

Source apportionment of particulate matter in a large city of southeastern Po Valley (Bologna, Italy)

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Abstract This study reports the results of an experimental research project carried out in Bologna, a midsize town in central Po valley, with the aim at characterizing local aerosol chemistry and tracking the main source emissions of airborne particulate matter. Chemical speciation based upon ions, trace elements, and carbonaceous matter is discussed on the basis of seasonal variation and enrichment factors. For the first time, source apportionment was achieved at this location using two widely used receptor models (principal component analysis/multi-linear regression analysis (PCA/MLRA) and positive matrix factorization (PMF)). Four main aerosol sources were identified by PCA/MLRA and

interpreted as: resuspended particulate and a pseudo-marine factor (winter street management), both related to the coarse fraction, plus mixed combustions and secondary aerosol largely associated to traffic and long-lived species typical of the fine fraction. The PMF model resolved six main aerosol sources, interpreted as: mineral dust, road dust, traffic, secondary aerosol, biomass burning and again a pseudo-marine factor. Source apportionment results from both models are in good agreement providing a 30 and a 33 % by weight respectively for PCA-MLRA and PMF for the coarse fraction and 70 % (PCA-MLRA) and 67 % (PMF) for the fine fraction. The episodic influence of Saharan dust

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transport on PM₁₀ exceedances in Bologna was identified and discussed in term of meteorological framework, composition, and quantitative contribution.

Keywords Particulate matter · PM₁₀ · PM_{2.5} · Bologna and Po Valley · Receptor modeling · Source apportionment · PIXE · Enrichment factors

Introduction

Air pollution has long been recognized as a serious concern due to its negative influence on the biotic and abiotic compartments of the Earth at both small and large scales, including climatic change. In the last two decades, airborne particulate matter (PM) has increasingly attracted the interest of the scientific community because, in spite of the ever improving efforts in abatement technologies, its concentration is locally still very high often exceeding the thresholds. Effects of PM hazards include damage to the environment and cultural heritage (Camuffo et al. 2001; Godoi et al. 2006; Nava et al. 2010) through direct and indirect effects such as respectively alteration of atmospheric chemistry and reactivity, climate change and biogeochemical cycles (Charlson et al. 1992; Finlayson-Pitts and Pitts 1986; Usher et al. 2003; Seinfeld and Pandis 2006; Forster et al. 2007) as well as adverse impacts on human health (Davidson et al. 2005; Pope and Dockery 2006; Pope et al. 2009).

The persistence of high levels of atmospheric pollution arises from a number of figures spanning from a generalized and huge increase in all the types of transportation from vehicles to maritime and aviation (EEA report 2011), building, soil use, urbanization and atmospheric circulation at every space and time scale. In this framework complexity in aerosol chemistry and phenomenology (Van Dingenen et al. 2004; Putaud et al. 2004; Prather et al. 2008; Putaud et al. 2010; Carslaw et al. 2010; Colb and Worsnop 2012), linking PM composition to its peculiar and transient mix of sources are still a matter of basic research. Although the formation mechanisms and chemical characterization of PM are still quite challenging, valuable tools for the identification of the emission spectrum over a location have long been available. Source apportionment techniques based upon chemical speciation and subsequent receptor modeling provide in facts a fundamental tool in order to obtain quantitative and reliable information about the number and types of sources of PM active in a given location. Such information is of crucial importance to understand the potential emission sources and to take corrective decisions within environmental policies in a given area. In the last decade, the use of these tools has provided an ever increasing application with the aim of solving PM sources mix in a innumerable series of

cases (see for example, Harrison et al. 1997; Querol et al. 2001; Marcazzan et al. 2003; Vallius et al. 2005; Kim et al. 2003a,b; Viana et al. 2007; Viana et al. 2008a; b and references therein; Yin et al. 2010; Masiol et al. 2012a; b; Pant and Harrison 2012).

If the choice of PM chemical species to characterize is fairly unlimited and to some extent arbitrary, though always experimentally demanding, data treatments enabling source apportionment include a relatively limited number of statistical techniques among which the most popular and effective are presently the principal component analysis followed by multi-linear regression analysis (PCA/MLRA, Thurston and Spengler 1985; Viana et al. 2006; Viana et al. 2008a; Almeida et al. 2006; Viana et al. 2008a) and the positive matrix factorization (PMF, Paatero and Tapper 1994; Lee et al. 1999; Kim et al. 2003a,b; Lee et al. 2008).

In this work, we present data of chemical speciation based on major inorganic ions, trace elements and carbonaceous matter collected in Bologna within the framework of the national project SITECOS (Integrated Study on national Territory for the characterization and the COntrol on atmospheric pollutantS), covering simultaneous and coherent PM monitoring in ten locations of the Italian peninsula in association with the large meteoroclimatic and environmental differences from north to south (Amodio et al. 2007). Bologna was one of the stations hosting SITECOS monitoring activity in the Po Valley. The whole Po Valley is recognized as one of the most polluted regions in Europe due to highest level of population and industrial density. Moreover, automotive, railing and flying transports have been regarded as important emission sources for this area (EC 2004). Extensive agricultural activity and related food industry is highly developed in the whole region.

The air quality in the Po Valley is usually very poor not only due to the aforementioned anthropogenic emissions, but also to its topography. Alps and Apennines mountain chains act as a shield against atmospheric circulation, leading to weak winds, low mixing heights and prolonged atmospheric stabilities, causing air mass stagnation and reduced pollutant dispersal both in the cold (extreme PM average concentrations) and in the warm (extreme photochemical levels) seasons.

Several studies on PM composition and source identification have been carried out in various urban locations of the Po Valley, e.g., in Turin (Gilli et al. 2007), Milan (Marcazzan et al. 2003; Lonati et al. 2005), Venice-Mestre (Rampazzo et al. 2008), Ispra (Rodríguez et al. 2005) and Bologna (Matta et al. 2002). Still, the whole region is a sort of large-scale laboratory deserving attention and efforts by the scientific community. A recent overview on receptor model techniques, European studies and sources can be found in Belis et al. (2013).

Fig. 1 Map and location of Bologna (44°29' N, 11°20' E) in the Italian Po Valley (Planiglobe, kk&w—digital cartography)



Bologna (44°29' N; 11°20' E) (Fig. 1) is a midsize city (380,000 inhabitants) reaching one million people including the metropolitan area. The territory is not directly affected by large-scale industrial facilities, however a recently upgraded municipal waste incinerator is active in the town outskirts and mechanical and food manufacturers are densely present in the whole area, together with agricultural activities. Due to its strategic location at the crossroad between north and south of Italy as well as of the western and eastern sides of the Po Valley, it is heavily interested by large-scale transportation (railway and aviation) but it is mainly affected by local and long-range light and heavy duty traffic. It is worth noting that besides the urban traffic, Bologna is an important crossroads between North and South Italy; moreover it is surrounded by much trafficked orbital roads.

This study mainly aims to evaluate the source contributions in an urban background site in Bologna by: (1) detecting the seasonal variations in PM chemical composition; (2) identifying and quantifying the main emission sources using PCA/MLRA (Viana et al. 2006) and PMF (Paatero and Tapper 1994; Paatero 1997; 1999) receptor

modeling techniques; (3) comparing the source apportionment results, and (4) evaluating the impact of long-range transport due to Saharan dust outbreaks. The results aim at providing a clear and quantitative knowledge of the main sources of airborne particles, enhancing the effectiveness of further control policies. Remarkably, though several papers have been published about Bologna airshed and its particulate matter, as far as the authors are aware, this is the first source apportionment study and, for the first time, trace elements have been accounted for.

Material and Methods

An urban background site (high-density residential area, distance >50 m from major streets) was placed in the courtyard of the Chemistry Dept., Bologna University, near the city center. PM₁₀ and PM_{2.5} were sampled on a daily simultaneous basis (24 h) in two main periods: a winter campaign and a summer campaign for a total of 84 days in 2006. Sampling was continuous within each campaign. Two

preliminary short-term campaigns were carried out in 2005: a very short campaign (only nine samples) was carried out during the summer 2005, in which only PM_{2.5} was sampled, whereas a simultaneous PM₁₀ and PM_{2.5} campaign was carried out during autumn 2005. Owing to the different experimental design these data could not be elaborated together with the former data. More details about the periods, the sampling and the analyses carried on the samples during the four campaigns are available as Supplementary Material Table 1.

Samplings were daily performed according to European standard EN 14907 (CEN 2005) using a HYDRA Dual (FAI, Italy) low-volume sampler and started at midnight. PM₁₀ was collected on PTFE (Whatman with support ring, 2 µm, Ø 47 mm) while PM_{2.5} was collected on quartz fiber filters (Schleicher and Schuell, Germany, Ø 47 mm) in agreement with SITECOS shared sampling strategy.

Blank filter mass and PM mass load were determined gravimetrically after 48 h conditioning at constant temperature and relative humidity in a drier. Filter weights were obtained as the average of at least three measurements using a micro-balance (nominal precision 1 µg). Each PM_{2.5} filter was cut in three aliquots. One quarter of the filter was sonicated in ultrapure water for 30 min and subsequently analyzed by isocratic ion chromatography with a Dionex ICS-90 for the determination of five major inorganic cations (NH₄⁺, Na⁺, Mg²⁺, K⁺ and Ca²⁺) and 3 anions (Cl⁻, NO₃⁻, SO₄²⁻). Cation set-up: precolumn, CG12A, column CS12A 4 µm; methanesulfonic acid (20 mM) as eluant. Anion set-up: precolumn, AG14A; column, AS14A 7 µm; Na₂CO₃ (8 mM) and NaHCO₃ (1 mM) as eluant.

The second aliquot was analyzed for total carbon (TC) using an elemental analyzer (CHN Flash Combustion, Termoquest, Milano), coupled to a muffle pretreatment (Nabertherm, Lilienthal) for 2 h at 450 °C. The collected samples were then analyzed for elemental carbon with a complete oxidation of OC at 350 °C for 3 h and 30 min. The third aliquot was stored for further analyses. Only for the autumn 2005 campaign, ICP-MS (Element 2 double focusing, with an HNO₃ pH 1.5 filter extraction) elemental analyses were performed on this third aliquot.

PM₁₀ samples on PTFE membranes were analyzed by particle-induced X-Ray emission (PIXE) at LNL-INFN laboratories (Padua, Italy) for the non-destructive quantitative determination of 19 elements (Na, Mg, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb, P). PIXE set-up was described in detail in Mittner et al. (1996) and involves a 1.8 MeV proton beam and a low-energy germanium detector. X-ray spectra from PIXE were fitted using GUPIX software package (Maxwell et al. 1995) to obtain concentration, minimum detection limits and % fit error for each element in each sample.

Filter blanks and field blanks were analyzed together with the samples in order to subtract their contribution to samples. Detection limit (LOD) was calculated as $LOD = +3.14 \sigma_b$ with as the arithmetic mean of the analyte concentration in the blanks and σ_b as its standard deviation. Experimental data lower than LOD were rejected at first and then substituted by LOD/2 only before applying multivariate statistical analyses, whereas data greater than LOD were subtracted by. Experimental uncertainty (RDS) was detected following Miller and Miller (1993); all the uncertainties were added up following the rules for error propagation. The relative percent error was in the range 3 % (for Na⁺) and 13 % (for Mg²⁺).

For ion chromatography, quality control was carried out by analyzing the synthetic rain water BCR®-408 and BCR®-409 (IRMM, Community Bureau of Reference of the European Community) certified reference materials. The quality and the accuracy of quantitative PIXE analyses were checked with NIST SRM 2783 Air Particulate thin film standard on Filter Media.

The influence of external PM contributions from African dust outbreaks over Bologna was investigated by the reconstruction of air mass backward trajectories using NOAA HYSPLIT v 9.4 model (Draxler 1999; Rolph 2003; Draxler and Rolph 2011). HYSPLIT set-up: starting at 00:00 h local time, at 50, 500, 1,000 m AGL, duration -90 h, 6 h step, model vertical velocity, GDAS1 meteorological data fields input data.

Results and Discussion

PM levels

A preliminary explorative data analysis was performed for each single campaign. Results are summarized in Table 1. Yearly, PM₁₀ mass concentration levels are in the 12.4–151.5 µg m⁻³ range, with an average (mean±standard deviation) of 44.5±24.2 µg m⁻³, while PM_{2.5} ranges from 7.9 to 124.3 µg m⁻³, with an average of 31.6±21.0 µg m⁻³.

Annual mean of PM₁₀ concentration was above the European annual PM₁₀ threshold of 40 µg m⁻³ fixed by 1999/30/EC (EC 1999), while the European 24 h PM₁₀ limit value of 50 µg m⁻³ was exceeded in 9 days during September–October 2005, 18 days during January–March 2006 and 5 days during June–July 2006 campaigns. Though PM_{2.5} thresholds were enforced in Italy in 2008, results from the present investigations clearly showed that not only this fraction represents a considerable mass contribution to PM₁₀ (up to 90 % in the winter), but also PM_{2.5} limits were frequently exceeded as presently regulated (2008/50/EC).

Table 1 Number of days when the elements have been found (*N*), arithmetic mean concentration and standard deviation (in microgram per cubic meter) for major and trace ions and elements obtained atBologna during the four campaign of the SITECOS project (summer 2005, autumn 2005, winter 2006, and summer 2006) in PM₁₀ and PM_{2.5}

	PM ₁₀	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb	P
AUTUMN 2005																				
N	24	0	0	24	0	0	0	0	0	0	24	24	24	24	24	24	24	0	24	0
mean	46	-	-	0.02	-	-	-	-	-	-	0.002	0.001	0.003	0.05	0.001	0.005	0.041	-	0.013	-
std dev	17	-	-	0.01	-	-	-	-	-	-	0.001	0.000	0.002	0.03	0.000	0.002	0.024	-	0.009	-
WINTER 2006																				
N	49	41	32	40	40	41	41	41	41	41	0	37	14	41	37	0	41	21	30	0
mean	51	0.23	0.05	0.11	0.5	1.2	1.1	0.32	1.2	0.03	-	0.006	0.02	0.67	0.006	-	0.08	0.01	0.03	-
std dev	31	0.15	0.03	0.07	0.3	0.7	0.8	0.18	0.8	0.02	-	0.003	0.01	0.37	0.004	-	0.054	0.005	0.018	-
SUMMER 2006																				
N	35	9	18	34	34	34	34	34	34	34	9	32	34	34	11	34	34	0	0	18
mean	35	0.09	0.05	0.26	0.8	1.1	0.05	0.27	1.2	0.04	0.006	0.004	0.016	0.7	0.004	0.02	0.03	-	-	0.024
std dev	11	0.07	0.03	0.24	0.6	0.4	0.11	0.13	0.5	0.03	0.003	0.001	0.007	0.4	0.002	0.006	0.008	-	-	0.007
	PM _{2.5}	EC	OC	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NH ₄ ⁺	Ca ⁺⁺	K ⁺	Mg ⁺⁺	Na ⁺		Cd		As		Mo		Hg	
SUMMER 2005																				
N	9	9	9	9	9	3	9	8	8	8	9		0		0		0		0	
mean	17.7	1.7	5.7	0.40	5.8	0.11	1.93	0.19	0.15	0.03	0.13		-		-		-		-	
std dev	4.3	0.4	4.8	0.09	2.5	0.04	1.08	0.07	0.07	0.01	0.05		-		-		-		-	
AUTUMN 2005																				
N	24	0	0	24	24	13	24	24	24	4	23		24		24		24		24	
mean	33	-	-	7.3	5.0	0.53	3.8	0.11	0.21	0.013	0.075		0.0005		0.0008		0.0005		0.0007	
std dev	18	-	-	6.9	2.8	0.21	2.1	0.04	0.19	0.004	0.078		0.0004		0.0005		0.0003		0.0008	
WINTER 2006																				
N	49	42	42	41	41	21	42	37	42	24	40		0		0		0		0	
mean	41	2.7	4.1	12.1	3.9	0.94	3.6	0.19	0.31	0.03	0.06		-		-		-		-	
std dev	26	1.3	2.0	9.4	2.0	0.84	2.3	0.11	0.21	0.02	0.04		-		-		-		-	
SUMMER 2006																				
N	35	34	34	34	34	13	34	32	34	30	0		0		0		0		0	
mean	21	1.7	4.0	0.74	5.2	0.66	1.55	0.32	0.39	0.04	-		-		-		-		-	
std dev	7	1.1	1.3	0.93	2.0	0.41	0.74	0.09	0.30	0.01	-		-		-		-		-	

Data on mixed layer height was obtained by the annual reports of the Regional Environmental Protection Agency ARPA-EMR; where this parameter is evaluated based on atmospheric modeling (ARPA-EMR (2013) meteorological pre-processor—data available at http://www.arpa.emr.it/sim/?qualita_aria/turbolenza). The mixing height typically shows winter minima and summer maxima and is inversely correlated with the PM₁₀ and PM_{2.5} seasonal trend in agreement with similar findings concerning the Po Valley (Matta et al. 2002; Lonati et al. 2008; Rampazzo et al. 2008).

The daily average concentrations of PM_{2.5} and PM₁₀ were found equal to 33 and 46 µg m⁻³ in autumn, 41 and 51 µg m⁻³ in winter, 21 and 35 µg m⁻³ in summer.

In most European sites, the PM_{2.5}:PM₁₀ ratio ranges from 0.4 to 0.9 with a slight increase from natural to urban background sites (Putaud et al. 2004; 2010). In this study, the

ratio among the two fractions varies seasonally, with values of 0.5–0.6 during the warm season and 0.8–0.9 during the cold period. In general, this difference is attributed to an increase in the coarse fraction under dryer summer conditions, due to higher resuspended dust during the warm season, as well as to different combustion source profiles in the two seasons.

Chemical characterization and seasonal patterns

Table 1 reports basic statistics of the chemical species measured in PM₁₀ and PM_{2.5}. During the whole period, the most abundant elements in PM₁₀ follow the order: Ca>S>Si>Cl>Fe>K>Na>Al>Mg>Zn>Ti>Pb>P>Br>Mn>Cu>Cr>Ni>V. These elements are mainly associated to natural sources, i.e., crustal material (Si, Al, Ca, Fe), sea spray

(Na and Cl), but also to secondary inorganic aerosol (SIA) and biomass burning (S and K, respectively). Anthropogenic-related elements (Cr, Cu, Zn, Pb) exhibit values slightly lower than in other Italian urban sites (e.g., Lucarelli et al. 2000; Marcazzan et al. 2003; Rampazzo et al. 2008) (Supplementary Material Table 2). The most abundant species in PM_{2.5} were nitrate, sulfate, ammonium, and the carbonaceous fraction. These latter species present concentrations comparable with other European sites located in the Mediterranean Region (Putaud et al. 2004; 2010). On average, the carbonaceous fraction represents about 17–20 % (cold period vs warm period value) of PM_{2.5} mass, while SIA accounts for 28 % of PM_{2.5} on the average (warm period average value 22 %, cold period average value 33 %).

The analyses carried out during the project about the partitioning of TC between organic and elemental carbon revealed that about 60–70 % of total carbon is composed of organic carbon while the elemental carbon account for only the 40–30 % (cold vs warm value). These values are in agreement with previous European studies (Putaud et al. 2010) that investigated the main chemical composition of several sites in Europe, including Bologna, and showed that total carbon in this area is mostly composed of organic carbon (69 %) and secondarily of elemental component (31 %). The seasalt contribution to PM₁₀ was calculated assuming that Na⁺ has only a marine origin and deriving the seasalt fraction of K⁺, Mg⁺⁺, Ca⁺⁺, Cl⁻ and SO₄²⁻ from the typical seawater ratios respect to Na⁺ (Riley and Chester 1971): the average value was found equal to 1 %.

The contribution of the crustal matter to PM₁₀ was estimated on the basis of the semi-empirical equation (Chan et al. 1997; Salma et al. 2001):

$$c(\text{crustal matter}) = 1.16 \times (c(\text{Al}) + 2.15c(\text{Si}) + 1.41c(\text{Ca}) + 1.67c(\text{Ti}) + 2.09c(\text{Fe}))$$

where $c(i)$ is the concentration of element i ; crustal matter contributes 13 % on the average, with a clear increase from the average value of 10 % during the cold period to the 17 % found during the warm period. This increase can be attributed to the above-mentioned increase of the coarse fraction due to dryer summer conditions but also to the incursion of a Saharan Dust in June 2006, which will be described with further details later on in this paper.

CO₃²⁻ were indirectly determined from the contents of Ca and Mg on the basis of the empirical relationship suggested by Querol et al. (1998), which assumes that the carbonate form is the dominant species for both elements; though experimentally unverified this hypothesis largely accommodates most situations including the local one where the pedological framework (alluvial plain) plus the building influence are reasonable sources of this component.

The contribution of carbonates to PM₁₀ was equal to 4–5 % (cold and warm value, respectively).

This first rough estimate of the PM₁₀ contributions of some “a priori” known sources gave us firstly an idea of the relevant contribution of SIA to particulate matter and of the high percentage due to crustal matter resuspension, increasing from winter to summer. The minor contribution of seasalt, which was expected due to the distance of Bologna from the sea, was confirmed by this first estimate.

The elemental composition largely follows the same seasonal behavior as PM₁₀, with higher values during the warm season, while S, K, Ca, and Fe do not present significant seasonal differences. Crustal tracers (Si, Al, Ti) and V exhibit higher concentrations during summer, usually attributed to an increase in soil resuspension and Saharan Dust contribution. This latter contribution is further investigated. During the cold season, nitrates contribute more than sulfates to PM_{2.5}, in good agreement with European data recorded in the last decade (Van Dingenen et al. 2004; Putaud et al. 2004; 2010). In fact, during the warm season the lower contribution of nitrates is partly due to incomplete collection of NH₄NO₃ due to its remarkable thermal instability (Schaap et al. 2002; Schaap et al. 2004a; b; Vecchi et al. 2009), while the increase of the photochemical oxidation of SO₂ leads to a relative raise of sulfates (Hueglin et al. 2005; Vecchi et al. 2004; Rodriguez et al. 2004).

The equivalence ratio between the experimental concentrations of nssSO₄²⁻ (determined as the difference between experimental SO₄²⁻ and seasalt sulfates, estimated by the typical seawater to Na⁺), NO₃⁻ and NH₄⁺ was calculated for the campaigns of autumn 2005, winter and summer 2006 in order to assess the degree of neutralization in the analyzed aerosol samples (see Supplementary Material, (Fig. 1a, b, c)). On the basis of the principle of electroneutrality, during the cold season the sum of sulfates and nitrates equivalents is not balanced by sufficient ammonium equivalents, which therefore calls for extra positive cations; this balancing fraction is attributed to H⁺ (whose measure is not straightforward) which therefore implies an acid character of aerosol (Pathak et al. 2004; Squizzato et al. 2013). In the warm season, cation deficit is substantially balanced by calcium as often observed in the warm season when soil resuspension increases adding carbonates to atmospheric bases available for acid neutralization (Alastuey et al. 2004).

Enrichment Factors

In order to acquire some preliminary information about the crustal and non-crustal sources of trace elements in particulate matter, crustal enrichment factors (EFs) were calculated during the cold and warm seasons. The enrichment factor

is defined as ((Lantzy and McKenzie 1979; Voutsas et al. 2002)

$$EF = (C_{\text{element}}/C_{\text{reference}})_{\text{air}} / (C_{\text{element}}/C_{\text{reference}})_{\text{crust}}$$

where C_{element} is the concentration of any element, $C_{\text{reference}}$ is the concentration of reference element. Generally, Al, Fe, or Si are chosen as reference elements. In this work, the average ratio of each trace element to Al in the crust (Bowen 1979) was used; in facts in an urban framework real soil composition may represent an arbitrary choice due to the dominant influence of traffic related sources (vehicles and pavement) and buildings (Marcazzan et al. 2003). By convention, an $EF \leq 10$ indicates a non-enriched element suggesting a crustal origin. $EFs \gg 10^4$ indicate that the element is enriched respect to the Earth's crust; according to the local conditions this enrichment may be attributed to the influence of anthropogenic sources locally active in the area.

Figure 2 reports the EF average values for the two analyzed periods. Lowest EF's were found for Mg, Al, Ti, Mn, K, and Fe, suggesting that these elements have a terrigenous origin. Na, Cr, Cu, Zn, but especially Cl and S are found to be enriched, particularly during the winter season. Anthropogenic sources may be relevant to these elements. The EF calculated for the data of autumn 2005 using Al as reference crustal element are presented in the Supplementary Material Fig. 2: all the elements apart from Mn and Fe are found to be enriched, and Cu, Zn, Pb, Cd, As, Mo, and Hg present very elevated EF value.

PCA/MLRA

PCA/MLRA receptor modeling was applied to the data of the period winter–summer 2006 (January–March and June–

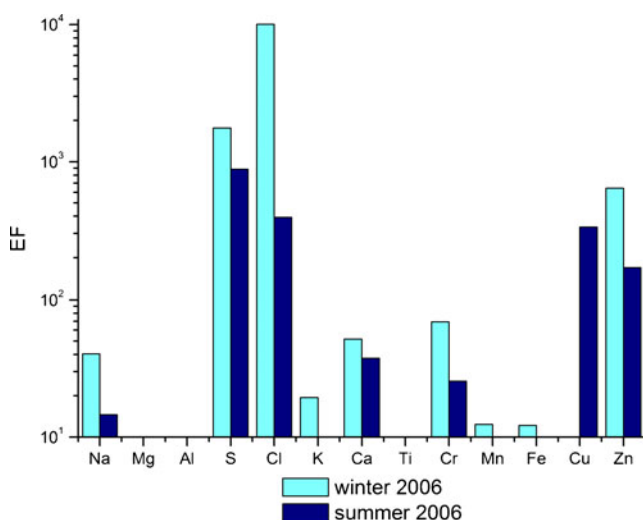


Fig. 2 Average values of enrichment factors of the analyzed elements during winter and summer 2006, calculated considering Si as reference crustal element

July 2006). As already highlighted in previous studies in the Po Valley (Matta et al. 2002; 2003) the major part of total aerosol mass is distributed in the fine size range. Moreover, as noted not only in the above-mentioned studies but also during a previous study carried out in Bologna on the size-segregated samples collected by means of a multi-stage high-volume cascade impactor (Andersen, Lab Automate Technologies) in this area (ARPA-EMR 2005), inorganic ions represent a substantial part of the total mass, and are typically present in the fine fraction ($<1.5 \mu\text{m}$). During this study, it was observed that in this area nitrate dominates the fractions below $1.5 \mu\text{m}$; nitrate is known to be a complex ion species owing to both remarkable volatility and chemical weakness when associated with ammonium and to post formation reactivity leading to displacement reactions with other aerosol species and to a size distribution shift towards coarser fractions. Crustal elements on the contrary dominate the coarse fraction, because of their mechanical origin: the coarse fraction is known to count very little in terms of number of f particles, but a lot as for the weight (Mitra et al. 2002; D'Alessio et al. 2005). Taking into account these considerations, in this study the ions data analyzed in the $\text{PM}_{2.5}$ fraction and the elemental data measured in PM_{10} were merged together.

Before applying multivariate statistical analysis, the overall dataset was subjected to a strict selection in order to optimize modeling conditions: variables with $>10\%$ values below the detection limit were discarded while if only a limited number of data was found lower than the LOD, they were substituted by $\text{LOD}/2$.

Before choosing the data for the analysis, a comparison between the PIXE analyzed elements in PM_{10} and the corresponding ion analyzed in $\text{PM}_{2.5}$ was also carried out. Na, Mg, and Ca are always more abundant in PM_{10} than in $\text{PM}_{2.5}$, which is reasonably linked to their mechanical (mostly crustal for Mg and Ca, marine for Na) origin. In order to prevent double counting in the working matrix PIXE data were kept for Na, Cl, and Ca; for Mg, the ion data were retained, as slightly more abundant, whereas the Cl^- data were discarded as the Cl data were far more abundant (see Table 1 for reference about the number of data available for each variable).

A good correlation was found between SO_4^{2-} determined in IC and the calculated SO_4^{2-} concentrations in PM_{10} ($r^2=0.75$) which means that S analyzed in PM_{10} had a prevailing secondary origin mostly lined to the presence of ammonium sulfate. K was often higher in PM_{10} than K^+ in $\text{PM}_{2.5}$, but for 19 samples the opposite was observed. For these samples, a contemporary increase of K^+ and OC and a general good correlation of K^+ with OC were observed ($r^2=0.78$ winter value, $r^2=0.40$ summer value): the overall conclusion of these observations is a probable link of K^+ to combustion sources, and in particular to biomass burning.

From these considerations, it was assumed that all the PM_{10} sulfur was in the sulfate form, and the IC sulfates data were kept instead of S; for K, the difference between the PIXE and IC values was calculated (K_{ins}) and K^+ and K_{ins} were treated as independent variable. A final matrix consisting of 20 variables and 76 observations was analyzed.

Results of the Varimax-rotated PCA on the standardized data (mean=0, standard deviation=1) revealed four factors (Table 2 and Fig. 3a, b, c, d), accounting for 80 % of the total variance. Communality, which represents the amount of variance of each variable explained by the model, showed high values for all the variables, except for K^+ and Mg^{++} (0.5 and 0.4, respectively), probably because of their low concentrations.

The first factor (42 % of the total variance) is clearly related to an anthropogenic source, being composed of Cr, Zn, Ni, Cu, nitrate, ammonium, EC, Cl, and secondarily OC and Fe. Chromium, copper, nickel and zinc have been extensively linked to various industrial processes and mostly to traffic (abrasion and corrosion of brakes, tires) (Wahlin et al. 2006; Alastuey et al. 2007; Lin et al. 2008; Thorpe and Harrison 2008; Gietl et al. 2010; Koçak et al. 2011), whereas NO_3^- and NH_4^+ are the main component of secondary ammonium nitrate formed through homogeneous and heterogeneous

reactions from gaseous NO_x and NH_3 (Schaap et al. 2004a; Pathak et al. 2009). This factor seems mainly associated with traffic, a relevant contribution in Bologna emissive profile, which seems to be confirmed by the results of the cluster (available as Supplementary Material Fig. 3) and factor analyses applied to the dataset of the autumn campaign in 2005 (not homogeneous with the subsequent sampling periods, as the analyses were all carried out on the $\text{PM}_{2.5}$ fraction) showing that the four variables Cr, Zn, NO_3^- , NH_4^+ are closely linked also to V, a tracer of diesel engines, widely used for both light and heavy vehicles in Italy. Since the industrial emissions in Bologna are not significantly high due to the lack of major industries (neither chemical industries nor energy production facilities are present in the territory), while the main industries are linked to manufacture activities, and since the city center is affected by heavy traffic roads (one of which close to the sampling site), the vehicular emissions appear as the most probable source for this association of elements. Thus, this source can be interpreted as a combination of secondary aerosol (mainly composed of nitrates coupled to ammonium) and traffic.

The second factor explains about 24 % of the total variance and mainly links typical crustal elements K_{ins} , Al, Si, Ca, Ti, Fe, Mn (loadings >0.6). This source was then

Table 2 Results of the VARIMAX rotated PCA on the standardized data. Loadings >0.6 are marked in bold, while loadings between 0.4 and 0.6 are in italics

	Factor 1	Factor 2	Factor 3	Factor 4
NO_3^-	0.92	0.00	0.22	0.10
SO_4^{2-}	0.09	0.29	0.81	−0.02
NH_4^+	0.80	0.00	<i>0.40</i>	0.07
K^+	0.18	−0.02	0.80	0.06
Mg^{++}	−0.47	0.16	0.18	0.62
OC	<i>0.54</i>	0.29	<i>0.55</i>	−0.15
EC	0.80	0.01	0.13	−0.07
Na	<i>0.49</i>	−0.16	−0.25	0.69
Al	−0.12	0.95	0.12	−0.08
Si	0.01	0.98	0.08	−0.05
Cl	0.67	−0.18	0.11	<i>0.55</i>
Ca	0.38	0.82	−0.04	0.09
Ti	0.06	0.98	0.08	−0.04
Cr	0.85	0.37	0.09	0.01
Mn	0.63	0.61	0.10	0.12
Fe	<i>0.43</i>	0.87	0.04	0.02
Ni	0.87	0.20	0.06	0.10
Cu	0.72	−0.03	−0.12	−0.09
Zn	0.90	0.19	0.15	0.13
K_{ins}	−0.12	0.80	0.22	−0.02
Eigenvalue	8.3	4.8	1.7	1.2
Variance (%)	41.7	24.1	8.4	5.8
Cumulative percent	41.7	65.8	74.2	80.0
Source	Traffic and ammonium nitrate	Crustal	Mixed combustion	“Pseudo-marine”

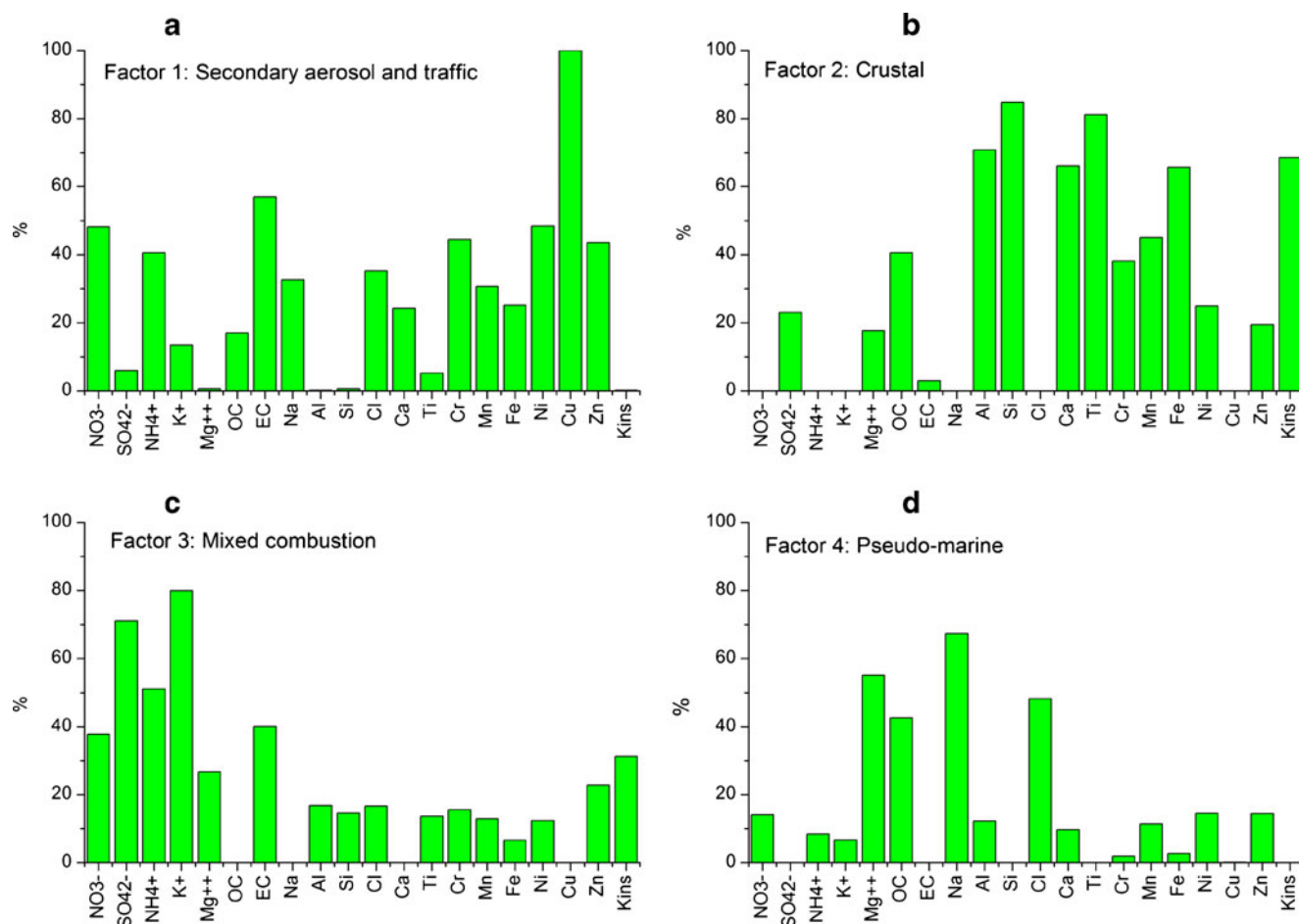


Fig. 3 a, b, c, d Source profiles illustrated as percentage of the species (%) in the four identified sources by the PCA model

interpreted as crustal material originated from soil resuspension (Qin et al. 2006; Mazzei et al. 2006; Vecchi et al. 2008). The influence of road dust cannot be excluded due to the pavement wear and to the abrasion occurring on mechanical parts, such as brake lining and drums (Fe, Mn) (Garg et al. 2000; Ijima et al. 2008; Thorpe and Harrison 2008; Bukowiecki et al. 2009; Gietl et al. 2010). A usual association of Fe with Cu was observed looking at the clusters of the single campaigns (an example of this observation can be found in Supplementary Fig. 3, referring to the period autumn 2005) and this can indicate a possible source from mechanical abrasion of vehicles (brakes). Fe also showed a significantly high linear correlation with Cu, Mn, Cr, Pb and Zn ($0.6 < R < 0.9$), all elements typically attributed to the abrasive/coarse contribution of vehicles, partly dropped from the matrix used in modeling for the reason explained, but reported as averages in Table 1.

The third factor (8 % variance) includes K^+ , SO_4^{2-} , and to a lesser extent NH_4^+ , OC. While K^+ was largely linked to combustion processes, including biomass burning (Morawska and Zhang 2002; Mahowald et al. 2005; Thurston et al. 2011; Masiol et al. 2012a), NH_4^+ and SO_4^{2-} are attributed to gas-to

particle reactions leading to the secondary ammonium sulfate formation. According to Ramadan et al. (2000) and/or Begum et al. (2004) for example, biomass burning sources are successfully identified by K and carbonaceous parameters, an evidence recently enforced and stressed by Pachon et al. (2013) who confirm the relevant role of potassium as an efficient tracer of biomass burning as compared to levoglucosan, an alternative tracer widely used to this scope. It is worth noting that in the present study ionic potassium in $PM_{2.5}$ was chosen for receptor modeling, representing the soluble/fine fraction of this element as compared to total potassium by PIXE in PM_{10} available in the present data set to which the former largely contributes, as previously discussed, when high correlation between K^+ and OC was described corroborating the tight association with biomass burning.

The last source is made up of Na, Cl, and Mg^{++} and accounts for 6 % of the total variance, representing the marine aerosol. Although Bologna is far distant from the coast (>100 km) and the influence of seasalt is very limited, as already highlighted by the “a priori” PM mass balance, this factor shows evidence of the occurrence of episodic transports of sea salt aerosol mainly in the coarse fraction.

Due to its distance from the Adriatic coast and to the weak circulation in this region, Bologna can rarely be reached by marine air masses, an occurrence usually more frequent in the winter, but in any case fairly rare (Bora episodes); therefore this seasalt component is mostly attributed to the use of road de-icing practice following snowfall as often reported (e.g., Furusjö et al. 2007; Belis et al. 2013) and will be named from now on as “pseudo-marine”.

The daily source contributions to the PM levels were then obtained by the regression of the Absolute Factorial Scores (AFS) on PM₁₀ concentrations following the methodology described in Thurston and Spengler (1985). Results of ANOVA show a statistically significant relationship (at a 99 % confidence level) for all the sources on PM masses. The adjusted coefficients of multiple determination indicate that the model explains 92 % of the PM₁₀ variability.

Figure 5a shows the percentage mass contribution of the four sources identified by PCA/MLRA to PM₁₀. On the average, the “mixed combustion” source mainly contributes to PM₁₀ mass, accounting for 36 %, followed by traffic and ammonium nitrate source, crustal and “pseudo-marine” particles, accounting for 32, 21, and 10 %, respectively.

The time series of PM₁₀ source contributions can be found in the Supplementary Material Fig. 4. The “pseudo-marine” contribution presents higher levels during the cold periods. The crustal source presents higher contribution during the summer, as already found by the empirical calculations for the PM mass balance; this is probably due to dryer conditions favoring the resuspension of crustal material. In addition, an influence of Saharan dust outbreaks cannot be excluded. A further elaboration including the back-trajectories analysis is subsequently presented to extract helpful information on the influence of long-range transports.

The traffic source contributes mainly during the cold season due to marked low-level atmospheric stability, while its dispersal is promoted during the warm season by marked instability and convection leading to a deeper mixed layer (Ponce et al. 2005; Marengo et al. 2006). The mixed combustion source is more intense during the warm period ruling out the potential role of the incinerator and of agricultural biomass burning at the end of the harvest and before the cold season rather than domestic heating typical of winter. The increase in sulfates during summer can be explained with enhanced photochemistry during the warm season: the oxidation kinetics of SO₂ (primary precursor emitted from the “mixed combustion” source) to sulfates are promoted during the warm season and have already been associated to higher levels during summer (Hueglin et al. 2005; Vecchi et al. 2004; Rodríguez et al. 2004).

PMF

PMF analysis was also performed on the same dataset, using the EPA PMF 3.0 software package. The final matrix used

for PMF modeling consists of 20 parameters (21 with PM₁₀)×76 observations in agreement with Pant and Harrison 2012 stating that a minimum of 50 points is suitable for the scope. The data consistency though not optimal for statistical purposes is widely coherent with published papers such as, for example, Qin and Oduyemi (2003), Furusjö et al. (2007), Callén et al. (2009). The chosen parameters were retained in order to fulfill the conditions of minimizing model uncertainty, with negligible or absent missing data.

Uncertainty was calculated as the analytical uncertainty plus one third of the LOD, in agreement with the widely used method by Reff et al. (2007). Missing (but higher than LOD) values were replaced by their median and the associated uncertainty was calculated as four times the species median, whereas data lower than LOD were replaced by LOD/2, while the associated uncertainty was taken as 0.83 LOD (Polissar et al. 2001; Reff et al. 2007).

Cu was treated as a weak variable due to a low signal-to-noise ratio (<2), therefore its uncertainty was tripled. Sodium was also added to the list of weak variables because of the presence of a large number of data below LOD during the warm season. The overall uncertainty of the dataset was also increased of a further 9 % to account for sampling uncertainties and the exclusion of some further species for which observations were missing (EPA 2008). PM₁₀ was set as the “total variable” and as such considered weak by default by the software.

PMF uses algorithms in order to find a solution that minimizes $Q(E)$ using various random starting points. For this study, 100 starting points were chosen for the elaboration of the results.

As the theoretical optimum value of $Q(E)$ (E residual matrix, $Q(E)$ object function to be minimized) should be roughly equal to the number of degrees of freedom for the data matrix (Qin and Oduyemi 2003; Yatkin and Bayram 2007; Furusjö et al. 2007) (1,520 in this case), and the two parameters IM (maximum scaled residuals mean of the modeled variables) and IS (maximum scaled residual standard deviation of the modeled variables) show a drastic decrease when the number of factors increases up to a critical value (Lee et al. 1999), the most physically feasible number of factors describing the system is 6.

The diagnostic parameters on the performance obtained by the PMF model such as intercept constant, slope of the regression line, standard error and r^2 with a factorization value of 6 were analyzed and are presented as Supplementary Material, Table 3.

The predicted PM₁₀ mass concentrations well reproduce the measured ones ($r^2=0.97$) and the scaled residuals are normally distributed.

The source profiles are reported in (Fig. 4a, b, c, d, e, f), whereas the contribution of the six identified sources on PM₁₀ can be found in (Fig. 5b). The first source (8 % of

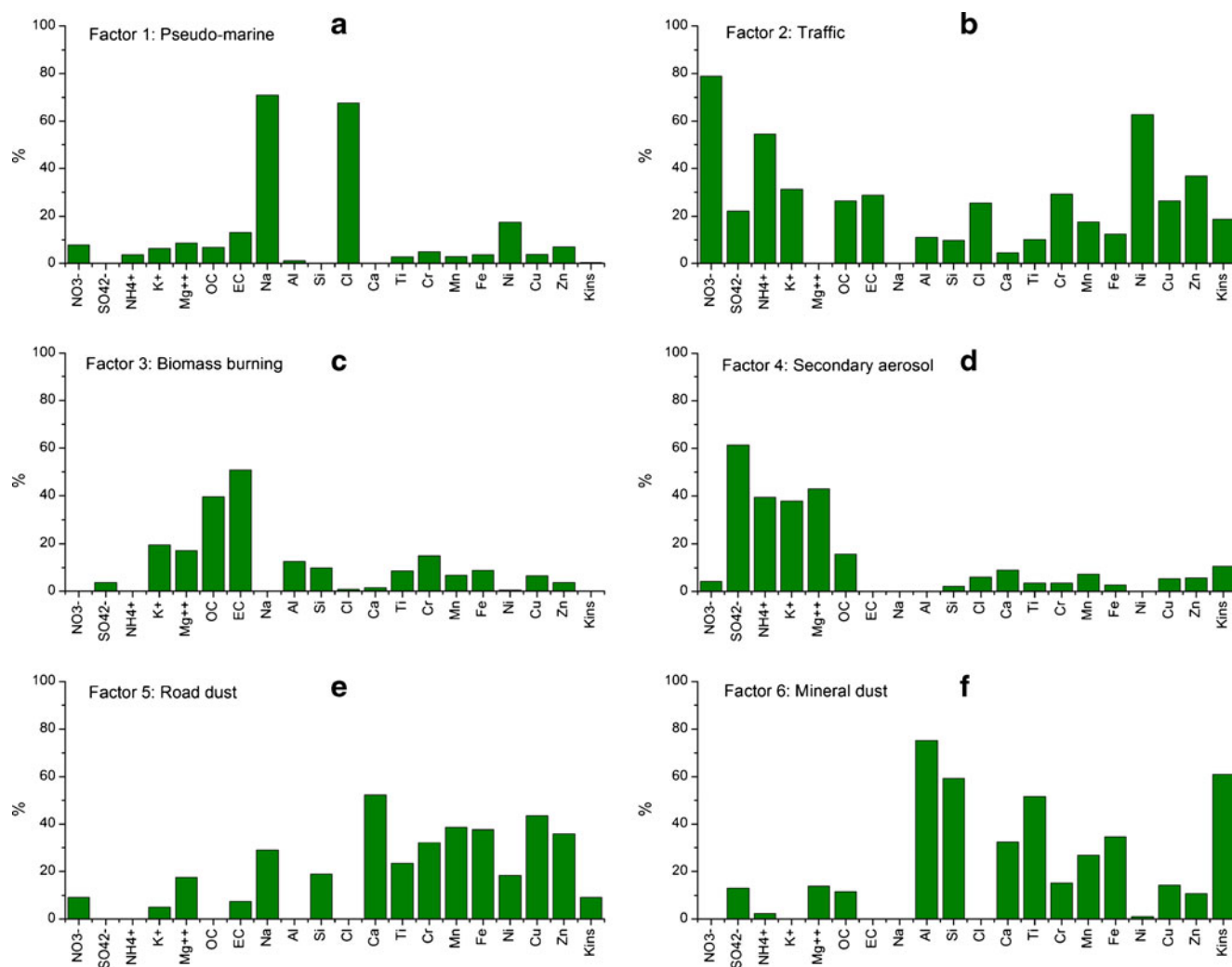


Fig. 4 a, b, c, d, e, f Source profiles illustrated as percentage of the species (%) in the six identified sources by the PMF model

PM₁₀) exhibits elevated contributions of Na and Cl clearly linked to the marine aerosol, but also to road salt in winter. The second source (35 % of PM₁₀) is interpreted as “secondary aerosol and traffic emissions”, with high contributions from NO₃⁻, NH₄⁺, Ni, Zn, K⁺, Cr, Cu, OC and EC. As already pointed out, discussing the results obtained by the PCA model, Ni, Cr, Cu, Zn can be linked to brakes and tire emissions (Garg et al. 2000; Bukowiecki et al., 2009; Wahlin et al. 2006; Thorpe and Harrison 2008; Ijima et al. 2008; Gietl et al. 2010), whereas NO₃⁻ and NH₄⁺ are the main component of secondary ammonium nitrate, formed through homogeneous reactions from gaseous NO_x and NH₃. Road traffic is a major source of NO_x, especially in a town like Bologna characterized by medium industries (mostly mechanical), agriculture and traffic; the increasing use of three-way catalysts on cars has presumably led to increasing emissions of NH₃ from vehicle exhausts (Sutton et al. 2000; Gilbert et al. 2003; Frati et al. 2006), caused by the reducing conditions inside the converter, though large-scale agriculture is

its main source. In the following this source will be referred to as “traffic”.

The third source (5 % of PM₁₀) exhibits contributions from OC, EC, and K⁺, Mg⁺⁺ to a lesser extent, and represents the biomass burning source (Morawska and Zhang 2002; Dan et al. 2004; Mahowald et al. 2005; Thurston et al. 2011; Masiol et al. 2012a; Pachon et al. 2013). High linear correlation among K⁺, sulfates and Cl⁻ ($R > 0.9$) all measured in PM_{2.5} and a slower but still significant linear correlation with Zn, a multisource species, suggests a likely influence of the municipal waste incinerator, whose relative importance requires further investigations.

The fourth source (26 % of PM₁₀) is linked to SO₄²⁻, Mg⁺⁺, NH₄⁺, K⁺ and represents the secondary aerosol (ammonium sulfate), mainly linked to the use of fuel oil from heavy duty vehicles, as suggested by the high good linear correlation coefficient between S/sulfates and the typical tracers of this source (V, Ni; sulfates-V $R = 0.73$ autumn 2005; sulfates-Ni $R = 0.64$ during autumn 2005 and winter

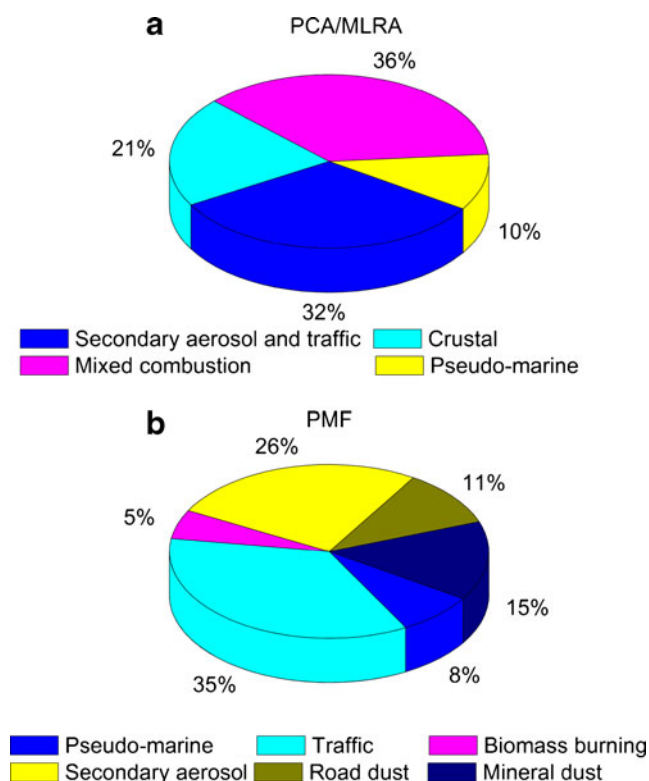


Fig. 5 Contribution of the sources to PM_{10} as resulting from the application of the **a** PCA/MLRA model; **b** PMF model

2006), whose data were not sufficient for the source apportionment but can be used for the purpose of gaining better insights as briefly outlined before going into the details of receptor modeling.

The fifth source (11 % of PM_{10}) is made up of Ca, Cu, Mn, Fe, Zn, Ni, Na. This source is thus attributed to the road dust associated to the abrasion of the mechanical parts of the vehicles (brakes, pads, drums, tires), as well as to the road dust asphalt, and is thus referred to as road dust.

The sixth source (15 % of PM_{10}) presents elevated shares from typical crustal elements (Al, Si, Ti, K_{ins} , Ca, Fe, Mn) and is identified as the mineral dust source.

With respect to the PCA/MLRA, the PMF model is able to distinguish between the mineral and road dust, and to split the ammonium sulfate from the traffic source.

The reconstructed time series of the four identified sources are reported as Fig. 6.

The “pseudo-marine” contribution presents higher levels during the cold periods. This is obviously also due to the winter use of seasalt as de-icing agents on the roads. The soil dust source yields a higher contribution in the warm season, in agreement with the empirical calculations for the PM mass balance and with the PCA/MLRA model as a result of enhanced resuspension under dry weather conditions. In addition, the influence of a Saharan dust transport during the summer period cannot be excluded. A further elaboration

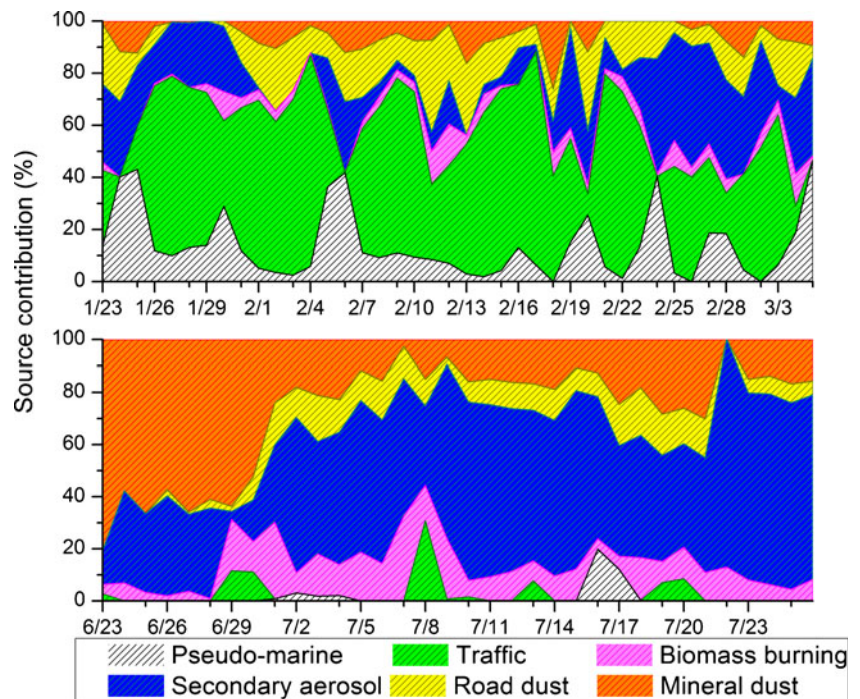
including the back-trajectories analysis is subsequently presented to extract helpful information on the influence of long-range transports across the Apennine range even in northern Italy.

The traffic source contributes mainly during the cold season probably because of the influence of the ammonium nitrate, more stable at low winter temperatures: in addition, the marked low-level atmospheric stability promotes the higher concentrations of most PM components during the cold season, while its dispersal is promoted during the warm season owing to marked instability and convection leading to a deeper mixed layer (Ponce et al. 2005). The road dust source, however, also shows a slight decrease from the winter to the summer season, which possibly means that a general decrease of the traffic from the cold to the warm season cannot be completely excluded. The biomass burning source is more intense during the warm period; as a consequence, it seems likely that this source is linked both to the agricultural biomass burning at the end of the harvest and possibly to the waste incinerator, rather than to domestic heating, which is instead typical of winter. The secondary aerosol (ammonium sulfate) source also shows an increase from the cold to the warm season. As pointed out before, the increase in sulfates during summer is due to enhanced photochemistry during the warm season as widely observed in the literature (Hueglin et al. 2005; Vecchi et al. 2004; Rodríguez et al. 2004).

Analysis of a case study occurred during the sampling campaigns

All the European plain zones, and in particular the Po Valley, are characterized by a typical trend of the PM concentrations, with a marked thermal gradient between summer and winter (Marcazzan et al. 2003; Matta et al. 2003). This result is mainly attributed to the variation of the thickness of the planetary boundary layer (PBL), i.e., the volume of air where the atmospheric pollutants are dispersed. The height of the PBL is directly proportional to the solar irradiance and because of the thermal expansion of the atmospheric gases and the trend of the turbulence is lower during the cold season and higher during the warm one. The overall result is a variation of the volume where the gases and PM can be dispersed. This results in the consequent rise of the winter concentrations of PM, mainly (but not only) due to the different dilution ratios. For this reason, generally, PM_{10} and $PM_{2.5}$ limit values set by the European legislation (1999/30/CE and 2008/50/CE) are frequently exceeded during the cold season in the whole Po Valley. The influence of additional sources during the cold season, such as domestic heating, along with frequent thermal inversions can also drop the dispersion of locally emitted pollutants in the lower atmosphere. Moreover, some peculiar

Fig. 6 Time series of the PM₁₀ source contribution resulting from the PMF model

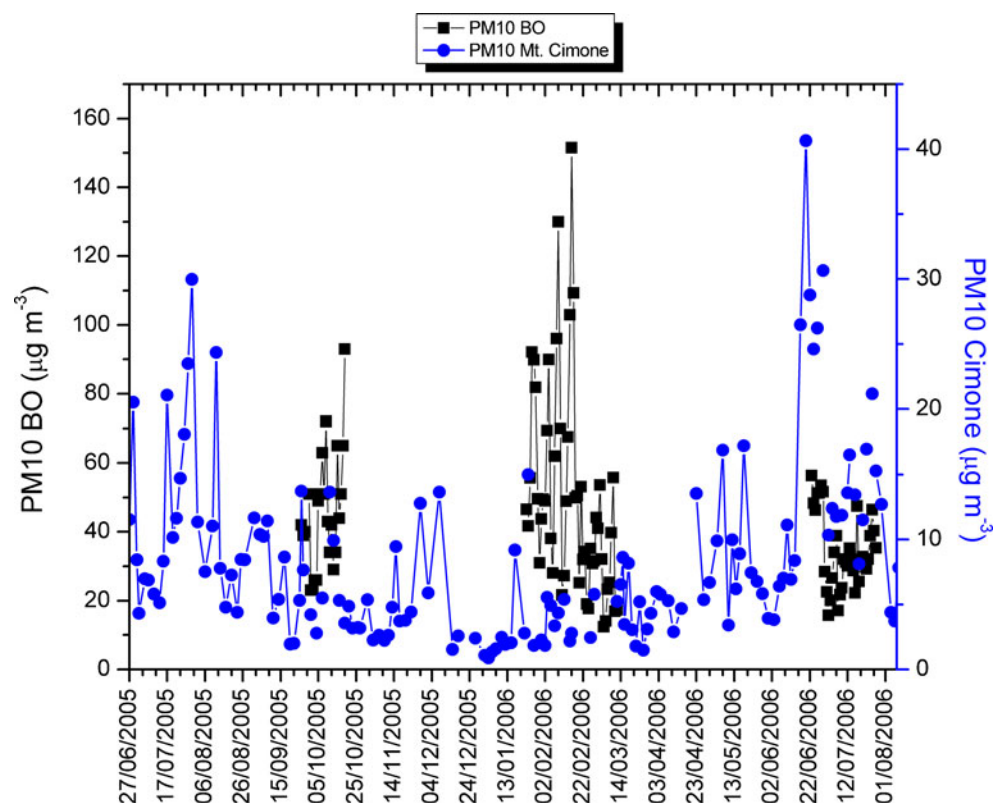


orographic characteristics of the Po Valley, which is surrounded by the Alps and Apennines mountain chains, can enhance the air mass stagnation with the consequent increase of the pollutants.

An interesting high PM value episode in June 2006 was investigated. This period was characterized by an anomalous

series (seven subsequent days, of which five exceeded the European limit value) of PM₁₀ concentrations in the range 46–56 $\mu\text{g m}^{-3}$. As previously recognized by, for example, Matassoni et al. (2009), Guarnieri et al. (2011), and Nava et al. (2012), this period was characterized by a Saharan dust outbreak, which strongly impacted overall Italy and in

Fig. 7 PM₁₀ mass load (in microgram per cubic meter) during the year 2006 at the Mt. Cimone site and in the city of Bologna. An increase in the end of June 2006 is evident at both sites



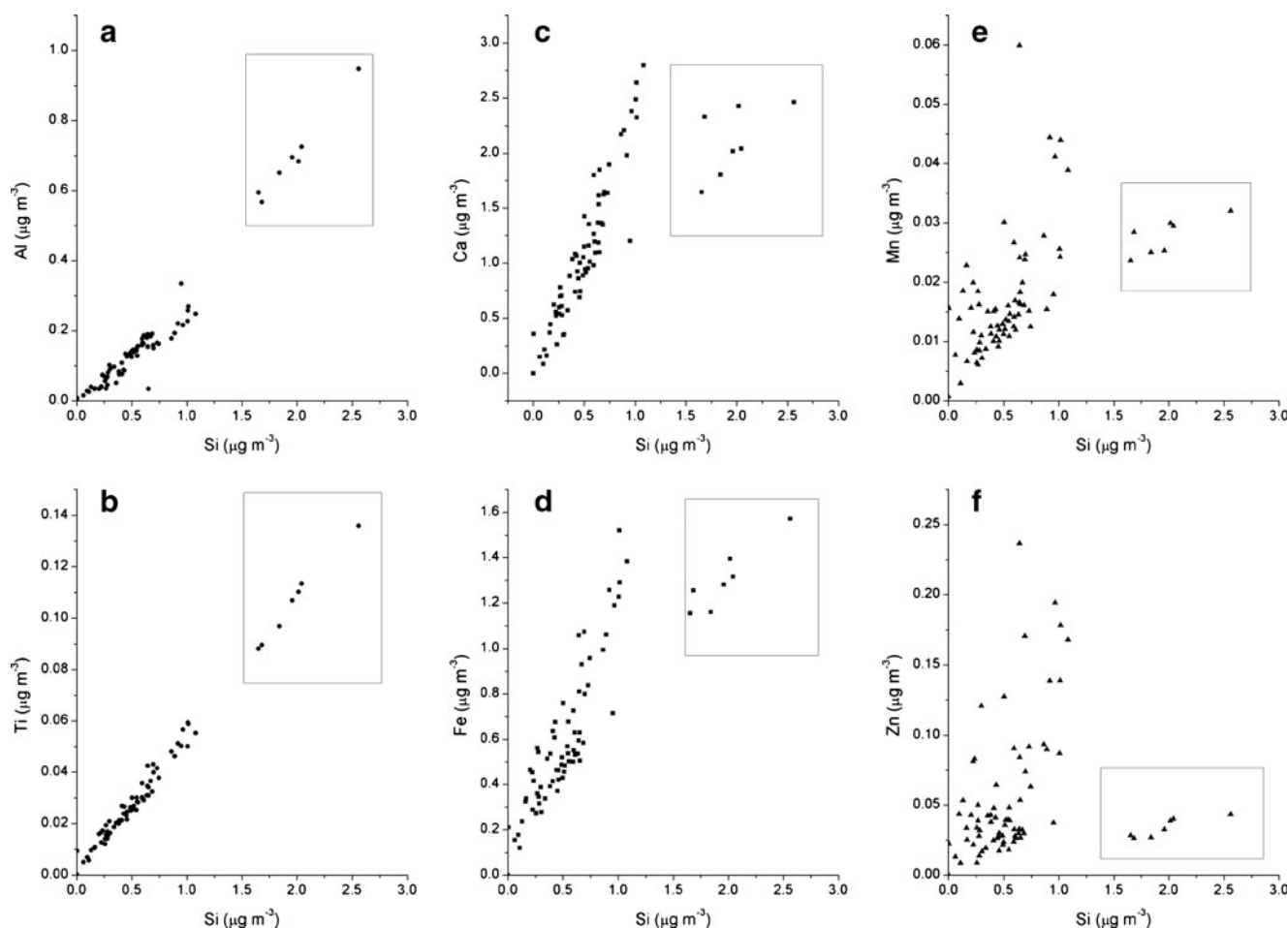


Fig. 8 Scatterplot of crustal elements during the period winter–summer 2006: **a** Al vs. Si; **b** Ti vs. Si; **c** Ca vs. Si; **d** Fe vs. Si; **e** Mn vs. Si; **f** Zn vs. Si. In the *rectangles*, the days of the SD transport event that happened at the end of June 2006 are identified

general the whole Mediterranean basin. The influence of this natural event in Bologna was quite remarkable owing both to its intensity and duration. As shown in Fig. 6, during this period the contribution of mineral dust to PM_{10} was very high (81 % on 23rd June, and then ranging from 52 to 67 % in the following 6 days till the end of June). Figure 7 reports the temporal trend of PM_{10} mass load during the period June–July 2006 in the city of Bologna and at a remote station (WMO-GAW) on Mt. Cimone ($44^{\circ}12' N$, $10^{\circ}42' E$, 2165 m a.s.l.). As it lies above the PBL during most of the year (Winkler et al. 1998), the Mt. Cimone background station is not influenced by common anthropogenic emissions due to cities and industrialized areas. For this reason, the measurements of atmospheric species carried out at this site can be considered representative for the South European free troposphere (Bonasoni et al. 2000; Fischer et al. 2000; Tositti et al. 2012).

In Fig. 8a–f, scatterplots of some elements during the joint period winter–summer 2006 are presented. The Saharan Dust event is identified by an oval in the Figure. The scatterplots highlight three clusters of elements: the first

one, to whom the Al–Si, Ti–Si couples belong, groups together elements which, sharing the same crustal source, exhibit elevated correlation values and keep the same ratio even during the SD event; for the second (Ca–Si, Fe–Si) and third (Mn–Si and Zn–Si) group the ratio is different during the SD event, and specifically it is slightly decreased for the second group while it is largely decreased for the third one. The analysis of the EF value shows that the typical crustal elements (Al, Ti) were enriched during the SD event, while the elements that can derive also from anthropogenic sources (brake pads, drums), as for example Mn, Cu, Cr, and Zn, result to be depleted.

The air mass origin analyzed with the help of the HYSPLIT-4 model and the Dust Regional Atmospheric Model DREAM (Fig. 9a, b, c), predicting the atmospheric life cycle of the eroded desert dust, show a transport of dust from the Sahara desert in that period. The synoptic situation, illustrated in (Fig. 9d, e), was characterized by an extended African high pressure and not by an episode with baric minimum over the Tyrrhenian Sea, which is instead a situation more typical during the transition seasons. Escudero

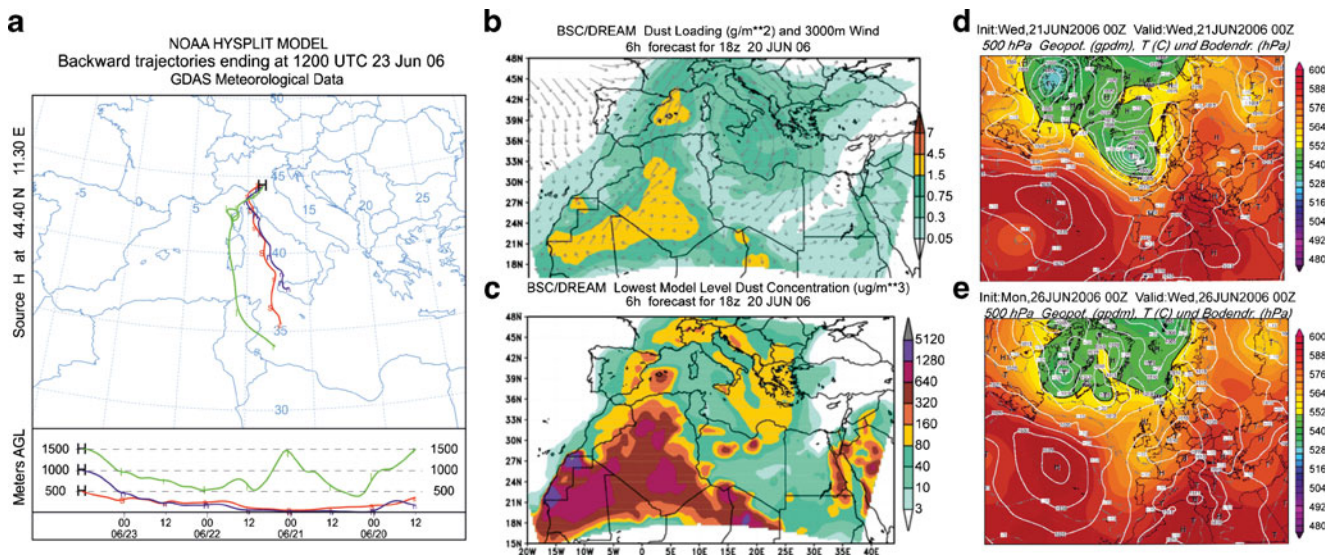


Fig. 9 **a** Back-trajectories calculated for the day 23/06/06, 12:00 UTC, by the HYSPLIT-4 model, for the city of Bologna (lat 44.40, lon 11.30) three arrival heights: 100, 500, 1,000 m AGL; **b** dust loading from the dust regional model DREAM for the day 20th June 2006; **c** lowest model level dust concentration resulting from the dust regional model

DREAM (<http://www.bsc.es/projects/earthscience/DREAM/>) for the day 20th June 2006; **d,e** Synoptic situation (500 hPa geopotential and ground level pressure in hPa) for the days 21 (**d**) and 26 June 2006 (**e**) (<http://www.wetterzentrale.de>)

et al. (2005) showed that the transport of air masses towards the Western Mediterranean basin can be originated by four meteorological scenarios: (1) a North African high located at surface levels, (2) an Atlantic depression, (3) a North African depression, and (4) a North African high located at upper levels (Querol et al. 2009). The high pressure system on North Africa (Morocco and Algeria) and the trough West of the African coast have been observed to be a typical synoptic configuration allowing for the transports of the dust for some thousands of kilometers in a short time, directly on the Mediterranean basin and Europe (Barkan et al. 2005; Meloni et al. 2008). Barkan et al. (2005) showed that it is the joint effect of the horizontal and vertical flows formed around the front between cold air and the African warm air that causes the uplifting of the dust and transportations over long distances. This phenomenon is an integral part of the West Africa monsoon system that develops starting from June (Guarnieri et al. 2011).

Conclusions

This study reports the results of an intensive particulate matter sampling campaign in Bologna, a large city in the Po Valley. This region is recognized to have high levels for many atmospheric pollutants in Europe and, then, is of primary importance for the related human health concerns. Major inorganic ions and elements were analyzed on $PM_{2.5}$ and PM_{10} , respectively, and two receptor modeling techniques have been successfully used to identify and characterize the most

influencing PM sources. Firstly, the application of a principal component analysis followed by a multi-linear regression on chemical data allowed to quantitatively identify four main sources: crustal dust, traffic and ammonium nitrate, mixed combustions and “pseudo-marine” aerosol. The mixed combustion was the source mainly contributing to the PM mass (36 %), followed by traffic and ammonium nitrate (32 %), crustal dust (21 %) and “pseudo-marine” aerosol (10 %). The multi-linear regression analysis also provided the percentage of each element in the sources composition. In a second step, the positive matrix factorization model was also applied on the same dataset. The second model is able to yield a more detailed source profile, splitting the crustal source between the mineral and the road dust component. Moreover, in the PMF model, the secondary aerosol source represented by ammonium sulfate is identified separately by the generic traffic source. The main source contributing to the PM levels is found to be the traffic (35 %), followed by the secondary aerosol (26 %), mineral dust (15 %), road dust (11 %), “pseudo-marine” (8 %) and biomass burning (8 %). Summing up the contribution of fine and coarse particles source, however, both the models indicate that about 70 % (66 % in the PMF and 68 % in the PCA/MLRA) of the PM is due to fine particulate (secondary aerosol, traffic, and biomass burning), while the remaining 30 % is instead due to coarse particulate source (dust and seasalt).

Even in the absence of significant industrial and energy production point sources, it is worth noting that all the receptor models employed in this study confirm the importance of anthropogenic sources associated mainly to traffic

and to regional scale processes affecting secondary aerosol formation especially during the cold season, in agreement with other authors (Marcazzan et al. 2003; Lonati et al. 2005; Putaud et al. 2004; 2010). Given the emissive pattern of the area and the relevant PM levels mainly affected by secondary fractions, it appears that main improvements in air quality standards are likely to succeed only if “tire” transports are more strictly regulated/substituted by less impacting technologies or policies, and if overall policies are set-up and shared over the whole Po Valley district.

Finally, an episode leading to excess PM₁₀ in June 2006 was investigated by means of meteorological analysis, back-trajectories, and aerosol chemistry pointing out a strong influence of long-range transports of Saharan dust. The episode was characterized by elevated PM₁₀ mass load not only in the urban sampling site in Bologna, but also at the high elevation WMO-GAW station of Mt. Cimone. A characteristic value of the ratio of some crustal elements (mean±standard deviation: Ca/Si=1.1±0.2, Fe/Si=0.68±0.05, Mn/Si=0.015±0.002, Zn/Si=0.020±0.008) was observed during this event, in agreement with, for example, Kong et al. (2011). The synoptic situation was characterized by an extended African high pressure, a situation that has been often observed to be responsible of elevated dust transport to Italy and to Central Europe.

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