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Source Apportionment of PM_{2.5} and PM₁₀ by Ionic and Mass Balance (IMB) in a traffic-influenced urban atmosphere, in Portugal

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Abstract

The recently developed Ion and Mass Balance (IMB) source apportionment methodology was applied to a traffic influenced urban aerosol, permitting the quantification of the contributions of 11 source components, or formation processes, which accounted for more than 96% of the measured aerosol mass loading. Main sources included exhaust and non-exhaust road vehicle emissions, biomass burning, secondary inorganic and organic pollutants, and primary soil and sea salt emissions. While in summer secondary carbonaceous matter is the predominant fraction, in winter biomass burning accounts, on average, for more than 40% of the PM_{2.5} aerosol. Comparison with Positive Matrix Factorization (PMF) showed the complementary characteristics of the two methodologies. PMF yielded 8 source profiles, including industry and oil combustion sources not discriminated by IMB. PMF is better at quantifying multiple component contributions to sources. IMB solves problems of collinearity between aerosol tracers and permits the discrimination of secondary formed pollutants.

1. Introduction

Atmospheric contamination by aerosols is one of the most important environmental problems worldwide, principally in urban areas, affecting billions of people, with great wellbeing impacts and economic costs to nature and human health (Ramanatham et al., 2001; Lohmann and Feichter, 2005; Poschl, 2005; Brunekreef and Fosberg, 2005; WHO, 2016). Urban atmospheric particulate pollution is a complex phenomenon involving a large number of anthropogenic and natural sources, such as industry, transport, building construction, domestic heating and sea spray and dust emissions, which produce primary particulate pollutants and secondary aerosols from gaseous and particulate precursors (Almeida et al., 2006; Oliveira et al., 2010; Mirante et al., 2014). As a result of these intrinsic and complex mix and interactions, the anthropogenic and natural activities responsible for the aerosol contamination are therefore difficult to account for.

The quantitative knowledge of the sources and processes intervening in aerosol contamination is essential for the design of efficient policies aiming at reducing atmospheric pollution, principally in urban areas where most people live and contamination levels are higher (Belis et al., 2013; Gulia et al., 2015; Zhu et al., 2018). The source apportionment of

emissions and formation processes, based on the measurement of aerosol levels and composition in the atmosphere, at the receptor, are tools frequently employed to estimate the causes of atmospheric contamination (Blanchard et al., 1999). Several types of receptor modelling are common in aerosol source apportionment and include Chemical Mass Balance, when the sources and their composition are identified, or multivariate models, otherwise (Hopke, 1985; Henry et al., 2004). Multivariate models use the relative variability of aerosol composition to identify a reduced number of independent variables, associated with sources and formation processes, and involve mathematical methodologies including factorial analysis and multilinear regression techniques (Pio et al., 1989; Pio et al., 1996). Presently, the most used multivariate receptor model is the Positive Matrix Factorization (PMF) because of the simplicity and availability of the software, and the relative advantages it provides concerning axis rotation, weight of measured variables, etc., by comparison with previous methodologies (Paatero and Tapper, 1994; Paatero, 1999; Reff et al., 2007; Salvador et al., 2016).

Besides these methods, other techniques have been employed in aerosol source apportionment, such as tracer enrichment, ionic balances and mass balances, usually as scrutinizing methods, to partially estimate the importance of specific sources (Watson et al., 2002). The European Commission recommends the parallel and complementary utilization of the panoply of methods available to, fully, elaborate source apportionments with a better accuracy in the accounting of particulate pollution sources (Belis et al., 2014).

Several authors, including ourselves, have published in the past the results of source apportionment scrutinising methodologies. Methods such as the relation between anions and cations constrained by the electro neutrality (Alastuey et al., 2005; Mirante et al., 2014), the direct mass balance of aerosol constituents applied to elements and compounds (Harrison et al., 2003; Johanson et al., 2009; Oliveira et al., 2010), or edge line estimation of source ratios associated with bibliographic information on source compositions (Henry, 2003; Pio et al., 2008; Pio et al., 2011), were employed. These methods successfully allowed to apportion fractions of the measured aerosol to sources and formation processes, including secondary inorganic and organic formation, or biomass burning during wild fires and residential heating.

In a recent publication, these different scrutinizing methodologies were used to evaluate, for the first time, the sources and formation processes contributing to the total aerosol Particulate Mass (PM) (Cardoso et al., 2018). This technique was called Ion and Mass Balance (IMB) and was applied to the PM₁₀ aerosol apportionment in a background marine environment frequently affected by strong Saharan dust intrusions, but with low levels of carbonaceous matter (Cape Verde Islands). The IMB method compared favourably with PMF applied to the same data, demonstrating its capabilities, as a complementary methodology, to detect and quantify sources and processes that were not clearly evaluated by PMF.

In the present publication, the IMB methodology was further tested, now applying it to a completely different data set: aerosol contamination at an urban traffic location with an important contribution of carbonaceous aerosol from different combustion sources. This data set includes PM_{2.5} and PM₁₀ aerosol sampled and measured in one of the main streets of Porto, Portugal, over one year. Therefore, it takes into account the different pollution drivers

acting in an urban area in summer and winter. The study was part of the AIRUSE LIFE+-project. Given that the aerosol composition and source apportionment by PMF has already been published, (Amato et al., 2016), it is now possible to independently test the current IMB methodology.

2. Aerosol Sampling and Analysis

The atmospheric aerosol was collected on the roof top (≈ 2.5 meters high) of the Air Quality Network monitoring station located on the kerbside of the Fernão de Magalhães Avenue, a major urban arterial route connecting the centre of Porto city to the inner circular motorway. The Porto region, located on the north coast of the Iberian Peninsula, is the second largest urban conurbation in Portugal, after Lisbon, with around 1.8 million habitants. Because of its location, Porto is influenced by sea-land breezes with winds from northwest that occur mostly in summer months. In the winter season, the lowering of the Azores anticyclone brings rainy low-pressure centres and fronts with winds blowing predominantly from southwest. According to the 30-year climate normal (1971-2000) provided by the Portuguese meteorological services (IPMA – *Instituto Português do Mar e da Atmosfera*), Porto has a temperate type of climate Csb (Köpen-Geiger classification) characterised by rainy winters and mild sunny and dry summers. The average monthly air temperature ranges between 9°C in January and 20°C in July, and the average values of the total amount of precipitation vary between 18 mm in July and 195 mm in December, with a total of around 1000 mm per year (IPMA, 2019).

The sampling campaign extended for approximately one year, during 2013-14, and was integrated in the European LIFE+-Project AIRUSE. Details of project objectives, region and site characteristics, sampling and analytical methodologies are published elsewhere (Custodio et al., 2016; Amato et al., 2016) and therefore only an integrated summary of the information is provided here.

Aerosol particles were collected in parallel, every 3 days, for 24 hours periods, with three samplers. A high-volume instrument with a PM₁₀ inlet, operating at a flow rate of 1.13 m³.min⁻¹, collected samples over pre-fired (550°C, 5h) quartz fibre filters. The sampler was equipped with a PM_{2.5} impactor to allow the fractional collection of PM_{2.5} and PM_{2.5-10} particles. The quartz filters were mainly used for the determination of the Elemental Carbon (EC) and Organic Carbon (OC) aerosol constituents. Two low volume samplers, equipped with PM_{2.5} or PM₁₀ inlets, were operated at flow rates of 2.3 m³.h⁻¹ to collect particles onto PTFE filters. These filters were used for the determination of total mass, water-soluble ions and major or trace elements.

The aerosol total mass concentration was determined by gravimetry, at 50% relative humidity and 20 °C, with a microbalance. Water-soluble anions (chloride, Cl⁻; nitrate, NO₃⁻; sulphate; SO₄²⁻; oxalate, C₂O₄²⁻; fluoride, F⁻; formate, HCOO⁻; acetate, CH₃COO⁻; methanesulfonate, CH₃SO₃⁻; glycolate, HOCH₂COO⁻) and cations (ammonium, NH₄⁺; sodium, Na⁺; potassium, K⁺; calcium, Ca²⁺; magnesium, Mg²⁺) were determined by ion chromatography in the Teflon filter deposit, after extraction with ultrapure water and filtration with a 0.45 µm pore PTFE syringe filter. All elements with Z > 10 were directly measured in Teflon filters by PIXE at

a 3 MV Tandatron accelerator with an external beam set-up (Lucarelli et al., 2018). Each sample was irradiated for ~5 min with a 3.2 MeV proton beam (~2 mm² spot, 5–50 nA intensity). A filter scanning was carried out to analyse most of the deposit area. PIXE spectra were fitted using the GUPIX code and elemental concentrations were obtained by a calibration curve from a set of thin standards of known areal density (Micromatter Inc.).

OC and EC were determined by filter heating and analysis of evolved CO₂ with a Non-Dispersive Infra-Red (NDIR) detector after light transmittance correction for charring. A home-made analyser was used. The heating program was similar to the EUSAAR2 protocol. Full description of the equipment, methodology, calibrations and inter-comparisons can be found in Pio et al., (1998) and Pio et al., (2011).

PM_{2.5} quartz filters were also used for the measurement of levoglucosan by liquid chromatography/amperometric detection after aqueous extraction (Caseiro et al., 2007). In the present data set levoglucosan was only measured in PM_{2.5}. Our previous measurements in Porto (Oliveira et al., 2007) showed that, on average, 86-87 % of levoglucosan is present in the aerosol fine fraction. Yttri et al., (2005), also found approximately 90% of levoglucosan in particles <2µm. Based on this information the levoglucosan mass fraction in PM₁₀ was estimated to be 1.11 times that obtained in PM_{2.5}.

Finally, quartz filters were used to measure carbonates by means of a procedure described by Pio et al., (1994), after acidification of the filter with phosphoric acid and quantification of the CO₂ evolved by NDIR. Probably as result of the granitic soil characteristics of the region and the influence of secondary acidic urban pollution, the carbonates were residual and only observed in PM_{2.5-10}.

With the different sampling and analytical methodologies, it was possible to obtain equal information for PM₁₀ and PM_{2.5} aerosol size fractions, concerning the compounds analysed. For the IMB analysis, only sampling days containing complete valid analytical information for both PM_{2.5} and PM₁₀ samples were considered, to allow a clear inter-comparison between size fractions. This reduced somewhat the data set to a total of 97 samples. Because of sampling and analytical uncertainties and, principally for compounds mostly concentrated in the fine fraction, in some days the amount in the PM_{2.5} fraction can be slightly higher than in the corresponding PM₁₀ fraction. This limits the ability to separately apportion sources associated with those compounds for the coarse aerosol fraction (PM_{2.5-10}). Therefore, only when feasible, for sources with important contributions to coarse particles, results are also discriminated as PM_{2.5-10}.

Besides the global apportionment for the total sampling campaign, partial evaluations for cold and hot seasonal periods were also estimated, to better infer sources and formation processes strongly influenced by season. Given the typical climate of Porto, summer samples were considered to be those collected between June 1st and September 30th (37 samples). Likewise, winter includes samples collected between November 1st and February 28th (27 samples).

3. Ionic and Mass Balance methodologies

When the aerosol composition is extensively evaluated, with the chemical analysis of major and trace elements, water-soluble inorganic ions, EC and OC, together with a few important specific tracers such as levoglucosan, it is possible to totally apportion by mass balance the measured aerosol mass, into classes that represent aerosol sources, or formation processes. Even with a thoroughly chemical analysis such as this, usually no more than 75% of the total mass can be directly accounted for, because oxygen, an important element present in organic matter, soil and sorbed/crystallised water, is not usually quantified. Therefore, inferences based on bibliographic information have to be assumed, to totally apportion the measured particulate mass. A thorough discussion about the IMB principles and constraints is presented in Cardoso et al., (2018). In that publication the methodologies for the sequential apportionment of the total aerosol mass were also fully detailed. In the present paper, to reduce repetition, just a brief description of IMB principles and methods is given, focusing mainly on alterations and adaptations to the present aerosol urban characteristics.

1-As a first step Al, Si and Ti were chosen as true major representative elements of soil sources, because of the good correlations between their respective concentrations and the similarity of inter-elements ratios with bibliographic information. Other major soil elements, such as Fe and Ca, may originate, in the present urban environment, from other important sources. The calculation of the soil dust contribution, either from natural origin, or from manmade soil resuspension in roads and building activities, is performed through equation 1:

$$\text{Soil} = 1.33 \cdot (2.14 \cdot \text{Si} + 1.89 \cdot \text{Al} + 1.67 \cdot \text{Ti}) \quad 1$$

where 1.33 is a multiplying coefficient, taken from Mason and Moore (1982) average crustal composition, to account for the contribution of other crust constituents. In the present dataset Al and Si were strongly correlated ($R=0.99$) with a Si/Al ratio of 1.7-1.9 (see Figure S1, in the Supplementary Information Section, for visualisation), very similar to the ratio observed in Cape Verde studies (1.64 – Cardoso et al., 2018) and quite different from the average crustal rock composition (Si/Al = 3.41-3.92; Mason and Moore, 1982; Wedepohl, 1995). The possible reasons for this discrepancy are discussed in Cardoso et al., (2018). Contrary to what happened with Cape Verde dusty aerosol, where Fe was chosen as the most representative dust element, here Fe is not included directly in equation 1 because in urban areas, subject to intense road traffic impact, large amounts of Fe are emitted by vehicles from sources such as break wear (Thorpe and Harrison, 2008; Pant and Harrison, 2013; Amato, 2018 and references there-in). In urban areas, Fe is usually a good tracer of non-exhaust road vehicle emissions.

2-Aluminium concentrations were used to estimate the soil contribution to Fe, Ca, Na^+ , Mg^{2+} , K^+ , Ca^{2+} , SO_4^{2-} , NO_3^- and Cl^- , based on minimum edge lines between Al and those compounds. Edge lines are here considered as representative ratios of the soil dust composition. To obtain more objective estimations and in coherence with our previous publications (Pio et al., 2011; Cardoso et al., 2018), edge lines are calculated by tracing a best-fit linear line through the five percent of total sample points with a lower $(Y - Y_{\min})/\text{Al}$ ratio (5 points, in our case). Y represents the element under consideration and $Y_{\min}$ is the

respective minimum measured concentration. As an example, two edge lines are presented in Figure 1 for Fe and Na⁺, in PM₁₀ samples. Other edge line examples can be found in Figure S2, in the Supplementary Information Section.

The Fe/Al edge line ratio (the slope of the lower edge linear best fit) presents a value comparable to crustal average ratios (Figure 1). The edge line methodology usually gives minimum contributions from the source under consideration, in the present case soil. However, it is possible that, as a result of natural variability of the source composition, somewhat higher source contributions to the compound in question may happen, on average. The methodology can give reliable results even when other sources of the compound Y are always present, if this presence is small and approximately constant for the samples used in the edge line estimation. If Y is always present the edge line will intercept the Y axis at a positive value equal to the minimum constant presence of Y from complementary sources.

From the above edge line procedure, it is possible to have a first estimation, in each sample, of the amounts of constituents, such as Fe_{soil}, Ca_{soil}, Ca²⁺_{soil}, Na⁺_{soil}, Mg²⁺_{soil}, K⁺_{soil}, SO₄²⁻_{soil}, NO₃⁻_{soil} and Cl⁻_{soil}, in soil dust.

3- A first estimation of sea salt Na⁺_{ssalt} and Mg²⁺_{ssalt} can be obtained from the differences between total Na⁺, or Mg²⁺, and soil Na⁺_{soil}, or Mg²⁺_{soil}, ion concentrations calculated in the previous step. These sea salt ion contributions are then recalculated to obtain a better Na⁺_{ss} and Mg²⁺_{ss} sea salt estimation by using minimum values and the Mg²⁺/Na⁺ ratio in sea water. If it is considered that during sea spray formation there is no ion fractionation the “true” Na⁺_{ss} and Mg²⁺_{ss} in the aerosol obeys to the Mg²⁺_{ss}/Na⁺_{ss} = 0.12 ratio (Turekian, 1968). Therefore, if Mg²⁺_{ssalt}/Na⁺_{ssalt} < 0.12, Mg²⁺_{ssalt} is chosen as the true Mg²⁺_{ss} concentration. Otherwise, Na⁺_{ssalt} is considered the true Na⁺_{ss} tracer. The Na⁺_{ssalt}-Na⁺_{ss} excess is considered to be part of soil contribution. Similar assumptions are made for Mg²⁺.

Fig. 1. Edge lines for Fe/Al and Na⁺/Al in PM₁₀, together with best-fit equations. Points in grey, red and blue represent samples taken in different seasonal periods. Points with a black edge were used to estimate the edge lines. The brown area represents the range of average crustal ratio, taken from Mason and Moore, (1982) and Wedepohl, (1995).

The previously estimated “true” sea salt Na^+_{ss} and $\text{Mg}^{2+}_{\text{ss}}$ enable the calculation of other important sea salt spray ions, using the salt ratios in seawater (Tukerian, 1968). Care needs to be taken to ensure that calculated sea salt ion contribution does not exceed the total ion amount present in the aerosol, especially for Cl^-_{ss} , because of possible volatilisation processes resulting from sea salt attack by atmospheric acidic pollutants (Pio and Lopes, 1998).

4-Determination of soil and sea salt contributions allows further estimation of excess Fe, Ca, Ca^{2+} and K^+ , by subtracting soil and/or sea salt values from the total measured ion concentrations. K^+ , principally in the fine fraction, is an important product and tracer of biomass burning. In urban areas Fe and Ca are also predominant products of non-exhaust road transport emissions (Kwak et al., 2013; Thorpe and Harrison, 2008).

5-When all the major particulate water-soluble ions are analysed, the electro-neutrality principle imposes an equality between the sum of anions and cations, for each sample, on an equivalent basis. This is the case for the present dataset, for which a ratio of approximately 0.9 between the sum of cations and anions and a linear correlation coefficient of 0.97 were observed (see Figure S3 in the Supplementary Information Section for better visualization). The small deficit of 10% of cations in relation to anions is, in part, possibly due to the presence of acidic compounds such as ammonium bisulphate or sulphuric acid, now that the H^+ cation was not directly analysed in the samples.

Therefore, using the principle of electro-neutrality, the anions not yet attributed to soil and sea salt were associated sequentially with the various non-soil and non-sea salt free cations in a sequence based on previous experimental and bibliographic evidence (Seinfeld and Pandis, 2016).

Firstly, free SO_4^{2-} , followed by free NO_3^- , (free means: in excess to soil and sea salt, or in excess of previous associations), are associated with NH_4^+ , until all ammonium is neutralized. Secondly, free NO_3^- is sequentially associated with free sea salt and free soil cations.

Thirdly, carbonates are totally associated with $\text{Ca}^{2+}_{\text{soil}}$ and $\text{Mg}^{2+}_{\text{soil}}$, in the soil. Sequentially, free SO_4^{2-} is associated with free sea salt and soil cations until all cations are neutralised. In samples where not all SO_4^{2-} is neutralised in the previous sequences, acidic sulphate in the form of ammonium bisulphate or sulphuric acid are considered to be present. In the balance, this excess is accounted for as H_2SO_4 .

In samples where there is an excess of Cl^- , by comparison with sea salt plus soil, the free chloride is associated with free soil cations until complete neutralization of either ions.

6-In urban polluted atmospheres carbonaceous matter is frequently the most important contributor to the aerosol mass. In the present samples OC+EC carbon constitutes, on average, 40% and 50% of total aerosol mass analysed in PM_{10} and $\text{PM}_{2.5}$, respectively. Therefore, the correct source apportionment of this class of substances is fundamental for a complete aerosol source evaluation. In the present study, carbonaceous matter concentrates almost exclusively in particles smaller than $2.5 \mu\text{m}$, principally in what concerns EC, for which more than 99%, on average, is in this size range.

In the present methodology, the concentrations of elemental and organic carbon from biomass burning (EC_{bb} and OC_{bb}) are estimated from the edge lines relating carbon with levoglucosan, as shown in Figure 2. The edge line methodology seems to be feasible in this situation because biomass burning emissions are independent from other sources of carbon. Edge line ratio estimations are probably more correct than bibliographic results taken from direct source composition measurements, because they constitute a local average of multiple burning conditions with a variety of biofuels and combustion devices that provide a large range of emission compositions. They also consider levoglucosan stability effects during transport and sampling processes (Hoffmann et al., 2010).

Figure 2 shows that levoglucosan (levog) tends to be much higher during winter, when home heating using biomass is frequent. Two to four summer samples with significant levoglucosan values are coincident with periods of forest fires in the region (Custódio et al., 2016). The ratios of $EC_{bb}/levog$ and $OC_{bb}/levog$ are approximately 3 and 6, respectively, giving an OC_{bb}/EC_{bb} ratio of 2. These values are somewhat in the extreme of ranges observed in direct measurements of biomass burning source emissions, although values in literature vary widely (Puxbaum et al, 2007; Piazzalunga et al., 2011; Vicente and Alves, 2018).

Gonçalves et al. (2010), after laboratory biomass burning experiments with an eco-labelled woodstove, obtained $OC_{bb}/levog=2.2-6.9$ and $EC_{bb}/levog=0.91-9.8$, for different wood species; the values of OC_{bb}/EC_{bb} ratio varied between 0.9 and 4.4. Gonçalves et al. (2011) measured $OC_{bb}/levog$ ratios of 3.0-3.4 in hot start emissions from pine wood burning in a traditional woodstove. Measurements with other 4 species in the same equipment gave ratios in the range 1-10. Burning the same species in a fireplace resulted in ratios in the range 1.7-10. The ratio of OC_{bb}/EC_{bb} in the same experiments ranged from 2 to 21 and 3 to 19 with hot start burning in fireplaces and woodstoves, respectively.

Fig. 2. Relation between levoglucosan and EC or OC, for $PM_{2.5}$ aerosol samples. The edge lines represent the ratios between levoglucosan and EC_{bb} (2.98) or OC_{bb} (5.90). Points in grey, red and blue represent samples take in different seasonal periods. Points with a black edge were used to estimate the edge lines.

The composition of biomass fuels in Porto region and respective combustion emissions were calculated and published by Gonçalves et al., (2012). From this inventory, as well as from specific emissions of Gonçalves et al., (2011), weighted ratio values of $OC_{bb}/levog=3.6$ and $EC_{bb}/levog=0.75$ were estimated.

On the other hand, edge lines estimation from rural PM_{10} measurements in an Aveiro rural site (data from Pio et al., 2007) gave $OC/levog=5$ and $EC/levog=0.8$.

The estimation of EC_{bb} and OC_{bb} from the above-referred edge lines allows, for each sample, the calculation of non-biomass burning carbon, by difference to total carbon. Figure 3 presents this information for $PM_{2.5}$ and PM_{10} . Non-biomass burning elemental carbon (EC_{nbb}) corresponds mostly to primary exhaust emissions from fossil fuel burning (EC_{ffp}). However, some of the EC_{nbb} may also result from non-exhaust road vehicle emissions by tyre wear, now that carbon black constitutes 22-30% of tyre mass (Milani et al., 2004; Thorpe and Harrison, 2008).

Non-biomass burning organic carbon (OC_{nbb}) includes the contribution of primary emissions from fossil fuel burning (OC_{ffp}) and secondary aerosol formation from primary gaseous and particulate compounds (OC_{sec}). Primary bio aerosols (OC_{bio}) (mainly in coarse fractions; Fröhlich-Nowoisky et al., 2016) and primary emissions from non-exhaust road vehicle tyre, brake and road wear in fine and coarse particles (OC_{nexh}) are also possible (Amato, 2018). Rubber hydrocarbons constitute 47-55% of the tyre mass (Milani et al., 2004; Thorpe and Harrison, 2008).

Estimation of non-exhaust carbon emissions using the edge line approach, by comparison, for example, with excess Fe emitted from non-exhaust sources of road vehicles (Fe_{nexh}), is not possible because, when daily averaged, exhaust and non-exhaust carbon emissions are highly correlated. Therefore, the subsequent estimations of EC_{ffp} and OC_{ffp} likely include minor amounts of non-exhaust road transport carbon emissions.

Figure 3 presents the inter-comparison between EC_{nbb} and OC_{nbb} , for $PM_{2.5}$ and PM_{10} particles. Edge lines in the Figure can be interpreted as representing the emission ratios between OC_{ffp} and EC_{ffp} , if the contribution from primary non-exhaust tyre, brake and road wear sources are neglected. The values calculated for Porto are 0.20 and 0.26, for $PM_{2.5}$ and PM_{10} , respectively. These values are of the order of those measured at kerb sites and road tunnels in the Iberian Peninsula, although in the lower end of the range. However, it should be born in mind that, here, carbon from biomass burning is excluded from the comparison. Pio et al., (2011), observed OC/EC minimum ratios of 0.29, for $PM_{2.5}$, and 0.33, for PM_{10} , in a roadway tunnel with only lightweight car traffic in Lisbon. Mirante et al., (2014), found minimum ratio values of 0.30 and 0.55 at a kerbside site in Madrid, for $PM_{2.5}$ and PM_{10} , respectively.

Fig. 3. Comparison between $EC-EC_{bb}=EC_{ffp}$ and $OC-OC_{bb}=OC_{nbb}$ in $PM_{2.5}$ and PM_{10} samples. Points in grey, red and blue represent samples taken in different seasonal periods. Points with a black edge were used to estimate the edge lines.

The determination of fossil fuel OC primary emissions enables, by difference to OC_{nbb} , to estimate excess OC that can be secondarily formed (OC_{sec}) or of primary biogenic origin in pollen, plant fragments or fungi (OC_{bio}). As OC_{bio} is usually residual, especially in fine particles in urban areas (Fröhlich-Nowoisky et al., 2016), this fraction will be referred to as OC_{sec} .

7- As usual, the sum of the source apportioned mass from previous steps constitutes, in average, to only 70% of the total particulate mass measured, because important components, such as oxygen in organic matter (OM) and sorbed water, were not taken into account. Gonçalves et al. (2010) calculated ratios of OM_{bb}/OC_{bb} of 1.2-2.4 based on PM organic speciation, for emissions from the biomass burning of three wood species in a woodstove. As this was achieved by mass balance it should be taken as an upper limit for the ratio. Reid et al., (2005) in a review of biomass burning emissions, suggested a range of 1.4-1.8 for the OM_{bb}/OC_{bb} mass ratio.

For the ambient aerosol, OM/OC ratio values in the range of 1.2-2.3 have been proposed by several authors (see Cardoso et al., 2018 and references there in) with lower values in urban areas at kerbsides and maximum ratios in conditions of long-range transport with extensive oxidation of primary particulate compounds and formation of secondary products from gaseous compounds (Turpin and Lim, 2001; Ervens et al., 2011).

Based on the bibliographic information, the following conversion factors were applied to calculate OM from OC: for biomass burning $OM_{bb}/OC_{bb}=1.6$; for primary organic mass emissions from fossil fuel burning the lower range documented in the literature was used ($OM_{ffp}/OC_{ffp}=1.2$); oppositely, the higher range values given in the bibliography were applied to secondary organic mass ($OM_{sec}/OC_{sec}=2.0$).

Sorption of air moisture by hygroscopic aerosol constituents and the formation of hydrates for some of the aerosol components are important because the total mass measurement is

performed at 20 °C and 50% relative humidity, in conditions of equilibrium with the water vapour present in the laboratory. A detailed discussion of the subject is given in Cardoso et al., (2018) and, therefore, it will not be repeated here. As an approach, it is considered that the different aerosol constituents behave independently in the interaction with ambient water vapour, and that a thermodynamic equilibrium exists between the condensed and gaseous phases. Therefore, sorbed water was independently estimated for each aerosol component, using the methodology and coefficients presented in Cardoso et al., (2018). In short, the following water/dry salt ratios were used: for sea salt, a ratio of 0.4 was applied, corresponding to the solid deliquescent point equilibrium, taken from Tang et al., (1997); for ammonium salts, a ratio of 0.4 was employed, from Tang and Munkelwitz (1994) and Xu et al., (1998); for the mass of polar organic molecules a water/OC ratio of 0.2, from Speer et al., (2003), was applied; for water-soluble soil dust and secondary dust inorganic compounds a ratio of 0.4 was adopted, based on the results of the ISORROPIA model (Nenes et al., 1998a, 1998b); finally, for insoluble minerals a ratio of 0.1 was used, based on Schuttlefield et al., (2007).

4. Results and Discussion

4.1. Aerosol Composition and Levels

The average concentrations, plus standard deviations, of measured total mass and aerosol constituents are presented in Table 1 for fine (PM_{2.5}) and coarse particles (PM_{2.5-10}). Only samples and constituents used in IMB apportionment were considered to be included in this table. Complementary information concerning analysed aerosol components not used in IMB apportionment are presented in Table S1, in the Supplementary Information Section.

From Table 1, it is possible to conclude that PM levels are similar in winter and summer for both fine and coarse particles. Fine particles contain most of the carbonaceous aerosol mass and also most of ammonium and sulphates. On the contrary, sodium, magnesium and chlorides are predominant in the coarse aerosol fraction. Elements such as Al, Si and Fe, as well as nitrates, distribute evenly between the two size fractions.

Ammonium, sulphates, Al and Si peak during summer, while chlorides and sodium are higher during winter.

Most of the PM₁₀ aerosol mass in the kerb side urban environment concentrates in the PM_{2.5} fine fraction. Therefore, for most of the aerosol components the amounts and conclusions are similar for PM_{2.5} and PM₁₀ measurements. Due to analytical limitations, the measured concentrations of water-soluble Na⁺ and Ca²⁺ were, in a few cases, slightly higher than the respective bulk concentrations of Na and Ca.

Table 1. Average (±standard deviation) concentrations measured in fine and coarse particles, for the total campaign and summer and winter periods, of aerosol constituents used in the IMB source apportionment methodology.

$\mu\text{g.m}^{-3}$	PM _{2.5}			PM _{2.5-10}		
	Year	Summer	Winter	Year	Summer	Winter
PM	25.8±15.2	28.8±16.6	28.8±6.2	8.9±4.7	8.6±4.2	7.8±6.1
EC	4.80±3.04	4.21±2.69	6.58±0.59	0.03±0.04	0.04±0.05	0.04±0.04
OC	5.86±4.79	5.96±4.57	8.34±6.14	0.34±0.23	0.45±0.30	0.28±0.12
levog	0.36±0.63	0.11±0.26	0.96±0.91	0.04±0.07	0.01±0.03	0.11±0.10
MSA	0.03±0.04	0.06±0.04	0.01±0.01	0.00±0.01	0.00±0.02	0.00±0.00
CO ₃ ²⁻				0.02±0.02	0.02±0.02	0.02±0.02
Cl ⁻	0.55±0.68	0.22±0.23	0.94±0.93	1.61±1.77	0.94±0.97	1.60±1.94
NO ₃ ⁻	1.07±1.00	0.81±0.68	1.64±1.32	0.89±0.76	1.16±0.82	0.53±0.64
SO ₄ ²⁻	2.10±1.95	3.17±2.54	1.14±0.48	0.38±0.80	0.56±1.14	0.16±0.40
NH ₄ ⁺	0.61±0.69	0.82±0.89	0.53±0.41	0.06±0.23	0.03±0.21	0.010±0.24
Na ⁺	0.53±0.69	0.43±0.26	0.61±0.60	1.18±1.00	0.91±0.64	1.00±1.04
Mg ²⁺	0.06±0.05	0.07±0.05	0.05±0.04	0.14±0.11	0.10±0.07	0.13±0.11
Ca ²⁺	0.14±0.14	0.21±0.18	0.11±0.11	0.16±0.11	0.18±0.10	0.11±0.14
K ⁺	0.20±0.17	0.21±0.20	0.29±0.18	0.06±0.05	0.06±0.04	0.04±0.07
Na	0.44±0.29	0.38±0.18	0.44±0.34	1.06±0.78	0.84±0.51	0.96±0.81
Mg	0.08±0.05	0.09±0.05	0.06±0.06	0.20±0.12	0.18±0.07	0.18±0.13
Al	0.23±0.30	0.41±0.39	0.10±0.10	0.23±0.22	0.38±0.24	0.13±0.14
Si	0.48±0.58	0.83±0.76	0.24±0.24	0.45±0.34	0.66±0.35	0.33±0.31
P	0.011±0.01	0.015±0.020	0.009±0.007	0.006±0.007	0.005±0.007	0.006±0.006
S	0.80±0.78	1.22±1.03	0.41±0.22	0.09±0.12	0.04±0.11	0.10±0.09
K	0.33±0.28	0.40±0.36	0.37±0.24	0.10±0.11	0.13±0.17	0.06±0.05
Ca	0.16±0.17	0.24±0.23	0.10±0.07	0.18±0.09	0.21±0.10	0.15±0.10
Ti	0.015±0.020	0.025±0.024	0.008±0.007	0.010±0.013	0.014±0.018	0.007±0.007
Mn	0.008±0.009	0.012±0.012	0.006±0.005	0.005±0.005	0.007±0.008	0.004±0.003
Fe	0.37±0.30	0.49±0.38	0.33±0.23	0.48±0.27	0.49±0.31	0.51±0.30
Cl	0.65±0.78	0.25±0.23	1.12±1.04	1.63±1.71	0.98±0.98	1.47±1.57
Zn	0.090±0.13	0.130±0.183	0.080±0.098	0.017±0.018	0.022±0.023	0.016±0.015
Cu	0.015±0.009	0.016±0.010	0.017±0.010	0.017±0.009	0.015±0.008	0.020±0.012

4.2. IMB Results

The application of the IMB methodology to the present aerosol data allowed the determination of 11 components, corresponding to the contributions of emissions or formation processes, namely, Insoluble Dust (**InsDu**), Soluble Dust (**SolDu**), Sea Salt (**SeaSalt**), secondary aerosol formation by reaction of inorganic acids with either dust (**SICdu**), sea salt (**SICss**) or ammonia (**SICam**), non-exhaust road traffic emissions from brakes and tyres (**n-Exhaust**), biomass burning emissions (**CARBbb**), (**Kbb**), direct carbonaceous matter emissions from vehicle exhausts (**CARBffp**) and organic matter from secondary origin (**CARBsec**). Some of these components are part of a single emission source,

such as CARBbb and Kbb, others such as CARBsec result from precursors emitted from a variety of sources.

In the present IMB evaluation it is not possible to differentiate between natural and anthropogenic dust and so both are treated and included together in the same source classes. However, the method allows to differentiate original dust from dust attacked by atmospheric acids. Previous studies in the Porto urban area demonstrated that, in the background urban and kerb side areas, resuspension by road traffic is a major contributor to aerosol dust (Oliveira et al., 2010). This latter study showed that, at roadside, more than 50-70% of coarse particles come from road resuspension, respectively in winter and summer. The values go up to as much as 90%, for the coarse fraction, during the day, in summer.

Figure 4 gives the average contribution of the different IMB sources for PM_{2.5} and PM₁₀, for the whole campaign and for summer and winter periods. Complementary information concerning IMB source contributions for individual samples can be found in Figure S4, in the Supplementary Information.

Fig. 4. IMB average source contributions to PM_{2.5} and PM₁₀, for the entire sampling campaign and for summer and winter periods. “Unacc” means unaccounted mass. Values are presented as μg.m⁻³ and percentage of total PM.

The contributions presented in Figure 4 include the sorbed water, attributed to each source. Sorbed water constitutes on average 12-14% of the weighted aerosol mass. Its inclusion in the IMB permits to close the mass balance within 96 to 101% of the measured aerosol mass, on average.

The results of IMB are also summarised in Table 2, for fine and coarse aerosol fractions. In the fine fraction, carbonaceous components and secondary inorganic matter are largely dominant. In the coarse size range, around 90% of the mass has a dust, sea salt or road traffic non-exhaust origin.

For the whole campaign, carbonaceous matter accounts for 47%, in PM₁₀, and more than 60%, in PM_{2.5}, of the total mass. In winter, the majority of carbonaceous mass results from biomass burning emissions, which contributes to more than 40% of the winter aerosol mass. During summer, secondary aerosol formation is the main fraction of the organic aerosol loading. Primary carbonaceous aerosol emission by vehicle exhaust is approximately constant over the year, accounting for 15-18% of the total fine aerosol mass.

Table 2. Contributions from sources estimated by IMB to fine and coarse particles, (in $\mu\text{g}\cdot\text{m}^{-3}$), for the entire campaign and for summer and winter periods (averages $\pm$ standard deviations). Predominant contributions are presented in bold.

Sources	PM _{2.5}			PM _{2.5-10}		
	Year	Summer	Winter	Year	Summer	Winter
SeaSalt	0.98 $\pm$ 1.33	0.38 $\pm$ 0.57	1.51 $\pm$ 1.80	3.94$\pm$4.24	2.13 $\pm$ 2.38	4.07$\pm$4.20
SICss	0.66 $\pm$ 0.80	0.95 $\pm$ 0.76	0.12 $\pm$ 0.21	1.11$\pm$1.43	1.38$\pm$1.70	0.56 $\pm$ 0.91
SICam	3.38$\pm$3.81	4.41$\pm$4.98	3.01 $\pm$ 2.29	0.32 $\pm$ 1.47	0.23 $\pm$ 1.57	0.56 $\pm$ 1.51
SICdu	1.54$\pm$1.02	1.44 $\pm$ 0.91	2.10$\pm$1.25	0.34 $\pm$ 1.42	0.87 $\pm$ 1.09	-0.32 $\pm$ 1.79
SolDu	0.42 $\pm$ 0.57	0.75 $\pm$ 0.74	0.17 $\pm$ 0.16	0.53 $\pm$ 0.49	0.82$\pm$0.58	0.34 $\pm$ 0.37
InsDu	1.61 $\pm$ 2.17	2.89$\pm$2.83	0.66 $\pm$ 0.85	1.51 $\pm$ 1.31	2.30$\pm$1.43	1.12 $\pm$ 1.10
n-Exhaust	0.38 $\pm$ 0.30	0.39 $\pm$ 0.32	0.46 $\pm$ 0.35	0.54 $\pm$ 0.42	0.35 $\pm$ 0.43	0.73$\pm$0.45
Kbb	0.22 $\pm$ 0.21	0.21 $\pm$ 0.22	0.35$\pm$0.25	0.01 $\pm$ 0.05	0.01 $\pm$ 0.05	-0.01 $\pm$ 0.07
CARBbb	4.65 $\pm$ 8.16	1.49 $\pm$ 3.36	12.4$\pm$11.7	0.07 $\pm$ 0.12	0.02 $\pm$ 0.05	0.19 $\pm$ 0.18
CARBffp	4.65 $\pm$ 2.78	4.80$\pm$2.71	4.69$\pm$3.13	0.30 $\pm$ 0.18	0.33 $\pm$ 0.19	0.27 $\pm$ 0.19
CARBsec	6.58 $\pm$ 5.55	9.92$\pm$6.68	4.18 $\pm$ 3.47	0.17 $\pm$ 0.43	0.43 $\pm$ 0.45	-0.08 $\pm$ 0.32
Unacc	0.69 $\pm$ 4.18	1.16 $\pm$ 4.92	-0.88 $\pm$ 3.49	0.09 $\pm$ 3.20	-0.25 $\pm$ 3.41	0.39 $\pm$ 3.28
SUM	25.8 $\pm$ 15.2	28.8 $\pm$ 16.6	28.8 $\pm$ 17.4	8.9 $\pm$ 4.7	8.6 $\pm$ 4.2	7.8 $\pm$ 6.1

The sea salt contribution to the local aerosol mass is concentrated in the coarse particles, with maximum values in winter. Suspended dust is equally distributed between fine and coarse fractions, with concentrations peaking during the summer season. An important fraction of the dust seems to be soluble, in part as a result of the reaction with atmospheric acidic constituents.

The formation of secondary inorganic compounds (SIC), by reaction of inorganic acids with ammonia, sea salt and dust, maximises in summer for SICam, concentrating almost exclusively in the fine aerosol fraction. SICss also forms predominantly in summer, accumulating, instead, in the coarse particles fraction. SICdu appears, mostly, in fine particles and occurs also in winter. This probably results from the fact that coarse dust at this kerbside site is mostly of local origin in the nearby road traffic, without enough residence time to enable secondary reactions.

Figure 5 depicts the SIC aerosol composition, for individual PM₁₀ samples, over the entire sampling campaign, using the IMB calculation methodology. Ammonium salts are mostly

formed by reaction with sulphuric acid, with some contribution from ammonium nitrate during winter periods, when temperature and humidity favour the condensation of this compound (Pio et al., 1992; Seinfeld and Pandis, 2016). In some samples, principally in summer, ammonium only partially neutralises sulphuric acid.

Sea salt reacts mostly with nitric acid. The reaction occurs throughout the year but peaks during summer when in some days most of the chlorine is volatilised from the sea salt (Pio and Lopes, 1998). HCl production from this reaction or from other formation processes contributes, together with HNO_3 and H_2SO_4 , to the production of secondary dust compounds. However, some of the sea salt excess chloride present, principally in winter, can be originated from biomass burning emissions (Alves et al., 2011).

Fig. 5. Contribution of different acids to the formation of SIC compounds in ammonium, sea salt and dust PM_{10} particles, on an equivalent basis, over the entire sampling campaign. Blue and orange shaded areas represent winter and summer periods, respectively.

4.3. Accuracy and errors

The accuracy of the IMB methodology is difficult to estimate quantitatively. A fully quantitative accounting for all errors would need inputs from experiments and literature,

which frequently have no available accuracy information or are subject to unknown and unpredictable errors.

Besides unexpected errors derived from hypothesized and applied source associations and formation mechanisms, the errors influencing the accuracy of the IMB source apportionment have the following origins and contributions: errors from sampling and chemical analysis; errors derived from the application of edge lines used to infer source compositions; errors associated with the application of coefficients taken from literature.

The sampling and measurement of aerosol mass and composition are prone to a significant number of errors, some of which can only be perceived qualitatively. Errors derive both from sampling and chemical analysis. Correct sampling is affected by the utilization of different sampling inlets and filters to separate and accumulate the aerosol mass for subsequent analysis. Gas-particle interferences in the filters during sampling and imprecisions in the size fractionation and sampling flow measurement are frequently the most important sampling errors. Analytical errors are associated with the presence of variable blanks in filters and the characteristics of analytical instrumentation. Most of these errors are of the order of 5-15%, but percentual analytical errors can be substantially higher for samples and compounds at levels near the analytical detection limit.

The evaluation of ratios of source components by the edge approach is also influenced by reasonable errors. An insight into the value of these errors can be achieved through the value of the correlation coefficients of the best fit edge lines. When the correlation coefficient R is near 1 the edge points have a low dispersion in relation to the best fit line and there is more confidence on the reasonability of the edge line approach. Using the R value more confidence on the source ratios can be put for component pairs such as Fe/Al and Na^+/Al in PM_{10} , or OC/Levog and Mg^{2+}/Al in $\text{PM}_{2.5}$ with R values above 0.98, than for the pairs NO_3^-/Al and OC/EC in PM_{10} or $\text{SO}_4^{2-}/\text{Al}$ or NO_3^-/Al in $\text{PM}_{2.5}$, with R values lower than 0.91. R tends to be in the lower part of the edge line R range for pairs with EC, indicating that this aerosol component is less accurately distributed across sources. This may derive from the high variability in EC source emissions, as indicates the literature, and the difficulty in correctly analyse EC. Although the errors in EC source distribution can be substantial, their impact on the amount of source contributions is probably small because EC is only a minor component of the carbonaceous aerosol.

The edge line approach implies that the aerosol has a constant relative composition, for the evaluated components, in the various aerosol samples. Minor relative concentration variations are considered by the linear best fit calculation but stronger source enrichment in some samples is possible. This originates an error by deficit to the contribution of the component to the source into question. This error is probably more important for the components of the carbonaceous aerosols and respective sources, such as biomass burning and primary carbonaceous emissions from road vehicles, because it is known from the literature that carbonaceous source composition is highly variable with time and with individual source. However, as shown in the next section, the IMB estimation of biomass burning contributions is quite similar to the quantification by PMF, an indication that these errors are possibly smaller than feared.

The third source of errors in IMB apportionment derives from the introduction of coefficients taken from literature, based in previous measurements and published calculations. The most important factors used in IMB are the soil coefficient in equation 2, coefficients to transform OC into OM and coefficients to estimate water in the various aerosol constituents. The scientific literature provides information on these coefficients mostly without estimation of errors. However, it is possible to infer the qualitative accuracy of some coefficients from the dispersion of proposed values in different publications. For the OM/OC ratio the published values vary between 1.2 and 2.3, depending from the oxidation state of the carbonaceous aerosol, being in the lower part of the range for fresh emissions from fossil fuel combustion and in the maxima values for biomass burning and old aerosol masses subject to gas-to-particle interaction. In the present IMB, different OM/OC factors were applied to carbonaceous matter, depending from the source/formation process type, which probably reduces the final error.

Another possibly important error is associated with the quantification of sorbed water by the different aerosol components. Probably the major error for water calculation derives from estimation of water sorbed in sea salt, both because of the hygroscopicity of the material and of the important sea salt amounts present in the coastal environment. A thorough discussion of the possible errors in soil and water estimation are given in the previous publication on IMB source apportionment (Cardoso et al., 2018) and therefore the reader should consult this publication for more detailed information. Furthermore, in the present case the impact of sea salt sorbed water on the whole aerosol loading is lower than in the previous situation of a site located in the middle of the ocean with low anthropogenic carbonaceous pollution. The IMB quantification of the sea salt source contribution agrees quite well with the PMF results (see next section) a strong indication of the reduced impact of errors in the methodology estimation.

It is necessary, however, to consider that the ionic balance and the measured PM constrain the sum of the errors (Malm et al., 1994; Andrews et al., 2000). Malm et al. (1994) used this comparison as a validation and self-consistency check for their reconstructed aerosol mass balance. Being the sum of estimated masses within 96 %–103 % of the $PM_{2.5}$ and within 98–101% of the PM_{10} total mass measured, the individual errors are probably limited (or of opposite directions, with mutual compensation).

4.4. Comparison with PMF

A good way to evaluate the capability of IMB to estimate aerosol source contributions is to make a comparison with other well-established source apportionment methodologies such as Positive Matrix Factorisation (PMF). PMF is the most trusted and used computational methodology to identify and quantify the contribution of sources and processes to atmospheric aerosol contamination. The US EPA PMF v5 was previously applied to the total $PM_{2.5}$ and PM_{10} aerosol data, together, to estimate source profiles and composition. Details of the methodology and results are available in Amato et al., (2016). Here only the PMF outcome results, in a comparison context with IMB, are discussed.

In the present comparison, the original profiles obtained by the application of PMF to the entire sampling data set (114 $PM_{2.5}$ + 118 PM_{10} samples) are used, but for a more correct

inter-comparison, of the individual and average source contributions, only the PMF outcomes for the coincident 97 PM_{2.5} and 97 PM₁₀ samples are considered. Therefore, the PMF average estimations presented here are slightly different from those published in Amato et al., (2016).

Fig. 6. PMF estimation of PM sources. a) Source composition in relation to measured major components; b) Averaged major components distributed by sources.

PMF could discriminate eight aerosol sources, or formation processes, in the Porto atmosphere. Figure 6 shows the fractional contribution of major aerosol constituents to each source profile, as well as average distributions of major aerosol components by PMF source profiles (minor aerosol elemental components, such as V, Ni, Cu, Sb and Sn, fundamental in establishing the PMF source profiles, are not detailed in the present discussion). A more classical view of the PMF source profiles can be found in Figures S5 of the Supplementary Information. The PMF source characterisation is the following: **Mineral**, including mainly soil constituents, namely Al and Si, resulting from natural or anthropogenic soil suspension; **SeaSalt**, containing Na and Cl transported as sea spray from the nearby ocean; **SecNitr**, formed by reaction of nitric acid with ammonia, sea salt and dust; **HOil+Sec**, containing mostly sulphur, ammonium and OC, as secondary compounds with origin in emissions from heavy oil combustion; **Industry**, mainly formed by OC and EC, from industrial emissions and containing most of the Zn element; **n-Exhaust**, with major contributions of Fe, EC and NO₃⁻, associated with non-exhaust vehicle emissions, such as brake and tyre wear, and road dust resuspension; **BioBur**, containing levoglucosan, K, OC and EC, with origin in the burning of biomass fuels; and **Exhaust**, mainly formed by OC and EC, attributed to emissions from combustion of fuels in internal engines of road vehicles.

The PMF eight source average contributions to the total aerosol mass, in the entire sampling campaign and during the summer and winter periods, are presented in Figure 7, for PM_{2.5} and PM₁₀. Exhaust, HOil+Sec, BioBur, Mineral and SeaSalt are the predominant aerosol sources, contributing in average to 80% of the aerosol loading. Exhaust does not vary appreciably with the period of the year, while Mineral is maximum during summer and BioBur and SeaSalt peak in winter.

Because of the different source specifications and organisation, it is not linear to compare IMB and PMF results. As a compromise, in each methodology various sources were

associated, allowing the comparison of **Exhaust** with the sum **CARBffp** + **CARBsec**, **Mineral** with **InsDu** + **SolDu** + **SICdu** and **SecNitr** + **HOil+Sec** with **SICss** + **SICam**. The average intercomparison between IMB and PMF, obtained after these adaptations, for the global sampling campaign and for the winter and summer seasons, is given in Table 3, discriminated for fine and coarse aerosol fractions. Figure 8 compares the two methodologies for individual samples in the PM₁₀ aerosol fraction.

Fig. 7. Average results from PMF apportionment, for PM_{2.5} and PM₁₀. The average contributions are given for the entire campaign and for the summer and winter periods. Values are presented in µg.m⁻³ and percentage of total PM.

From the table and the figure it is possible to conclude that both methodologies give quite similar source attributions, over the seasons, for Sea Salt and Biomass Burning, with PMF producing in average, principally in summer, somewhat more sea salt mass (10%, for PM₁₀) than the IMB methodology. This can be in part the result of IMB minimisation in correcting Na⁺_{ssalt} and Mg²⁺_{ssalt} to Na⁺_{ss} and Mg²⁺_{ss}, (see point 3 in the previous Section), and the contamination of Sea Salt with NH₄⁺ and NO₃⁻, in the PMF profile (see Figure 6).

Table 3. IMB and PMF source contributions, (in µg. m⁻³), for the fine and coarse aerosol fractions, averaged over the whole campaign and for summer and winter periods.

	Sources	Year		Summer		Winter	
		IMB	PMF	IMB	PMF	IMB	PMF
PM2.5	Sea Salt	1.0	1.1	0.4	0.5	1.5	1.5
	Mineral	3.6	3.8	5.1	7.7	2.9	0.7
	Biomass Burning	4.9	4.2	1.7	1.2	12.8	11.8
	Exhaust	11.2	8.0	14.7	8.2	8.9	8.6
	non-Exhaust	0.4	1.2	0.4	0.9	0.5	1.8
	Secondary	4.0	4.8	5.4	7.4	3.1	2.4
	Industry		1.3		2.0		1.2
	SUM	25.1	24.5	27.6	28.0	29.7	28.1
PM2.5-10	Sea Salt	3.9	4.3	2.1	2.8	4.1	4.0
	Mineral	2.4	2.6	4.0	4.4	1.1	1.1
	Biomass Burning	0.1	0.0	0.0	0.0	0.2	0.1
	Exhaust	0.5	-0.1	0.8	-0.1	0.2	-0.1
	non-Exhaust	0.5	1.8	0.4	1.1	0.7	2.2
	Secondary	1.4	1.8	1.6	2.3	1.1	1.4
	Industry		-0.1		0.0		-0.1
	SUM	8.9	10.4	8.9	10.5	7.4	8.5

The similarity of results for Biomass Burning (for PM₁₀, IMB=1.04 PMF + 0.55 $\mu\text{g.m}^{-3}$; R=0.96) is a good indication of the correctness of the edge line approach to the estimation of EC_{bb} and OC_{bb}, in the IMB methodology, although the estimated levoglucosan, OC_{bb} and EC_{bb} ratios are in the limit of ranges reported in the literature for biomass burning experiments. The edge line approach considers the regional variability in biofuel and burning conditions, as well as levoglucosan atmospheric stability effects (Hoffmann et al., 2010).

In spite of the differences in source classifications between the two methodologies, there is also a reasonable agreement between secondary inorganic compounds (in PM₁₀, IMB =0.71 PMF + 0.79 $\mu\text{g.m}^{-3}$; R=0.93), but with IMB calculating 30% less mass, in average, than PMF. That might be the result of not including SIC_{du} in IMB and including secondary OC and soil components in the PMF profiles (see Figure 6). In IMB, all OC_{sec} is apportioned into a separate source classification (CARBsec).

Where an important discrepancy between IMB and PMF source apportionments can be observed is in the mineral/soil component. Although, on average for the whole campaign, the results are similar, individual sample observation shows that while in winter, when dust contamination is lower, the IMB gives higher contributions, in summer, during dusty periods, the PMF calculates the double of soil contamination. In winter, probably the almost exclusive source of Mineral is local road dust resuspension. While IMB does not discriminate the sources of dust, PMF may attribute one fraction of road dust to the non-exhaust source (see the PMF non-exhaust source profile in Figure 6). From Table 3 that seems to happen, principally for fine particles. We have no clear explanation to justify the differences observed in the summer. Even adding SIC_{du} to the Mineral component and not discriminating dust between sources in IMB, apportionment of dust by this methodology is only half of PMF. However, it is necessary to take into account that the PMF mineral profile includes OC, from the possible occurrence of organic matter in the soil. Also, only 30% of the PMF profile mass is attributed to the measured aerosol components. Even if the measured mass of soil constituents is multiplied by 2 to account for soil associated oxygen, there is still 40% of the profile mass unaccounted in PMF.

Fig. 8. Comparison of source contributions, between IMB and PMF, for individual PM₁₀ samples. The regression line, equation and R values are estimated for the whole sampling campaign.

The two methodologies also do not compare well in the non-exhaust car emissions, with PMF giving a much higher contribution. The IMB n-Exhaust source only includes iron oxides, in excess to soil (Fe_{nexh}), and oxides of calcium not attributed to soil and sea salt, (Ca_{nexh}). The PMF profile (see Figure 6), besides these elements, contains also an important contribution from EC and reasonable values of nitrate and soil constituents. While for soil elements there is a clear justification in road dust resuspension by the traffic, for nitrate it is less clear this association with vehicle non-exhaust sources. The large presence of EC, without OC, is also strange, now that elements from non-exhaust sources such as Fe occur predominantly in the coarse size range while EC occurs almost exclusively in measured fine particles. Since EC represents approximately 30% of the PMF non-exhaust source profile, (Figure 6), the amount

of EC in this profile estimated for winter by PMF, for coarse particles, is around $0.7 \mu\text{g.m}^{-3}$, more than one order of magnitude higher than the real measured values (see Tables 1 and 3 for evaluation). In our opinion, the inclusion of EC in the PMF profile results from the joint application of PMF to $\text{PM}_{2.5}$ and PM_{10} samples and the collinearity of vehicle exhaust and non-exhaust emissions (on a daily average basis) in this kerb site where both sources are local and there is not enough time for differentiated deposition of fine and coarse particles. From Figure 6 it is possible to calculate, for PMF, the ratio Fe/Al in Mineral, which amounts to 0.80, very similar to the value of 0.83 estimated in Figure 1 by the edge line approach, for soil, which is a good indication of the performance of the IMB methodology in this situation.

On average, the IMB and PMF methodologies give similar outputs for the exhaust source profile, in winter. In summer IMB tends to produce higher contributions than PMF. Figure 8 shows an important dispersion of values with a correlation coefficient of only 0.73. To understand the differences, it is important to consider that IMB concentrates all non-biomass burning carbon into CABffp and CARBsec, while PMF also attributes appreciable amounts of carbon to Industry, n-Exhaust, HOil+Sec and Mineral. The excess of IMB values in summer is in part due to the presence of important secondary organic mass that in PMF is also distributed through HOil+Sec and Industry.

The results of the IMB and PMF inter-comparison, presented in Table 3 and Figure 8, were statistically evaluated with the Excel Data Analysis Tools. A two-sample student t-Test analysis, assuming unequal population variances, was used to test for the equality of IMB and PMF population means. The statistical results confirm the qualitative intercomparison interpretation and conclusions presented in previous paragraphs. At the 95% confidence level, the null hypothesis is confirmed for the pairs **IMB SeaSaltt/PMF SeaSalt**, **IMB SICss+SICam/PMF SecNitr+HOil** and **IMB BiomBurn/PMF BiomBurn**. At the same confidence level, the null hypothesis was rejected for the **IMB n-Exhaust/PMF n-Exhaust** and **IMB CARBffp+CARBsec/PMF Exhaust** pairs. For the **IMB CARBffp+CARBsec/PMF Exhaust** pair, the null hypothesis was confirmed, however, if applied only to the winter period. Although the differences reported and discussed in the previous paragraphs, the pair **IMB InsDu+SolDu+SICdu/PMF Mineral** showed, statistically, to be part of populations with the same averages, at the 95% confidence level.

5. Conclusions

$\text{PM}_{2.5}$ and PM_{10} aerosol samples, collected at the kerb side of one of the most traffic congested urban avenues in Porto city, Portugal, were evaluated quantitatively in relation to main sources and formation processes by a new source apportionment methodology based on an Ionic and Mass Balance (IMB) approach.

The IMB methodology estimated 11 components of emission sources or formation processes, including exhaust and non-exhaust road vehicle emissions, biomass burning, secondary inorganic and organic pollutants, and primary soil and sea salt emissions, which, on average, accounted for 96 to 102% of measured $\text{PM}_{2.5}$ or PM_{10} mass. Some of these components are part of a single emission source, such as CARBbb and Kbb; others, such as CARBsec, result from precursors emitted from a variety of sources.

While in summer, secondary carbonaceous matter is the predominant fraction, in winter, biomass burning accounts, on average, for more than 40% of the PM_{2.5} aerosol. As three quarters of the PM₁₀ aerosol mass is concentrated in fine particles, most of the obtained sources are mainly found in PM_{2.5}. The coarse aerosol fraction is almost exclusively formed by sea spray and its reaction products, dust and non-exhaust road vehicles emissions.

The IMB results were compared with the PMF source apportionment of the same aerosol samples. The PMF source classes are different from the IMB and therefore it is not linear to totally inter-compare both methodologies. Furthermore, PMF identifies 2 additional sources (industry and oil-combustion). Results are almost equal for biomass burning and sea salt sources. They are also reasonably similar for the exhaust source and the formation of secondary inorganic compounds, being possible to explain the differences based on the corresponding IMB and PMF characteristics. There is a reasonable to marked difference for soil dust and non-exhaust sources. Some of these differences possibly result from collinearity problems in PMF. PMF has the advantage of a higher potential for identifying sources such as the industrial and oil-combustion, which are easily assigned by specific tracers; also, the multivariate analysis evaluates the possible ‘unknown’ sources present. On the other hand, IBM yields very relevant information on source patterns, because it is able to decompose source contributions in specific sub-contributions.

The inter-comparison demonstrates that IMB and PMF are complementary and that the utilization of both methodologies, together, allows a better insight into the contribution of sources and processes to the urban aerosol loading. The PMF is better in evaluating sources that have a contribution from a variety of measured constituents. IMB enables the identification of collinearity between aerosol tracers and the discrimination of secondary pollutants.

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Supplementary information

Table S1. Average ($\pm$ standard deviation) concentrations measured in fine and coarse particles, for the whole campaign and for summer and winter periods, of aerosol constituents not used in the IMB source apportionment methodology.

$\mu\text{g}\cdot\text{m}^{-3}$	PM _{2.5}			PM _{2.5-10}		
	Total	Summer	Winter	Total	Summer	Winter
Oxalate	0.174 $\pm$ 0.140	0.222 $\pm$ 0.157	0.170 $\pm$ 0.124	-0.003 $\pm$ 0.068	0.010 $\pm$ 0.062	-0.025 $\pm$ 0.087
MSA	0.0343 $\pm$ 0.0360	0.0548 $\pm$ 0.0430	0.0100 $\pm$ 0.0070	-0.0005 $\pm$ 0.0116	0.0010 $\pm$ 0.0177	-0.0002 $\pm$ 0.0025
V	0.0032 $\pm$ 0.0030	0.0048 $\pm$ 0.0040	0.0019 $\pm$ 0.0012	0.0005 $\pm$ 0.0013	0.0005 $\pm$ 0.0015	0.0006 $\pm$ 0.0012
Cr	0.0020 $\pm$ 0.0016	0.0025 $\pm$ 0.0021	0.0019 $\pm$ 0.0013	0.0026 $\pm$ 0.0016	0.0026 $\pm$ 0.0018	0.0030 $\pm$ 0.0016
Ni	0.0025 $\pm$ 0.0023	0.0036 $\pm$ 0.0030	0.0019 $\pm$ 0.0012	0.0004 $\pm$ 0.0006	0.0005 $\pm$ 0.0008	0.0003 $\pm$ 0.0006
Se	0.0004 $\pm$ 0.0003	0.0005 $\pm$ 0.0004	0.0004 $\pm$ 0.0003	0.0002 $\pm$ 0.0005	0.0003 $\pm$ 0.0006	0.0000 $\pm$ 0.0003
Br	0.0074 $\pm$ 0.0073	0.0076 $\pm$ 0.0044	0.0099 $\pm$ 0.0124	0.0032 $\pm$ 0.0043	0.0022 $\pm$ 0.0035	0.0029 $\pm$ 0.0050
Sr	0.0010 $\pm$ 0.0010	0.0012 $\pm$ 0.0014	0.0008 $\pm$ 0.0004	0.0012 $\pm$ 0.0014	0.0012 $\pm$ 0.0016	0.0010 $\pm$ 0.0012
Zr	0.0022 $\pm$ 0.0019	0.0026 $\pm$ 0.0023	0.0022 $\pm$ 0.0019	0.0026 $\pm$ 0.0023	0.0028 $\pm$ 0.0027	0.0027 $\pm$ 0.0020
Li	0.0006 $\pm$ 0.0006	0.0009 $\pm$ 0.0008	0.0003 $\pm$ 0.0004	0.0002 $\pm$ 0.0004	0.0003 $\pm$ 0.0004	0.0000 $\pm$ 0.0003
Co	0.0002 $\pm$ 0.0001	0.0002 $\pm$ 0.0002	0.0002 $\pm$ 0.0001	0.0000 $\pm$ 0.0001	0.0001 $\pm$ 0.0001	0.0000 $\pm$ 0.0001
Ga	0.0002 $\pm$ 0.0001	0.0003 $\pm$ 0.0002	0.0001 $\pm$ 0.0000	0.0001 $\pm$ 0.0001	0.0001 $\pm$ 0.0001	0.0000 $\pm$ 0.0000
As	0.0008 $\pm$ 0.0005	0.0008 $\pm$ 0.0005	0.0010 $\pm$ 0.0006	0.0001 $\pm$ 0.0004	0.0001 $\pm$ 0.0004	0.0000 $\pm$ 0.0004
Rb	0.0015 $\pm$ 0.0015	0.0021 $\pm$ 0.0021	0.0014 $\pm$ 0.0011	0.0004 $\pm$ 0.0007	0.0005 $\pm$ 0.0010	0.0001 $\pm$ 0.0003
Y	0.0001 $\pm$ 0.0001	0.0002 $\pm$ 0.0001	0.0001 $\pm$ 0.0000	0.0000 $\pm$ 0.0001	0.0001 $\pm$ 0.0001	0.0000 $\pm$ 0.0000
Nb	0.0005 $\pm$ 0.0004	0.0006 $\pm$ 0.0005	0.0003 $\pm$ 0.0003	0.0002 $\pm$ 0.0004	0.0001 $\pm$ 0.0004	0.0000 $\pm$ 0.0002
Mo	0.0004 $\pm$ 0.0006	0.0004 $\pm$ 0.0006	0.0005 $\pm$ 0.0009	0.0004 $\pm$ 0.0004	0.0004 $\pm$ 0.0004	0.0005 $\pm$ 0.0004
Cd	0.0003 $\pm$ 0.0003	0.0003 $\pm$ 0.0003	0.0004 $\pm$ 0.0004	0.0000 $\pm$ 0.0001	0.0000 $\pm$ 0.0001	0.0000 $\pm$ 0.0001
Sn	0.0048 $\pm$ 0.0050	0.0037 $\pm$ 0.0044	0.0068 $\pm$ 0.0050	0.0036 $\pm$ 0.0048	0.0024 $\pm$ 0.0022	0.0049 $\pm$ 0.0046
Sb	0.0054 $\pm$ 0.0103	0.0034 $\pm$ 0.0048	0.0048 $\pm$ 0.0067	-0.0001 $\pm$ 0.0085	0.0007 $\pm$ 0.0039	0.0020 $\pm$ 0.0021
Cs	0.0001 $\pm$ 0.0001	0.0002 $\pm$ 0.0001	0.0001 $\pm$ 0.0000	0.0000 $\pm$ 0.0001	0.0000 $\pm$ 0.0001	0.0000 $\pm$ 0.0000
Ba	0.0095 $\pm$ 0.0077	0.0118 $\pm$ 0.0083	0.0099 $\pm$ 0.0087	0.0118 $\pm$ 0.0082	0.0109 $\pm$ 0.0064	0.0121 $\pm$ 0.0087
La	0.0002 $\pm$ 0.0003	0.0004 $\pm$ 0.0004	0.0001 $\pm$ 0.0001	0.0001 $\pm$ 0.0002	0.0001 $\pm$ 0.0003	0.0000 $\pm$ 0.0001
Ce	0.0005 $\pm$ 0.0007	0.0008 $\pm$ 0.0009	0.0004 $\pm$ 0.0003	0.0003 $\pm$ 0.0006	0.0003 $\pm$ 0.0007	0.0001 $\pm$ 0.0002
W	0.0005 $\pm$ 0.0007	0.0006 $\pm$ 0.0010	0.0006 $\pm$ 0.0005	0.0000 $\pm$ 0.0006	-0.0001 $\pm$ 0.0009	-0.0001 $\pm$ 0.0004
Pb	0.0123 $\pm$ 0.0132	0.0141 $\pm$ 0.0163	0.0163 $\pm$ 0.0133	0.0011 $\pm$ 0.0038	0.0010 $\pm$ 0.0038	0.0007 $\pm$ 0.0029
Bi	0.0002 $\pm$ 0.0002	0.0004 $\pm$ 0.0003	0.0002 $\pm$ 0.0002	0.0001 $\pm$ 0.0002	0.0001 $\pm$ 0.0002	0.0002 $\pm$ 0.0002

Fig. S1. Relation between Aluminium and Silicon, in PM₁₀ and PM_{2.5} aerosol samples. The brown area represents the range of average crustal ratio taken from Manson and Moore, (1982) and Wedepohl, (1995).

Fig. S2. Edge lines for estimation of soil contribution, in PM₁₀, presented together with best-fit equations. Points in grey, red and blue represent samples taken in different seasonal periods. Points with a black edge were used to estimate the edge lines. The brown area represents the range of average crustal ratios, taken from Mason and Moore, (1982) and Wedepohl, (1995).

Fig. S3. Comparison between the sum of measured anions and cations for PM_{2.5} (left figures) and PM₁₀ (right figures). The lower figures include non-analysed H⁺, calculated from the ionic balance determination of H₂SO₄.

Fig. S4. Daily variability of source contributions to PM_{2.5} and PM₁₀, together with mass values directly measured, in IMB source apportionment. Blue and orange shaded areas represent winter and summer periods, respectively.

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Fig. S5. PMF source profiles and constituent fractional contributions

Fig. S6. Daily variability of source contributions to $PM_{2.5}$ and PM_{10} , together with mass values directly measured, in PMF source apportionment. Blue and orange shaded areas represent winter and summer periods, respectively.