Source Apportionment and Macro Tracer: Integration of Independent Methods for Quantification of Woody Biomass Burning Contribution to PM$_{10}$

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ABSTRACT

During the last few years, the rise in woody biomass burning (BB) for household heating has caused an increase in PM mass concentrations, particularly for the fine fraction, in Europe, as reported by the European Environmental Agency. Estimating the contribution from biomass combustion to airborne particulate matter is therefore an important issue in air quality governance, due to its potential health and environmental impacts.

Wood burning's contribution to PM$_{10}$ was estimated in winter at a rural site in southern Italy by means of two independent methods: source apportionment analysis with Positive Matrix Factorization (BB$_{PMF}$) and the macro tracer approach, based on levoglucosan concentrations (BB$_{Levo}$). PM$_{10}$ and PM$_{2.5}$ samples were collected every 24 h and every 8 h, respectively, and analyzed to determine the organic and elemental carbon, levoglucosan, inorganic ions and elements.

The results obtained via these methods showed good agreement (r = 0.85), with a linear correlation slope of about 1, and provide a reliable assessment of the BB contribution.

Woody biomass combustion contributed significantly to the PM$_{10}$ (on average, slightly less than 30% of the total mass) during winter. The combination of the independent methods proposed here may be used as a methodology for refining the BB contribution to air pollution.

Keywords: Biomass combustion; Particulate matter; Levoglucosan; PMF; Emission sources.

INTRODUCTION

National and international environmental policies point out the need for identifying and quantifying the contribution of emission sources to atmospheric concentrations, distinguishing also the contribution of the local and regional sources from the long-range transported pollutants. Air Quality Directives (Council Directive 2008/50/EC; Council Directive 2004/107/EC) reinforce the importance of having information on pollution sources for the development of efficient air quality plans and for the evaluation of human risk-exposure.

Identification and quantification of the air pollution sources have been performed with various methodologies such as explorative methods, emission inventories, photochemical and dispersion models (Lagrangian, Gaussian and Eulerian models) and receptor models (Viana *et al.*, 2008; Belis *et al.*, 2014). The receptor models (RMs, e.g., Principal Component Analysis, Multilinear Engine, Chemical Mass Balance) are mathematical or statistical procedures that are able to provide information on the contribution of emitting sources at a specific receptor site using *in-situ* measured experimental data and solving a mass balance equation, some of which may run also without the knowledge of the pollution sources.

One of the most commonly RMs used is the Positive Matrix Factorization (PMF, P. Paatero, Helsinki, Finland; Paatero and Tapper, 1994) that explains the correlation between the different measured species (carbonaceous fractions, inorganic ions, trace metals, etc.) through their linear combinations. These combinations, resulting in clustered "factors" (sources), originate from hidden common trends of species.

In the last years the international research community, e.g., European Commission with the Forum for Air quality Modelling (FAIRMODE; http://fairmode.jrc.ec.europa.eu/) and United States Environmental Protection Agency (https://www.epa.gov/scram/air-pollutant-receptor-modeling) have dealt with source apportionment matter and some basic guidelines and procedures (Belis *et al.*, 2014; Norris *et al.*, 2014; Pernigotti *et al.*, 2016) are in continuous improvement for joint assessment protocols among all the

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scientific subject involved in air quality evaluation (Karagulian *et al.*, 2012; Belis *et al.*, 2015a, b).

Source apportionment is gaining relevance in highly polluted areas to identify the main emission sources affecting air quality in order to propose/develop/implement protocols and strategies aiming at the reduction of air pollution.

Among the most relevant anthropogenic emission sources (such as vehicular traffic, industrial and agriculture activities), an important contribution is given by biomass-based household heating appliances during wintertime. In the last years, woody biomass burning (BB) for domestic or residential heating has increased its diffusion driven by climate and energy policy and the higher costs of other fuels (EC Commission Stuff Working Document, 2014; EC Renewable Energy Progress Report, 2015).

The incomplete or inefficient combustion of wood biomass in conditions typical of small and medium domestic heating device use has been recognized as an important source of particulate matter (PM_{10}, $PM_{2.5}$, PM_1) and other air pollutants harmful to human health (EC Commission Staff Working Document, 2014; WHO, 2015, www.eea.europa.eu/publications/air-quality-in-europe-2015/download).

Quantification of BB contribution is still challenging due to mixing of sources, heating device type, species of wood and combustion conditions, and meteorology. BB contribution to PM is usually estimated by using RMs (Bernardoni *et al.*, 2011; Waked *et al.*, 2014; Petralia *et al.*, 2017) or specific macro tracer approaches (Sdizat *et al.*, 2006; Schmidl, 2008; Piazzalunga *et al.*, 2011; Shahid *et al.*, 2019).

The macro tracer approach is based on the identification of markers (such as levoglucosan or ^{14}C) that are directly related to biomass combustion emissions allowing thus the estimation of BB contribution to the mass concentration of PM. Levoglucosan and its stereoisomers, mannosan and galactosan, are monosaccharide anhydrides produced by pyrolysis processes at temperatures higher than 300°C of cellulose and hemicellulose, respectively, and are considered specific markers of BB (Simoneit *et al.*, 1999; Fine *et al.*, 2002; Gelencsér *et al.*, 2007; Yttri *et al.*, 2011; Nielsen *et al.*, 2017). Levoglucosan may undergo degradation processes in the atmosphere due to oxidation reactions with radicals present in the ambient air; in particular, the reactions with the OH radical have been widely studied (Hennigan *et al.*, 2010; Hoffman *et al.*, 2010; Lai *et al.*, 2014). In fact, levoglucosan atmospheric lifetime could vary widely between 1.2 and 3.9 days (Lai *et al.*, 2014) under different environmental condition (temperature [T] and relative humidity [RH]), OH concentration, other atmospheric radical concentrations and levoglucosan mixing state together with inorganic salt and soot (Hennigan *et al.*, 2010; Hoffman *et al.*, 2010; Lai *et al.*, 2014). As a consequence, the use of levoglucosan for estimating the contribution of BB to PM is under debate since the possible underestimation due to the marker degradation, particularly in summer atmospheric conditions and/or sampling aged PM (Busby *et al.*, 2016). The macro tracer approach proposed by Schmidl *et al.* (2008) estimates the BB contribution to PM_{10} depending

on the levoglucosan atmospheric concentration through a specific conversion factor related to the wood species burnt and BB fuel type (logs or pellets). This method, already applied in Italy (Piazzalunga *et al.*, 2011), results in more precise site specific conversion factor assessment and so for BB contribution estimation, since it considers the species and fuel type actually burnt at certain area.

Despite the wide application of these methods, both show advantages and limits. PMF allows to obtain information on the contribution of emission sources in a specific receptor site without knowing *a priori* the different types of sources persisting at a site; on the contrary, the contribution, in terms of absolute concentration value, could be underestimated. Indeed, the analytical speciation of the chemical composition of PM is never complete, because of the difficulties in determining the water content, in establishing a complete and specific geochemical characterization of various metal oxide, and in assessing the best organic matter (OM) quantification (Sciare *et al.*, 2005; Bae *et al.*, 2006; Terzi *et al.*, 2010; Perrino *et al.*, 2013; Perrino *et al.*, 2014; Genga *et al.*, 2017). The lack of this information affects considerably PM_{10} mass reconstruction from the characterized species (Belis *et al.*, 2014). Macro tracer approach allows to estimate the BB contribution to PM from a single tracer (levoglucosan) but this evaluation is highly dependent on the knowledge of local type of solid biomass fuel (logs, chips, pellets, bark and sawdust) and wood species consumption inventory as well as on levoglucosan degradation processes; both factors lead to the uncertainty or underestimation of the real BB contribution.

This study estimates the BB contribution to PM_{10} samples collected at a rural site located in the south of Italy during winter by applying PMF and macro tracer methods in an independent and complementary way. The simultaneous application of these methods may improve our possibility to correctly evaluate the BB contribution to air pollution leading to a more accurate and "realistic" quantification and to obtain more reliable site specific BB evaluation.

MATERIALS AND METHODS

PM Sampling and Measurement Techniques

The aerosol was sampled in a coastal zone in Apulia (Italy) (Fig. 1(a)) at three sites: Cisternino (40.74278°N; 17.41583°E), Torchiarolo-Lendinuso (40.5175°N; 18.07889°E) and Torchiarolo-Fanin (40.48945°N; 18.04723°E). Cisternino (Ci) site is defined as rural site, while Torchiarolo-Lendinuso (TL) and Torchiarolo-Fanin (TF) are classified as suburban sites (according to the criteria in Italian Decr. Leg. 13 agosto 2010, n. 155). Ci is located 11 km from the sea and at an elevation of 400 m, TL and TF are located 0.7 and 5 km away from the sea respectively at an elevation of 30 m a.s.l. The area around the urban sites is moderately urbanized but highly agricultural, characterized by olive groves, vineyards, non-irrigated arable areas and complex crops. All these land-cover typologies determine soils exposure by the wind erosion with eventual re-suspension phenomena of soil and dust material. The distances of Torchiarolo from larger cities
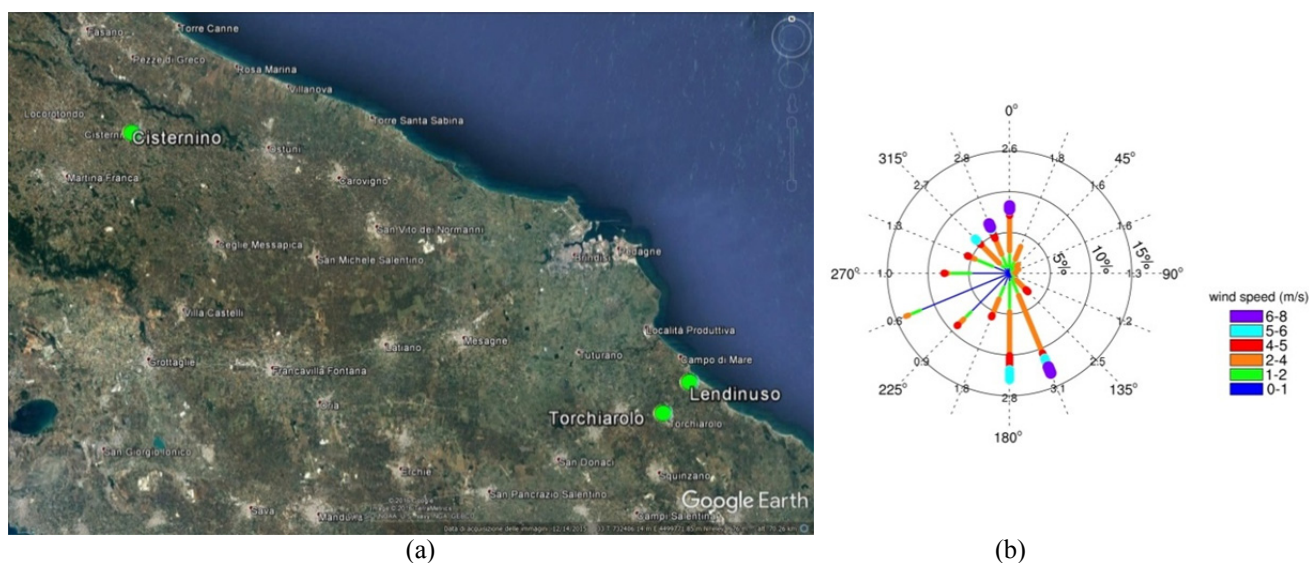
Fig. 1. Sampling sites: (a) Torchiarolo (Torchiarolo-Fanin [TF]), Cisternino (Cisternino [Ci]), Lendinuso (Torchiarolo-Lendinuso [TL]) (elab. from https://www.google.com/earth/). (b) Wind rose.

in the region are 16 km NNW and 16 km SSE for Brindisi and Lecce respectively, while Taranto is located 65 km WSW. The nearest medium size towns are San Pietro Vernotico (4 km W) and Squinzano (5 km S). The four lane motorway Strada Statale 613 is located around 600 meters W-SW. The prevalent directions of wind during the sampling period were WSW and S-SSE and the wind velocities vary from weak (up to 2–4 m s^{-1}) to moderate (up to 6–8 m s^{-1}) (Fig. 1(b)).

PM$_{10}$ was sampled in all three sites with FAI Hydra Dual Sampler. At TF, the measurements were carried out with the following instruments: Sunset Laboratory Model-4 Semi-Continuous OCEC Field Analyzer, Aerodyne Aerosol Chemical Speciation Monitor (ACSM), FAI Hydra Dual Sampler (equipped with PM$_{2.5}$ sampling head) and VAISALA MAWS 100 weather station.

24-hour PM$_{10}$ samples were collected on polytetrafluoroethylene (PTFE) membranes and quartz fiber filters for 30 consecutive days, from 23 January to 21 February 2016; 29 parameters were quantified: organic carbon (OC), elemental carbon (EC), inorganic ions (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg^{2+}, Ca^{2+}), elements (Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ba, W, Pb, Sc, Ce, Rb) and gravimetric PM$_{10}$. The chemical characterization of PM$_{10}$ was used as input for PMF (PMF 5.0, USEPA) to identify the emission sources. Only at TF was possible to investigate the macro tracer contribution of biomass combustion using a set of additional parameters such as mass concentration of levoglucosan, PM$_{2.5}$ with 8-h time resolution and on-line EC and OC with 2-h time resolution.

ACSM on-line measurements were conducted from 21 January to 23 February 2016, with 30-min time-resolution. Data were then pooled and mediated over 8 h or 24 h in post processing operations, to make species time series data homogeneous in order to perform right comparisons and correlations. ACSM measures the major non-refractory (at 600°C) components of PM$_1$ (NR-PM$_1$) such as Organic

Matter (OM), nitrate (NO$_3^-$), sulfate (SO$_4^{2-}$), ammonium (NH$_4^+$), chloride (Cl$^-$), providing loadings for 100 different macro-molecules (individuated by their mass-to-charge, m/z): In particular, the m/z 60 is associated to levoglucosan (Alfarra *et al.*, 2007) and so used for comparison with the laboratory levoglucosan measurements.

Gravimetric determination of PM$_{10}$ and PM$_{2.5}$ was carried out according to UNI EN 12341 and UNI EN 14907 methods. PM gravimetric mass was determined using an electronic balance (0.01 mg resolution; model AX205, Mettler Toledo).

Water soluble inorganic ions concentrations (Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, K$^+$, NH$_4^+$, Ca^{2+}, Mg^{2+}) in 24-h PM$_{10}$ samples were determined according to CEN/TR16269 method. Teflon filters were extracted in 18-MΩ Milli-Q$^®$ water in ultrasonic bath (32 min) and analyzed by ion chromatography (IC). The detail of the analytical procedure can be found in Malaguti *et al.* (2015a).

EC and OC mass concentrations were determined in 24-h PM$_{10}$ samples by means of a Thermal/Optical Carbon Analyzer (Sunset Laboratory Inc.) according to CEN/TR16243:2011 method. On-line EC-OC mass concentrations were measured with Semi-Continuous OC-EC Field Analyzer (Model-4, Sunset Laboratory Inc.) every 2 h. The NIOSH-like (RT-QUARTZ-840) thermal optical transmittance protocol was used both for off-line and on-line analysis. Detailed information about the analytical procedures are reported in Malaguti *et al.* (2015b).

Metals and trace elements (Na, Mg, S, Al, Si, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Ba, W, Pb, Sb, Sc, Ce, Rb) were estimated using energy-dispersive X-ray fluorescence (ED-XRF; NEX CG, Rigaku). The calibration was carried out by means of Standard Reference Material$^®$ NIST 2783 Air Particulate on Filter Media. The Method Detection Limit (MDL) and combined relative standard uncertainty are reported in Supplementary Material (Table S1).

Anhydrosugars (levoglucosan, mannosan and galactosan)

were analyzed using High-Performance Anion Exchange Chromatography (HPAEC; Dionex™ ICS-5000, Thermo Scientific™) equipped with Thermo Scientific™ Dionex™ CarboPac™ MA1 Analytical (4 × 250 mm) & Guard (4 × 50 mm) Columns and Pulsed Amperometric Detection (PAD; Dionex™ ED50A Stand-Alone Electrochemical Detector & Electrochemical Detector Conductivity Cells, Thermo Scientific™). Four squares (1 cm² each) portions of quartz fiber filter from 8 h PM2.5 samples were extracted with 2 mL of 18-MΩ Milli-Q® water in ultrasonic bath (32 min). Extracted water was filtered to remove debris with a 0.22 μm pore size nylon syringe filter (0.2 μm, Acrodisc® Nylon membrane, Pall®).

A good resolution between anhydrosugars (levoglucosan, mannosan and galactosan) and sugar alcohols (Arabitol, Sorbitol) was achieved (Fig. 2) developing an analytical method starting from Iinuma *et al.* (2009) consisting of a gradient elution of a 1 M aqueous sodium hydroxide (NaOH) solution at a flow rate of 0.4 mL min⁻¹. Method Detection Limit (MDL) for levoglucosan was evaluated equal to 9.2 ng m⁻³ by EPA method ($MDL = t_{(n-1, 1-\alpha=0.99)} \times SD$ where *SD SD* is the standard deviation of eight replicate standard solution), while the combined relative standard uncertainty (ε_R) was 0.07.

Biomass Burning Identification Methods: Positive Matrix Factorization (PMF) and Macro Tracer Approaches
PMF

PMF (USEPA PMF 5.0, Norris *et al.*, 2014; PMF2, Paatero, 2004) was applied to chemical data obtained from PM₁₀ samples collected at the three sites investigated.

PMF performs the decomposition of the measured concentrations dataset (*X* matrix) into three different matrices containing the sources, following the mass balance formula:

$$X = G \cdot F + E,$$

where *G* is the sources' contribution (time variations) matrix, *F* is the sources' profiles (such as fingerprint) matrix, and *E* is the residual (mass not explained by the model) matrix.

PMF can be run on a number of cases (each sampling occasion) which must be minimum three times the number of variables (in our study, 19 different parameters/species) (Belis *et al.*, 2014). The PMF was applied to a dataset (n = 1767) of 19 measured parameters in 93 daily samples collected at TF, Ci and TL.

The selected data followed the quality criteria defined by Belis *et al.* (2014) and Norris *et al.* (2014) for each parameter: Only measurements parameters having both 50% of values above detection limit (ADL) and a signal-to-noise ratio (S/N) value > 1 were considered. The parameters so used for source profile identification with PMF analysis were EC, OC, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Al, Si, Ti, V, Mn, Fe, Ni, Cu, Zn, all considered as "strong" according to Norris *et al.* (2014); total-gravimetric PM₁₀ was considered as total variable and set as "default to weak" (Norris *et al.*, 2014). This assumption distributed the PM mass among the different sources leading to an almost realistic estimation of PM₁₀ sources. The retrieval of the entire PM₁₀ mass is particularly required for calculation of biomass combustion factor as explained in Section "Estimations of BB Contribution to PM₁₀-Comparison between Macro Tracer Method and PMF Method". Levoglucosan filter concentrations were not included in the PMF input dataset in order to avoid its eventual influence on source profile definitions and on BB factor calculation. The "Results" section ("Estimations of BB Contribution to PM₁₀-PMF and Source Apportionment") shows two reconstructed PM₁₀ mass: The sum of the masses of all the speciated elements reconstructed by PMF (Σspec) and as the sole component PM₁₀ reconstructed mass coming from PMF output (PM₁₀_comp).

For identification and confirmation, the resulting factors profiles were compared to emissive profiles in SPECIEUROPE database (Pernigotti *et al.*, 2016) and other literature reference-profiles (cit. lit. in Section "Estimations of BB Contribution to PM₁₀-PMF and Source Apportionment").

Macro Tracer Method

BB contribution to PM was estimated by macro tracer method proposed by Schmidl *et al.* (2008) on the basis of
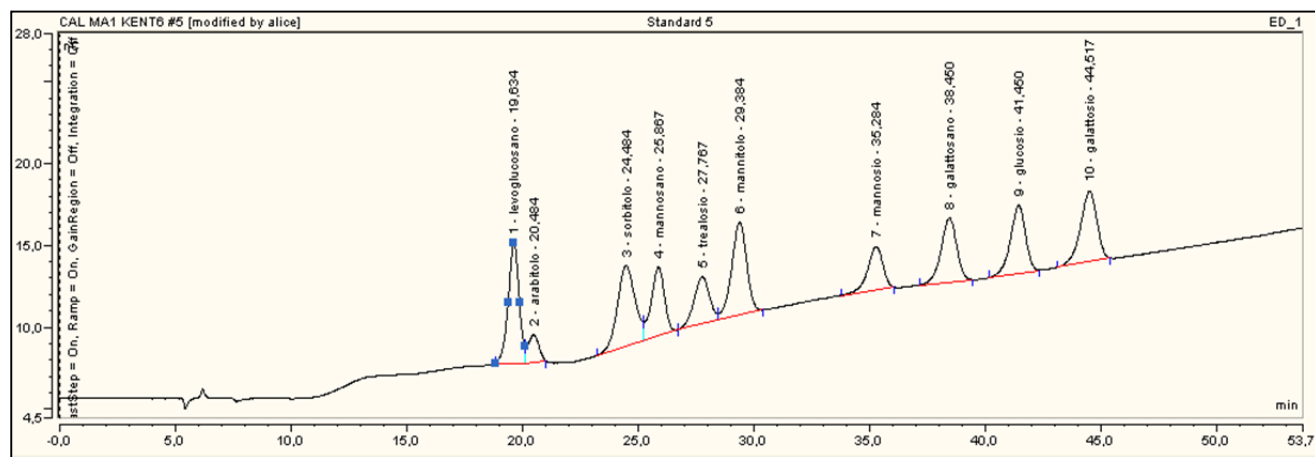
Fig. 2. Anhydrosugars HPAEC-PAD chromatogram.

wood species and woody fuel type (firewood, pellets or logs).

According to this approach, PM_{10} mass contribution from biomass burning can be calculated from levoglucosan concentration (BB_{Levo}) as follows:

$$BB_{Levo} \,(\mu g\ m^{-3}) = F_{Wn(1;2;3)} \times [Levoglucosan] \,(\mu g\ m^{-3}) \quad (1)$$

where F_W is a conversion factor calculated considering both the woody species burnt in the area of study and the relative spread of pellet burning appliances:

$$F_W = 100 ⁄ \{c\ Beech \times 4.1 + c\ Oak \times 13.3 + c\ Spruce \times 10.7 + c\ Larix \times 15.1 + c\ Pellet \times 10.1\} \quad (2)$$

where c_i is the weight of each woody species and woody fuel type in the examined site.

This formula takes into account endemic woody species for Austrian and alpine regions where this approach has been developed and applied (Schmidl *et al.*, 2008; Piazzalunga *et al.*, 2011). The woody species mainly burned in Apulia are about 70% olive, approximately 10% beech and oak, 10% other local species (e.g., almond tree) according to Spagnolo *et al.* (2014) and the remaining 10% is associated to pellet combustion.

The emission factors for olive and for the other endemic species burnt in the study area were not available; therefore, three different hypotheses were considered in the formula proposed by Schmidl. Olive woody biomass emission factor was assumed to be the equal to that reported for oak wood combustion (1) (as in equation F_{W1}), beech wood combustion (2) (F_{W2}) and a combination of 50% oak and 50% beech (3) (in F_{W3}). Oak and beech were selected as representative of the upper and lower limit of hardwood species PM_{10} emission factors (Kistler *et al.*,

2012):

$$F_{W1} = 100 ⁄ \{0.05\ Beech \times 4.1 + 0.85\ Oak \times 13.3 + 0.1\ Pellet \times 10.1\} = 8$$

$$F_{W2} = 100 ⁄ (\{0.85\ Beech \times 4.1 + 0.05\ Oak \times 13.3 + 0.1\ Pellet \times 10.1\} = 19$$

$$F_{W3} = 100 ⁄ \{0.45\ Beech \times 4.1 + 0.45\ Oak \times 13.3 + 0.1\ Pellet \times 10.1\} = 11$$

RESULTS AND DISCUSSION

Samples Characterization

Table 1 shows the mean, median, standard deviation, minimum and maximum values, 25th and 75th percentile concentrations calculated for 24-h samples at TF site for PM_{10}, $PM_{2.5}$, OC, EC and levoglucosan. Descriptive statistics for EC, OC, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Al, Si, Ti, V, Mn, Fe, Ni, Cu, Zn of samples from the three examined sites are reported in Supplementary Materials (Table S2).

PM_{10} shows a mean concentration value of 32 $\mu g\ m^{-3}$ with a minimum value of 17 $\mu g\ m^{-3}$ and a maximum value 58 $\mu g\ m^{-3}$. Daily PM_{10} limit value of 50 $\mu g\ m^{-3}$ set by AQ Directive 50/2008 was exceeded four times during the sampling campaign, on 28 January and 2, 15 and 16 February with 56 $\mu g\ m^{-3}$, 54 $\mu g\ m^{-3}$, 58 $\mu g\ m^{-3}$ and 52 $\mu g\ m^{-3}$, respectively. On the 15 and the 16 of February a Saharan dust intrusion event occurred (Fig. S1), based on Al concentration value > 1.0 $\mu g\ m^{-3}$ and Ca/Al ratio < 2 (according to Koçak *et al.* (2012)).

Daily $PM_{2.5}$ concentrations reached the highest values on 28 January with 52 $\mu g\ m^{-3}$, almost equal to PM_{10} and the mean value over the sampling campaign was ca. 22 $\mu g\ m^{-3}$. During the campaign, the fine fraction represented on average about 70% of PM_{10} daily concentrations.

Table 1. Main statistical parameters values calculated for 24-h time resolution (PM_{10}, $PM_{2.5}$, OC, EC, levoglucosan) and 8-h time resolution ($PM_{2.5}$, OC, EC, levoglucosan) concentrations.

		PM_{10}	$PM_{2.5}$	$PM_{2.5}/PM_{10}$	EC	OC	Levoglucosan
		$\mu g\ m^{-3}$	$\mu g\ m^{-3}$	%	$\mu gC\ m^{-3}$	$\mu gC\ m^{-3}$	$\mu g\ m^{-3}$
	Mean	32	22	67	1.1	8.3	0.71
	Median	28	16	68	0.79	6.3	0.55
	SD	13	13	21	0.75	5.3	0.46
24 h	25th Percentile	21	13	52	0.49	4.5	0.41
	75th Percentile	45	25	82	1.8	11.5	0.97
	Min	17	7	28	0.18	2.2	0.15
	Max	58	52	110	2.5	19	1.9

		$PM_{2.5}$	EC	OC	Levoglucosan
		$\mu g\ m^{-3}$	$\mu gC\ m^{-3}$	$\mu gC\ m^{-3}$	$\mu g\ m^{-3}$
	Mean	22	1.4	8.7	0.73
	Median	16	1.0	6.2	0.42
	SD	17	1.2	6.9	0.78
8 h	25th Percentile	9.5	0.54	3.5	0.195
	75th Percentile	29	1.8	11	1.0
	Min	2.2	0.090	0.90	0.053
	Max	84	4.9	33	4.1

Levoglucosan was detected in all the collected samples, confirming the presence of woody biomass combustion as PM emission source in the sampling site. Daily levoglucosan concentrations vary from a minimum value of 0.15 μg m^{-3} on 18 February to a maximum value of 1.9 μg m^{-3} on 30 January, with a mean value of 0.75 μg m^{-3}.

At higher time resolution (8 h), PM$_{2.5}$ concentrations vary from 2 μg m^{-3} to 84 μg m^{-3} and levoglucosan from 0.053 μg m^{-3} to 4.1 μg m^{-3}. As expected ACSM's m/z 60 and levoglucosan time series showed a good agreement, both showing temporal patterns similar to that of PM$_{2.5}$ with higher concentrations from 4:00 p.m. to 8:00 a.m. (Fig. 3). More likely these high values are due to house-heating/cooking activities. A similar trend observed for the EC/OC data support this hypothesis. This daily cycle of biomass burning indicators suggests the presence of significant local source rather than long-range transport. Generally, the major emission sources of fine OC and EC at urban-suburban areas are traffic, domestic heating, cooking and industrial activities (Piazzalunga *et al.*, 2011). The high correlation coefficients between the woody biomass combustion tracers (levoglucosan and m/z 60) and PM$_{2.5}$ and EC/OC (Table 2) suggest that the biomass burning (domestic heating and cooking activities) is one of the most relevant sources of fine PM at the sampling site (Tzompa-Sosa *et al.*, 2016).

Estimations of BB Contribution to PM$_{10}$

PMF and Source Apportionment

PMF analysis identified 9 factors (sources): fresh marine aerosol, soil dust, biomass combustion (BB), vehicular traffic emission, industrial/port activity, re-suspended dust, nitrate-rich secondary aerosol, sulfate-rich secondary aerosol and aged marine aerosol. In this section, the data

for the biomass combustion source are shown and discussed; the other sources are reported in Supplementary Material (Fig. S2).

BB factor (Fig. 4) is well isolated, since it shows a profile characterized almost exclusively by K$^+$, typically used as indicator of biomass burning in European source apportionment studies (Rodriguez *et al.*, 2004; Andersen *et al.*, 2007; Petralia *et al.*, 2017), together with OC and EC with a relative contribution of 48.9%, 41.6% and 40.4%, respectively. Furthermore, the EC/OC ratio (equal to 0.12) is in accordance with data previously reported on emissions from residential BB by Szidat *et al.* (2006); it is noteworthy the elevated correlation (r = 0.85) between 24-h levoglucosan and 24-h OC apportioned to BB by PMF.

Fig. 5 reports the mass contribution to PM$_{10}$ (μg m^{-3}) for Σspec and for PM$_{10\_comp}$ related to each factor. Fig. 6 shows the daily sources apportionment derived from the sum of all the speciated elements (Σspec) and for parameter PM$_{10\_comp}$; for a more immediate interpretation, similar sources have been clustered: secondary inorganic aerosol, sea salt and soil dust come from clustering respectively nitrate-rich secondary aerosol and sulfate-rich secondary aerosol, fresh marine aerosol and aged marine aerosol, and soil dust and re-suspended dust.

Σspec is not sufficient to reconstruct the daily gravimetric PM$_{10}$ mass concentration (Fig. 6(a)), while if PM$_{10\_comp}$ is considered in the PMF (Fig. 6(b)), the agreement between source reconstructed mass concentration and measured daily gravimetric PM$_{10}$ mass concentration increases (Table 3). In particular, in Table 4 the single source contributions to PM$_{10}$ are reported for the clustered sites. Even though the sources mass contribution to PM$_{10}$ may differ among the two mass reconstructions (for BB Σspec is 5.0 μg m^{-3} while considering PM$_{10\_comp}$ apportioned mass is 7.8 μg m^{-3}), the
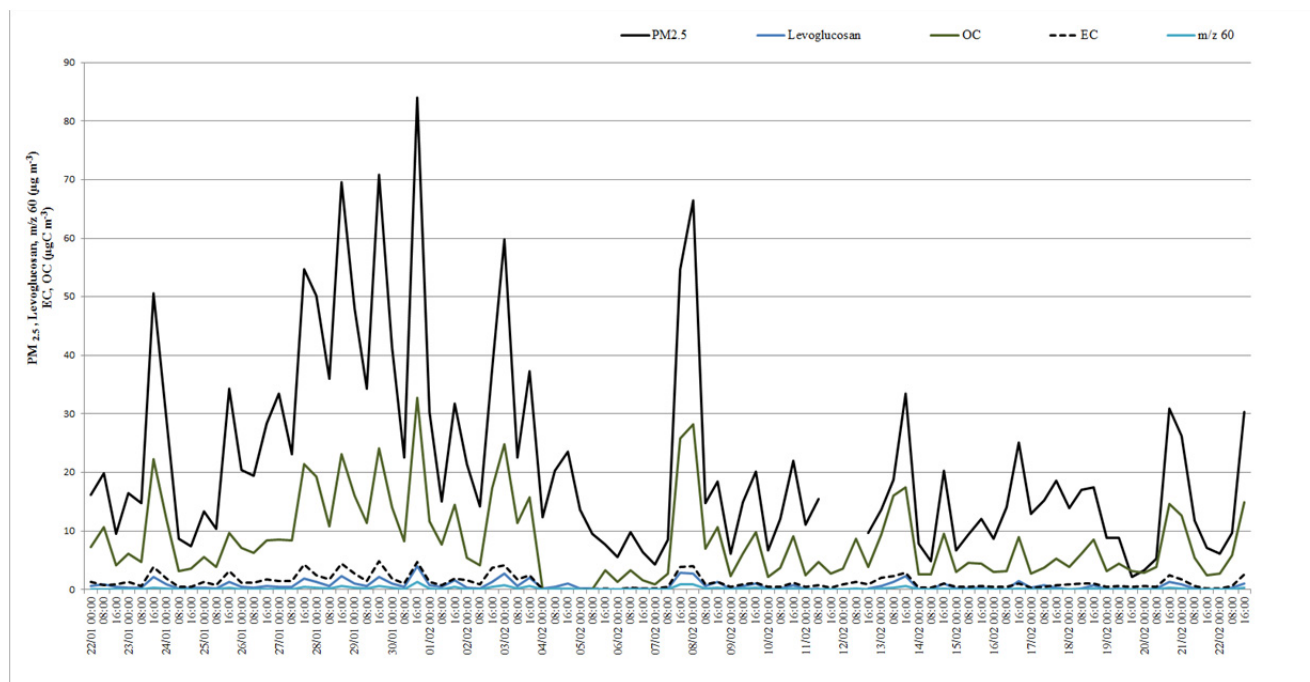

Fig. 3. 8-h concentration of PM$_{2.5}$, levoglucosan, EC, OC, and m/z 60 during field campaign.

Table 2. Levoglucosan, EC, OC, and PM_1 BB tracers (m/z 60) linear correlation coefficients.

	EC	OC	Levoglucosan	m/z 60
$PM_{2.5}$	0.92	0.93	0.90	0.88
EC		0.95	0.88	0.85
OC			0.93	0.92
Levoglucosan				0.97

relative contribution (Table S3) does not vary significantly (for BB the relative contribution is 20.2% and 20.3% for Σspec and PM_{10_comp}, respectively).

The comparison of sources mass concentration obtained with Σspec and PM_{10_comp} shows remarkable difference for specific sources and in particular for BB, for which the difference is of 40%. This discrepancy is related almost completely to the difference between OM and OC, since the organic fraction enters in PMF analysis as OC. To support this conclusion, we compared the BB OC-to-OM conversion factor, f_{BB} equal to 1.86, reported in Genga *et al.* (2017) and Philip *et al.* (2014), with the one calculated here (f_{BB_PMF}):

$$f_{BB\_PMF} = [OC_{BB} + (PM_{10\_comp} - PM_{10\Sigma spec})]/OC_{BB}$$

where OC_{BB} is the OC apportioned by PMF to biomass burning factor. The obtained f_{BB_PMF} value (equal to 1.70) is in good agreement with the literature value, therefore supporting our conclusion that the difference between PM_{10_comp} and Σspec is related to the uncertainties in the quantification of OM starting from OC data.

As reported in "Biomass Burning Identification Methods: Positive Matrix Factorization (PMF) and Macro Tracer Approaches" Section, PM_{10_comp} is considered more representative of gravimetric measured PM_{10} (Fig. S3) since it reproduces almost completely the PM_{10} mass, associated to all the sources; for clearness and for comparison with the macro tracer approach from now on we will refer just to BB obtained from PM_{10_comp} PMF (BB_{PMF}).

BB Macro Tracer Approach

In order to calculate the BB_{Levo} contribution to PM_{10}, 8-h levoglucosan concentrations were averaged every 24 h and multiplied for the conversion factors (F_{W1}, F_{W2}, and F_{W3}) calculated, as reported in "Biomass Burning Identification Methods: Positive Matrix Factorization (PMF) and Macro Tracer Approaches" Section.

Although PM_{10} and BB_{Levo} contributions show the same
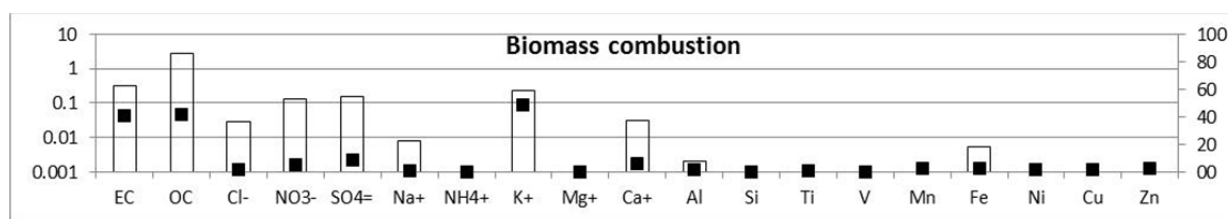
Fig. 4. Biomass burning factor profile obtained from PMF analysis; vertical bars (principal *y*-axis): mass concentration (µg m^{-3}) of the single element in the factor; black squares (secondary *y*-axis): % contribution of the single element in the factor over the totality of factors.
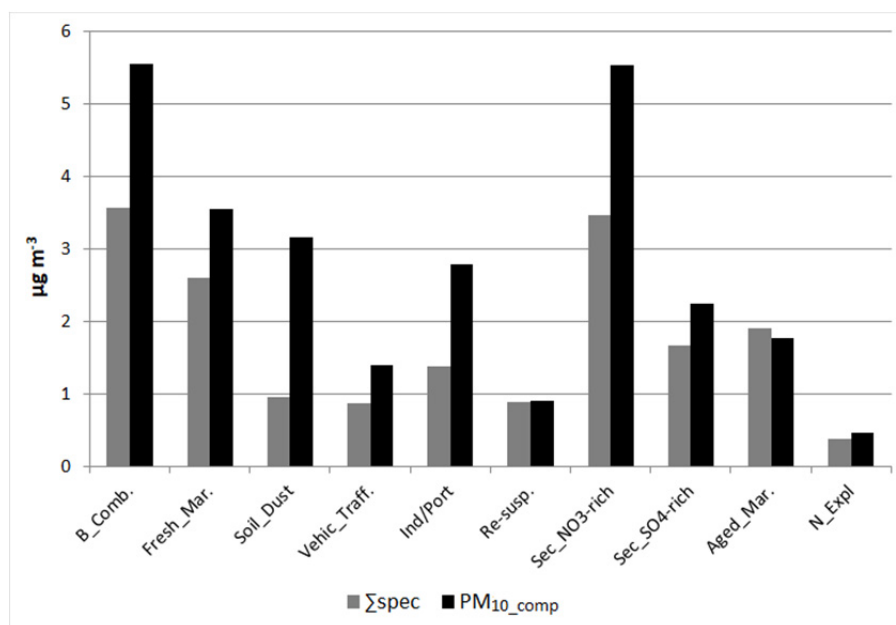
Fig. 5. Mass contribution (µg m^{-3}) of factors to Σspec (grey bars) and mass contribution (µg m^{-3}) of PM_{10_comp} (black bars) attributable to each factor. N_Expl: unexplained mass.
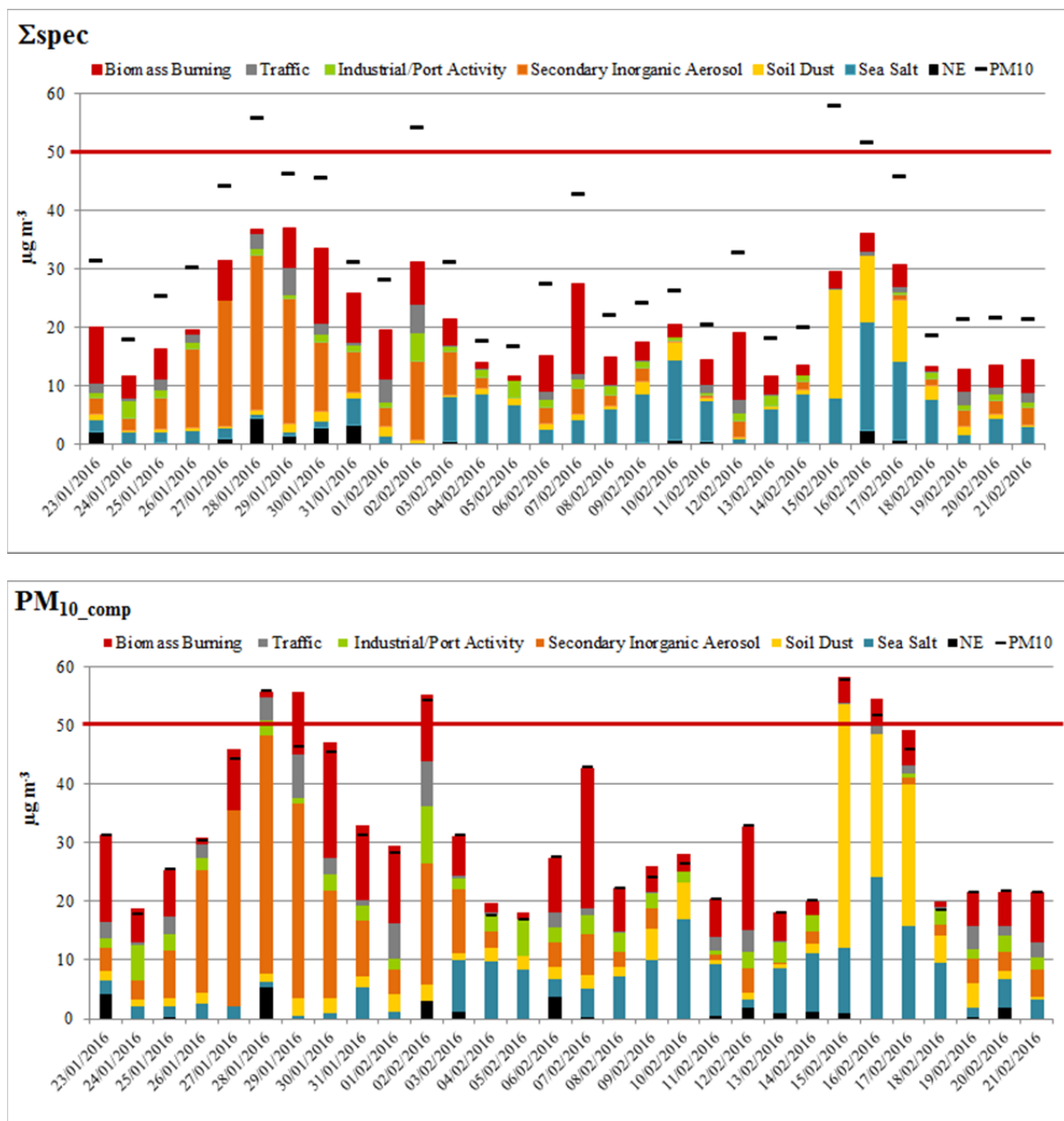
Fig. 6. Daily sources apportionment derived from the sum of all the speciated elements, (a) Σspec and (b) for parameter PM$_{10\_comp}$. Secondary inorganic aerosol, sea salt and soil dust come from clustering respectively nitrate-rich secondary aerosol and sulfate-rich secondary aerosol, fresh marine aerosol and aged marine aerosol, soil dust and re-suspended dust.

Table 3. Mean, median, standard deviation, minimum and maximum values for PM$_{10}$ and Σspec and PM$_{10\_comp}$ mass reconstruction.

	PM$_{10}$	Σspec	PM$_{10\_comp}$
	µg m^{-3}	µg m^{-3}	µg m^{-3}
Mean	32	21	32
Median	28	19	28
SD	13	8	13
25th Percentile	21	14	20
75th Percentile	45	29	45
Min	17	12	17
Max	58	37.0	57

trend, their maximum and minimum concentration values differ in occurring days. The highest BB$_{Levo}$ mass concentration value was recorded on 30 January, with 15, 21 and 36 µg m^{-3} depending on the specific F_W considered while the lowest occurred on 18 February, with 1.2, 1.7, and 2.9 µg m^{-3}. The relative BB$_{Levo}$ contribution to PM$_{10}$ shows maximum value on 12 February (35, 49, and 84%) and minimum on 18 February (6, 8, and 14%) (Table 5).

The BB$_{Levo}$ daily contribution to PM$_{10}$ estimated with macro tracer method ranges from 18 to 44%, depending on the specific F_W value (Table 5) and on the conversion factor used in Eq. (1). In order to evaluate the F_W more representative of the specific conditions of the studied area

Table 4. Σspec and PM_{10_comp} sources mass concentration data (NE: unexplained mass).

| | Biomass Burning | | Traffic | | Secondary Inorganic Aerosol | | Soil Dust | | Sea Salt | | Industrial/Port Activity | | NE | |
	Σspec µg m⁻³	PM_{10_comp} µg m⁻³	Σspec µg m⁻³	PM_{10_comp} µg m⁻³	Σspec µg m⁻³	PM_{10_comp} µg m⁻³	Σspec µg m⁻³	PM_{10_comp} µg m⁻³	Σspec µg m⁻³	PM_{10_comp} µg m⁻³	Σspec µg m⁻³	PM_{10_comp} µg m⁻³	Σspec µg m⁻³	PM_{10_comp} µg m⁻³
Mean	5.0	7.8	1.3	2.0	5.5	8.3	2.2	5.0	5.2	6.2	1.3	2.6	1.0	0.8
Median	4.0	6.2	0.8	1.3	2.7	4.1	0.82	2.1	4.3	5.0	1.2	2.5	0.37	0.1
SD	3.7	5.8	1.4	2.1	7.1	11	4.0	9.0	4.4	5.7	0.96	2.0	1.2	1.4
25th Percentile	2.8	4.4	0.22	0.35	1.2	1.9	0.5	1.3	1.9	1.9	0.84	1.7	0.083	0.0
75th Percentile	6.8	11	1.8	2.9	6.4	9	1.6	3.0	7.7	9.3	1.4	2.8	1.3	1.1
Min	0.63	1.0	0.011	0.017	0.18	0.015	0.17	0.54	0.76	0.48	0.39	0.79	0.021	0.0
Max	15	24	4.9	7.7	26	41	18	41	19	24	4.8	9.7	4.4	5.3

Table 5. Relative BB contribution to PM_{10} calculated by means of F_{W1}, F_{W2} and F_{W3}.

	BB % PM_{10} F_{W1}	BB % PM_{10} F_{W2}	BB % PM_{10} F_{W3}
Mean	18	44	26
Median	18	43	25
SD	8	20	12
25th Percentile	11	27	16
75th Percentile	23	55	32
Min	6	14	8
Max	35	84	49

the comparison of the independent results from PMF and macro tracer has been performed as reported in the following section.

Comparison between Macro Tracer Method and PMF Method

Since levoglucosan concentrations are available just for TF site, only the data from this site were extracted from the PMF output dataset and compared with the macro tracer results. BB contribution to PM_{10} calculated by means of the two independent methods (BB_{PMF} and BB_{Levo}) were analyzed by linear correlation. BB_{Levo} calculated with F_{W3} best fitted the BB_{PMF} values with *r* value equal to 0.85 and a slope value equal to 0.9 (Fig. 7): The slope value close to 1 indicates a tight correspondence between the data series obtained with the two independent methods. BB_{PMF} varies from 1.0 µg m⁻³ to 24 µg m⁻³ with a mean value of 7.8 µg m⁻³, while BB_{Levo}, calculated with F_{W3}, from 1.7 µg m⁻³ to 21 µg m⁻³ with a mean value of 8.5 µg m⁻³. The relative contribution to gravimetric PM_{10} is 25% and 26% for BB_{PMF} and BB_{Levo} respectively.

BB is the main source of PM in the studied area, accounting for about 30% (range from a minimum of 10% to a maximum of 50%). Nava *et al.* (2015) reported a comparable value of BB contribution to PM_{10} (37%) for a Centre of Italy site, confirming the relevant contribution of BB in suburban areas of Italy.

Even though levoglucosan may undergo atmospheric degradation processes, in our case we can speculate a relative chemical stability considering the agreement with the calculated daily BB mass contribution by the two methods.

As already explained in Section "Biomass Burning Identification Methods: Positive Matrix Factorization (PMF) and Macro Tracer Approaches", the F_{W3} assumes an olive emission coefficient intermediate between oak and beech ones. Since in the studied area olive is the most burned wood species (about 70%; Spagnolo *et al.*, 2014) we tried to determine a hypothetical olive emission factor *x* from the data of the daily BB_{PMF} contributions:

$$x = \{100 - [(F_{W\_PMF} \times 0.05 \text{ Beech} \times 4.1) + (F_{W\_PMF} \times 0.05 \text{ Oak} \times 13.3) + (F_{W\_PMF} \times 0.1 \times \text{Pellet} \times 10.1)]\}/(F_{W\_PMF} \times 0.8)$$

where
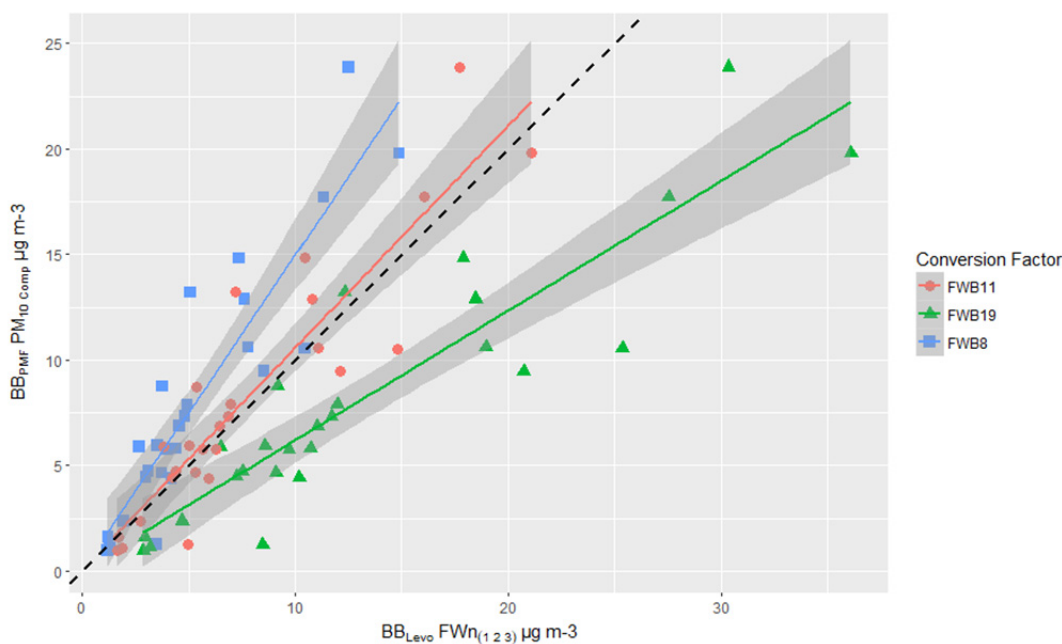$F_{W\_PMF} = BB_{PMF}$ (µg m⁻³)/[*Levoglucosan*] (µg m⁻³).

Fig. 7. BB_{PMF} and BB_{Levo} F_W (11, 19, 8) linear correlation.

Calculated olive emission factor results on average equal to 12. This value, derived from mathematical calculations and theoretical approximations, should be confirmed by further experimental emission tests on olive wood but represents to our knowledge the first proposed conversion factor for this wood species. Interestingly Fourtziou *et al.* (2017) reported a relation factor between levoglucosan and night PM_1 equal to 11.25 as representative for samplings in Greece where olive wood biomass is used for domestic heating. However, Maenhaut *et al.* (2016) reported a conversion factor for Flanders region equal to 22.6. This value is higher than the values here considered representative for olive biomass burning but is in line with other conversion factors reported for other northern Europe regions: In Finland, Saarnio *et al.* (2012) reported a factor equal to 24, equal to median value reported in Switzerland (Gianini *et al.*, 2013). Higher conversion factors have been also reported, for example by Ducret-Stich *et al.* (2013) for a Swiss Alpine valley (factor equal to 37).

CONCLUSIONS

Gravimetric measurements and detailed chemical characterizations of PM were performed in the study area to identify the main emission sources, with particular attention to BB. The daily values for PM_{10} varied between 9 µg m^{-3} and 51 µg m^{-3}, with the fine fraction representing, on average, about 70% of the concentration.

PMF was shown to be a good method for quantifying the emission sources, although the difference between the sum of the reconstructed speciation parameters (Σspec) and the experimentally measured gravimetric PM_{10} remains an issue to be solved. On the other side, the macro tracer approach, developed and applied mostly in the Alpine region, easily facilitated the evaluation of BB, although the

available conversion factors (F_W) do not cover the entire variety of woody biomass burned in Europe.

These two methods (PMF and the macro tracer approach) showed good agreement, as confirmed by the correlation coefficient (r = 0.85) and the slope (close to 1). The values for the mean concentration as well as the minimum and maximum values from the 24-h BB_{PMF} and BB_{Levo} series were, in fact, comparable: 7.8 vs. 8.5 µg m^{-3} for the average, 1.0 vs. 1.7 µg m^{-3} for the minimum and 24 vs. 21 µg m^{-3} for the maximum. BB was identified as one of the most significant sources of PM_{10} in the study area, contributing, on average, slightly less than 30%, with a maximum of 50% and a minimum of 10%.

Comparing the results from these two independent methods also allowed us to determine a possible conversion factor that is specific to the studied area and potentially representative of olive wood burning. Furthermore, the good agreement between the methods led us to identify and exclude an underestimation of the BB contribution in the macro tracer approach due to levoglucosan degradation. Levoglucosan is thus confirmed as a valid tracer for BB during winter in the examined area, exhibiting a daily-cycle (over 8 h) that corresponds to the expected house-heating/cooking activities, with higher concentrations during the late afternoon and night.

Integrating these two methods therefore results in a good methodology for realistically and independently quantifying BB's contribution to PM. Applying this approach to other case studies may further confirm the utility of this dual evaluation and of identifying specific conversion factors (F_w). These conversion factors, mathematically identified and demonstrated with *ad hoc* tests, can also be used in simple and cheap procedures to routinely evaluate BB in the long term, increasing our knowledge of BB's impact on air quality in every region of Europe. Furthermore, establishing a

database of F_w values that are representative of different geographical areas may enable the development of automated instruments for the real time quantification of BB.

The two methods, each with its specific strengths and weaknesses, converge when evaluating BB in the studied area. We recommend that this integrated approach be considered a state of the art procedure for the quantification of BB.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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