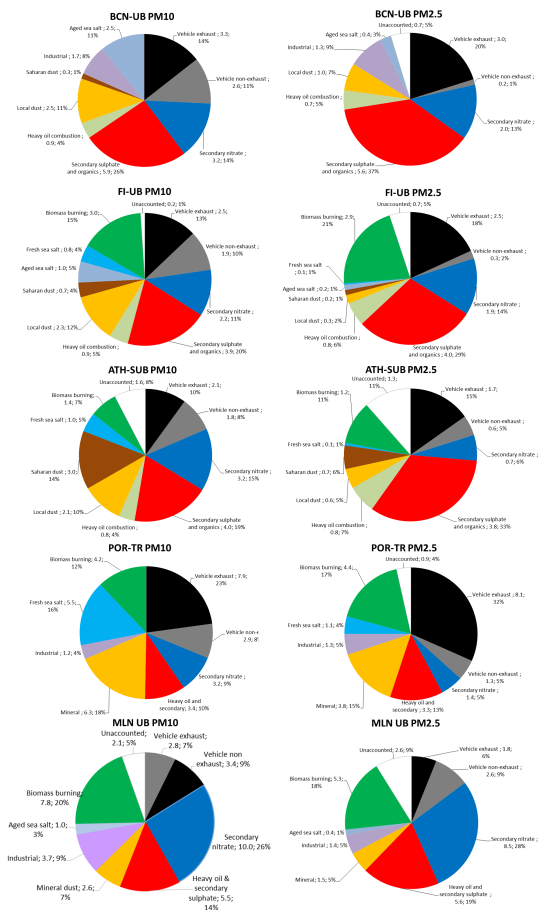


Figure 4. Average contribution (%) of PM₁₀ and PM_{2.5} sources from January 2013 to February 2014.

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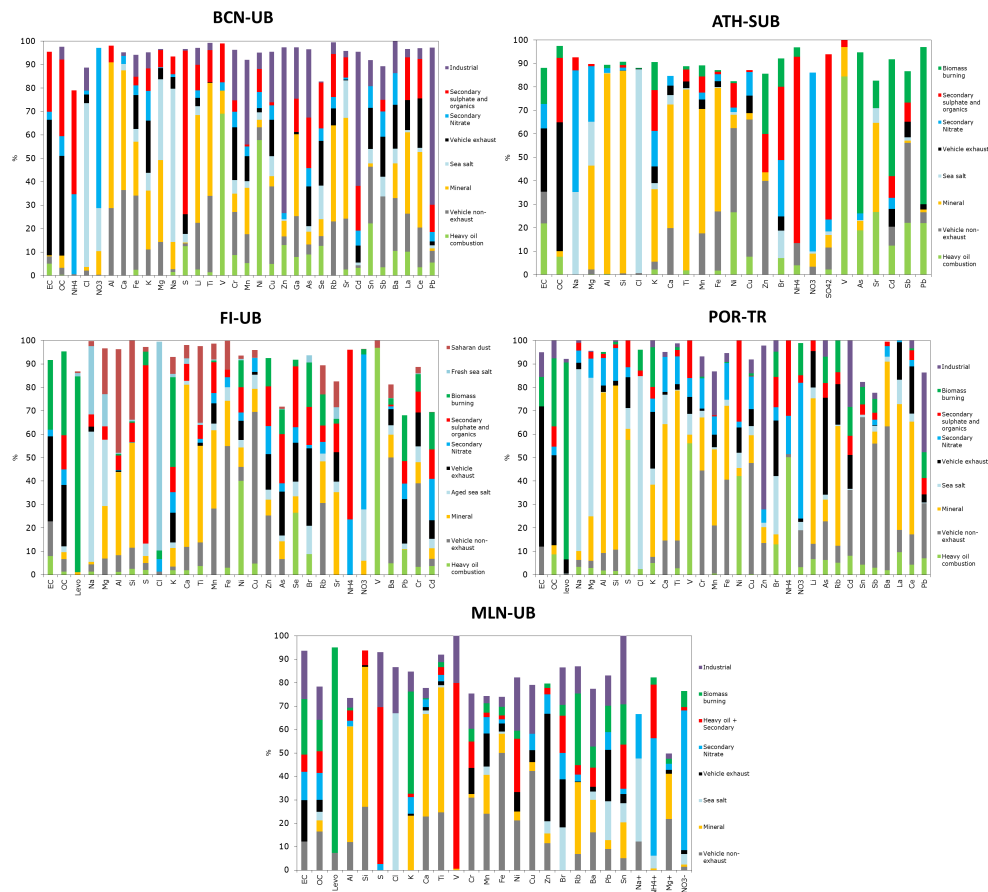


Figure 5. Percentage of species explained by each factor at each site. Average of PM₁₀ and PM_{2.5}

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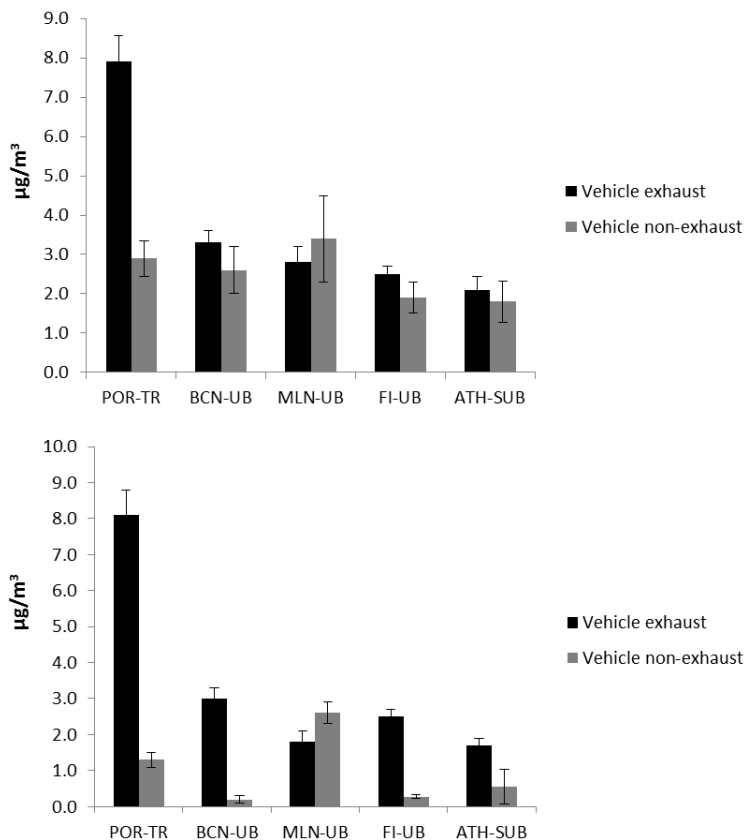


Figure 6. Mean contributions (and standard error) for traffic-related sources at the five AIRUSE cities for PM₁₀ (top) and PM_{2.5} (bottom).

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