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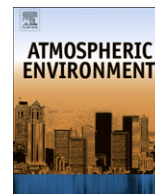
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Saharan dust impact in central Italy: An overview on three years elemental data records

S. Nava^{a,*}, S. Becagli^b, G. Calzolari^a, M. Chiari^a, F. Lucarelli^a, P. Prati^c, R. Traversi^b, R. Udisti^b, G. Valli^d, R. Vecchi^d

^a Department of Physics and Astronomy, University of Florence and I.N.F.N., Via Sansone 1, 50019 Sesto Fiorentino (FI), Italy

^b Department of Chemistry "Ugo Schiff", University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino (FI), Italy

^c Department of Physics, University of Genova and I.N.F.N., Via Dodecaneso 33, 16146, Genova, Italy

^d Department of Physics, Università degli Studi di Milano and I.N.F.N., Via Celoria 16, 20133, Milano, Italy

HIGHLIGHTS

- ▶ PIXE is very effective to quantify the actual mineral dust contribution to PM.
- ▶ The impact of Saharan intrusions on PM10 is extremely variable from case to case.
- ▶ Desert dust concentrations up to 20–25 $\mu\text{g m}^{-3}$ during the most intense episodes.
- ▶ Saharan dust determinant for PM10 daily limit exceedance in 2% of analysed samples.

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ABSTRACT

In southern European countries, Saharan dust may episodically produce significant increases of PM10, which may also cause the exceedance of the PM10 daily limit value established by the European Directive (2008/50/EC). The detection with very high sensitivity of all the elements that constitute mineral dust makes PIXE technique a very effective tool to assess the actual impact of these episodes.

In this work, a review of long-term series of elemental concentrations obtained by PIXE has been accomplished with the aim of identifying the occurrence of Saharan dust transport episodes over long periods in Tuscany and characterising them in terms of composition and impact on PM concentration, tracing back their contribution to the exceedances of the PM10 limit value.

The impact of the different Saharan intrusions on PM10 showed a very high variability. During the most intense episodes (which occurred with a frequency of few times per year) the calculated soil dust concentration reached values as high as 25–30 $\mu\text{g m}^{-3}$, to be compared with background values of the order of 5 $\mu\text{g m}^{-3}$. The Saharan dust contribution was decisive to cause the exceedance of the PM10 daily limit value in the 1–2% of the days considered in the present work.

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1. Introduction

Saharan dust is a major component of Particulate Matter (PM) on a global scale. Although the majority of the transport events take place in a low-latitude belt (towards the Atlantic Ocean), Saharan dust gives an important contribution to PM also in the European area, where it may episodically produce significant increases of the PM10 (Particulate Matter with aerodynamic diameter lower than 10 μm) concentration levels, especially in southern European countries (Querol et al., 2009).

The current European Directive (2008/50/EC) confirms the PM10 standards established by the previous one (1999/30/EC), i.e. an annual limit value of 40 $\mu\text{g m}^{-3}$ and a daily limit value (DLV) of 50 $\mu\text{g m}^{-3}$ with a maximum allowed number of exceedances of 35 times a year. However, if an exceedance can be attributed to a natural event, including the atmospheric resuspension or transport of natural particles from dry regions, rather than to anthropogenic sources, it can be discounted by the State Members of the European Union after scientific validation. As a consequence, in case of DLV exceedance, the estimate of African dust contribution to PM10 concentration has become a primary task for both scientists and policy makers.

In the absence of a single, standard recognised procedure, during last years different approaches have been proposed to face

* Corresponding author. Tel.: +390554572727.

E-mail address: nava@fi.infn.it (S. Nava).

this task, mainly by methods that involve the use of back-trajectories and satellite images to track Saharan dust transports from the sources. However, these tools alone are in general not sufficient as the transit of air masses coming from Sahara does not necessarily imply high PM concentrations at ground level. A model-based method has been proposed by Mitsakou et al. (2008) to estimate the contribution of desert dust to PM₁₀ in Greece, while other approaches focused on the analysis of PM₁₀ concentration time sequences (Ganor et al., 2009). During the last decade several papers appeared in the literature concerning the desert dust contribution to PM in Spain (see for example Rodriguez et al., 2001; Escudero et al., 2005, 2007; Querol et al., 2009). The reported approaches mainly rely on the use of back-trajectory calculations and satellite data to identify Saharan episodes. The net contribution of African dust to PM₁₀ is then calculated (Escudero et al., 2007), on a daily basis, by subtracting the PM₁₀ regional background (RB) level from the PM₁₀ concentration values measured in rural background sites only on dust-days. The RB level is calculated by applying the monthly moving 30th percentile to the PM₁₀ time series, after the exclusion of dust-days. This method was tuned and applied on multi-year periods over Spain, and validated by chemical analyses as well.

Many authors characterised Saharan dust events observed in Italy (see for example Prodi and Fea, 1979; Marcazzan et al., 1993; Bonelli et al., 1996; Barnaba and Gobbi, 2004; Meloni et al., 2007; Cristofanelli et al., 2009; Pavese et al., 2009), but only few recent works have focused on the assessment of the desert dust contribution to PM₁₀ limit values (Gobbi et al., 2007; Perrino et al., 2009; Matassoni et al., 2009; Pederzoli et al., 2010). A very similar approach to that reported in (Escudero et al., 2007) was used in the works of Matassoni et al. (2009) and Pederzoli et al. (2010). It should be noted that in both these works the PM₁₀ regional background was calculated by analogy with the Spanish method, but no experimental validation of its “exportability” to the Italian case has been accomplished so far. As clearly explained in Matassoni et al. (2012), two key points of this method, i.e. the selection of a proper network of rural background stations and the accounting of days with or without anthropogenic or Saharan dust contributions, are particularly critical in Italy where many rural stations are “near-city” stations and may be affected by different anthropogenic contributions, also from farming and industry.

None of the aforementioned methods rely on PM elemental composition measurements, despite their high potentialities in both Saharan episodes identification and direct quantitative assessment of their contribution. Nevertheless, as the impact of desert dust at ground level is well characterised by an increase of all soil-related elements and changes in elemental ratios, field campaigns followed by elemental analysis can indeed be very effective to assess the real impact of these episodes on PM at ground level (Marcazzan et al., 1993; Bonelli et al., 1996; Borbély-Kiss et al., 2004; Chiari et al., 2005; Marengo et al., 2006; Nicolás et al., 2008). The choice of methods not relying on elemental data is mainly due to cost and time required for reliable chemical speciation analysis. This is also the reason why Saharan dust compositional studies are often focused on the analysis of a few specific episodes or, in any case, they cover limited time periods (less than one year) and a limited number of sampling sites.

In this context, the development of rapid analytical methods that allow the assessment of the concentration of all soil-related elements on a large number of samples, in short measuring times, would be very useful. Particle Induced X-ray Emission (PIXE) technique can fulfil these requirements, as it allows the simultaneous detection, with high sensitivity, of elements that compose mineral dust (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe, Sr, Zr). Improving the technique capabilities, it is possible to quantify the crustal element

concentrations in less than 1 min per sample (Calzolari et al., 2006; Lucarelli et al., 2010).

Since nineties, several aerosol sampling campaigns have been carried out by the authors in Tuscany (central Italy). In this work, a review of these PIXE data-sets has been accomplished aiming at: (1) identifying the occurrence of Saharan dust transport episodes over long periods in Tuscany, (2) characterising them in terms of composition and impact on PM concentration and (3) tracing back their contribution to exceedances of the PM₁₀ limit value. Backward trajectory calculations (HYSPLIT transport model by NOAA Air Resource Laboratory (Draxler and Rolph, 2003)) have been performed for all the sampling days as an additional tool for confirming the Saharan origin and, in general, for studying correlations between elemental composition and air mass trajectories.

2. Methods

2.1. Field campaigns

For this work we selected three field campaigns performed in Tuscany, from 1997 to 2006, where PM₁₀ samples were collected on a daily basis (from midnight to midnight).

The first campaign (Lucarelli et al., 2004) was carried out from January 1997 to January 1998, in Florence, at a traffic site (FL_TS in the following). About 250 PM₁₀ samples were collected by an APM-1 air sampler (ELECOS, Rome, Italy) on 47 mm diameter mixed cellulose ester membrane filters; the PM₁₀ mass was automatically measured by the β -absorption technique.

The second campaign (Chiari et al., 2005) was carried out from September 2002 to June 2003, in Montelupo Fiorentino, a small town located about 20 km west of Florence characterised by the presence of a large number of ceramic and glass factories (MF_IS in the following). About 180 PM₁₀ samples were collected on 47 mm TEFLON filters, by an IND PNS15D sequential sampler ($2.3 \text{ m}^3 \text{ h}^{-1}$).

The third campaign was carried out within the PATOS (Particolato Atmosferico in TOScana) project, from September 2005 to September 2006, in six sampling sites representative of areas with different characteristics: Florence – urban background (FL_UB), Prato – traffic site (PO_TS), Capannori (Lucca) – urban background (CA_UB), Arezzo – traffic site (AR_TS), Grosseto – urban background (GR_UB) and Livorno – suburban/rural background (LI_SB). About 1000 PM₁₀ samples were collected by three low volume ($2.3 \text{ m}^3 \text{ h}^{-1}$) samplers (HYDRA Dual Sampler), which were moved every 15 days from three sampling sites (FL_UB, CA_UB and GR_UB) to the other three (AR_TS, PO_TS and LI_SB). In both the second and third campaigns the PM daily mass concentrations were obtained by weighing the filters by an analytical balance in controlled conditions of temperature ($20 \pm 1 \text{ }^\circ\text{C}$) and relative humidity ($50 \pm 5\%$).

Although the samples collected in these campaigns have been analysed by different analytical techniques, this work mainly focuses on the analysis of elemental concentrations (in particular of crustal elements) measured by PIXE.

2.2. PIXE analysis

PIXE analyses of samples collected during the PATOS campaign were performed at the 3 MV Tandetron accelerator at the LABEC laboratory (Calzolari et al., 2006), while samples collected during the other campaigns were analysed at the 3 MV KN3000 Van de Graaff accelerator (now decommissioned), using a similar set-up (Chiari et al., 2005).

Each sample was irradiated for about 5–10 min with a proton beam of 3 MeV energy and intensity ranging from 5 nA to 50 nA (depending on the sample load and the collecting substratum), over

a spot of $\sim 2 \text{ mm}^2$; during irradiation, the filter was moved in front of the beam in order to scan and analyse most of the deposit area. PIXE spectra were fitted using the GUPIX code (Campbell et al., 2010) and elemental concentrations were obtained via a calibration curve from a set of thin standards of known areal density (Micromatter Inc.). The results presented in this work are based on analytical data for Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe and Sr. Minimum detection limits (MDLs) are in average $10\text{--}20 \text{ ng m}^{-3}$ for Na, $5\text{--}10 \text{ ng m}^{-3}$ for Mg, Al, Si, K, Ca, and $1\text{--}3 \text{ ng m}^{-3}$ for Mn, Fe, Sr. The uncertainties were determined by a sum of independent uncertainties on certified standard sample thickness (5%), peak areas (from 2 to 20% or higher when concentrations approach MDLs) and sampling parameters (of the order of few percent). The concentrations of lighter elements (Na, Mg, Al and Si) were corrected for self-absorption effects, i.e. lower energy X-rays attenuation inside aerosol particles (Calzolari et al., 2010; Formenti et al., 2010).

2.3. Data analysis

As a preliminary analysis, the measured elemental time patterns were observed to identify simultaneous episodic increases in the concentration of crustal elements, as this may be a first hint of the occurrence of dust events. When PM₁₀ was collected in more than one sampling site, like in the case of PATOS, we also looked at simultaneous peaks in the different locations, since this behaviour may suggest the impact of long-range transported soil dust affecting all the regional area, while the observation of different patterns from site to site clearly points out at the contribution of local sources (e.g. local dust resuspension). To distinguish between local soil dust resuspension and Saharan dust intrusions, an analysis of elemental ratios was also accomplished.

For all the studied periods we calculated backward trajectories using the HYSPLIT model at different end-point altitudes (from 500 to 2000 m a.g.l.) and for different hours of the day (0, 6, 12 and 18 UTC). These data were used with the twofold aim of supporting the Saharan origin hypothesis of the episodes identified by PIXE and investigating connections between elemental composition and air mass trajectories. On the basis of these calculations, all the sampling days were classified as “HYSPLIT Saharan days (HSDs)” and “HYSPLIT non-Saharan days (HnSDs)”. Elemental concentrations and elemental ratios during HSDs and HnSDs were thus compared.

To quantify the impact of the identified Saharan intrusions on PM₁₀ concentration, we first calculated the concentration of the soil dust component and then we estimated the desert dust contribution, by subtracting the local/background soil dust fraction, as explained in Section 3.2.

3. Results and discussion

3.1. Elemental signatures

In Fig. 1 the time pattern of the Al concentration, for all the sampling campaigns, is shown.

Although several concentration peaks during HSDs may be clearly observed, other peaks of comparable intensity may be seen also during HnSDs, probably due to local dust contributions. Conversely, in some cases we found back-trajectories coming from Sahara but no (or very low) increase in the concentration of crustal elements was observed. For some of these days, the reason is the PM scavenging due to the rain; for the others, possible explanations are: a weak uptake of dust over the desert, the dust lost by deposition during the transport and/or the weakness of the entrainment mechanism at the sampling site.

During the 1997–1998 sampling campaign in Florence, the most intense HSD-peak occurred in May: the concentrations of crustal

elements started increasing on May 12 and returned to “background” values on May 16. Other less intense HSD-peaks occurred in March, July, August, October, November, December and January. However, during the cold season the rain limited the duration and the intensity of these episodes. During the 2002–2003 campaign in Montelupo Fiorentino, two intense HSD-peaks occurred in November: the concentrations of crustal elements started increasing on November 14 and abruptly decreased on November 17 due to the strong rain, which lasted until November 25; when the rain stopped, the concentrations increased again (November 26 and 27). During the PATOS project, a very high increase in the concentrations of crustal elements, lasting several days, was observed in June, simultaneously in all the sampling sites, and back-trajectory calculations confirmed the Saharan origin. Other less intense simultaneous HSD-peaks occurred in September, November, May and August. The huge Saharan intrusions of November 2002 and June 2006 were also detected in other sampling sites in Italy, from Sicily to central-northern Italy (Matassoni et al., 2009).

To distinguish between local soil dust and Saharan dust, a stringent signature may be given by elemental ratios (Bonelli et al., 1996; Borbély-Kiss et al., 2004; Marengo et al., 2006). In Fig. 2, Si-Fe, Al-Ca and Ti-Fe scatter plots for the PATOS campaign are shown. A quite nice separation between HSDs and HnSDs can be observed, especially for higher concentrations, i.e. when the impact of the Saharan dust at ground level is higher. However, for low concentrations the separation is less evident and the quite high dispersion of the elemental ratios, especially during HnSDs, prevents the possibility of a reliable Saharan attribution based on this criterion alone.

To summarise this information, main crustal element ratios have been averaged over two different groups of samples: HnSDs and “peak-HSDs”, i.e. HSDs with some increase in the concentration of crustal elements excluding all the cases with very low (or lower than neighbour days) concentrations. Mean values and standard deviations are reported in Table 1. Apart from differences that may be noted from site to site, some common features can be observed. In all the cases, during Saharan intrusions the Al/Ca, Si/Ca, Ti/Ca, Al/Fe, Si/Fe and Ti/Fe ratios increase, while the Si/Al, Ti/Al and Ti/Si ratios decrease; conversely, the Ca/Fe ratio does not show a well defined trend. The statistical significance of these differences in elemental ratio means between the two groups of samples (HnSDs and peak-HSDs) has been evaluated for all sampling sites using a Student's *t*-test: in most of the cases obtained *p*-values were well below 0.01, with the exception of Ca/Fe and Ti/Si ratios. Conversely, the elemental ratios that show the most significant differences between Saharan and non-Saharan days are those involving either Fe or Ca (especially Al/Fe and Si/Fe, *p*-value $< 10^{-6}$), probably due to a Fe and Ca enrichment of local PM with respect to the Saharan dust. Elemental ratios including Fe are however also the most site-dependent as the concentration of this element increases in areas that are more impacted by anthropogenic sources. The Si/Al ratio shows the most reproducible values in all the sampling sites and a significant (*p*-value < 0.001) slight decrease during Saharan days. This trend may be explained by a higher contribution during Saharan intrusions of agglomerated clay minerals with respect to bulk crustal material (Rahn, 1976).

Similar results were found in two remote sites in northern and central Italy: the Stelvio National Park (Bonelli et al., 1996) and the Mt. Cimone Global Atmospheric Watch (GAW) station (Marengo et al., 2006). In both works, a decrease of the Si/Al ratio and an increase of Ti/Fe, Ti/Ca and Al/Ca ratios are indicated as the more effective fingerprints of African dust transport events. Reported values for the Si/Al ratio during these events (and during days not affected by Saharan intrusions), i.e. 2.3 (2.7) at Mt. Cimone and 2.4 (2.8) at the Stelvio National Park, match very well with those found in this work.

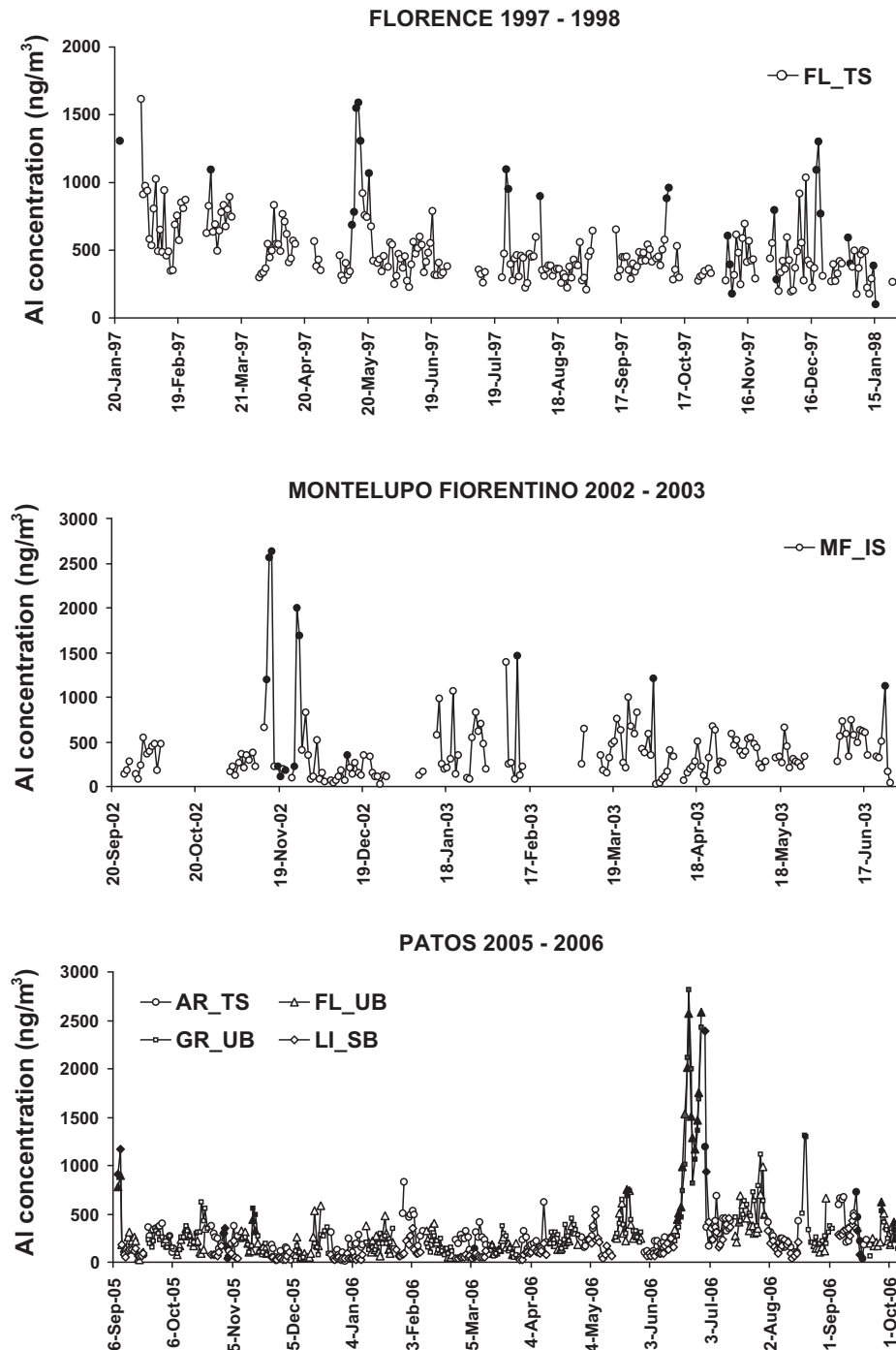


Fig. 1. Al concentration time trends. Days identified as Saharan intrusions on the basis of calculated backward trajectories (HSDs) are shown as black points.

3.2. Saharan dust contribution to PM₁₀ concentration

The soil dust component was estimated from the measured elemental concentrations following a wide used approach, i.e. the sum of oxides algorithm (Eldred et al., 1987; Malm et al., 1994; Miranda et al., 1994; Marcazzan et al., 2001), with some alterations as discussed in the following. Namely, it was calculated as the sum of all the main crustal element oxides (Na_2O , MgO , SiO_2 , Al_2O_3 , TiO_2 , K_2O , CaO , Fe_2O_3):

$$[\text{soil dust}] = 1.35 [\text{Na}] + 1.66 [\text{Mg}] + 1.89 [\text{Al}] + 2.14 [\text{Si}] + 1.21 [\text{K}] + 1.40 [\text{Ca}] + 1.67 [\text{Ti}] + 1.43 [\text{Fe}]$$

Some corrections were however applied to this formula to take into account sea-salt contributions to Na and Mg and possible anthropogenic contributions to the other elements. The sea salt fraction of Na and Mg was calculated using the measured Cl concentration and the Na/Cl and Mg/Cl ratios reported in Bowen (1979), i.e. 0.56 and 0.07, respectively. Due to possible Cl losses in aerosol samples (Seinfeld, 1986; Singh, 1995), this approach may overestimate the non-sea salt component of Na (nssNa) and Mg (nssMg). For this reason, we also looked at the time trends of the calculated nssNa and nssMg to verify the absence of significant residual peaks in correspondence of the identified sea-salt aerosol transport events. Following the approach reported in Marcazzan

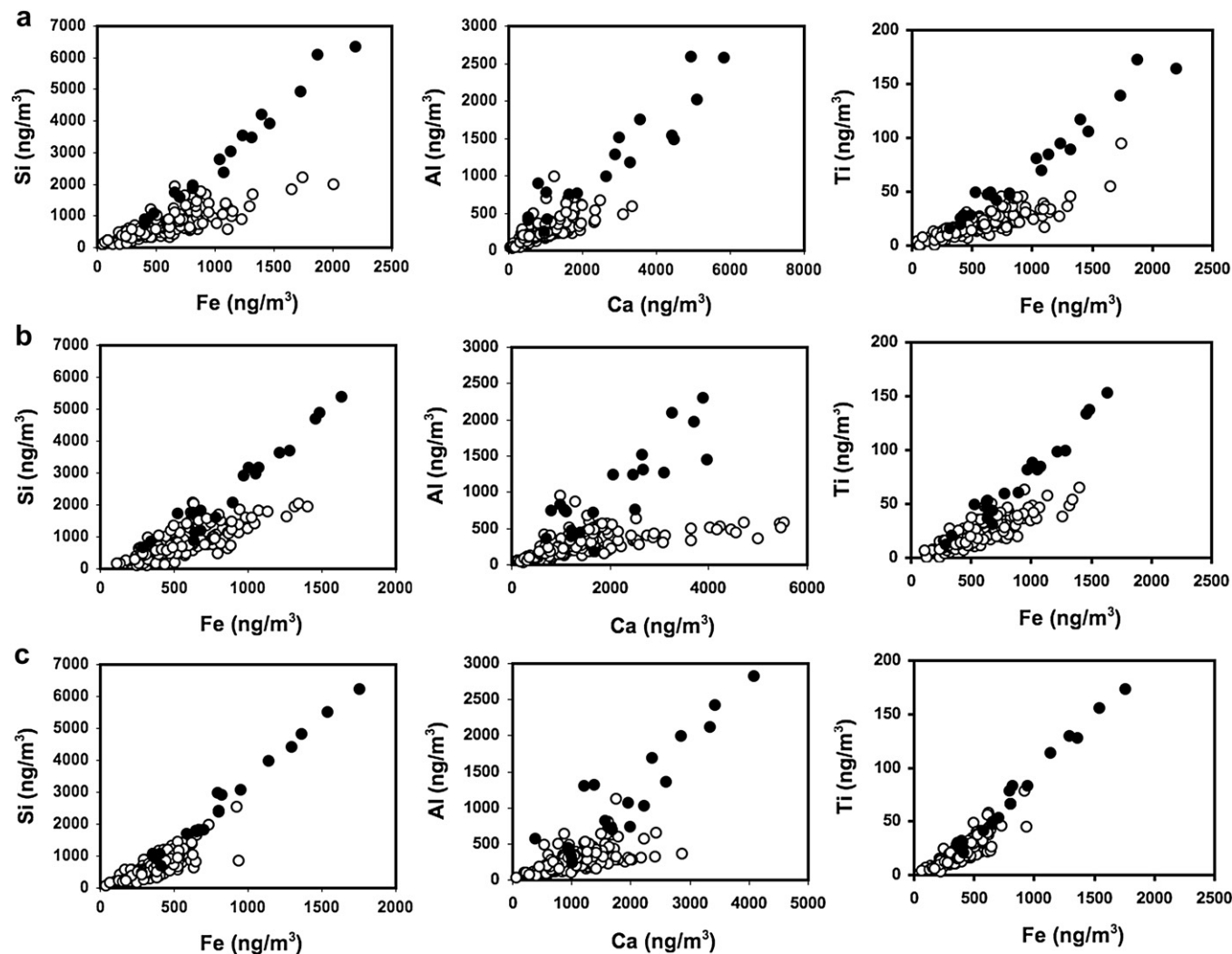


Fig. 2. Si–Fe, Al–Ca and Ti–Fe scatter plots during the PATOS campaign for the sampling sites of FL_UB (a), CA_UB (b) and GR_UB (c). Days identified as Saharan intrusions on the basis of calculated backward trajectories (HSDs) are shown as black points.

et al. (2001), possible anthropogenic contributions to Si, K, Ca, Ti and Fe were estimated by the use of aerosol-crust Enrichment Factors (EFs), which were calculated with respect to Al and adopting the crust composition profile reported in Mason (1966).

Evident anthropogenic contributions were identified only for Fe (high EFs in the traffic sites, with values up to 15–20) and K (high EFs during the cold season due to biomass burning, with values up to some tens in all sampling sites and up to one hundred in CA_UB):

Table 1
Mean values (black and bold) and standard deviations (not bold) of crustal element ratios during Saharan intrusions (HSDs with significant concentration peaks, “peak-HSDs”) and during days not affected by long-range dust transport episodes (HnSDs).

	Si/Al		Ti/Al		Ti/Si		Al/Ca		Si/Ca		Ti/Ca		Al/Fe		Si/Fe		Ca/Fe		Ti/Fe	
FLORENCE 97-98 (FL_TS)																				
Peak-HSDs	2.5	0.3	0.092	0.018	0.037	0.007	0.41	0.16	0.99	0.34	0.037	0.015	0.51	0.10	1.2	0.2	1.4	0.4	0.047	0.014
HnSDs	2.7	0.3	0.107	0.022	0.040	0.008	0.27	0.07	0.72	0.16	0.028	1.007	0.27	0.06	0.7	0.2	1.0	0.3	0.029	0.009
MONTELUPO 02-03 (MLJS)																				
Peak-HSDs	2.5	0.2	0.065	0.010	0.027	0.005	0.44	0.09	1.09	0.14	0.029	0.009	1.32	0.19	3.3	0.5	3.0	0.6	0.085	0.010
HnSDs	2.9	0.4	0.092	0.041	0.033	0.016	0.31	0.13	0.85	0.26	0.029	0.025	0.73	0.24	2.1	0.6	2.6	0.9	0.062	0.017
PATOS 05-06 (FL_UB)																				
Peak-HSDs	2.4	0.2	0.064	0.005	0.027	0.002	0.49	0.21	1.14	0.36	0.031	0.010	1.13	0.15	2.7	0.3	2.5	0.6	0.072	0.010
HnSDs	2.7	0.4	0.082	0.019	0.030	0.006	0.29	0.12	0.76	0.27	0.022	0.009	0.46	0.22	1.2	0.5	1.7	0.6	0.036	0.013
PATOS 05-06 (CA_UB)																				
Peak-HSDs	2.4	0.2	0.067	0.004	0.028	0.003	0.56	0.17	1.32	0.33	0.037	0.011	1.21	0.16	2.9	0.4	2.3	0.5	0.081	0.009
HnSDs	2.9	0.4	0.087	0.027	0.030	0.009	0.22	0.11	0.61	0.23	0.018	0.007	0.50	0.23	1.4	0.6	2.5	0.9	0.040	0.013
PATOS 05-06 (GR_UB)																				
Peak HSDs	2.3	0.1	0.063	0.003	0.028	0.001	0.62	0.20	1.42	0.44	0.039	0.013	1.40	0.19	3.2	0.4	2.4	0.4	0.088	0.012
HnSDs	2.6	0.3	0.083	0.040	0.031	0.014	0.26	0.12	0.67	0.27	0.020	0.009	0.67	0.23	1.8	0.6	2.8	0.9	0.052	0.014

the contributions of these elements were thus corrected dividing their concentrations by the corresponding EFs. The first day of the year was eliminated from all datasets due to significant contributions from fireworks to Al, Mg, Ti and Cl concentrations.

The time trends of the calculated soil dust concentrations for the different sampling campaigns are shown in Fig. 3. As already observed for crustal elements, during HSDs the increments with respect to background soil dust values are very different from case to case, ranging from null or negligible to significant or very strong. Conversely, some quite intense soil dust peak may be observed also during HnSDs, due to local dust contributions.

The soil dust mean values and standard deviations, calculated for the different sampling campaigns excluding Saharan days, are reported in Table 2. In the absence of African dust inputs the soil dust concentration is on average $2.5\text{--}7.4\text{ }\mu\text{g m}^{-3}$ and it accounts for about 15–20% of the PM₁₀ mass while during the most intense Saharan dust episodes (Fig. 3) it reaches values as high as $20\text{--}30\text{ }\mu\text{g m}^{-3}$.

To quantify the net Saharan dust contribution, an estimated soil dust background value was calculated by applying a 30-days moving average to the soil dust time series, after an a-priori exclusion of Saharan-days. The Saharan dust contribution was then

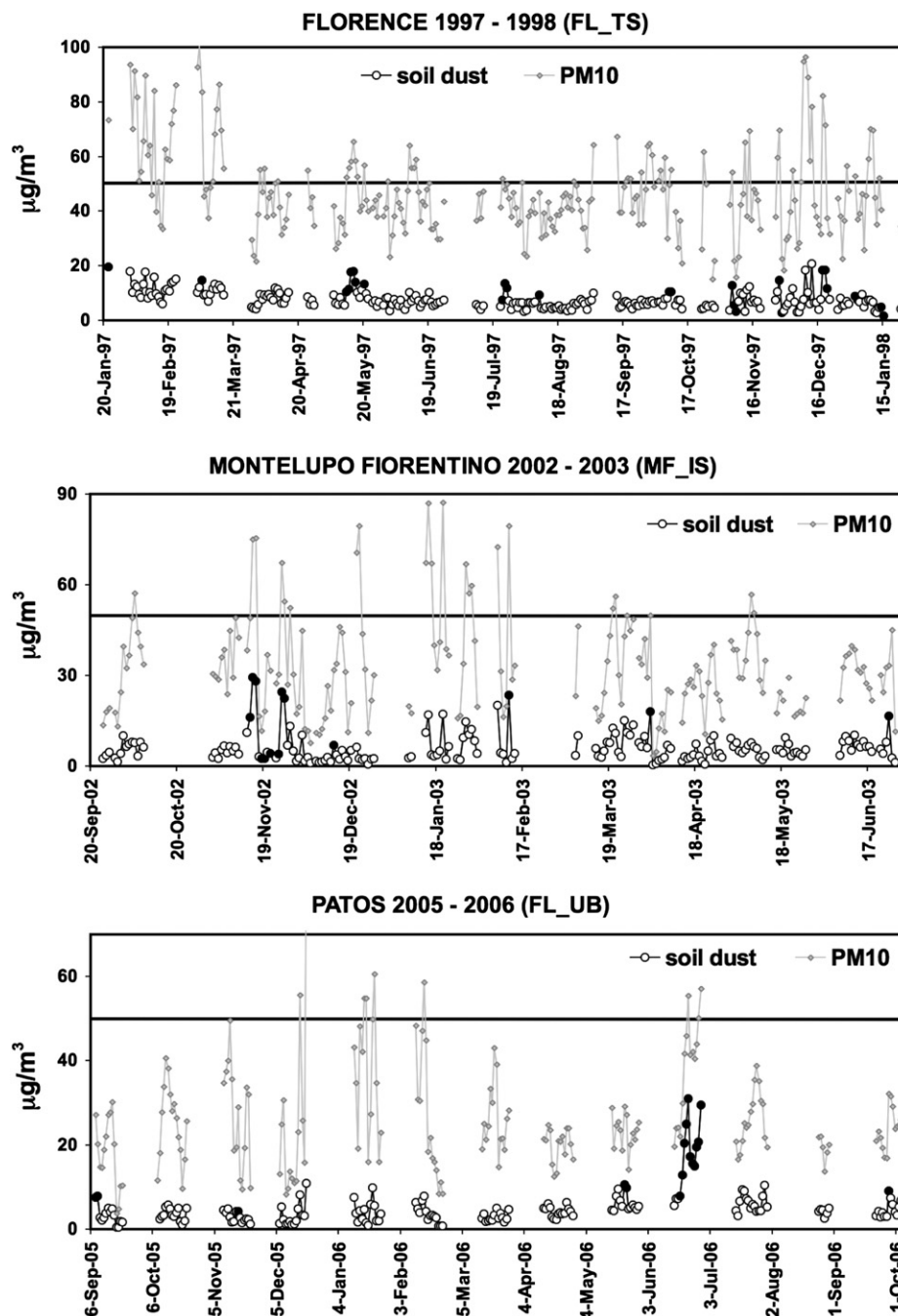


Fig. 3. Concentration time trends of PM₁₀ (grey line, open grey squares) and soil dust (black line, open and solid black circles). Days identified as Saharan intrusions on the basis of calculated backward trajectories (HSDs) are shown as black solid circles in the soil dust time trend. The $50\text{ }\mu\text{g m}^{-3}$ PM₁₀ daily limit value is also shown.

Table 2

Soil dust concentration during non-Saharan days (HnSDs) in the different sampling sites: average \pm standard deviation ($\mu\text{g m}^{-3}$) and percentage on the PM10 mass concentration.

	Soil dust (Saharan days excluded)	
	Mean \pm st.dev. ($\mu\text{g m}^{-3}$)	Percentage of PM10 (%)
FLORENCE 97-98 (FL_TS)	7.4 ± 3.0	16%
MONTELUPO 02-03 (ML_IS)	5.7 ± 4.3	18%
PATOS 05-06 (FL_UB)	4.1 ± 2.3	16%
PATOS 05-06 (CA_UB)	5.2 ± 2.8	13%
PATOS 05-06 (GR_UB)	4.7 ± 2.1	21%
PATOS 05-06 (AR_TS)	4.5 ± 2.3	16%
PATOS 05-06 (PO_TS)	5.5 ± 2.4	16%
PATOS 05-06 (LI_SB)	2.5 ± 1.7	15%

calculated, for each Saharan-day, as the difference between the total soil dust daily concentration and the soil dust background value (calculated for the same day). In order to estimate the uncertainty introduced by the background subtraction, the distributions of the absolute differences between the soil dust concentrations and the moving average daily values during non-Saharan days were analysed. Median values of the absolute difference were about $1 \mu\text{g m}^{-3}$ in all the sampling sites ($0.5 \mu\text{g m}^{-3}$ in the suburban/rural background station LI_SB), but daily absolute differences up to several $\mu\text{g m}^{-3}$ were also observed due to short local resuspension episodes. As expected, these episodes were more frequent and intense in sampling sites more affected by human activities. On the basis of these observations, in the following discussion we assume as not measurable the contribution of all the intrusions with a Saharan dust concentration lower than $1\text{--}2 \mu\text{g m}^{-3}$. It is worth noting that the use of rural background stations may lower this limit and improve the accuracy and sensitivity of this approach.

During the PATOS campaign, the highest Saharan dust concentrations (up to $29 \mu\text{g m}^{-3}$) were reached during the intense and lasting episode of June 2006, while lower contributions ($3\text{--}8 \mu\text{g m}^{-3}$) were observed during three less intense episodes. In the Montelupo Fiorentino campaign, the desert dust reached values of the order of $20 \mu\text{g m}^{-3}$ during the most intense events of November 2002. Quite high concentration levels ($10\text{--}14 \mu\text{g m}^{-3}$) turned out also for other three intrusions, while a lower contribution ($3 \mu\text{g m}^{-3}$) was estimated for the episode of December 2002. During the Florence campaign, quite high Saharan dust concentrations ($3\text{--}11 \mu\text{g m}^{-3}$) were observed during the episodes of May, January and July. High levels turned out also for other 3 episodes in November and December, but in these cases the intensity and duration were limited by the rain.

The mean net dust contributions to PM10 for the different campaigns, estimated by averaging the calculated Saharan dust concentrations over all the analysed samples (assuming null concentrations for all non-Saharan days) were about: $0.6 \mu\text{g m}^{-3}$ (Florence, 1997–1998), $0.8 \mu\text{g m}^{-3}$ (Montelupo Fiorentino, 2002–2003) and $0.5 \mu\text{g m}^{-3}$ (PATOS, 2005–2006). As all the campaigns lasted about one year and the analysed samples covered the great majority of the days, these values may be considered in first approximation as the net Saharan dust annual means.

As can be observed in Fig. 3, the PM10 concentration exceeded the DLV in several occasions during days of Saharan dust intrusion. In Table 3 the estimated Saharan dust concentration during these episodes is reported, together with the PM10 concentration. In the PATOS campaign, the only DLV exceedances during Saharan days took place during the episode of June: the PM10 concentration exceeded the $50 \mu\text{g m}^{-3}$ limit barely of few $\mu\text{g m}^{-3}$ and the contribution of Saharan dust was clearly determinant. It is worth noting that these were the only days of limit overcoming during

Table 3

PM10 DLV exceedances during days of Saharan dust intrusions. PM10 and Saharan dust concentrations (absolute values and percentage on PM10) are reported. The total number of analysed samples and PM10 exceedances for the different campaigns are also indicated (in brackets).

Sampling site (n° samples, n° exceedances)	Date	PM10 $\mu\text{g/m}^3$	Saharan dust $\mu\text{g/m}^3$ (%)
PATOS 05-06 (FL_UB) (179, 12)	22-Jun-06	56	25 (44%)
	27-Jun-06	51	14 (29%)
	28-Jun-06	57	23 (40%)
PATOS 05-06 (CA_UB) (200, 49)	27-Jun-06	51	16 (32%)
	28-Jun-06	52	19 (36%)
PATOS 05-06 (GR_UB) (181, 2)	22-Jun-06	51	29 (48%)
	28-Jun-06	51	26 (43%)
PATOS 05-06 (LI_SB) (164, 1)	30-Jun-06	52	19 (37%)
MONTELUPO 02-03 (ML_IS) (177, 21)	15-Nov-02	74	25 (32%)
	16-Nov-02	75	24 (30%)
	25-Nov-02	67	21 (31%)
	26-Nov-02	55	19 (34%)
	12-Feb-03	80	14 (18%)
FLORENCE 97-98 (FL_TS) (253, 91)	02-Apr-03	50	12 (23%)
	22-Jan-97	74	8.1 (11%)
	6-Mar-97	84	3.3 (4%)
	12-May-97	52	3.9 (7%)
	13-May-97	56	4.5 (8%)
	14-May-97	58	11 (19%)
	15-May-97	65	11 (17%)
	16-May-97	59	7 (12%)
	17-May-97	53	3.5 (7%)
	20-May-97	57	6.6 (12%)
	23-Jul-97	52	2.0 (4%)
	25-Jul-97	50	6.3 (13%)
	9-Oct-97	55	4.4 (8%)
	6-Nov-97	54	6.2 (11%)
	27-Nov-97	60	2.9 (5%)
	28-Nov-97	70	6.1 (9%)
	18-Dic-97	82	10 (13%)
	19-Dic-97	71	11 (15%)
	2-Jan-98	53	2.8 (5%)

summer for all the sampling sites of PATOS and the only ones in absolute for the less polluted sampling sites (LI_SB and GR_UB). In Montelupo Fiorentino, 6 DLV exceedances out of 21 were observed during Saharan days: 4 during the intense episodes of November, 1 in February and 1 in April. Despite the high Saharan dust concentrations, the African contribution was clearly decisive only in 3 days. Very high PM10 concentrations were found in the 1997–1998 campaign in Florence: the limit was exceeded 91 times on a total of 253 analysed samples, but only in six cases the desert dust contribution was determinant. All these cases, with only one exception, took place in spring–summer, during the high and lasting episode of May and during the shorter intrusion of July. During autumn/winter, many PM10 standard exceedances took place with high PM10 values, but the Saharan dust contribution was determinant only in one of them.

As aforementioned, the intense Saharan intrusions of November 2002 and June 2006 are also reported in Matassoni et al. (2009). In this work, the November 15–17 episode is quoted as the only one responsible for simultaneous DLV exceedance in all the sampling sites, from Sicily (Southern Italy) to the Po Valley (northern Italy), while the episode of June 2006 caused DLV exceedances in all the sites with the exception of the Po Valley one, i.e. from Sicily up to the Apennine mountain chain which divides northern from central Italy.

4. Conclusions

The analysis of extended elemental data set allowed the identification of several Saharan dust transport episodes in Tuscany (central Italy). One of the main features of these episodes is the very

high variability in their impact on PM₁₀ at the ground level. The increments in the concentrations of crustal elements during days classified as Saharan intrusions (on the basis of back-trajectory calculations) are very different from case to case, ranging from null or negligible, with respect to background values, to significant or very strong. During the most intense episodes, which occurred with a frequency of few times per year, the calculated soil dust concentration reached values as high as 25–30 $\mu\text{g m}^{-3}$, to be compared with background values of the order of 5 $\mu\text{g m}^{-3}$. The mean net Saharan dust contribution to PM₁₀ was however quite low (in the 0.5–0.8 $\mu\text{g m}^{-3}$ range, for the different campaigns). The DLV exceedances that may be ascribed to the Saharan dust contribution turned out to be 6 during the Florence 1997–1998 campaign (253 analysed samples, 91 exceedances), 4 during the Montelupo Fiorentino 2002–2003 campaign (179 samples, 23 exceedances) and 4 during the PATOS 2005–2006 campaign (160–200 samples, up to 50 exceedances, depending on the sampling site). This corresponds to an average incidence of about 1–2% of the days (3–8 times per year).

These results are in reasonable agreement with those found by other authors by the application of the “Spanish approach” (Matassoni et al., 2009; Pederzoli et al., 2010; Querol et al., 2009). However, some caution should be taken in this comparison as the sampling sites in those works were all rural/background stations and do not cover the Tuscany region, an area of relatively high latitude (42°–44°) within the Mediterranean Basin (MB), but still below the Apennine mountain chain (which divides northern from central Italy). As expected, the values found in the present work are in between those reported for the North MB (number of DLV exceedances due to African dust outbreaks, *N*, less than 2 and mean annual net desert dust contribution to PM₁₀, ND, less than 2 $\mu\text{g m}^{-3}$) and those found in the more impacted Mediterranean areas (East MB, *N* ~ 20–26 and ND 9–10 $\mu\text{g m}^{-3}$; South and South-West MB, *N* ~ 14–16 and ND 5–6 $\mu\text{g m}^{-3}$).

The approach described in this work turned out to be a very effective tool to determine the actual contribution of Saharan dust at ground level. In this case we used pre-existent PIXE data sets, which were obtained using “standard” experimental conditions; however, if only crustal elements are of interest, one day of measurement may be sufficient to analyse all the samples collected during a one-year-long campaign: this capability makes PIXE analysis a feasible approach to study the impact of Saharan dust over representative long periods and in several sampling sites. The joint use of adequate methods for African dust outbreak identification (air mass back trajectory calculation, satellite image observation, aerosol model application, etc.) and PIXE measurements on aerosol samples collected by an extended station network may provide an effective tool to trace back the contribution of desert dust to PM₁₀ quality standards. This approach may be also used to validate cheaper methods that do not require speciation analysis (but just PM₁₀ concentration measurements), like the one proposed and adopted in Spain (Escudero et al., 2007).

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References

- Barnaba, F., Gobbi, G.P., 2004. Aerosol seasonal variability over the Mediterranean region and relative impact of maritime, continental and Saharan dust particles over the basin from MODIS data in the year 2001. *Atmospheric Chemistry and Physics* 4, 2367–2391.
- Bonelli, P., Braga Marazzan, G.M., Cereda, E., 1996. Elemental composition and air trajectories of African dust transported in northern Italy. In: Guerzoni, S., Chester, R. (Eds.), *The Impact of Desert Dust across the Mediterranean*. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 275–283.
- Borbély-Kiss, I., Kiss, A.Z., Koltay, E., Szabo, Gy., Bozo, L., 2004. Saharan dust episodes in Hungarian aerosol: elemental signatures and transport trajectories. *Journal of Aerosol Science* 35, 1205–1224.
- Bowen, H.J.M., 1979. *Environmental Chemistry of the Elements*. Academic Press, New York.
- Calzolari, G., Chiari, M., García-Orellana, I., Lucarelli, F., Migliori, A., Nava, S., Taccetti, F., 2006. The new external beam facility for environmental studies at the Tandemtron accelerator of LABEC. *Nuclear Instruments and Methods in Physics Research B* 249, 928–931.
- Calzolari, G., Chiari, M., Lucarelli, F., Nava, S., Portarena, S., 2010. Proton induced γ -ray emission yields for the analysis of light elements in aerosol samples in an external beam set-up. *Nuclear Instruments and Methods in Physics Research B* 268, 1540–1545.
- Campbell, J.L., Boyd, N.I., Grassi, N., Bonnick, P., Maxwell, J.A., 2010. The Guelph PIXE software package IV. *Nuclear Instruments and Methods in Physics Research B* 268, 3356–3363.
- Chiari, M., Lucarelli, F., Mazzei, F., Nava, S., Paperetti, L., Prati, P., Valli, G., Vecchi, R., 2005. Characterization of airborne particulate matter in an industrial district near Florence by PIXE and PESA. *X-ray Spectrometry* 34, 323–329.
- Cristofanelli, P., Marinoni, A., Arduini, J., Bonafè, U., Calzolari, F., Colombo, T., Decesari, S., Duchi, R., Facchini, M.C., Fierli, F., Finessi, E., Maione, M., Chiari, M., Calzolari, G., Messina, P., Orlandi, E., Roccatò, F., Bonasoni, P., 2009. Significant variations of trace gas composition and aerosol properties at Mt. Cimone during air mass transport from North Africa e contributions from wildfire emissions and mineral dust. *Atmospheric Chemistry and Physics* 9, 4603–4619.
- Draxler, R.R., Rolph, G.D., 2003. HYSPLIT Model, NOAA ARL READY. Website: <http://www.arl.noaa.gov/ready/hysplit4.html>.
- Eldred, R.A., Cahill, T.A., Feeney, P.J., 1987. Particulate monitoring at US National Parks using PIXE. *Nuclear Instruments and Methods in Physics Research B* 22, 289–295.
- Escudero, M., Castillo, S., Querol, X., Avila, A., Alarcón, M., Viana, M.M., Alastuey, A., Cuevas, E., Rodríguez, S., 2005. Wet and dry African dust episodes over Eastern Spain. *Journal of Geophysical Research* 110, D18S08 10.1029.
- Escudero, M., Querol, X., Avila, A., Cuevas, E., 2007. Origin of the exceedances of the European daily PM limit value in the regional background areas of Spain. *Atmospheric Environment* 41, 730–744.
- Formenti, P., Nava, S., Prati, P., Chevallier, S., Klaver, A., Lafon, S., Mazzei, F., Calzolari, G., Chiari, M., 2010. Self-attenuation artifacts and correction factors of light element measurements by X-ray analysis: Implication for mineral dust composition studies. *Journal of Geophysical Research* 115, D01203. <http://dx.doi.org/10.1029/2009JD012701>.
- Ganor, E., Stupp, A., Alpert, P., 2009. A method to determine the effect of mineral dust aerosols on air quality. *Atmospheric Environment* 43, 5463–5468.
- Gobbi, G.P., Barnaba, F., Ammannato, L., 2007. Estimating the impact of Saharan dust on the year 2001 PM₁₀ record of Rome, Italy. *Atmospheric Environment* 41, 261–275.
- Lucarelli, F., Mandò, P.A., Nava, S., Prati, P., Zucchiatti, A., 2004. One-year study of the elemental composition and source apportionment of PM₁₀ aerosols in Florence, Italy. *Journal of the Air & Waste Management Association* 54, 1372–1382.
- Lucarelli, F., Nava, S., Calzolari, G., Chiari, M., Udisti, R., Marino, F., 2010. Is PIXE still a useful technique for the analysis of atmospheric aerosols? The LABEC experience. *X-Ray Spectrometry* 40, 162–167.
- Malm, W.C., Sisler, J.F., Huffman, D., Eldred, R.A., Cahill, T.A., 1994. Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research* 99, 1347–1370.
- Marazzan, G.M., Bonelli, P., Della Bella, E., Fumagalli, A., Ricci, R., Pellegrini, U., 1993. Study of regional and long-range transport in an Alpine station by PIXE analysis of aerosol particles. *Nuclear Instruments and Methods in Physics Research B* 75, 312–316.
- Marazzan, G.M., Vaccaro, S., Valli, G., Vecchi, R., 2001. Characterisation of PM₁₀ and PM_{2.5} particulate matter in the ambient air of Milan (Italy). *Atmospheric Environment* 35, 4639–4650.
- Marenco, F., Bonasoni, P., Calzolari, F., Ceriani, M., Chiari, M., Cristofanelli, P., D’Alessandro, A., Fermo, P., Lucarelli, F., Mazzei, F., Nava, S., Piazzalunga, A., Prati, P., Valli, G., Vecchi, R., 2006. Characterization of atmospheric aerosols at Monte Cimone, Italy, during summer 2004: source apportionment and transport mechanisms. *Journal of Geophysical Research* 111, D24202. <http://dx.doi.org/10.1029/2006JD007145>.
- Matassoni, L., Pratesi, G., Centioli, D., Cadoni, F., Malesani, P., Caricchia, A.M., Di Menno di Buccianico, A., 2009. Saharan dust episodes in Italy: influence on PM₁₀ daily limit value (DLV) exceedances and related synoptic. *Journal of Environmental Monitoring* 11, 1586–1594.

- Matassoni, L., Pratesi, G., Centioli, D., 2012. Comments on “Quantification of Saharan dust contribution to PM₁₀ concentrations over Italy during 2003–2005”. *Atmospheric Environment* 46, 680–681.
- Mason, B., 1966. *Principles of Geochemistry*, third ed.. Wiley, New York.
- Meloni, D., Di Sarra, A., Biavati, G., De Luisi, J.J., Monteleone, F., Pace, G., Piacentino, S., Sferlazzo, D., 2007. Seasonal behavior of Saharan dust events at the Mediterranean island of Lampedusa in the period 1999–2005. *Atmospheric Environment* 41, 3041–3056.
- Miranda, J., Cahill, T.A., Morales, J.R., 1994. Determination of elemental concentrations in atmospheric aerosols in Mexico City using proton induced X-Ray emission, proton Elastic scattering and Laser absorption. *Atmospheric Environment* 28, 2299–2306.
- Mitsakou, C., Kallos, G., Papantoniou, N., Spyrou, C., Solomos, S., Astitha, M., Housiadas, C., 2008. Saharan dust levels in Greece and received inhalation doses. *Atmospheric Chemistry and Physics* 8, 7181–7192.
- Nicolás, J., Chiari, M., Crespo, J., Garcia-Orellana, I., Lucarelli, F., Nava, S., Pastor, C., Yubero, E., 2008. Quantification of Saharan and local dust impact in an arid Mediterranean area by the positive matrix factorization (PMF) technique. *Atmospheric Environment* 42 (39), 8872–8882.
- Pavese, G., De Tomasi, F., Calvello, M., Esposito, F., Perrone, M.R., 2009. Detection of Sahara dust intrusions during mixed advection patterns over south-east Italy: a case study. *Atmospheric Research* 92, 489–504.
- Pederzoli, A., Mircea, M., Finardi, S., Di Sarra, A., Zanini, G., 2010. Quantification of Saharan dust contribution to PM₁₀ concentrations over Italy during 2003–2005. *Atmospheric Environment* 44, 4181–4190.
- Perrino, C., Canepari, S., Catrambone, M., Dalla Torre, S., Rantica, E., Sargolini, T., 2009. Influence of natural events on the concentration and composition of atmospheric particulate matter. *Atmospheric Environment* 43, 4766–4779.
- Prodi, F., Fea, G., 1979. A case of transport and deposition of Saharan dust over the Italian Peninsula and southern Europe. *Journal of Geophysical Research* 84, 6951–6960.
- Querol, X., Peya, J., Pandolfi, M., Alastuey, A., Cusack, M., Perez, N., Moreno, T., Viana, M., Mihalopoulos, N., Kallos, G., Kleanthous, S., 2009. African dust contributions to mean ambient PM₁₀ mass-levels across the Mediterranean Basin. *Atmospheric Environment* 43, 4266–4427.
- Rahn, K.A., 1976. Silicon and aluminum in atmospheric aerosols: crust-air fractionation? *Atmospheric Environment* 10, 597–601.
- Rodriguez, S., Querol, X., Alastuey, A., Kallos, G., Kakaliagou, O., 2001. Saharan dust contributions to PM₁₀ and TSP levels in southern and Eastern Spain. *Atmospheric Environment* 35, 2433–2447.
- Seinfeld, J.H., 1986. *Atmospheric Chemistry and Physics of Air Pollution*. Wiley, New York.
- Singh, H.B., 1995. *Composition, Chemistry and Climate of the Atmosphere*. Van Nostrand Reinhold, New York.