



## Biomass burning contributions estimated by synergistic coupling of daily and hourly aerosol composition records



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### HIGHLIGHTS

- PMF has been applied to both daily and hourly aerosol compositional data-sets.
- Unexpectedly very high biomass burning contributions were found in Central Italy.
- Multi-elemental high time resolved PIXE data allowed a clear source identification.

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### ABSTRACT

Biomass burning (BB) is a significant source of particulate matter (PM) in many parts of the world. Whereas numerous studies demonstrate the relevance of BB emissions in central and northern Europe, the quantification of this source has been assessed only in few cities in southern European countries. In this work, the application of Positive Matrix Factorisation (PMF) allowed a clear identification and quantification of an unexpected very high biomass burning contribution in Tuscany (central Italy), in the most polluted site of the PATOS project. In this urban background site, BB accounted for 37% of the mass of PM10 (particulate matter with aerodynamic diameter <10 μm) as annual average, and more than 50% during winter, being the main cause of all the PM10 limit exceedances.

Due to the chemical complexity of BB emissions, an accurate assessment of this source contribution is not always easily achievable using just a single tracer. The present work takes advantage of the combination of a long-term daily data-set, characterized by an extended chemical speciation, with a short-term high time resolution (1-hour) and size-segregated data-set, obtained by PIXE analyses of streaker samples. The hourly time pattern of the BB source, characterised by a periodic behaviour with peaks starting at about 6 p.m. and lasting all the evening–night, and its strong seasonality, with higher values in the winter period, clearly confirmed the hypothesis of a domestic heating source (also excluding important contributions from wildfires and agricultural wastes burning).

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### 1. Introduction

Biomass burning (BB), which is generally defined as combustion of any non-fossilized vegetative or organic fuel, is a significant source of particulate matter (PM) in many parts of the world: on a global scale, it is the largest source of primary fine carbonaceous aerosols (Akagi et al., 2011). The use of BB for domestic heating is increasing in many European countries, as it is considered a renewable energy source and it is in general less expensive than methane and oil combustion. The

recent economical crisis further pushed the domestic use of wood (and similar materials) burning.

In the last years, many studies have been carried out to evaluate the BB contribution to PM because of its impact on air quality, human health, and climate change (Szidat et al., 2007, 2009; Gelencsér et al., 2007; Piazzalunga et al., 2011, Saarikoski et al., 2008; Viana et al., 2013). However, when several sources are simultaneously responsible of air pollution, it is often difficult to unravel the different contributions and to assess the impact of BB source only. The use of different kinds of biomass fuels (wood chips, bark, waste wood, straw, etc.) and different combustion technologies (operating at different temperatures) is reflected by the large variability of source profiles reported in literature for this source. Moreover, the reactivity, the volatility and to some extent the hygroscopicity of organic compounds, including also main BB

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tracers like levoglucosan, may compromise the basic assumptions for receptor models and strongly increase difficulties and uncertainties in source apportionment.

Next to carbonaceous particles, which dominated biomass burning emissions especially in the older and less efficient combustion systems, many inorganic elements-compounds are emitted by these processes, like potassium salts (KCl,  $K_2SO_4$ ,  $KNO_3$ ,  $K_2CO_3$ ), metals (Zn, Pb) and also refractory compounds including the elements Ca, Mg and Si (Jöller et al., 2007; Khalil and Rasmussen, 2003; Christensen et al., 1998; Obernberger, 1998). Although there are several potential chemical markers, an easy assessment of this source contribution using a single specific (and robust) tracer is hampered by the chemical complexity of these emissions. In this context, multi-elemental composition measurements can be very useful. In particular, the possibility of measuring elemental concentrations with high time resolution may be of great help in disentangling the contribution of this source by means of receptor models, like Positive Matrix Factorisation (PMF).

In the framework of the regional project PATOS (Particolato Atmosferico in TOScana), PM has been collected in 6 sampling sites in Tuscany both with daily and hourly time resolution: daily PM10 (i.e. particulate matter with aerodynamic diameter  $<10\ \mu\text{m}$ ) samples have been collected for 1 year and analysed by different techniques in order to obtain a complete chemical composition characterization (elements, ions, elemental and organic carbon); hourly fine ( $<2.5\ \mu\text{m}$ ) and coarse ( $2.5\text{--}10\ \mu\text{m}$ ) PM samples have been collected for shorter periods by the Streaker sampler and hourly elemental concentrations have been obtained by Particle Induced X-ray Emission (PIXE) analysis. Unexpectedly, the urban background site of Capannori, a small town near Lucca, resulted to be the most polluted among the sampling sites, with average PM10 concentration and number of daily exceedances even higher than those registered in the kerf sites.

In this paper, results concerning the BB source identification and characterisation in this highly polluted sampling site will be shown, with some comparison with the other sites of the PATOS project. To our best knowledge, whereas a discrete number of studies on BB have been accomplished in Northern Italy (Bernardoni et al., 2011, 2013; Pastorello et al., 2011; Piazzalunga et al., 2011), this is the first time that a strong impact of BB is demonstrated for central Italy. More in general, while numerous studies demonstrate the relevance of BB emissions on PM in many urban and suburban environments in central and northern Europe (see for example, Puxbaum et al., 2007; Saarikoski et al., 2008; Szidat et al., 2009; Favez et al., 2009), the quantification of this source has been assessed only in few cities in southern Europe (Alves et al., 2011; Gonçalves et al., 2012; Karanasiou et al., 2009; Minguillón et al., 2011; Reche et al., 2012; Viana et al., 2013). Only in one recent study (Giannoni et al., 2012), levoglucosan has been used to trace biomass burning in PM2.5 samples collected in Tuscany (Florence and Livorno): relatively high levoglucosan concentrations, similar to those reported for northern Italy, were found in the cold season, thus suggesting a possible significant impact of domestic heating; however contributions to PM were not quantified.

## 2. Methods

Aerosol samples were collected from September 2005 to September 2006, in six sampling sites in Tuscany (Central Italy) representative of areas with different characteristics (Fig. S1): Florence – urban background (FL\_UB), Prato – traffic site (PO\_TS), Capannori (Lucca) – urban background (CA\_UB), Arezzo – traffic site (AR\_TS), Grosseto – urban background (GR\_UB) and Livorno – suburban/rural background (LI\_SB). About 1000 PM10 samples were collected on a daily basis (from midnight to midnight) by three low volume ( $2.3\ \text{m}^3/\text{h}$ ) samplers (HYDRA Dual Sampler), each of them equipped with two inlets in order to simultaneously collect the aerosol on Teflon and Quartz fibre filters.

The samplers were relocated every 15 days from three sampling sites (FL\_UB, CA\_UB and GR\_UB) to the other three (AR\_TS, PO\_TS and LI\_SB).

PM10 daily mass concentrations were obtained by weighing the Teflon filters by an analytical balance in controlled conditions of temperature ( $20 \pm 1\ ^\circ\text{C}$ ) and relative humidity ( $50 \pm 5\ \%$ ). Samples collected on Teflon filters were then analysed by PIXE (Lucarelli et al., 2010, 2014) to measure the concentrations of all the elements with atomic number  $Z > 10$  with the external set-up described in Calzolari et al. (2006), by Ion Chromatography (IC) to quantify the soluble component (sample extraction in ultra-pure MilliQ water in ultrasonic bath) of inorganic cations, inorganic anions and low molecular weight organic anions (Becagli et al., 2011), and by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) to assess the soluble component (sample extraction in ultrasonic bath with MilliQ water acidified at pH 1.5–2 with ultra-pure nitric acid) of selected metals (Traversi et al., 2014). Samples collected on Quartz fibre filters were analysed by a CHN Analyzer (Thermo 1112) to measure Total Carbon (TC) concentration and estimate Elemental Carbon (EC) and Organic Carbon (OC) components according to the method proposed by Zappoli et al. (1999).

In particular, ~400 daily samples (~200 on Teflon and ~200 on Quartz fibre filters) were collected and analysed for the CA\_UB site.

During shorter periods (1–2 weeks for each site) the aerosol was also collected by a low volume ( $0.06\ \text{m}^3/\text{h}$ ) two-stage streaker sampler (D'Alessandro et al., 2003; Crespo et al., 2010; Amato et al., 2011; Dall'Osto et al., 2013). Briefly, in this device, particles are separated on different stages by a pre-impactor and an impactor. The pre-impactor removes PM with aerodynamic diameter  $D_{ae} > 10\ \mu\text{m}$ . The impactor deposits the aerosol coarse fraction ( $2.5\ \mu\text{m} < D_{ae} < 10\ \mu\text{m}$ ) on a Kapton foil while the fine fraction ( $D_{ae} < 2.5\ \mu\text{m}$ ) is collected on a Nuclepore filter. The two collecting substrata (Kapton and Nuclepore) are paired on a cartridge which rotates at constant speed for a week: this produces a circular continuous deposition of particulate matter ("streak") on both stages. PIXE analysis of these samples by a properly collimated proton beam, scanning the deposit in steps corresponding to 1 h of aerosol sampling, provided the elemental concentrations with hourly time resolution (Lucarelli et al., 2010).

Positive Matrix Factorisation (PMF) has been applied to the whole data set (separately on daily and hourly samples) aiming at the identification and the quantification of the major aerosol sources, using the EPA PMFv3 software. PMF is an advanced factor analysis technique based on a weighted least square fit approach (Paatero and Tapper, 1994); it uses realistic error estimates to weigh data values and imposes non-negativity constraints in the factor computational process. Briefly, the PMF factor model may be written as  $X = G \cdot F + E$ , where  $X$  is a known  $n$  by  $m$  matrix of the  $m$  measured chemical species in  $n$  samples;  $G$  is an  $n$  by  $p$  matrix of source contributions to the samples (i.e. time variations of the  $p$  factor scores);  $F$  is a  $p$  by  $m$  matrix of factors composition (often called source profiles).  $E$  is defined as a residual matrix: it represents the difference between the measured concentrations ( $X$ ) and those reproduced by the model ( $G \cdot F$ ). The PMF objective is determining the  $G$  and  $F$  factor matrices that minimize the sum of the squares of the inversely weighed residuals with uncertainty estimates of the data points. Furthermore, PMF constrains all the elements of

$G$  and  $F$  to be non-negative, meaning that sources cannot have negative species concentration ( $f_{kj} \geq 0$ ) and samples cannot receive a negative source contribution ( $g_{ik} \geq 0$ ).

Input data were prepared using the procedure suggested by Polissar (Polissar et al., 1998) and PMF results for different number of factors and multiple values of FPEAK were systematically explored to find out the most reasonable solution (20 pseudorandom initializations were run for each test).

For daily samples,  $G$  and  $F$  matrices were normalized by multilinear regression analysis, i.e. by regressing the total PM10 mass concentration measured for each sample against the factor scores, to obtain absolute source profiles and contributions. For hourly data, only elemental

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