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Estimation of local and external contributions of biomass burning to PM2.5 in an industrial zone included in a large urban settlement

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Abstract:	A total of 85 PM2.5 samples were collected at a site located in a large industrial zone (Porto Marghera, Venice, Italy) during a one year-long sampling campaign. Samples were analyzed to determine water soluble inorganic ions, elemental and organic carbon and levoglucosan and results were processed to investigate the seasonal patterns, the relationship between the analyzed species and the most probable sources by using a set of tools, including: (i) conditional probability function (CPF), (ii) conditional bivariate probability function (CBPF), (iii) concentration weighted trajectory (CWT) and (iv) potential source contribution function (PSCF) analyses. Furthermore, the importance of biomass combustions to PM2.5 was also estimated. Average PM2.5 concentrations ranged between 54 µg m-3 and 14 µg m-3 in the cold and warm period, respectively. The mean value of total ions was 11 µg m-3 (range 1-46 µg m-3): the most abundant ion was nitrate with a share of 34% followed by sulfate (23%), ammonium (11%), potassium (3%) and chloride (3%). Levoglucosan accounted for 1.2% of the PM2.5 mass and its concentration ranged from few ng m-3 in warm periods to 2.6 µg m-3 during winter. Average concentrations of levoglucosan during the cold period were higher than those found in other European urban sites. This result may indicate a great influence of biomass combustions on particulate matter pollution. Elemental and organic carbon (EC, OC) showed similar behavior, with the highest

	contributions during cold periods and lower during summer. The ratios between biomass burning indicators (K+, Cl-, NO3-, SO42-, levoglucosan, EC and OC) were used as proxy for the biomass burning estimation and the contribution to the OC and PM2.5 were also calculated by using the LG/OC and LG/PM2.5 ratios and were estimated to be 29% and 18%, respectively.
Response to Reviewers:	Dear Editor, The authors are grateful to the referees for reviewing the manuscript. All suggestions have been addressed and the text has been rewritten and completed accordingly. A point to point reply is reported here below. We are confident that the manuscript has significantly improved after the revision. The authors are also grateful to the Editor and Editorial office for their help. Kind regards, Bruno Pavoni Note: The Referee questions are in italics, in normal text are the old parts and their revisions Reviewer #1.The manuscript by Benetello et al. discusses the contribution of both regional and local sources of biomass burning to PM2.5 concentrations in the Po valley, Italy. The authors present time-integrated data on ambient OC, EC, inorganic ions and levoglucosan, as well as the results of multiple receptor modeling and back trajectory analyses (such as conditional probability function and concentration weighted trajectories, among other methods). The manuscript and discussions therein are very well-articulated, and the analyses are presented elegantly. Quality of the manuscript and importance of the topic certainly warrant a publication in ESPR. Below are a few (minor) comments that can help further improve the quality of this already well-written manuscript prior to publication: Line 41: Please define IARC. Definition added Line 42: Please define fine mode particulate matter. “from 10% to 70% to fine mode particulate matter” Rewritten: “from ~10% to 70% to fine mode particulate matter (PM2.5)” Line 134: "probably" should be changed to "probable". Corrected Line 187: TC is not defined anywhere in the text. From the numbers it seems that it refers to "total carbon" and is calculated as the sum of EC and OC. This needs to be clarified. Added: (TC=OC+EC) Line 189-191: It is worthwhile to present the actual correlation matrix with all correlation values in either SI or the main text. The correlation matrix has been added in the “supplementary material” part. Line 212-235 (section 4.3). There are logical issues in the interpretation of OC/EC ratio in this section. First of all, OC and EC can both have very diverse source origins. Analyzing the OC/EC ratio as an indicator of the extent of biomass burning is too simplistic to be true, and can be significantly biased depending on location/season. As an example, the authors first attribute the higher OC/EC concentration in winter compared to summer to higher biomass burning. Few lines later temperature difference and partitioning of OC in the particle phase is noted as another factor affecting this comparison. The extent to which each of these factors contributes to OC levels is, however, unclear. Another effect totally ignored in these discussions is the secondary formation of OC, which can enhance the OC levels during summer without affecting EC concentrations. Accordingly, OC/EC ratios in many regions of the world where SOA formation is substantial during summer seasons (such as southwestern United States) is higher during the warmer season compared to the colder seasons. It is, overall, insightful to discuss the OC/EC ratios and compare them to what was found

	in literature, but interpretation of this ratio (in the absence of more deterministic carbonaceous species parameters such as WSOC or WIOC) should be made with caution given the numerous factors that affect both OC and EC levels. Old Text Sudheer and Sarin (2008) discuss the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. Further, this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for PM2.5 in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam (Viana et al., 2007) and could be related to wood burning emissions characterized by low EC/TC ratios during the cold period as observed by Zdráhal et al. (2002).The use of EC and OC relationship can be useful to distinguish their origin (Xu et al. 2012). EC may be used as a tracer for primary emissions of carbonaceous compounds; for this reason, variations of the OC/EC ratio range can be consider as an indicator, because it may identify changes in emission sources, source areas or processes (Viana et al. 2007). OC/EC ratios of 9, 1.1 and 2.7 reported by Watson et al. (2001), discern biomass burning, vehicle emissions and coal combustion sources, respectively. Lonati et al. (2007) reported a mean OC/EC ratio of 8.6 for the cold season and 4.2 for the warm one in Milan. Other Italian OC/EC values were in a range of 4.0–5.6 in Genoa, 4.3–13.4 in Florence and 4.5–8.2 in Milan (Vecchi et al. 2008). In this study, the mean OC/EC ratios for the cold period were 4±2 (range 1.8 - 10.1), while 1.7±0.5 (range 1.1–3.3) for the warm period and were generally similar to those found in most European cities. In fact, OC/EC mean ratios obtained by Viana et al. (2007) were 4.7, 3.1, 4.4 for winter time and 2.8, 2.6, 3.5 during the summer period in Amsterdam, Barcelona and Ghent, respectively. Generally, lower OC/EC ratios indicate fossil-fuel combustion, while higher ratios underline the influence from biomass burning sources (Ram and Sarin 2010). Low temperature and mixing layer heights during winter play an important role to increase the OC/EC ratio; for this reason, ratio values were higher during cold period (Vecchi et al. 2008; Li et al. 2012). This pattern was observed in studies in Italy (e.g. Vecchi et al. 2008) and in other countries like China (e.g. Dan et al. 2004; Li et al. 2012). Figure 2 shows correlations, the temporal variation of EC and OC concentrations and OC/EC ratio for PM2.5. Different EC-OC correlation coefficient (R2) of 0.53 and 0.42 were observed during cold and warm periods, respectively. This result suggests the presence of different sources for EC and OC especially in summer, since the relative rates of OC and EC releases are not proportional to each other. Rewritten: “Sudheer and Sarin (2008) discussed the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. In addition this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for PM2.5 in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam by Viana et al. (2007), who related it to wood burning emissions characterized by low EC/TC ratios during the cold period and cited Zdráhal et al. (2002) as a confirmation. The use of EC and OC relationship can be useful to distinguish their origin (Turpin and Huntizicker 1995; Xu et al. 2012). EC may be used as a tracer for primary emissions of carbonaceous compounds; for this reason, variations of the OC/EC ratio range can be considered as an indicator, because it may identify changes in emission sources, source areas or processes (Viana et al. 2007). In this study, the mean OC/EC ratio for the cold period was 4±2 (range 1.8 - 10.1), while 1.7±0.5 (range 1.1–3.3) for the warm one. The annual range was comparable with that of 0.6-8.4 and 0.7-15.4 reported by Giannoni et al. (2012) and Khan et al. (2016), respectively, while other Italian OC/EC values were in a range of 4.0–5.6 in Genoa, 4.3–13.4 in Florence and 4.5–8.2 in Milan (Vecchi et al. 2008). With respect to this study, similar winter OC/EC mean ratios were obtained by Viana et al. (2007): 4.7, 3.1, 4.4, while higher values (2.8, 2.6, 3.5) were observed during the summer period in Amsterdam, Barcelona and Ghent, respectively. The temporal variation (Fig. 2), with high OC/EC values during cold period and lower

during the warm one, was observed also in other studies (e.g. Lonati et al. 2007; Khan et al. 2016). High OC/EC ratios could underline the influence of biomass burning sources (Ram and Sarin 2010), or the formation of secondary organic aerosol (SOA, Chow et al. 1994; Turpin and Huntizicker 1995). During winter, when the highest ratios were observed, several factors can lead to higher OC concentrations compared to EC: i) lower temperatures, which promote the aerosol particle phase of organic compounds, ii) higher local contributions from household heating systems or biomass burning, which characterize colder months, and iii) lower mixing layer heights that enhance the SOA formation due to the accumulation of gaseous precursors (Viana et al. 2007; Vecchi et al. 2008; Li et al. 2012). In addition, the strong daily variability in winter, due to local contributions, may increase the OC values, whereas regional-scale SOA during summer leads to homogeneous contributions and to lower OC variability (Viana et al. 2007).
Fig. 2 shows linear regressions between OC and EC: different EC-OC coefficient of determination (R2 = 0.53 and 0.42) were obtained during cold and warm periods, respectively. These results suggest the presence of different sources for EC and OC especially in summer, when the relative rates of OC and EC releases are less proportional to one another."

A sentence has been also added in the conclusion section:
"The OC/EC ratios mean values were higher during colder months, the annual range was 1.1-10.1 and comparable with other Italian studies. A large variability of OC was observed during the cold period probably due to local contribution, while during the warm one, the regional-scale SOA leads to homogenous contributions and to lower OC variability."

Line 229-230: the impact of temperature on increasing OC/EC level is expected, but not the mixing height. Mixing height variation is expected to have comparable impact on EC and OC concentration, hence no substantive impact on the ratio. This statement needs to be corrected.
Old Text:
"Low temperature and mixing layer heights during winter play an important role to increase the OC/EC ratio; for this reason, ratio values were higher during cold period"
Corrected with (see also previous reply):
"During winter, when the highest ratios were observed, several factors can lead to higher OC concentrations compared to EC: i) lower temperatures, which promote the aerosol particle phase of organic compounds, ii) higher local contributions from household heating systems or biomass burning, which characterize colder months, and iii) lower mixing layer heights that enhance the SOA formation due to the accumulation of gaseous precursors (Viana et al. 2007; Vecchi et al. 2008; Li et al. 2012). In addition, the strong daily variability in winter, due to local contributions, may increase the OC values, whereas regional-scale SOA during summer leads to homogeneous contributions and to lower OC variability (Viana et al. 2007) ".
Reviewer #2: The authors are presenting a study about the influence of biomass burning on air quality at industrial-urban site in Northern Italy. The topic of the study is recent in Europe, and the data on biomass burning are still incomplete. Even though several source apportionment studies from this region are published, there is still a need for new studies to elucidate the contribution of biomass burning to airborne particulate matter and to support the local administration and decision-makers to improve the air quality. The work appears to be well done and the interpretations of the authors are very reasonable. I would suggest publishing the article manuscript with minor revisions:

Section 2, line 106-108: Rephrase the sentence.
"Previous studies showed that all these sources clearly affect air quality in Venice and significantly apportion to PM mass and its component (PAHs, inorganic ions and elements)"

Rephrased:
"Previous studies showed that all these sources clearly affect the air quality in Venice, by varying the PM mass and its chemical composition (PAHs, inorganic ions and elements)"

Section 3.1, line 128-129: How many field blanks did you use?
We used 5 field blanks.

Section 3.3, line 151-152: What was the reason for the model set-up? Do you expect different analysis results with starting heights of e.g. 100 m AGL and 500 m AGL?
The model set-up was made by considering the Planetary Boundary Layer (PBL) variations. During the cold period, the mixing height is below 500 m. PBL variations were observed also during the day. At night, the PBL drops down to below 100 m (Pecorari et al. 2013).

Section 4.3, line 212-217: Rephrase the paragraph and refer to the primary sources e.g. Sudheer and Sarin 2008 discuss the TC/EC ratio and Vianna et al., 2007 refer to the study conducted in Ghent by Zdráhal et al. (2002).
Old text:
Fossil fuel and biomass burning sources can be distinguished by using the EC/TC ratio (Sudheer and Sarin 2008). Further, this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for PM2.5 in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam and could be related to wood burning emissions characterized by low EC/TC ratios during the cold period (Viana et al. 2007).

Rewritten:
“Sudheer and Sarin (2008) discussed the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. In addition this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for PM2.5 in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam by Viana et al. (2007), who related it to wood burning emissions characterized by low EC/TC ratios during the cold period and cited Zdráhal et al. (2002) as a confirmation.”

Section 4.5, line 285-286: Rephrase the sentence according to the Figure 3.
Text and Figure 3 have been corrected:

Old text:
Results of CPF and CBPF are shown in Fig. 3. During the cold period, the higher probabilities (Fig. 3a) are reached toward south, south-east (PM2.5, OC, LG) and also west and north-west for K+, where a large rural area is located. In the warm period (Fig. 3b) CPF plots highlight the higher probabilities for wind blowing from the north-west sector i.e. in the direction of the mainland characterized especially by the conurbation of Mestre and the farmland.

Revised text:
Results of CPF and CBPF are shown in Fig. 3. During the cold period, higher probabilities in CPF plots (Fig. 3a) are reached for PM2.5, OC, LG and K+ toward south, south-east. In the warm period (Fig. 3b) CPF plots highlight higher probabilities for wind blowing from the north-west sector i.e. in the direction of the mainland characterized by the conurbation of Mestre and the farmland.
.
Section 4.5, line 289-292: Rephrase the sentence and add the WS intervals for the different WD.
In the bivariate polar plots interesting features can be seen. They show that the significant profile contributions are associated with low wind speed conditions from the north-west sector, indicating that biomass combustion can be an important local source of pollution, but also with high wind from north, north –west and from south-east, in the cold and warm period respectively. This highlights a probable external contribution for PM and biomass burning tracers.

Corrected:

In the bivariate polar plots (CBPF) interesting features can be seen. They show that significant profile contributions are associated with low wind speed conditions (< ~2 m s-1) from the north-west sector (rural area), indicating that biomass combustion can be an important local source of pollution (Fig. 3a). However, the high wind speed (> 3 m s-1) from north, north –west and from south-east, in the cold and warm period, respectively could suggests a probable external contribution for PM and biomass burning tracers (Fig. 3a and 3b).
Section 4.6: What was the reason for the CWT analysis of the biomass burning traces (OC, LG, K+) and not ratios (OC/PM2.5, LG/OC, K+/OC) as for the PSCF analysis and vice versa? Do the results of the two analyses match or differ since you analyse traces/ratios with the CWT and the PSCF?
As in the study of Squizzato and Masiol (2015) the outputs of the two approaches were very similar, it was considered redundant to apply both on the same variables. CWT are applied on LG, OC e K+ for the first time in the Venice area. So far CWT have been reported only for ions (Squizzato and Masiol 2015; Masiol et al. 2015)
The choice of not using ratios, e.g. OC/PM2.5 in CWT computations was based on the fact that scarce data for PM are available in the central-western European regions (Fra-UK) for back trajectory use. In addition, when using datasets based on low concentrations, the information extent that can be obtained is very limited (Hsu et al. 2003).

Section 4.6, line 318: How can you explain a probable contribution of LG/OC from the North Sea in summer?
This is not so clear and deserves further investigation. However some studies (e.g. Saarnio et al. 2010; Karlsson et al. 2013)report the role of the transport from east Europe of air masses to northern europe. These masses come from regions where in especially in summer large biomass combustion occurs. In addition the long distance transport from these areas has been detected also in UK (Witham and Mannin 2007). In the last decade United Kingdom replaced coal in the large power utilities with wood pellet and burned about 4.7 tons of pellets for industrial use in 2014 (about 60% of EU-28 Industrial wood pellet consumption) (AEBIOM, 2015).

Section 4.7, line 339-351: Unify text and Table 2 wood combustion versus biomass combustion.
Corrected in the text

Section 4.7, line 327-332: Compare the results found here with other European studies if possible.
Added text:
“On the other hand, considering some European studies, LG/OC mean values during fall-winter seasons were in the range 1-8% (Giannoni et al. 2012; Elsasser et al. 2012; Crilley et al. 2015; Pietrogrande et al. 2016)”
Figure 3: Correct the captions CPF/CBPF and unify the units.

Figure 3 was modified

Added references

AEBIOM, European Biomass Association, 2015. AEBIOM statistical report 2015, European Bioenergy Outlook, Key findings 2015. Brussels, Belgium. Available at: http://www.aebiom.org/library/statistical-reports/statistical-report-2015/.
Karlsson PE, Ferma M, Tømmervik H, Hole LR, Karlsson GP, Ruoho-Airola T, Aas W, Hellsten S, Akselsson C, Mikkelsen TN, Nihlgård B (2013) Biomass burning in eastern Europe during spring 2006 caused high deposition of ammonium in northern Fennoscandia. Environ Poll 176: 71-79
Pecorari E, Squizzato S, Masiol M, Radice P, Pavoni B, Rampazzo G (2013) Using a photochemical model to assess the horizontal, vertical and time distribution of PM2.5 in a complex area: Relationships between the regional and local sources and the meteorological conditions. Sci Tot Environ 443: 681–691
Saarnio K, Aurela M, Timonen H, Saarikoski S, Teinilä K, Mäkelä T, Sofiev M, Koskinen J, Aalto PP, Kulmala M, Kukkonen J, Hillamo R (2010) Chemical composition

	of fine particles in fresh smoke plumes from boreal wild-land fires in Europe. Sci Tot Environ 408: 2527–2542 Witham C, Manning A (2007) Impacts of Russian biomass burning on UK air quality. Atmos Environ 41: 8075–8090
Additional Information:	
Question	**Response**
§Are you submitting to a Special Issue?	No

Estimation of local and external contributions of biomass burning to $PM_{2.5}$ in an industrial zone included in a large urban settlement

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Abstract

A total of 85 $PM_{2.5}$ samples were collected at a site located in a large industrial zone (Porto Marghera, Venice, Italy) during a one year-long sampling campaign. Samples were analyzed to determine water soluble inorganic ions, elemental and organic carbon and levoglucosan and results were processed to investigate the seasonal patterns, the relationship between the analyzed species and the most probable sources by using a set of tools, including: (i) conditional probability function (CPF), (ii) conditional bivariate probability function (CBPF), (iii) concentration weighted trajectory (CWT) and (iv) potential source contribution function (PSCF) analyses. Furthermore, the importance of biomass combustions to $PM_{2.5}$ was also estimated. Average $PM_{2.5}$ concentrations ranged between 54 µg m^{-3} and 14 µg m^{-3} in the cold and warm period, respectively. The mean value of total ions was 11 µg m^{-3} (range 1-46 µg m^{-3}): the most abundant ion was nitrate with a share of 34% followed by sulfate (23%), ammonium (11%), potassium (3%) and chloride (3%). Levoglucosan accounted for 1.2% of the $PM_{2.5}$ mass and its concentration ranged from few ng m^{-3} in warm periods to 2.6 µg m^{-3} during winter. Average concentrations of levoglucosan during the cold period were higher than those found in other European urban sites. This result may indicate a great influence of biomass combustions on particulate matter pollution. Elemental and organic carbon (EC, OC) showed similar behavior, with the highest contributions during cold periods and lower during summer. The ratios between biomass burning indicators (K^+, Cl^-, NO_3^-, SO_4^{2-}, levoglucosan, EC and OC) were used as proxy for the biomass burning estimation and the contribution to the OC and $PM_{2.5}$ were also calculated by using the LG/OC and LG/$PM_{2.5}$ ratios and were estimated to be 29% and 18%, respectively.

Keywords: $PM_{2.5}$**,** Levoglucosan**,** Inorganic ions**,** OC/EC ratio**,** Biomass burning

1. Introduction

In 2013, outdoor air pollution and airborne particulate matter (PM) have been classified as human carcinogens (Group 1)by IARC (International Agency for Research on Cancer). Elemental (EC) and organic (OC) carbon are major PM components and are ubiquitous in the Earth's troposphere. It was estimated that carbonaceous species contribute from ~10% to 70% to fine mode particulate matter ($PM_{2.5}$) (Kanakidou et al. 2005; Fuzzi et al. 2006): in European rural, urban and kerbside sites, EC ranges from 5% to 21%, while OM (organic matter expressed as 1.4*OC) from 15% to

26% of $PM_{2.5}$ (Putaud et al. 2010).The European Directive 2008/50/EC (EC 2008) has included EC and OC as parameters to be monitored all over Europe.

Combustions are recognized as one of the main impacting sources of worldwide airborne pollution (Gaffney and Marley 2009) and mainly emit carbonaceous material in both gaseous and aerosol phases (Andreae and Merlet 2001). The combustion of biomasses (biomass burning, BB) is among the main sources of carbonaceous PM, along with fossil-fuel and industrial emissions. BB involves a large number of potential sources and fuels, e.g., wildfires (Knorr et al. 2012), savanna/forest fires (Ofosu et al. 2013), agricultural burning of crop residues (Hays et al. 2005), domestic (Akagi et al. 2011) and many other open fires (Lemieux et al. 2004, and references therein). BB emissions have several adverse implications on human health (e.g., Laumbach and Kipen 2012; Kodgule and Salvi 2012), visibility and global climate (Keywood et al. 2013).

Generally, BB aerosol consists in a non-uniform mixing of high molecular-weight organics, soot and potassium (e.g., Lee et al. 2015). Some compounds are usually used as tracers for BB: water soluble-potassium (K^+), levoglucosan(1,6-anhydro-β-D-glucopyranose) and even organic carbon are the most widely used ones (Simoneit et al. 1999). Levoglucosan, as well as other anhydrosugars, is formed during pyrolysis of materials containing cellulose (present in every type of wood) and hemicellulose at high temperature (> than 300°C) (Simoneit et al. 1999; Puxbaum et al. 2007): for this reason, it is a good BB tracer. On the contrary, potassium should be used with caution: although it is largely emitted by BB, it also derives from other different sources, such as crustal dust, sea-salt, coal usage, waste incinerators and others (Duan et al. 2004; Wang et al. 2007; Caseiro et al. 2009; Giannoni et al. 2012; Mkoma et al. 2013).

In Europe, BB emissions are generally released into the atmosphere from wild fires (especially in southern Europe), from agricultural fires (in Eastern Europe) and from fireplaces and wood stoves (in central and north Europe) (Caseiro et al. 2009). However, in countries where agriculture is an important economic sector, the combustion of biomass (e.g. agricultural waste etc) results an important source of particulate matter (Maenhaut et al. 2012; Mkoma et al. 2013, Vassura et al. 2014).

The Po Valley (N Italy) is one of the remaining hot-spots for air quality in Europe, i.e. some European standards for air quality are not always met (including PM_{10} and $PM_{2.5}$). Although a large number of studies have been performed for investigating the main sources of PM in Po Valley (e.g., Bernardoni et al. 2011; Perrone et al. 2012; Masiol et al. 2014a; Tositti et al. 2014), data on BB are still incomplete. This lack of data represents a serious gap, since recent studies have

reported that biomass combustion cause a significant increase of air pollution (Vecchi et al. 2008; van Drooge and Perez Ballesta 2009; Piazzalunga et al.2010, 2011; Belis et al. 2011; Giannoni et al. 2012; Perrone et al. 2012; Piazzalunga et al.2013a,b; Masiol et. al. 2014b, Khan et. al. 2016) and the use softwood (i.e. pellets, briquettes, logs and chips) is becoming a renewable alternative to replace the use of methane (Pignatelli et al. 2008; Pastorello et al. 2011).

In the Veneto region (NE Italy),wood consumption for domestic heating and cooking was estimated to reach ~2 million tons/year (Francescato and Antonini 2010; ARPAV 2015). However, the burning of weeds and twigs deriving by mowing, pruning or cleanups of agricultural land and forest is a very common technique in Italy, and its estimation is problematic. This is partially due to uncertainties in estimating the amount of burned biomasses since ~56% of wood biomass are self-produced (38%) or traded/sold between private individuals (18%) (ARPAV 2015).

This study aims to investigate the potential local and external contributions of BB sources to $PM_{2.5}$ in an industrial zone included in a large urban settlement of Northern Italy.$PM_{2.5}$ samples have been collected at an industrial site close to an important urban area (Mestre and Venice) during a1 year-long sampling campaign. A total of 85 samples were selected to represent cold and warm periods and analyzed to determine water soluble inorganic ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}), carbonaceous components (EC, OC) and levoglucosan. Data have been processed to investigate the seasonal behavior, the relationship among analyzed species and to evaluate the importance of BB in the study area. The main goal of this study is to define the influence of biomass burning to air quality, at first by using inorganic ions and carbonaceous species (levoglucosan, EC, OC and TC), then by estimating the biomass burning contribution on OC and $PM_{2.5}$ levels. Moreover, conditional probability function (CPF), conditional bivariate probability function (CBPF), concentration weighted trajectory (CWT) and potential source contribution function (PSCF) analysis have been used to estimate the most probable emitting locations of biomass burning compounds and external contributions.

2. **Area of study**

The Venice conurbation is located in the northeastern part of Italy, in the Po Valley (Fig.1). It counts more than 270 000 inhabitants, most of them concentrated in Mestre on the mainland. The sampling station was located at Malcontenta within the industrial district of Porto Marghera (Lat. N 45.4382 – Long. E 12.2055). This site is included in the monitoring network of the regional environmental agency (ARPAV), and is placed close to the industrial settlement. The main facilities of the industrial area include thermal power plants, chemical and metallurgical works and oil refineries. Since this area is included in the conurbation of Mestre, the site is also influenced by typical urban sources (e.g.: domestic heating during cold period, light duty vehicle emissions) and emissions from heavy traffic coming from

the A57 (part of the E70 connecting Barcelona to Kiev) and E55 (Helsingborg –Kalamáta) motorways. Previous studies showed that all these sources clearly affect the air quality in Venice, by varying the PM mass and its chemical composition (PAHs, inorganic ions and elements) (Masiol et al. 2012a,b; Squizzato et al. 2014; Masiol et al.2014a). Unfavorable weather conditions and orographic features cause pollutant accumulation in the study area, so that the European limits for PM_{10} and $PM_{2.5}$ are frequently exceeded (Masiol et al. 2012c).

3. Experimental methods

3.1 Sampling campaign and analytical methods

Details of the sampling procedures were given elsewhere (Squizzato et al. 2012). Briefly, all samples were collected daily (24 h) on quartz fiber filters (Ø = 47 mm; Whatman QMA) with low volume samplers following the European standard EN 14907:2005 (2.3 m^3 h^{-1}) (CEN, 2005). The sampling campaign started on December 20, 2008, and ended on November 27, 2009. Within this period, a total of 85 samples (41 collected during the warm period and 44 during the cold period) were selected to analyze elemental and organic carbon (EC, OC), levoglucosan (LG) and water soluble inorganic ions. After sampling, filters were stored at -20°C in the dark until analyses.

Two aliquots were punched from each filter for the analysis. The first one (1 cm^2 or 1.5 cm^2) has been analyzed by the Sunset Lab OC-EC Aerosol Analyzer (*Thermal Optical Transmittance (TOT)-method*) for OC and EC. In the present study, the NIOSH 5040 protocol (US EPA 2003) was used. Analyses were carried out by following the procedure of carbon speciation established by Birch and Cary (1996).

The second one (1 cm^2) has been analyzed for levoglucosan and ions following the procedure described in Piazzalunga et al. (2010, 2013b and references therein) with an Ion Chromatograph (Dionex) equipped with an Ion Pac AS14A (Dionex) column for anions (Cl^-, NO_3^- and SO_4^{2-}), a CS12A (Dionex) column for cations (Na^+, Ca^{2+}, NH_4^+ and Mg^{2+}) and a Carbopac PA-10 column with an amperometric detector for LG. Details of analytical procedure are provided as supplementary material. Field blanks (n=5) were treated in the same way as the other samples and the mean of their results was routinely subtracted from the sample values.

The quality and accuracy of quantitative analyses were systematically checked by analyzing the standard reference material SRM1649a and 1648 (NIST, USA). The recovery of each analyzed compound was >75%.

3.2Conditional probability function and conditional bivariate probability function

In order to evaluate the most probable source area of $PM_{2.5}$, LG, OC and K^+, the conditional probability function (CPF) and conditional bivariate probability function (CBPF) (Uria-Tellaetxe and Carslaw 2014 and references therein) were performed for cold and warm periods by using the "Openair" package. Meteorological data have been provided by Ente

della Zona Industriale di Porto Marghera.

CPF is an important tool to identify a source area by estimating the probability that a pollutant species exceeds a specified value within a particular wind sector (Uria-Tellaetxe and Carslaw 2014). In this study the 75th percentile has been used as threshold value.

The conditional bivariate probability function (CBPF) adds more information on the nature of the sources (or chemical species), because each source type can be influenced by wind speed. In this view, wind speed represents a third variable which is coupled to ordinary CPF (Uria-Tellaetxe and Carslaw 2014).

3.3 Back trajectories, CWT and PSCF computation

Back-trajectory analysis allows to indicate the origin of an air mass investigating the potential effects of long-range transports (Abdalmogith and Harrison 2005). This method traces the history of air masses passing over a geographical area at a defined time (Squizzato and Masiol 2015). In this study, back-trajectories analysis was realized using "Openair" package in R (Carslaw 2015) considering the density of air masses (i.e. where the air masses spent most of their time) on pre-calculated back trajectories using the HYSPLIT trajectory model (Hybrid Single Particle Lagrangian Integrated Trajectory Model) (Draxler and Rolph 2015; Rolph 2015). Our model set-up parameters included 4 days (-96 h) run time, starting height of 20 m AGL, GDAS data fields. In this work, back-trajectories were used to investigate two episodes of high OC, LG and K^+ concentrations occurred during the cold period.

External contributions due to long range transport processes were evaluated by applying CWT (concentration weighted trajectory), a Trajectory Statistical Method (TSM) based on back-trajectory analysis. CWT approach is a method that combines weighting trajectories with concentrations (Hsu et al. 2003). In each grid cell, each concentration is used as a weighting factor to evaluate the residence times of all trajectories and then it is divided by the cumulative residence time from all trajectories (Cheng et al. 2013).

PSCF model is able to identify locations of sources that influenced aerosol concentrations over the study area. PSCF allows to obtain values combining aerosol composition data with air parcel back-trajectory calculations. This method is a conditional probability that an air parcel with a specific pollutant concentration arrives at a receptor site after having passed through a specific geographical area (Biegalski and Hopke 2004). In this study, PSCF model was applied to investigate the source regions of LG/OC, K^+/OC and OC/$PM_{2.5}$ which are the most important biomass burning indicator.

4. Results and discussion

4.1. *$PM_{2.5}$ mass and its ion composition*

Table1 presents concentrations of $PM_{2.5}$ mass and water-soluble inorganic ions in aerosol collected during the 2008-2009 campaign in Malcontenta. It is well known that the Po Valley is one of the hotspots of $PM_{2.5}$ in Europe and often standard air quality fixed by the European Directive 2008/50/EC (annual average 25 µg m^{-3}) are not met and PM_{10} regulatory daily limits exceeded, because of local weather conditions and external transport, especially in winter season (Traversi et al. 2008; Fattore et al. 2011; Masiol et al. 2015). $PM_{2.5}$ concentrations range between 54 µg m^{-3} and 14 µg m^{-3} as average values in the cold and warm period, respectively, in agreement with the typical behavior of the studied area. The average concentration of the three anions followed the sequence of $NO_3^- > SO_4^{2-} > Cl^-$, while the five cations followed the order $NH_4^+ > K^+ > Ca^{2+} > Na^+ > Mg^{2+}$. Total ions represented 15-53% of $PM_{2.5}$ (annual average 31%) and the most abundant ion was nitrate with an average of 34% of total ions, mostly present during winter time. The second most abundant ion was sulphate 23% (22% non-sea-salt (nss-SO_4^{2-})) followed by ammonium 11% and both potassium and chloride 3%. The reaction between gaseous HNO_3 and marine NaCl leads to a decrease of Cl^- concentrations during warm period caused by its volatilization as HCl (Aldabe et al. 2011). Obtained data for SO_4^{2-} were similar to those found by Masiol et al. (2015): no seasonal trend were observed. Nevertheless, the oxidation of SO_2 to SO_4^{2-} due to summer solar radiation is responsible for its increase during the warm period rather than during the cold one (Aldabe et al. 2011). On the contrary, lower values for NO_3^- levels are recorded during summer because the formation of gaseous HNO_3 is favored and a negative artifact during sampling cannot be excluded (Vecchi et al. 2009; Aldabe et al. 2011). A seasonal trend was observed for NH_4^+ confirming that during summer the reaction between ammonium and NaCl gives volatile NH_4Cl (Aldabe et al. 2011).

4.2. *Concentrations of OC, EC and levoglucosan (Carbonaceous species)*

As reported in Table 1, the higher concentrations of LG, OC, EC, and TC (TC=OC+EC) were detected during the cold period, while lower mean concentrations were observed during the warm period. Both meteorological factors and source variations can explain the same seasonal trend of carbonaceous species and PM mass (Mkoma et al. 2013). A Spearman correlation was applied and all these compounds were significantly correlated at $p<0.05$ during the cold period ($0.64<r_s<0.98$), while during the warm period the significant correlation was lower ($0.46<r_s< 0.97$) with the exception of LG which resulted non-correlated (Table SI1). The concentration of levoglucosan ranged from close to zero to 2.6 µg m^{-3}, with an average value of 0.66 µg m^{-3} and an amounts of 1.2% in the $PM_{2.5}$. Levoglucosan annual cycle was also demonstrated in previous studies: it is quite stable during the winter period and has a significant decrease during summer due to photochemical processes (Hoffmann et al. 2010). During winter, levoglucosan mean values obtained in north Europe ranged between 0.04 µg m^{-3} (Copenhagen) and 0.17 µg m^{-3} (Oslo) (Yttri et al. 2005; Hedberg et al. 2006; Oliveira et al. 2007; Szidat et al. 2009); for southern Europe Reche et al. (2012) reported a mean value of

0.06 μg m^{-3} in Barcelona. The data of the present study resulted to be higher and ranged from 0.06 to 2.6 μg m^{-3} (mean value 1.2 μg m^{-3}) and were comparable to those observed in the Lombardy region (Piazzalunga et al. 2010, 2011).This underlines that in the area of Venice – Mestre, wood is still used as heating material in domestic and/or industrial heating, especially in winter. As reported by Giannoni et al. (2012), lower levoglucosan concentrations during the warm period could represent background levels and could be caused by long range transport of pollutants, dry vegetation and/or agricultural biomass combustion. TC accounted for 36% and 23.4% of the $PM_{2.5}$ mass in cold and warm periods, respectively. TC concentrations ranged from 1.5 to 48.7 μg m^{-3}, with an average of 12.1 μg m^{-3}. Among the carbonaceous components, OC was the most abundant, accounting for 78.4% of TC and 28% of $PM_{2.5}$ during the cold period and 62% of TC and 14% of $PM_{2.5}$ in the warm period. The mean value was 9.4 μg m^{-3} in a range between 0.9 – 41 μg m^{-3}. During this sampling period, the abundance of OC in $PM_{2.5}$ varied from 8.5% to 40%, with an average of 21.5%. EC constituted around 9% of the total $PM_{2.5}$ mass and 38% of the TC during the warm period, while represented around 7.8% of $PM_{2.5}$ and 21.5% of the TC during the cold period.

4.3. *EC/TC and OC/EC ratios*

Sudheer and Sarin (2008) discussed the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. In addition this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for $PM_{2.5}$ in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam by Viana et al. (2007), who related it to wood burning emissions characterized by low EC/TC ratios during the cold period and cited Zdráhal et al. (2002) as a confirmation.

The use of EC and OC relationship can be useful to distinguish their origin (Turpin and Huntizicker 1995; Xu et al. 2012). EC may be used as a tracer for primary emissions of carbonaceous compounds; for this reason, variations of the OC/EC ratio range can be considered as an indicator, because it may identify changes in emission sources, source areas or processes (Viana et al. 2007). In this study, the mean OC/EC ratio for the cold period was 4±2 (range 1.8 - 10.1), while 1.7±0.5 (range 1.1–3.3) for the warm one. The annual range was comparable with that of 0.6-8.4 and 0.7-15.4 reported by Giannoni et al. (2012) and Khan et al. (2016), respectively, while other Italian OC/EC values were in a range of 4.0–5.6 in Genoa, 4.3–13.4 in Florence and 4.5–8.2 in Milan (Vecchi et al. 2008). With respect to this study, similar winter OC/EC mean ratios were obtained by Viana et al. (2007): 4.7,

3.1, 4.4, while higher values (2.8, 2.6, 3.5) were observed during the summer period in Amsterdam, Barcelona and Ghent, respectively.

The temporal variation (Fig. 2), with high OC/EC values during cold period and lower during the warm one, was observed also in other studies (e.g. Lonati et al. 2007; Khan et al. 2016). High OC/EC ratios could underline the influence of biomass burning sources (Ram and Sarin 2010), or the formation of secondary organic aerosol (SOA, Chow et al. 1994; Turpin and Huntizicker 1995). During winter, when the highest ratios were observed, several factors can lead to higher OC concentrations compared to EC: i) lower temperatures, which promote the aerosol particle phase of organic compounds, ii) higher local contributions from household heating systems or biomass burning, which characterize colder months, and iii) lower mixing layer heights that enhance the SOA formation due to the accumulation of gaseous precursors (Viana et al. 2007; Vecchi et al. 2008; Li et al. 2012). In addition, the strong daily variability in winter, due to local contributions, may increase the OC values, whereas regional-scale SOA during summer leads to homogeneous contributions and to lower OC variability (Viana et al. 2007).

Fig. 2 shows linear regressions between OC and EC: different EC-OC coefficient of determination (R^2 = 0.53 and 0.42) were obtained during cold and warm periods, respectively. These results suggest the presence of different sources for EC and OC especially in summer, when the relative rates of OC and EC releases are less proportional to one another.

4.4. *Relationships among biomass burning indicators*

During combustion processes, K^+ and Cl^- content in the fluids of plants volatilize and, due to nucleation or condensation reactions, are converted into the particulate phase (Alves et al. 2010). Hence, during biomass combustion, great quantities of K-rich particles are released, because this ion is considered the major electrolyte of the cytoplasm. This is the reason why high K^+ levels normally characterize biomass burning source, while fossil-fuel emission produces little K^+ (Pio et al. 2008; Satsangi et al. 2012; Mkoma et al. 2013). Consequently, K^+/EC and K^+/OC ratios can be used to distinguish biomass burning emissions from other sources as fossil fuel combustion (Duan et al. 2004; Satsangi et al. 2012; Vicente et al. 2013). Unfortunately, to our knowledge, in Venice-Mestre area, there are no reported values of ratios of such chemical species from biomass burning, whereas few are reported for the Po Valley (Belis et al. 2011, Piazzalunga et al. 2011). Low K^+/EC values reported in literature were in a range from 0.025 to 0.09 and indicate fossil fuel combustion, while high values in a range from 0.21 to 0.46 are representative of biomass burning (Andreae 1983). Data obtained in this study showed mean values of 0.2±0.1 and 0.05±0.09 for the cold and the warm seasons, respectively, denoting a major contribution of biomass burning during winter. The K^+/OC ratio in Malcontenta varied from 0.03 to 0.15 with an average of 0.05±0.02 during the cold period and from 0.001 to 0.32 with an average of

0.03±0.06 during the warm period. Similarly, K^+/OC ratios for various types of biomass burning ranged between 0.01 (both extratropical forest and biofuel burning) and 0.1 (Savanna and grassland): agricultural residue burning presented a ratio between 0.04-0.13 (Andreae and Merlet 2001). A good significant Spearman's correlation (at $p < 0.05$) was obtained between K^+ and OC during the cold period ($r_s = 0.91$),revealing that the OC origin is linked to biomass combustion (Mkoma et al. 2013). On the other hand, a low but also significant Spearman's correlation was observed during the warm season ($r_s = 0.49$). A similar result was obtained for the K^+/EC correlation: good significant Spearman's correlation (at $p < 0.05$) during cold period ($r_s = 0.77$) and insignificant during the warm season ($r_s = 0.25$). Cl^-/EC ratio was also calculated. Obtained data were 0.2±0.2 as a mean value of cold period (range close to 0-0.96) and 0.05±0.1 as a mean of warm period (range 0.016-0.62). Ferek et al. (1998) and Yamasoe et al. (2000) reported Cl^-/EC ratios of 0.44 and in a range 0.15-0.17, for cerrado fires in Brazil, while a higher value equal to 2.39 was obtained by Andreae et al. (1998) for Savanna fires in Africa. This discrepancy could be caused by the influence of industrial emissions, sea-salt aerosol etc., which may enormously increase this ratio (Yamasoe et al. 2000; Saud et al. 2013).

However, two episodes, that occurred on 7th June and on 5th September, were characterized by high values of K^+/OC and K^+/EC ratios. In particular, the K^+/OC and K^+/EC ratios of 7th June were 0.20 and 0.37, respectively. On 5th September these values were 0.32 and 0.51.

The ratio for nss-SO_4^{2-}/EC was found to be 1.0±0.7 and 2.5±1.6 for cold and warm periods, respectively, with an annual average of 1.7±1.4, while nss-SO_4^{2-}/OC ratios were 0.26±0.19 during the cold period and 1.4±0.8 during the warm one, with an annual average of 0.8±0.8. These ratios were higher than those found in the literature (Mkoma et al. 2013; Pipalatkar et al. 2014). Only Sudheer and Sarin (2008) reported a ratio of ~15 for nss-SO_4^{2-}/EC recorded in Bay of Bengal. Similarly, NO_3^-/EC and NO_3^-/OC were found to be 2.7±3.3 and 0.6±0.4 during cold period, while 0.5±0.4 and 0.3±0.2 during summertime, respectively. NO_3^-/EC ratio recorded in this study during warm period was similar to those found by Pipalatkar et al. (2014). However, our NO_3^-/EC and NO_3^-/OC ratios were higher than those calculated by Gillies et al. (2001) from road tunnel aerosol which were 0.13 and 0.17 respectively in $PM_{2.5}$, suggesting the influence of biomass burning to our receptor site.

Both K^+ and levoglucosan are recognized markers of biomass combustion (Fraser and Lakshmanan 2000; Mullaugh et al. 2014). The temporal trend of levoglucosan coincided with that of K^+ and the two species were positively and significantly correlated during this study ($r_s = 0.88$ at $p < 0.05$), similarly to what it was observed in other studies (Urban et al. 2012, Mullaugh et al. 2014). This indicates that it is acceptable to use K^+ as a biomass burning tracer especially in winter. In Austria, Caseiro et al. (2009) found a LG/K^+ ratio in a range 0.9-1.7 during the cold period. Our values varied from 0.09 to 2.35 during the cold period and the range was extremely lower during the warm period (close

to 0–0.3) with respect to the range of 0.22-0.56 reported by Caseiro et al. (2009),probably because of the lower wood combustion in this season near the sampling site.

4.5. *Conditional probability function*

Results of CPF and CBPF are shown in Fig. 3. During the cold period, higher probabilities in CPF plots (Fig. 3a) are reached for $PM_{2.5}$, OC, LG and K^+ toward south, south-east. In the warm period (Fig. 3b) CPF plots highlight higher probabilities for wind blowing from the north-west sector i.e. in the direction of the mainland characterized by the conurbation of Mestre and the farmland.

In the bivariate polar plots (CBPF) interesting features can be seen. They show that significant profile contributions are associated with low wind speed conditions (< ~2 m s^{-1}) from the north-west sector (rural area), indicating that biomass combustion can be an important local source of pollution (Fig. 3a). However, the high wind speed (> 3 m s^{-1}) from north, north –west and from south-east, in the cold and warm period, respectively could suggests a probable external contribution for PM and biomass burning tracers (Fig. 3a and 3b).

4.6. *Potential contribution of long-range transport*

Fig. 4 shows the frequency of back trajectories calculated over the study period. Most trajectories originate over the eastern part of the Po Valley, indicating that the influence of long-range transport on aerosol composition could be negligible rather than the regional origin.

The analysis of the potential effects of long-range transport on a regional scale through the CWT model clearly indicates some predominant source areas for potential transboundary transport. During the cold period, OC, LG and K^+ appear influenced by high external contribution when air masses are coming from Central Europe (Fig. 5). Moreover an increase in LG concentration can be also observed for air masses coming from East Europe, highlighting a widespread distribution of this species.

In the warm period K^+ concentrations appear not influenced by external transport, whereas OC shows the highest concentration from the warmer European area. This feature can be related the presence of OC as secondary organic aerosol, which is more easily formed in conditions of high temperature and intense solar radiation, that enhance photochemical reactions (Zhang et al. 2012). LG shows the highest concentration over the Alpine area, where the biomass burning is common throughout the year. In a recent study conducted by ARPAV, the largest use of biomass in the Veneto region was observed in the Belluno province, which is located in the Alpine area (ARPAV, 2015).

Single high-polluted episodes have been also investigated. Two episodes of high OC, LG and K^+ concentrations occurred during the campaign: 1) from 8th to 12th January and 2) from 12th to 15th January. Fig. 6 shows the single back-

trajectories associated with the daily concentration of OC, LG and K^+ in order to explain if the origin of high pollutant concentrations may be local or due to long-range transport. Both episodes showed that the passage of back trajectories over the central-eastern part of Europe could promote the enrichment of air masses with pollutant species, having in this way a high impact over the Eastern Po Valley.

The PSCF results calculated on the ratio of the most important biomass burning indicators are shown in Fig. 7. All the considered ratios showed large variability both in the whole period and the seasons. During summer, the $OC/PM_{2.5}$ and LG/OC ratios show the highest probabilities over the Austria, Hungary and Slovenia, with a probable contribution of LG/OC also from the North Sea. Different behavior was observed for K^+/OC which is present over central Italy and mostly over Tunisia and Algeria. During winter time, the major source of LG/OC could be firstly the Mediterranean area and secondly the Alpine region of the North-East Italy. The $OC/PM_{2.5}$ source area is more distributed over the Eastern-Central Europe, while K^+/OC is more located over the study area and Dolomites. On annual base, LG/OC and K^+/OC are mostly localized over the Alps, while $OC/PM_{2.5}$ in the Eastern Europe.

4.7. *Estimate of the contribution of biomass burning to OC and $PM_{2.5}$*

The use of tracers can be an important tool to define the source identification. Since levoglucosan is considered a good tracer for biomass burning activities, it was used in this study to evaluate the biomass burning contribution to OC and $PM_{2.5}$. In particular, the most considered tool is the LG/OC ratio (Zhang et al. 2008; Mkoma et al. 2013). In Beijing, Zhang et al. (2008) recorded a LG/OC ratio of 2.1% as annual average in $PM_{2.5}$ while Mkoma et al. (2013) a value of 3-4% in $PM_{2.5}$ and PM_{10} for Tanzania. On the other hand, considering some European studies, LG/OC mean values during fall-winter seasons were in the range 1-8% (Giannoni et al. 2012; Elsasser et al. 2012; Crilley et al. 2015; Pietrogrande et al. 2016). In our study, the mean LG/OC ratio of all sampling period was 4±5%, with a decrease from cold to warm periods. During winter, the mean LG/OC ratio was 8±3% (range 0.4-13%)and it was close to 0 in summer. However, large variability of this ratio can be caused by combustion efficiency/conditions, technologies or composition of burned fuel (branches, leaves, wood, etc.) (Yttri et al. 2009).

The $LG/PM_{2.5}$ ratio calculated for all period was 1.2±1.4%. During cold season, this ratio was 2.4±0.9% (range 0.07-3.6%) and it was comparable with that of Piazzalunga et al. (2011) for PM_{10}. Also in this case, lower values were recorded during summer months.

Several studies provided emission factors for various type of biomass combustion (i.e. savanna, agricultural waste, residential wood burning etc), by considering emissions of trace gases and aerosol from biomass burning (Andreae and Merlet 2001; Szidat et al. 2006; Wang et al. 2007).

Actually, results of burning tests on biomass (considering both type of wood and plants) in Italy and also in Europe are still scarce; further, limited information is available on the types of burning plants of the Veneto region. To estimate the per cent contribution of biomass combustion to OC, the factor calculated by Szidat et al. (2006) by averaging literature data of emission ratios was used in this work. The percent contributions of biomass burning to the OC during cold and warm periods are given in Table 2. In the same way, the contribution to $PM_{2.5}$ was calculated. In this case, the emission ratio considered was that of Andreae and Merlet (2001) for agricultural residues. As an annual average, 18% of the $PM_{2.5}$ originated from biomass burning, especially during the cold period. This value was higher than that reported in other studies (Wang et al. 2007; Reche et al. 2012). The contribution to OC was on average 29% for all the sampling campaign and, during wintertime, the biomass burning contributed for 56±20% to OC. Results obtained from other studies reported average contributions in the range 19-50% in PM10 during the cold period (Szidat et al. 2006; Piazzalunga et al. 2011). A very little contribution of biomass burning to OC and $PM_{2.5}$ occurs also during the warm period, particularly at the end of July (27th and 28th) and in September (3rd). This underlines a source of biomass burning pollution in Venice-Mestre area also in summer season, probably for agricultural activities.

Conclusions

This study is the first one that investigates the importance of biomass burning in the Venice-Mestre area by determining the concentrations of $PM_{2.5}$, OC, EC, TC, LG and inorganic ions in the station of Malcontenta. $PM_{2.5}$ values above 100 µg m^{-3}were recorded in two occasions, and highlighted the critical situation for air quality of Po Valley due to weather conditions, external transport and orographic features. Results showed that wood is still used and biomass burning can be an additional local source of particulate air pollution, in particular during the cold period. Because few data are available in Italy, this study also provides an estimation of biomass burning in the Venice-Mestre area. The main findings of this work can be summarized as follows:

- Total ions accounted for 15-35% of $PM_{2.5}$ with an annual average of 31%. Nitrate was the most abundant ion (34%) followed by sulphate (23%), ammonium (11%) and both potassium and chloride (3%).
- TC accounted for 36% and 23.4% of $PM_{2.5}$ in the cold and warm period, respectively. During cold period, OC and EC represented 78.4% and 21.5% of TC, while during warm period 62% and 38%, respectively.
- LG concentrations were higher during the cold period and comparable to those found in the Lombardy region rather than to those of other European urban sites, thus underlining that in the study area, wood is still used especially in winter.
- The EC/TC and relationships among biomass burning indicators denoted a major contribution of biomass burning during winter, probably because of the lower wood combustion during warm period near the sampling

site.

- The OC/EC ratios mean values were higher during colder months, the annual range was 1.1-10.1 and comparable with other Italian studies. A large variability of OC was observed during the cold period probably due to local contribution, while during the warm one, the regional-scale SOA leads to homogenous contributions and to lower OC variability.
- CPF and CBPF showed that wind speed and wind directions can play an important role on the transport of biomass burning indicators, which could be linked with both local and external contributions.
- A CWT model, applied on OC, LG and K^+, was used to identify the potential transboundary transport. Results indicate that Eastern and Central Europe can influence the Eastern part of Po plain. In fact, two episodes of high biomass burning indicator concentrations were also investigated confirming that events of high-pollution may be due to the transport of air masses from polluted areas.
- The PSCF analysis was applied on the ratios of the biomass burning indicators. Results confirmed the variability of LG/OC, K^+/OC and OC/$PM_{2.5}$ among the seasons indicating that biomass burning is important in the North-East Italy and Central Europe.
- The contribution of biomass burning to OC and $PM_{2.5}$ was on average 29% and 18%, respectively. This contribution was found important mostly during the cold period, but a little contribution, occurred also in the warm period, revealed that wood is still an important source of pollutants from biomass burning also in summer because of agricultural activities.

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Disclaimer

We would like to stress that the views expressed in this study are exclusively of the authors and do not necessarily correspond to those of ARPAV.

References

Abdalmogith SS, Harrison RM (2005) The use of trajectory cluster analysis to examine the long-range transport of secondary inorganic aerosol in the UK. *Atmos Environ* **39**: 6686–6695

Akagi SK, Yokelson RJ, Wiedinmyer C, Alvarado MJ, Reid JS, Karl T, Crounse JD, Wennberg PO (2011) Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos Chem Phys*, **11**(9): 4039-4072

Aldabe J, Elustondo D, Santamaría C, Lasheras E, Pandolfi M, Alastuey A, Querol X, Santamaría JM (2011) Chemical characterization and source apportionment of $PM_{2.5}$ and PM_{10} at rural, urban and traffic sites in Navarra (North of Spain). *Atmospheric Research* **102**: 191–205

Alves CA, Gonçalves C, Pio CA, Mirante F, Caseiro A, Tarelho L, Freitas MC, Viegas DX (2010) Smoke emissions from biomass burning in a Mediterranean shrubland. *Atmos Environ* **44**: 3024-3033

Andreae MO (1983) Soot carbon and excess fine potassium: Long-range transport of combustion-derived aerosol. Science, **220**: 1148-1151

Andreae MO, Merlet P (2001) Emission of trace gases and aerosols from biomass burning. Global Biogeochemical Cycles, Vol. 15, NO. 4: 955-966

Andreae MO, Andreae TW, Annegarn H, Beer J, Cachier H, le Canut P, Elbert W, Maenhaut W, Salma I, Wienhold FG, Zenker T (1998) Airborne studies of aerosol emissions from savanna fires in southern Africa: 2. Aerosol chemical composition. *J Geophys Res* VOL. 103, NO. D24, PAGES 32,119-32,128

ARPAV (Environmental Protection Agency of Veneto Region) (2015) Indagine sul consumo domestico di biomasse legnose in Veneto: risultati dell'indagine campionaria e stima delle emissioni in atmosfera, p. 35 [in italian]. Available at: http://www.arpa.veneto.it/temi-ambientali/aria/file-e-allegati/Consumi%20domestici%20legna%20in%20Veneto_1.0.pdf

Belis CA, Cancelinha J, Duane M, Forcina V, Pedroni V, Passarella R, Tanet G, Douglas K, Piazzalunga A, Bolzacchini E, Sangiorgi G (2011) Sources for PM air pollution in the Po Plain, Italy: I. Critical comparison of methods for estimating biomass burning contributions to benzo (a) pyrene. *Atmos Environ* **45**(39): 7266-7275

Bernardoni V, Vecchi R, Valli G, Piazzalunga A, Fermo P (2011) PM_{10} source apportionment in Milan (Italy) using time-resolved data. *Sci Total Environ* **409**(22):4788-4795

Biegalski SR, Hopke PK (2004) Total Potential Source Contribution Function Analysis of trace elements determined in aerosol samples collected near Lake Huron. *Environ Sci Technol* **38**: 4276-4284

Birch ME, Cary RA (1996) Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust. *Aerosol Sci Technol* **25**:221 – 241

Carslaw DC (2015) The openair manual — open-source tools for analysing air pollution data. Manual for version 1.1-4, King's College London

Caseiro A, Bauer H, Schmidl C, Pio CA, Puxbaum H (2009) Wood burning impact on PM_{10} in three Austrian regions. *Atmos Environ* **43**: 2186–2195

CEN (2005) European Standard EN 14907: Ambient air quality -- Standard gravimetric measurement method for the determination of the $PM_{2.5}$ mass fraction of suspended particulate matter. European Committee for Standardization, Brussels, Belgium

Cheng I, Zhang P, Blanchard P, Dalziel J, Tordon R (2013) Concentration-weighted trajectory approach to identifying potential sources of speciated atmospheric mercury at an urban coastal site in Nova Scotia, Canada. *Atmos. Chem. Phys* **13**: 6031–6048

Chow JC, Watson JG, Fujita EM, Lu Z, Lawson DR (1994) Temporal and spatial variations of PM2.5 and PM10 aerosol in the Southern California air quality study. *Atmos Environ* **28**(12):2061-2080

Crilley LR, Bloss WJ, Yin J, Beddows DCS, Harrison RM, Allan JD, Young DE, Flynn M, Williams P, Zotter P , Prévôt ASH, Heal MR, Barlow JF, Halios CH, Lee JD, Szidat S, Mohr C (2015) Sources and contributions of wood smoke during winter in London: assessing local and regional influences. *Atmos Chem Phys* **15**: 3149–3171

Draxler RR, Rolph GD (2015) HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website (http://www.arl.noaa.gov/HYSPLIT.php). NOAA Air Resources Laboratory, College Park, MD.

Duan F, Liu X, Yu T, Cachier H (2004) Identification and estimate of biomass burning contribution to the urban aerosol organic carbon concentrations in Beijing. *Atmos Environ* **38**: 1275–1282

EC (2008) Council Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of European Communications. L152/1, 11/6/2008.

Elsasser M, Crippa M, Orasche J, De Carlo PF, Oster M, Pitz M, Cyrys J, Gustafson TL, Pettersson BC, Schnelle-Kreis J, Prévôt ASH, Zimmermann R (2012) Organic molecular markers and signature from wood combustion particles in winter ambient aerosols: aerosol mass spectrometer (AMS) and high time-resolved GC-MS measurements in Augsburg, Germany. *Atmos Chem Phys* **12**: 6113–6128

Engling G, Zhang Y-N, Chan C-Y, Sang X-F, Lin,M, Ho K-F, Li Y-S, Lin C-Y, Lee JJ (2011) Characterization and sources of aerosol particles over the southeastern Tibetan Plateau during the Southeast Asia biomass-burning season. *Tellus*, **63B**: 117–128

Fattore E, Paiano V, Borgini A, Tittarelli A, Bertoldi M, Crosignani P, Fanelli R (2011) Human health risk in relation to air quality in two municipalities in an industrialized area of Northern Italy. *Environ Res* **111**: 1321–1327

Ferek RJ, Reid JS, Hobbs PV (1998) Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. *J Geophys Res* (D24), 32107-32118

Francescato V, Antonini E (2010) La combustione del legno - Fattori di emissione e quadro normativo. Veneto Agricoltura – Settore Bioenergie e Cambiamento Climatico (in italian)

Fraser MP, Lakshmanan K (2000) Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. *Environ Sci Technol* **34**: 4560-4564

Fuzzi S, Andreae MO, Huebert BJ, Kulmala M, Bond TC, Boy M, Doherty SJ, Guenther A, Kanakidou M, Kawamura K, Kerminen V-M, Lohmann U, Russell LM, Pöschl U (2006) Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change. *Atmos Chem Phys* **6**: 2017-2038

Gaffney JS, Marley NA (2009) The impacts of combustion emissions on air quality and climate–From coal to biofuels and beyond. *Atmos Environ* **43**(1): 23-36

Giannoni M, Martellini T, Del Bubba M, Gambaro A, Zangrando R, Chiari M, Lepri L, Cincinelli A (2012) The use of levoglucosan for tracing biomass burning in $PM_{2.5}$ samples in Tuscany (Italy). *Environ Pollut* **167**: 7-15

Gillies JA, Gertler AW, Sagebiel JC, Dippel WA (2001) On-road particulate matter ($PM_{2.5}$and PM_{10}) emissions in the Sepulveda Tunnel, Los Angeles, California. *Environ Sci Technol* **35**: 1054–1063.

Hays MD, Fine PM, Geron CD, Kleeman MJ, Gullett BK (2005) Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. *Atmos Environ* **39**(36): 6747-6764.

Hedberg E, Johansson C, Johansson L, Swietlicki E, Brorström-Lundén E (2006) Is levoglucosana suitable quantitative tracer for wood burning? Comparison with receptor modeling on trace elements in Lycksele, Sweden. *J Air Waste ManageAssoc* **56**: 1669–78.

Hoffmann D, Tilgner A, Iinuma Y, Herrmann H (2010) Atmospheric stability of levoglucosan: a detailed laboratory and modeling study. *Environ Sci Technol* **44**: 694-699

Hsu Y, Holsen TM, Hopke PK (2003) Comparison of hybrid receptor models to locate PCB sources in Chicago. *Atmos Environ* **37**: 545–562.

Kanakidou M, Seinfeld JH, Pandis SN, Barnes I, Dentener FJ, Facchini MC, van Dingenen R, Ervens B, Nenes, Swietlicki E, Putaud JP, Balkanski Y, Fuzzi S, Horth J, Moortgat GK , Winterhalter R, Myhre CEL, Tsigaridis K, Vignati E, Stephanou EG, Wilson J (2005) Organic aerosol and global climate modelling: a review. *Atmos Chem Phys* **5**(4):1053-1123

Keywood M, Kanakidou M, Stohl A, Dentener F, Grassi G, Meyer CP, Torseth K, Edwards D, Thompson AM, Lohmann U, Burrows J (2013) Fire in the air: Biomass burning impacts in a changing climate. Critical Reviews in *Environ Sci Technol*, **43**(1): 40-83

Khan Md B, Masiol M, Formenton G, Di Gilio A, de Gennaro G, Agostinelli C, Pavoni B (2016) Carbonaceous $PM_{2.5}$ and secondary organic aerosol across the Veneto region (NE Italy). *Sci Total Environ* **542**: 172–181

Knorr W, Lehsten V, Arneth A (2012) Determinants and predictability of global wildfire emissions. *Atmos Chem Phys* **12**(15): 6845-6861

Kodgule R, Salvi S (2012) Exposure to biomass smoke as a cause for airway disease in women and children. *Current opinion in allergy and clinical immunology* **12**(1): 82-90

Laumbach RJ, Kipen HM (2012) Respiratory health effects of air pollution: update on biomass smoke and traffic pollution. *Journal of allergy and clinical immunology*, **129**(1):3-11

Lee AKY, Willis MD, Healy RM, Wang JM, Jeong C-H, Wenger JC, Evans GJ, Abbatt JPD (2015) Single particle characterization of biomass burning organic aerosol (BBOA): evidence for non-uniform mixing of high molecular weight organics and potassium. *Atmos Chem Phys* **16**: 5561-5572

Lemieux PM, Lutes CC, Santoianni DA (2004) Emissions of organic air toxics from open burning: a comprehensive review. *Prog Energy Combust Sci* **30**(1): 1-32

Li P-H, Han B, Huo J, Lu B, Ding X, Chen L, Kong S-F, Bai Z-P, Wang B (2012) Characterization, Meteorological Influences and Source Identification of Carbonaceous Aerosols during the Autumn-winter Period in Tianjin, China. *Aerosol and Air Quality Research*, **12**: 283–294

Lonati G, Ozgen S, Giuliano M (2007) Primary and secondary carbonaceous species in $PM_{2.5}$ samples in Milan (Italy). *Atmos Environ* **41**: 4599–4610.

Maenhaut W, Vermeylen R, Claeys M, Vercauteren J, Matheeussen C, Roekens E (2012) Assessment of the contribution from wood burning to the PM_{10} aerosol in Flanders, Belgium. *Sci Total Environ* **437**: 226–236

Masiol M, Centanni E, Squizzato S, Hofer A, Pecorari E, Rampazzo G, Pavoni B (2012a) GC-MS analyses and chemometric processing to discrimate the local and long-distance sources of PAHs associated to atmospheric $PM_{2.5}$. *Environ Sci Pollut Res* **19** (8): 3142 – 3151

Masiol M, Hofer A, Squizzato S, Piazza R, Rampazzo G, Pavoni B (2012b) Carcinogenic and mutagenic risk associated to airborne particle-phase polycyclic aromatic hydrocarbons: A source apportionment. *Atmos Environ* **60**: 375 – 382

Masiol M, Squizzato S, Ceccato D, Rampazzo G, Pavoni B (2012c) A chemometric approach to determine local and regional sources of PM_{10} and its geochemical composition in a coastal area. *Atmos Environ* **54**: 127-133

Masiol M, Squizzato S, Rampazzo G, Pavoni B (2014a) Source apportionment of $PM_{2.5}$ at multiple sites in Venice (Italy): spatial variability and the role of weather. *Atmos Environ* **98**: 78-88

Masiol M, Formenton G, Giraldo G, Pasqualetto A, Tieppo P, Pavoni B (2014b) The dark side of the tradition: the polluting effect of Epiphany folk fires in the eastern Po Valley (Italy). *Sci Total Environ* **473-474**: 549-564.

Masiol M, Benetello F, Harrison RM, Formenton G, De Gaspari F, Pavoni B (2015) Spatial, seasonal trends and transboundary transport of $PM_{2.5}$inorganic ions in the Veneto region (Northearstern Italy). *Atmos Environ* **117**: 19-31

Mkoma SL, Kawamura K, Fu PQ (2013) Contributions of biomass/biofuel burning to organic aerosols and particulate matter in Tanzania, East Africa, based on analyses of ionic species, organic and elemental carbon, levoglucosan and mannosan. *Atmos Chem Phys* **13**: 10325–10338

Mullaugh KM, Byrd JN, Brooks Avery Jr G, Mead RN, Willey JD, Kieber RJ (2014) Characterization of carbohydrates in rainwater from the Southeastern North Carolina. *Chemosphere* **107**: 51–57.

Ofosu FG, Hopke PK, Aboh IJ, Bamford SA (2013) Biomass burning contribution to ambient air particulate levels at Navrongo in the Savannah zone of Ghana. *J Air Waste Manage Assoc*, **63**(9): 1036-1045

Oliveira C, Pio C, Alves C, Evtyungina M, Santos P, Gonçalves V, Nunes T, Silvestre AJD, Palmgren F, Wåhlin P, Harrad S (2007) Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the North and South of Europe. *Atmos Environ* **41**: 5555–5570

Pastorello C, Caserini S, Galante S, Dilara P, Galletti F (2011) Importance of activity data for improving the residential wood combustion emission inventory at regional level. *Atmos Environ* **45**(17), 2869–76

Perrone MG, Larsen BR, Ferrero L, Sangiorgi G, De Gennaro G, Udisti R, Zangrando R, Gambaro A, Bolzacchini E (2012) Sources of high $PM_{2.5}$concentrations in Milan, Northern Italy: Molecular marker data and CMB modelling. *Sci Total Environ **414***: 343–355

Piazzalunga A, Fermo P, Bernardoni V, Vecchi R, Valli G, De Gregorio MA (2010) A simplified method for levoglucosan quantification in wintertime atmospheric particulate matter by high performance anion-exchange chromatography coupled with pulsed amperometric detection. *Int J Environ Anal Chem* **90**(12): 934 – 947

Piazzalunga A, Belis C, Bernardoni V, Cazzuli O, Fermo P, Valli G, Vecchi R (2011) Estimates of wood burning contribution to PM by the macro-tracer method using tailored emission factors. *Atmos Environ* **45**: 6642-6649

Piazzalunga A, Anzano M, Collina E, Lasagni M, Lollobrigida F, Pannocchia A, Fermo P, Pitea D (2013a) Contribution of wood combustion to PAH and PCDD/F concentrations in two urban sites in Northern Italy. *J Aerosol Sci* **56**:30–40

Piazzalunga A, Bernardoni V, Fermo P, Vecchi R (2013b) Optimisation of analytical procedures for the quantification of ionic and carbonaceous fractions in the atmospheric aerosol and applications to the ambient samples. *Anal Bioanal Chem* **405** (2-3): 1123 – 1132

Pietrogrande MC, Bacco D, Ferrari S, Ricciardelli I, Scotto F, Trentini A, Visentin M (2016) Characteristics and major sources of carbonaceous aerosols in $PM_{2.5}$ in Emilia Romagna Region (Northern Italy) from four-year observations. *Sci Total Environ* **553**:172–183

Pignatelli T, D'Elia I, Vialetto G, Bencardino M, Contaldi M (2008) The use of biomass: synergies and trade-offs between Climate Change and Air Pollution, Italy. 17th Annual International Emission Inventory Conference. Portland, OR: US Environmental Protection Agency.

Pio CA, Legrand M, Alves CA, Oliveira T, Afonso J, Caseiro A, Puxbaum H, Sanchez-Ochoa A, Gelencsér A (2008) Chemical composition of atmospheric aerosols during the 2003 summer intense forest fire period. *Atmos Environ* **42**: 7530–7543

Pipalatkar P, Khapardel VV,Gajghate DG, Bawase MA (2014) Source Apportionment of $PM_{2.5}$ Using a CMB Model for a Centrally Located Indian City. *Aerosol and Air Quality Research*,**14**: 1089–1099

Putaud J-P, van Dingenen R, Alastuey A, Bauer H., Birmili W, Cyrys, J, Flentje H, Fuzzi S, Gehrig R, Hansson H C, Harrison RM, Herrmann H, Hitzenberger R, Hüglin C, Jones A M, Kasper-Giebl A, Kiss G, Kousa A, Kuhlbusch T A J, Loschau G, Maenhaut W, Molnar A, Moreno T, Pekkanen J, Perrino C, Pitz M, Puxbaum H, Querol X, Rodriguez S, Salma I, Schwarz J, Smolik J, Schneider J, Spindler G, ten Brink H, Tursic J, Viana M, Wiedensohler A, Raes F (2010) A European aerosol phenomenology-3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos Environ* **44**: 1308-1320

Puxbaum H, Caseiro A, Sánchez-Ochoa A, Kasper-Giebl A, Claeys M, Gelencsér A, Legrand M, Preunkert S, Pio C, (2007) Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. *J Geophys Res* **112**: D23S05, doi:10.1029/2006JD008114

Ram K, Sarin MM (2010). Day-night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic Plain: Implications to secondary aerosol formation. *Atmos Environ* **45**: 460-468.

Reche C, Viana M, AmatoF, Alastuey A, Moreno T, Hillamo R, Teinilä K, Saarnio K, Seco R, Peñuelas J, Mohr C, Prévôt ASH, Querol X (2012) Biomass burning contributions to urban aerosols in a coastal Mediterranean City. *Sci Total Environ* **427-428**: 175–190

Rolph GD (2015) Real-time Environmental Applications and Display system (READY) Website (http://www.ready.noaa.gov). NOAA Air Resources Laboratory, College Park, MD

Satsangi A, Pachauri T, Singla V, Lakhani A, Kumari KM (2012) Organic and elemental carbon aerosols at a suburban site. *Atmos Res* **113**: 13–21

Saud T, Saxena M, Singh DP, Saraswati, Dahiya M, Sharma SK, Datta A, Gadi R, Mandal TK (2013) Spatial variation of chemical constituents from the burning of commonly used biomass fuels in rural areas of the Indo-Gangetic Plain (IGP), India. *Atmos Environ* **71**:158-169

Sudheer AK, Sarin MM (2008) Carbonaceous aerosols in MABL of Bay of Bengal: Influence of continental outflow. *Atmos Environ* **42**: 4089–4100

Simoneit BRT, Schauer JJ, Nolte CG, Oros DR, Elias VO, Fraser MP, Rogge WF, Cass GR (1999) Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmos Environ* **33**: 173-182

Squizzato S, Masiol M, Innocente E, Pecorari E, Rampazzo G, Pavoni B (2012) A procedure to assess local and long-range transport contributions to $PM_{2.5}$ and secondary inorganic aerosol. *J Aerosol Sci* **46**:64–76

Squizzato S, Masiol M, Visin F, Canal A, Rampazzo G, Pavoni B (2014) The $PM_{2.5}$ chemical composition in an industrial zone included in a large urban settlement: main sources and local background. *Environ Sci Process Impacts* **16**: 1913-1922

Squizzato S, Masiol M (2015) Application of meteorology-based methods to determine local and external contributions to particulate matter pollution: A case study in Venice (Italy). *Atmos Environ* **119**: 69–81

Szidat S, Jenk TM, Synal H-A, Kalberer M, Wacker L, Hajdas I, Kasper-Giebl A, Baltensperger U (2006) Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by 14C. *J Geophys Res*, VOL. 111, D07206, doi:10.1029/2005JD006590.

Szidat S, Ruff M, Perron N, Wacker L, Synal HA, Hallquist M, Shannigrahi AS, Yttri KE, Dye C, Simpson D (2009) Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Göteborg, Sweden. *AtmosChem Phys* **9**: 1521–1535

Tositti L, Brattich E, Masiol M, Baldacci D, Ceccato D, Parmeggiani S, Stracquadanio M, Zappoli S (2014) Source apportionment of particulate matter in a large city of southeastern Po Valley (Bologna, Italy).*Environ Sci PollutRes* **21**(2): 872-890

Traversi D, Degan R, De Marco R, Gilli G, Pignata C, Ponzio M, Rava M, Sessarego F, Villani S, Bono R (2008) Mutagenic properties of $PM_{2.5}$ air pollution in the Padana Plain (Italy) before and in the course of XX Winter Olympic Games of "Torino 2006". *Environ Int* **34**: 966–970

Turpin BJ and Huntzicker JJ (1995) Identification of Secondary Organic Aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmos Environ* **29(**23) 3527-3544

Urban RC, Lima-Souza M, Caetano-Silva L, Queiroz MEC, Nogueira RFP, Allen AG, Cardoso AA, Held G, Campos MLAM (2012) Use of levoglucosan, potassium, and water-soluble organic carbon to characterize the origins of biomass-burning aerosols. *Atmos Environ* **61**: 562-569

Uria-Tellaetxe I, Carslaw DC (2014) Conditional bivariate probability function for source identification. Environmental Modelling & Software **59**: 1-9.

US EPA (2003) DIESEL PARTICULATE MATTER 5040 (as Elemental Carbon). NIOSH Manual of Analytical Methods (NMAM), Fourth Edition.

van Drooge BL, Perez Ballesta P (2009). Seasonal and daily source apportionment of polycyclic aromatic hydrocarbon concentrations in PM_{10} in a semirural European area. *Environ Sci Technol* **43**: 7310–7316

Vassura I, Venturini E, Marchetti S, Piazzalunga A, Bernardi E, Fermo P, Passarini F (2014) Markers and influence of open biomass burning on atmospheric particulate size and composition during a major bonfire event. *Atmos Environ* **82**:218-225

Vecchi R, Chiari M, D'Alessandro A, Fermo P, Lucarelli F, Mazzei F, Nava S, Piazzalunga A, Prati P, Silvani F, Valli G (2008) A mass closure and PMF source apportionment study on the sub-micron sized aerosol fraction at urban sites in Italy. *Atmos Environ* **42**: 2240–2253

Vecchi R, Valli G, Fermo P, D'Alessandro A, Piazzalunga A, Bernardoni V (2009) Organic and inorganic sampling artefacts assessment. *Atmos Environ* **43**(10): 1713-1720

Viana M, Maenhaut W, ten Brink HM, Chi X, Weijer E, Querol X, Alastuey A, Mikuška P, Večeřa, Z (2007) Comparative analysis of organic and elemental carbon concentrations in carbonaceous aerosols in three European cities. *Atmos Environ* **41**: 5972–5983

Vicente A, Alves C, Calvo AI, Fernandes AP, Nunes T, Monteiro C, Almeida SM, Pio C (2013) Emission factors and detailed chemical composition of smoke particles from the 2010 wildfire season. *Atmos Environ* **71**: 295-303

Wang Q, Shao M, Liu Y, William K, Paul G, Li X, Liu Y, Lu S (2007) Impact of biomass burning on urban air quality estimated by organic tracers: Guangzhou and Beijing as cases. *Atmos Environ* **41**: 8380–8390

Xu L, Chen X, Chen J, Zhang F, He C, Zhao J, Yin L (2012) Seasonal variations and chemical compositions of $PM_{2.5}$ aerosol in the urban area of Fuzhou, China. *Atmos Res* **104-105**: 264–272

Yamasoe MA, Artaxo P, Miguel AH, Allen AG (2000) Chemical composition of aerosol particles from direct emissions of vegetation fires in the Amazon Basin: water-soluble species and trace elements. *Atmos Environ* **34**:1641-1653

Yttri KE, Dye C, Braathen O-A, Simpson D, Steinnes E (2009) Carbonaceous aerosols in Norwegian urban areas. *Atmos Chem Phys* **9**: 2007–2020

Yttri KE, Dye C, Slørdal LH, Braathen O-A (2005) Quantification of monosaccharide anhydride by liquid chromatography combined with mass spectrometry: application to aerosol samples from an urban and a suburban site influenced by small-scale wood burning. *J Air Waste Manage Assoc* **55**:1169–1177

Zdráhal Z, Oliveira J, Vermeylen R, Claeys M, Maenhaut W (2002) Improved method for quantifying levoglucosan and related monosaccharide anhydrides in atmospheric aerosols and application to samples from urban and tropical locations. *Environ. Sci. Technol* **36**: 747-753

Zhang T, ClaeysM, Cachier H, Dong S, Wang W, Maenhaut W, Liu X (2008) Identification and estimation of the biomass burning contribution to Beijing aerosol using levoglucosan as a molecular marker. *Atmos Environ* **42**: 7013–7021

Zhang X, Liu Z, Hecobian A, Zheng M, Frank NH, Edgerton ES, Weber RJ (2012) Spatial and seasonal variations of fine particle water-soluble organic carbon (WSOC) over the southeastern United States: implications for secondary organic aerosol formation. *Atmos Chem Phys* **12**: 6593–6607

Table 1

Table 1 - Mean concentrations and concentration ranges of $PM_{2.5}$, inorganic ions, carbonaceous components and levoglucosan in Malcontenta during the whole, cold and warm periods.

	Total period (n = 85)		Cold period (n = 44)		Warm period (n = 41)	
	Mean-SD	Range	Mean-SD	Range	Mean-SD	Range
$PM_{2.5}$ (µg m^{-3})	36 ± 27	6.4 - 134.6	54 ± 27	13.3 - 134.6	16 ± 6	6.4 – 38.3
OC (µg m^{-3})	9 ± 9	0.9 - 41.3	16 ± 9	2.9 - 41.3	2 ± 1	0.9 – 4.4
EC (µg m^{-3})	3 ± 2	0.6 - 7.7	4 ± 2	0.7 - 7.7	1.4 ± 0.5	0.6 – 2.5
TC (µg m^{-3})	12 ± 11	1.5 - 48.7	20 ± 11	3.8 – 48.7	4 ± 1	1.5 – 6.8
LG (ng m^{-3})	658 ± 851	0.01 - 2656	1272 ± 787	61 – 2656	0.5 ± 1.6	0.01 - 8
Cl^-(µg m^{-3})	0.4 ± 0.5	0.002 - 2.2	0.8 ± 0.5	0.002 – 2.2	0.1 ± 0.1	0.02 – 0.6
NO_3^-(µg m^{-3})	5 ± 7	0.2 – 39.2	9 ± 8	0.5 – 39.2	0.6 ± 0.4	0.2 – 2.2
SO_4^{2-}(µg m^{-3})	3 ± 2	0.004 – 11.6	3 ± 1	0.004 - 6	3 ± 2	0.6 – 11.6
Nss-SO_4^{2-}(µg m^{-3})*	3 ± 2	0.001 – 11.5	3 ± 1	0.001 – 6	3 ± 2	0.6 – 11.6
NH_4^+(µg m^{-3})	2 ± 1	0.003 – 6.9	2 ± 1	0.003 – 6.9	0.9 ± 0.6	0.003 – 2.5
Na^+(µg m^{-3})	0.2 ± 0.3	0.01 – 1.3	0.4 ± 0.4	0.01 – 1.3	0.1 ± 0.1	0.04 – 0.7
K^+(µg m^{-3})	0.5 ± 0.6	0.003 – 0.3	0.9 ± 0.6	0.07 – 2.3	0.1 ± 0.1	0.003 – 0.5
Mg^{2+}(µg m^{-3})	0.05 ± 0.05	0.008 – 2.6	0.06 ± 0.04	0.01 – 0.2	0.04 ± 0.1	0.008 – 0.3
Ca^{2+}(µg m^{-3})	0.3 ± 0.2	0.07 – 1.1	0.3 ± 0.2	0.07 – 1.1	0.3 ± 0.2	0.2 – 1.1
Σ ions (µg m^{-3})	11 ± 9	1.4 - 46	17 ± 10	2.6 - 46	5 ± 3	1.4 – 17.3

***Nss-SO_4^{2-}were calculated as $[SO_4^{2-}]$– 0.25·$[Na^+]$.**

Table 2 - Mean and range of percent contribution of biomass burning (BB) to the OC and $PM_{2.5}$ during 2008-2009 cold and warm period campaigns in Malcontenta.

	Contribution of BB to the OC(%)		Contribution of BB to the $PM_{2.5}$(%)	
	Cold period	Warm period	Cold period	Warm period
Mean ± SD	56 ± 20	0.1 ± 0.4	34 ± 13	0.05 ± 0.14
Min –Max	3 - 85	Close to 0 – 2	1 - 53	Close to 0 – 0.7

Here, the contributions of biomass burning to OC and $PM_{2.5}$ were calculated using the following equation: $(LG/OC \text{ or } PM_{2.5})_{measured}/(LG/OC \text{ or } PM_{2.5})_{reference}$.

Figure-1

Figure 1 – Area of study (Images from Google Earth) with wind roses (wind speed in m s^{-1}) of cold and warm periods.

Figure-2

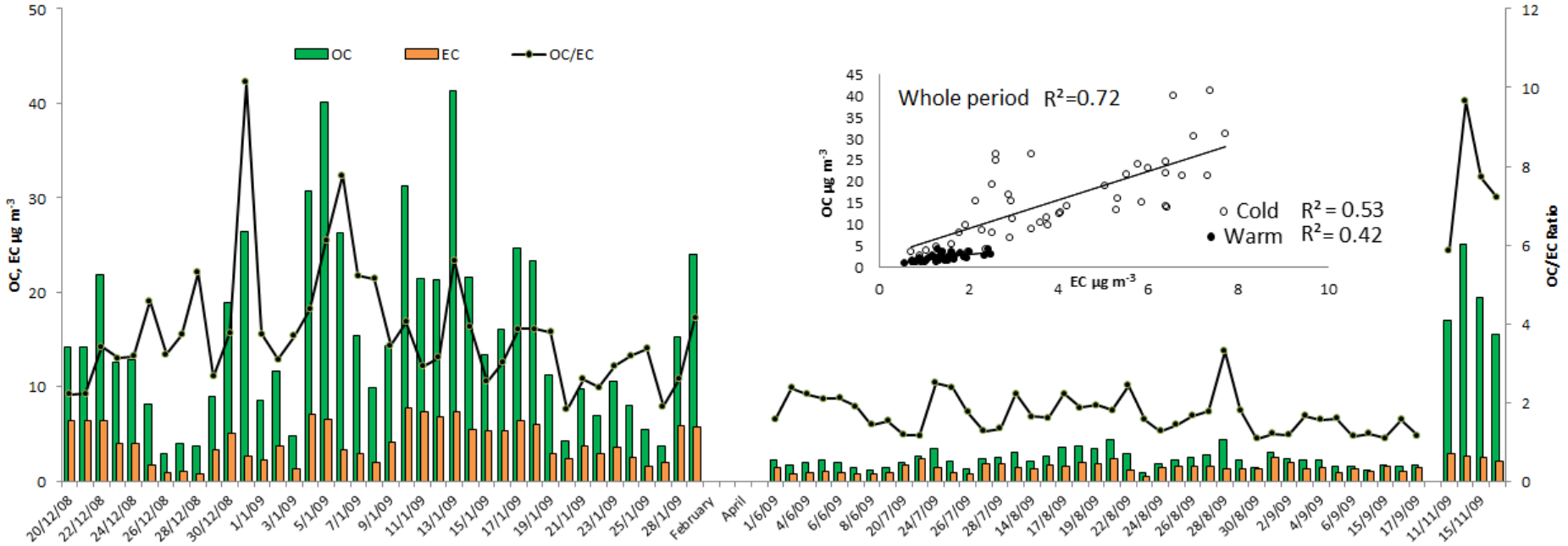

Figure 2 – Correlations, temporal variation of OC and EC concentrations and OC/EC ratio for $PM_{2.5}$ aerosol.

Figure 3

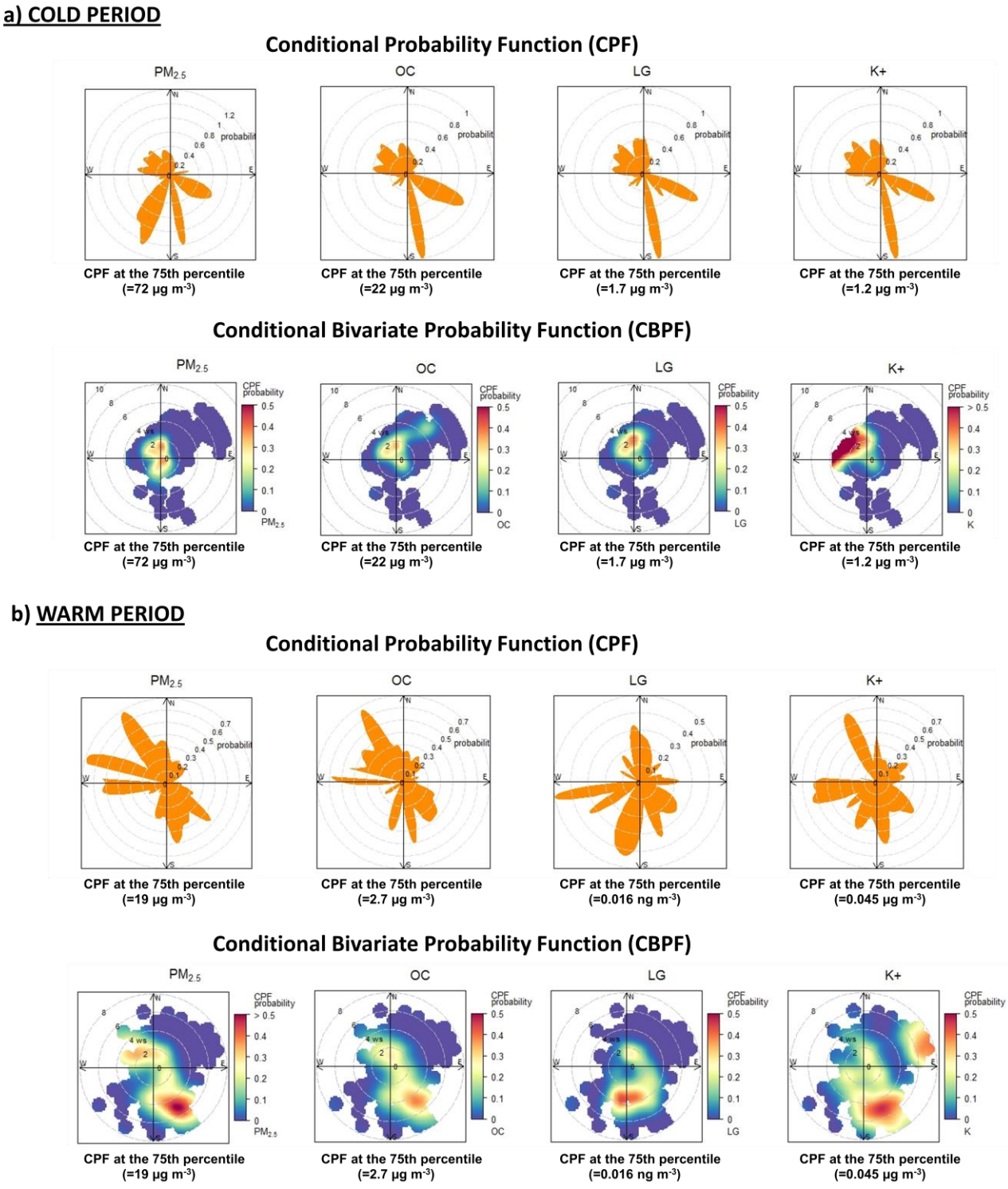

Figure 3 – CPF and CBPF plot for LG, K^+ and OC for concentrations >75th percentile. Wind speed (ws) is in m s^{-1}.

Figure-4

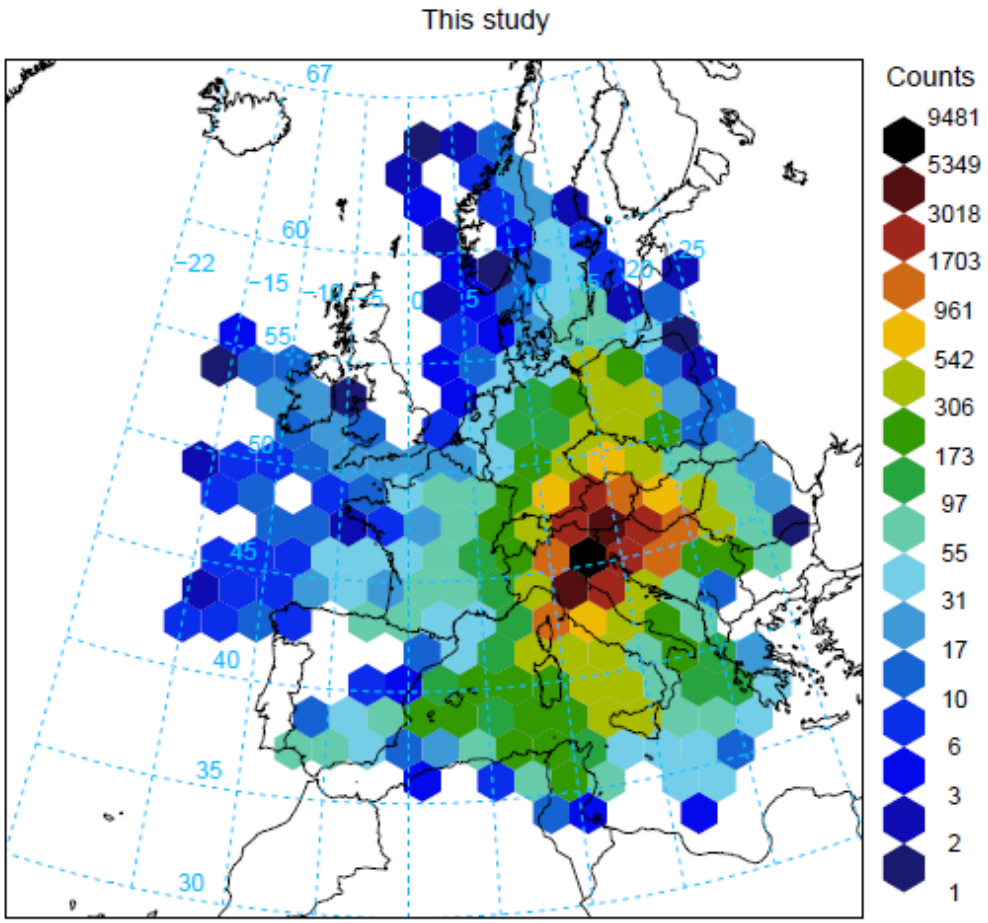

Figure 4 – Gridded back trajectory frequencies.

Figure-5

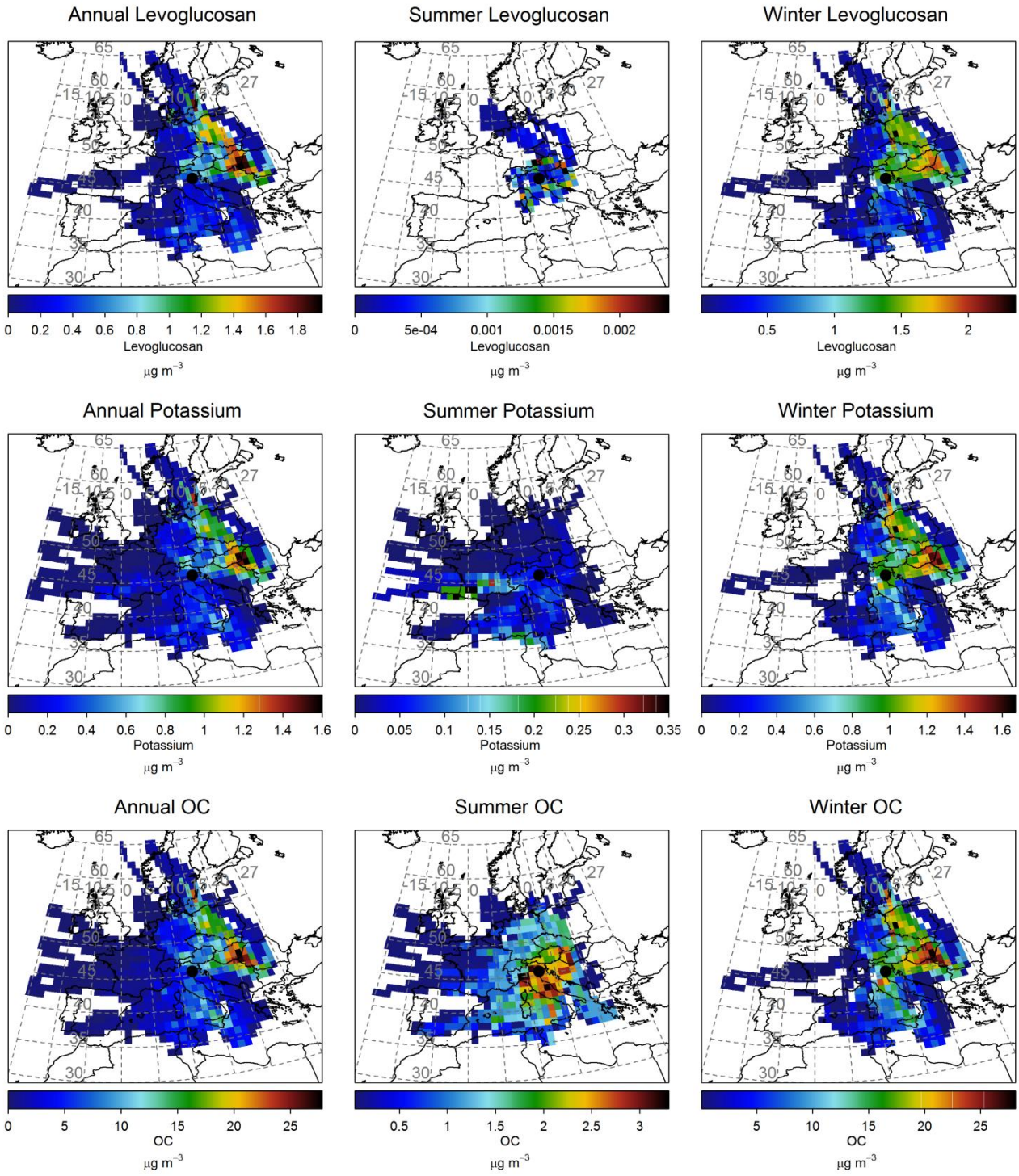

Figure 5 – CWT analysis for OC, K^+ and LG for the whole period, summer and winter seasons. Concentrations are in µg m^{-3}.

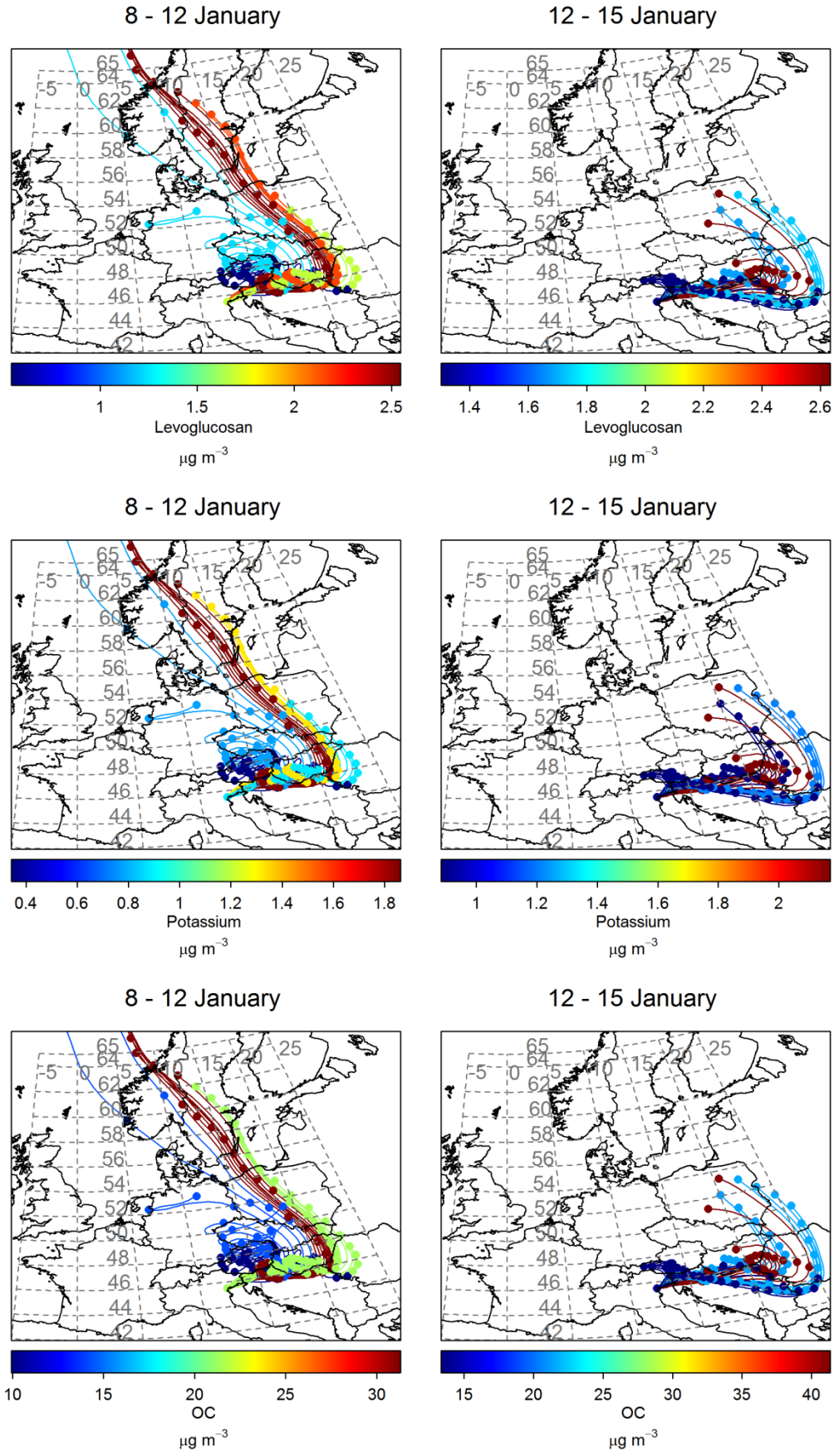

Figure 6 – Single back-trajectories during two high concentration events of biomass burning indicators.

Figure-7

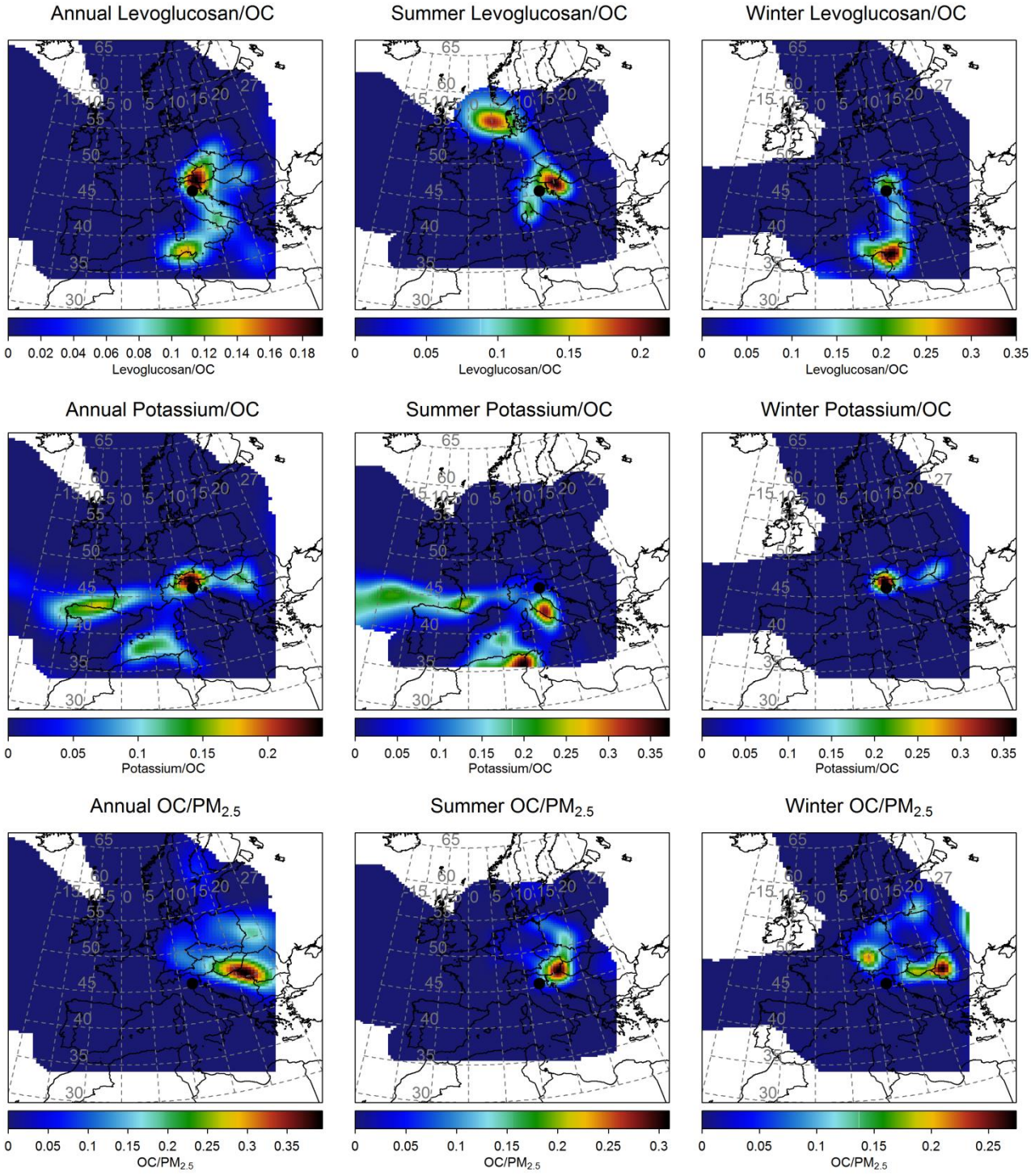

Figure 7 – PSCF analysis for LG/OC, K^+/OC and OC/$PM_{2.5}$ for the whole period, summer and winter seasons.

Dear Editor,

The authors are grateful to the referees for reviewing the manuscript. All suggestions have been addressed and the text has been rewritten and completed accordingly. A point to point reply is reported here below.

We are confident that the manuscript has significantly improved after the revision.

The authors are also grateful to the Editor and Editorial office for their help.

Kind regards,

Bruno Pavoni

Note:

The Referee questions are in italics, in normal text are the old parts and their revisions

Reviewer #1.The manuscript by Benetello et al. discusses the contribution of both regional and local sources of biomass burning to PM2.5 concentrations in the Po valley, Italy. The authors present time-integrated data on ambient OC, EC, inorganic ions and levoglucosan, as well as the results of multiple receptor modeling and back trajectory analyses (such as conditional probability function and concentration weighted trajectories, among other methods). The manuscript and discussions therein are very well-articulated, and the analyses are presented elegantly. Quality of the manuscript and importance of the topic certainly warrant a publication in ESPR. Below are a few (minor) comments that can help further improve the quality of this already well-written manuscript prior to publication:

Line 41: Please define IARC.

Definition added

Line 42: Please define fine mode particulate matter.

"from 10% to 70% to fine mode particulate matter"

Rewritten:
"from ~10% to 70% to fine mode particulate matter ($PM_{2.5}$)"

Line 134: "probably" should be changed to "probable".

Corrected

Line 187: TC is not defined anywhere in the text. From the numbers it seems that it refers to "total carbon" and is calculated as the sum of EC and OC. This needs to be clarified.

Added: (TC=OC+EC)

Line 189-191: It is worthwhile to present the actual correlation matrix with all correlation values in either SI or the main text.

The correlation matrix has been added in the "supplementary material" part.

Line 212-235 (section 4.3). There are logical issues in the interpretation of OC/EC ratio in this section. First of all, OC and EC can both have very diverse source origins. Analyzing the OC/EC ratio as an indicator of the extent of biomass burning is too simplistic to be true, and can be significantly biased depending on location/season. As an example, the authors first attribute the higher OC/EC concentration in winter compared to summer to higher biomass burning. Few lines later temperature difference and partitioning of OC in the particle phase is noted as another factor affecting this comparison. The extent to which each of these factors contributes to OC levels is, however, unclear. Another effect totally ignored in these discussions is the secondary formation of OC, which can enhance the OC levels during summer without affecting EC concentrations. Accordingly, OC/EC ratios in many regions of the world where SOA formation is substantial during summer seasons (such as southwestern United States) is higher during the warmer season compared to the colder seasons. It is, overall, insightful to discuss the OC/EC ratios and compare them to what was found in literature, but interpretation of this ratio (in the absence of more deterministic carbonaceous species parameters such as WSOC or WIOC) should be made with caution given the numerous factors that affect both OC and EC levels.

Old Text

Sudheer and Sarin (2008) discuss the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. Further, this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for PM2.5 in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam (Viana et al., 2007) and could be related to wood burning emissions characterized by low EC/TC ratios during the cold period as observed by Zdráhal et al. (2002).The use of EC and OC relationship can be useful to distinguish their origin (Xu et al. 2012). EC may be used as a tracer for primary emissions of carbonaceous compounds; for this reason, variations of the OC/EC ratio range can be consider as an indicator, because it may identify changes in emission sources, source areas or processes (Viana et al. 2007). OC/EC ratios of 9, 1.1 and 2.7 reported by Watson et al. (2001), discern biomass burning, vehicle emissions and coal combustion sources, respectively. Lonati et al. (2007) reported a mean OC/EC ratio of 8.6 for the cold season and 4.2 for the warm one in Milan. Other Italian OC/EC values were in a range of 4.0–5.6 in Genoa, 4.3–13.4 in Florence and 4.5–8.2 in Milan (Vecchi et al. 2008). In this study, the mean OC/EC ratios for the cold period were 4±2 (range 1.8 - 10.1), while 1.7±0.5 (range 1.1–3.3) for the warm period and were generally similar to those found in most European cities. In fact, OC/EC mean ratios obtained by Viana et al. (2007) were 4.7, 3.1, 4.4 for winter time and 2.8, 2.6, 3.5 during the summer period in Amsterdam, Barcelona and Ghent, respectively. Generally, lower OC/EC ratios indicate fossil-fuel combustion, while higher ratios underline the influence from biomass burning sources (Ram and Sarin 2010). Low temperature and mixing layer heights during winter play an important role to increase the OC/EC ratio; for this reason, ratio values were higher during cold period (Vecchi et al. 2008; Li et al. 2012). This pattern was observed in studies in Italy (e.g. Vecchi et al. 2008) and in other countries like China (e.g. Dan et al. 2004; Li et al. 2012).
Figure 2 shows correlations, the temporal variation of EC and OC concentrations and OC/EC ratio for PM2.5. Different EC-OC correlation coefficient (R2) of 0.53 and 0.42 were observed during cold and warm periods, respectively. This result suggests the presence of different sources for EC and OC especially in summer, since the relative rates of OC and EC releases are not proportional to each other.

Rewritten:

"Sudheer and Sarin (2008) discussed the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. In addition this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for $PM_{2.5}$ in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam by Viana et al. (2007), who related it to wood burning emissions characterized by low EC/TC ratios during the cold period and cited Zdráhal et al. (2002) as a confirmation.

The use of EC and OC relationship can be useful to distinguish their origin (Turpin and Huntizicker 1995; Xu et al. 2012). EC may be used as a tracer for primary emissions of carbonaceous compounds; for this reason, variations of the OC/EC ratio range can be considered as an indicator, because it may identify changes in emission sources, source areas or processes (Viana et al. 2007). In this study, the mean OC/EC ratio for the cold period was 4±2 (range 1.8 - 10.1), while 1.7±0.5 (range 1.1–3.3) for the warm one. The annual range was comparable with that of 0.6-8.4 and 0.7-15.4 reported by Giannoni et al. (2012) and Khan et al. (2016), respectively, while other Italian OC/EC values were in a range of 4.0–5.6 in Genoa, 4.3–13.4 in Florence and 4.5–8.2 in Milan (Vecchi et al. 2008). With respect to this study, similar winter OC/EC mean ratios were obtained by Viana et al. (2007): 4.7, 3.1, 4.4, while higher values (2.8, 2.6, 3.5) were observed during the summer period in Amsterdam, Barcelona and Ghent, respectively.

The temporal variation (Fig. 2), with high OC/EC values during cold period and lower during the warm one, was observed also in other studies (e.g. Lonati et al. 2007; Khan et al. 2016). High OC/EC ratios could underline the influence of biomass burning sources (Ram and Sarin 2010), or the formation of secondary organic aerosol (SOA, Chow et al. 1994; Turpin and Huntizicker 1995). During winter, when the highest ratios were observed, several factors can lead to higher OC concentrations compared to EC: i) lower temperatures, which promote the aerosol particle phase of organic compounds, ii) higher local contributions from household heating systems or biomass burning, which characterize colder months, and iii) lower mixing layer heights that enhance the SOA formation due to the accumulation of gaseous precursors (Viana et al. 2007; Vecchi et al. 2008; Li et al. 2012). In addition, the strong daily variability in winter, due to local contributions, may increase the OC values, whereas regional-scale SOA during summer leads to homogeneous contributions and to lower OC variability (Viana et al. 2007).

Fig. 2 shows linear regressions between OC and EC: different EC-OC coefficient of determination (R^2 = 0.53 and 0.42) were obtained during cold and warm periods, respectively. These results suggest the presence of different sources for EC and OC especially in summer, when the relative rates of OC and EC releases are less proportional to one another."

A sentence has been also added in the conclusion section:

"The OC/EC ratios mean values were higher during colder months, the annual range was 1.1-10.1 and comparable with other Italian studies. A large variability of OC was observed during the cold period probably due to local contribution, while during the warm one, the regional-scale SOA leads to homogenous contributions and to lower OC variability."

Line 229-230: the impact of temperature on increasing OC/EC level is expected, but not the mixing height. Mixing height variation is expected to have comparable impact on EC and OC concentration, hence no substantive impact on the ratio. This statement needs to be corrected.

Old Text:

"Low temperature and mixing layer heights during winter play an important role to increase the OC/EC ratio; for this reason, ratio values were higher during cold period"

Corrected with (see also previous reply):

"During winter, when the highest ratios were observed, several factors can lead to higher OC concentrations compared to EC: i) lower temperatures, which promote the aerosol particle phase of organic compounds, ii) higher local contributions from household heating systems or biomass burning, which characterize colder months, and iii) lower mixing layer heights that enhance the SOA formation due to the accumulation of gaseous precursors (Viana et al. 2007; Vecchi et al. 2008; Li et al. 2012). In addition, the strong daily variability in winter, due to local contributions, may increase the OC values, whereas regional-scale SOA during summer leads to homogeneous contributions and to lower OC variability (Viana et al. 2007) ".

Reviewer #2: The authors are presenting a study about the influence of biomass burning on air quality at industrial-urban site in Northern Italy. The topic of the study is recent in Europe, and the data on biomass burning are still incomplete. Even though several source apportionment studies from this region are published, there is still a need for new studies to elucidate the contribution of biomass burning to airborne particulate matter and to support the local administration and decision-makers to improve the air quality. The work appears to be well done and the interpretations of the authors are very reasonable. I would suggest publishing the article manuscript with minor revisions:

Section 2, line 106-108: Rephrase the sentence.

"Previous studies showed that all these sources clearly affect air quality in Venice and significantly apportion to PM mass and its component (PAHs, inorganic ions and elements)"

Rephrased:
"Previous studies showed that all these sources clearly affect the air quality in Venice, by varying the PM mass and its chemical composition (PAHs, inorganic ions and elements)"

Section 3.1, line 128-129: How many field blanks did you use?

We used 5 field blanks.

Section 3.3, line 151-152: What was the reason for the model set-up? Do you expect different analysis results with starting heights of e.g. 100 m AGL and 500 m AGL?

The model set-up was made by considering the Planetary Boundary Layer (PBL) variations. During the cold period, the mixing height is below 500 m. PBL variations were observed also during the day. At night, the PBL drops down to below 100 m (Pecorari et al. 2013).

Section 4.3, line 212-217: Rephrase the paragraph and refer to the primary sources e.g. Sudheer and Sarin 2008 discuss the TC/EC ratio and Vianna et al., 2007 refer to the study conducted in Ghent by Zdráhal et al. (2002).

Old text:
Fossil fuel and biomass burning sources can be distinguished by using the EC/TC ratio (Sudheer and Sarin 2008). Further, this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for $PM_{2.5}$ in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam and could be related to wood burning emissions characterized by low EC/TC ratios during the cold period (Viana et al. 2007).

Rewritten:

"Sudheer and Sarin (2008) discussed the EC/TC ratio as a way to distinguish fossil fuel and biomass burning sources. In addition this ratio could identify emissions also from different types of biomass burning (Andreae and Merlet 2001). Engling et al. (2011) reported a value of 0.23 ± 0.10 for $PM_{2.5}$ in Tengchong County impacted by biomass burning activities; our ratios were 0.22±0.06 and 0.38±0.06 during cold and warm periods, respectively, reaching the highest values in summer and following a clear decrease in winter. This behavior was also observed in Amsterdam by Viana et al. (2007), who related it to wood burning emissions characterized by low EC/TC ratios during the cold period and cited Zdráhal et al. (2002) as a confirmation."

Section 4.5, line 285-286: Rephrase the sentence according to the Figure 3.

Text and Figure 3 have been corrected:

Old text:
Results of CPF and CBPF are shown in Fig. 3. During the cold period, the higher probabilities (Fig. 3a) are reached toward south, south-east ($PM_{2.5}$, OC, LG) and also west and north-west for K+, where a large rural area is located. In the warm period (Fig. 3b) CPF plots highlight the higher probabilities for wind blowing from the north-west sector i.e. in the direction of the mainland characterized especially by the conurbation of Mestre and the farmland.

Revised text:
Results of CPF and CBPF are shown in Fig. 3. During the cold period, higher probabilities in CPF plots (Fig. 3a) are reached for $PM_{2.5}$, OC, LG and K^+ toward south, south-east. In the warm period (Fig. 3b) CPF plots highlight higher probabilities for wind blowing from the north-west sector i.e. in the direction of the mainland characterized by the conurbation of Mestre and the farmland.
.

Section 4.5, line 289-292: Rephrase the sentence and add the WS intervals for the different WD.

In the bivariate polar plots interesting features can be seen. They show that the significant profile contributions are associated with low wind speed conditions from the north-west sector, indicating that biomass combustion can be an important local source of pollution, but also with high wind from north, north –west and from south-east, in the cold and warm period respectively. This highlights a probable external contribution for PM and biomass burning tracers.

Corrected:

In the bivariate polar plots (CBPF) interesting features can be seen. They show that significant profile contributions are associated with low wind speed conditions (< ~2 m s^{-1}) from the north-west sector (rural area), indicating that biomass combustion can be an important local source of pollution (Fig. 3a). However, the high wind speed (> 3 m s^{-1}) from north, north –west and from south-east, in the cold and warm period, respectively could suggests a probable external contribution for PM and biomass burning tracers (Fig. 3a and 3b).

Section 4.6: What was the reason for the CWT analysis of the biomass burning traces (OC, LG, K^+) and not ratios (OC/PM2.5, LG/OC, K+/OC) as for the PSCF analysis and vice versa? Do the results of the two analyses match or differ since you analyse traces/ratios with the CWT and the PSCF?

As in the study of Squizzato and Masiol (2015) the outputs of the two approaches were very similar, it was considered redundant to apply both on the same variables. CWT are applied on LG, OC e K^+ for the first time in the Venice area. So far CWT have been reported only for ions (Squizzato and Masiol 2015; Masiol et al. 2015)

The choice of not using ratios, e.g. OC/$PM_{2.5}$ in CWT computations was based on the fact that scarce data for PM are available in the central-western European regions (Fra-UK) for back trajectory use. In addition, when using datasets based on low concentrations, the information extent that can be obtained is very limited (Hsu et al. 2003).

Section 4.6, line 318: How can you explain a probable contribution of LG/OC from the North Sea in summer?

This is not so clear and deserves further investigation. However some studies (e.g. Saarnio et al. 2010; Karlsson et al. 2013)report the role of the transport from east Europe of air masses to northern europe. These masses come from regions where in especially in summer large biomass combustion occurs. In addition the long distance transport from these areas has been detected also in UK (Witham and Mannin 2007). In the last decade United Kingdom replaced coal in the large power utilities with wood pellet and burned about 4.7 tons of pellets for industrial use in 2014 (about 60% of EU-28 Industrial wood pellet consumption) (AEBIOM, 2015).

Section 4.7, line 339-351: Unify text and Table 2 wood combustion versus biomass combustion.

Corrected in the text

Section 4.7, line 327-332: Compare the results found here with other European studies if possible.

Added text:
"On the other hand, considering some European studies, LG/OC mean values during fall-winter seasons were in the range 1-8% (Giannoni et al. 2012; Elsasser et al. 2012; Crilley et al. 2015; Pietrogrande et al. 2016)"

Figure 3: Correct the captions CPF/CBPF and unify the units.

Figure 3 was modified

Added references

AEBIOM, European Biomass Association, 2015. AEBIOM statistical report 2015, European Bioenergy Outlook, Key findings 2015. Brussels, Belgium. Available at: http://www.aebiom.org/library/statistical-reports/statistical-report-2015/.

Karlsson PE, Ferma M, Tømmervik H, Hole LR, Karlsson GP, Ruoho-Airola T, Aas W, Hellsten S, Akselsson C, Mikkelsen TN, Nihlgård B (2013) Biomass burning in eastern Europe during spring 2006 caused high deposition of ammonium in northern Fennoscandia. *Environ Poll* **176**: 71-79

Pecorari E, Squizzato S, Masiol M, Radice P, Pavoni B, Rampazzo G (2013) Using a photochemical model to assess the horizontal, vertical and time distribution of $PM_{2.5}$ in a complex area: Relationships between the regional and local sources and the meteorological conditions. *Sci Tot Environ* **443**: 681–691

Saarnio K, Aurela M, Timonen H, Saarikoski S, Teinilä K, Mäkelä T, Sofiev M, Koskinen J, Aalto PP, Kulmala M, Kukkonen J, Hillamo R (2010) Chemical composition of fine particles in fresh smoke plumes from boreal wild-land fires in Europe. *Sci Tot Environ* **408**: 2527–2542

Witham C, Manning A (2007) Impacts of Russian biomass burning on UK air quality. *Atmos Environ* **41**: 8075–8090