

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

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20 **Abstract**

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

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

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

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42 **Keyword: PM_{2.5}, urban area, sources, PMF, atmospheric circulation**

43 **1. Introduction**

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

53 Urban air quality represents a major public health burden and is a long-standing concern to
54 European citizens. Major decreases in the pollutant levels in Europe have been observed since the
55 1950s. The implementation of the first European Commission Directive on Ambient Air Quality in
56 1980, regularly updated since then, has not eliminated important disparities in exposure to air
57 pollution between and within European countries (Pascal et al., 2013).

58 In urban areas, combustion and traffic-related emissions (exhaust and non-exhaust emissions) often
59 represents the main primary sources of PM. However, other sources can affect air quality (e.g.:
60 industrial activities, road dust resuspension, sea-salt) depending on the characteristics of the study
61 area. In addition, organic and inorganic secondary particles formed in the atmosphere from
62 chemical processes involving precursor gases emitted from different sources, represent a large
63 fraction of fine PM mass (e.g.: Aldabe et al., 2011; Perrone et al., 2012; Masiol et al., 2014a).
64 Therefore, the identification and the apportionment of all sources is importance to make effective
65 corrective decisions with respect to environmental management policies.

66 Treviso (Veneto, Italy) is located in the eastern part of the Po valley, between the coastal plain and
67 the peri-Alpine region. The Po Valley is characterized by densely urbanized areas and widely

68 dispersed anthropogenic activities (intensive agriculture and industrial activities), implying a high
69 density of air pollutant sources. This situation, coupled with frequent stagnant meteorological
70 conditions, leads to non-compliance with the EU air quality standards, not only in the largest
71 metropolitan areas (e.g. Milan) but also in small and mid-sized communities (Wang et al., 2016).
72 Treviso can represent an illustrative example of urban and industrial development in one mid-sized
73 city in the Po Valley affected by typical urban sources and small industrial zones (e.g.:
74 manufacturing industry) spread throughout the vicinity. The area is also characterized by the
75 presence of the “A. Canova” airport whose operations (landings, units providing power to the
76 aircraft on the ground, the traffic due to the airport ground service, maintenance work, heating
77 facilities) can contribute to the deterioration of air quality (Li et al., 2013; Masiol and Harrison,
78 2014).

79 Recently, attention was focused on the largest urban areas in the Po Valley such as Milan, Bologna,
80 and Venice (e.g.: Vecchi et al., 2008; Perrone et al., 2012; Masiol et al., 2014a; Tositti et al., 2014)
81 with a few studies focusing on smaller cities (e.g.: Belis et al., 2011). However, the understanding
82 of pollution source characteristics and behavior is essential in these smaller urban areas to develop
83 and adopt appropriate air quality action policies.

84 The objectives of this study are to evaluate the impacts of different emissions sources on PM_{2.5}
85 concentrations and composition, and comparing two different sampling sites: the first one located
86 inside the airport boundary, close to the runway and the second one near the historic centre of
87 Treviso. Data have been analysed to assess the compositional differences, to determine PM_{2.5}
88 sources and their contributions and to evaluate the influence of air mass transport on the ambient
89 PM. Non-parametric tests, positive matrix factorization (PMF), conditional bivariate probability
90 function (CBPF) and concentration weighted trajectory (CWT) have been used in a multiple
91 chemometric approach to understand the multiple-scale (proximate, local, regional) areas from
92 which different sources affect on PM_{2.5} compositions and concentrations.

94 **2. Material and methods**

95 *2.1 Study area and main emission sources*

96 Treviso is located in the Veneto region in the eastern part of the Po Valley, enclosed between the
97 coastal plain and the pre-Alpine area, about 30 km north of Venice. The main activities include
98 agriculture and small and medium size industries. Although the population is much smaller than the
99 main cities of Veneto region (Treviso 81,668; Venice 285,647; Verona 259,544; Padua 213,647),
100 the population density of 1457 inhabitants km⁻² is one of the higher values in the region (ISTAT,
101 2011). Treviso and the surrounding municipalities (e.g.: Quinto di Treviso, Zero Branco, Paese)
102 form a commercial production system involving more than 136,000 employees: 23,940 commuters
103 moving every working day into the system, 25,654 others moving out of the system and 86,921 that
104 move within the system (ISTAT, 2011). Located between Treviso and Quinto di Treviso, the “A.
105 Canova” airport represents an important node in the Italian airports network (Ministero delle
106 Infrastrutture, 2015) with about 1300 flights per month (Assaeroporti, 2015).
107 A project to characterize the impact of the activities of Treviso “A. Canova” airport on air quality
108 and PM composition in the vicinity established two sampling sites to evaluate the differences in PM
109 composition, concentrations, and sources between the airport site and the urban site (Fig. 1):

- 110 • The AIR site was located inside the “A. Canova” airport, close to the runway (~ 150 m). The
111 airport area is adjacent to two important and trafficked roads (SR515 Noalese, ~ 200 m
112 northward; SR53 Postumia, ~ 2.3 km eastward). In addition, it borders the urban area of
113 Quinto di Treviso on the west and a rural area towards the south;
- 114 • The TV site is a station of the ARPAV (local environmental protection agency for Veneto
115 region) regional monitoring network (Treviso-Via Lancieri di Novara), categorized as urban
116 background location (ARPAV, 2013a). It is in a residential area close to the historical city
117 centre of Treviso.

118 Based on the 2010 emission inventory (ISPRA, 2015), PM_{2.5} primary emissions mainly result from
119 residential heating (41%), combustion in manufacturing industries (22%), and road transport (20%)
120 in the province of Treviso. Gaseous pollutant emissions are associated with combustion in
121 manufacturing industry (SO₂, 68%), road transport (NO_x, 61%; CO, 44%), and residential heating
122 (CO, 44%). Elements are estimated to be emitted mainly by combustion in manufacturing industry
123 (As, Cd, Cu, Ni, Pb and Zn) and road transport (Cu and Zn). Table 1 reports a summary of
124 disaggregated data at provincial level and municipality level for Treviso and Quinto di Treviso
125 (ARPAV, 2015). Detailed descriptions of the specific activities for each emission inventory group
126 are available in the EMEP/CORINAIR (European Monitoring and Evaluation Program CORE
127 INventory AIR emissions) guidebook (EEA, 2007).

128 *2.2 Experimental*

129 PM_{2.5} samples were collected daily during a winter period (December 21, 2012 –February 21,
130 2013).

131 For the AIR samples, PM_{2.5} was collected using a low volume sampler (Skypost PM, Tecora, 38.33
132 l min⁻¹) on quartz fiber filters and PM_{2.5} mass was measured by gravimetric determination
133 (microbalance with 0.1 µg sensitivity) on filters preconditioned for 48 h at constant temperature
134 (20°C) and relative humidity (50%).

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

141 A total of 55 samples for each site were collected simultaneously and then analysed to determine
142 their inorganic compositions. Samples were cut into two portions. The first one was used to

143 determine major inorganic ions (Na^+ , NH_4^+ , Cl^- , NO_3^- , SO_4^{2-}) via water extraction and ion exchange
144 chromatography (IC). The second one was acid digested to quantify elements *via* ICP-OES (Al, Ca,
145 Mg, S, K, Ti, Mn, Fe and Zn) and ICP-MS (V, Ni, Cu, As, Cd, Sb and Pb). Analytical methods are
146 reported elsewhere (Squizzato et al., 2012; 2014) and a detailed description of the methods is
147 provided as supplementary materials (SI1 and Table SI1).

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

151 The quality of the analytical procedures was checked by blanks, by evaluating detection limits
152 (DLs), recoveries, accuracy, and repeatability. The accuracies of quantitative analyses were
153 assessed by analysing certified liquid standards (TraceCERT, Fluka) and standard reference
154 materials for elements (SRM 1648, NIST). The recoveries of ions and elements were in the range of
155 80–110%.

156 Common meteorological data including wind speed and direction, air temperature, relative
157 humidity, solar radiation and precipitations were hourly measured in Canizzano near the AIR
158 sampling site (Fig. 1) by Ente della Zona Industriale di Porto Marghera supported by AIRTRE.
159 Gaseous pollutants (NO_x , NO, NO_2 , CO and SO_2) were hourly monitored at the Canizzano and
160 Treviso sites by Ente della Zona Industriale and ARPAV, respectively.

161

162 2.3 Data treatment

163 Among the analysed ions and elements, the final dataset includes 19 variables: Al, Ca and Mg have
164 not been considered in the statistical analyses because of the high percentage of data below the
165 detection limit (>70%). To model all of the $\text{PM}_{2.5}$ mass, the approach proposed by Hopke et al.
166 (2003) and Zhao et al. (2007) was followed. An unknown mass variable and its uncertainty (UNM,
167 undetermined mass) was calculated for each sample to estimate the unmeasured carbon mass
168 concentration: (i) elements were considered as oxides; (ii) nitrate and sulfate were converted in

169 ammonium nitrate and ammonium sulfate, respectively; (iii) a reconstructed mass (RM) has been
170 calculated as sum of oxides, ammonium nitrate, ammonium sulfate and other ions (Na^+ , Cl^- , K^+)
171 and (iv) the undetermined mass resulted from the difference between $\text{PM}_{2.5}$ measured mass and RM.
172 Details of the procedure are provided in the supplementary materials (SI2). The undetermined mass
173 represents about 62% and 54% of the $\text{PM}_{2.5}$ mass measured at the AIR and TV, respectively.
174 Because of their relative proximity, the sampling sites can be considered to be influenced by the
175 same sources. According to recent studies (Mooibroek et al., 2011; Jang et al., 2013; Masiol et al.,
176 2014a; Kara et al., 2015), a multiple-receptor sites PMF has been performed using USEPA PMF
177 5.0. PMF was performed following the rules and suggestions found in the user manual (USEPA,
178 2014) and in Reff et al. (2007).
179 Data and uncertainties were handled according to Polissar et al. (1998): (1) data < DLs were set as
180 $\text{DL}/2$, with an uncertainty of $5/6$ of the corresponding DL; (2) data > DLs were matched with
181 uncertainties determined by compounding errors from the most uncertain components with the
182 addition of $1/3$ of the DLs. Details of PMF settings, regression diagnostics, base model
183 displacement error estimation and bootstrap results are provided as supplementary materials (SI3,
184 Table SI2, Figure SI1).

185

186 **3. Results and discussion**

187 *3.1 Meteorology of the study area*

188 The sampling period was characterized by low wind speed (1.4 m s^{-1} on mean) blowing from north-
189 northeast (Fig. 1), low temperatures (4°C), a few days with high levels of precipitation and
190 generally stable condition associated to low mixing layer heights mainly during December and
191 January. Fig. 2 report the daily precipitation and the daily average mixing layer height (H_{mix}).
192 H_{mix} was extracted from the NOAA ARL GDAS1 data (National Oceanic and Atmospheric
193 Administration, Atmospheric Resources Laboratory, Global Data Assimilation System).

194 Low average temperatures were recorded during December 2012 associated with low wind speed
195 (0.7 m s^{-1} on average) and high relative humidity. The final days of 2012 were characterized by
196 stable conditions, temperatures above the mean (4°C), thermal inversions, low mixing layer heights
197 ranging between 49 m and 96 m, fog and low rainfall. January 2013 had colder temperatures than
198 December but still had stable conditions with some foggy days alternating to brief atmospheric
199 disturbances (rain and some snow episodes). After January 17th, the weather became sunny and
200 cold with temperature below 0°C during the night with some thermal inversion episodes. Mixing
201 layer heights increased in the second week of January and low heights were again observed in the
202 final days of the month. February 2013 was characterized by scattered rain and snow episodes and
203 by higher mixing layer height ranging between 86 m and 317 m (ARPAV, 2013b; ARPAV, 2014).
204 These meteorological conditions favor the formation of ammonium nitrate (low temperature
205 enhances the movement of the equilibrium to the particle phase) and the low mixing layer heights
206 coupled with low wind speed limit the dispersion of pollutants resulting in high concentration of
207 particulate matter and poorer air quality.

208

209 *3.2 PM concentrations, composition*

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

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

216 Ion contributions to $\text{PM}_{2.5}$ (express as sum of analysed species) amounts $17 \mu\text{g m}^{-3}$ at both sites,
217 accounting for the 33% and 43% of $\text{PM}_{2.5}$ mass at the AIR and TV sites, respectively. The bulk of
218 this contribution is the secondary inorganic constituents (expresses as sum of NH_4^+ , NO_3^- and SO_4^{2-})
219 that represents 30% and 38% of $\text{PM}_{2.5}$ mass at the AIR and TV sites, respectively. Similar to those

220 observed in other area of the Po Valley, nitrate concentrations exceed sulfate during cold periods.
221 Particulate nitrate is favored by low temperatures and higher NO_x emissions in winter from space
222 heating emissions, such that it represents more than 60% of the secondary inorganic components.
223 S and K are major elemental components followed by Al > Ca > Fe > Mg > Zn > Pb > Cu > Mn >
224 Ni > Ti > Sb > V > As > Cd. However, Al, Ca and Mg were found to have high percentages of
225 values below the detection limit. Their presence in samples can be treated as sporadic events that do
226 not represent the average conditions. Sulfur and potassium are mainly present in the ionic form
227 (SO₄²⁻ and K⁺) at both the AIR and TV sites. Other elements account for only a small amount of
228 PM_{2.5}, accounting for only 1% of the mass.

229 Intersite differences have been evaluated using the Mann Whitney non-parametric test (U-test)
230 (Table 2). PM_{2.5}, water soluble inorganic ions, Fe, Zn, Cd, Sb, V and O₃ show no statistically
231 significant differences. These results suggest that PM_{2.5} and these species present an area-wide
232 distribution due to common emission sources and formation processes.

233

234 At the AIR site, an excess of sulfur and potassium compared to the ionic form (SO₄²⁻ and K⁺,
235 respectively) can be observed (Table 2). The excess of sulfur and potassium was calculated as the
236 mass concentration difference between the elemental and the ionic form. Therefore, considering the
237 proximity of the sampling site to the runway, the relationship with aircraft emission was
238 investigated.

239 Among the analysed elements, the excess of sulfur showed good correlations with Zn ($r = 0.5$), and
240 Sb ($r = 0.6$). Similarly, the excess of potassium presented good correlations with Ti ($r = 0.4$), Zn (r
241 $= 0.5$), Pb ($r = 0.4$), Sb ($r = 0.6$) and the excess of sulfur ($r = 0.6$). Zn and S have been linked to tyre
242 detritus/smoke in runway dust (Amato et al., 2010; Li et al., 2013), Sb to brake dust and Pb is a
243 component of 100 octane aviation gas fuel used in general aviation aircraft (Federal Aviation
244 Administration, 2001). Ti can be from the resuspension of dust/soil particles by anthropogenic
245 activities (Amato et al., 2010). The small excess of potassium over potassium ion could also be due

246 to the resuspension of soil on the runway and the open land in the proximity of the sampling site
247 due to aircraft landing (Watson et al., 2001).

248 Despite the observed correlations, it cannot be totally excluded the contribution of vehicular traffic.
249 There is a severe shortage of data on the elemental composition of $PM_{2.5}$ emitted by aircraft, these
250 studies report that emissions are composed of various trace elements mainly originating from fuels,
251 lubricating oils, tyre wear, engine wear and corrosion, which are similar to those emitted from the
252 vehicular traffic (Masiol and Harrison, 2014 and references therein).

253

254 With the aim of identifying the elements more directly related to human activities and working
255 cycles, the concentrations observed at week-ends (Saturday, Sunday and holidays) and on week-
256 days have been examined and statistically differences tested by using Mann-Whitney U-test. No
257 significant differences were observed for $PM_{2.5}$ concentrations ($p > 0.05$). However, Na^+ , Fe and Mn
258 concentrations increase during working-days (+72%, +59%, +132%, respectively) at the AIR site.
259 Reductions in the traffic intensity during the week-end can explain these differences. Lawrence et
260 al. (2013) observed a good correlation between Na and traffic volume (samples were collected at a
261 tunnel entrance and exit) and associated Na to road salting to prevent ice forming on the road
262 surface. Moreover, several studies suggest Fe and Mn as marker for brake wear, tyre wear, and re-
263 suspension of non-exhaust vehicle emissions (Pant and Harrison, 2013 and references therein).
264 Differently, the TV site data show an increase for NH_4^+ (+18%), SO_4^{2-} (+20%), K^+ and K (+41%
265 and +31%, respectively) during the weekend. K^+ is usually considered as a marker of biomass
266 burning (e.g.: Cerasi Urban et al., 2012) and recently also ammonium and sulfate have been
267 observed in high pollution episodes from biomass burning (Karlsson et al., 2013). The sampling site
268 is located in a residential area. Thus, it is plausible that on weekends the biomass burning for
269 domestic heating increases.

270

271 *3.3 Identification and apportion of $PM_{2.5}$ sources*

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

277

278 The first factor profile accounts for K⁺, Cl⁻ and UNM with some amounts of Zn, Pb and Sb. It
279 accounts for 38% (21 μg m⁻³) and 37% (15 μg m⁻³) on mean of PM_{2.5} mass at AIR and TV,
280 respectively. K⁺ and Cl⁻ have been widely used as tracers of wood combustion and biomass burning
281 (e.g.: Johnson et al., 2006; Ryu et al., 2007) and the modelled elements have been associated with
282 wood pellet and cord wood combustion (Boman et al., 2006; Chandrasekaran et al., 2012; Wiinikka
283 et al., 2013). The UMN is likely to be the substantial amounts of organic carbon associated with
284 wood combustion. The peak of combustion contribution on January 6 supports this interpretation: in
285 the Veneto Region on the eve of Epiphany, a religious celebration (between January 5th and January
286 6th). At this time, thousands of bonfires burn wooden material particularly in the rural areas of
287 Venice and Treviso and causing an increase of PM_{2.5}, PM₁₀, K⁺ and total carbon levels (Masiol et
288 al., 2014b). Moreover, the biomass combustion source contributions are statistically significant
289 correlated with NO_x and CO (AIR: $r_{NO_x} = 0.6$; $r_{CO} = 0.7$; TV: $r_{NO_x} = 0.6$; $r_{CO} = 0.7$) in both sites.
290 This factor represents the biomass burning (wood and pellets) for domestic heating and other wood
291 burning activities.

292 This interpretation is also consistent with those reported in the last released emissions inventory
293 (ISPRA, 2015) that assigns a large part of primary PM_{2.5} and CO emissions to the group 2 - Non-
294 industrial combustion systems (41% and 44%, respectively), in particular to the sub-group
295 Residential heating (96% and 93%, respectively).

296

297 The second and third factors represent the secondary inorganic component of PM_{2.5} associated with
298 ammonium nitrate (NH₄⁺, NO₃⁻) and ammonium sulfate (NH₄⁺, SO₄²⁻). Ammonium nitrate and
299 ammonium sulfate apportion average 32% (18 μg m⁻³) and 13% (7 μg m⁻³), respectively, of PM_{2.5}
300 mass at the AIR site and 29% (12 μg m⁻³) and 13% (6 μg m⁻³), respectively, the TV site. These
301 secondary ions derive from gas-to-particle conversion processes. Similar contribution and trend can
302 be observed at both stations during the sampling period highlighting a widespread pollution of these
303 components (Fig. 4).

304

305 In the fourth factor, As, Cd and V are associated suggesting the presence of an industrial source that
306 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,
307 respectively. These elements can be related to industrial emissions from brick and ceramic factories,
308 glass making, non-ferrous metal production, and iron and steel manufacturing (Pacyna and Pacyna,
309 2001; Sánchez de la Campa et al., 2010; Taiwo et al., 2014). Although a large industrial zone is not
310 present, several small industrial activities affect the study area including those mentioned above
311 (Figure SI2).

312

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

320

321 The final factor includes Na⁺, Ni, and Cu as major species and minor amounts of Zn, Ti. It
322 contributes for 3% (2 μg m⁻³) and 14% (6 μg m⁻³) of PM_{2.5} mass at the AIR and TV sites,

323 respectively. This association can be related to the resuspension of road-dust, as non-exhaust
324 emissions (Ni, Cu, Zn) from tyre wear and brake wear, salt used for deicing (Na^+) and to the
325 abrasion of road surface (Ti) (Pant and Harrison, 2013 and references therein).

326

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

338 The highest concentrations of ammonium nitrate at the TV site can be addressed to the greater
339 availability of HNO_3 from high emissions of NO_x than at the AIR site. Despite this, ammonium
340 nitrate is correlated between the AIR and TV sites.

341 Changes in source contributions can be compared with the evolution of the mixing layer height in
342 Fig. 4. It can be observed that the higher concentrations of ammonium nitrate and combustion were
343 reached in correspondence of the lowest mixing layer heights that favor the accumulation processes
344 and lead to a homogeneity on source concentrations over the area. Ammonium sulfate shows a
345 different behavior. Higher concentrations were associated both to the lowest and to the highest
346 H_{mix} , thus the levels of ammonium sulfate might depend both on accumulation processes and on
347 intrusion of polluted air masses from farther areas during high H_{mix} events in the final days of
348 February.

349 Levels of traffic non-exhaust, industrial and resuspended dust do not appear influenced by Hmix
350 evolution.

351

352 *3.4 Influence of atmospheric circulation on PM and its sources*

353 To better understand the changing PM_{2.5} concentrations, the influence of atmospheric circulation
354 has been evaluated. The relationships between source contributions and ground-wind circulation
355 patterns were investigated by using CBPF (conditional bivariate probability function) analysis.

356 Computation of CBPF has been done by using Openair package for R (Carslaw, 2015).

357 Furthermore, external contributions due to long range transport processes were evaluated by
358 applying CWT (concentration weighted trajectory), a Trajectory Statistical Method (TSM) based on
359 back-trajectory analysis. In this study CWT has been computed by using TrajStat software (Wang et
360 al., 2009).

361

362 *3.4.1 Conditional bivariate probability function*

363 The conditional bivariate probability function (CBPF) couples ordinary CPF with wind speed as a
364 third variable, allocating the observed pollutant concentration to cells defined by ranges of wind
365 direction and wind speed rather than to only wind direction sectors. The CPF is defined as $CPF =$
366 m_{θ}/n_{θ} , where m_{θ} is the number of samples in the wind sector θ with concentrations greater than
367 some 'high' concentration ($> 75^{\circ}$ percentile, in this study), and n_{θ} is the total number of samples in
368 the same wind sector (Kim et al., 2003; Kim and Hopke, 2004). The extension to the bivariate case
369 provides more information on the nature of the sources (or chemical species) because different
370 source types can have different wind speed dependencies (Uria-Tellaetxe and Carslaw, 2014)
371 Computed CBPF plots are presented in Figure 5 and 6.

372 Ammonium nitrate shows that the highest probabilities at the AIR site were associated to wind
373 blowing from north, west and south both for weak, moderate and strong winds (Fig. 5) in
374 correspondence of the runway, trafficked roads and the residential area of Quinto di Treviso. High

375 probabilities towards south-west can also be observed at TV where the major highways are located
376 (Fig. 1). This pattern suggests both local formation/accumulation processes (associated to low wind
377 speed and to a greater availability of HNO₃ from high emissions of NO_x) and transport from farther
378 areas of ammonium nitrate.

379 Probabilities associated with ammonium sulfate increase with wind blowing from east at both sites.

380 The highest probabilities associated with combustion occur for winds characterized by low speeds
381 (2 m s⁻¹) blowing from south-west where the residential area of Quinto and Treviso are located.

382 The industrial source shows a preferential wind direction from south and east at TV (Fig. 6).

383 Alternatively, the highest probabilities were obtained with winds from the northeast and northwest
384 at the airport site where several small industries are located. Details of production activities and
385 their position relative to the sampling site are provided in the supplementary materials (Fig. SI2;
386 Table SI3).

387 At the AIR site, traffic non-exhaust emissions exhibit high probabilities associated for low wind
388 speeds, suggesting a source close to the sampling site such as the SR515 Noalese, one of the more
389 important trafficked roads of the area (Fig. 1). Conversely, in TV site high probabilities are
390 associated to wind blowing from south where the ring road of Treviso historical center is located.

391 The highest probabilities for resuspended dust were associated to moderate and high wind speeds
392 that enhance the resuspension process at both AIR and TV, supporting the interpretation of PMF
393 results.

394

395 3.4.2 Concentration weighted trajectory

396 CWT is a method of weighting trajectories with associated concentrations (Hsu et al., 2003). In this
397 procedure, each grid cell gets a weighted concentration obtained by averaging sample
398 concentrations that have associated trajectories that crossed that grid cell as follows, i.e. each
399 concentration is used as a weighting factor for the residence times of all trajectories in each grid cell
400 and then divided by the cumulative residence time from all trajectories (Hsu et al., 2003; Cheng et

401 al., 2013). In summary, weighted concentration fields show concentration gradients across potential
402 sources and highlight the relative significance of potential sources (Hsu et al., 2003).

403 In this study, 96 hours back-trajectories were computed by using the HYSPLIT model and global
404 data assimilation system (GDAS1) meteorological data fields (Draxler and Rolph, 2013; Rolph,
405 2013). The starting height was set at 100 m a.s.l. and 4 trajectories per day were computed per each
406 sampling day (at 3, 9, 15 and 21 UTC). Considering the proximity of the sampling sites, AIR site
407 coordinates were used as starting point. The geographical domain was divided into 1° by 1° grid
408 cells according to the meteorological data fields. The obtained maps are reported in Fig. 7.

409

410 High external contribution can be observed for combustion source only when air mass coming from
411 the Atlantic area and passing across the United Kingdom (12% of cases). This could be attributed to
412 the impact of wood pellet combustion for power generation in United Kingdom. In the last decade,
413 the United Kingdom replaced coal in their largest power utilities with wood pellet and burned about
414 4.7 tons of pellets for industrial use in 2014 (about 60% of EU-28 Industrial wood pellet
415 consumption) (AEBIOM, 2015).

416

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

420 During winter, high daily external contributions of ammonium sulfate have been already observed
421 in the Venice area (Squizzato and Masiol, 2015) when air masses coming from East-Europe, where
422 SO₂, the main precursor of sulfate aerosol and ammonium sulfate, still reaches high concentrations
423 (>10 µg m⁻³) (e.g., Poland, Romania, Serbia, Bulgaria, Greece and Turkey) (EEA, 2015).

424 This confirms what previously observed on CBPF that shows high probabilities associated both
425 with low wind speed (local emissions) and with moderate and strong winds.

426 Industrial source shows high probabilities on CBPF both for weak and strong wind, representing the
427 local and long range transport processes influence, respectively. In fact, high concentration gradient
428 is showed by CWT when trajectories coming from East Europe. Hence, a transboundary
429 contribution cannot be excluded for this source.

430 Results of CWT are interesting and may have significant implications for air quality assessment and
431 mitigation measures adopted, or to adopt, in the study area. $PM_{2.5}$ is a critical pollutant in the
432 Northern Italy due to the frequent exceeding of European air quality standards. All identified
433 sources apportion to a significant mass of $PM_{2.5}$ and among the main ones, ammonium sulfate and
434 industrial appear strongly influenced by external contributions. Changes in ammonium nitrate levels
435 can be addresses both to local formation process (favored by high levels of NO_x and
436 low temperatures, typical conditions during winter) and to long-range transport. On the contrary,
437 combustion source that contributes for a large part of $PM_{2.5}$ mass appears mainly linked to local
438 emissions. Under this scenario, effective mitigation strategies should consider these evidences.

439

440 **4. CONCLUSIONS**

441 $PM_{2.5}$ samples have been collected at two sites in Treviso (Po Valley, Italy), within one of the most
442 polluted areas in Europe. The main inorganic components of PM were determined (water soluble
443 inorganic ions and elements) and data have been processed to highlight compositional differences,
444 to determine PM sources and their contribution and to evaluate the influence of air masses
445 movements. A set of chemometrics tools have been used helping in understanding PM dynamics.
446 Therefore, the main findings can be summarized as follows:

- 447 • A widespread pollution has been highlighted for $PM_{2.5}$, water soluble inorganic ions, Fe, Zn,
448 Cd, Sb, V and O_3 ;
- 449 • Six sources of $PM_{2.5}$ have been identified and quantify: combustion, ammonium nitrate,
450 ammonium sulfate, industrial, traffic non-exhaust and resuspended dust. Combustion,
451 ammonium nitrate and ammonium sulfate are strong correlated between the two sites but

452 ammonium nitrate source shows statistically different contributions as well as industrial, traffic
453 non-exhaust and resuspended dust, probably due to the characteristics of the sampling sites.

- 454 • High external contribution can be observed for combustion source only when air mass coming
455 from the Atlantic area passing over the United Kingdom (only 12% of cases), indicating that the
456 local emissions has a strong effect on combustion concentrations during the sampling period;
- 457 • Ammonium sulfate appears strongly influenced by external contributions whereas ammonium
458 nitrate and industrial contributions can be addresses both to local and external contribution;
- 459 • Traffic non-exhaust and resuspended dust do not appear influenced by external contributions, as
460 expected. CBPF calculated on traffic non-exhaust contributions shows high probabilities towards
461 the south in the TV site and toward west in the AIR site in correspondence of trafficked roads
462 and also airport runway in AIR site. Highest levels of resuspended dust are probably associated
463 to moderate winds that enhance the resuspension both in AIR and TV.

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

471

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478

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641

642 **Table captions**

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

645

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

649

650 **Figure captions**

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

654

655 **Figure 2. Precipitations and daily average mixing layer height (H_{mix}) during the sampling**
656 **period.**

657

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

660

661 **Figure 4. Time series obtained by PMF analysis and daily average mixing layer height (H_{mix})**
662 **during the sampling period.**

663

664 **Figure 5. CBPF plots computed on source contributions for TV and AIR site for PMF factors:**
665 **combustion, ammonium nitrate and ammonium sulfate.**

666

667 **Figure 6. CBPF plots computed on source contributions for TV and AIR site for PMF factors:**
668 **industrial, traffic non-exhaust and resuspended dust.**

669

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