

# Application of meteorology-based methods to determine local and external contributions to particulate matter pollution: A case study in Venice (Italy)

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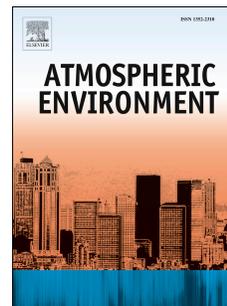
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Application of meteorology-based methods to determine local and external contributions to particulate matter pollution: A case study in venice (Italy)

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6 **APPLICATION OF METEOROLOGY-BASED**  
7 **METHODS TO DETERMINE LOCAL AND**  
8 **EXTERNAL CONTRIBUTIONS TO**  
9 **PARTICULATE MATTER POLLUTION: A**  
10 **CASE STUDY IN VENICE (ITALY)**

11  
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**ABSTRACT**

The air quality is influenced by the potential effects of meteorology at meso- and synoptic scales. While local weather and mixing layer dynamics mainly drive the dispersion of sources at small scales, long-range transports affect the movements of air masses over regional, transboundary and even continental scales. Long-range transport may advect polluted air masses from hot-spots by increasing the levels of pollution at nearby or remote locations or may further raise air pollution levels where external air masses originate from other hot-spots. Therefore, the knowledge of ground-wind circulation and potential long-range transports is fundamental not only to evaluate how local or external sources may affect the air quality at a receptor site but also to quantify it. This review is focussed on establishing the relationships among  $PM_{2.5}$  sources, meteorological condition and air mass origin in the Po Valley, which is one of the most polluted areas in Europe. We have chosen the results from a recent study carried out in Venice (Eastern Po Valley) and have analysed them using different statistical approaches to understand the influence of external and local contribution of  $PM_{2.5}$  sources. External contributions were evaluated by applying Trajectory Statistical Methods (TSMs) based on back-trajectory analysis including (i) back-trajectories cluster analysis, (ii) potential source contribution function (PSCF) and (iii) concentration weighted trajectory (CWT). Furthermore, the relationships between the source contributions and ground-wind circulation patterns were investigated by using (iv) cluster analysis on wind data and (v) conditional probability function (CPF). Finally, local source contribution have been estimated by applying the Lenschow' approach.

In summary, the integrated approach of different techniques has successfully identified both local and external sources of particulate matter pollution in an European hot-spot affected by the worst air quality.

**Keywords:  $PM_{2.5}$ , local and external contributions, meteorology-based methods**

69 **1. INTRODUCTION**

70 Since mid 90s, the European Community has adopted increasingly stringent standards for reduction  
71 of emissions to improve air quality. Such efforts have generally led to an overall improvement of air  
72 quality in most of the EU Countries. However, there are still some European regions that are  
73 affected by high levels of air pollutants - the so-called hot-spots. Among others, Northern Italy,  
74 Benelux, some Eastern Countries and greater urban areas such London and Paris deserve particular  
75 attention because of their high population density.

76 Generally, the main causes of high air pollution levels in hot-spots are the additive effects of: (i)  
77 heavy local emissions from many anthropogenic sources; (ii) peculiar weather and/or orographic  
78 features limiting the dispersion of locally emitted pollutants and (iii) the regional or even trans-  
79 boundary transport of polluted air masses from external source areas. The first cause is primarily  
80 related to the levels of urbanization and industrialization: since most hot-spots lie in densely  
81 anthropised areas which are affected by relatively heavy emissions from traffic, energy production  
82 and industrial activities. Beyond the local emission sources, air quality may be further influenced by  
83 the potential effects of meteorology at meso- and synoptic scales. While local weather and mixing  
84 layer dynamics mainly drive the dispersion of sources at small scales, long-range transports affect  
85 the movements of air masses over regional, trans boundary and even continental scales and may  
86 have two opposite but potentially concurrent effects: (i) they can advect polluted air masses from  
87 hot-spots by increasing the level of pollution at near areas or even remote locations, and/or (ii) they  
88 may further raise air pollution levels where external air masses originate from other hot-spots.

89 Therefore, the knowledge of ground-wind circulation and potential long-range transports is essential  
90 to evaluate how and how much local or external sources may affect the air quality at a receptor site.

91 The main goal of this study is to establish a relationship among  $PM_{2.5}$  sources, meteorological  
92 condition and air mass origin through the application of a multiple methods and tools. The results of  
93 a recent source apportionment study carried out in Venice (Eastern Po Valley) over three sites were  
94 evaluated using various statistical approaches to determine the influence of external and local  
95 contribution on identified  $PM_{2.5}$  sources. External contributions were evaluated by applying  
96 Trajectory Statistical Methods (TSMs) based on back-trajectory analysis: (i) back-trajectories  
97 cluster analysis; (ii) potential source contribution function (PSCF) and (iii) concentration weighted  
98 trajectory (CWT). Furthermore, the relationships between the source contributions and ground-wind  
99 circulation patterns were investigated using (iv) cluster analysis on wind data and (v) conditional  
100 probability function (CPF). Finally, local source contributions have been estimated following the  
101 approach proposed by Lenschow et al. (2001).

102 The application of multiple techniques has identified both local and external sources of particulate  
103 matter pollution in an European hot-spot affected by worst air quality. We strongly believe that the

104 proposed approaches will be useful for the future air quality assessment studies and reduction  
105 strategies.

106

## 107 **2. MATERIALS AND METHODS**

### 108 *2.1 Study area*

109 While Northern Italy has fulfilled the same mitigation processes adopted by other European  
110 Countries towards emissions reduction, it has not fully benefited in terms of substantial reduction of  
111 air pollution. As of today, the Po Valley is one of the most polluted areas in the Europe for  
112 particulate matter (PM), ozone and nitrogen oxides (EEA, 2015). Local emissions are expected to  
113 be more important in Po Valley than in other European areas (Maurizi et al., 2013) although  
114 Gilardoni et al. (2011) showed that local sources mainly affect fine PM (aerodynamic diameter less  
115 than 2.5  $\mu\text{m}$ ,  $\text{PM}_{2.5}$ ) during winter while the influence of regional air masses from the nearby Po  
116 Valley dominates in summer. Moreover, the generation of secondary aerosol is known to form over  
117 the Valley that rapidly build-up air pollution after clean-air episodes which is governed by the  
118 particular topology and meteorological conditions of the plain (Larsen et al., 2012; Masiol et al.,  
119 submitted).

120 Venice is located between the eastern edge of the Po Valley and the Adriatic Sea. Along with the  
121 city of Mestre, they form a large coastal urban municipality hosting 270,000 inhabitants. The  
122 emission scenario includes sources of PM such as high density residential areas, heavy traffic roads  
123 mostly congested during peak hours, a motorway and a motorway-link part of the main European  
124 routes E55 and E70, an extended industrial area (Porto Marghera) with a large number of different  
125 installations, including incineration plants and a large thermoelectric power plant burning coal and  
126 refuse-derived fuel, the artistic glassmaking factories in the island of Murano, heavy shipping traffic  
127 providing public/commercial and tourist transports and an international airport. The apportionment  
128 of the most relevant PM sources and their spatial and seasonal changes (Masiol et al., 2012a;2014b)  
129 as well as the regional and local influence of PM and secondary aerosol have been investigated  
130 (Squizzato et al., 2012; Masiol et al., submitted). Moreover, the potential influence of local or long-  
131 range transports upon PM mass and PM-bound pollutants were investigated in a series of sparse  
132 studies (e.g., Masiol et al., 2010; 2012a,b; Squizzato et al., 2012; 2014), but its role on standard  
133 breaching has not yet comprehensively assessed.

### 134 *2.2 Experimental*

135 A year-long  $\text{PM}_{2.5}$  sampling campaign (February 2009 - January 2010) was carried out at the three  
136 sites indicative of different environments (Fig. 1):

- 137 • a semi-rural background coastal site (SRB) installed on a coastal lighthouse upwind of the major  
138 local emission sources;
- 139 • an urban background site (URB) established in a high density residential zone of Mestre, very  
140 close (~50 m) to the main traffic roads;
- 141 • an industrial site (IND) placed downwind of Porto Marghera and the surrounding area that has  
142 extensive road and shipping traffic.

143 Four time periods were selected for chemical analysis: spring (March-April 2009), summer (June-  
144 July 2009), autumn (September-October 2009) and winter (December 2009-January 2010). Filters  
145 were cut into two portions: one to determine major inorganic ions via ion exchange chromatography  
146 (IC) (after water extraction) and the second to quantify elements via ICP-OES and ICP-MS after  
147 acid digestion. Analytical methods are reported elsewhere (Squizzato et al., 2012; 2014).

148 Common weather data including wind speed and direction, air temperature, relative humidity, solar  
149 radiation and precipitations were hourly measured at two stations near the sampling sites (Fig. 1):  
150 ARPAV Cavallino-Treporti was chosen as being representative of SRB, while EZI5 (part of the  
151 network of Ente della Zona Industriale di Porto Marghera) for URB and IND. Wind data were  
152 homogenized and appropriate corrections were applied when necessary. The wind speeds  $< 0.5 \text{ m}$   
153  $\text{s}^{-1}$  (anemometer detection limit) were assumed as calm wind whereas uncertain data or hours with  
154 fast changes in wind direction were excluded from the analysis.

### 155 *2.3 Overview of back-trajectories and trajectory-based models*

156 There are number of methods that are currently used in air pollution studies to account for long-  
157 range transports (Fleming et al., 2012 and references therein). Back-trajectory analysis is a  
158 commonly-used tool for tracing the history of air masses passing over a location at a defined time.  
159 Briefly, interpolated measured or modelled meteorological fields are used to infer backward in time  
160 the most probable paths of infinitesimally small particles of air that at the time zero are located at a  
161 starting point. In this study, back-trajectories were computed using HYSPLIT (Draxler and Rolph,  
162 2015; Rolph, 2015). Our model set-up parameters included 4 days (-96 h) run time, starting height  
163 of 20 m AGL, NCEP/NCAR Reanalysis data fields.

164 It is important to stress that back-trajectories are potentially associated with large uncertainties  
165 (Stohl, 1998) mostly due to the oversimplification of the atmosphere in that dispersion is not  
166 accounted for. Moreover, back-trajectories may be highly variable when run at different hours in a  
167 day, causing further uncertainty when associated with daily pollutant data. To overcome large  
168 uncertainties, the confidence of back-trajectories was tested using different starting heights and  
169 hours: errors associated with a single trajectory were reduced by simulating four trajectories for  
170 each sampling day (at 3:00, 9:00, 15:00 and 21:00). Taking into account the range of associated

171 uncertainties, the use of multiple trajectory-based models over long periods may yield more robust  
172 results than the use of individual trajectories and may provide useful information about the external  
173 source areas.

174 Back-trajectory modelling combined with atmospheric concentrations measured at the receptor site  
175 are commonly referred to Hybrid Receptor Models (HRMs) (Han et al., 2007) or Trajectory  
176 Statistical Methods (TSMs) (Kabashnikov et al., 2011; Brereton and Johnson, 2012). Most used  
177 TSMs are: Potential Source Contribution Function (PSCF) (Hsu et al., 2003; Pekney et al., 2006;  
178 Kim et al., 2005; Gildemeister et al., 2007; Han et al., 2007), Gridded Frequency Distributions  
179 (GFD) (Weiss-Penzias et al., 2011), Concentration Fields Analysis (Rutter et al., 2009),  
180 Concentration-Weighted Trajectory (CWT) (Seibert et al., 1994) and Residence Time Weighted  
181 Concentration (RTWC) (Hsu et al., 2003; Han et al., 2007). All these methods essentially count the  
182 frequency of back-trajectory segment endpoints in grid cells that make up the geographical domain  
183 of interest for the receptor site (Cheng et al., 2013).

184 In this study three methods have been used, moreover an approach to determine the uncertainties  
185 associated with PSCF is also proposed. Details of each method are provided as supplementary  
186 material:

- 187 • *Cluster analysis on back-trajectories*: the principal purpose of back trajectories clustering is  
188 to group trajectories having similar geographic origins and histories. The subsequent  
189 coupling of clusters with chemical data associated to air pollutants is a simple but powerful  
190 way to infer insights into the potential contribution of long-range transports from different  
191 pathways.
- 192 • *PSCF*: It was initially developed to identify the likely locations of the regional PM sources  
193 (Lee and Hopke, 2006; Pekney et al., 2006) and calculates the probability that a source is  
194 located at latitude  $i$  and longitude  $j$ . The basis of PSCF is that if a source is located at  
195 coordinates  $i$  and  $j$ , an air parcel back-trajectory passing through that location indicates that  
196 material from the source can be collected and transported along the trajectory to the receptor  
197 site. The PSCF value can be interpreted as the conditional probability that concentrations  
198 larger than a given criterion value are related to the passage of air parcels through a grid cell  
199 with this PSCF value during transport to the receptor site (Hsu et al., 2003). This method is  
200 deficient in the determination of the statistical significance of its outcome and is suitable for  
201 identifying possible source regions (Dvorska et al., 2008 and references therein). Generally,  
202 PSCF values of 0.00–0.50 are considered as low whereas the values of 0.51–1.00 are  
203 considered as high.
- 204 • *CWT*: the concentration weighted trajectory is a method of weighting trajectories with  
205 associated concentrations (Hsu et al., 2003). In this procedure, each grid cell gets a weighted

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

- 212 • *Evaluation of the uncertainties associated with PSCF*: despite the scientific literature  
213 proposes different methods, at today there is not a unique standardized technique for  
214 assessing the better estimates of the PSCF probabilities and their uncertainties. For example,  
215 Pekney et al. (2006) used weighting functions multiplied by PSCF values for reducing the  
216 effect of spurious large ratios in grid cells, while Lupu and Maenhaut (2002) and Hopke et  
217 al. (1995) applied bootstrap techniques to estimate the statistical significance and the  
218 uncertainties of the calculated PSCF values, respectively. Bootstrapping is not yet  
219 implemented in the Openair package, however the package used weighted PSCF values  
220 depending on the number of values in each cell (weights factors range from 0.15 to 2). The  
221 bootstrapping techniques are widely used in chemometrics and provide accurate tools for  
222 yielding estimates in cases where other methods are simply not available (Wehrens et al.,  
223 2000). This way, the uncertainties associated to PSCF values in this study were estimated  
224 externally by using a non-parametric bootstrap method. Briefly,  $n=500$  subsamples  
225 including 80% of the total number of trajectories were re-sampled without replacement from  
226 the original dataset and PSCF was then re-run for each subsample. The 500 new PSCFs  
227 maps were then merged to assess the average values and their associated standard deviations  
228 for each cell in the grid domain. The uncertainties over the average results were then  
229 expressed as average  $\pm$  standard deviation.

#### 231 2.4 Overview of wind-based methods

232 The effectiveness of coupling air pollution data with wind data fields for identifying and accounting  
233 local sources was largely demonstrated in a number of studies using very different approaches and  
234 techniques (e.g., Ashbaugh et al., 1985; Kaufmann and Whiteman, 1999; Kim et al., 2003; Carslaw  
235 et al., 2006; Viana et al., 2006; Masiol et al., 2012a; Uria-Tellaetxe and Carslaw, 2014). Such  
236 approaches are based on the assumption that air pollutants emitted from a source are transported by  
237 local winds. As a consequence, the levels of pollution recorded at a receptor site under downwind  
238 conditions from the source should be higher when air blows from different sectors. However, these  
239 methods generally disregard many issues linked to the dispersion of pollutants in the atmosphere,  
240 e.g., the influence of atmospheric stability and turbulence on dilution of pollutants, the effects of the

241 mixing layer height on wind dynamics, the concentration-wind speed dependencies for certain  
242 pollutants, the street canyon and urban canopy layer effects, etc. Despite the limitations, methods  
243 for coupling air pollution with wind data are very useful in extracting information on local source  
244 contributions and locations. Wind-based methods applied in this study aim to couple source  
245 apportionment results with local wind fields recorded at ground:

- 246 • *Cluster of wind data*: The hourly data of wind speed and direction from the weather station  
247 were processed by extracting their scalar components  $u$  and  $v$  relative to the North–South  
248 and West–East axes (Kaufmann and Whiteman, 1999; Darby, 2005). In this study the hourly  
249 values of the components were separately summed to obtain daily data, which represents the  
250 resultant vector of the air movement. A hierarchical cluster analysis using the Ward's  
251 method and the squared Euclidean distance measure were then performed on these  
252 components.
- 253 • *CPF*: the conditional probability function (Kim et al., 2003; Kim and Hopke, 2004) analyses  
254 local source impacts from varying wind directions using the source contribution estimates  
255 from PMF coupled with the time-resolved wind directions. The CPF estimates the  
256 probability that a given source contribution from a given wind direction will exceed a  
257 predetermined threshold criterion. The sources are likely to be located at the directions that  
258 have high conditional probability values (Kim et al., 2005). Details are reported as  
259 supplementary material.

260

### 261 *2.5 Lenschow approach*

262 Local contributions can be estimated using the method proposed by Lenschow et al. (2001). Briefly,  
263 the method essentially compares the PM levels and components (PMF sources, in this case)  
264 measured in sites affected by different emission scenarios (semi-rural, urban and industrial, in this  
265 case). In this study we assumed that: (i) the differences of particulate matter and its chemical  
266 components between URB and IND can be attributed to the local influence of urban and industrial  
267 area, respectively and (ii) SRB represents a rural background station affected by regional sources  
268 with little contribution from the urban and industrial area. Only URB and IND samples with higher  
269 concentration than SRB have been considered.

270

## 271 **4. RESULTS AND DISCUSSION**

### 272 *4.1 Overview on PMF results*

273 A multiple-site positive matrix factorization receptor model was performed over 448 PM<sub>2.5</sub> samples  
274 and 19 variables. Details of adopted methods and results are exhaustively reported in Masiol et al.  
275 (2014b). Six factors associated with potential sources were extracted and apportioned, namely:

- 276 • secondary sulphate (made up of  $\text{SO}_4^{2-}$  and  $\text{NH}_4^+$ );
- 277 • ammonium nitrate and combustions ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$  plus combustion tracers  $\text{K}^+$  and  $\text{Cl}^-$ )
- 278 linked to gas-to-particles conversion processes involving  $\text{NH}_3$  and  $\text{NO}_x$  (emitted both from
- 279 industries and traffic) and various combustion processes:  $\text{K}^+$  was associated to biomass
- 280 combustion processes (Kundu et al., 2010) and the association  $\text{K}^+$ -  $\text{Cl}^-$  was attributed to
- 281 gasoline vehicle emissions (Spencer et al., 2006);
- 282 • fossil fuels (V, Ni);
- 283 • traffic, mainly related to primary traffic emissions and road dust resuspension (Fe, Ti, Mn,
- 284 Cu, Ba,  $\text{Mg}^{2+}$ );
- 285 • industrial (Zn, Pb,  $\text{Mg}^{2+}$ );
- 286 • glassmaking (As, Cd).

287 The quantification of sources revealed that on annual basis the most impacting source in all the sites

288 is ammonium nitrate and combustions, accounting for  $\sim 12 \mu\text{g m}^{-3}$  at all the sites, i.e. 47% of the

289  $\text{PM}_{2.5}$  mass in SRB and 38 % in URB and IND. Ammonium sulphate is the second largest

290 contributor, accounting for  $5.6 \mu\text{g m}^{-3}$  (24 % in SRB and 17 % in URB and IND sites). As a matter

291 of fact, such sources account for most of the  $\text{PM}_{2.5}$  mass (71% in SRB and 55% in URB and IND)

292 and their mass contributions are identical at all the sites, indicating that they are homogeneously

293 distributed throughout the area.

294

295 On the contrary, the remaining sources show different and variable contributions at the three sites.

296 This result is an early indication of their potential strong component of local origin: industrial

297 source contributes  $7.1 \mu\text{g m}^{-3}$  in IND,  $4.8 \mu\text{g m}^{-3}$  in URB and  $3.6 \mu\text{g m}^{-3}$  in SRB, followed by road

298 traffic ( $5.5 \mu\text{g m}^{-3}$  in URB,  $3.3 \mu\text{g m}^{-3}$  in IND and  $0.6 \mu\text{g m}^{-3}$  in SRB), fossil fuels ( $2.9 \mu\text{g m}^{-3}$  in

299 IND,  $2.1 \mu\text{g m}^{-3}$  in URB and  $1.9 \mu\text{g m}^{-3}$  in SRB) and glassmaking ( $1.7 \mu\text{g m}^{-3}$  in URB,  $1.1 \mu\text{g m}^{-3}$

300 in IND and  $1 \mu\text{g m}^{-3}$  in SRB).

301

#### 302 *4.2 Results of trajectory-based methods*

303 Seven clusters are identified using the measure of the Euclidean distance and are named according to

304 their common origin. Five clusters are linked to long-range transports from Atlantic, Central

305 Europe, Northern Europe, Eastern EU and Western Mediterranean. Remaining two clusters are

306 associated with more local transports from East-Austria and from South/Central Italy. Fig. 1 shows

307 the frequency of trajectories passing through the grid cells in the grid domain and the average

308 trajectories associated to each identified cluster. The number of trajectories in each cluster is

309 reported in Table 1: a large number of trajectories pass over the Po Valley or blow from East-

310 Europe. These latter two clusters depict the two overwhelming pathways during the sampling

311 campaign. The potential effects of long-range/regional transports are then assessed by averaging the  
312 levels of  $PM_{2.5}$  and source contributions overall the study period: Table 1 reports the average  
313 concentrations calculated for each cluster as well as the percentage of differences with respect to the  
314 mean of the overall sampling period in the semi-rural background coastal site as considered affected  
315 to regional sources with little contribution from the urban and industrial area. Generally, results  
316 show an evident increase of  $PM_{2.5}$  and ammonium sulphate when air masses originated from  
317 Eastern Europe (+ 40 % and + 124 %, respectively), ammonium nitrate increases when air masses  
318 come from Atlantic and Western Mediterranean area (+ 35 % and + 17 %, respectively) and fossil  
319 fuel source when air masses blow from South (+ 60 %). On the contrary, industrial, glass making  
320 and traffic only slightly increases when masses move from Eastern Europe and in East-Austria.  
321 Results also show significant drops of concentrations of  $PM_{2.5}$ , ammonium nitrate and fossil fuels  
322 for Central and Northern Europe clusters.

323  
324 Generally, PSCF and CWT analyses return very similar results, but they give some more clues  
325 about the potential source location. Resulting PSCF plots for  $PM_{2.5}$  and PMF sources are shown in  
326 Fig. 2, while their associated uncertainties are provided as Figure SIIa and SIIb. Maps are  
327 calculated over the whole sampling campaign and are not smoothed because the low number of  
328 trajectories used (only trajectories with concentrations >75th percentile). Uncertainties calculated  
329 by bootstrapping the trajectories are generally low for all the variables, allowing to extract the  
330 following information. High probabilities (range 0.5-0.6) of high levels of fossil fuels combustion  
331 and ammonium nitrate are found in Po Valley, while industrial, ammonium sulphate and road traffic  
332 contributions show elevated probabilities in East-Europe (range 0.3 - 0.7) and glass-making source  
333 from Eastern and Southeastern Countries. With respect to the glass-making sources, it should be  
334 noted that near SRB sampling site, there is a local glass-making industry. Hence, the increase of  
335 probability can be due to the mix of local air masses with external air masses and not necessarily  
336 only from an external contribution.

337 Although CWT distributes concentration along the trajectories similarly to PSCF, this method has  
338 an advantage that it distinguishes major sources from moderate ones by calculating concentration  
339 gradients (Hsu et al., 2003). CWT maps presented in Fig. 3a and 3b demonstrates smoothed data  
340 split for sampling seasons. The concentration gradients indicate Po Valley and East-Europe as  
341 significant contributors of  $PM_{2.5}$  and related PMF sources. Seasonally, high external contribution  
342 can be observed during spring and winter, reaching  $40 \mu g m^{-3}$  and  $30 \mu g m^{-3}$  for  $PM_{2.5}$  and  
343 ammonium nitrate, respectively. In addition, other sources show potential external contribution  
344 during summer (fossil fuels combustion and glass-making) and autumn (ammonium sulphate,

345 industrial, road-traffic and glassmaking). In particular, the external contributions of ammonium  
346 sulphate from East-Europe reach  $14 \mu\text{g m}^{-3}$  during autumn and winter.

347

348 Results of trajectory-based methods are interesting for a number of reasons and may have  
349 significant implications for air quality assessment and mitigation measures adopted, or to adopt, in  
350 the study area.  $\text{PM}_{2.5}$  is a critical pollutant in Venice and in the Northern Italy due to the frequent  
351 exceeding of European air quality standards.

352

353 Ammonium nitrate and combustion source is the main contributor of  $\text{PM}_{2.5}$  apportioned by the PMF  
354 analysis and also has PSCF and CWT maps quite identical to  $\text{PM}_{2.5}$  for source locations,  
355 probability/concentrations and seasonal trends. Under this scenario, it is evident that it plays a key  
356 role in breaching of  $\text{PM}_{2.5}$  standards. Although the source apportionment has not separated the two  
357 main components behind this source (likely because of the limitation to distinguish elemental and  
358 organic carbon), results indicate they have likely a similar potential origin, which is principally  
359 linked to weather conditions and anthropogenic emissions. Nitrate aerosol mainly derives from the  
360 atmospheric oxidation of  $\text{NO}_2$  and the combustion of fossil fuels (road traffic and industries) is by  
361 far the dominant source of nitrogen oxides in Europe. Moreover, nitrate is a semi-volatile  
362 compound and its partitioning is favoured toward particle-phase in coldest periods. Similarly,  
363 combustion emissions generally increase in coldest periods due to contributions from domestic  
364 heating and the recent increase of the number of pellet stoves in use in Northern Italy is expected to  
365 boost this trend. Results of PSCF and CWT show a strong potential contribution from regional  
366 transports from Po Valley (spring, autumn, winter) and from Central (spring) and Eastern (winter)  
367 Europe. These findings are in line with the EEA airbase maps (EEA, 2015), which clearly show that  
368 Northern Italy, Central Europe and in minor extent some Eastern Countries are affected by the  
369 highest annual average levels of measured  $\text{NO}_2$ . The seasonal behaviour is also consistent with  
370 results, since spring and winter were the coldest periods during the sampling campaign. Moreover,  
371 carbonaceous matter that can be considered mainly related to combustion processes presents the  
372 highest contribution in central Europe and the ratio  $\text{TC}/\text{PM}_{10}$  is generally larger in this area (Putaud  
373 et al., 2010).

374

375 The increasingly high standard for fossil fuels and industrial emissions in Central Europe have lead  
376 a significant drop of  $\text{SO}_2$  levels in Central and Western Europe to concentrations well below  $10 \mu\text{g}$   
377  $\text{m}^{-3}$  (EEA, 2015). However,  $\text{SO}_2$  still reach high concentrations ( $>10 \mu\text{g m}^{-3}$ ) in some Eastern and  
378 Southeastern locations (e.g., Poland, Romania, Serbia, Bulgaria, Greece and Turkey). Since  $\text{SO}_2$  is  
379 the main precursor of sulphate aerosol and ammonium sulphate account for 17 % -24 % of total

380 PM<sub>2.5</sub> mass in Venice, results of this study indicate a strong influence of trans-boundary transports.  
381 However, many studies attribute SO<sub>2</sub> and ammonium sulphate aerosol in the Mediterranean area  
382 also to the high maritime traffic in particular for the role of SO<sub>2</sub> as gaseous precursor on secondary  
383 formation processes (e.g.: Cesari et al., 2014; Salameh et al., 2015), nevertheless shipping emissions  
384 are not the main trigger of PM pollution episodes encountered in the Mediterranean basin (Salameh  
385 et al., 2015).

386 Moreover, a recent study conducted in the Veneto region (Masiol et al., 2015) demonstrated that  
387 sulphate levels are constant, showing similar daily trends and mean throughout the region and  
388 highlighting that both the accumulation/removal processes in the region are similar. In regards to  
389 SO<sub>2</sub>, Sacca Fisola (a Venice monitoring station close to the Grand Canal where cruise ships pass)  
390 shows similar concentration to the IND site on annual mean (ARPAV, 2011). IND site is affected  
391 by industrial activities (petrochemical plant, coal power plant) and shipping traffic. Therefore,  
392 despite maritime traffic contributes strongly to pollutant source in the coastal area, in the study area  
393 it can be considered negligible with respect to other contributions.

394  
395 Although glass-making industry source is considered of local origin because the emissions from the  
396 Island of Murano, the high probability in PSCF and the high concentration gradient in CWT are not  
397 surprising. The trajectories coming from SE are often associated with typical wind regimes called  
398 “Scirocco”, which bring hot and wet air masses from the Adriatic region. Under this wind regime,  
399 the Island of Murano is just upwind to the sampling sites and the results of trajectory analyses may  
400 be subjected to an artefact. However, a transboundary origin cannot be excluded for this source. The  
401 elemental tracer in this source (As and Cd) can be also linked to industrial processes, mining and  
402 other anthropogenic activities (Moreno et al., 2006; Lim et al., 2010).

#### 403 404 *4.3 Cluster on wind data and CPF*

405 Five groups of days with similar atmospheric circulation patterns were found in data obtained from  
406 both the weather stations. A 15 % cut-off level has been applied while processing data. Average  
407 wind speeds (Ws) and predominant directions were then plotted for the full period and each group  
408 in Fig. 4. Kruskal-Wallis test has been applied to highlight which sources are statistically different  
409 (p value < 0.05) respect to the average conditions (all sampled days) among the identified groups.

410  
411 Group 1 (N=44) includes days with prevailing wind from quadrant I, with high speeds and very low  
412 percentage of calm wind hours (0.5 %). Fast north-easterly winds called “bora” form peculiar cold  
413 and gusty downslope windstorms blowing over the Adriatic Sea and bringing air masses from  
414 Northern Europe. Generally, in the study area these conditions may cause increased sea-spray

415 generation and dispersion of pollutants (Masiol et al. 2010). In fact, in these conditions, a general  
416 decrease of all contributions can be observed in all three sites, in particular for industrial, glass-  
417 making and ammonium nitrate show a clear drop in contributions (-54 %, -48 %, -83 % on mean,  
418 respectively) and are statistically different to the full period mean. Group 2 (N=93) includes days  
419 with middle intensity winds blowing mainly from N-NE, other directions are negligible. This group  
420 is mainly composed of autumn and winter days and can represent the atmospheric circulation  
421 occurring during cold periods. In these days, fossil fuels contribution decrease and, on the contrary  
422 an increase in industrial component can be observed in IND (+39 %) and URB sites (+42 %) as  
423 well as traffic (+35 % and +34 % in IND and URB, respectively). This shows that the wind speed is  
424 decisive in the dispersion of pollutants and even a small decrease could lead to a widespread  
425 accumulation of pollutants.

426 Group 3 (N=75) includes conditions with ~50 % of winds from quadrant I and ~50 % of winds from  
427 the quadrant II. Winds from quadrant II are frequent mainly during the warmer seasons, in fact no  
428 winter days are included due to the sea-breeze circulation, but they can describe a peculiar wind  
429 pattern called “Scirocco,” bringing warm air masses from southern Adriatic and Mediterranean  
430 regions. Fossil fuels, industrial and ammonium nitrate are statistically different to the full period  
431 mean: fossil fuels shows an increase in contribution (+49% and +21% in IND and URB,  
432 respectively) while industrial and ammonium nitrate contributions decrease with the lowest  
433 contributions reached in SRB (-51% and -55%, respectively). The highest wind speed (2.0 - 2.7 m s<sup>-1</sup>)  
434 favours the dispersion of these sources but enhance the transport of fossil fuel related compounds.  
435 Moreover, the decrease on ammonium nitrate contribution can be also linked to the fact that winter  
436 samples (enriched in nitrate and ammonium) are not included in this group.

437 Group 4 includes only spring days (SRB=31; IND=27; URB=29) characterized by wind blowing  
438 from SE. In these conditions clean air from Adriatic Sea results in low contributions of all sources  
439 except fossil fuels combustion. Similar to group 3, wind from II quadrant enhances the input of  
440 fossil component (+44 %, +80 % and +61 % in IND, URB and SRB respectively). Group 5 (N=11)  
441 includes days characterized by a high percentage of wind calm (about 20 %), low speeds (1 - 1.9  
442 m/s) and no prevailing direction. These “stagnation” conditions were associated to the rise of  
443 locally emitted pollutants (Masiol et al., 2010); in fact an increase of industrial and ammonium  
444 nitrate contribution can be observed in all three sites (+30 % and +50 % on mean, respectively).  
445 Among the identified sources, industrial, ammonium nitrate and fossil fuel combustion appear more  
446 sensitive to atmospheric circulation changes. In particular, fossil fuels contribution enhance in days  
447 characterized by wind blowing from SE (group 3 and 4) while industrial and ammonium nitrate  
448 levels are most affected by the different wind speed. Despite this, our analysis does not help in

449 understanding the source locations with respect to each sampling site, may be due to a widespread  
450 pollution condition that affects the study area.

451 In this view, the application of CPF method provides the most probable sources of pollution for  
452 each location. CPF values for each sources that apportion to PM<sub>2.5</sub> are plotted in polar coordinates in  
453 Fig. 5. CPF permits to better highlight the possible location of each identified source. The highest  
454 probabilities are reached to the sources characterized by a significant local contribution (traffic,  
455 industrial and glass-making) whereas the probability associated to ammonium nitrate and  
456 ammonium sulphate tends to be lower according to their secondary origin and the homogeneous  
457 distribution in the study area (Squizzato et al., 2012).

458 Traffic shows high probability toward east in all three sites and south in URB and IND site in  
459 correspondence with the street located near the sampling sites.

460 In SRC the highest probability for industrial contribution is reached toward north: this may be due  
461 to the influence of the engineering works for the construction of high-tide preventing dams at the  
462 Venice Lagoon entrance.

463 The highest probability for glass-making is reached toward south and east in IND site due to the  
464 emissions of local industries in Murano Island, located east of the site. Fossil fuels shows the  
465 highest probability associated to wind blowing from SE. This highlights the influence of the  
466 combustion processes occurring in the industrial zone on URB and IND site. In regards to SRB site,  
467 the increase of probability can be due to the ship traffic toward Venice.

468

#### 469 *4.5 Lenschow approach*

470 Yearly, local sources contribute for 9.8  $\mu\text{g m}^{-3}$  of PM<sub>2.5</sub> amounting to 28 % and 30 % of masses in  
471 URB and IND site respectively (Table 2). Seasonally, the highest local contributions were observed  
472 in spring and winter both in URB (11.3  $\mu\text{g m}^{-3}$  and 15.5  $\mu\text{g m}^{-3}$ ) and IND site (10.4  $\mu\text{g m}^{-3}$  and  
473 12.5  $\mu\text{g m}^{-3}$ ) whereas the highest percentage was reached in summer (31 % in URB and 40.5 % in  
474 IND site). Among the identified sources, ammonium nitrate and ammonium sulphate show the  
475 lowest local contribution (31 % and 26 % respectively) confirming the results obtained applying the  
476 CWT, highlighting high external contribution for these sources. Traffic sources show the highest  
477 local contribution (83 % and 74 % in URB and IND site respectively), followed by glass making,  
478 industrial and fossil fuels combustion.

479 During heavy PM events (> 75<sup>th</sup> percentile) local contribution on PM expressed in  $\mu\text{g m}^{-3}$  increases  
480 (20.4  $\mu\text{g m}^{-3}$ ) whereas the local contribution percentages are similar to the average conditions (28.4  
481 % and 27.7 %, respectively). Nevertheless, considering the mass percentage, no significant  
482 variations have been observed for all periods and samples for PM and its sources. Fossil fuels

483 source represents an exception: during these events the local contribution reaches the 56 % and the  
484 63 % in URB and IND respectively that is about twice the average percentage of samples.  
485 On this basis, local contribution is important and it is strongly affected to local atmospheric  
486 circulation that governs the level of PM and its component. During high polluted episodes the local  
487 contributions do not increase and the increase of PM and related sources can be addresses to  
488 external contribution.

489

## 490 **Conclusions**

491 The knowledge of ground-wind circulation and potential long-range transports is fundamental to  
492 evaluate how and how much local or external sources may affect the air quality at a receptor site.  
493 In this study, the results of a recent source apportionment study carried out in Venice (Eastern Po  
494 Valley) are used as input for different statistical approaches. Meteorology-based methods (back-  
495 trajectories and wind-based methods) have been used to determine the influence of external and  
496 local contribution on identified PM<sub>2.5</sub> sources.

497 About applied methodologies some consideration can be done:

- 498 • Cluster on back-trajectories represents an easy but effective method to evaluate the potential  
499 effects of long-range/regional transports. It helps in understanding the area of origin but  
500 does not provide a precise location.
- 501 • Generally, PSCF and CWT analyses return very similar results to cluster but they give some  
502 more clues about the potential source location.
- 503 • Despite CWT distributes concentration along the trajectories similarly to PSCF, this method  
504 has an advantage: it distinguishes major sources from moderate ones by calculating  
505 concentration gradients and it becomes more effective in estimating of external  
506 contributions.
- 507 • Cluster on wind data partially help in understanding the source locations respect to each  
508 sampling site. The analysis can be affected to widespread pollution condition and the wind  
509 speed component tends to dominates in the interpretations of results respect to direction.
- 510 • The application of CPF provides understanding of the most probable sources location, with  
511 the highest probability associated to the local sources respect to the external ones (e.g. road  
512 traffic).
- 513 • Lenschow's approach represents a useful method to estimate local contribution but it  
514 requires to have a good knowledge of the study area and its emission sources and more than  
515 one measurement sites at least one of these considerable as a background site. This may be a  
516 limitation to its applicability.

517 Obtained results highlighted the complexity of atmospheric dynamics in the study area and our  
518 influence on PM and sources levels: (i) external contributions are a not negligible intake of PM<sub>2.5</sub>  
519 and (ii) local atmospheric circulation determines different levels of source contribution and some  
520 specific direction have been detected.

521 PM sources contributions are influenced by external contribution coming mainly from Po Valley  
522 and East-Europe. Seasonally, high external contribution can be observed during spring and winter  
523 reaching 40  $\mu\text{g m}^{-3}$  and 30  $\mu\text{g m}^{-3}$  for PM<sub>2.5</sub> and ammonium nitrate, respectively. Moreover, the  
524 external contributions of ammonium sulphate, that represent the second PM mass source, reach 14  
525  $\mu\text{g m}^{-3}$  during autumn and winter over East-Europe.

526 Among the identified sources, industrial, ammonium nitrate and fossil fuel combustion appear more  
527 sensitive to local atmospheric circulation changes. In particular, fossil fuels contribution enhance in  
528 days characterized by wind blowing from SE while industrial and ammonium nitrate levels are most  
529 affected by the different wind speed. Other sources do not show a strong dependence on the wind  
530 direction.

531 Lenschow's approach has allowed to estimate the local contribution on PM and its sources: yearly,  
532 local sources contribute for 9.8  $\mu\text{g m}^{-3}$  of PM<sub>2.5</sub> amounting to 28 % and 30 % of masses in URB and  
533 IND site, respectively. During heavy PM events the local contribution percentage are similar to the  
534 average conditions (28.4 % and 27.7 %, respectively), hence the increase of PM and related sources  
535 can be mainly addresses to external contribution. Only fossil fuels represent an exception: during  
536 these events the local contribution reaches the 56 % and the 63 % in URB and IND, respectively,  
537 about twice the average percentage of samples.

538

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546

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## 690 **Table captions**

691  
692 **Table 1. Average concentrations ( $\mu\text{g m}^{-3}$ ) and percentage difference respect to all samples mean ( $\Delta\%$ )**  
693 **in SRB samples of PM<sub>2.5</sub> and source contributions for each identified back-trajectories cluster.**

694 **Table 2. Local contribution expressed in  $\mu\text{g m}^{-3}$  and % estimated using Lenschow' approach for URB**  
695 **and IND site.**

## 696 **Figure captions**

697  
698 **Fig. 1. Sampling site locations (a), gridded back trajectory frequencies (b) and back-**  
699 **trajectories clusters (c).**

700 **Fig. 2. PSCF probabilities for PM<sub>2.5</sub> and identified sources (75<sup>th</sup> percentile).**

701 **Fig. 3a. CWT for PM<sub>2.5</sub>, ammonium nitrate and ammonium sulphate sources.**

702 **Fig. 3b. CWT for industrial, traffic, glassmaking and fossil fuel combustion sources.**

703 **Fig. 4. Results of cluster analysis on wind data: box-plots and wind roses for each identified**  
704 **cluster (Chs = wind calm hours; Ws = average wind speed). Boxes represent inter-quartile**

705 ranges; squared dots are the median, while whiskers represent quartiles  $\pm$  (1.5\*inter-quartile  
706 ranges).

707 **Fig. 5. CPF plots for the highest 25% of the mass contributions.**

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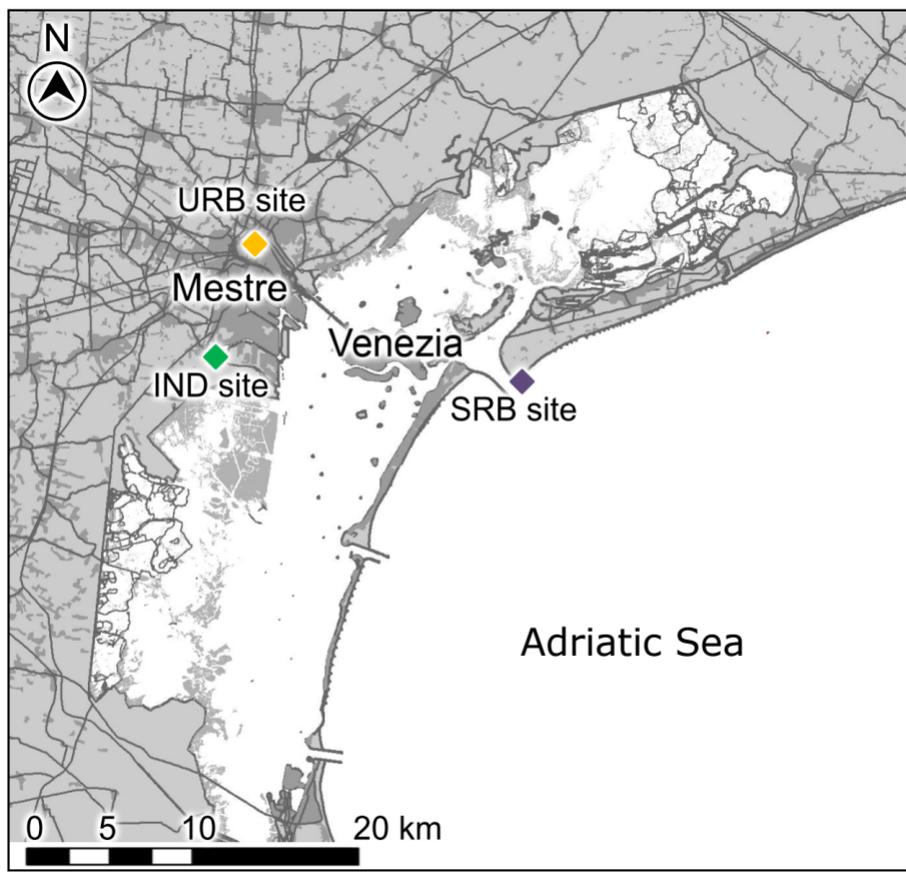
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**Table 1. Average concentrations ( $\mu\text{g m}^{-3}$ ) and percentage difference respect to all samples mean ( $\Delta\%$ ) in SRB samples of  $\text{PM}_{2.5}$  and source contributions for each identified back-trajectories cluster.**

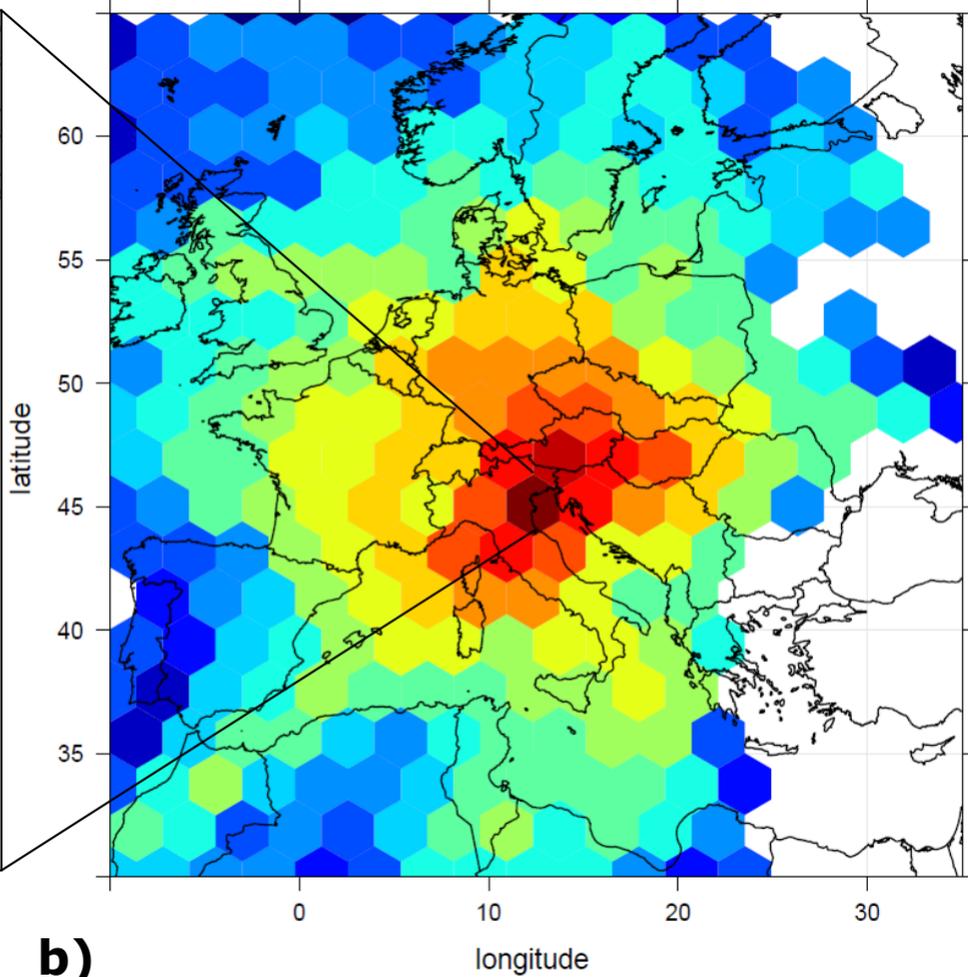
	$\text{PM}_{2.5}$		Industrial		Fossil fuels		Amm. Nitrate		Glass-making		Amm. Sulfate		Road traffic	
	Mean	$\Delta$ (%)	Mean	$\Delta$ (%)	Mean	$\Delta$ (%)	Mean	$\Delta$ (%)	Mean	$\Delta$ (%)	Mean	$\Delta$ (%)	Mean	$\Delta$ (%)
Atlantic (N=7)	23.6	-5	3.1	-13	2.2	15	15.8	35	1.6	57	1.0	-83	0.2	-75
Central EU (N=18)	16.2	-35	2.9	-21	2.1	11	7.8	-33	0.7	-30	2.2	-62	0.6	-16
Northern EU (N=14)	15.6	-37	2.4	-34	1.1	-45	9.0	-24	0.8	-27	2.0	-66	0.4	-32
East – Austria (N=42)	26.4	7	4.5	24	1.7	-10	12.0	2	1.4	33	6.1	2	0.9	35
Eastern EU (N=21)	34.6	40	5.8	62	0.9	-54	12.5	7	1.2	18	13.4	124	0.9	39
South (N=37)	25.0	1	2.3	-36	3.1	60	12.3	5	0.8	-26	6.3	5	0.5	-23
Western MED (N=15)	24.9	1	3.4	-5	1.5	-24	13.7	17	0.8	-21	5.1	-14	0.6	-11
All samples	24.7		3.6		1.9		11.7		1.0		6.0		0.7	

**Table 2. Local contribution expressed in  $\mu\text{g m}^{-3}$  and % estimated using Lenschow' approach for URB and IND site.**

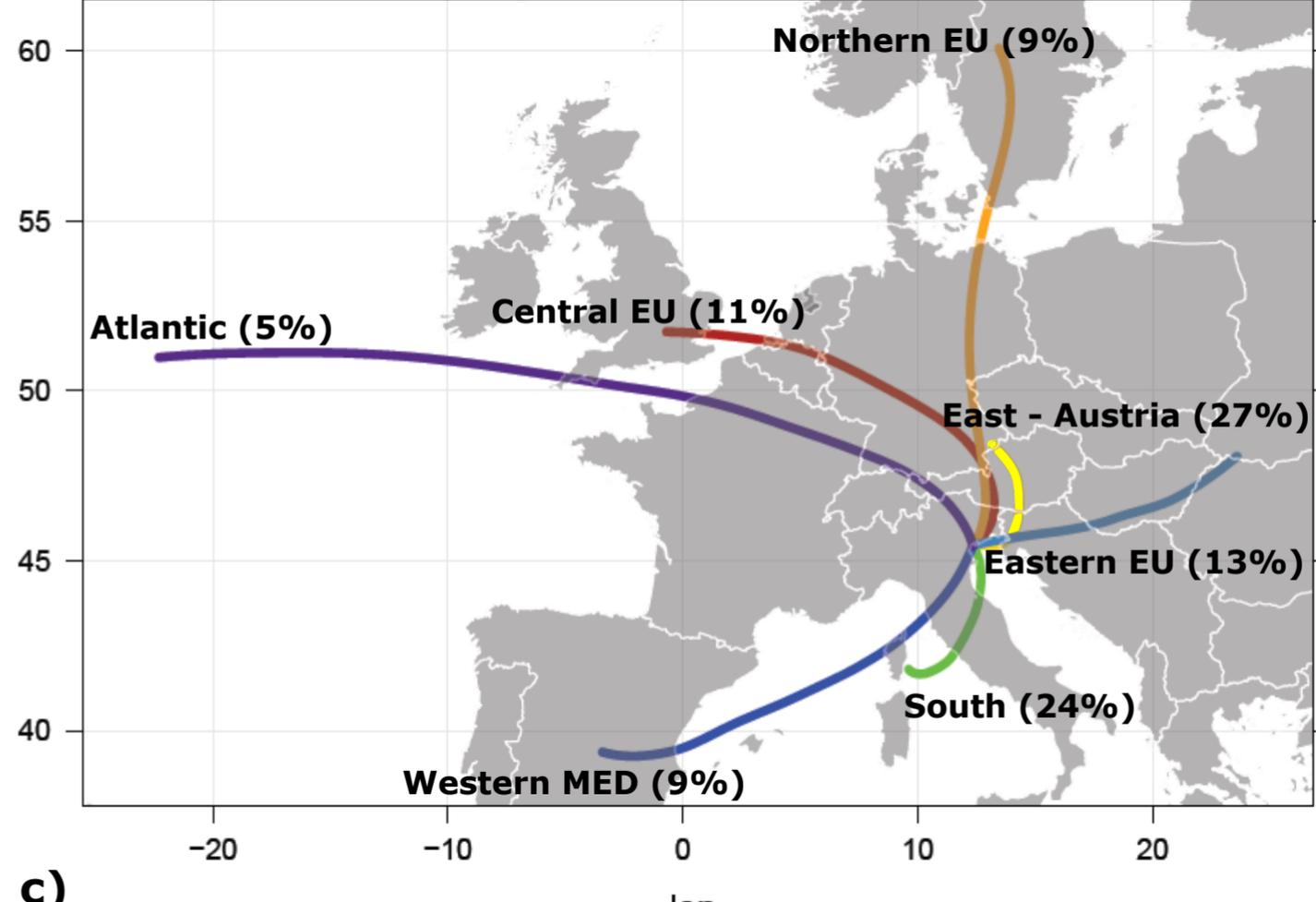
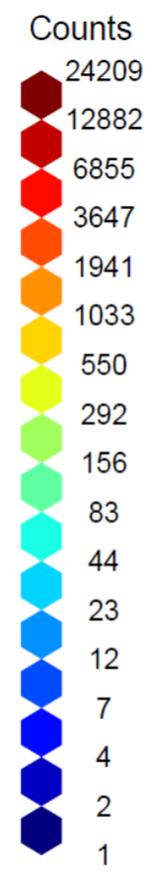
	PM <sub>local</sub>		Industrial <sub>local</sub>		Fossil <sub>local</sub>		Amm. nitrate <sub>local</sub>		Glass <sub>local</sub>		Amm. sulfate <sub>local</sub>		Traffic <sub>local</sub>	
	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%	$\mu\text{g m}^{-3}$	%
<b>Via Lissa (URB)</b>														
All samples	9.8	27.7	2.5	40.0	1.3	34.8	5.6	31.0	1.2	58.8	1.0	25.6	5.2	82.8
Spring	11.3	26.3	2.5	52.2	1.2	32.0	6.2	20.5	1.6	67.7	1.8	39.0	5.0	86.9
Summer	4.5	31.2	1.7	32.5	1.4	32.2	0.8		1.2	59.3	0.5	20.1	2.5	76.3
Autumn	5.7	24.5	1.6	42.9	1.6	43.2	4.5	50.3	1.1	64.3	0.7	23.9	6.9	84.7
Winter	15.5	28.6	3.3	31.8	0.2	42.5	5.9	30.1	1.1	44.4	1.2	25.7	5.1	81.2
Heavy PM Events (>75 <sup>th</sup> percentile)	20.4	28.4	4.4	41.8	2.5	56.3	7.9	24.6	1.3	51.7	1.8	19.1	6.1	80.9
<b>Malcontenta (IND)</b>														
All samples	9.8	29.9	4.6	53.8	1.9	54.6	5.1	34.0	1.1	57.5	1.3	31.3	3.4	74.3
Spring	10.4	31.7	4.9	69.3	2.0	46.1	6.3	36.7	1.4	69.5	1.8	42.8	5.1	91.3
Summer	8.9	40.5	3.7	52.8	1.9	40.0	3.6	55.2	1.3	67.3	0.5	28.3	0.6	58.5
Autumn	6.6	25.4	3.1	48.2	2.3	64.4	2.3	39.9	0.5	44.0	1.5	33.0	3.5	75.2
Winter	12.5	24.8	5.9	48.4	1.1	81.9	5.6	28.2	0.8	38.0	1.4	26.6	2.9	66.9
Heavy PM Events (>75 <sup>th</sup> percentile)	17.6	27.2	6.9	46.0	1.8	62.6	6.0	26.4	0.9	41.8	1.5	20.8	3.6	66.4



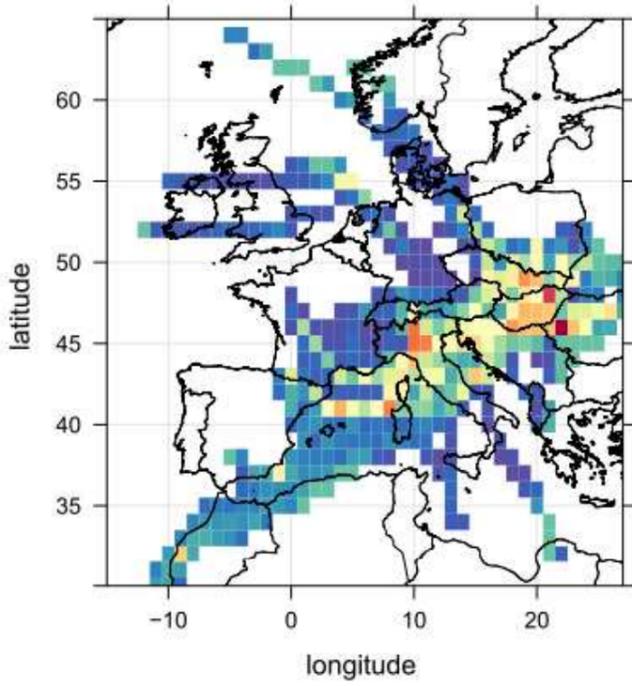
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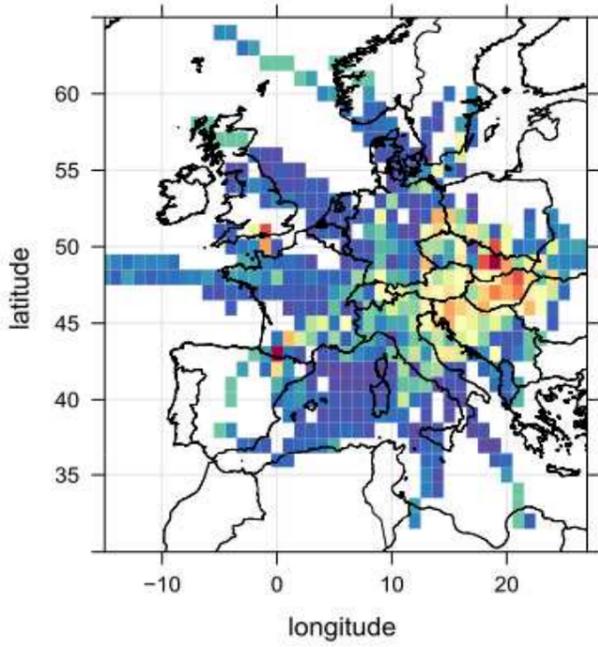
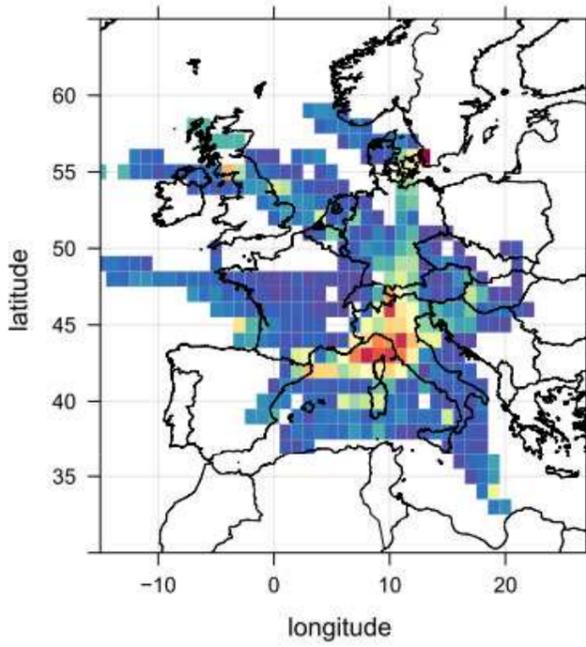
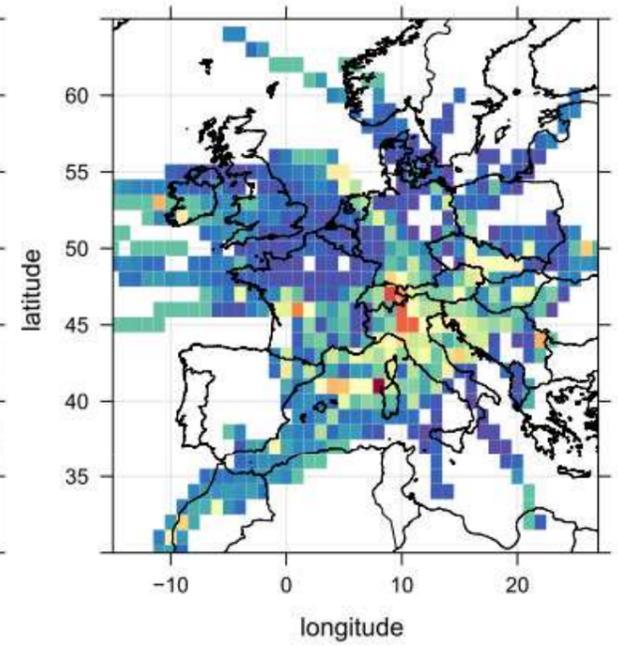
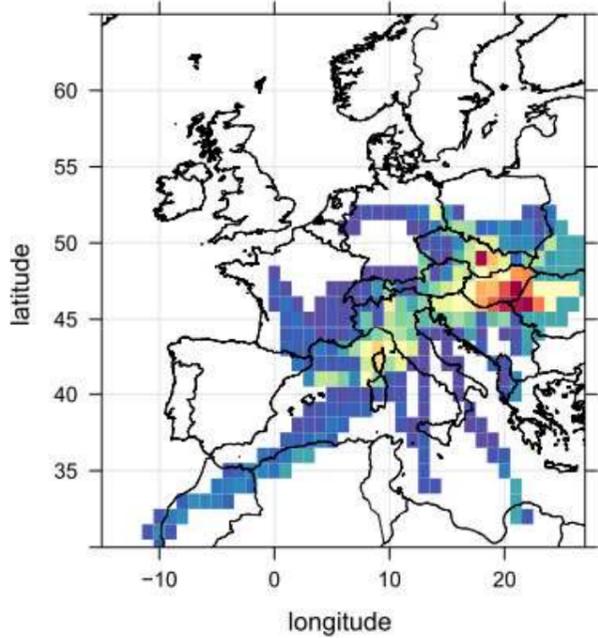
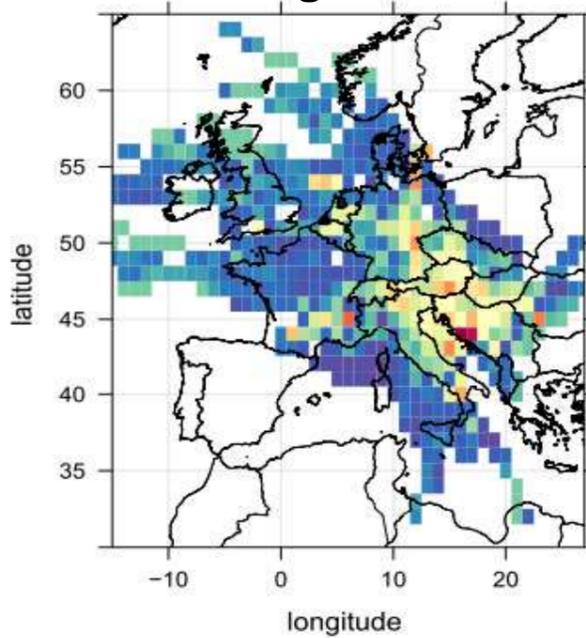
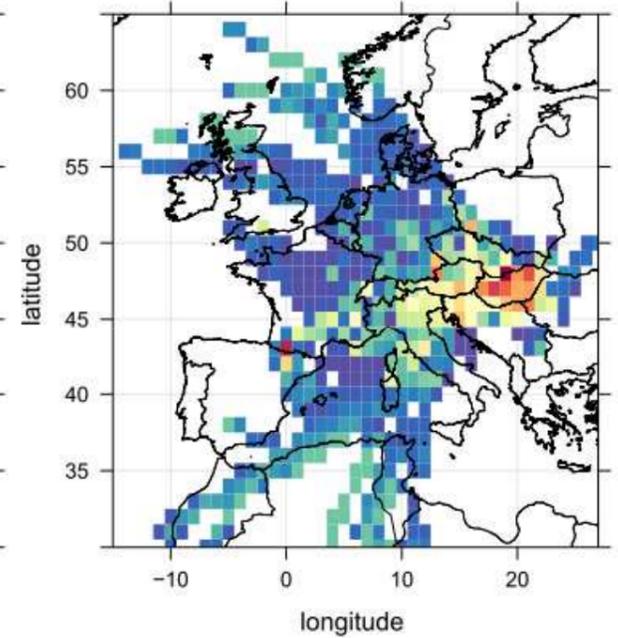
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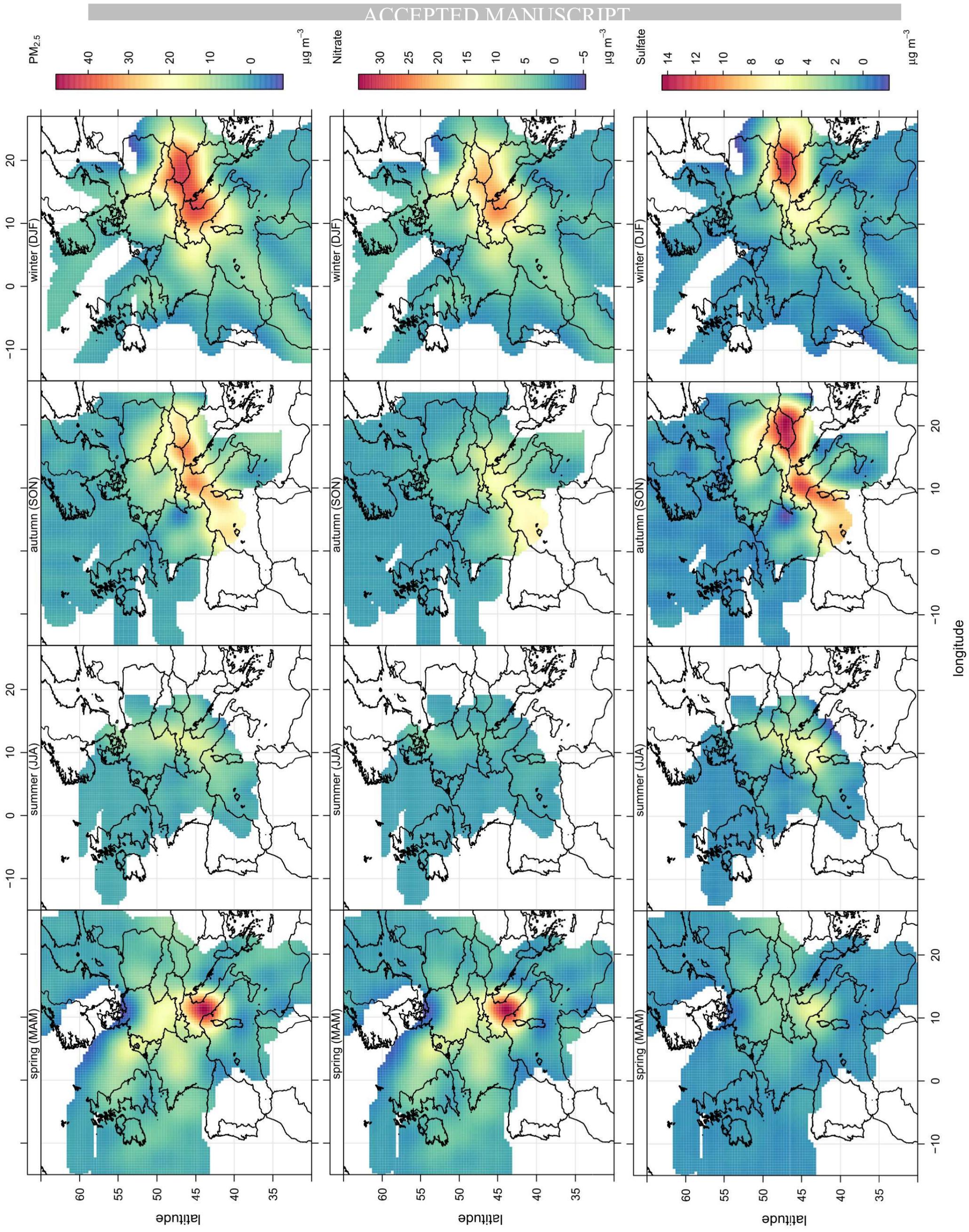


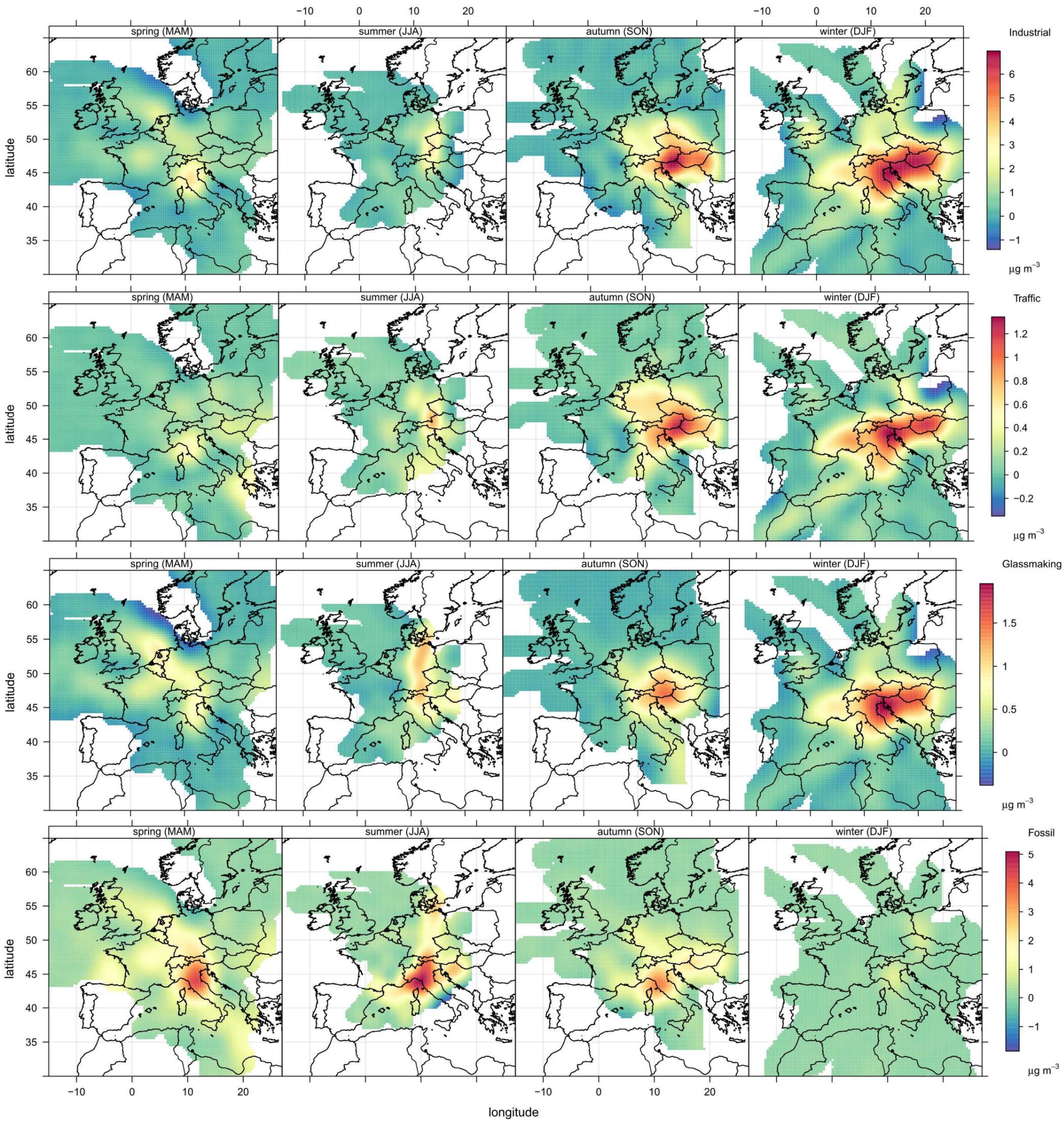
c)

**PM<sub>2.5</sub>****PSCF probability**

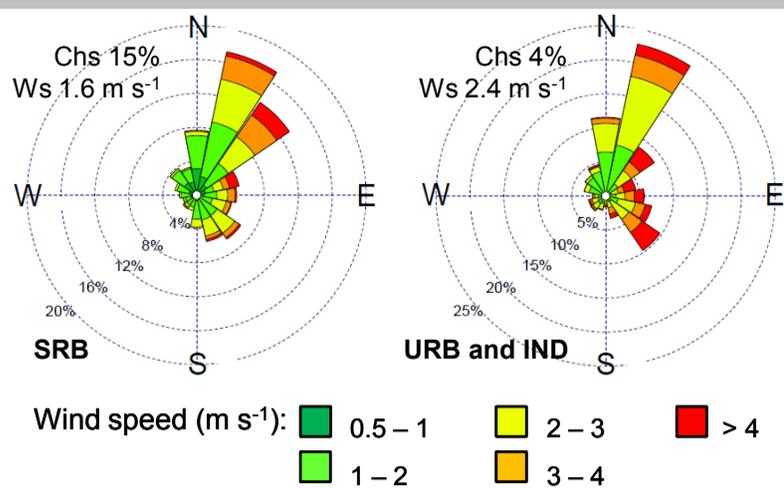
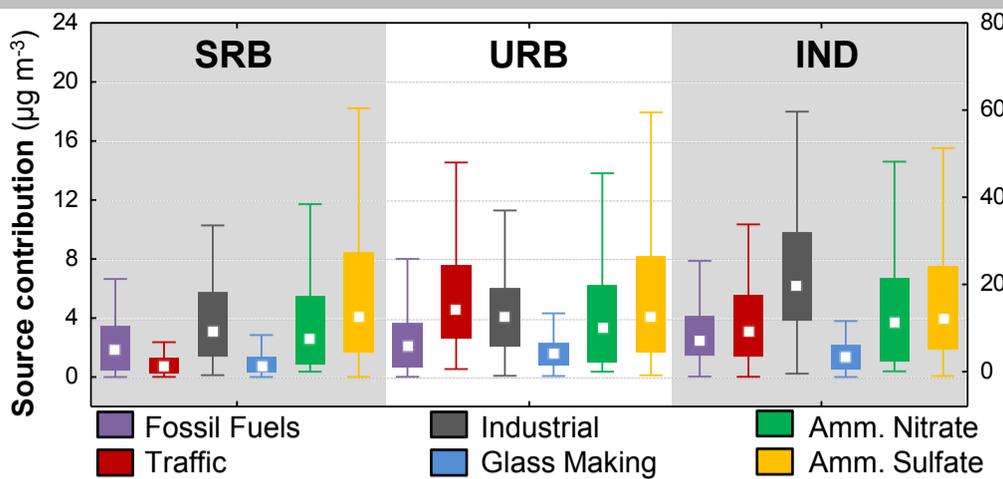
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**Industrial****Fossil fuels****Ammonium nitrate****Ammonium sulfate****Glass-making****Traffic**

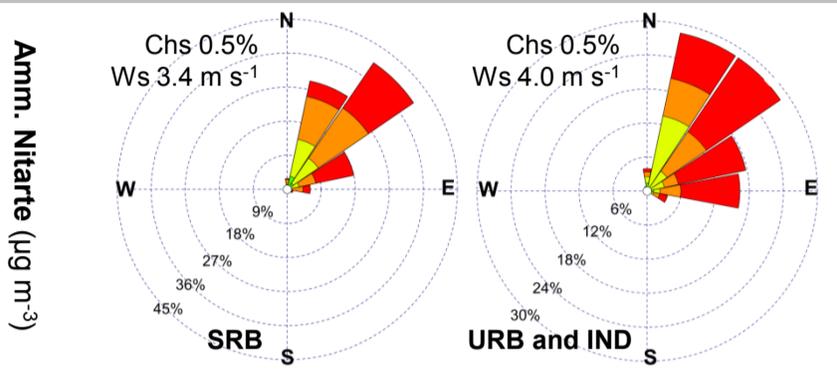
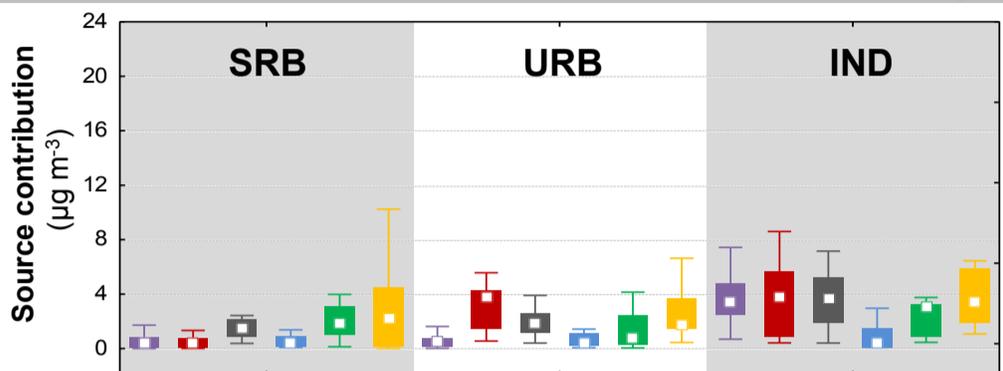




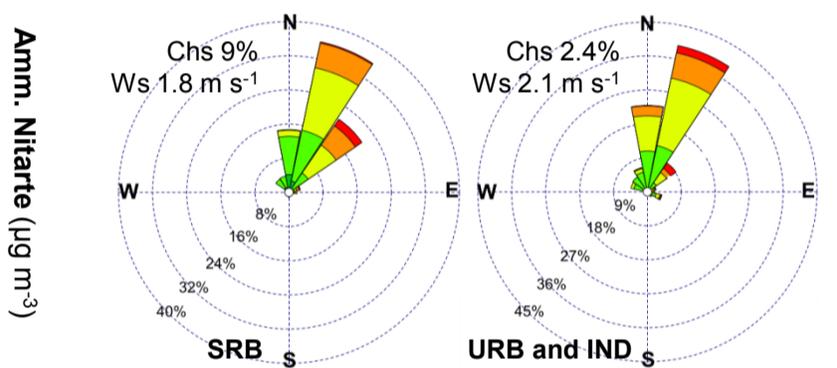
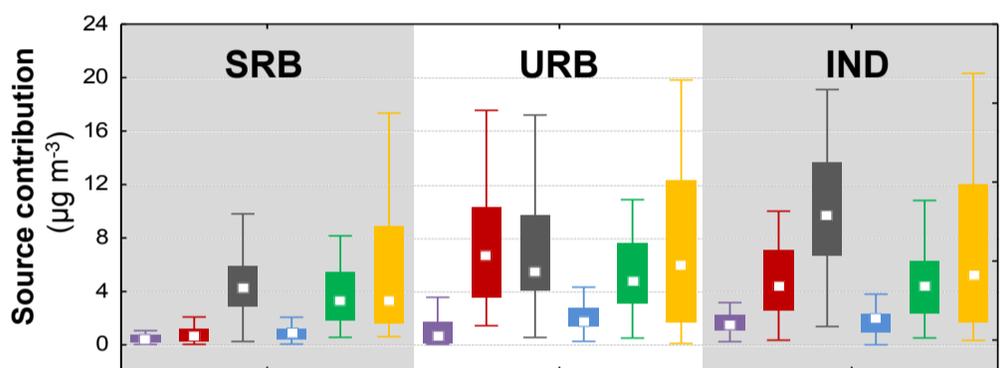
# ALL: full period



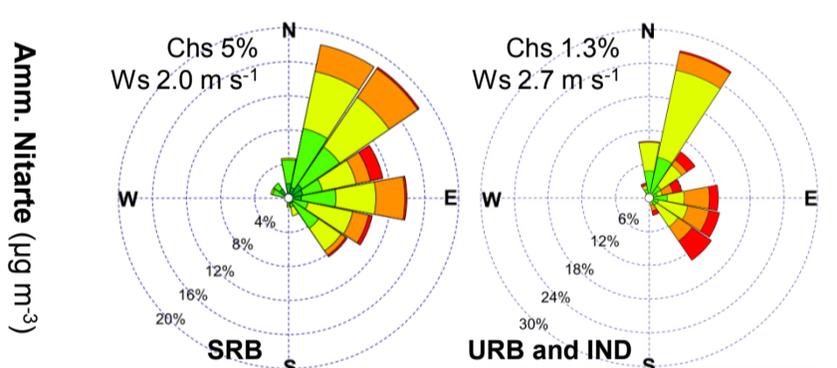
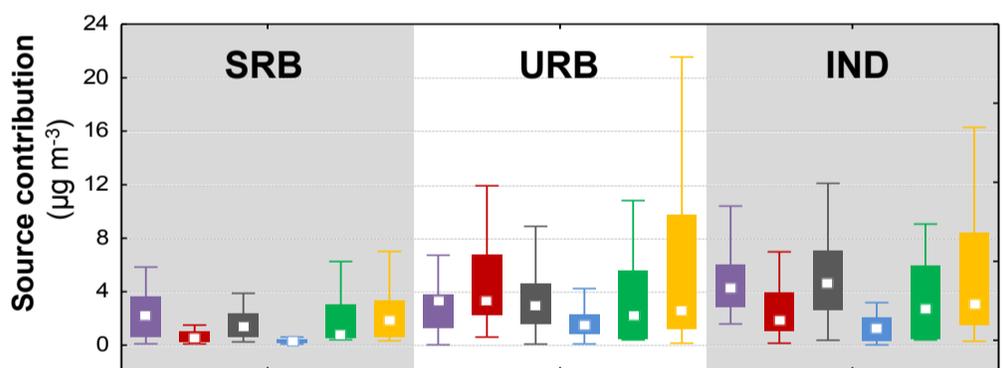
## Group 1



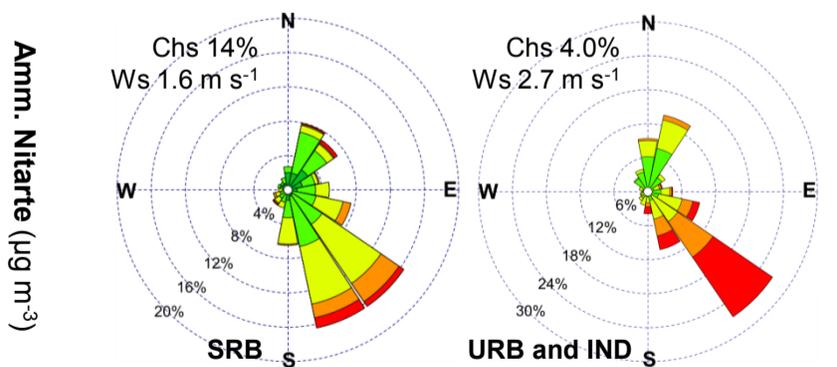
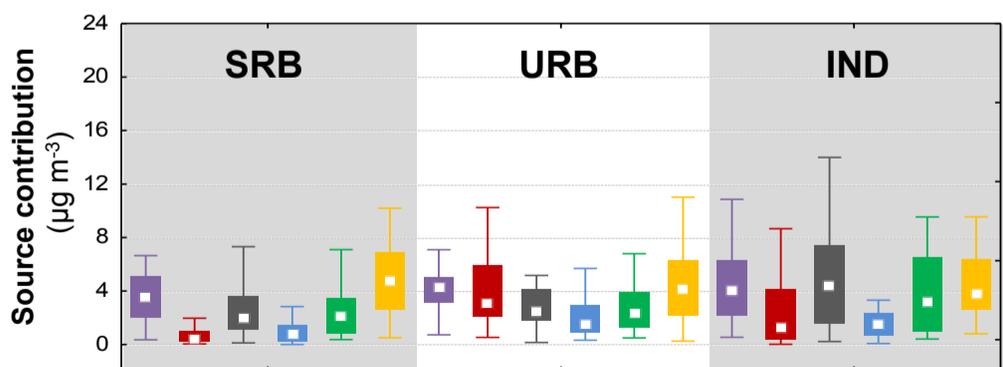
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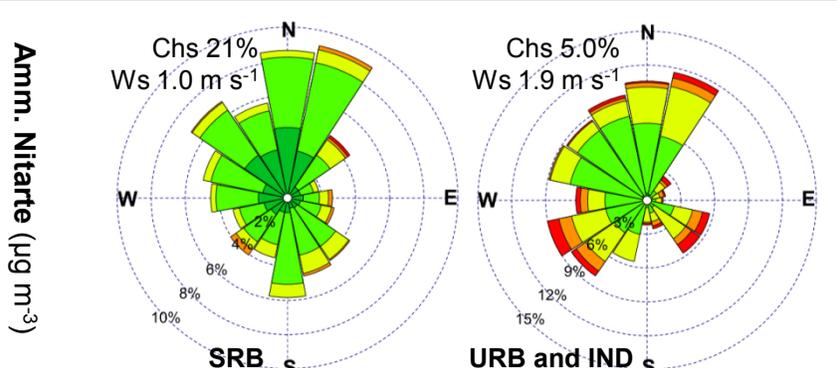
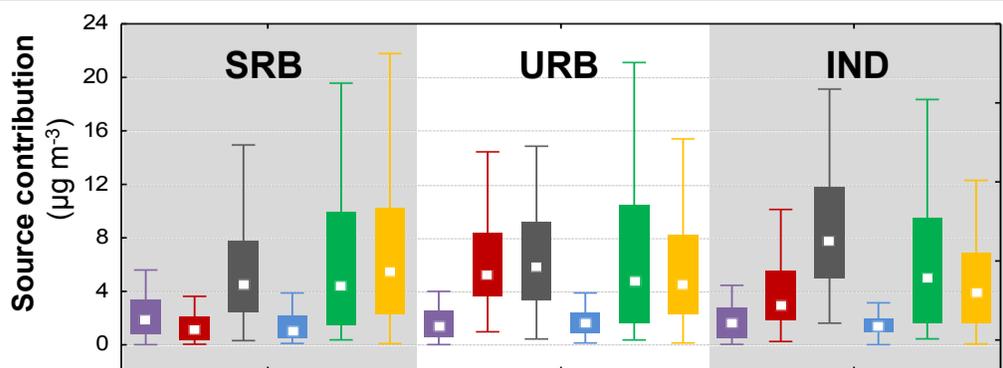
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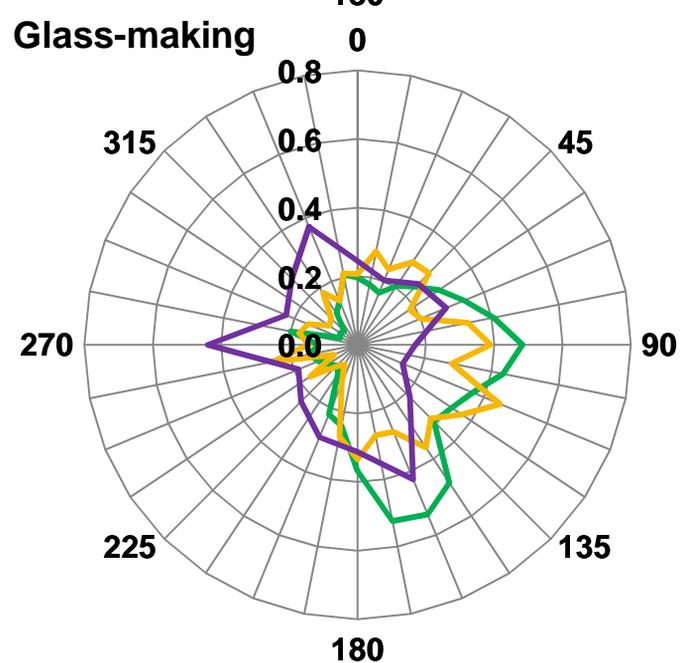
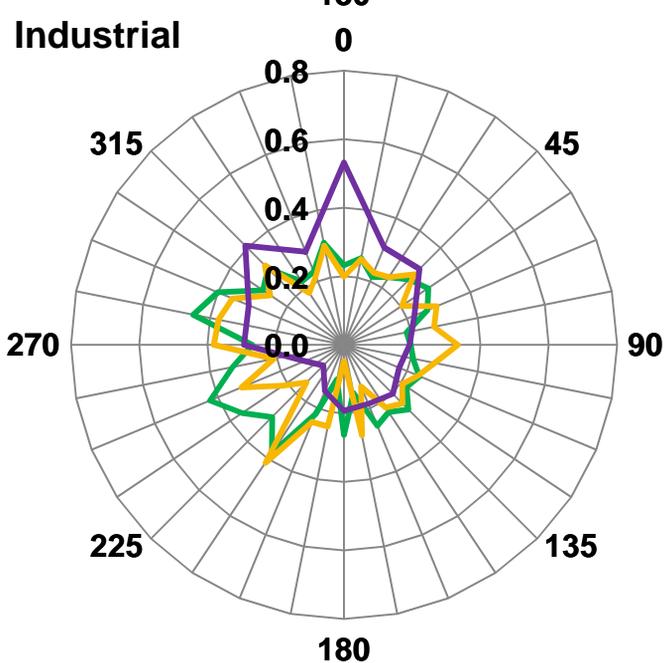
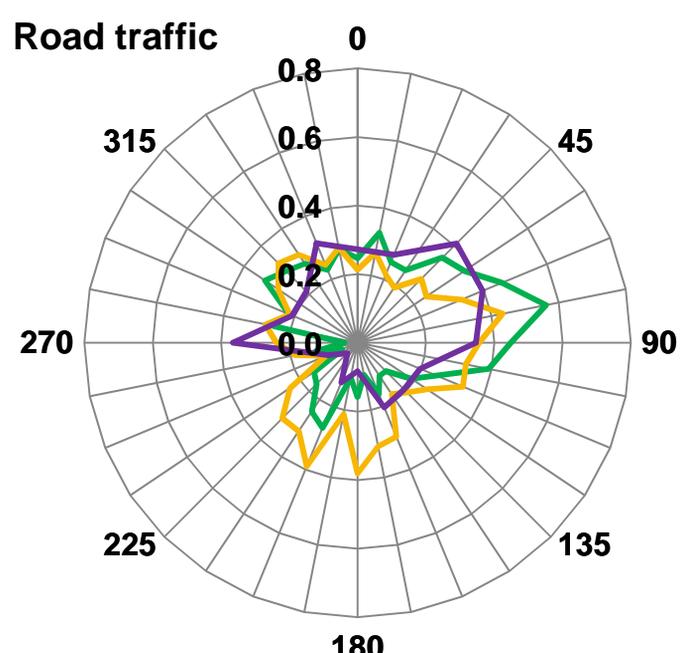
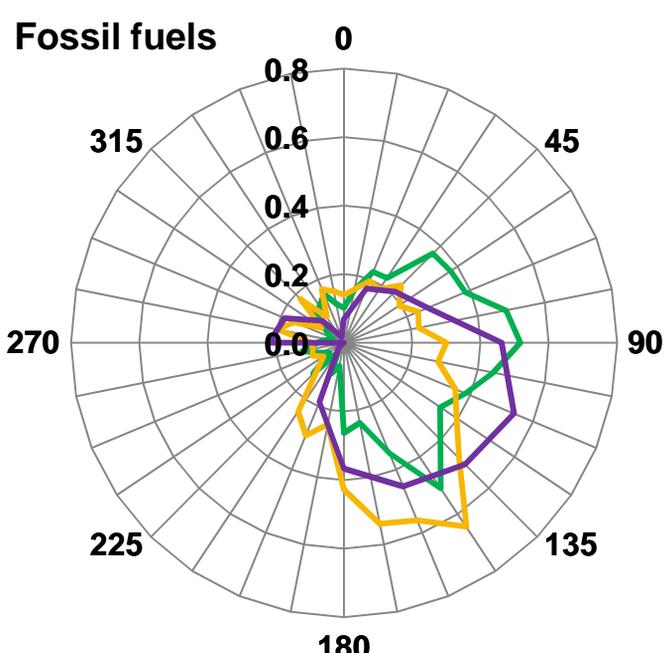
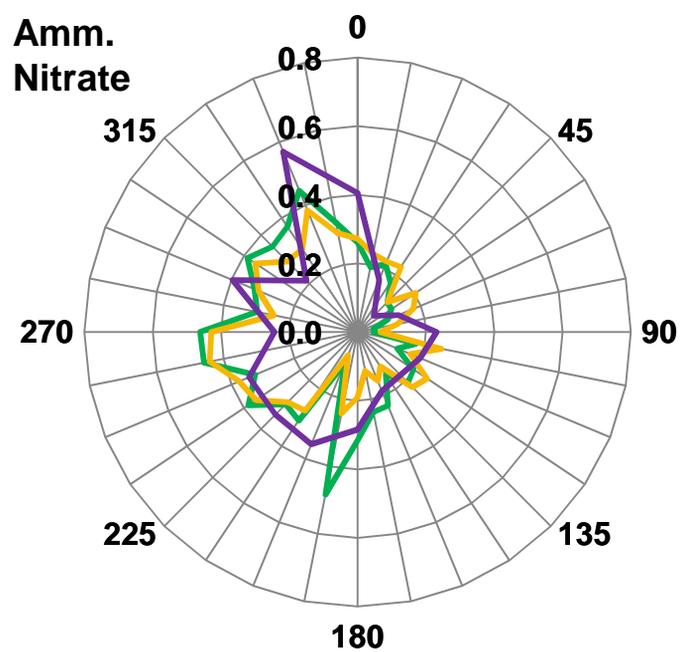
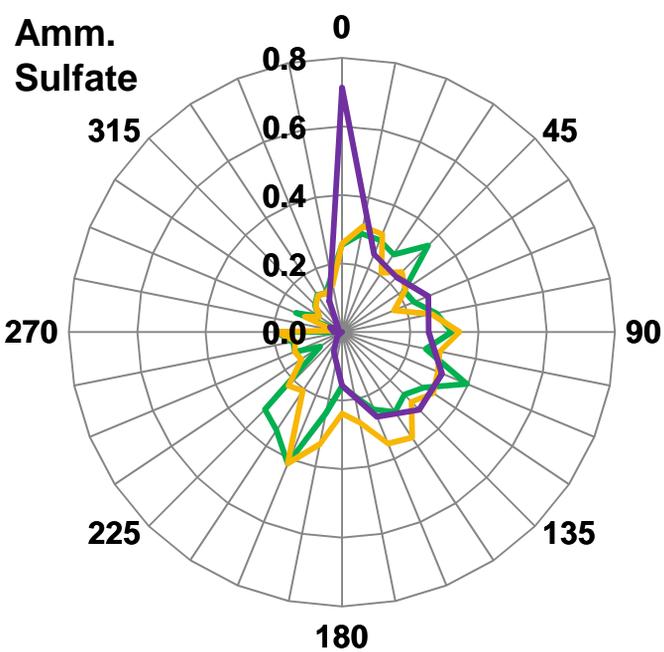


## Group 4



## Group 5





SRB
  URB
  IND

**HIGHLIGHTS**

- PM<sub>2.5</sub> local and external sources have been evaluated in an European hot-spot area
- Meteorology-based methods have been applied to source apportionment results
- External contributions were evaluated applying Trajectory Statistical Methods
- Effects on PM sources of ground-wind circulation patterns were also investigated
- Local source contributions have been estimated following the Lenschow' approach

### Cluster analysis on back-trajectories

The principal purpose of back trajectories clustering is to group trajectories having similar geographic origins and histories. The subsequent coupling of clusters with chemical data associated to air pollutants is a simple but powerful way to infer insights into the potential contribution of long-range transports from different pathways. There are several ways in which clustering can be performed several measures of the similarity (e.g., Carlslaw, 2015). The Euclidean distance ( $d$ ) parameter is the most common technique used in a number of studies (e.g., Abdalmogith and Harrison, 2005; Owega et al., 2006; Borge et al., 2007; Markou and Kassomenos, 2010; Rozwadowska et al., 2010). It that can be defined as:

$$d_{1,2} = \left( \sum_{i=1}^n ((X_{1i} - X_{2i})^2 + (Y_{1i} - Y_{2i})^2) \right)^{1/2} \quad (\text{Eq. 1})$$

where  $X_1$ ,  $Y_1$  and  $X_2$ ,  $Y_2$  are the latitude and longitude coordinates of back trajectories 1 and 2, respectively, and  $n$  is the number of back trajectory points (96 hours in this case). In this study a non-hierarchical clustering method (K-Means) has been applied. The appropriate number of clusters has been selected by using the analysis of the total spatial variance (TSV), individuating when a large change in TSV occurs.

### PSCF

The PSCF was initially developed to identify the likely locations of the regional PM sources (Lee and Hopke, 2006; Pekney et al., 2006) and calculates the probability that a source is located at latitude  $i$  and longitude  $j$ . The basis of PSCF is that if a source is located at coordinates  $i$  and  $j$ , an air parcel back-trajectory passing through that location indicates that material from the source can be collected and transported along the trajectory to the receptor site. PSCF solves:

$$PSCF = \frac{m_{ij}}{n_{ij}} \quad (\text{Eq. 2})$$

where  $n_{ij}$  is the total number of end points that fall in the  $ij$ th cell and  $m_{ij}$  is the number of end points in the same cell that are associated with samples that exceeded the threshold criterion (Carlsaw, 2015). The PSCF value can be interpreted as the conditional probability that concentrations larger than a given criterion value are related to the passage of air parcels through a grid cell with this PSCF value during transport to the receptor site (Hsu et al., 2003). This method is suitable for obtaining first knowledge of possible source regions (Dvorska et al., 2008 and references therein). Generally, PSCF values of 0.00–0.50 are considered as low, values of 0.51–1.00 are considered as high. In this study, PSCF has been calculated using the 75th percentile of source contribution as threshold criterion.

**CWT**

The main limitation of PSCF analysis is that grid cells can have the same PSCF values from samples of slightly higher or extremely higher criterion concentrations. As a consequence, larger sources cannot be distinguished from moderate ones. The 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):

$$C_{ij} = \frac{1}{\sum_{l=1}^M \tau_{ijl}} \sum_{l=1}^M C_l \tau_{ijl} \quad (\text{Eq. 3})$$

Where  $C_{ij}$  is the average weighted concentration in the grid cell  $(i,j)$ .  $C_l$  is the measured concentration (source contributions in this study),  $\tau_{ijl}$  is the number of trajectory endpoints in the grid cell  $(i,j)$  associated with the  $C_l$  sample, and  $M$  is the number of samples that have trajectory endpoints in grid cell  $(i,j)$ . In summary, weighted concentration fields show concentration gradients across potential sources and highlight the relative significance of potential sources (Hsu et al., 2003).

**CPF**

The conditional probability function (Kim et al., 2003a; Kim and Hopke, 2004) analyses local source impacts from varying wind directions using the source contribution estimates from PMF coupled with the time-resolved wind directions. The CPF estimates the probability that a given source contribution from a given wind direction will exceed a predetermined threshold criterion. CPF is defined as:

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \quad (\text{Eq. 4})$$

where  $m_{\Delta\theta}$  is the number of occurrences from wind sector  $\Delta\theta$  (11.25 degree) that exceeded the threshold criterion, and  $n_{\Delta\theta}$  is the total number of data from the same wind sector. To minimize the effect of the atmospheric dilution, the daily fractional contributions from each source relative to the total of all sources were used rather than the absolute source contributions (Kim et al., 2003a). The same daily fractional contribution was assigned to each hour of a given day to match the hourly wind data; hence 24 h was set as threshold criterion for  $n_{\Delta\theta}$ . Calm winds ( $< 1 \text{ m s}^{-1}$ ) were excluded from this analysis due to the isotropic behaviour of wind vane under calm winds. The threshold

criterion has been fixed to the upper 25<sup>th</sup> percentile of the fractional contribution of each source according to most previous studies (Kim et al., 2003b; Kim and Hopke, 2004; Kim et al., 2005). The sources are likely to be located at the directions that have high conditional probability values (Kim et al., 2005).

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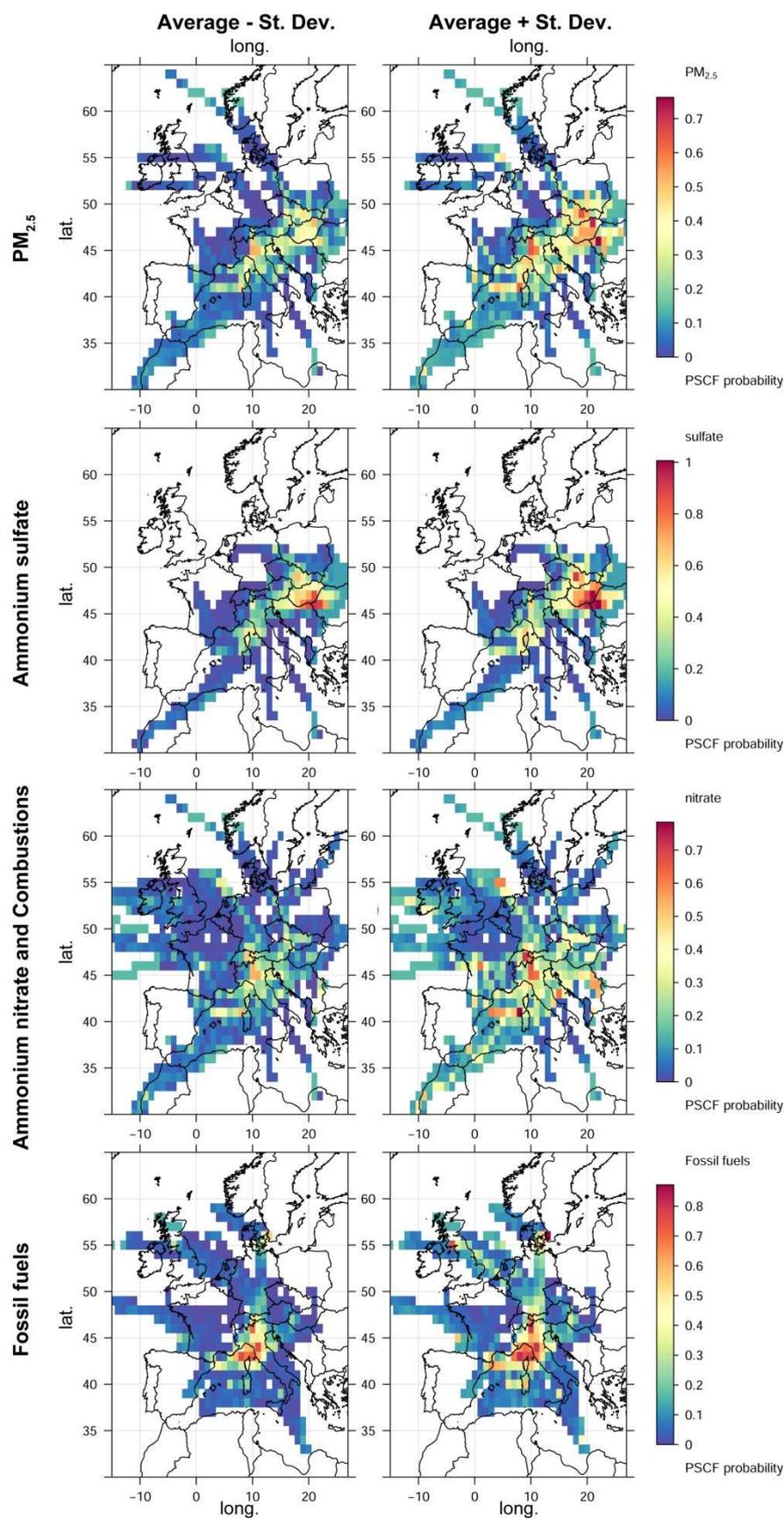
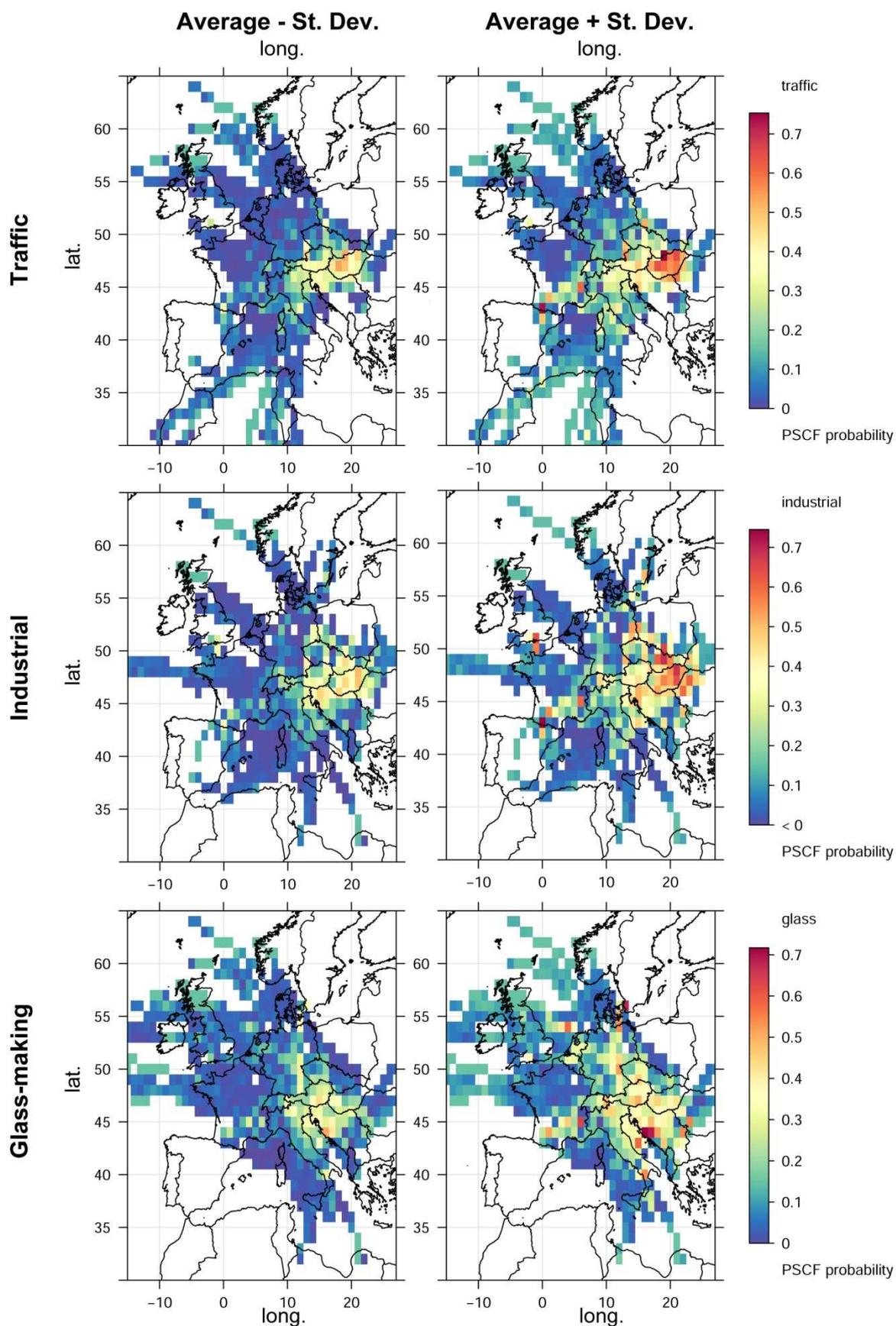


Figure SI1a. Associated uncertainties for PSCF expressed as average $\pm$ standard deviation of  $n=500$  bootstrap resamples.



**Figure SI1b. Associated uncertainties for PSCF expressed as average  $\pm$  standard deviation of  $n=500$  bootstrap resamples.**