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A multi-year source apportionment of PM2.5 at multiple sites in the southern Po Valley (Italy)

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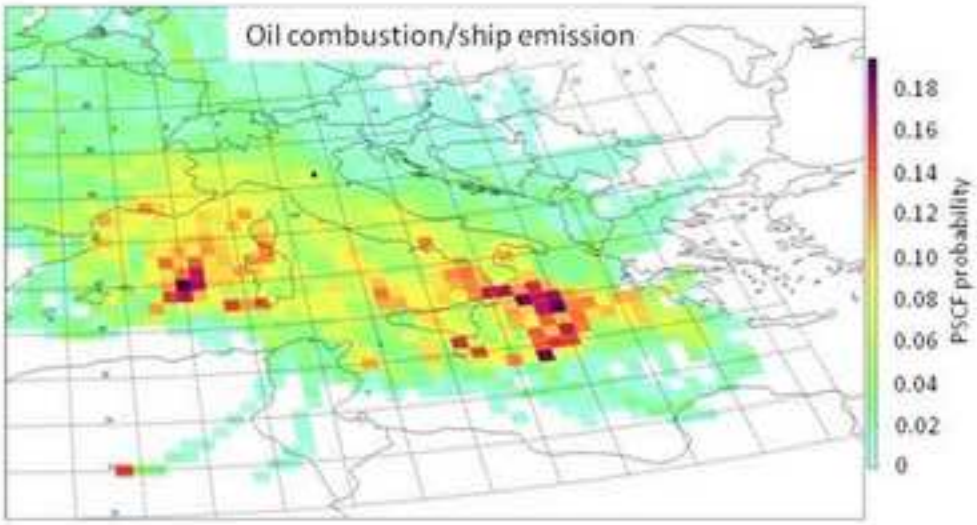
Corresponding Author:	Fabiana Scotto, master's degree Regional Agency for Prevention, Environment and Energy of Emilia-Romagna, Italy ITALY
First Author:	Fabiana Scotto, master's degree
Order of Authors:	Fabiana Scotto, master's degree
	Dimitri Bacco
	Stefano Lasagni
	Arianna Trentini
	Vanes Poluzzi
	Roberta Vecchi
Abstract:	A source apportionment study was carried out at four sites in the southern Po Valley, one of the most polluted regions in Europe. PM2.5 daily samples were collected from April 2013 to October 2017 at one rural site (San Pietro Capofiume, Bologna) and three urban background locations (cities of Bologna, Parma, Rimini) representative of different geographical area types across the region. A Positive Matrix Factorization (PMF) was performed and six major PM2.5 sources were identified: traffic with dust resuspension, biomass burning, oil combustion/ship emission, mix anthropogenic (not found at the rural site), ammonium nitrate and ammonium sulfate with organics. Factors related to secondary components explain almost 50% or even more of the PM2.5 total mass in all seasons. Traffic and biomass burning were confirmed as the most relevant primary contributors to PM2.5. A not negligible contribution of biomass burning resulted in Rimini during the summer, suggesting other possible sources of wood combustion, such as cooking or open burning of agricultural pruning. Agriculture is not singled out as a PMF factor, but a rough estimate based on ammonium concentrations and ammonia data from emission inventory indicates a contribution from this source of about 10% of PM2.5 mass, resulting the single productive activity with the highest impact on PM2.5 at the investigated sites. For two factors an important extra-regional contribution resulted from back trajectory analysis: oil combustion/ship emission is related to long-range transport of air masses overpassing the Mediterranean sea and concentration-weighted trajectory showed a provenience of secondary sulfate from Eastern Europe.
Suggested Reviewers:	Adriana Pietrodangelo adriana.pietrodangelo@iia.cnr.it expertise in atmospheric aerosol characterisation and source apportionment
	Willy Maenhaut willy.maenhaut@ugent.be expertise in atmospheric aerosol characterisation and source apportionment
	Evangelia Diapouli ldiapouli@ipta.demokritos.gr expertise in atmospheric aerosol characterisation and source apportionment
	Dennis Mooibroek dennis.mooibroek@rivm.nl expertise in atmospheric aerosol characterisation and source apportionment

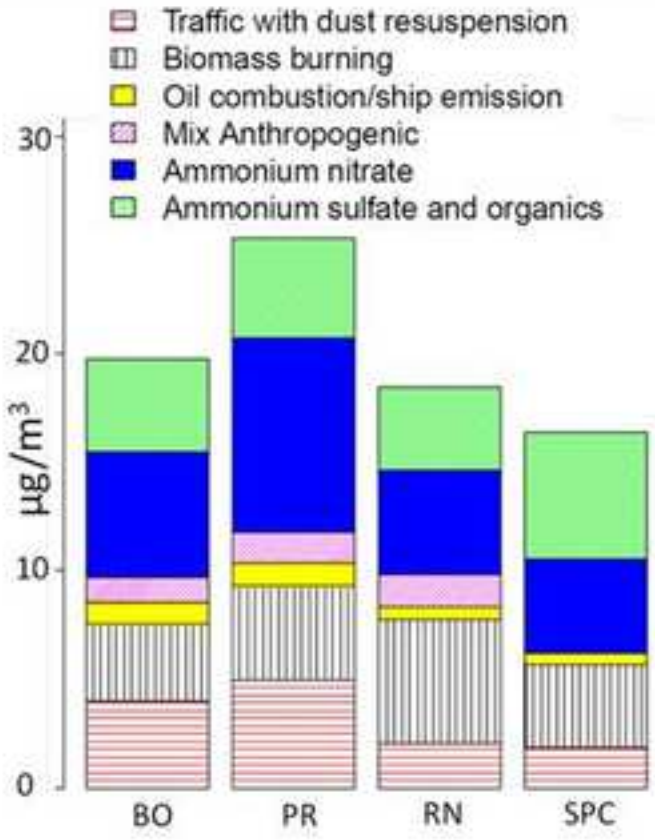
	Jan Hovorka jan.hovorka@natur.cuni.cz expertise in atmospheric aerosol characterisation and source apportionment
Opposed Reviewers:	
Response to Reviewers:	

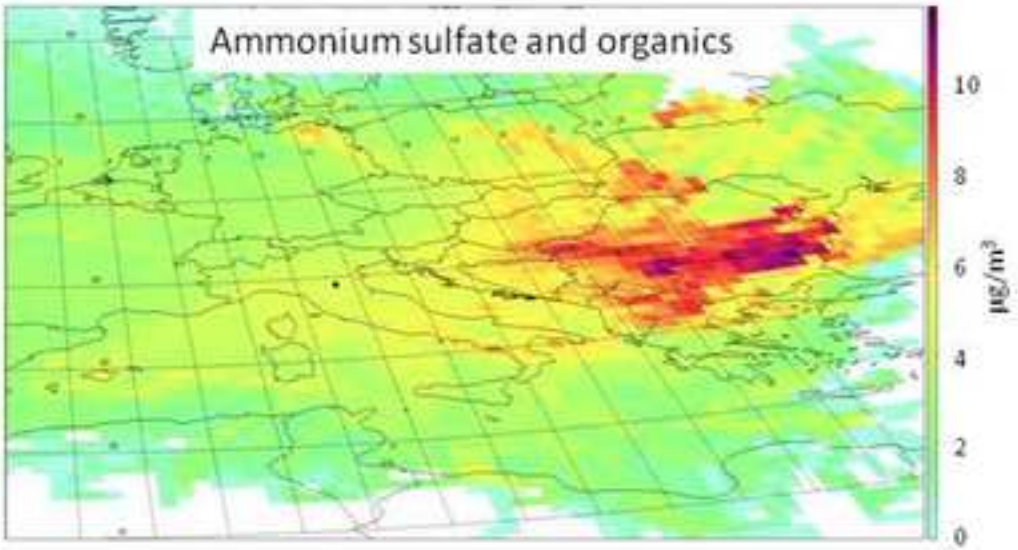
Highlights

- Source apportionment in Po Valley was performed using a Positive Matrix Factorization
- Chemical profiles of identified factors resulted very similar at the 4 sites
- Secondary component accounts for about half of total PM2.5 at urban sites
- Back-trajectories analysis and polar plots explored local or long range contributions
- Oil combustion and ammonium sulfate factors highlighted an extra-border provenience

Graphical Abstract







A multi-year source apportionment of $PM_{2.5}$ at multiple sites in the southern Po Valley (Italy)

Fabiana Scotto[a], Dimitri Bacco[a], Stefano Lasagni[b], Arianna Trentini[a], Vanes Poluzzi[a], Roberta Vecchi[c]

[a]Regional Agency for Prevention, Environment and Energy (Arpae), Emilia-Romagna, Italy. Largo Caduti del Lavoro, 6 - 40122 – Bologna, Italy

[b]European Training Foundation, viale Settimio Severo, 10133 - Torino, Italy

[c]Department of Physics, Università degli Studi di Milano and INFN-Milan, via Celoria, 16, 20133 - Milan (Italy)

Fabiana Scotto e-mail: fscotto@arpae.it

Dimitri Bacco e-mail: dbacco@arpae.it

Stefano Lasagni e-mail: stefano.lasagni@etf.europa.eu

Arianna Trentini e-mail: atrentini@arpae.it

Vanes Poluzzi e-mail: vpoluzzi@arpae.it

Roberta Vecchi e-mail: roberta.vecchi@unimi.it

Corresponding author: Fabiana Scotto, phone number: +390515281254; +393494514209

Abstract

A source apportionment study was carried out at four sites in Emilia-Romagna region, southern Po Valley, one of the most critical regions in Europe in terms of atmospheric pollution. $PM_{2.5}$ daily samples were collected during 4 years from April 2013 to October 2017 at one rural site (San Pietro Capofiume) and three urban background locations in the cities of Bologna, Rimini, Parma which show different features and are located in the, central, coastal and inner part of the investigated region. Samples were analyzed to achieve a complete chemical characterization (carbon fractions, ions, and elements). A source apportionment analysis by Positive Matrix Factorization (PMF) was performed and six $PM_{2.5}$ factors were identified at all sites but the rural one (where 5 out of 6 of them were detected); the factors were associated to traffic with dust resuspension, biomass burning, oil combustion/ship emission, mix anthropogenic (not found at the rural site), ammonium nitrate and ammonium sulfate with organics. Chemical profiles of factors were very

similar among all the 4 sites, indicating that main pollution sources are basically the same at the 4 sites, while some differences emerged with regard to source contributions. Factors related to secondary components seem to explain almost 50% or even more of $PM_{2.5}$ mass concentration in all seasons. Traffic and biomass burning are the most relevant contributors to $PM_{2.5}$ in terms of primary components. A not negligible contribution of biomass burning results in Rimini during the summer, suggesting other possible sources of wood combustion, such as cooking or open burning of agricultural pruning bonfires. Agriculture is not singled out as a PMF factor, but a rough estimate based on ammonium concentrations and ammonia data from emission inventory indicates a contribution from this source of about 10% of $PM_{2.5}$ mass, thus resulting the single productive activity with the highest impact on $PM_{2.5}$ at the investigated sites. Back trajectory analysis points at the relevant extra-regional contributions to two factors; indeed, oil combustion/ship emission is related to long-range transport of air masses overpassing the Mediterranean sea and secondary sulfate from Eastern Europe countries occasionally impacts on the Po Valley.

Keywords: $PM_{2.5}$, Po Valley, Source apportionment, Positive Matrix Factorization, Back-trajectories.

1. Introduction

The Po Valley, Northern Italy, is a highly polluted region (EEA, 2019), due to both relevant anthropogenic emissions from industrial, agricultural, and transport sectors and poor atmospheric dispersion conditions. Therefore, this region is a pollution hotspot even at rural locations and not only in urban and industrial settlements (Gilardoni et al., 2020). It is noteworthy that Italy has been recently (November 2020) ordered to pay pecuniary penalties from the Court of Justice of the European Union, for having "persistently and systematically" breached EU rules against fine particulate matter (PM) air pollution and the Po Valley was explicitly mentioned among the zones where daily limit values have been exceeded from 2008 (EU, Judgment of the court. 2020). With around 16 million inhabitants and a 46 x 103 km2-wide floodplain/hilly territory, the Po Valley is a densely inhabited and anthropized area so that as a whole it can be considered an extended megacity (WMO/IGAC, 2012). In addition, the valley is surrounded from mountain chains on the south side (Apennines) and on the west and north side (Alps): this favors air stagnation promoted by shallow mixing layer height and low winds (Deserti et al., 2001; Vecchi et al., 2019) and prevents pollutants dispersion promoting also the formation of secondary compounds. Wintertime thermal inversions and widespread fog events are frequent, leading to the buildup of particulate matter (PM) concentrations (Perrino et al., 2014; Caserini et al., 2017, Brege et al., 2018, Gilardoni et al., 2020; Masiol et al. 2020; and references therein). Although over the past decade the regional authorities in the Po valley have implemented air quality plans, PM levels did not drop below the EU limits. In order to improve air quality and comply with Directive 2008/50/EC and the European strategy ‘Clean Air for Europe’, in 2017 the PREPAIR LIFE Integrated project (LIFE 15 IPE IT 013) was undertaken with the goal of planning common actions in the Po Valley regions and in Slovenia (Raffaelli et al., 2020).

Particulate matter causes health effects being linked to allergy, cardiovascular and respiratory symptoms (Nozza et al., 2021 and references therein), low neonatal birth weight (Han et al., 2018) and life-expectancy reduction (Pope et al., 2009). Furthermore, PM damages the environment in many ways: it interacts with clouds affecting climate (IPCC. 2013), decreases atmospheric visibility (Bäumer et al., 2008; Vecchi et al., 2018); can interfere with the Earth’s radiation budget (Fountoukis et al., 2020); causes ecosystems acidification (Narita et al., 2019) and threatens cultural heritage (Nava et al., 2010).
The present source apportionment study is based on PM2.5 data series collected during 4 years at four sites in the southern Po Valley; to our knowledge no other source apportionment study in the Po Valley has been carried out with such long continuous time series at multiple sites. Receptor models constitute a complementary approach to studies based on emission inventories and transport models. In particular, Positive Matrix Factorization (PMF) was here applied as it is a well-known and widely used approach (Belis et al., 2020); it provides estimates of source contributions together with their chemical profiles at a receptor site using the measured PM chemical composition as input data(Paatero and Tapper, 1994).

Identifying the sources of particulate matter facilitates understanding the mechanisms of formation and transformation of PM, in order to be able to support politicians in building effective PM abatement strategies and to check the effectiveness of undertaken measures. It also allows distinguishing between anthropogenic and natural sources, as well as between primary sources and secondary components. Secondary components like sulfates and nitrates play a fundamental role in fine PM mass concentrations, especially in the Po Valley (Thunis et al., 2021) and are of major importance for the realization of effective abatement measures. Recently (Giannadaki et al., 2018; and references therein) has pointed at the fundamental role of agriculture and livestock activities worldwide, thus also in Europe and in the Po Valley. These activities are mainly responsible for ammonia emissions (NH_3); it reacts with other gaseous precursors such as SO_2 and NO_x and forms ammonium sulfate ($(NH_4)_2SO_4$) and ammonium nitrate (NH_4NO_3), the main secondary inorganic aerosol (SIA) components in PM. The relevance impact of these components was proved in this study too. PMF results were further examined in order to understand the differences or similarities among sources contribution and profiles among the sites; between urban sites and the rural one and among urban sites representative of dissimilar territorial conditions (see Section 2.1). The role of wind speed and direction and back trajectories was investigated in order to understand pollutant transports from extra-regional sources (Diémoz et. al., 2019). Last but not least, results of this source apportionment study have been already used by Ottone (2020) in order to investigate the risk of adverse birth outcomes.

2. Materials and Methods

2.1 Sampling sites characteristics

Samples were collected at four monitoring stations with different characteristics (Fig. 1): one rural background site (San Pietro Capofiume - SPC) and three urban background sites in the central (Bologna - BO), coastal (Rimini - RN), and inner (Parma - PR) part of the Emilia-Romagna region. The monitoring sites have been described in detail in a previous paper (Ricciardelli et al. 2017). Briefly, Bologna is a metropolitan city with about 400000 inhabitants, largely impacted by agricultural and industrial activities and located at the crossroads of major motorways and railway national lines. Parma has about 200000 inhabitants; located half way between Bologna and Milan, it is impacted by both industrial and agricultural activities located in the Po Valley. Rimini has about 150000 inhabitants and overlooks the Adriatic coast, which is a peculiar area, both because of its meteorological features and the anthropogenic pressure due to tourism. During the period of this study, the overall average number of tourists present in the summer months June - August exceeded 11 million (Emilia-Romagna region statistics). San Pietro Capofiume is a rural site located 30 km north-east of Bologna, in the middle of the countryside, far from major primary sources and thus very interesting for atmospheric studies (see e.g. Decesari et al., 2014; Wolf et al., 2015; Sandrini et al., 2016; Paglione et al., 2020; Gilardoni et al, 2020).

Sites were chosen in order to represent the different types of geographical and meteo-climatic areas across the region (Bonafè et al., 2011). The spatial distribution of these stations provides an exposure assessment of nearly half of the regional population; indeed, epidemiological studies exploiting the Supersito project results were also carried out (Ottone et al., 2020, Ranzi et al., 2016).

Fig.1 - Map of the sampling sites area.

2.2 Sampling methods and chemical analyses

The datasets here analyzed refer to the periods 1 April 2013 – 31 March 2015 and 15 October 2015 – 14 October 2017. Sampling was carried out continuously on a daily basis at all sites; 10 samples per month were devoted to chemical analyses in PR, RN and SPC and 27 samples per month in BO. Therefore, the final datasets comprised about 1200 samples for BO and 400-450 samples for the other three sites. During the time period April 2013 - October 2017, the largest available time series for every site was kept as input to the receptor model; opposite, the comparison among sites was carried out selecting only data in common.

Daily $PM_{2.5}$ were collected with samplers equipped with parallel sampling lines (SWAM, FAI Instruments, Rome, Italy operated at a flow-rate of 38.3 L min^{-1} according to UNI EN 12341:2014) using quartz fiber filters (Whatman® QM-A filters, diameter: 47 mm). On these samples – after suitable chemical pretreatment - major ions (by Ion Chromatography), levoglucosan (by High Performance Liquid Chromatography Mass Spectrometry), and elements (by Inductively Coupled Plasma Mass Spectrometry) were assessed. Samples devoted to carbonaceous component analyses were collected using a low-volume $PM_{2.5}$ sampler (Skypost PM, TCR-TECORA Instruments, Milan, Italy) operated at a flow-rate of 38.3 L min^{-1} during the warm months (from April to October) and 16.6 L min^{-1} (using a suitable inlet) during the cold season in order to reduce filter overloading (Costa et al., 2016). Quartz fiber filters (PALL Tissu Quartz 2500 QAO-UP 2500) were pre-baked for 5 h at 800° C in order to eliminate any absorbed organic material. EC/OC/TC concentrations were retrieved by thermo-optical transmission analysis using EUSAAR2 thermal protocol (Cavalli et al., 2010).
Daily $PM_{2.5}$ mass concentration was retrieved by β-ray attenuation operated in SWAM Dual channel and SWAM Monochannel instruments (FAI Instruments, Rome, Italy).
Details about instruments, sampling and analytical procedures are reported in previous papers (Costa et al., 2016; Ricciardelli et al., 2017; Ottone et al., 2020).
Detection of levoglucosan started from 2015 and it was achieved by formation of anhydrosugar acetate adducts [M+CH3COO]- in the negative electrospray mode using an electrospray ionization source (ESI) (Engling et al., 2006).

Details on QA/QC procedures have been reported elsewhere (Ricciardelli et al. 2017, Costa et al., 2016). Briefly, every day a four points linear calibration curve is processed at the beginning of the sequence and each 20 samples for IC, HPLC-MS and ICP-MS analysis. Instrumental blanks of the analytical system and a standard solution are analyzed and the results reported in process control charts (i.e. Shewhart control charts, UNI ISO 7870-2:2014) to check instrument performance over time. Daily standard control solution is measured every 10 samples to check the efficiency of the calibration curve with a ±10% tolerance from the expected concentration. Furthermore, ICP-MS calibration curves are checked with 2 certified standards (NIST SRM 2583 and NIES CRM n°8).

EC/OC analysis performances are checked by instrument internal standard (methane) and a sucrose standard solution, according to UNI EN 16909 (Costa et al., 2016; Panteliadis et al., 2015).

Elements detection limits were calculated as three times the standard deviation of the blank because the average values of the black were directly subtracted to the measures, according to UNI EN 14902. Detection limit values of levoglucosan, EC, OC and ions were calculated as three time the standard deviation of the blank and it was added to the average value of the blank, which was not subtracted to the samples in this case, according to aforementioned regulations (and to UNI EN 16913 for ions).

Meteorological data for all the investigated sites were provided by Hydro-Meteo-Climate Service of the Regional Agency for the Prevention, Environment and Energy of Emilia-Romagna.

2.3 Data pre-treatment and receptor modeling procedure

Receptor models are widely used to identify the sources that mainly impact a site and to retrieve time series of source contributions. Among various receptor modeling approaches, Positive Matrix Factorization (PMF) is a factorial decomposition technique based on a weighted least square fit approach: it uses uncertainty values to weigh the concentration data and imposes non-negativity constraints on chemical profiles and contributions of identified factors in order to limit the space of the possible solutions. Detailed information on the PMF methodology can be found elsewhere (e.g. Paatero and Tapper, 1994; Paatero et al., 2014). Similar to other receptor models approaches, PMF aims at solving the mass conservation equation between the measured species concentrations and source emissions as a linear combination of p factors, as follows: $x_{ij} = \left(\sum_p g_{ip} \times f_{pj}\right) + e_{ij}$

where x_{ij} represents the measured data for species j in sample i; g_{ip} represents the PM mass contribution of factor (source) p in the sample i, f_{pj} represents the fraction of species j in the PM ascribed to factor p; and e_{ij} is the residual of each sample and species obtained by the difference between the fitted and the observed value. In matrix form, G and F matrices have to be determined in the equation X=G·F+E, where X is the known matrix of measured concentrations; G is the matrix of source contributions; F is the matrix of factors

composition (source profiles) and E is the residual matrix. Goal of the PMF is determining non-negative G and F matrices that minimize the Q-function, which represents the sum of the squares of the residuals between observed and predicted values, inversely weighted to the uncertainty estimates.

In this work, EPA-PMF 5.0 (US EPA, 2014) was applied to each dataset in order to single out $PM_{2.5}$ sources. Chemical species used in this study are summarized in Table 1. Generally, it is recommended to neglect species with more than 50% of values below detection limit (BDL) unless these are source tracer or if they present a reasonable signal-to-noise ratio (Belis et al. 2019); therefore, in this study Al, Ba, Br^-, Ca^{2+}, Ca, Cr, K, Mg, Mg^{2+}, Na^+, and PO_4^{3-} were excluded. Despite the high number of BDL, we kept some species such as La because of its importance as marker for crustal material, given the lack of other typical tracers such as Si; Cl^- as it is a marker of sea spray (Calzolai et al., 2015) and also a component in biomass burning aerosol (Venturini et al., 2014; Hovorka et al. 2015); Ni which is, together with V, a known tracer for heavy oil combustion and ship emissions (see e.g. Becagli et al., 2012; Viana et al. 2014). Finally, Cl^-, Ni, Zn, and La were classified as weak variables in all datasets, Fe was set as weak only for data related to SPC site.
As a consequence of the data reduction described above, a poor characterization of crustal component resulted as typical tracers such as Ca, Al, Mg, and Si were excluded and only La was kept. Anyway, in our previous paper (Ricciardelli et al., 2017), crustal fraction in $PM_{2.5}$ samples was estimated due to the availability of such tracers and it accounted on average for 1.0 μg m^{-3}, corresponding to 3% of $PM_{2.5}$ at the urban background site of BO during winter 2012/2013. Based on these results, we can assume that generally crustal material is not a relevant component of $PM_{2.5}$ mass (few percents) in the investigated area.
Input uncertainties to PMF were estimated following Zabalza et al. (2006) for chemical species; $PM_{2.5}$ uncertainty was set equal to 2.5 μg/m^3, on the basis of previous intercomparisons between paired samplers.
BDL values were provided by the analytical laboratory and used when concentrations were below the detection limit (Belis et al. 2019). Detailed information about uncertainties, treatment of missing values and exclusion of outliers is available in the Supplementary Material.

Table 1 – $PM_{2.5}$ mass and chemical components concentrations at the investigated sites. Mean and standard deviation (to be interpreted as concentration variability) are expressed in μg/m^3. The number of available data is also reported. DL stands for detection limit and N.A. for not available.

	Bologna (BO)				Parma (PR)				Rimini (RN)				San Pietro Capofiume (SPC)			
	# data>=D	# data<D	mean	Standard deviation	# data>=D	# data<D	mean	Standard deviation	# data>=D	# data<DL	mean	Standard deviation	# data>=D	# data<DL	mean	Standard deviation
PM2.5	1313	23	21	17	496	17	27	21	453	41	21	19	474	21	18	13
OC	1284	4	4.75	3.28	494	2	4.55	3.01	490	0	5.34	4.48	485	0	4.58	3.59
EC	1324	0	1.31	0.89	486	10	1.13	0.90	488	3	1.28	0.91	484	1	0.83	0.69
Levoglucosar	627	60	0.235	0.305	274	24	0.231	0.301	285	13	0.378	0.452	215	42	0.204	0.287
Na^+	134	1196	0.073	0.075	48	456	0.077	0.049	158	340	0.125	0.122	48	437	0.078	0.174
NH_4^+	1322	5	2.236	2.241	502	2	2.875	2.674	493	5	2.233	2.394	485	0	2.249	2.008
K^+	1024	304	0.135	0.174	405	99	0.162	0.176	416	82	0.200	0.218	385	100	0.148	0.169
Mg^{2+}	80	1248	0.010	0.015	38	466	0.012	0.013	85	413	0.018	0.021	40	445	0.010	0.011
Ca^{2+}	204	1124	0.103	0.076	159	345	0.202	0.149	82	416	0.128	0.093	81	404	0.134	0.137
Cl^-	566	762	0.162	0.230	245	257	0.194	0.252	270	228	0.228	0.282	193	292	0.131	0.165
Br^-	3	1327	0.000	0.003	0	502	N.A.	N.A.	1	497	0.000	0.002	0	485	N.A:	N.A.
NO_3^-	1263	67	4.253	6.944	496	6	6.232	8.186	461	37	4.402	7.223	473	12	4.485	6.345
SO_4^{2-}	1328	2	2.171	1.406	500	2	2.392	1.504	497	1	2.234	1.427	484	1	2.102	1.377
PO_4^{3-}	187	1143	0.075	0.178	51	451	0.050	0.175	46	452	0.045	0.098	54	431	0.059	0.135
Al	138	1172	0.02410	0.04465	25	479	0.02811	0.04518	36	462	0.01880	0.04464	39	441	0.02087	0.04128
As	1317	13	0.00045	0.00045	503	1	0.00046	0.00040	490	8	0.00035	0.00029	483	2	0.00046	0.00042
Cr	145	1152	-0.00006	0.00256	69	434	-0.00012	0.00344	49	440	0.00085	0.00713	43	408	-0.00012	0.00414
Fe	953	357	0.09596	0.07722	405	99	0.08638	0.06348	376	122	0.07725	0.07545	289	191	0.06468	0.15215
Mn	1053	277	0.00270	0.00205	457	47	0.00323	0.00205	422	76	0.00267	0.00214	397	88	0.00234	0.00191
Ni	407	903	0.00119	0.00135	161	343	0.00124	0.00124	141	357	0.00122	0.00176	138	342	0.00182	0.00431
V	1321	9	0.00092	0.00099	500	4	0.00087	0.00090	492	6	0.00115	0.00104	478	7	0.00098	0.00106
Zn	718	579	0.01607	0.01432	280	223	0.01652	0.01608	233	265	0.01333	0.01253	227	251	0.01405	0.01415
Cd	1285	26	0.00015	0.00026	488	16	0.00012	0.00011	486	12	0.00015	0.00024	470	10	0.00013	0.00014
Pb	1307	3	0.00420	0.00544	504	0	0.00386	0.00341	497	1	0.00357	0.00399	479	1	0.00348	0.00296
Sn	1249	81	0.00136	0.00136	436	68	0.00119	0.00097	439	59	0.00087	0.00077	420	65	0.00095	0.00100
Sb	1139	171	0.00094	0.00644	423	81	0.00053	0.00053	376	122	0.00051	0.00041	390	90	0.00058	0.00056
Ba	79	1218	0.00293	0.00773	25	479	0.00279	0.01111	29	469	0.00280	0.00669	22	458	0.00348	0.01878
Ca	5	1325	-0.02	0.41	2	502	0.00	0.42	0	498	N.A.	N.A.	1	484	-0.04	0.35
K	425	885	0.15	0.24	160	344	0.15	0.23	208	290	0.21	0.32	189	291	0.15	0.22
Mg	7	1323	0.00	0.12	2	502	0.00	0.14	1	497	-0.01	0.09	7	478	0.00	0.12
La	832	498	0.000041	0.000045	374	130	0.000059	0.000065	283	215	0.000031	0.000028	234	251	0.000032	0.000036

* Data available only on the two-year period 2015-2107

Solutions with 3 to 12 factors were explored and the more robust base-case solution presented 6 factors for BO, PR and RN sites, and 5 factors for SPC. The 7-factor solution (or six-factor for SPC), presented exactly the same sources as the 6-factor one with the addition of a factor with a unique element and no characteristic time pattern. As the origin of this seventh factor was not clear, the 6-factor solution (5-factor for SPC) was considered the most robust one showing a clear physical meaning. Solutions with fewer factors, on the other hand, mixed more sources in the same factor.

Positive Matrix Factorization analyses were performed with different settings in terms of categorization of variables, exclusion or inclusion of species with high number of BDL values or low signal to noise ratio, treatment of outliers, and extra-modelling uncertainty (see e.g. PMF manual for definitions, US-EPA, 2014). PMF results obtained with rotational tools for multiple values of fpeak (in the range -1.5 – 1.5) as well as the imposition of constraints were also systematically explored (50 pseudorandom initializations were run in each test) thus refining the base-case solution obtained at each site. A number of criteria were applied to each dataset in order to evaluate different solutions, including the assessment of realistic source profiles, statistical fitting of the model, check of the stability of solutions over 200 runs, analysis of scaled residuals, inspection of G-space plots (Paatero et al., 2005), and bootstrap and displacement error estimation. The Q/Q_{exp} ratio was monitored with increasing number of factors, as a large decrease indicates an enhanced explanatory power of the fitting model, while a small drop suggests little improvement ascribed to added factors (Crilley et al., 2017; Belis et al., 2019). The key criterion applied was based on extracting chemical

profiles and temporal variation of source contributions with physical meaning and with a high degree of specificity (e.g. secondary aerosol components like sulfates and nitrates differentiated from primary aerosol contributions). In the final solution retrieved at all sites, chemical components were reproduced fairly well by the model (correlation coefficient $R^2 > 0.7$) and only in a minor number of cases input variables were poorly modelled ($R^2 < 0.5$) due to many BDL values and/or the presence of isolated peaks; by performing multiple PMF runs excluding and including these species, results were not substantially different so that all variables were kept. Details on fitting parameters of PMF solutions are reported in Supplementary Material (Table S1)

Random and rotational uncertainty in PMF solutions was investigated by Bootstrap resample, Displace Error Estimation (DISP) and Bootstrap Error Estimation and Bootstrap Displacement Error Estimation (BS-DISP) (Paatero et al, 2014). Uncertainties on average $PM_{2.5}$ mass apportionment to each factor were calculated as interval between 5^{th} and 95^{th} percentile of bootstrap displacement error estimation (100 bootstrap resamples) and are reported in Supplementary Material (Table S2 – S5).

Statistical analysis was performed using RStudio (RStudio Team, 2020) with R.3.6.0 (R Core Team, 2013).

2.4 Back-trajectories analysis

Back-trajectories were used to analyze the potential source regions of PMF factors for which an important extra-regional contribution resulted from the polar plots. Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) was used to derive 72 hours back-trajectories at each station; the latter were computed at 00, 06, 12 and 18 UTC every day during the studied period (March 2013 - October 2017) at the height of 500 m and 100 m above ground level (a.g.l.) (see section 3.2 for details about the choice of these 2 different heights). The HYSPLIT model - developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) - is one of the most widely used models for atmospheric trajectory calculations. The meteorological data input used for running the HYSPLIT model are the reanalysis files, with a 2.5-degree latitude-longitude global grid. Such a coarse resolution was the best compromise available at the time we started the back-trajectories calculation; although being too large to resolve mesoscale sub-synoptic processes, it is still suitable for our purposes, since we are interested in a large-scale flow pattern.

Single back-trajectories were analyzed for each site (Fig. S1), and Potential Source Contribution Function (PSCF) and Concentration-Weighted Trajectory (CWT) methods were employed (Fig. 5 and Fig.S2) . In order to achieve a more statistically robust result about the source regions, trajectories computed at the four sites were combined together with the PSCF and CWT analysis.

The PSCF value for a given grid cell (i, j) is defined as $PSCF_{ij}=W_{ij}*M_{ij}/N_{ij}$, where M_{ij} represents the number of model trajectory endpoints within the same grid cell (i,j) that correspond to days exceeding a specific threshold (here the 90th percentile) for the factor; N_{ij} is the total number of model trajectory endpoints within the grid cell (i, j); W_{ij} is an arbitrary weight function to reduce the effect of small N_{ij} values.

The concentration weighted trajectory (CWT) is a method weighting pollutant concentration using the air mass residence time in each cell (Stohl, 1996). In this method, each grid cell is assigned a concentration which is the average of concentrations associated to trajectories crossing that grid cell, as described by the following equation: $CWT_{ij} = W_{ij}\frac{1}{\sum_{l=1}^{M}\tau_{ijl}}\sum_{l=1}^{M} C_l\tau_{ijl}$, where CWT_{ij} is CWT value for the grid cell (i, j); M is the total number of trajectories; i is the index of the specific trajectory; C_l is the factor contribution related to the corresponding trajectory l; τ_{ijl} is the residence time in the ijth grid cell for the trajectory i. In summary, CWT method shows factor concentration gradients across potential origin areas thus helping to identify the relative importance of potential sources.

The Openair package (Carslaw and Ropkins, 2012) was used for the back-trajectories analysis.

3 Results

3.1 Factors resolved by PMF model

The final PMF solution was optimized at each site selecting rotated and constrained solutions as summarized in Table S1 (Supplementary Material). As already mentioned, at all urban background sites the same 6 factors were singled out and tentatively associated to the following sources: Traffic with dust resuspension; Biomass burning; Oil combustion/ship emission; Mix anthropogenic; Secondary Nitrate; Secondary Sulfate and Organics. Apart from the "mix anthropogenic" factor which is missing at the SPC rural background site, the other 5 are the same as those identified at the urban background sites. It is noteworthy that PMF analysis did not single out a marine aerosol factor at the coastal site of RN; indeed, Na^+ and Cl^- present a large percentage of BDL values thus preventing the identification of this source. Although it might seem an oddity, previous receptor model studies in the Eastern part of the Po Valley have detected a sea-salt factor only in PM_{10} (see e.g. Bologna: Tositti et al., 2014 Venice area: Masiol et al., 2012); and generally not in $PM_{2.5}$ (see e.g. Rimini: Venturini et al., 2014; Treviso: Squizzato et al., 2017; Venice area: Masiol et al., 2014; Masiol et al., 2020). This does not exclude that there may be sporadic contributions from marine air masses but in general the contribution of this source to $PM_{2.5}$ mass can be considered negligible.

Factors chemical profiles (Fig. 2) are very similar at all sites – especially when looking at trace species - and time series show correlations that vary according to the degree of the local nature of the factor. Similarities

between chemical profiles of PMF factors have been quantitatively defined by Pearson correlation coefficients and Standardized Identity Distance (SID) calculated according to Belis et al. (2015) and reported in Supplementary Material (Table S6 – S7), together with correlation between time series (Table S8). The comparison between the "traffic with resuspended dust" singled out by PMF at the rural site SPC vs. all the urban background sites shows the lowest correlation, for both chemical profiles and time series; indeed, at the rural site a possible anthropogenic mix contribution that is not individually resolved might be present, as reported in section 3.1.1. Details are discussed further in Sections 3.1.1.-3.1.6.

$PM_{2.5}$ average source apportionment for the whole investigated period is reported in Fig. 3 and seasonal averages are reported in table 2. In this paper, the "warm period" comprises the period from 15 May to 14 September and the "cold season" is defined as the period from 1 November to 31 March; this selection was performed analyzing meteorological parameters and the $PM_{2.5}$ chemical composition over the 4 years at the 4 sites.

Fig. 2 - Source profiles of factors identified by the PMF analysis at the 4 sites.

Fig. 3 – Source apportionment for the period 2013-2017 at the 4 sites.

Table 2

Seasonal apportionment in $\mu g/m^3$ and in percentage at the 4 sites. In order to ensure better comparability among the sites, the averages were calculated only on samples available at all 4 sites during the 4-years period of investigation. Results are quite similar when they are calculated on the whole time series available for each site (see tables S2-S5 for a comparison with overall average).

	Traffic with dust resuspension	Biomass burning	Oil combustion	Mix anthropogenic	Ammonium nitrate	Ammonium sulfate and organics
	Overall average (4 years)					
BO	4.0 (20.2%)	3.5 (17.9%)	1.0 (5.1%)	1.1 (5.7%)	5.8 (29.3%)	4.3 (21.7%)
PR	4.9 (19.5%)	4.3 (17.1%)	1.1 (4.3%)	1.4 (5.7%)	8.9 (35.3%)	4.6 (18.1%)
RN	2.0 (11%)	5.7 (31.1%)	0.6 (3.1%)	1.5 (8.2%)	4.8 (25.8%)	3.9 (20.9%)
SPC	1.9 (11.4%)	3.8 (23.5%)	0.5 (3.1%)		4.3 (26.4%)	5.8 (35.7%)
	Warm period					
BO	2.9 (28%)	0.9 (9%)	1.0 (9.9%)	0.6 (6%)	0.1 (0.7%)	4.8 (46.4%)
PR	4.1 (30.5%)	1.1 (8.1%)	1.3 (9.8%)	0.7 (5.1%)	0.2 (1.5%)	6.0 (45%)
RN	1.9 (19.7%)	1.9 (19.9%)	0.6 (6.7%)	0.8 (8.7%)	0.3 (3.1%)	4.0 (42%)
SPC	1.5 (15.3%)	0.8 (7.6%)	0.5 (5.2%)		0.6 (5.5%)	6.6 (66.3%)
	Cold period					
BO	4.8 (18.2%)	5.8 (21.9%)	1.0 (3.9%)	1.4 (5.2%)	9.7 (36.7%)	3.8 (14.2%)
PR	5.4 (16.4%)	7.2 (22%)	1.0 (3.1%)	1.8 (5.6%)	13.8 (42.2%)	3.6 (10.8%)
RN	2.1 (8.3%)	9.2 (36.4%)	0.5 (2%)	1.9 (7.6%)	7.9 (31.3%)	3.6 (14.4%)
SPC	2.1 (9.6%)	6.4 (30.3%)	0.5 (2.4%)		7.0 (32.6%)	5.3 (25.1%)

3.1.1 Traffic with dust resuspension

The factor profile is characterized by chemical species typical of both exhaust (mainly EC and OC) and non-exhaust emissions, such as clutch, brake and tire wear abrasion (e.g. Fe, Mn, Ni, Sb, Sn, Zn) or road dust resuspension (e.g. La, Fe, Mn) (Viana et al., 2008; Pant and Harrison, 2013; Amato et al., 2016; Charron et al., 2019). At SPC rural site the chemical profile of this factor shows contributions from Cd, Pb, and As as well as a relevant presence of Sn and Sb while at the urban background sites these elements are found in the mix-anthropogenic factor profile. Therefore, this factor at the rural site probably represents a medium-range air mass transport from urban areas, generally including emissions from anthropogenic activities such as vehicular traffic, service and production activities with the first one being the most relevant.

Traffic with dust resuspension is the major $PM_{2.5}$ source during the warm season accounting for about 10% - 20% of the $PM_{2.5}$ mass with the sites of PR and BO showing the largest absolute and relative contributions. An expection is RN where biomass burning accounts for about 20% of $PM_{2.5}$ also during the warm season, as described in Section 3.1.2. This factor is not characterized by a strong seasonality (see Table 2); indeed, the PMF solution shows a decrease in traffic absolute contribution during warm season because of the better atmospheric dilution although its relative share increases due to the lower impact of other factors such as biomass burning and secondary nitrate. It is interesting that in RN during warm season this factor shows the greatest increase in relative terms and the least decrease in terms of absolute concentration in $\mu g/m^3$; this city is heavily impacted by tourists in summertime and recorded the presence of about 13 and a half million tourists during the warm season from May to September in the years 2013-2017 (Emilia-Romagna region statistics).

At all 4 sites a decrease in traffic source contribution is observed during the weekend and the decrease is even larger when considering only holidays; this effect was also confirmed by Mann Whitney test (Mann and Whitney, 1947) indicating statistically significant decrease when comparing Sundays and feast days at all 4 sites (from 24% in SPC to 42% in BO).

The traffic factor is the one with the lowest correlation among the sites (correlation coefficient r varying between 0.44 and 0.64), revealing its local character. As already mentioned, the rural site SPC presents the lowest correlation coefficients for both time series and chemical profiles (see Table S6 – S8 in the Supplementary Material).

Polar plots of the factor named traffic with resuspended dust (see Fig. 4 and Fig. S3 in the Supplementary Material) evidence a clear local origin for traffic with prevalent direction pointing at the presence of trafficked roads. Figure 4 shows the polar plots (average over all seasons) positioned on the road map. At SPC polar plots suggest a provenience from West (i.e. from the highway about 13 km away) pointing to a more aged traffic aerosol, consistent with the rural character of this site. At PR the origin seems almost exclusively local, consistent with the location of the sampling site in a park in the city center. At BO there is a notable local origin and the polar plots also indicate a predominant origin from East, probably at the ring road and the E45 and A13 motorways. In RN, in addition to the indication of a local origin, a provenance from North can be observed pointing at the state road which is very busy and fairly close to the site (about 600 m). To exclude possible long-range contributions, back trajectories analysis was also performed.

Fig. 4 – Polare plots for Traffic and resuspended dust at the 4 sites.

3.1.2 Biomass burning (BB)

The chemical profile is characterized by the presence of K^+, Cl^-, EC, and OC, and some elements (Zn, Cd, As, and Pb) which do not impact on $PM_{2.5}$ mass very much but are relevant for their possible effects on human health (Bell et al., 2014; Pun et al., 2014; Basagaña et al., 2015). K^+ is often considered a tracer for biomass burning in many studies (Larsen et al. 2012; Pachon et al. 2013; Venturini et al., 2014; Zhu et al., 2017; Ikemori et al., 2021) and Cl^- was also found to be typically emitted by wood combustion, although less frequently (AIRUSE Project, 2014; Venturini et al., 2014; Hovorka et al. 2015). It is noteworthy that potassium chloride in a previous study performed in 2011-2012 (Venturini et al., 2014) was found to be a tracer of biomass burning at a marine location (Riccione) nearby the RN site. Literature works (Narodoslawsky and Obernberger 1996; Anttila et al. 2008; Gu et al. 2011; Hansen et al. 2001; Hovorka et al. 2015) reported the presence of elements such as Pb, Cd, Zn, and As in the BB profile.

BB represents an important source of particulate matter: at all sites it explains most of $PM_{2.5}$ mass during cold season and it is detected during warm season too. Depending on the site, it accounts for 15% - 30% (Fig. 3) of $PM_{2.5}$ mass on a yearly basis; 20% - 35% in the cold season and 10% - 20% during warm season

(see Table 2). Lower contributions were typically observed in PR and BO while biomass burning in RN gave the highest absolute and relative contributions. Levoglucosan data were not included in this PMF analysis because available only from 15 October 2015. However, levoglucosan concentrations were used in data post-processing to verify results correctness. Correlation between biomass burning PMF factor and levoglucosan concentrations resulted in fairly good agreement with Pearson correlation coefficients of 0.79 for BO, 0.87 for PR, 0.89 for RN and 0.91 for SPC.

The relevance of BB in RN is confirmed by the levoglucosan average concentration which, during the period October 2015-October 2017, is 1.4 times higher than at the other sites (the same calculation performed on the biomass burning contribution from PMF gives a factor 1.5). Looking at the K^+ to levoglucosan ratio, an indication about the possible contribution of K^+ with a crustal origin in RN can be retrieved; however, this ratio is smaller in RN than at the other sites so that an overestimation of biomass burning at the site of RN can be excluded.

The significant impact on BB at RN during summer was confirmed by an ad-hoc study carried out in 2018 with 2 intensive campaigns (in summertime and wintertime) not published yet. Results suggested that the relevance of this source at RN site is likely connected to agriculture and cooking activities as already reported for other areas in the literature; indeed, it is normal practice that crop straw is burned in fields after harvest (Cao et al., 2006; McCarty, 2009; Singh et al., 2014). Farmland straw burning has been recognized as the main source of local air pollution in China, and has become the focus of public attention in both summer and autumn (Xie et al., 2016). About cooking combustion, Alves et al. (2012) in a European study estimated that around 10% of the OC mass in the urban areas originates from cooking emissions. Vicente et al. (2018) experimentally quantified and characterized the gaseous and particulate matter ($PM_{2.5}$) emissions from charcoal combustion in a typical brick barbecue grill and they found that particle emissions were of the same order of magnitude as those from traditional residential wood burning appliances. As PM chemical composition from these sources is quite similar, it is not possible the disentanglement of emissions from charcoal and from other biomass combustion sources.

From polar plots analysis (Fig. S4) biomass burning seems to be a very local factor at all sites and in all seasons and especially in winter when the $PM_{2.5}$ shares attributable to this factor are very high. It is interesting to note that the site of RN shows a clear local origin in cold and warm seasons. According to this analysis the highest levels of biomass burning in this site cannot be ascribed to transported aerosols.

3.1.3 Oil combustion/ship emission

Sulfate, V, and Ni are commonly reported in literature as tracers for oil combustion or ship emission (Mazzei et al. 2008; Becagli et al., 2012; Pey et al. 2013; Bove et al., 2014; Viana et al. 2014; Gregoris 2021). Therefore, the PMF factor with the chemical profile characterized by such components may be related to emissions from power plants, refineries and ships as well. High correlations among the factor temporal

409 contributions at the four sites (r ranging from 0.71 to 0.89 between all pairs of sites, decreasing with
410 distance, Table S8 in the Supplementary Material) suggest a long range transport of air masses impacted by
411 naval traffic. This is also confirmed by the meteorological analysis (see Section 3.2) showing the
412 provenience of air mass from Mediterranean Sea in the days before peaks in factor contribution (see Fig.
413 5a). Sometimes high contributions are registered in concomitance with a Saharan dust event (identified
414 through back-trajectories analysis indicating that air mass originated from North African regions) which
415 could explain the presence of crustal elements such as Fe and La in the chemical profile.
416 The presence of SO_4^{2-} is common in PMF factors related to marine aerosol (Calzolai et al., 2015; Becagli et
417 al., 2017) and – more generally – to aged aerosol (Belis et al., 2013) or air masses which experienced a long-
418 range transport; indeed, residence time of sulfate in atmosphere is estimated between 3 and 9 days
419 (Seinfeld and Pandis, 2016). A study based on five years of data collected in Lampedusa - an island in the
420 center of the Mediterranean sea in southern Italy (Becagli et al., 2012) - reported that in the Central
421 Mediterranean sea several SO_2 sources (anthropogenic, marine biogenic, crustal, volcanic) contribute to
422 non-sea salt sulfate detected in aerosol samples.
423 In addition, the factor shows a marked seasonality with higher absolute and relative contributions during
424 the warm months, in agreement to the evidence of autumn-winter minima and spring-summer maximum
425 in the desert dust transport events at Mt. Cimone (Duchi et al., 2016) and reflecting the enhanced vertical
426 transport of air masses from the lower troposphere and planetary boundary layer during the warm season
427 (Marinoni et al., 2008; Carbone et al., 2014). Higher planetary boundary layer during the warm season plays
428 an important role, by favoring the circulation of air masses at low altitude and therefore the transport of air
429 masses coming from the sea. In addition to favorable weather conditions for atmospheric transport, during
430 summer months in the Mediterranean sea both the number of passenger vessels and small vessels is the
431 largest, probably for the increased recreational travel (Jalkanen et al., 2016).Therefore, it seems plausible
432 to relate this factor to air masses which travelled over the Mediterranean basin and were enriched with
433 ship emissions. Polar plots (Fig. S5) confirm a long-range transport and suggest that this factor is related to
434 air masses coming mainly from the Tyrrhenian and Adriatic seas as observed during strong winds events.
435 This is evident during warm seasons, when contributions to $PM_{2.5}$ are higher. Since this is a factor related to
436 long-range air mass transport, a more detailed analysis of the origin of the air masses was carried out (see
437 Section. 3.2).
438 This factor accounts for up to 5 % of $PM_{2.5}$ mass as an annual average and up to 10% during the warm
439 season.
440
441 *3.1.4 Mix anthropogenic*
442 This factor probably includes production and service activities which have not a well-defined chemical
443 fingerprint, but are related to quite different profiles associated to a variety of anthropogenic sources with

specific characteristics. In Emilia-Romagna the production sector comprises small and medium-sized industries spread throughout the territory. In the three provinces considered in this study there are energy plants, food industries, mechanical factories (including packaging) and ceramic industries. In each of the 3 provinces there is a municipal waste incinerator.

The chemical profile of this factor is mainly characterized by the presence of trace elements (As, Zn, Cd, Pb, Ni, Mn, Sb, Sn). These trace elements are mostly associated to PM industrial emissions as reported in many receptor modeling studies (Taiwo et al., 2014, Pernigotti et al., 2016). EEA (2012) reported that industrial processes (Industrial Processes, Energy use in industry and Energy Production and distribution) make a significant contribution to the total EU-27 emissions of heavy metals (65% Pb, 56% Cd). In published source apportionment studies, elements like Zn, Pb, As, Mn, and Cd were found in chemical profile of "industrial activities" factor (Thomaidis et al., 2003; Reche et al., 2012; Pey et al., 2013); As, Pb, and Zn in "ceramic industry" factor (Pandolfi et al., 2008; Sánchez de la Campa et al., 2010); Zn, Cd and Pb were also suggested as incinerator emission markers (Gratz and Keeler, 2011; Venturini et al, 2013; Lucarelli et al., 2019). In receptor modelling studies, chemical profiles of industrial emissions is very diverse depending on many factors such as the type of industry and the emission control measures in place in industrial plants. The choice and availability of industrial emission tracers in receptor models affects the ability to discriminate among specific source emissions. It is also noteworthy that industrial emissions are often characterized by huge peaks lasting only few hours (see e.g. Taiwo et al., 2014); thus, without high time resolved data the identification of the specific contribution can be hard to detect (see e.g. Forello at al., 2019 and 2020). The reported contribution of industry to PM mass is highly variable too, even when source apportionment studies are carried out at industrial sites (see e.g. Taiwo et al., 2014). In our study, this factor accounts for 5-10% of $PM_{2.5}$ mass at all urban sites as annual average. As already mentioned, it is not identified as a separate factor at the rural site where a possible contribution of anthropogenic activities is included in the traffic factor (with traffic component dominating), that explains about 10% of $PM_{2.5}$ mass. This mix-anthropogenic factor is not characterized by a distinct seasonality in relative terms although higher absolute contributions are typically observed during the cold season when poor dispersion conditions frequently occur.

Polar plots (Fig. S6) point at a local origin at all sites and in both cold and warm seasons; this observation is consistent with the fact that it is not identified by PMF at the rural site of SPC.

3.1.5 Ammonium Nitrate

Ammonium and nitrate are dominant species in this factor profile suggesting the presence of ammonium nitrate salt (Gu et al. 2011; Amato et al. 2016; Farao et al. 2014; Masiol et al. 2017); it is interesting to note that 90-100% of the nitrate detected in the samples is accounted for in this factor. The contribution is almost negligible in summer (5% at maximum) and accounts for 30-40% of $PM_{2.5}$ during cold season at all

sites thus pointing at the relevant role of ammonium nitrate in the Po Valley during wintertime as already reported e.g. by Vecchi et al. (2018).

Strong seasonality of this factor is typical and it is due to meteorological conditions, because high temperatures maintain ammonium nitrate in gas phase (Seinfeld and Pandis, 2016) and possible sampling artifacts can promote ammonium nitrate losses from the filters (Vecchi et al., 2009a). During winter nitrate contributions at the rural site are lower than at other sites while during summer the opposite situation occurs. In summertime 2012, during a field campaign at SPC, Sandrini et al. (2016) observed ammonium nitrate formation during nighttime with concentrations on average 5 times higher at the rural site than in BO and concluded that lower average temperatures and higher average relative humidity recorded during the night in SPC with respect to BO probably played an important role.

Temporal patterns of PMF contributions show very high correlations among sites (r between 0.84 and 0.90) highlighting once again the homogeneity of this component at the regional scale.

In the chemical profile, small contributions due to OC, K^+, and Cl^- suggest that this factor has also a connection with biomass burning emissions which are also characterized by the same seasonal pattern. Recently, Forello et al. (2020) reported a similar chemical profile related to a factor mixing nitrate and aged aerosols.

Also ammonium nitrate polar plots (Fig. S7) evidence a clear local origin, especially during the cold season, when it accounts for more than 30% of $PM_{2.5}$ mass (during warm season its contribution is minimal).

3.1.6 Ammonium Sulfate and Organics

This factor is characterized by the presence of organic aerosol and secondary inorganic ions like ammonium and sulfate, probably in the form ammonium sulfate or bi-sulfate (Andriani et al. 2011; Gu et al. 2011; Bove et al. 2014; Masiol et al. 2017). In the same factor not negligible shares of As (about 20%), known as charcoal combustion tracer (Larsen et al., 2008), have been also observed.

This factor accounts for about 64-99% of the sulfate detected in the samples; it explains 20% of $PM_{2.5}$ annual average mass at urban sites and about 35% at the rural site of SPC. This factor presents a high correlation among the sites (Pearson correlation coefficient varying from 0.67 and 0.82). During the warm season, when the photochemical activity is stronger (Amato et al., 2009), absolute values are slightly higher while percent contributions are consistently higher and vary from about 40% in RN to about 65% in SPC. The occurrence of high sulfate concentrations in the Po Valley was observed in previous works (Vecchi et al., 2009b; Squizzato et al., 2012; Canepari et al., 2014) and it was explained by air masses transport from Eastern Europe, where sulfur-rich fuels are still in use (while this is not the case in Italy). During wintertime, the occurrence of low mixing layer heights and foggy days with high relative humidity likely promote the formation of sulfate through heterogeneous phase chemical reactions.

Sulfate is commonly referred to be a continental background component deriving from long range air masses transport such as marine traffic or coal-fired power plants located in Eastern Europe (Hamed et al., 2007); indeed, SO_2 – i.e. the sulfate precursor - tends to spread homogeneously because of its thermal stability and its relatively long life time in the atmosphere (Seinfeld and Pandis, 2016). The presence of As in the profile suggests coal-fired power plants as potential source.

For the ammonium sulfate and organics, it is interesting to observe the non-local origin of this factor (Fig. S8) , with a provenance from the East, during the cold season. A more detailed analysis was carried out to investigate the long-range provenience of this factor (see Section 3.2).

3.1.7 Comparison of source contribution observed in previously published work for the same region

Previous source apportionment studies on $PM_{2.5}$ carried out in the Po Valley (Amato et al., 2016; Farao et al., 2014; Larsen et al., 2012; Masiol et al., 2020; Squizzato et al., 2017; Tositti et al., 2014; Venturini et al., 2014) found the same factors as those reported in this study, although sometimes differently aggregated (as in the case of secondary aerosol components that can be found in a single factor) or disaggregated (as in the case of traffic and crustal material that here are combined into a single factor). The relevance of the secondary component is confirmed by all studies and the overall contribution of nitrate and sulfate to $PM_{2.5}$ mass concentration varies from about 50% (Amato et al., 2016) up to 75% (Larsen et al., 2012). Thunis et al. (2020) reported that in the Po Valley the relative contribution of secondary inorganic $PM_{2.5}$ component ranges between 40 and 50%, and is quite homogeneously distributed over the entire area. Traffic and BB factors are the first two anthropogenic factors at the various investigated sites, with alternating importance depending on the study. A factor characterized by V and Ni was also found by Masiol et al. (2020); in Amato et al.(2016) and Farao et al. (2014) a factor including V, Ni, and sulfate was discussed. Other factors of anthropogenic origin are sporadically reported in some studies e.g. Amato et al. (2016), Farao et al. (2014), and Squizzato et al. (2017) reported about a generic industry factor, while Venturini et al. (2014) found a factor associated with natural gas home appliances. Regarding factors of natural origin, the crustal factor is sometimes found as a separate factor (Amato et al., 2016; Masiol et al., 2020) accounting for about 5% to $PM_{2..5}$, sometimes together with the non-exhaust component (Squizzato et al., 2017) or with other components (Larsen et al., 2012; Farao et al., 2014).

3.2 Back-trajectories analysis

In order to better understand aerosol transport processes, for the non-local factors we analyzed back-trajectories retrieved by Hysplit model. Polar plots in fact use local wind speed and direction data and are more suitable for detecting the influence of potential local sources (Carslaw et al., 2006; Carslaw and Beevers, 2013), while PSCF and CWT consider long range air mass transports (Cheng,2015; Kim, 2020).

Back-trajectories analysis was carried out to better understand the oil combustion/ship emission (Fig. 5a) and the ammonium sulfate and organics (Fig. 5b) PMF factors, for which the polar plots have suggested an extra-regional contribution. We also investigated the traffic factor (Fig. 5c) because polar plots highlighted also a provenance from distinct directions at the different investigated sites although a local origin was evident. This was attributed to roads near to the sampling site (max 13 km for the rural site) but the possibility of aerosol transport from longer distance was also checked. In addition, an analysis of the back trajectories was carried out for $PM_{2.5}$ total mass (Fig. 5d).

Concentration weighted trajectory (CWT) approach has been applied to investigate the origins of ammonium sulfate and organics PMF factor, traffic with resuspended dust PMF factor and total $PM_{2.5}$ mass. As reported in Section 2.4, for each cell this method provides a weighted concentration obtained by averaging sample concentrations associated to trajectories which crossed that grid cell. In this way, the CWT method shows concentration gradients across potential source areas. A different approach was used for oil combustion/ship emission factor. Time series contributions due to oil combustion/ship emission are characterized by few huge peaks which occur mainly during spring or summer. For this reason, days with contributions over the 90^{th} percentile were analyzed with Potential Source Contribution Function (PSCF). Back trajectories were calculated at a height of 500 m a.g.l. (above ground level) for this analysis, because the days with concentrations $<90^{th}$ percentile of this factor are almost all in the warm season with higher planetary boundary layer (PBL). For CTW analysis, since this elaboration considers every day of the year, back trajectories were calculated at a height of 100 m a.g.l., according to Sogacheva et al. (2007) who calculated the back-trajectories at SPC site too.

In the vast majority of cases when oil combustion/ship emission factor contributions exceeded 90^{th} percentile, air masses overpassed Mediterranean Sea in the previous days (Fig. S1). In addition, PSCF analysis showed a significant probability of high levels occurrence in the investigated area in the following 72 hours (Fig. 5a). These observations underline that the impact of naval traffic in this factor is remarkable. CWT analysis for secondary sulfate and organics points to Eastern Europe provenance; similar findings for the Po Valley were already reported e.g. by Bernardoni et al. (2011), Canepari et al. (2014) and Masiol et al. (2020).

There is no evidence of an extra-regional origin for the traffic factor, apart from some cells in the south east Mediterranean which are also evident in the analysis on $PM_{2.5}$ mass concentrations and hardly can be related to the traffic factor.

$PM_{2.5}$ mass concentration origin seems to be originated partly from the same area as the ammonium sulfate factor. It is also highlighted the south east Mediterranean area, where the oil combustion/ship emission factor was observed too. However, it is unlikely that the latter is responsible for high levels of $PM_{2.5}$, given its low contributions in terms of mass concentrations. A possible interpretation for these cells located in the south east of the Mediterranean might be given considering wintertime cases (Fig. S2) when

582 air masses have crossed these cells during synoptic scale weather conditions related to local atmospheric
583 conditions favouring stagnation (Finardi and Pellegrini, 2004). This is only a possible interpretation that can
584 be further verified and investigated; higher spatial resolution of the input meteorological files will also be
585 necessary for a more accurate analysis.
586
587 Fig. 5 – (a) Seasonal Potential Source Contribution Function (PSCF) for *Oil combustion/ship emission*
588 calculated on 90th percentile, over 72 hours. The PSCF value in a cell is the number of high ($\geq$ 90th
589 percentile) concentration values divided by the total number of trajectory points in the cell. 72 hours long
590 back trajectories are calculated at the 4 sites at 500 m a.g.l. between 01/04/2013 and 14/10/2017 at 0:00,
591 6:00, 12:00 and 18:00
592 Concentration-Weighted Trajectory (CWT) method applied on *Secondary sulfate and organics* (b) daily
593 concentrations, on *Traffic with resuspended dust* (c), and on $PM_{2.5}$ mass (d). Each grid cell is assigned an
594 average of concentrations associated to trajectories crossing that grid cell. 72 hours long back trajectories
595 are calculated at the 4 sites at 100 m a.g.l. between 01/04/2013 and 14/10/2017 at 0:00, 6:00, 12:00 and
596 18:00.
597
598 ***4 Discussion***
599 This study showed the similarity and peculiarities of 4 sites representative of different areas of southern Po
600 Valley (Fig. 1). The similarity is certainly given by the fact that main pollution sources – as also identified by
601 PMF - are the same at the 4 sites and their chemical profile is largely comparable. Excluding SPC, they are
602 all urban background sites chosen to maximize the representativeness of population exposure to
603 particulate matter and to avoid locations strongly impacted by local sources. PMF results (Table 2) showed
604 that at BO and PR source contributions to $PM_{2.5}$ from different factors were very similar; opposite, $PM_{2.5}$ in
605 RN resulted largely accounted for by biomass burning emissions in both cold and warm season thus
606 pointing at the role of cooking and agricultural activities in addition to residential heating. As concerns SPC,
607 contributions from the different sources were typical of a rural background site.
608 As for local sources of primary origin, traffic gave the most relevant contribution in BO and PR urban areas
609 as annual average; opposite, biomass burning contribution was higher than traffic one in RN and, as
610 expected, at the rural site SPC. During wintertime, biomass burning accounted for the largest part of $PM_{2.5}$
611 mass at all sites; wintertime is also when daily limits imposed on PM_{10} concentration (50 µg/m^3 for not
612 more than 35 days in solar year, Directive 2008/50/CE) are more often exceeded in the investigated area.
613 However, biomass burning contribution does not become null even during the warm season although a
614 huge decrease in its contribution can be observed (see Table 2). This result suggests that, in addition to
615 domestic heating, wood burning cooking and open burning of agricultural pruning bonfires are not
616 negligible sources of biomass burning, especially during warm season. The non-ideal combustion mode

typical of wood combustion activities mentioned above and the lack of abatement systems likely lead to an increase in emissions. More than the other locations considered in this study, RN is an important tourist destination with many pizzerias and restaurants with wood ovens and large campsites with areas dedicated to grilling; in addition, the habit of disposing of agricultural pruning with large open-air bonfires is quite common in this area. These motivations can explain the significant contribution of biomass burning (20%) in RN during summertime.

An increasing number of studies are highlighting the effects of wood burning on human health. A systematic review of health effects from air pollution (http://bit.ly/WHO_EU2013) concluded that there are no reasons to consider particulate matter deriving from biomass burning less toxic than particulate matter from other sources. A recent study (Corsini et al., 2017; Marabini et al., 2017) performed in Northern Italy on ultrafine particles evidenced both pro-inflammatory and genotoxic effects due to biomass burning aerosols; literature studies (see e.g. Corsini et al., 2019; and references therein) all over the world also report about health effects due to biomass burning emissions. Pollution from domestic heating with solid fuel has caused about 1 million DALYs ("Disability-Adjusted Life Years" = Years of Life Lost + Years Lived with Disability) in Europe in 2010 (Economic Commission for Europe, 2014). Exposure to $PM_{2.5}$ from bush fires has been associated with out-of-hospital cardiac arrest (Dennekamp et al., 2015; Haikerwal, 2015).

These results suggest to take into account the opportunity to monitor and regulate summertime biomass combustion activities as they were detected as non-negligible sources of $PM_{2.5}$ with possible health effects. Monitoring such activities is not straightforward as they are characterized by variable and episodic emissions and assessing them in a reliable way with traditional methods (emission inventory, fixed-site monitoring stations and even passive samplers or mobile stations) is not easy. In agricultural countries, however, new techniques have been successfully used for fire detection, such as satellite remote sensing (Schreuder M. and Mavko M., 2010; Verma et al., 2019, Temudo et al., 2020) and low-cost sensor operated on commercial drones (Vreeland et al., 2018).

An industrial factor is not singled out clearly but it is included in a generic "mix anthropogenic" source and has less relevance compared to the aforementioned factors, not exceeding 10% of the $PM_{2.5}$ mass as primary contribution. This is in line with what emerged in previous European studies (Belis et al., 2013, Giardullo, 2016) but it is in contrast with the general perception of the Italian population, who often considers industry the first polluting factor (Giardullo, 2016).

The long-range factor associated to oil combustion/ship emissions was quite unexpected, especially because the impact was not only observed at the coastal site but also in the inner part of the region. Further extensive investigations are still needed to definitively clarify if these are emissions due to ships or refinery plants or a mix of both. The contribution due to this factor is on average similar to the anthropogenic mix one, accounting for a few percents (on average less than 5%) of $PM_{2.5}$ mass. It is

651 detected mainly during the warm season, therefore, it does not give a significant contribution to
652 exceedances of the $PM_{2.5}$ EU target value (25 μg/m^3); nevertheless, V and Ni which characterize the
653 chemical profile of this factor could threaten human health (Bell et al., 2014; Pun et al., 2014; Basagaña et
654 al., 2015) despite they are not relevant in terms of $PM_{2.5}$ mass. This factor accounts for 30-45 % of the total
655 Ni (element subject to regulatory limits, according to Directive 2004/107/CE, UE, 2004b) detected at the
656 investigated sites (32% in PR, 37% in BO, 44% in SPC and 45% in RN).
657 This study confirms also the role of secondary aerosol components, which account for about half of $PM_{2.5}$
658 mass at urban sites and for about two thirds of the mass concentration at the rural one, showing a marked
659 seasonal trend with ammonium sulfate dominating in the warm season and ammonium nitrate being the
660 most abundant component during the cold season. The Po Valley is one of the large hot-spots for ammonia
661 emissions in Europe (e.g. EAA, 2012; Carozzi et al., 2013; Van Damme et al., 2018) so that nitrates and
662 sulfates are typically in the form of ammonium nitrate and ammonium sulfate. As expected, the relative
663 contribution from secondary aerosols at the rural site of SPC (about 60%) is higher than at urban sites
664 (about 45%-55%) due to the minor influence of primary contributions. It is noteworthy that the relative
665 contribution of secondary inorganic aerosol detected in the Po Valley – especially in rural locations - is
666 typically higher than the median values found on European sites and comparable only to concentrations
667 observed in the Netherlands (Belis et al., 2013); indeed, the wintertime weather conditions of the Po Valley
668 favor accumulation and condensation processes which promote ammonium nitrate formation from
669 gaseous precursors such as nitrogen oxides and ammonia (Perrone et al., 2012; Stanier et al., 2012;
670 Ricciardelli et al., 2017). According to the regional emissions inventory (Emilia-Romagna region, 2017), NO_x
671 is originated almost exclusively from combustion processes, mainly related to transport and to a lesser
672 extent to production activities, heating, and agricultural machinery while ammonia is originated for more
673 than 98% by agricultural and livestock activities.
674 Considering that NH_4^+ originates from NH_3 in atmosphere, it can be roughly estimated that also 98% of the
675 ammonium detected in $PM_{2.5}$ samples derives from agricultural and livestock activities; therefore, in our
676 study an amount estimated in 2.4 μg/m^3 of ammonium originates from these emissions, i.e. about 11% of
677 the average $PM_{2.5}$ mass. This quantity is roughly calculated but it is probably an underestimation of the real
678 impact of agriculture in the investigated area, because it takes into account only ammonia and does not
679 consider other emissions related to agricultural and livestock activities, such as those related to combustion
680 or resuspension induced by agricultural machinery and to the use of pesticides, and field burning of
681 agricultural wastes (these ones accounted for in the biomass burning factor, in our study).
682 The impact of pollution attributable to agriculture and livestock is commonly underestimated by the
683 population. From the Prepair survey (Marongiu et al., 2019), emerges that in Emilia-Romagna only one out
684 of four respondents considers agricultural and livestock as activities which impact much or very much on air
685 pollution, while domestic heating, transport, and industry are considered to give a huge contribution by

more than half to around two thirds of respondents. Giardullo (2016) reported that there is a big difference between the PM_{10} imputable to this factor and the one perceived by the Italian population. Currently, recent studies agree on the impact of agricultural emissions on health and environment worldwide. Literature works (e.g. Bessagnet et al., 2014; Giannadaki et al., 2018; and references therein) highlighted the high contribution of NH_3 and in general emissions linked to agriculture in fine aerosol formation and levels. Lelieved et al. (2015) estimated that in eastern Europe, Russia, USA, and East Asia agricultural emissions are responsible for the largest relative contribution to $PM_{2.5}$ and on mortality linked to outdoor air pollution in 2010. Giannadaki et al. (2018) estimated for Italy a reduction of 75% in mortality attributable to $PM_{2.5}$ and relative cost range, in a scenario where agricultural emissions are eliminated. Pozzer et al. (2017) reported that reducing by 50% the agricultural emissions of NH_3, a reduction of $PM_{2.5}$ equal to 2.4 μg/m^3 could be obtained in the Po Valley region. Lovarelli et al. (2020), by discussing the role of agriculture and livestock activities in Po Valley during Covid-19 quarantine, pointed at the need for lowering agricultural NH_3 emissions to improve the air quality and underlined the importance of a combined role of all productive sectors in abating $PM_{2.5}$. The impact of agriculture and intensive livestock farms definitely claim for further investigation in the Po Valley where these activities have a great economic importance (Banca d'Italia, 2018).

As confirmed by the sulfate–to-ammonium diagnostic ratio found in the secondary sulfate PMF factor, sulfate is almost exclusively present as ammonium sulfate, produced by photochemistry and heterogeneous phase reactions from SO_2 gaseous precursor. According to available emissions inventory, almost all SO_2 in Po Valley can be ascribed to production activities (80%); SO_2 concentrations recorded in Emilia-Romagna in the period 2013-2017 were extremely low, almost always lower than the limit of quantification (14 μg /m^3) (Arpae, 2018). As already discussed in Section 3.2, transport of air masses enriched in sulfate from Eastern Europe countries to the Po Valley were clearly identified in this work and also reported in literature (Hamed et al., 2007; Bernardoni et al., 2011; Canepari et al., 2014, Masiol et al. 2020); it is thus of interest to assess how much of the secondary sulfate is of local origin and therefore its abatement can be carried out through local policies and how much of it is of extra-border origin and cannot be decreased with actions taken at regional or national level.

More complex is the attribution of the organic component which can derive from many sources; anyway, as described in Section 3.1.5, an important signal of an aged biomass burning is clearly identified by PMF at almost all sites; indications about the relevance of biomass burning in the secondary organic aerosol production has been reported in recent studies (e.g. Gilardoni et al., 2016; Forello et al., 2020; Paglione et al., 2020).

Last but not least, a consideration about the epidemiological aspects is appropriate due to the huge population living in the Po Valley. There is a growing body of epidemiologic research on source-specific

associations of $PM_{2.5}$ on a variety of health outcomes; results from this study have been already used by Ottone (2020) who showed a statistically significant association between the risk of preterm birth and 3 factors identified by PMF, i.e. traffic, oil combustion/ship emission and secondary sulfate and organics. Secondary sulfates and organics and oil combustion/ship emission account for a significant part of $PM_{2.5}$ mass (both as absolute and relative contribution) especially during the warm season; also traffic relative contribution is larger in the warm season. These findings are consistent with previous studies that have shown a stronger effect of particulate matter on health during the warm season compared to the cold one (Nawrot et al., 2007; Stafoggia et al., 2008; Samoli et al., 2013) although the mechanisms underneath call for further investigations.

5 Conclusions

This paper reports about results retrieved by a source apportionment analysis over a period of four years, at four sites in the Emilia-Romagna region considered representatives of different areas of southern Po Valley. As far as we know, this is the first multi-site study with such a temporal covering performed in the well-known European pollution hot-spot located in northern Italy.

Results about major sources impacting on the investigated area highlight the need for structural coordinated interventions throughout the entire basin. In order to further decrease the background concentrations of air pollution, coordinated and large-scale actions are needed. The relevance of secondary aerosols in $PM_{2.5}$ mass concentration strongly suggests that unfavorable climatic conditions which promote air mass stagnation and pollution build-up make it difficult to lower concentration values. Therefore, to achieve significant pollution reduction in this area huge efforts in emission abatement are needed, more than those required in other Italian and European regions. Expensive and demanding interventions must be targeted as much as possible through a coordinated effort played by all the regions located in the Po Valley.

This study confirms traffic and biomass burning as the most relevant contributors to $PM_{2.5}$ in terms of primary components. Noteworthy is the not negligible contribution of biomass burning in RN during summer suggesting that other possible sources of wood combustion, such as open burning of agricultural pruning bonfires and cooking play a role in $PM_{2.5}$ concentrations. Indeed, these activities are characterized by a not ideal combustion process and do not have abatement systems, therefore they can be significant $PM_{2.5}$ sources. These emissions deserve further study and new monitoring techniques following examples reported in recent literature works.

Agricultural and livestock activities were not singled out by PMF analysis (mainly due to the lack of specific source tracers) but a rough estimate based on ammonium concentrations and ammonia data from emission inventory indicates a contribution from this source of at least 10% to which the exhaust off-road vehicles emissions and pruning burnings (accounted for in the biomass burning factor) must be added.

754 Agriculture and livestock seem to be therefore the productive activity with the highest impact on $PM_{2.5}$ at
755 the investigated sites. This is in agreement with the known literature and with the recently growing number
756 of studies on these productive activities and it is not unexpected due to paramount importance that these
757 activities have in Po Valley.
758 Specific industrial emissions were not identified by PMF although at urban sites a generic factor defined as
759 anthropogenic mix accounted for 5 - 10% of $PM_{2.5}$ mass.
760 Lastly, PMF analysis shows a minor but clear contribution from heavy oils combustion/ship emissions,
761 which is related to long-range transport of air masses overpassing Mediterranean and whose possible
762 impact on health must be further investigated. With regard to the cross-border contribution, we also
763 emphasize the relevance of the secondary sulfate coming from Eastern Europe countries. This specific
764 contribution has not been quantified but clearly emerges from the back-trajectories analysis.

765

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774

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Credit Author Statement

Author contributions

Fabiana Scotto:, Writing - original draft, Methodology, Conceptualization, Formal analysis, Data curation

Dimitri Bacco: Data curation; Methodology; Writing - review & editing

Stefano Lasagni: Methodology, Formal analysis, Writing - review & editing

Arianna Trentini: Writing - review & editing

Vanes Poluzzi: Project administration, Writing - review & editing

Roberta Vecchi Methodology; Supervision; Validation; Writing - original draft

Figure1

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Figure3

April 2013 − October 2017

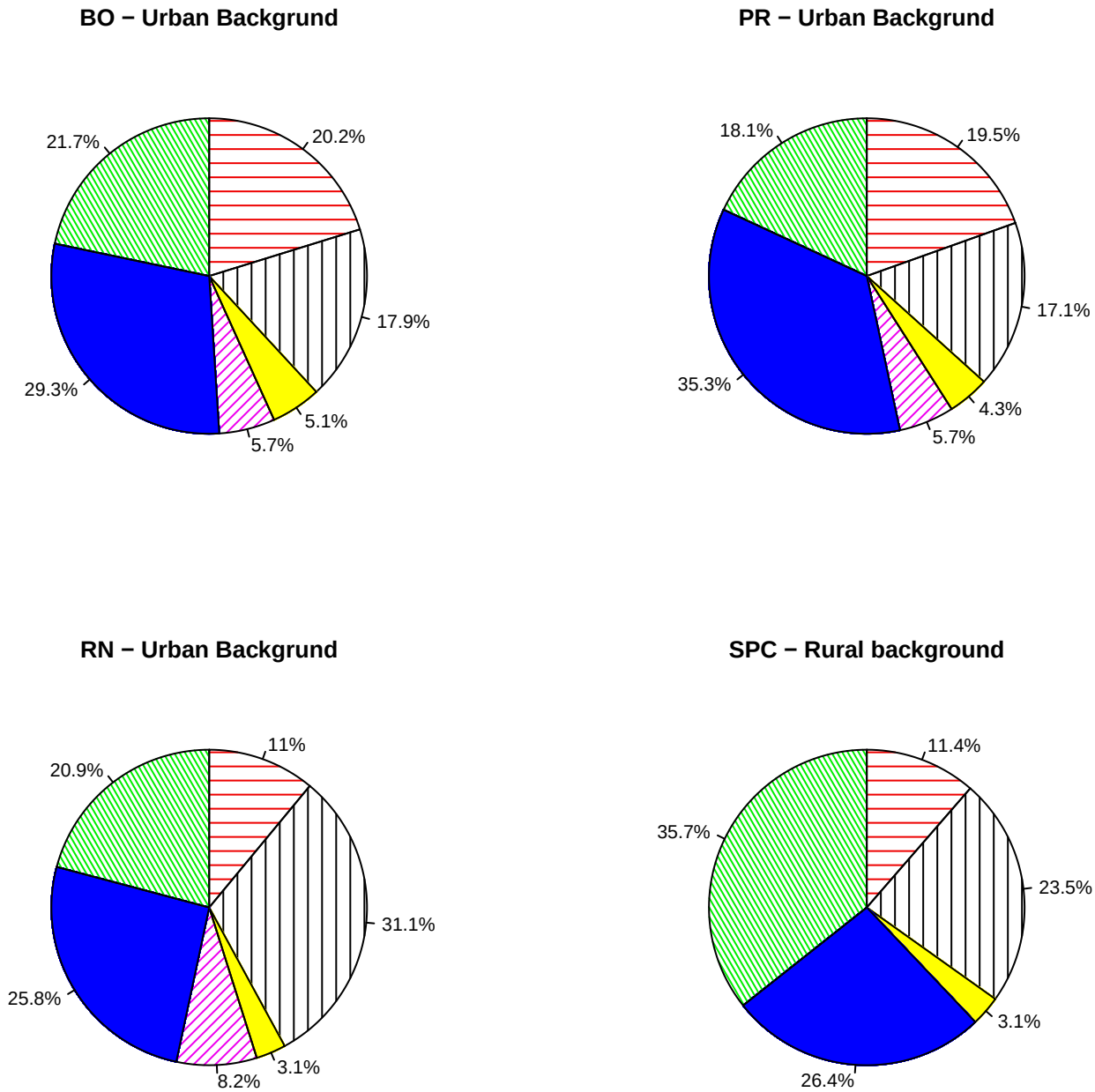

Figure 2

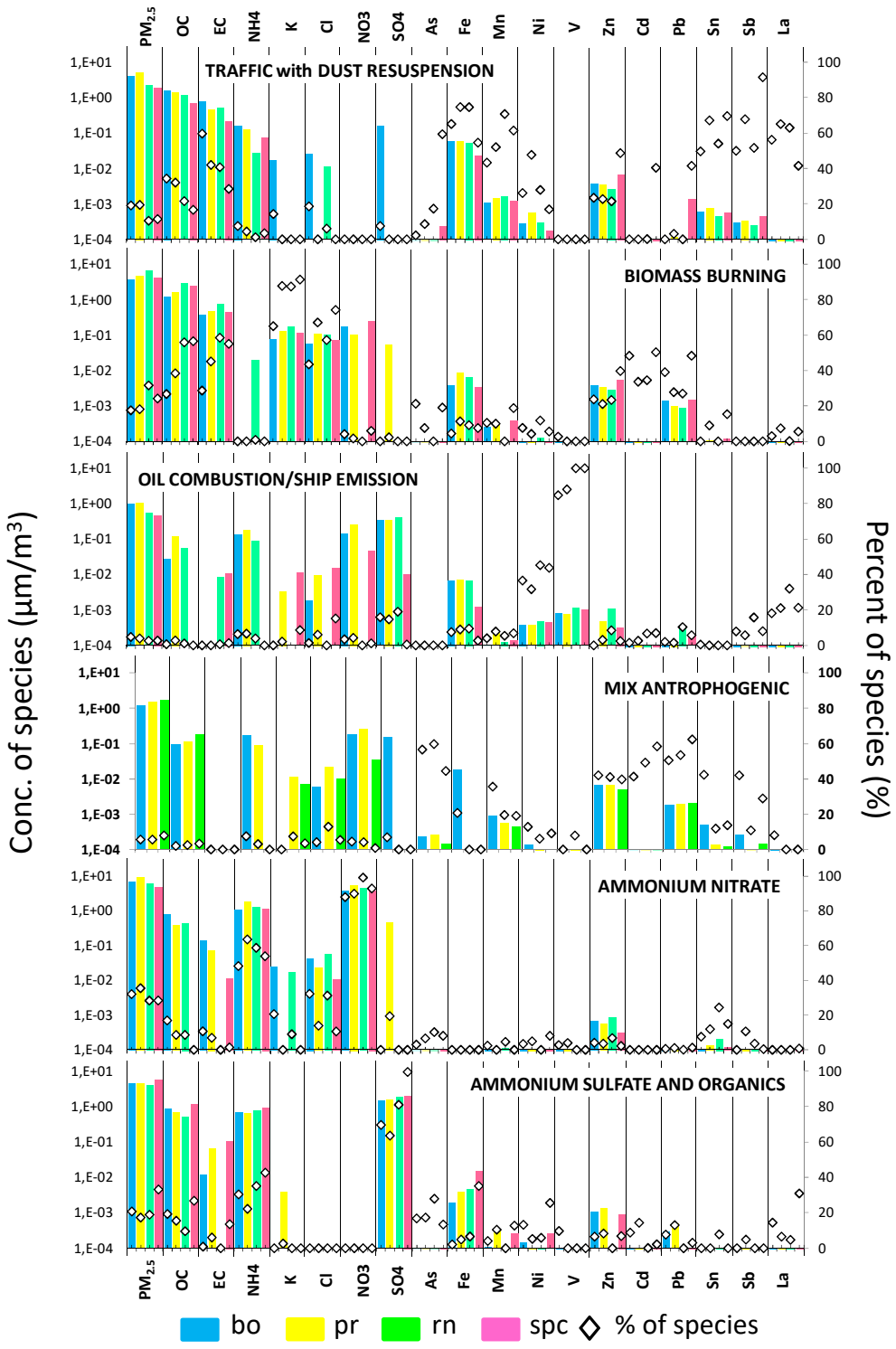

Figure 4

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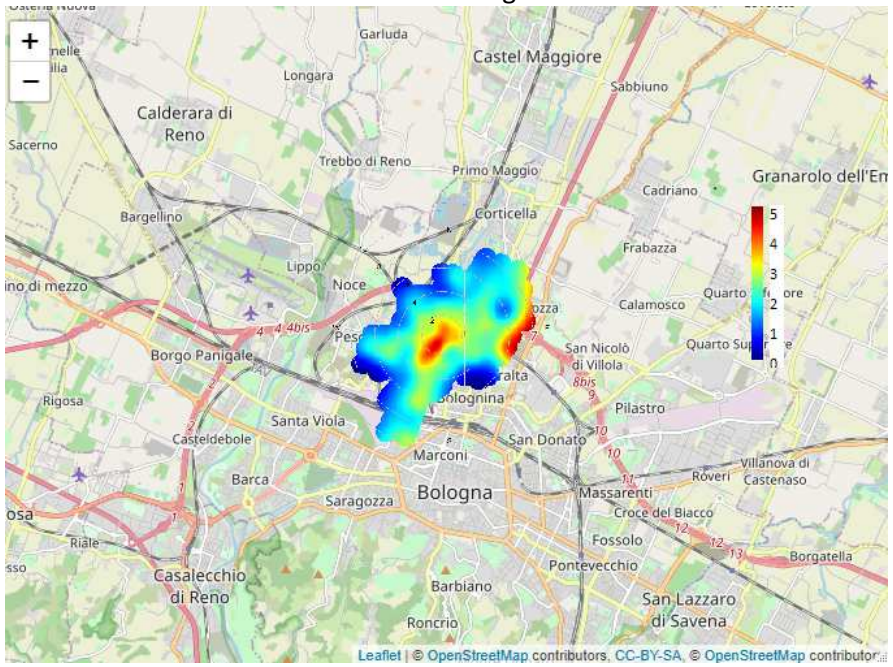
BO – Urban background



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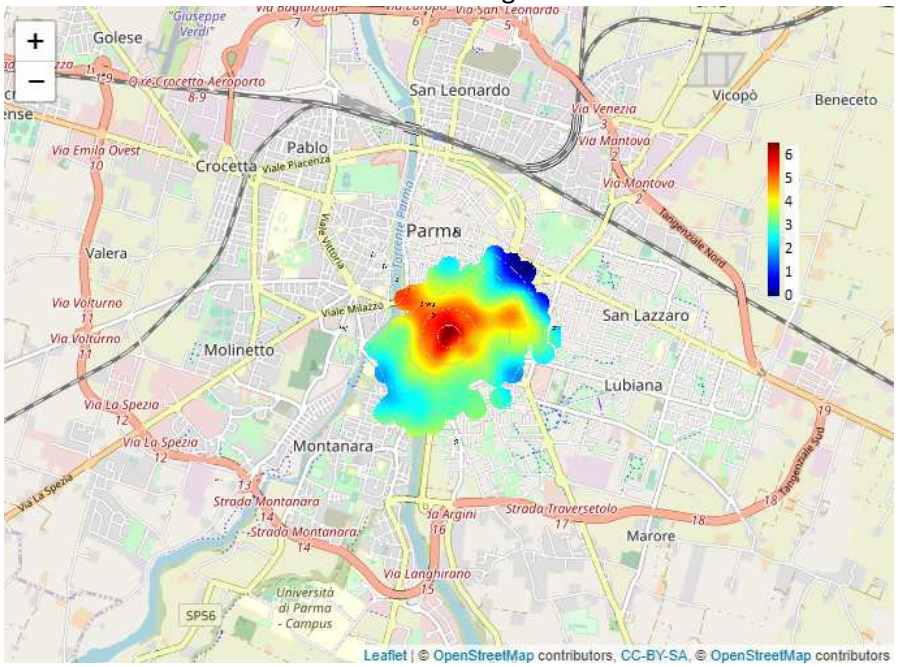

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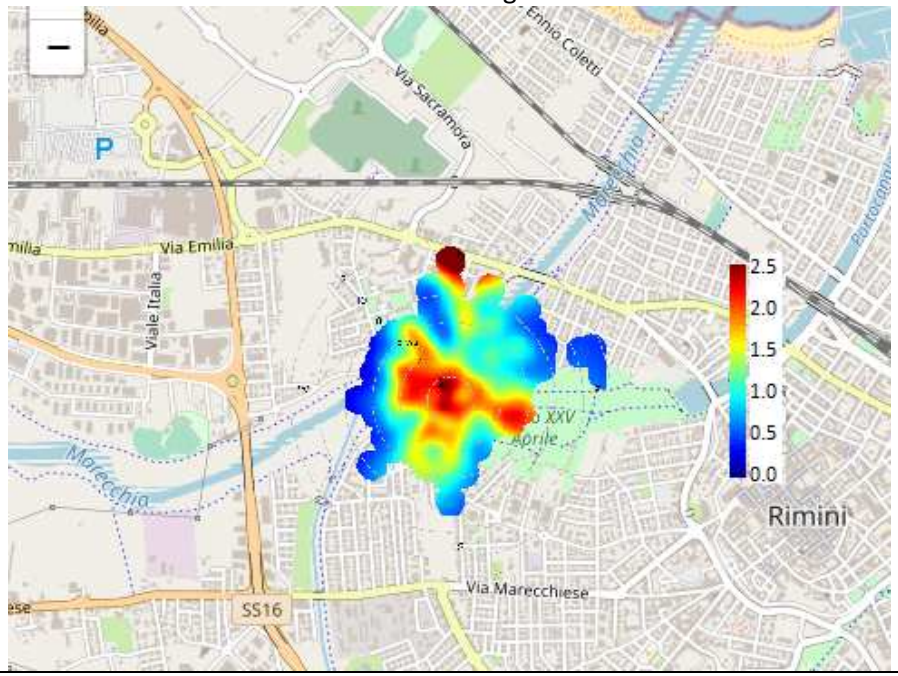

SPC – Rural background

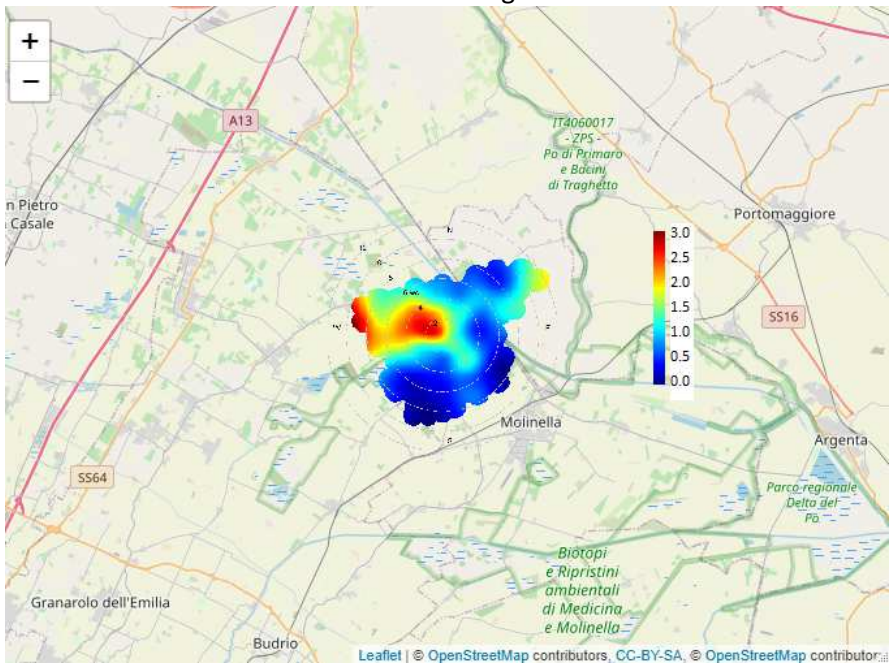

Figure 5