Urban air quality in a mid-size city – PM$_{2.5}$ composition, sources and identification of impact areas: from local to long range contributions

Authors: Squizzato Stefania$^{1,2*}$, Cazzaro Marta$^1$, Innocente Elena$^1$, Visin Flavia$^1$, Philip K. Hopke,$^2$ Rampazzo Giancarlo$^1$

$^1$Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca’ Foscari Venezia, Via Torino 155, 30172 Venezia Mestre, Italy

$^2$Center for Air Resources Engineering and Science, Clarkson University, Box 5708, Potsdam, New York 13699, USA

* To whom correspondence should be addressed.

Email: stefania.squizzato@unive.it; stefania.squizzato81@gmail.com
Abstract

Urban air quality represents a major public health burden and is a long-standing concern to European citizens. Combustion processes and traffic-related emissions represent the main primary particulate matter (PM) sources in urban areas. Other sources can also affect air quality (e.g., secondary aerosol, industrial) depending on the characteristics of the study area. Thus, the identification and the apportionment of all sources is of crucial importance to make effective corrective decisions within environmental policies.

The aim of this study is to evaluate the impacts of different emissions sources on PM$_{2.5}$ concentrations and compositions in a mid-size city in the Po Valley (Treviso, Italy). Data have been analysed to highlight compositional differences (elements and major inorganic ions), to determine PM$_{2.5}$ sources and their contributions, and to evaluate the influence of air mass movements. Non-parametric tests, positive matrix factorization (PMF), conditional bivariate probability function (CBPF), and concentration weighted trajectory (CWT) have been used in a multi-chemometrics approach to understand the areal-scale (proximate, local, long-range) where different sources act on PM$_{2.5}$ levels and composition.

Results identified three levels of scale from which the pollution arose: (i) a proximate local scale (close to the sampling site) for traffic non-exhaust and resuspended dust sources; (ii) a local urban scale (including both sampling site and areas close to them) for combustion and industrial; and (iii) a regional scale characterized by ammonium nitrate and ammonium sulfate. This approach and results can help to develop and adopt better air quality policy action.

Keyword: PM$_{2.5}$, urban area, sources, PMF, atmospheric circulation
1. Introduction

Ambient airborne particles have diverse physicochemical properties, sources, and impacts. The impacts include effects on transport, transformation, and deposition of chemical species, radiative forcing and human health. Therefore, many countries or politico-economic unions such as the European Union have developed policies and implemented legislation to limit and reduce exposure to ambient particulate matter (PM). However, the diversity of ambient PM composition complicates identifying the specific causal association between exposure to PM and adverse human health effects, the contribution of different sources to ambient PM at different locations, and the consequent formulation of policy actions to cost-effectively reduce harm caused by ambient PM (Heal et al., 2012).

Urban air quality represents a major public health burden and is a long-standing concern to European citizens. Major decreases in the pollutant levels in Europe have been observed since the 1950s. The implementation of the first European Commission Directive on Ambient Air Quality in 1980, regularly updated since then, has not eliminated important disparities in exposure to air pollution between and within European countries (Pascal et al., 2013).

In urban areas, combustion and traffic-related emissions (exhaust and non-exhaust emissions) often represent the main primary sources of PM. However, other sources can affect air quality (e.g.: industrial activities, road dust resuspension, sea-salt) depending on the characteristics of the study area. In addition, organic and inorganic secondary particles formed in the atmosphere from chemical processes involving precursor gases emitted from different sources, represent a large fraction of fine PM mass (e.g.: Aldabe et al., 2011; Perrone et al., 2012; Masiol et al., 2014a).

Therefore, the identification and the apportionment of all sources is importance to make effective corrective decisions with respect to environmental management policies.

Treviso (Veneto, Italy) is located in the eastern part of the Po valley, between the coastal plain and the peri-Alpine region. The Po Valley is characterized by densely urbanized areas and widely
dispersed anthropogenic activities (intensive agriculture and industrial activities), implying a high
density of air pollutant sources. This situation, coupled with frequent stagnant meteorological
conditions, leads to non-compliance with the EU air quality standards, not only in the largest
metropolitan areas (e.g. Milan) but also in small and mid-sized communities (Wang et al., 2016).
Treviso can represent an illustrative example of urban and industrial development in one mid-sized
city in the Po Valley affected by typical urban sources and small industrial zones (e.g.: manufacturing industry) spread throughout the vicinity. The area is also characterized by the
presence of the “A. Canova” airport whose operations (landings, units providing power to the
aircraft on the ground, the traffic due to the airport ground service, maintenance work, heating
facilities) can contribute to the deterioration of air quality (Li et al., 2013; Masiol and Harrison,
2014).
Recently, attention was focused on the largest urban areas in the Po Valley such as Milan, Bologna,
and Venice (e.g.: Vecchi et al., 2008; Perrone et al., 2012; Masiol et al., 2014a; Tositti et al., 2014)
with a few studies focusing on smaller cities (e.g.: Belis et al., 2011). However, the understanding
of pollution source characteristics and behavior is essential in these smaller urban areas to develop
and adopt appropriate air quality action policies.
The objectives of this study are to evaluate the impacts of different emissions sources on PM$_{2.5}$
concentrations and composition, and comparing two different sampling sites: the first one located
inside the airport boundary, close to the runway and the second one near the historic centre of
Treviso. Data have been analysed to assess the compositional differences, to determine PM$_{2.5}$
sources and their contributions and to evaluate the influence of air mass transport on the ambient
PM. Non-parametric tests, positive matrix factorization (PMF), conditional bivariate probability
function (CBPF) and concentration weighted trajectory (CWT) have been used in a multiple
chemometric approach to understand the multiple-scale (proximate, local, regional) areas from
which different sources affect on PM$_{2.5}$ compositions and concentrations.
2. Material and methods

2.1 Study area and main emission sources

Treviso is located in the Veneto region in the eastern part of the Po Valley, enclosed between the coastal plain and the pre-Alpine area, about 30 km north of Venice. The main activities include agriculture and small and medium size industries. Although the population is much smaller than the main cities of Veneto region (Treviso 81,668; Venice 285,647; Verona 259,544; Padua 213,647), the population density of 1457 inhabitants km$^{-2}$ is one of the higher values in the region (ISTAT, 2011). Treviso and the surrounding municipalities (e.g.: Quinto di Treviso, Zero Branco, Paese) form a commercial production system involving more than 136,000 employees: 23,940 commuters moving every working day into the system, 25,654 others moving out of the system and 86,921 that move within the system (ISTAT, 2011). Located between Treviso and Quinto di Treviso, the “A. Canova” airport represents an important node in the Italian airports network (Ministero delle Infrastrutture, 2015) with about 1300 flights per month (Assaeroporti, 2015).

A project to characterize the impact of the activities of Treviso “A. Canova” airport on air quality and PM composition in the vicinity established two sampling sites to evaluate the differences in PM composition, concentrations, and sources between the airport site and the urban site (Fig. 1):

- The AIR site was located inside the “A. Canova” airport, close to the runway (~ 150 m). The airport area is adjacent to two important and trafficked roads (SR515 Noalese, ~ 200 m northward; SR53 Postumia, ~ 2.3 km eastward). In addition, it borders the urban area of Quinto di Treviso on the west and a rural area towards the south;

- The TV site is a station of the ARPAV (local environmental protection agency for Veneto region) regional monitoring network (Treviso-Via Lancieri di Novara), categorized as urban background location (ARPAV, 2013a). It is in a residential area close to the historical city centre of Treviso.
Based on the 2010 emission inventory (ISPRA, 2015), PM$_{2.5}$ primary emissions mainly result from residential heating (41%), combustion in manufacturing industries (22%), and road transport (20%) in the province of Treviso. Gaseous pollutant emissions are associated with combustion in manufacturing industry (SO$_2$, 68%), road transport (NO$_x$, 61%; CO, 44%), and residential heating (CO, 44%). Elements are estimated to be emitted mainly by combustion in manufacturing industry (As, Cd, Cu, Ni, Pb and Zn) and road transport (Cu and Zn). Table 1 reports a summary of disaggregated data at provincial level and municipality level for Treviso and Quinto di Treviso (ARPAV, 2015). Detailed descriptions of the specific activities for each emission inventory group are available in the EMEP/CORINAIR (European Monitoring and Evaluation Program CORINe INventory AIR emissions) guidebook (EEA, 2007).

2.2 Experimental

PM$_{2.5}$ samples were collected daily during a winter period (December 21, 2012 –February 21, 2013).

For the AIR samples, PM$_{2.5}$ was collected using a low volume sampler (Skypost PM, Tecora, 38.33 1 min$^{-1}$) on quartz fiber filters and PM$_{2.5}$ mass was measured by gravimetric determination (microbalance with 0.1 µg sensitivity) on filters preconditioned for 48 h at constant temperature (20°C) and relative humidity (50%).

At TV site, PM$_{2.5}$ was determined on cellulose nitrate membrane filters (Ø 0.8 µm) by using a beta attenuation monitor (SM200, OPSIS, $^{14}$C polymethyl methacrylate source beta rays, 16.67 l min$^{-1}$) and samples were provided by ARPAV - Department of Treviso. A comparison between pairs of filters measured with both methods (gravimetric and beta attenuation) has been routinely done by ARPAV technicians to ensure the quality of the technical protocols adopted in UNI EN 12341:2001 (Masiol et al., 2013).

A total of 55 samples for each site were collected simultaneously and then analysed to determine their inorganic compositions. Samples were cut into two portions. The first one was used to
determine major inorganic ions (Na$^+$, NH$_4^+$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) via water extraction and ion exchange chromatography (IC). The second one was acid digested to quantify elements via ICP-OES (Al, Ca, Mg, S, K, Ti, Mn, Fe and Zn) and ICP-MS (V, Ni, Cu, As, Cd, Sb and Pb). Analytical methods are reported elsewhere (Squizzato et al., 2012; 2014) and a detailed description of the methods is provided as supplementary materials (SI1 and Table SI1).

Field blanks were prepared and analysed together with the samples and the sample values obtained were routinely blank corrected. Limits of detection (LODs) were calculated as three times the standard deviation of field blanks (Table SI1).

The quality of the analytical procedures was checked by blanks, by evaluating detection limits (DLs), recoveries, accuracy, and repeatability. The accuracies of quantitative analyses were assessed by analysing certified liquid standards (TraceCERT, Fluka) and standard reference materials for elements (SRM 1648, NIST). The recoveries of ions and elements were in the range of 80–110%.

Common meteorological data including wind speed and direction, air temperature, relative humidity, solar radiation and precipitations were hourly measured in Canizzano near the AIR sampling site (Fig. 1) by Ente della Zona Industriale di Porto Marghera supported by AIRTRE. Gaseous pollutants (NO$_x$, NO, NO$_2$, CO and SO$_2$) were hourly monitored at the Canizzano and Treviso sites by Ente della Zona Industriale and ARPAV, respectively.

### 2.3 Data treatment

Among the analysed ions and elements, the final dataset includes 19 variables: Al, Ca and Mg have not been considered in the statistical analyses because of the high percentage of data below the detection limit (>70%). To model all of the PM$_{2.5}$ mass, the approach proposed by Hopke et al. (2003) and Zhao et al. (2007) was followed. An unknown mass variable and its uncertainty (UNM, undetermined mass) was calculated for each sample to estimate the unmeasured carbon mass concentration: (i) elements were considered as oxides; (ii) nitrate and sulfate were converted in
ammonium nitrate and ammonium sulfate, respectively; (iii) a reconstructed mass (RM) has been calculated as sum of oxides, ammonium nitrate, ammonium sulfate and other ions (Na\(^+\), Cl\(^-\), K\(^+\)) and (iv) the undetermined mass resulted from the difference between PM\(_{2.5}\) measured mass and RM. Details of the procedure are provided in the supplementary materials (SI2). The undetermined mass represents about 62% and 54% of the PM\(_{2.5}\) mass measured at the AIR and TV, respectively. Because of their relative proximity, the sampling sites can be considered to be influenced by the same sources. According to recent studies (Mooibroek et al., 2011; Jang et al., 2013; Masiol et al., 2014a; Kara et al., 2015), a multiple-receptor sites PMF has been performed using USEPA PMF 5.0. PMF was performed following the rules and suggestions found in the user manual (USEPA, 2014) and in Reff et al. (2007).

Data and uncertainties were handled according to Polissar et al. (1998): (1) data < DLs were set as DL/2, with an uncertainty of 5/6 of the corresponding DL; (2) data > DLs were matched with uncertainties determined by compounding errors from the most uncertain components with the addition of 1/3 of the DLs. Details of PMF settings, regression diagnostics, base model displacement error estimation and bootstrap results are provided as supplementary materials (SI3, Table SI2, Figure SI1).

3. Results and discussion
3.1 Meteorology of the study area
The sampling period was characterized by low wind speed (1.4 m s\(^{-1}\) on mean) blowing from north-northeast (Fig. 1), low temperatures (4\(^\circ\)C), a few days with high levels of precipitation and generally stable condition associated to low mixing layer heights mainly during December and January. Fig. 2 report the daily precipitation and the daily average mixing layer height (Hmix). Hmix was extracted from the NOAA ARL GDAS1 data (National Oceanic and Atmospheric Administration, Atmospheric Resources Laboratory, Global Data Assimilation System).
Low average temperatures were recorded during December 2012 associated with low wind speed (0.7 m s\(^{-1}\) on average) and high relative humidity. The final days of 2012 were characterized by stable conditions, temperatures above the mean (4°C), thermal inversions, low mixing layer heights ranging between 49 m and 96 m, fog and low rainfall. January 2013 had colder temperatures than December but still had stable conditions with some foggy days alternating to brief atmospheric disturbances (rain and some snow episodes). After January 17th, the weather became sunny and cold with temperature below 0°C during the night with some thermal inversion episodes. Mixing layer heights increased in the second week of January and low heights were again observed in the final days of the month. February 2013 was characterized by scattered rain and snow episodes and by higher mixing layer height ranging between 86 m and 317 m (ARPAV, 2013b; ARPAV, 2014). These meteorological conditions favor the formation of ammonium nitrate (low temperature enhances the movement of the equilibrium to the particle phase) and the low mixing layer heights coupled with low wind speed limit the dispersion of pollutants resulting in high concentration of particulate matter and poorer air quality.

### 3.2 PM concentrations, composition

Table 2 summarizes the average concentrations of PM\(_{2.5}\), ions, elements and gaseous pollutants at AIR and TV site.

Mean PM\(_{2.5}\) concentrations were 55 and 44 µg m\(^{-3}\) at the AIR and TV sites, respectively. At the TV site PM\(_{10}\) concentrations were also available. The mean PM\(_{10}\) was 58 µg m\(^{-3}\) during the sampling period. On average, the PM\(_{2.5}\) to PM\(_{10}\) ratio was 0.76, highlighting that the fine fraction represented the majority of the PM\(_{10}\).

Ion contributions to PM\(_{2.5}\) (express as sum of analysed species) amounts 17 µg m\(^{-3}\) at both sites, accounting for the 33% and 43% of PM\(_{2.5}\) mass at the AIR and TV sites, respectively. The bulk of this contribution is the secondary inorganic constituents (expresses as sum of NH\(_4^+\), NO\(_3^-\) and SO\(_4^{2-}\)) that represents 30% and 38% of PM\(_{2.5}\) mass at the AIR and TV sites, respectively. Similar to those
observed in other area of the Po Valley, nitrate concentrations exceed sulfate during cold periods.

Particulate nitrate is favored by low temperatures and higher NOx emissions in winter from space heating emissions, such that it represents more than 60% of the secondary inorganic components. S and K are major elemental components followed by Al > Ca > Fe > Mg > Zn > Pb > Cu > Mn > Ni > Ti > Sb > V > As > Cd. However, Al, Ca and Mg were found to have high percentages of values below the detection limit. Their presence in samples can be treated as sporadic events that do not represent the average conditions. Sulfur and potassium are mainly present in the ionic form (SO_4^{2-} and K^+) at both the AIR and TV sites. Other elements account for only a small amount of PM_{2.5}, accounting for only 1% of the mass.

Intersite differences have been evaluated using the Mann Whitney non-parametric test (U-test) (Table 2). PM_{2.5}, water soluble inorganic ions, Fe, Zn, Cd, Sb, V and O_3 show no statistically significant differences. These results suggest that PM_{2.5} and these species present an area-wide distribution due to common emission sources and formation processes.

At the AIR site, an excess of sulfur and potassium compared to the ionic form (SO_4^{2-} and K^+,
respectively) can be observed (Table 2). The excess of sulfur and potassium was calculated as the mass concentration difference between the elemental and the ionic form. Therefore, considering the proximity of the sampling site to the runway, the relationship with aircraft emission was investigated.

Among the analysed elements, the excess of sulfur showed good correlations with Zn (r = 0.5), and Sb (r = 0.6). Similarly, the excess of potassium presented good correlations with Ti (r = 0.4), Zn (r = 0.5), Pb (r = 0.4), Sb (r = 0.6) and the excess of sulfur (r = 0.6). Zn and S have been linked to tyre detritus/smoke in runway dust (Amato et al., 2010; Li et al., 2013), Sb to brake dust and Pb is a component of 100 octane aviation gas fuel used in general aviation aircraft (Federal Aviation Administration, 2001). Ti can be from the resuspension of dust/soil particles by anthropogenic activities (Amato et al., 2010). The small excess of potassium over potassium ion could also be due
to the resuspension of soil on the runway and the open land in the proximity of the sampling site
due to aircraft landing (Watson et al., 2001).

Despite the observed correlations, it cannot be totally excluded the contribution of vehicular traffic.

There is a severe shortage of data on the elemental composition of PM$_{2.5}$ emitted by aircraft, these
studies report that emissions are composed of various trace elements mainly originating from fuels,
lubricating oils, tyre wear, engine wear and corrosion, which are similar to those emitted from the
vehicular traffic (Masiol and Harrison, 2014 and references therein).

With the aim of identifying the elements more directly related to human activities and working
cycles, the concentrations observed at week-ends (Saturday, Sunday and holidays) and on week-
days have been examined and statistically differences tested by using Mann-Whitney U-test. No
significant differences were observed for PM$_{2.5}$ concentrations ($p > 0.05$). However, Na$^+$, Fe and Mn
concentrations increase during working-days (+72%, +59%, +132%, respectively) at the AIR site.

Reductions in the traffic intensity during the week-end can explain these differences. Lawrence et
al. (2013) observed a good correlation between Na and traffic volume (samples were collected at a
tunnel entrance and exit) and associated Na to road salting to prevent ice forming on the road
surface. Moreover, several studies suggest Fe and Mn as marker for break wear, tyre wear, and re-
suspension of non-exhaust vehicle emissions (Pant and Harrison, 2013 and references therein).

Differently, the TV site data show an increase for NH$_4^+$ (+18%), SO$_4^{2-}$ (+20%), K$^+$ and K (+41%
and +31%, respectively) during the weekend. K$^+$ is usually considered as a marker of biomass
burning (e.g.: Cerasi Urban et al., 2012) and recently also ammonium and sulfate have been
observed in high pollution episodes from biomass burning (Karlsson et al., 2013). The sampling site
is located in a residential area. Thus, it is plausible that on weekends the biomass burning for
domestic heating increases.

### 3.3 Identification and apportion of PM$_{2.5}$ sources
Six factors were extracted from the PMF model. Modelled PM$_{2.5}$ mass concentrations correlated well with the measured PM$_{2.5}$ ($r^2 = 0.92$). The scaled residuals were symmetrically distributed. The source profiles obtained are given in Fig. 3 and the time series of each source are provided in Fig. 4. Results were interpreted on the basis of the presence of known tracers for specific sources and the likely major emission sources in the study area.

The first factor profile accounts for K$^+$, Cl$^-$ and UNM with some amounts of Zn, Pb and Sb. It accounts for 38% (21 $\mu$g m$^{-3}$) and 37% (15 $\mu$g m$^{-3}$) on mean of PM$_{2.5}$ mass at AIR and TV, respectively. K$^+$ and Cl$^-$ have been widely used as tracers of wood combustion and biomass burning (e.g.: Johnson et al., 2006; Ryu et al., 2007) and the modelled elements have been associated with wood pellet and cord wood combustion (Boman et al., 2006; Chandrasekaran et al., 2012; Wiinikka et al., 2013). The UMN is likely to be the substantial amounts of organic carbon associated with wood combustion. The peak of combustion contribution on January 6 supports this interpretation: in the Veneto Region on the eve of Epiphany, a religious celebration (between January 5th and January 6th). At this time, thousands of bonfires burn wooden material particularly in the rural areas of Venice and Treviso and causing an increase of PM$_{2.5}$, PM$_{10}$, K$^+$ and total carbon levels (Masiol et al., 2014b). Moreover, the biomass combustion source contributions are statistically significant correlated with NO$_x$ and CO (AIR: $r_{NOx} = 0.6$; $r_{CO} = 0.7$; TV: $r_{NOx} = 0.6$; $r_{CO} = 0.7$) in both sites. This factor represents the biomass burning (wood and pellets) for domestic heating and other wood burning activities.

This interpretation is also consistent with those reported in the last released emissions inventory (ISPRA, 2015) that assigns a large part of primary PM$_{2.5}$ and CO emissions to the group 2 - Non-industrial combustion systems (41% and 44%, respectively), in particular to the sub-group Residential heating (96% and 93%, respectively).
The second and third factors represent the secondary inorganic component of PM$_{2.5}$ associated with ammonium nitrate (NH$_4^+$, NO$_3^-$) and ammonium sulfate (NH$_4^+$, SO$_4^{2-}$). Ammonium nitrate and ammonium sulfate apportion average 32% (18 µg m$^{-3}$) and 13% (7 µg m$^{-3}$), respectively, of PM$_{2.5}$ mass at the AIR site and 29% (12 µg m$^{-3}$) and 13% (6 µg m$^{-3}$), respectively, the TV site. These secondary ions derive from gas-to-particle conversion processes. Similar contribution and trend can be observed at both stations during the sampling period highlighting a widespread pollution of these components (Fig. 4).

In the fourth factor, As, Cd and V are associated suggesting the presence of an industrial source that represent on mean 10% (6 µg m$^{-3}$) and 5% (2 µg m$^{-3}$) of the PM$_{2.5}$ mass at the AIR and TV sites, respectively. These elements can be related to industrial emissions from brick and ceramic factories, glass making, non-ferrous metal production, and iron and steel manufacturing (Pacyna and Pacyna, 2001; Sánchez de la Campa et al., 2010; Taiwo et al., 2014). Although a large industrial zone is not present, several small industrial activities affect the study area including those mentioned above (Figure SI2).

The fifth factor is characterized by Fe, Ti, and Mn association and apportions 2 µg m$^{-3}$ (3%) and 1 µg m$^{-3}$ (3%) of PM$_{2.5}$ at the AIR and TV sites, respectively. This factor has a good correlation with NO$_x$ (AIR: $r_{NOx} = 0.4$; TV: $r_{NOx} = 0.5$) at both sites. This fraction could represent the non-exhaust emissions from vehicular traffic. Metals are emitted from various exhaust-related sources (i.e.: fuel and lubricant combustion, catalytic converters) but these elements are most likely to arise from non-exhaust sources like brake wear and muffler ablation considering that the levels of trace elements emitted in the exhaust are very low (Pant and Harrison, 2013 and references therein).

The final factor includes Na$^+$, Ni, and Cu as major species and minor amounts of Zn, Ti. It contributes for 3% (2 µg m$^{-3}$) and 14% (6 µg m$^{-3}$) of PM$_{2.5}$ mass at the AIR and TV sites,
respectively. This association can be related to the resuspension of road-dust, as non-exhaust emissions (Ni, Cu, Zn) from tyre wear and brake wear, salt used for deicing (Na⁺) and to the abrasion of road surface (Ti) (Pant and Harrison, 2013 and references therein).

Similar to PM composition, inter-site differences were evaluated applying the Mann-Whitney U-test and the Pearson correlation coefficient to detect which sources can be mainly associated with local sources emissions relative to widespread pollution across the study area. Combustion, ammonium nitrate, ammonium sulfate, and traffic non-exhaust are strongly correlated between the two sites ($r=0.8$, $r=0.8$, $r=0.8$, and $r=0.6$, respectively). No correlation was observed for the resuspended dust and industrial source. Source contributions to PM were statistically different ($p$-value < 0.005) between the two sites for ammonium nitrate, industrial, traffic non-exhaust, and resuspended dust. Thus, the contributions of ammonium nitrate, industrial, traffic, and resuspended dust are likely influenced by local emissions close to sampling sites. Alternatively, changes in ammonium sulfate and combustion contributions are likely to be related to transport and widely dispersed sources across the region.

The highest concentrations of ammonium nitrate at the TV site can be addressed to the greater availability of HNO₃ from high emissions of NOₓ than at the AIR site. Despite this, ammonium nitrate is correlated between the AIR and TV sites. Changes in source contributions can be compared with the evolution of the mixing layer height in Fig. 4. It can be observed that the higher concentrations of ammonium nitrate and combustion were reached in correspondence of the lowest mixing layer heights that favor the accumulation processes and lead to a homogeneity on source concentrations over the area. Ammonium sulfate shows a different behavior. Higher concentrations were associated both to the lowest and to the highest Hmix, thus the levels of ammonium sulfate might depend both on accumulation processes and on intrusion of polluted air masses from farther areas during high Hmix events in the final days of February.
Levels of traffic non-exhaust, industrial and resuspended dust do not appear influenced by Hmix evolution.

3.4 Influence of atmospheric circulation on PM and its sources

To better understand the changing PM$_{2.5}$ concentrations, the influence of atmospheric circulation has been evaluated. The relationships between source contributions and ground-wind circulation patterns were investigated by using CBPF (conditional bivariate probability function) analysis. Computation of CBPF has been done by using Openair package for R (Carslaw, 2015).

Furthermore, 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. In this study CWT has been computed by using TrajStat software (Wang et al., 2009).

3.4.1 Conditional bivariate probability function

The conditional bivariate probability function (CBPF) couples ordinary CPF with wind speed as a third variable, allocating the observed pollutant concentration to cells defined by ranges of wind direction and wind speed rather than to only wind direction sectors. The CPF is defined as $\text{CPF} = \frac{m_\theta}{n_\theta}$, where $m_\theta$ is the number of samples in the wind sector $\theta$ with concentrations greater than some ‘high’ concentration (> 75° percentile, in this study), and $n_\theta$ is the total number of samples in the same wind sector (Kim et al., 2003; Kim and Hopke, 2004). The extension to the bivariate case provides more information on the nature of the sources (or chemical species) because different source types can have different wind speed dependencies (Uria-Tellaetxe and Carslaw, 2014)

Computed CBPF plots are presented in Figure 5 and 6.

Ammonium nitrate shows that the highest probabilities at the AIR site were associated to wind blowing from north, west and south both for weak, moderate and strong winds (Fig. 5) in correspondence of the runway, trafficked roads and the residential area of Quinto di Treviso. High
probabilities towards south-west can also be observed at TV where the major highways are located (Fig. 1). This pattern suggests both local formation/accumulation processes (associated to low wind speed and to a greater availability of HNO₃ from high emissions of NOₓ) and transport from farther areas of ammonium nitrate.

Probabilities associated with ammonium sulfate increase with wind blowing from east at both sites. The highest probabilities associated with combustion occur for winds characterized by low speeds (2 m s⁻¹) blowing from south-west where the residential area of Quinto and Treviso are located.

The industrial source shows a preferential wind direction from south and east at TV (Fig. 6). Alternatively, the highest probabilities were obtained with winds from the northeast and northwest at the airport site where several small industries are located. Details of production activities and their position relative to the sampling site are provided in the supplementary materials (Fig. SI2; Table SI3).

At the AIR site, traffic non-exhaust emissions exhibit high probabilities associated for low wind speeds, suggesting a source close to the sampling site such as the SR515 Noalese, one of the more important trafficked roads of the area (Fig. 1). Conversely, in TV site high probabilities are associated to wind blowing from south where the ring road of Treviso historical center is located. The highest probabilities for resuspended dust were associated to moderate and high wind speeds that enhance the resuspension process at both AIR and TV, supporting the interpretation of PMF results.

3.4.2 Concentration weighted trajectory

CWT is a method of weighting trajectories with associated concentrations (Hsu et al., 2003). In this procedure, each grid cell gets a weighted concentration obtained by averaging sample concentrations that have associated trajectories that crossed that grid cell as follows, i.e. each concentration is used as a weighting factor for the residence times of all trajectories in each grid cell and then divided by the cumulative residence time from all trajectories (Hsu et al., 2003; Cheng et
al., 2013). In summary, weighted concentration fields show concentration gradients across potential sources and highlight the relative significance of potential sources (Hsu et al., 2003).

In this study, 96 hours back-trajectories were computed by using the HYSPLIT model and global data assimilation system (GDAS1) meteorological data fields (Draxler and Rolph, 2013; Rolph, 2013). The starting height was set at 100 m a.s.l. and 4 trajectories per day were computed per each sampling day (at 3, 9, 15 and 21 UTC). Considering the proximity of the sampling sites, AIR site coordinates were used as starting point. The geographical domain was divided into 1° by 1° grid cells according to the meteorological data fields. The obtained maps are reported in Fig. 7.

High external contribution can be observed for combustion source only when air mass coming from the Atlantic area and passing across the United Kingdom (12% of cases). This could be attributed to the impact of wood pellet combustion for power generation in United Kingdom. In the last decade, the United Kingdom replaced coal in their largest 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).

Other sources, except traffic non-exhaust and resuspended dust that represent the local emissions, show high potential external contribution from wider areas: north and north-west Europe (ammonium nitrate), central and north-east Europe (ammonium sulfate), east Europe (industrial).

During winter, high daily external contributions of ammonium sulfate have been already observed in the Venice area (Squizzato and Masiol, 2015) when air masses coming from East-Europe, where SO$_2$, the main precursor of sulfate aerosol and ammonium sulfate, still reaches high concentrations (>10 $\mu$g m$^{-3}$) (e.g., Poland, Romania, Serbia, Bulgaria, Greece and Turkey) (EEA, 2015).

This confirms what previously observed on CBPF that shows high probabilities associated both with low wind speed (local emissions) and with moderate and strong winds.
Industrial source shows high probabilities on CBPF both for weak and strong wind, representing the local and long range transport processes influence, respectively. In fact, high concentration gradient is showed by CWT when trajectories coming from East Europe. Hence, a transboundary contribution cannot be excluded for this source. Results of CWT are interesting and may have significant implications for air quality assessment and mitigation measures adopted, or to adopt, in the study area. PM$_{2.5}$ is a critical pollutant in the Northern Italy due to the frequent exceeding of European air quality standards. All identified sources apportion to a significant mass of PM$_{2.5}$ and among the main ones, ammonium sulfate and industrial appear strongly influenced by external contributions. Changes in ammonium nitrate levels can be addresses both to local formation process (favored by high levels of NO$_x$ and low temperatures, typical conditions during winter) and to long-range transport. On the contrary, combustion source that contributes for a large part of PM$_{2.5}$ mass appears mainly linked to local emissions. Under this scenario, effective mitigation strategies should consider these evidences.

4. CONCLUSIONS

PM$_{2.5}$ samples have been collected at two sites in Treviso (Po Valley, Italy), within one of the most polluted areas in Europe. The main inorganic components of PM were determined (water soluble inorganic ions and elements) and data have been processed to highlight compositional differences, to determine PM sources and their contribution and to evaluate the influence of air masses movements. A set of chemometrics tools have been used helping in understanding PM dynamics. Therefore, the main findings can be summarized as follows:

- A widespread pollution has been highlighted for PM$_{2.5}$, water soluble inorganic ions, Fe, Zn, Cd, Sb, V and O$_3$;
- Six sources of PM$_{2.5}$ have been identified and quantify: combustion, ammonium nitrate, ammonium sulfate, industrial, traffic non-exhaust and resuspended dust. Combustion, ammonium nitrate and ammonium sulfate are strong correlated between the two sites but
ammonium nitrate source shows statistically different contributions as well as industrial, traffic
non-exhaust and resuspended dust, probably due to the characteristics of the sampling sites.

- High external contribution can be observed for combustion source only when air mass coming
from the Atlantic area passing over the United Kingdom (only 12% of cases), indicating that the
local emissions has a strong effect on combustion concentrations during the sampling period;

- Ammonium sulfate appears strongly influenced by external contributions whereas ammonium
nitrate and industrial contributions can be addresses both to local and external contribution;

- Traffic non-exhaust and resuspended dust do not appear influenced by external contributions, as
expected. CBPF calculated on traffic non-exhaust contributions shows high probabilities towards
the south in the TV site and toward west in the AIR site in correspondence of trafficked roads
and also airport runway in AIR site. Highest levels of resuspended dust are probably associated
to moderate winds that enhance the resuspension both in AIR and TV.

Results pointed out three levels of scale from which the pollution arose: (i) a proximate local scale
(close to the sampling site) for traffic non-exhaust source and resuspended dust; (ii) a local scale
(including both sampling site and areas close to them) for combustion, ammonium nitrate,
industrial; (iii) a regional scale characterized by external contribution for ammonium nitrate,
ammonium sulfate and partially industrial source. In this view, the proposed approach and results
can help to develop and adopt better air quality policy action both at local and at regional scale.
More effective inter-regional and inter-state policy actions should be also evaluated.

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Table captions

Table 1. Emission inventory: primary contribution of each sources to the PM and gaseous pollutant.

Table 2. Basic statistics of concentrations of PM$_{2.5}$, major ions, elements and gaseous pollutants for each site for the period December 21, 2012 –February 21, 2013. Statistically significant U tests ($p < 0.05$) are in bold.

Figure captions

Figure 1. Sampling sites (Airport and Treviso – Via Lancieri di Novara) and meteorological station (Canizzano) location (image from Google Earth). Wind rose shows the prevalent wind directions during the sampling period.

Figure 2. Precipitations and daily average mixing layer height (Hmix) during the sampling period.

Figure 3. Factor profiles obtained by PMF analysis expressed as concentration of species in μg m$^{-3}$ (left axis) and percentage of species sum (right axis).

Figure 4. Time series obtained by PMF analysis and daily average mixing layer height (Hmix) during the sampling period.

Figure 5. CBPF plots computed on source contributions for TV and AIR site for PMF factors: combustion, ammonium nitrate and ammonium sulfate.
Figure 6. CBPF plots computed on source contributions for TV and AIR site for PMF factors: industrial, traffic non-exhaust and resuspended dust.

Figure 7. CWT on source contributions estimated by PMF analysis.