

### Citation for published version

Cruz Minguillón, M. [María], Schembari, A. [Anna], Triguero-Mas, M. [Margarita], de Nazelle, A. [Audrey], Dadvand, P. [Payam], Figueras, F. [Francesc], ... & Querol, X. [Xavier] (2012). Source apportionment of indoor, outdoor and personal PM2.5 exposure of pregnant women in Barcelona, Spain. *Atmospheric Environment*, 59, 426-436.

#### DOI

<https://doi.org/10.1016/j.atmosenv.2012.04.052>

#### HANDLE

<http://hdl.handle.net/10609/150633>

### Document Version

This is the Accepted Manuscript version.

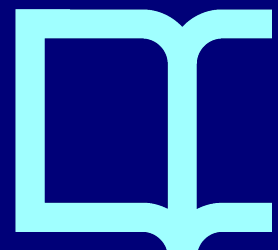
The version published on the UOC's O2 Repository may differ from the final published version.

### Copyright and Reuse

This manuscript version is made available under the terms of the Creative Commons Attribution Non Commercial No Derivatives license (CC-BY-NC-ND) <http://creativecommons.org/licenses/by-nc-nd/4.0/>, which allows others to download it and share it with others as long as they credit you, but they can't change it in any way or use them commercially.

### Enquiries

If you believe this document infringes copyright, please contact the UOC's O2 Repository administrators: [repositori@uoc.edu](mailto:repositori@uoc.edu)



## **Source apportionment of indoor, outdoor and personal PM<sub>2.5</sub> exposure of pregnant women in Barcelona, Spain**

M.C. Minguillón a,\* , A. Schembari b,c,d, M. Triguero-Mas b,c,d, A. de Nazelle b,c,d, P. Dadvand b,c,d, F. Figueras e, J.A. Salvado a, J.O. Grimalt a, M. Nieuwenhuijsen b,c,d, X. Querol a

a Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain

b Centre for Research in Environmental Epidemiology (CREAL), Barcelona, Spain

c IMIM (Hospital del Mar Research Institute), Barcelona, Spain

d CIBER Epidemiología y Salud Pública (CIBERESP), Spain

e Department of Maternal-Fetal Medicine, ICGON, Hospital Clinic-IDIBAPS, University of Barcelona, Spain

\* Corresponding author. Tel.: +34 934006100. E-mail address: mariacruz.minguillon@idaea.csic.es (M.C. Minguillón).

### **Abstract**

Exposure to air pollution has been shown to adversely affect foetal development in the case of pregnant women. The present study aims to investigate the PM composition and sources influencing personal exposure of pregnant women in Barcelona. To this end, indoor, outdoor and personal exposure measurements were carried out for a selection of 54 pregnant women between November 2008 and November 2009. PM<sub>2.5</sub> samples were collected during two consecutive days and then analysed for black smoke (BS), major and trace elements, and polycyclic aromatic hydrocarbons (PAHs) concentrations. Personal information such as commuting patterns and cosmetics use was also collected.

PM<sub>2.5</sub> concentrations were higher for personal samples than for indoor and outdoor environments. Indoor, outdoor and personal BS and sulphate concentrations were strongly correlated, although some specific indoor and outdoor sulphate sources may exist. Average trace elements concentrations were similar indoor, outdoor and for personal exposure, but the correlations were moderate for most of them. Most of the PAHs concentrations showed strong correlations indoor - outdoor.

A source apportionment analysis of the PM composition data by means of a Positive Matrix Factorization (PMF) resulted in the identification of six sources for the outdoor and indoor environments: secondary sulphate, fueloil + sea salt (characterized by V, Ni, Na and Mg), mineral, cigarette (characterized by K, Ce, Cd, benzo(k)fluoranthene and benzo(ghi)perylene), road traffic (characterized by BS and low weight PAHs), and industrial (characterized by Pb, Sn, Cu, Mn and Fe). For personal exposure two specific sources

were found: cosmetics (characterized by abundance of Ca, Li, Ti and Sr and the absence of Al) and train/subway (characterized by Fe, Mn, Cu and Ba). The contribution of the sources varied widely among women, especially for cigarette (from zero to up to 4  $\mu\text{g m}^{-3}$ ), train/subway (up to more than 6  $\mu\text{g m}^{-3}$ ) and cosmetics (up to more than 5  $\mu\text{g m}^{-3}$ ). The source contributions showed generally strong correlations indoor - outdoor although the infiltration efficiencies varied among homes. This study emphasizes the importance of relying on personal exposure in epidemiological studies assessing the impact of air pollution on human health.

## **1.Introduction**

Exposure to air pollution has been shown to increase mortality and morbidity in adults and children (Cohen et al., 2005; Stafoggia et al., 2008; Perez et al., 2009; Zanobetti and Schwartz, 2009). It has been also suggested to adversely affect foetal development (Sapkota et al., 2010; Shah and Balkhair, 2011; van den Hooven et al., 2011; Vrijheid et al., 2011). Maternal exposure to ambient air pollution has been associated with the risk of low birth weight, preterm birth, intra-uterine growth retardation, and congenital anomalies (Sapkota et al., 2010; Shah and Balkhair, 2011; van den Hooven et al., 2011; Vrijheid et al., 2011). Active and passive smoking have been reported to increase blood concentrations of metals in pregnant women (Vardavas et al., 2011).

Personal exposure depends on the pollutant concentrations in the surrounding microenvironments (e.g. indoor and outdoor microenvironments, and during transport) and personal time-activity. Pregnant women may have different mobility patterns compared to the general population, spending more time at home or walking (Choi et al., 2008; Nethery et al., 2008). Therefore general ambient measurements, which are commonly used in epidemiological studies, may not provide a good characterization of the personal exposure (Nerriere et al., 2005; Kornartit et al., 2010). Assessment of the influence of different PM sources on personal exposure and its relation with the monitored outdoor concentrations is essential for assessing the possible health effects estimated from monitoring data on outdoor concentrations. Previous studies suggested that improvement of exposure assessment could have an important impact on the effect estimates (Ritz et al., 2007; Sapkota et al., 2010; Setton et al., 2010; Shah and Balkhair, 2011; Vrijheid et al., 2011).

Studies on personal, indoor and outdoor air pollution started many years ago (Dockery and Spengler, 1981). More recently, studies on PM concentrations, composition and sources affecting outdoor and indoor environments have been carried out (e.g. Arhami et al., 2010; Pekey et al., 2010; Kliucininkas et al., 2011). Others have specifically assessed PM concentrations and composition of personal exposure (Niu et al., 2010; Wheeler et al., 2011). However, only a few encompassed a complete characterisation of PM sources for indoor, outdoor and personal samples, and these were carried out in the US (Hopke et al.,

2003; Larson et al., 2004), where the results may be different to European cities as a consequence of differences in city structure, vehicle fleet composition, fuel types, and activity habits. In this respect, Barcelona has a specific geography, a high traffic density in comparison to other European cities (e.g. four times higher number of registered vehicles per km<sup>2</sup> than London), and a large proportion of the vehicles using diesel (DGT, [http://www.dgt.es/portal/es/seguridad\\_vial/estadistica/parque\\_vehiculos/por\\_provincia\\_tipo\\_y\\_carburante/](http://www.dgt.es/portal/es/seguridad_vial/estadistica/parque_vehiculos/por_provincia_tipo_y_carburante/)). Furthermore Barcelona has many semi-tall buildings and relatively narrow streets leading to the known street canyon effect (Mirzaei and Haghghat, 2012). Within this context the ARIBA project (Air Pollution and Pregnancy in Barcelona) was defined to evaluate the relation between the atmospheric pollution and different reproductive outcomes. Within this project, the aim of the present study was to investigate the PM composition of outdoor and indoor microenvironments and its influence on personal exposure of pregnant women. This study also aimed to identify the sources for these particles and their relationship between the different microenvironments and individual maternal exposures in Barcelona.

## **2.Methods**

### **2.1.Study population and time-activity data**

A total of 54 pregnant women were recruited during the first, second or third trimester of pregnancy from those visiting the obstetrics department at Hospital Clinic, Barcelona. Hospital Clinic is a major university hospital providing services to about one million inhabitants (Figueras et al., 2008). Sixteen dates were randomly selected between September 2008 and September 2009 and the pregnant women that had a hospital appointment on those dates were invited to participate in the study (n = 434). Women volunteering to participate were Spanish-speaking women resident in Barcelona metropolitan area during November 2008 to November 2009. Participation in the study entailed providing personal and home characteristic information, and collaborating in the measurement of personal and home-based air pollution. The study protocol was approved by the Clinical Research Ethical Committee of the Parc de Salut MAR, Barcelona, Spain (Ethics approval No. 2008/3115/I).

Information on the surroundings of the women's homes included presence of green spaces, street canyons, construction works, and traffic lanes. Data on personal time-activity was collected using a revised version of the EXPOLIS (population exposures to key air pollutants in six European cities, <http://www.ktl.fi/expolis>) Time-Microenvironment-Activity-Diary (TMAD) which provides information on the time spent by the participants in various microenvironments and activities (Hänninen et al., 2004a). Each participant was asked to record a microenvironment/activity category for every 30 min during the sampling period (two consecutive days, see Section 2.2). The diary also included data on smoking (active or passive).

A sub-sample of volunteers was interviewed for the use of powder cosmetics during the sampling period. More details are provided by Schembari et al. (submitted for publication).

## **2.2. Air quality measurements**

Air quality measurements were carried out indoors (living room, when possible) and outdoors (balcony, window or patio) of the women's homes between November 2008 and November 2009. Moreover, personal samples were collected. The women carried the personal samplers positioning inlets near their breathing zone. Each sampling round consisted in two consecutive days (weekdays) of sampling simultaneously for indoor and outdoor environments and personal exposure. The sampling rounds were repeated twice for 11 of the 54 women.

Identical instruments were used for indoor, outdoor and personal samples. PM<sub>2.5</sub> samples were collected on 37 mm Teflon filters (Pall, Eas Hills, NY) held in a BGI PM<sub>2.5</sub> cyclone working at 4 L min<sup>-1</sup> (GK 2.05) following the EXPOLIS protocol (Hänninen et al., 2004b). Flow rate was adjusted at the beginning of each measurement to 4 L min<sup>-1</sup> with a rotameter (RM67, BGI, USA) and checked at the end of each measurement. After sampling, PM<sub>2.5</sub> concentrations were determined gravimetrically. To this end, the filters were weighted on a 6 figure balance (Mettler Toledo MX5) in a humidity and temperature controlled room, following the procedure PRO.002-Teflon filter Weighing Revision: 01 (20/02/09) (ULTRA protocol, Exposure and risk assessment for fine and ultra- fine particles in ambient air, <http://www.ktl.fi/ultra/adobe/out/sop-abs.pdf>). The detection limit for PM<sub>2.5</sub> concentration was 1.4 µg m<sup>-3</sup>.

In indoor and outdoor environments, there was an additional sampler to collect PM<sub>2.5</sub> on quartz filters using similar instrumentation as that described above.

## **2.3. Analyses of the collected PM<sub>2.5</sub>**

### **2.3.1. Black smoke analyses**

The reflectance of the PM<sub>2.5</sub> teflon filters was measured by a Smoke Stain Reflectometer (Diffusion Systems Limited Model 43, Hanwell, London) according to the Standard Operating Procedure (a modification of ISO 9835, Determination of a Black Smoke Index) of the EXPOLIS study (Koistinen et al., 1999; Hänninen et al., 2002). The absorbance was calculated using the formula  $a = (A/2V) \ln (RF/R0)$ , following the Standard Operating Procedure ULTRA/KTL-L-1.1, where  $a$  = absorption coefficient;  $A$  = area of the Teflon filter membrane = 37 mm;  $V$  = volume of air sampled;  $RF$  = reflectance of the sampled filter in percentage;  $R0$  = reflectance of the blank filters in percentage. The detection limit was  $0.2 \times 10^{-5}/m$ . Black smoke (BS) concentrations were determined based on the absorbance ( $a$ ) as  $BS = 1.5a/2.5$

(Cyrus et al., 2003).

### **2.3.2. Major and trace elements analyses**

The collected teflon filters were acid digested (HNO<sub>3</sub>:HF:HClO<sub>4</sub>) following the procedure described by Querol et al. (2001) and the resulting solution was analysed by means of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for the major and trace elements concentration determination, respectively. Approximately 10 mg of the reference material NIST 1633b were added to a fraction of a blank filter to check the accuracy of the analysis of the acidic digestions. Laboratory blank filters were analysed following the same methodology and concentrations were subtracted to those found in the samples in order to calculate the ambient concentrations. Concentration uncertainties were estimated as described by Escrig Vidal et al. (2009).

### **2.3.3. Polycyclic aromatic hydrocarbons (PAHs) analyses**

PAHs were analysed only for indoor and outdoor samples collected on quartz filters by a Thermo DSQII (ThermoQuest, Manchester, USA) gas chromatograph (GC) mass spectrometer in electron impact mode (EI, 70 eV ionization energy). Quantitative data for PAHs were obtained using external standards. The reported data were corrected by the internal and surrogate standards. Recoveries for the overall procedure were obtained from surrogate data: anthracene-d10  $55 \pm 10\%$ , benz[a]anthracene-d12  $64 \pm 8\%$ , benzo[b]fluoranthene-d12  $98 \pm 13\%$  and benzo[ghi]perylene-d12  $86 \pm 11\%$ . Procedural blanks were performed with each set of eleven samples. Additional information can be found in Section S1 of the Supplementary Material.

On average, the sum of the analysed species concentrations (black smoke, major and trace elements and PAHs) was 24-33% of the bulk PM<sub>2.5</sub> measured concentration. The composition of the remaining 67-76% is discussed in Section 3 (Results and Discussion).

## **2.4. Source apportionment**

A source apportionment analysis of the PM composition data was carried out by means of a Positive Matrix Factorization (PMF; Paatero and Tapper, 1994), using EPA Positive Matrix Factorization 3.0 software (<http://www.epa.gov/heasd/products/pmf/pmf.html> [4th April 2012]). The objective of multivariate receptor modelling was to obtain  $p$  independent factors, each one representing different sources of emissions as well as their elemental composition and the amount that they contribute to the total signal. The PMF method is based on the mass conservation principle:

$$x_{ij} = \sum_{k=1}^p g_{ik}f_{kj} + e_{ij} \quad (1)$$

With  $i= 1, 2, \dots, n$ ;  $j=1,2,\dots,m$ ;  $k=1, 2, \dots,p$ ;  $x_{ij}$  is the  $j$ th species concentration measured in the  $i$ th sample,  $g_{ik}$  is the contribution of the  $k$ th source to the  $i$ th sample,  $f_{kj}$  is the concentration of the  $j$ th species in the  $k$ th source and  $e_{ij}$  is the residual associated with the  $j$ th species concentration measured in the  $i$ th sample.

The values  $g_{ik}$  and  $f_{kj}$  are adjusted until a minimum for the objective function  $Q$  for a given number of factors  $p$  is found:

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left( \frac{x_{ij} - g_{ik}f_{kj}}{\sigma_{ij}} \right)^2 \quad (2)$$

where  $\sigma_{ij}$  is the user defined uncertainty for the  $j$ th species in the  $i$ th sample. This uncertainty was calculated as 10% of the concentration for BS and PAHs, and it was estimated as described by Escrig Vidal et al. (2009) for major and trace elements.

Two separate PMF analyses were performed, one using the outdoor and indoor datasets together, and the other using only the personal dataset. One of the women was excluded from the PMF analysis due to the extremely high concentrations of some elements, which would bias the output of the PMF. Samples with missing data were also excluded. In total, 4 indoor samples, 4 outdoor samples and 3 personal samples were excluded; and 122 outdoor + indoor samples and 62 personal samples were used. Selection of the species included in the model was done depending on their signal to noise ratio (S/N, Equation (3)), the percentage of samples above detection limit and the significance of the species (knowledge of its presence in possible PM sources in the area). From all the PAHs analysed, the two light PAHs with the highest S/N (phenanthrene and anthracene) and the two heavy PAHs with the highest S/N (benzo(k)fluoranthene and benzo(ghi)perylene) were used.

$$\left( \frac{S}{N} \right)_j = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - s_{ij})^2}{\sum_{i=1}^n s_{ij}^2}} \quad (3)$$

The average outdoor source apportionment to PM<sub>2.5</sub> was completed by adding some components not analysed in the present study and by re-calculating the mineral source contribution. To this end, data from an urban background site in Barcelona during the sampling period of the present study (November 2008-November 2009; Reche et al., 2012) was used, including nitrate, ammonium and organic matter (OM) concentrations (calculated as 1.6 times the organic carbon (OC) concentration). The mineral source

contribution was re-calculated to include the contribution of SiO<sub>2</sub> in this source. This was calculated based on the mineral source contribution, the Al<sub>2</sub>O<sub>3</sub> content in this source and the ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>  $\frac{1}{4}$  3.

### 3. Results and discussion

#### 3.1. PM<sub>2.5</sub> concentrations and composition

PM<sub>2.5</sub> concentrations were 20  $\mu\text{g m}^{-3}$ , 24  $\mu\text{g m}^{-3}$ , and 27  $\mu\text{g m}^{-3}$ , on average (arithmetic means), for outdoor, indoor, and personal samples, respectively. Indoor/outdoor ratios varied between 0.5 and 4.9. Outdoor and indoor PM<sub>2.5</sub> concentrations were not strongly correlated, although after removing some outliers the correlation was relatively strong (square Pearson correlation coefficient,  $R^2 = 0.42$ , Fig. S1). This indicates that there was certain penetration of outdoor sources to indoor environments. Personal PM<sub>2.5</sub> concentrations showed a relatively strong correlation with indoor PM<sub>2.5</sub> concentrations ( $R^2 = 0.66$  after removing 5 outliers (points that are far from linearity in the scatter plot), Fig. S1), whereas the correlation was not strong with outdoor PM<sub>2.5</sub> concentrations ( $R^2 = 0.18$  after removing 6 outliers, Fig. S1). This indicates the high variability in PM<sub>2.5</sub> concentrations in different environments affecting the personal exposure (indoor home, commuting, indoor work, outdoors, etc.). This is in agreement with previous studies carried out in Barcelona, which found that outdoor PM<sub>2.5</sub> measurements do not correlate strongly with personal exposure to PM<sub>2.5</sub> (Jacquemin et al., 2007); and with studies carried out in France showing the spatial heterogeneity of personal exposure to airborne metals (Nerriere et al., 2007). A more detailed analysis of the correlations can be found in Schembari et al. (submitted for publication). No direct influence of the proximity to a street canyon on the outdoor and indoor PM<sub>2.5</sub> concentrations was observed (Fig. S2).

Average concentrations (across all women) of major PM<sub>2.5</sub> components are shown in Fig. 1a. One of the women was excluded from the average, due to especially high concentrations of some components (and trace elements, as shown below in this section) attributed to the influence of metallurgy processing nearby her home. The concentrations recorded for this woman are shown separately and labelled as 'metallurgy' in Fig. 1a. Concentrations of Ca, Fe, K, Mg and Na were clearly higher in the metallurgy environment with respect to the average of the rest of the environments, whereas BS and sulphate concentrations were comparable. Most of the components had similar average concentrations outdoors and indoors. Al<sub>2</sub>O<sub>3</sub>, Ca and Fe average concentrations were slightly higher outdoors than indoors, which could be partially attributed to the influence of dust resuspension outdoors. On the contrary, average K concentration was higher indoors (Fig. 1a and b), which could be attributed to the influence of indoor sources. No clear correlation was observed between indoor K concentrations with any of our recorded indoor activities. Nevertheless, it should be noted that the highest indoor K concentration (corresponding also to the highest K indoor/outdoor ratio) coincides with the maximum time reported as exposure to cigarette smoke indoors.



In general, outdoor and personal species concentrations were poorly correlated (Table 1). Nevertheless, some species showed strong correlations for indoor-outdoor and/or for indoor-personal concentrations. This was the case of BS, which was homogeneously spread across different microenvironments, probably indicating the high penetration from outdoor to indoor environments. This agrees with Gotschi et al. (2002), who found stronger indoor-outdoor correlations for BS concentrations than for bulk PM<sub>2.5</sub> in several European cities. Mg demonstrated the strongest indoor-outdoor correlation, but there was a weak indoor-personal correlation. K showed a strong indoor-personal correlation supporting the hypothesis of a cigarette origin for this element. The weak indoor-outdoor, indoor-personal and outdoor-personal correlations for SO<sub>4</sub><sup>2-</sup> (R<sup>2</sup> = 0.17e0.38) could be due to several outliers, but a clear defined linear trend was observed in the scatter plots (Fig. S3). Therefore, we may conclude that SO<sub>4</sub><sup>2-</sup> has a regional origin (resulting in a clear linear trend in the scatter plots indoor-outdoor-personal), which agrees with findings by Jacquemin et al. (2007), who found strong correlations between personal and outdoor SO<sub>4</sub><sup>2-</sup> concentrations in Barcelona. Nevertheless, there is evidence that there are additional SO<sub>4</sub><sup>2-</sup> sources that would not be transported between different micro- environments, hence being responsible for the outliers in our scatter plots.

The average concentrations of trace elements (across all women) are presented in Fig. 2a. Concentrations corresponding to the metallurgy-influenced area are shown separately. Concentrations of Zn, Cu, Pb, Mn, Mo, Ni, Sn, Cr, Sb, As, Rb, Li and Co were clearly higher in the metallurgy environment with respect to the average of the rest of the environments, which agrees with the trace elements associated to metallurgy processing identified by Querol et al. (2007). Most of the elements showed similar average concentrations outdoors and indoors, as shown also by the indoor/ outdoor ratios (Fig. 2b). As for major species, in general, outdoor and personal trace elements concentrations were poorly correlated with R<sup>2</sup> ranging from <0.01 to 0.16 (Table 1), except for V, Sn and Tl, which showed strong correlations outdoor-personal, coinciding with strong correlations indoor-outdoor and indoor-personal. This indicates that these elements had a high penetration and were quite homogeneous in different microenvironments. Other elements with strong indoor-outdoor correlations were Ti, Mn, Zn, Rb and Pb, from which only Rb also showed a strong indoor-personal correlation. Ce and Y had the highest indoor/ outdoor ratios (Fig. 2b), attributed to the influence of a specific indoor source, such as cigarette smoke (discussed in Section 3.2). Although average concentrations were quite similar indoor, outdoor and for personal exposure, the correlations were moderate for most of the species, and hence personal measurements are needed in order to assess the personal exposure.

Indoor and outdoor PAHs concentrations were generally strongly correlated (Table 1), indicating also widespread distribution and high penetration outdoor-indoor of these compounds. Nevertheless, their average composition indoors and outdoors showed some differences. In outdoor environments lower molecular weight PAHs (between fluorene and benzo[e]pyrene) were found in higher concentrations than

in indoor environments. Conversely, the PAHs of highest molecular weight (between benzo [a]pyrene and dibenz[ah]anthracene) were found in higher concentrations indoors than outdoors.

Examination of the ratios between compounds of the same molecular weight is useful for identifying some of the main sources contributing to the atmospheric PAHs mixtures (Sicre et al., 1987). These ratios were rather similar for both indoor and outdoor environments. Thus, the phenanthrene/(anthracene + phenanthrene) ratios were 0.80 and 0.82 indoors and outdoors, respectively. The fluoranthene/(fluoranthene + pyrene) and benz[a]anthracene/(chrysene + triphenylene + benz[a]anthracene) ratios were 0.48 and 0.46, and 0.33 and 0.36 indoors and outdoors, respectively. These ratios are very similar to those found in emissions from gasoline vehicles (Grimmer and Hildebrandt, 1975). The benzo[e] pyrene/(benzo[e]pyrene + benzo[a]pyrene) ratios were 0.53 and 0.67, indoors and outdoors, respectively. These ratios are intermediate between those found in emissions from gasoline and from diesel vehicles (Aceves, 1993). The indeno[1,2,3,-cd]pyrene/(benzo [ghi]perylene + indeno[1,2,3,-cd]pyrene) ratios were 0.38 and 0.35, indoors and outdoors, respectively. These ratios are similar to those found in emissions from diesel vehicles (Aceves, 1993). These ratios did not indicate a substantial difference in composition between indoor and outdoor environments, suggesting that these PAHs may have a dual origin from traffic emissions of gasoline and diesel vehicles. However, the higher indoor concentrations of the heavier molecular weight PAHs suggest that indoor particles may accumulate a higher proportion of those originating from this second source.

The sum of the analysed species concentrations was on average 24-33% of the bulk PM<sub>2.5</sub> measured concentration. The remaining mass was thought to be mainly organic matter (OM), and in much lower proportion silica, nitrate, and ammonium, for which the concentrations were not determined for the collected samples of this study. Concentrations of some of these species during our sampling period are available from a Barcelona urban background site (Reche et al., 2012). After adding these concentrations, 29-38% of the bulk PM<sub>2.5</sub> remains undetermined. Further details are given in the source apportionment Section 3.2.

The correlation coefficients among outdoor-indoor, personal-indoor and personal-outdoor sum of species concentrations were similar to those of bulk PM<sub>2.5</sub> measured concentrations (Figs. S1 and S4). Therefore, the strong or weak correlations cannot be attributed to either the analysed or non- analysed components. A complete analysis of all the samples would be needed for more conclusive results.

### **3.2. Source apportionment**

Six sources were identified by PMF for the indoor + outdoor datasets: sulphate, fueloil + sea salt, cigarette, mineral, road traffic and industrial (Fig. 3). Three of these sources were also identified in the

personal dataset: sulphate, fueloil + sea salt, and cigarette. The sulphate source is attributed to the formation of secondary sulphate, commonly found in most source apportionment studies (Viana et al., 2008). The fueloil + sea salt source was characterized by V, Ni, Na and Mg; and in the personal dataset there is also some influence of BS on this source. The inclusion of these two sources (fueloil and sea salt) into a single one in the PMF probably reflects the contribution of some regional background with the influence of these two sources and therefore the model is not able to separate them. Several previous studies have also attributed a source characterised by V and Ni to a background contribution (Viana et al., 2008). The cigarette source was mainly characterized by K, Ce, Cd, benzo(k)fluoranthene and benzo(ghi)perylene. The last two compounds were only analysed in the indoor and outdoor samples, and therefore the personal profile does not include those. K is a known tracer of biomass combustion sources (Pio et al., 2008); Ce is attributed to the use of lighters, since it is a component of the lighters flint (Kilbourn, 1988); Cd is present in cigarette smoke (Miranda et al., 2012); and benzo(k)fluoranthene and benzo(ghi)perylene are also present in the cigarette smoke (Kleeman et al., 2008). The mineral source was characterized by Al<sub>2</sub>O<sub>3</sub>, Ca, Ti, Fe, Li, Rb and Sr, which are typical known mineral species. This mineral source may be attributed to soil resuspension, influence of construction works and natural mineral sources. Given the similar chemical profile of these sources, the model is not able to separate them, but it identifies a single source with this mineral chemical profile. The road traffic source was characterized by BS, phenanthrene and anthracene (low weight PAHs characteristic from fresh emissions). The industrial source was characterized by Pb, Sn, Cu, Mn and Fe, which is similar to the industrial source profile found in Barcelona by other outdoor studies with large datasets (Amato et al., 2009).

For the personal dataset, the road traffic and industrial sources were also identified but merged in a single source, reflecting the influence of the urban background cocktail. Moreover, two additional sources were identified for the personal dataset: cosmetics and train/subway (Fig. 3). The cosmetics source was characterized by abundance of Ca, Li, Ti and Sr and the absence of Al, which makes the main difference for not identifying this source as a mineral source. The presence of Ti and Ca in cosmetics has been documented by several studies (Kaida et al., 2004; Cengiz et al., 2006; Di Maiuta and Schwarzentruher, 2011) and is included in the European inventory of cosmetics ingredients (Commission Decision, 2006/257/EC). Some personal care products may contain nanoparticles of titanium dioxide that are used as active ingredients in sunscreen products. In the present study, the identification of such a factor could be attributed to powder cosmetics containing these ingredients. Hopke et al. (2003) identified a personal care products factor, with a similar source profile to the cosmetics factor found in this study. The main difference is the lack of calcium in the Hopke et al. (2003) profile, most likely due to the fact that the Hopke et al. (2003) source consisted in personal care products other than make up. The train/subway source was characterized by the presence of Fe, Mn, Cu and Ba, which coincides with train emissions profiles from other studies

(Aarnio et al., 2005; Chillrud et al., 2005; Bukowiecki et al., 2007). The relation of the contribution of these sources (cosmetics and train/subway) with the activities reported in the diary further confirms the identification of such sources, as discussed later in this section. The number of sources was chosen based on the physical meaning of the different options and based on the Q values found for different number of factors (Fig. S5).

Our source apportionment was based on the sum of the analysed components (species), which were 24-33% of the sampled bulk PM<sub>2.5</sub>. Hence, the contribution of each source only includes the contribution of the source to the sum of the analysed species concentrations, excluding other possible components present in the source but not analysed. Although the average contributions give a broad view of the sources (Fig. 4), the contribution of the different sources varied widely among women, as indicated by high standard deviations of the source contributions (data not shown). Bearing this in mind, the average contributions of bulk PM<sub>2.5</sub> ( $\pm$ standard deviation) were 9-15% ( $\pm$ 6-10%) for secondary sulphate, 4-5% ( $\pm$ 3-4%) for road traffic, 1-2% ( $\pm$ 1%) for industry, 2% ( $\pm$ 2%) for fueloil + sea salt (only for indoor and outdoor environments), 5% ( $\pm$ 4%) for fueloil + sea salt + BS (only for personal exposure), 5-6% ( $\pm$ 4-5%) for mineral source (only for indoor and outdoor environments), 2-3% ( $\pm$ 2-3%) for cigarette, 3% ( $\pm$ 4%) for train/subway (only for personal exposure), and 2% ( $\pm$ 4%) for cosmetics (only for personal exposure). As for bulk PM<sub>2.5</sub> concentrations, no direct influence of the proximity to a street canyon was found for the road traffic contribution to outdoor concentrations (Fig. S6).

The highest variations in the contributions were observed for cigarette, train/subway and cosmetics sources. This could be due to the fact that these sources widely depend on the behavioural and time-activity patterns of the women. On the contrary, the rest of the sources belonged to the Barcelona urban environment and therefore their contribution was always present. For these sources, the variation was mostly due to the temporal variation in the influence of these sources, given that the sampling rounds were carried out at different times of the year for different women.

The highest cigarette contributions (up to 4  $\mu\text{g m}^{-3}$ ) were observed for women exposed to tobacco more than 30 min per two days sampling period (Fig. S7a). The contribution of train/subway was below 1  $\mu\text{g m}^{-3}$  for women not using train or subway during the study, whereas it was much higher (up to more than 6  $\mu\text{g m}^{-3}$ ) for women using subway and/or train (Fig. S7b). Nevertheless there was a weak correlation between the train/subway contribution and the time spent in train and subway ( $R^2 < 0.1$ ), i.e. the contribution of this source does not depend directly on the time spent inside the train. This may indicate that the highest exposure to specific train/subway pollutants takes place on the platforms and not inside the trains, as found in the London subway (Seaton et al., 2005). The cosmetics contribution was much lower (less than 3  $\mu\text{g m}^{-3}$ ) for women using powder cosmetics from zero to two days per week, than for women using powder cosmetics three to seven days per week (Fig. S7c). In this latter case, contributions reached more than 5  $\mu\text{g m}^{-3}$ .

m-3, which is similar to the highest contributions found by Hopke et al. (2003) for personal care products. These variations further confirm the identification of the sources as such, since the contributions varied accordingly to the reported exposure in the women diaries.

The completed average outdoor source apportionment (Fig. 4) resulted in a mineral contribution of 9% of the bulk PM<sub>2.5</sub>. Nitrate and ammonium average concentrations accounted for 8% and 9% of the bulk PM<sub>2.5</sub>, respectively. These are secondary compounds, the precursors of which can be originated by different sources, such as traffic (NO<sub>x</sub>) and sewer systems (NH<sub>3</sub>). OM average concentration accounted for 21% of the bulk PM<sub>2.5</sub>. This OM can have different origins, such as road traffic or biogenic emissions, among others (Minguillón et al., 2011). With the completed outdoor source apportionment, only 26% of the bulk PM<sub>2.5</sub> remains non-analysed, which could be attributed to the water uptake of the filter and hygroscopic PM components.

The contributions to the indoor environments were correlated with and similar to the corresponding contributions to the outdoors for most of the sources (Fig. 5). The most correlated were fueloil + sea salt ( $R^2 = 0.70$ ), sulphate ( $R^2 = 0.36$ , but a strong correlation was observed when some outliers were removed), road traffic ( $R^2 = 0.66$ ) and industry ( $R^2 = 0.73$ ), which could indicate the penetration of these sources from outdoors into indoors. These findings are in agreement with Larson et al. (2004), who also found strong indoor-outdoor correlations for mobile and secondary sources. The mineral source contributions were less correlated ( $R^2 = 0.40$ ), suggesting the possible different sources of indoor and outdoor mineral dust. The cigarette contribution was larger for personal exposure than for indoor and outdoor environments and the indoor-outdoor and the personal-outdoor correlations were poor ( $R^2 = 0.22$  and  $R^2 = 0.01$ , respectively), indicating the local influence of this source. The personal-outdoor correlation was quite strong for the sulphate source, despite the relatively low Pearson correlation coefficient ( $R^2 = 0.15$ ) due to some outliers, indicating the secondary nature of this source, which makes its contribution quite homogeneous and independent of the specific place. There was a very weak correlation ( $R^2 = 0.04$ ) between the road traffic contributions to the outdoor environment and to the personal exposure, indicating that this source varies widely with the location, despite the high penetration indoors as shown by the high indoor-outdoor correlation. To better evaluate these indoor-outdoor variations, the indoor/outdoor ratios of source contributions were examined, and they showed the same results as explained above (Fig. S8). Nevertheless, the wide range of indoor/outdoor ratios indicates the variations in infiltration efficiencies among homes, which is in agreement with previous studies (Allen et al., 2003).

#### **4. Conclusions**

PM<sub>2.5</sub> concentrations were higher for personal samples than for indoor and outdoor environments. Outdoor-indoor PM<sub>2.5</sub> correlation was moderate, outdoor-personal PM<sub>2.5</sub> correlation was poor and

indoor-personal PM<sub>2.5</sub> correlation was relatively strong.

Outdoor dust resuspension was evidenced by the higher mineral concentrations in outdoor samples. High K indoor concentrations were attributed to the influence of indoor sources, particularly cigarette smoke, supported by a strong indoor-personal correlation for K concentrations. Strong correlations for indoor-outdoor and/or for indoor-personal were found for BS, indicating the homogeneity of this pollutant in our evaluated microenvironments. Sulphate concentrations were similar in all environments, although some specific indoor and outdoor SO<sub>2</sub>- sources may have a local influence.

Although average trace elements concentrations were quite similar indoor, outdoor and for personal exposure, the correlations were moderate for most of the species, indicating the need for personal measurements in order to assess the personal exposure. PAHs concentrations were in general highly correlated indoor and outdoor suggesting high penetration of these species. The ratios between different PAHs concentrations indicate that the influence from road traffic could be due to both gasoline and diesel vehicles.

Six sources were identified by PMF for the indoor + outdoor datasets: secondary sulphate, fueloil + sea salt, mineral, cigarette, road traffic, and industrial. For the personal dataset, sulphate, fueloil + sea salt, and cigarette were also identified, whereas the road traffic and industrial sources were merged in a single source, reflecting the influence of the urban background cocktail. Two specific personal sources were found: cosmetics and train/subway. The contribution of the different sources varied widely among women, with secondary sulphate being the largest contributor. The high variations in the contributions of cigarette, train/subway and cosmetics sources were due to the woman time-activity.

The contributions to indoor environments were similar to and correlated with the corresponding outdoors for most of the sources, especially fueloil + sea salt, sulphate, road traffic, and industry. The mineral source contributions indoor vs. outdoor were less correlated, which indicates the possible different sources of mineral dust outdoors and indoors. The cigarette source had a higher influence indoors compared to outdoors, and it was even higher on the personal exposure, with poor correlations indoor-outdoor and outdoor-personal. The wide range of indoor/outdoor ratios indicates the variations in infiltration efficiencies among homes.

The results found in this study support the necessity of an assessment of the influence of different PM sources on personal exposure, as a base for further epidemiological studies.

## **Acknowledgements**

The work was conducted as part of ARIBA (Air Pollution and Pregnancy in Barcelona) funded by a Fondo de Investigación Sanitaria (FIS) grant (PI081109) by the ISCIII. M.C. Minguillón was funded by the JAE-Doc CSIC program, co-funded by the European Social Fund (ESF). A. Schembari was funded by an

ISCIII scholarship (PFIS e FI10/00476). P. Dadvand was funded by the Spanish Ministry of Science and Innovation by a Juan de la Cierva grant (JCI-2011-09937).

## References

- Aarnio, P., Yli-Tuomi, T., Kousa, A., Mäkelä, T., Hirsikko, A., Hämeri, K., Räsänen, M., Hillamo, R., Koskentalo, T., Jantunen, M., 2005. The concentrations and composition of and exposure to fine particles (PM<sub>2.5</sub>) in the Helsinki subway system. *Atmospheric Environment* 39, 5059e5066.
- Aceves, M., 1993. Seasonally dependent size distributions of aliphatic and polycyclic aromatic hydrocarbons in urban aerosols from densely populated areas. *Environment Science Technology* 27, 2896e2908.
- Allen, R., Larson, T., Sheppard, L., Wallace, L., Liu, L.J.S., 2003. Use of real-time light scattering data to estimate the contribution of infiltrated and indoor-generated particles to indoor air. *Environmental Science and Technology* 37, 3484e3492.
- Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., Hopke, P.K., 2009. Quantifying road dust resuspension in urban environment by multilinear engine: a comparison with PMF<sub>2</sub>. *Atmospheric Environment* 43, 2770e2780.
- Arhami, M., Minguillón, M.C., Polidori, A., Schauer, J.J., Delfino, R.J., Sioutas, C., 2010. Organic compound characterization and source apportionment of indoor and outdoor quasi-ultrafine particulate matter in retirement homes of the Los Angeles Basin. *Indoor Air* 20, 17e30.
- Bukowiecki, N., Gehrig, R., Hill, M., Lienemann, P., Zwicky, C.N., Buchmann, B., Weingartner, E., Baltensperger, U., 2007. Iron, manganese and copper emitted by cargo and passenger trains in Zürich (Switzerland): size-segregated mass concentrations in ambient air. *Atmospheric Environment* 41, 878e889.
- Cengiz, E., Wissing, S.A., Müller, R.H., Yazan, Y., 2006. Sunblocking efficiency of various TiO<sub>2</sub>-loaded solid lipid nanoparticle formulations. *International Journal of Cosmetic Science* 28, 371e378.
- Cohen, A.J., Anderson, H.R., Ostro, B., Pandey, K.D., Krzyzanowski, M., Künzli, N., Gutschmidt, K., Pope, A., Romieu, I., Samet, J.M., Smith, K., 2005. The global burden of disease due to outdoor air pollution. *Journal of Toxicology and Environmental Health e Part A* 68, 1301e1307.
- Commission Decision 2006/257/EC of 09 February 2006 Amending Decision 96/ 335/EC Establishing an Inventory and a Common Nomenclature of Ingredients Employed in Cosmetic Products.
- Cyrys, J., Heinrich, J., Hoek, G., Meliefste, K., Lewné, M., Gehring, U., Bellander, T., Fischer, P., Van Vliet, P., Brauer, M., Wichmann, H.E., Brunekreef, B., 2003. Comparison between different traffic-related particle indicators: elemental carbon (EC), PM<sub>2.5</sub> mass, and absorbance. *Journal of Exposure Analysis and Environmental Epidemiology* 13, 134e143.

Chillrud, S.N., Grass, D., Ross, J.M., Coulibaly, D., Slavkovich, V., Epstein, D., Sax, S.N., Pederson, D., Johnson, D., Spengler, J.D., Kinney, P.L., Simpson, H.J., Brandt- Rauf, P., 2005. Steel dust in the New York City subway system as a source of manganese, chromium, and iron exposures for transit workers. *Journal of Urban Health* 82, 33e42.

Choi, H., Perera, F., Pac, A., Wang, L., Flak, E., Mroz, E., Jacek, R., Chai-Onn, T., Jedrychowski, W., Masters, E., 2008. Estimating individual-level exposure to airborne polycyclic aromatic hydrocarbons throughout the gestational period based on personal, indoor, and outdoor monitoring. *Environmental Health Perspectives* 116, 1509e1518.

Di Maiuta, N., Schwarzentruher, P., 2011. Molecular detection of bacteria in calcium carbonate powder used in cosmetic formulations. *International Journal of Cosmetic Science* 33, 426e431.

Dockery, D.W., Spengler, J.D., 1981. Personal exposure to respirable particulates and sulfates. *Journal of the Air Pollution Control Association (United States)* 31,153e159.

Escrig Vidal, A., Monfort, E., Celades, I., Querol, X., Amato, F., Minguillón, M.C., Hopke, P.K., 2009. Application of optimally scaled target factor analysis for assessing source contribution of ambient PM10. *Journal of the Air and Waste Management Association* 59, 1296e1307.

Figueras, F., Meler, E., Iraola, A., Eixarch, E., Coll, O., Figueras, J., Francis, A., Gratacos, E., Gardosi, J., 2008. Customized birthweight standards for a Spanish population. *European Journal of Obstetrics & Gynecology and Reproductive Biology* 136, 20e24.

Gotschi, T., Oglesby, L., Mathys, P., Monn, C., Manalis, N., Koistinen, K., Jantunen, M., Hanninen, O., Polanska, L., Kunzli, N., 2002. Comparison of black smoke and PM2.5 levels in indoor and outdoor environments of four European cities. *Environmental Science & Technology* 36, 1191e1197.

Grimmer, G., Hildebrandt, A., 1975. Investigations on the carcinogenic burden by air pollution in man. XIII. Assessment of the contribution of passenger cars to air pollution by carcinogenic polycyclic hydrocarbons. *Zentralblatt fur Bakter- iologie. Hygiene. Krankenhaushygiene Betriebshygiene Preventive Medizin e Abt. 1 Orig. B* 161, 104e124.

Hänninen, O.O., Koistinen, K.J., Kousa, A., Keski-Karhu, J., Jantunen, M.J., 2002. Quantitative analysis of environmental factors in differential weighing of blank Teflon filters. *Journal of the Air and Waste Management Association* 52, 134e139.

Hänninen, O.O., Alm, S., Katsouyanni, K., Künzli, N., Maroni, M., Nieuwenhuijsen, M.J., Saarela, K., Srám, R.J., Zmirou, D., Jantunen, M.J., 2004a. The EXPOLIS study: implications for exposure research and environmental policy in Europe. *Journal of Exposure Analysis and Environmental Epidemiology* 14, 440e456.

Hänninen, O.O., Lebret, E., Ilacqua, V., Katsouyanni, K., Künzli, N., Srám, R.J., Jantunen, M., 2004b. Infiltration of ambient PM2.5 and levels of indoor generated non-ETS PM2.5 in residences of four



European cities. *Atmospheric Environment* 38, 6411e6423.

Hopke, P.K., Ramadan, Z., Paatero, P., Norris, G.A., Landis, M.S., Williams, R.W., Lewis, C.W., 2003. Receptor modeling of ambient and personal exposure samples: 1998 Baltimore particulate matter epidemiology-exposure study. *Atmospheric Environment* 37, 3289e3302.

Jacquemin, B., Lanki, T., Sunyer, J., Cabrera, L., Querol, X., Bellander, T., Moreno, N., Peters, A., Pey, J., Pekkanen, J., 2007. Levels of outdoor PM<sub>2.5</sub>, absorbance and sulphur as surrogates for personal exposures among post-myocardial infarction patients in Barcelona, Spain. *Atmospheric Environment* 41, 1539e1549.

Kaida, T., Kobayashi, K., Adachi, M., Suzuki, F., 2004. Optical characteristics of titanium oxide interference film and the film laminated with oxides and their applications for cosmetics. *Journal of Cosmetic Science* 55, 219e220.

Kilbourn, B.T., 1988. Metallurgical applications of yttrium and the lanthanides. *Journal of Metals* 40, 22e25.

Kleeman, M.J., Robert, M.A., Riddle, S.G., Fine, P.M., Hays, M.D., Schauer, J.J., Hannigan, M.P., 2008. Size distribution of trace organic species emitted from biomass combustion and meat charbroiling. *Atmospheric Environment* 42, 3059e3075.

Kliucininkas, L., Martuzevicius, D., Krugly, E., Prasauskas, T., Kauneliene, V., Molnar, P., Strandberg, B., 2011. Indoor and outdoor concentrations of fine particles, particle-bound PAHs and volatile organic compounds in Kaunas, Lithuania. *Journal of Environmental Monitoring* 13, 182e191.

Koistinen, K.J., Kousa, A., Tenhola, V., Hänninen, O., Jantunen, M.J., Oglesby, L., Kuenzli, N., Georgoulis, L., 1999. Fine particle (PM<sub>2.5</sub>) measurement methodology, quality assurance procedures, and pilot results of the EXPOLIS study. *Journal of the Air and Waste Management Association* 49, 1212e1220.

Kornartit, C., Sokhi, R.S., Burton, M.A., Ravindra, K., 2010. Activity pattern and personal exposure to nitrogen dioxide in indoor and outdoor microenvironments. *Environment International* 36, 36e45.

Larson, T., Gould, T., Simpson, C., Liu, L.J.S., Claiborn, C., Lewtas, J., 2004. Source apportionment of indoor, outdoor, and personal PM<sub>2.5</sub> in Seattle, Washington, using positive matrix factorization. *Journal of the Air and Waste Management Association* 54, 1175e1187.

Minguillón, M.C., Perron, N., Querol, X., Szidat, S., Fahrni, S.M., Alastuey, A., Jimenez, J.L., Mohr, C., Ortega, A.M., Day, D.A., Lanz, V.A., Wacker, L., Reche, C., Cusack, M., Amato, F., Kiss, G., Hoffer, A., Decesari, S., Moretti, F., Hillamo, R., Teinilä, K., Seco, R., Peñuelas, J., Metzger, A., Schallhart, S., Müller, M., Hansel, A., Burkhardt, J.F., Baltensperger, U., Prévôt, A.S.H., 2011. Fossil versus contemporary sources of fine elemental and organic carbonaceous particulate matter during the DAURE campaign in Northeast Spain. *Atmospheric Chemistry and Physics* 11, 12067e12084.

Miranda, K., Dionísio, A.G.G., Pessoa Neto, O.D., Gomes, M.S., Pereira-Filho, E.R., 2012. Determination

of Cd levels in smoke condensate of Brazilian and Paraguayan cigarettes by thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS). *Microchemical Journal* 100, 27e30.

Mirzaei, P.A., Haghghat, F., 2012. A procedure to quantify the impact of mitigation techniques on the urban ventilation. *Building and Environment* 47, 410e420.

Nerriere, É., Zmirou-Navier, D., Blanchard, O., Momas, I., Ladner, J., Le Moullec, Y., Personnaz, M.B., Lameloise, P., Delmas, V., Target, A., 2005. Can we use fixed ambient air monitors to estimate population long-term exposure to air pollutants? The case of spatial variability in the Genotox ER study. *Environmental Research* 97, 32e42.

Nerriere, E., Guegan, H., Bordigoni, B., Hautemaniere, A., Momas, I., Ladner, J., et al., 2007. Spatial heterogeneity of personal exposure to airborne metals in French urban areas. *Science of the Total Environment* 373, 49e56.

Nethery, E., Brauer, M., Janssen, P., 2008. Time-activity patterns of pregnant women and changes during the course of pregnancy. *Journal of Exposure Science and Environmental Epidemiology* 19, 317e324.

Niu, J., Rasmussen, P.E., Wheeler, A., Williams, R., Chénier, M., 2010. Evaluation of airborne particulate matter and metals data in personal, indoor and outdoor environments using ED-XRF and ICP-MS and co-located duplicate samples. *Atmospheric Environment* 44, 235e245.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5, 111e126.

Pekey, B., Bozkurt, Z.B., Pekey, H., Dogan, G., Zararsiz, A., Efe, N., Tuncel, G., 2010. Indoor/outdoor concentrations and elemental composition of PM<sub>10</sub>/PM<sub>2.5</sub> in urban/industrial areas of Kocaeli City, Turkey. *Indoor Air* 20, 112e125.

Perez, L., Medina-Ramón, M., Künzli, N., Alastuey, A., Pey, J., Pérez, N., Garcia, R., Tobias, A., Querol, X., Sunyer, J., 2009. Size fractionate particulate matter, vehicle traffic, and case-specific daily mortality in Barcelona, Spain. *Environmental Science and Technology* 43, 4707e4714.

Pio, C.A., Legrand, M., Alves, C.A., Oliveira, T., Afonso, J., Caseiro, A., Puxbaum, H., Sanchez-Ochoa, A., Gelencsér, A., 2008. Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period. *Atmospheric Environment* 42, 7530e7543.

Querol, X., Alastuey, A., Rodriguez, S., Plana, F., Ruiz, C.R., Cots, N., Massagué, G., Puig, O., 2001. PM<sub>10</sub> and PM<sub>2.5</sub> source apportionment in the Barcelona metropolitan area, Catalonia, Spain. *Atmospheric Environment* 35, 6407e6419.

Querol, X., Viana, M., Alastuey, A., Amato, F., Moreno, T., Castillo, S., Pey, J., de la Rosa, J., Sánchez de la Campa, A., Artñano, B., Salvador, P., García Dos Santos, S., Fernández-Patier, R., Moreno-Grau, S., Negral, L., Minguillón, M.C., Monfort, E., Gil, J.I., Inza, A., Ortega, L.A., Santamaría, J.M., Zabalza, J., 2007. Source origin of trace elements in PM from regional background, urban and industrial sites of Spain. *Atmospheric Environment* 41, 7219e7231.

Reche, C., Viana, M., Amato, F., Moreno, T., Alastuey, A., Hillamo, R., Teinilä, K., Saarnio, K., Seco, R., Peñuelas, J., Mohr, C., Prévôt, A., Querol, X., 2012. Biomass burning contributions to urban aerosols in a coastal Mediterranean city. *Science of the Total Environment* 427e428, 175e190.

Ritz, B., Wilhelm, M., Hoggatt, K.J., Ghosh, J.K.C., 2007. Ambient air pollution and preterm birth in the environment and pregnancy outcomes study at the University of California, Los Angeles. *American Journal of Epidemiology* 166, 1045e1052.

Sapkota, A., Chelikowsky, A.P., Nachman, K.E., Cohen, A.J., Ritz, B., 2010. Exposure to particulate matter and adverse birth outcomes: a comprehensive review and meta-analysis. *Air Quality, Atmosphere and Health*, 1e13.

Schembari, et al. Personal, indoor and outdoor air pollution levels in pregnant women. *Atmospheric Environment*, ATMENV-D-12e00397, submitted for publication.

Seaton, A., Cherrie, J., Dennekamp, M., Donaldson, K., Hurley, J.F., Tran, C.L., 2005. The London underground: dust and hazards to health. *Occupational and Environmental Medicine* 62, 355e362.

Setton, E., Marshall, J.D., Brauer, M., Lundquist, K.R., Hystad, P., Keller, P., Cloutier- Fisher, D., 2010. The impact of daily mobility on exposure to traffic-related air pollution and health effect estimates. *Journal of Exposure Science and Environmental Epidemiology* 21, 42e48.

Shah, P.S., Balkhair, T., 2011. Air pollution and birth outcomes: a systematic review. *Environment International* 37, 498e516.

Sicre, M.A., Marty, J.C., Saliot, A., Aparicio, X., Grimalt, J., Albaiges, J., 1987. Aliphatic and aromatic hydrocarbons in different sized aerosols over the Mediterranean Sea: occurrence and origin. *Atmospheric Environment* 21, 2247e2259.

Stafoggia, M., Schwartz, J., Forastiere, F., Perucci, C.A., 2008. Does temperature modify the association between air pollution and mortality? A multicity case- crossover analysis in Italy. *American Journal of Epidemiology* 167, 1476e1485.

van den Hooven, E.H., Pierik, F.H., de Kluizenaar, Y., Willemsen, S.P., Hofman, A., van Ratingen, S.W., Zandveld, P.Y.J., Mackenbach, J.P., Steegers, E.A.P., Miedema, H.M.E., Jaddoe, V.W.V., 2011. Air pollution exposure during pregnancy, ultrasound measures of fetal growth, and adverse birth outcomes: a prospective cohort study. *Environmental Health Perspectives* 120, 150e156.

Vardavas, C.I., Patelarou, E., Grandér, M., Chatzi, L., Palm, B., Fthenou, E., Roumeliotaki, T., Koutis, A., Kafatos, A., Vrijheid, M., Connolly, G.N., Murphy, S., Vahter, M., Kogevinas, M., 2011. The association between active/passive smoking and toxic metals among pregnant women in Greece. *Xenobiotica* 41, 456e463.

Viana, M., Kuhlbusch, T.A.J., Querol, X., Alastuey, A., Harrison, R.M., Hopke, P.K., Winiwarter, W., Vallius, M., Szidat, S., Prévôt, A.S.H., Hueglin, C., Bloemen, H., Wählin, P., Vecchi, R., Miranda, A.I.,

Kasper-Giebl, A., Maenhaut, W., Hitenberger, R., 2008. Source apportionment of particulate matter in Europe: a review of methods and results. *Journal of Aerosol Science* 39, 827e849.

Vrijheid, M., Martinez, D., Manzanares, S., Dadvand, P., Schembari, A., Rankin, J., Nieuwenhuijsen, M., 2011. Ambient air pollution and risk of congenital anomalies: a systematic review and meta-analysis. *Environmental Health Perspectives* 119, 598e606.

Wheeler, A.J., Wallace, L.A., Kearney, J., Van Ryswyk, K., You, H., Kulka, R., Brook, J.R., Xu, X., 2011. Personal, indoor, and outdoor concentrations of fine and ultrafine particles using continuous monitors in multiple residences. *Aerosol Science and Technology* 45, 1078e1089.

Zanobetti, A., Schwartz, J., 2009. The effect of fine and coarse particulate air pollution on mortality: a national analysis. *Environmental Health Perspectives* 117, 898e903

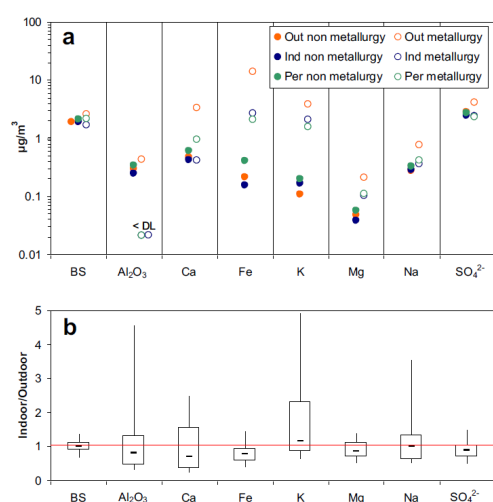


Fig. 1. a) Outdoor (Out), indoor (Ind) and personal (Per) average major components concentrations excluding one of the women and for this specific woman in a metallurgy-influenced environment. b) Indoor/outdoor ratios for major components concentrations excluding data below detection limit (<DL). Extremes of the whiskers indicate 10th and 90th percentiles. Grey line (red in the web version) indicates an indoor/outdoor ratio equal to 1.

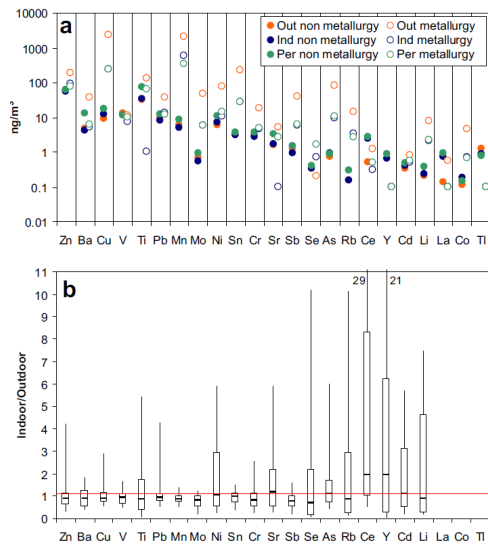
**Table 1** Average concentrations, number of data points >DL (detection limit), and square Pearson correlation coefficients between indoor, outdoor and personal species concentrations (only those >DL, and excluding those corresponding to the woman living in a metallurgy-processing-influenced environment). In bold  $R^2 > 0.80$ .

	Ind Ave	Out Ave	Per Ave	Ind $n > DL$	Out $n > DL$	Per $n > DL$	Ind-Out $R^2$	Ind-Per $R^2$	Out-Per $R^2$
PM <sub>2.5</sub>	24	20	27	<b>61</b>	<b>61</b>	<b>62</b>	<b>0.18</b>	<b>0.44</b>	<b>0.04</b>
BS	1.9	1.9	2.1	<b>61</b>	<b>61</b>	<b>62</b>	<b>0.54</b>	<b>0.63</b>	<b>0.31</b>
Al <sub>2</sub> O <sub>3</sub>	0.2	0.3	0.3	<b>52</b>	<b>50</b>	<b>53</b>	<b>0.24</b>	<b>0.06</b>	<b>0.02</b>
Ca	0.4	0.5	0.6	<b>59</b>	<b>60</b>	<b>60</b>	<b>0.11</b>	<b>0.27</b>	<b>0.06</b>
Fe	0.2	0.4	0.4	<b>59</b>	<b>58</b>	<b>62</b>	<b>0.24</b>	<b>0.00</b>	<b>0.00</b>
K	0.2	0.2	0.2	<b>44</b>	<b>42</b>	<b>46</b>	<b>0.02</b>	<b>0.54</b>	<b>0.00</b>

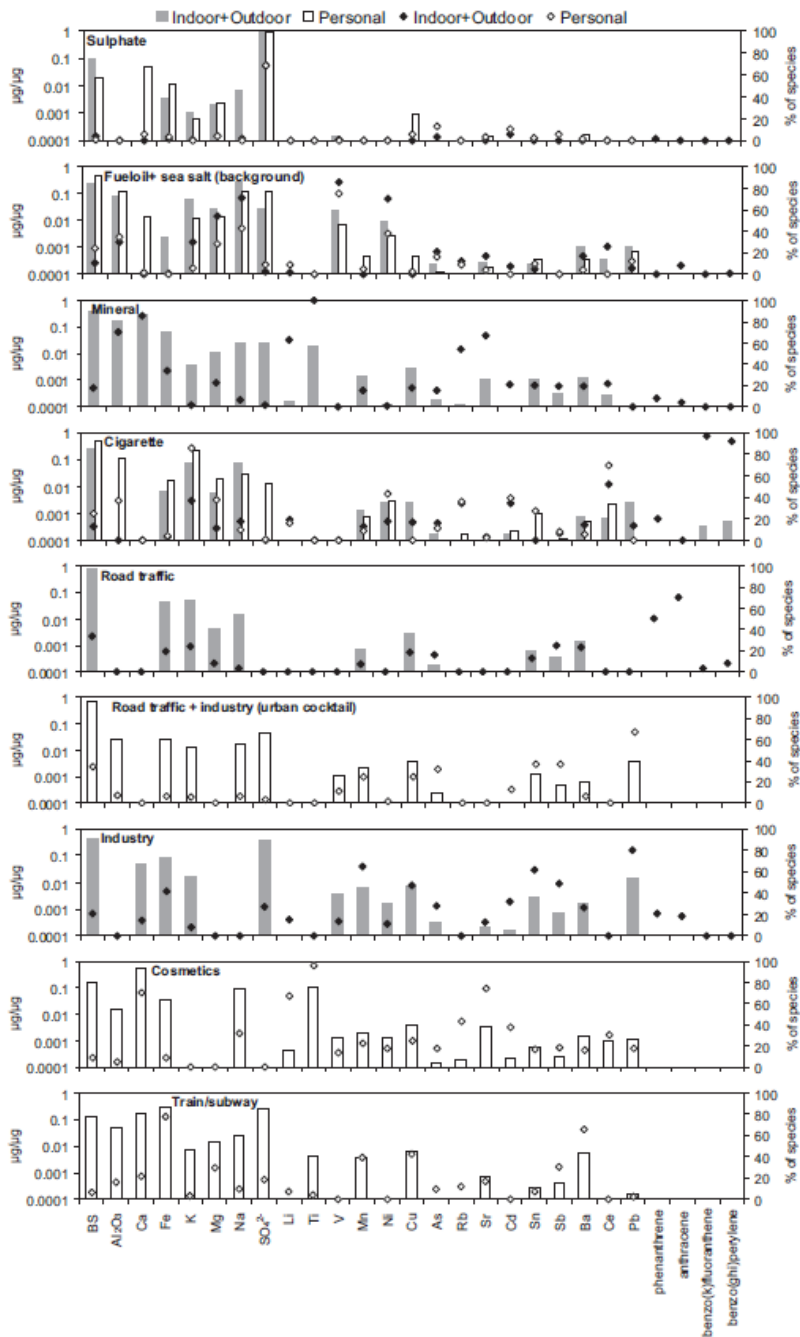
	Mg	0.04	0.05	0.06	38	38	45	0.78	0.29	0.37
	Na	0.3	0.3	0.3	60	55	58	0.10	0.07	0.14
	P	0.01	0.01	0.01	1.1	8	10	0.28	0.21	0.72*
4	SO <sup>2-</sup>	2.4	2.8	2.6	61	59	62	0.38	0.18	0.17
	Li	0.3	0.3	0.4	15	18	21	0.01	0.32	0.05
	Ti	32.6	33.9	75.1	54	52	60	0.55	0.14	0.13
	V	11.5	12.7	11.7	58	56	60	0.93	0.88	0.83
	Cr	2.9	3.4	3.7	52	54	58	0.30	0.19	0.02
	Mn	14.0	38.0	13.7	59	58	62	0.70	0.09	0.03
	Co	0.2	0.2	0.2	6	2	5	**	**	**
	Ni	7.4	7.1	10.8	53	52	58	0.08	0.11	0.00
	Cu	15.8	45.9	21.1	59	58	62	0.00	0.15	0.10
	Zn	54.7	61.0	62.9	61	58	61	0.60	0.07	0.07
	As	1.1	2.0	1.0	57	50	56	0.04	0.15	0.01
	Se	0.3	0.4	0.4	20	24	24	0.13	0.04	0.10
	Rb	0.2	0.4	0.3	12	11	22	0.59	0.87	0.16
	Sr	1.7	1.6	3.4	59	55	62	0.04	0.02	0.06
	Y	0.7	0.9	0.9	26	24	23	0.01	0.00	0.00
	Zr	35.8	40.7	34.5	35	35	41	0.01	0.11	0.00
	Nb	0.2	0.2	0.4	8	7	15	0.44	0.93*	0.00
	Mo	0.6	1.4	1.0	45	47	54	0.23	0.02	0.01
	Cd	0.4	0.4	0.5	29	27	36	0.14	0.59	0.00
	Sn	3.5	6.6	4.1	59	57	62	0.73	0.59	0.56
	Sb	1.0	1.9	1.6	50	54	56	0.00	0.04	0.00
	Ba	4.1	5.2	13.2	59	58	62	0.04	0.01	0.00
	La	0.7	0.1	0.9	27	4	35	**	0.56	**
	Ce	2.5	0.5	2.7	47	37	52	0.06	0.48	0.03
	Hf	0.6	0.5	0.6	20	17	17	0.30	0.03	0.00
	Tl	0.9	1.2	0.8	5	6	6	0.87	0.65	0.91
	Pb	8.3	10.2	12.4	55	49	56	0.54	0.05	0.03
	Fluorene	19.3	24.4		64	64		0.16		
	Phenanthrene	135.4	175.8		64	64		0.39		
	Anthracene	34.6	37.9		64	64		0.49		
	Fluoranthene	145.8	274.4		64	64		0.24		
	Pyrene	161.	323.8		64	64		0.27		
	Retene	67.7	211.4		64	64		0.67		
	Benzo[a]anthracene	93.2	143.1		64	64		0.42		
	Chrysene b triphenylene	194.	259.1		64	64		0.21		
	Benzo[b o j]fluoranthene	138.8	155.1		64	64		0.44		
	Benzo[k]fluoranthene	129.4	141.7		64	64		0.51		
	Benzo[a]fluoranthene	34.5	33.1		64	64		0.76		
	Benzo[e]pyrene	181.	199.4		64	64		0.39		
	Benzo[a]pyrene	116.	114.1		64	64		0.68		
	Perylene	27.2	25.0		64	64		0.47		
	Indene[1,2,3-cd]pyrene	136.	116.0		64	64		0.46		
	Benzo[ghi]perylene	218.5	212.6		64	64		0.50		
	Dibenzo[ah]anthracene	30.3	25.1		64	64		0.52		

\*Due to a single high pair of points.

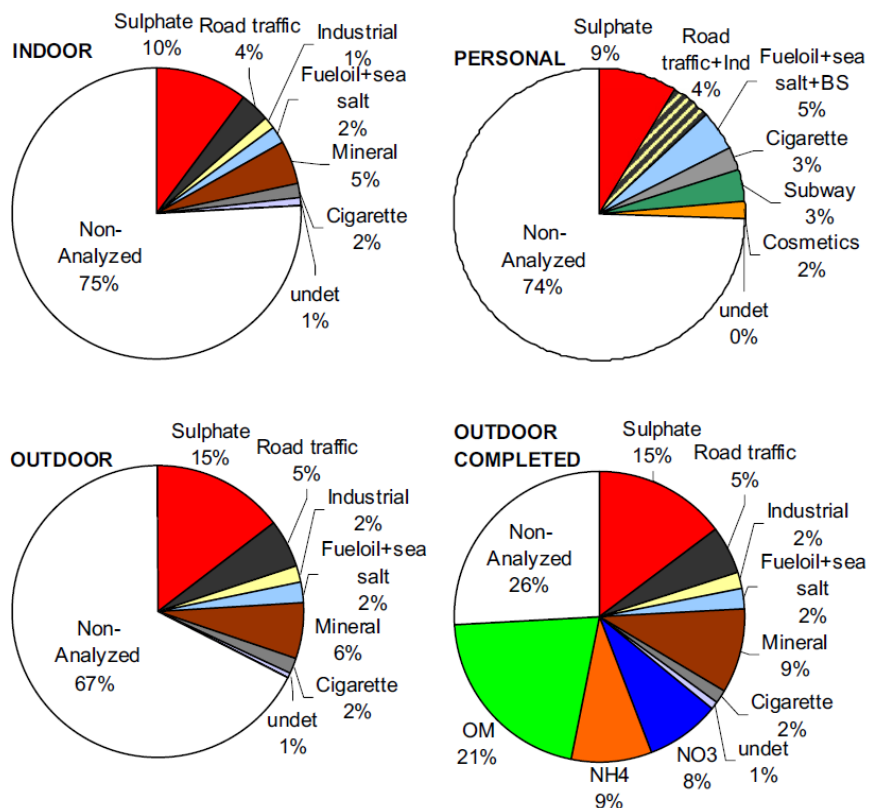
\*\*Due to low availability of data, it is not possible to calculate the  $R^2$ .



**Fig. 2.** a) Outdoor (Out), indoor (Ind) and personal (Per) average trace elements concentrations excluding one of the women and for this specific woman in a metallurgy- influenced environment. Note that the y-axis is in logarithmic scale. b) Indoor/outdoor ratios for trace elements concentrations excluding data  $<DL$ . Extremes of the whiskers indicate 10th and 90th percentiles. Indoor/outdoor ratios not shown for La, Co and Tl because of low data availability. Grey line (red in the web version) indicates an indoor/outdoor ratio equal to 1.

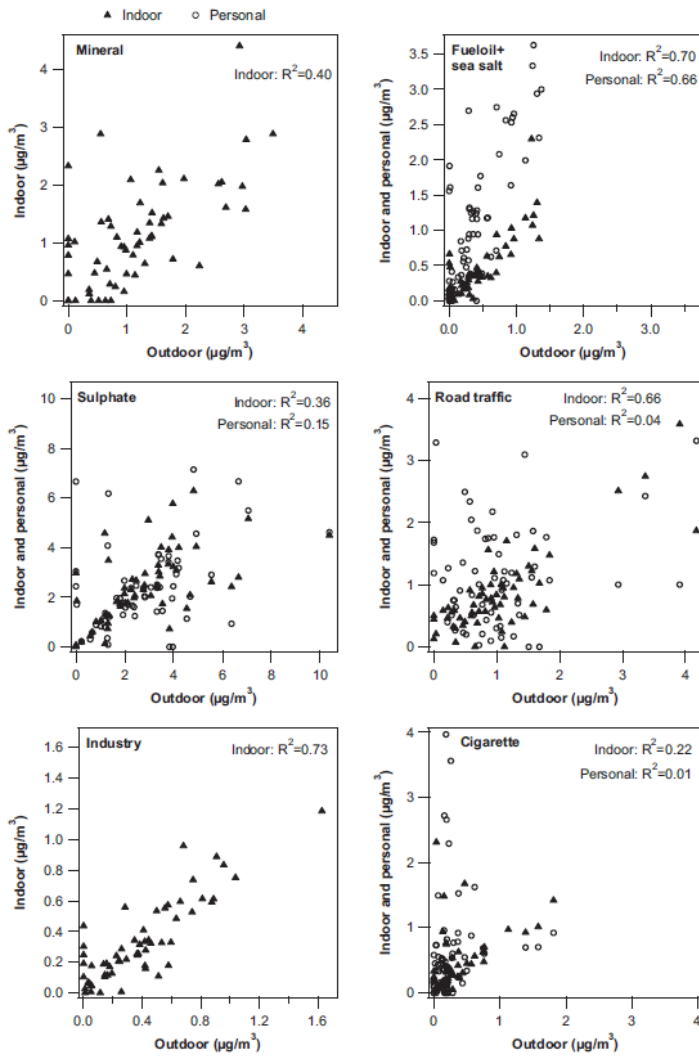


**Fig. 3.** Source profiles (bars, mg mg<sub>-1</sub>, left axis) identified for indoor and outdoor samples together and for personal samples, and percentage of ambient species concentration apportioned by each source (diamonds, right axis).



**Fig. 4.** Average source contribution to PM<sub>2.5</sub> for indoor, outdoor and personal samples. Outdoor completed includes average NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and OM concentrations in Barcelona from November 2008 to November 2009, and the mineral source has been recalculated to include the SiO<sub>2</sub> (as 3\*Al<sub>2</sub>O<sub>3</sub>).





**Fig. 5.** Source contribution to indoor environment and personal exposure vs. source contribution to outdoor environment for each of the sources.