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NATURAL SOURCES AND HEAVY METALS[†]

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Summary - PTS, PM10 and PM2.5 samples have been collected at a rural site of south-east Italy (40° 20' 13'' N; 18° 6' 47'' E) from June to October, 2004 to investigate natural and anthropogenic contributions on particulate matter and heavy metal mass concentrations. It is shown that sharp-peak particulate-matter concentrations have been recorded during most African dust outbreaks occurred over south-east Italy. In particular, PM10 concentrations exceeding the 24-hour limit value of 50 μg/m^3 have been monitored during dust events.
Al, Cd, Cr, Cu, Fe, Mn, V, Ni, Pb, and Zn metal concentrations have been evaluated by an inductively coupled plasma atomic emission spectrometer and Al mass concentrations >500 ng/m^3 have been observed in PTS and PM10 samples during the advection of African dust particles. Accordingly to geochemical calculations Al, Fe, and Mn, have a significant crustal origin while, Cd, Cu, Pb, and Zn are of anthropogenic origin. Moreover, Fe resulted predominant in the coarse particle fraction, while Ni, Pb, V, and Zn were predominant in the fine particle fraction. It is also shown that Cd, Mn, Ni, Pb, and V concentrations never exceeded guide and/or limit values recommended by the World Health Organization and the European Council Directives.

INTRODUCTION

In the last years several studies have demonstrated that the atmospheric particulate matter (PM) besides affecting climate[1] has a large impact on human health.[2] In fact, epidemiological studies have revealed that the atmospheric particulate matter has a clear correlation with the number of daily deaths and hospitalizations due to pulmonary and cardiac disease responses.[3]

It has also been observed that the atmospheric particle impact on public health besides composition is quite dependent on particle's size. Size influences the site deposition in the human respiratory tract and hence the degree of toxicity that may be experienced. As a consequence the European Council Directive 1999/30/CE has established that the PM10 limit value for human health

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protection is 40 μg/m^3 for annual daily limit, and 50 μg/m^3 for 24-hour limit value. The 24-hour limit value cannot be exceeded more than 35 times/year. The possibility of limiting the PM2.5 mass concentrations is at present under evaluation. It is worth noting that particle size may reflect origin and formation of airborne particles: larger sized particles are often of natural origin while, small particles quite often are of anthropogenic origin or may result from gas to particle conversion reactions in the atmosphere. Sea spray, crustal erosions, volcanic emissions, and dust outbreaks are the main natural sources of atmospheric particles and natural emissions may interfere considerably in the particulate matter monitoring around large natural emission sources. North Africa is the major source of atmospheric particles of desert origin close to Europe and several authors[4-7] have demonstrated the significant impact of the long range transport of North African dust on particulate matter concentrations recorded at several sites of southern Europe. A peculiar property of dust particles is their ability to be transported over long distances from source regions.

The aim of this preliminary work is to investigate the impact of Sahara dust outbreaks on mass concentrations of 24-hour PTS, PM10, and PM2.5 samples, which have been collected at a rural site of south-east Italy (40° 20' 13'' N; 18° 6' 47'' E) that is about 800 km away from the northern Africa coast. Particulate matter samples have been collected from June to October, 2004 since the most intense dust activity over North Africa starts in April-May and extends to August-September.[8] Seven-day analytical backtrajectories and satellite images have been used to infer the advection of Saharan dust over the monitoring site. The Sahara dust impact on Al, Cd, Cr, Cu, Fe, Mn, V, Ni, Pb, and Zn mass concentrations has also been evaluated. Mass concentration evaluations mainly of heavy metals are a valuable tool to characterize air quality and to infer the presence of long range transported pollutants. The World Health Organization[9] and the European Council Directives 1999/30/CE have established limits and/or risk values of some heavy metals of specific health concern.[10]

Besides results and discussion, details on monitoring site, few notes on particulate matter sampling and metal analysis techniques are given in the following paper sections.

EXPERIMENTAL

Sampling location and systems

24-hour PTS, PM10, and PM2.5 samples have been collected from June to October, 2004 at the Physics Department of Lecce's University (40° 20' 13'' N; 18° 6' 47'' E). A rural site on the flat Salentum peninsula, which is located 7 km away from the town of Lecce, about 17 and 19 km from the Adriatic and Ionian Sea, respectively, and about 800 km from the northern Africa coast. Sampling has been carried out at the top of a small building ~ 35 m a.s.l. by a low volume (2.3 m^3/h) FH 95 KF (ESM Andersen) particulate sampler equipped with PTS, PM10, and PM2.5 inlets. Airborne particles have been collected on 47 mm diameter cellulose nitrate filters with 0.8 μm pore size and filter loads have been determined by the gravimetric method with a 10 μg-resolution Sartorius balance.

Metals analysis

An inductively coupled plasma atomic emission spectrometer ICP-AES model Liberty 110 (Varian Inc., Palo Alto, USA) has been used for heavy metals analysis. The instrument was equipped with a vertical torch inert to hydrofluoric acid and an ultrasonic nebulizer CETAC model U-5000AT$^+$ (Cetac Technologies Inc., Omaha, Nebraska, USA).

A microwave system MILESTONE model MLS-1200 MEGA (Milestone, Bergamo, Italy) has been used to accomplish the dissolution of the samples. Details on sample preparation and analysis technique are reported elsewhere.[11]

Dust event characterization

Seven-day analytical backtrajectories provided by NASA (http://aeronet.gsfc.nasa.gov/) have been used to characterize the advection of Sahara dust particles over the monitoring site. Analytical backtrajectories are provided twice a day, at 00:00 and 12:00 UTC, respectively for four different pressure levels (950 hPa, 850 hPa, 700 hPa and 500 hPa).

Moreover, true-colour images obtained from the Sea Wide Field-of-view Sensor (SeaWiFS, http://seawifs.gsfc.nasa.gov) on board of the NASA SeaStar spacecraft and from the Moderate Resolution Imaging Spectroradiometer (MODIS, http://modis.gsfc.nasa.gov/) on board of the Earth Observing System, have been used to get clear views of dust particles suspended over the south-east Mediterranean basin and hence over the monitoring site.

RESULTS AND DISCUSSION

Figure 1 shows 24-hour PTS, PM10, and PM2.5 mass concentrations as a function of the time of the year. 49, 43, and 19 samples of PTS, PM10, and PM2.5, respectively have been collected from June to October, 2004. Uncertainties on mass concentration values are lower than 5%. We observe that PTS, PM10, and PM2.5 mass concentrations vary in the range 15-83 $\mu g/m^3$, 7-90 $\mu g/m^3$, and 17-63 $\mu g/m^3$, respectively. Figure 1a also reveals that mass concentrations of PTS and PM10 samples are characterized by a rather similar variability range and temporal evolution pattern. Latter results may indicate that PM10 particles were dominant in PTS samples during our sampling period. Conversely, Fig. 1b shows that PM2.5 mass concentrations are on average lower than that of PTS and PM10 concentrations monitored during rather close time intervals. We observe from Fig. 1a that the 24-hour limit value of 50 $\mu g/m^3$ is exceeded several times by the PM10 samples collected from June to October, 2004. These results have led us to investigate the impact of African dust outbreaks on the mass concentration of collected samples. The dotted vertical lines on the top of Figs. 1a and 1b define approximately dusty-days, accordingly to satellite images and analytical backtrajectories. We believe that the intense dust outbreak that has occurred over our monitoring site during July 7-11, 2004 can be considered responsible of the PM10 mass concentration of 83±4 $\mu g/m^3$ retrieved by sampling atmospheric particles from 08:00 UTC of July 8, to 08:00 UTC of July 9.

Figure 2 shows the 7-day analytical backtrajectories of (a) July 8 at 12:00 UTC and (b) of July 9 at 12:00 UTC. Both plots reveal that north-west Africa is the source region of the 700 and 500 hPa backtrajectories reaching the monitoring site.

The SeaWiFS true colour image of Figure 3 shows that a dust plume (light-black pattern) extends all over the central east Mediterranean basin on July 9. Dust outbreaks have also occurred from September 13 to17, from October 8 to 11, and from October 20 to 24 (Fig. 1). Hence, we observe from Fig. 1a that peaks of 24-hour PM10 samplings exceeding the limit value of 50 $\mu g/m^3$, have also been obtained during sampling times not affected by African dust particles.

Work is on progress to investigate the main sources of these additional PM10 peak values. However, larger particulate matter mass concentrations have on average been sampled during dust events. Figure 1b shows that PM2.5 concentrations of about 60 $\mu g/m^3$ have been monitored during the September-October dust events. It is worth noting that the dust particle impact on ground collected particulate matter is quite dependent on the Sahara dust outbreak intensity. Moreover, the dust particle impact on PTS, PM10, and PM2.5 concentrations depends on sedimentation effects occurring during the dust particle transport: dust layers directly advected over the sampling site are expected to be richer of large size particles as a consequence of the reduced contribution of sedimentation effects during their transport. In fact, large particles play a major role in controlling

the dry deposition of mineral particles.[12] Figure 1 reveals that the July 7-11 dust event has significantly affected the PM10 concentration and less the PM2.5 concentration.

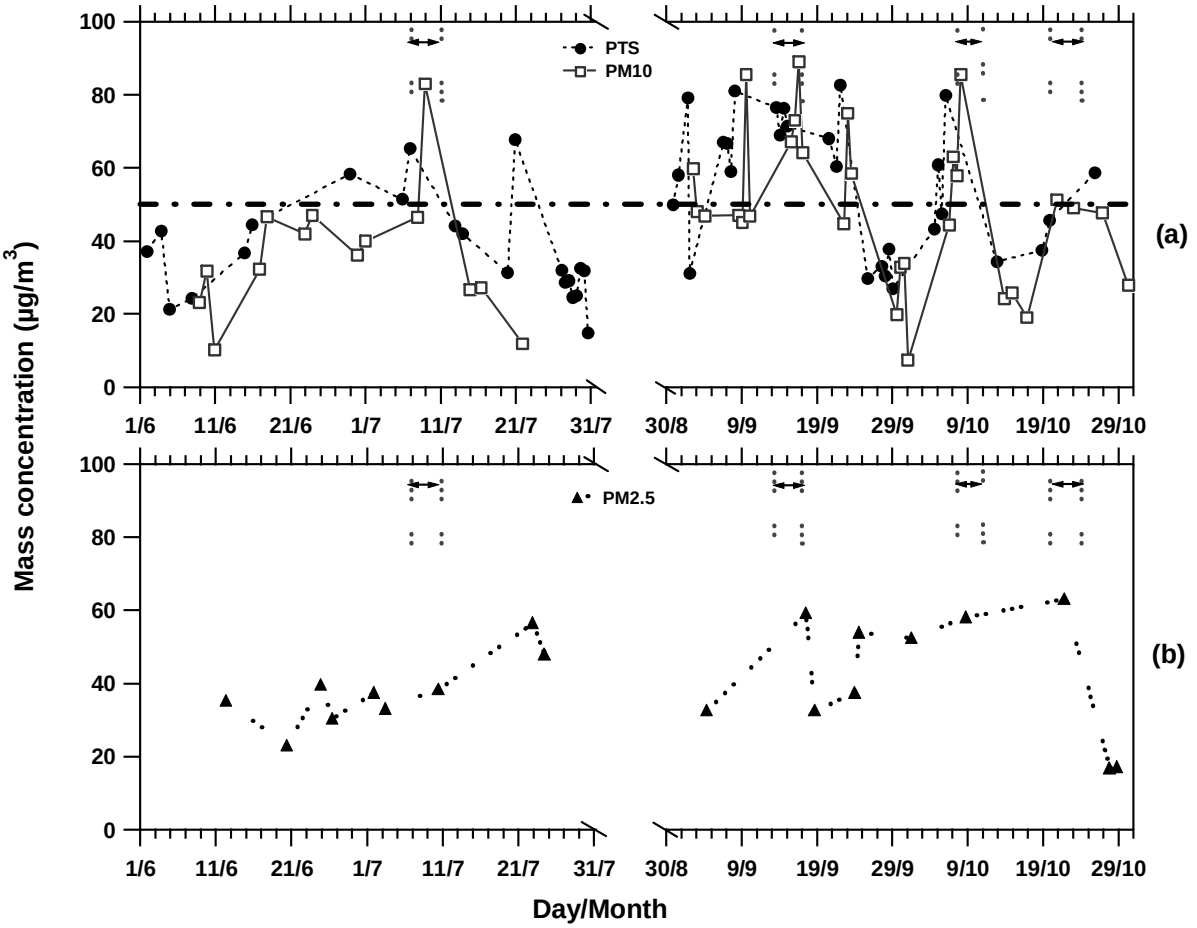

FIG. 1 - (a) PTS and PM10, and (b) PM2.5 mass concentrations of 24h-samplings collected from June to October, 2004.

Mass concentrations of heavy metals (Cd, Cr, Cu, Fe, Mn, V, Ni, Pb, and Zn) and of Al have been determined for 25 PTS, 20 PM10 and 13 PM2.5 samples randomly chosen during the sampling period. Tables 1, 2, and 3 report mean (Mean), maximum (Max), and minimum (Min) value of the mass concentration retrieved for each element in the analyzed PTS, PM10, and PM2.5 samples, respectively. Besides Mean, Max, and Min mass concentration values, 1 standard deviation (Sd) and the number of times (*N*) the element has been observed in the investigated samples are also given in Table 1, 2, and 3 to better summarize the data concerning the investigated elements. Uncertainties on metal mass concentrations are lower than 5% for Al, Fe, Mn, and Cd, while are lower than 8% for Cr, Cu, V, Ni, Pb, and Zn.

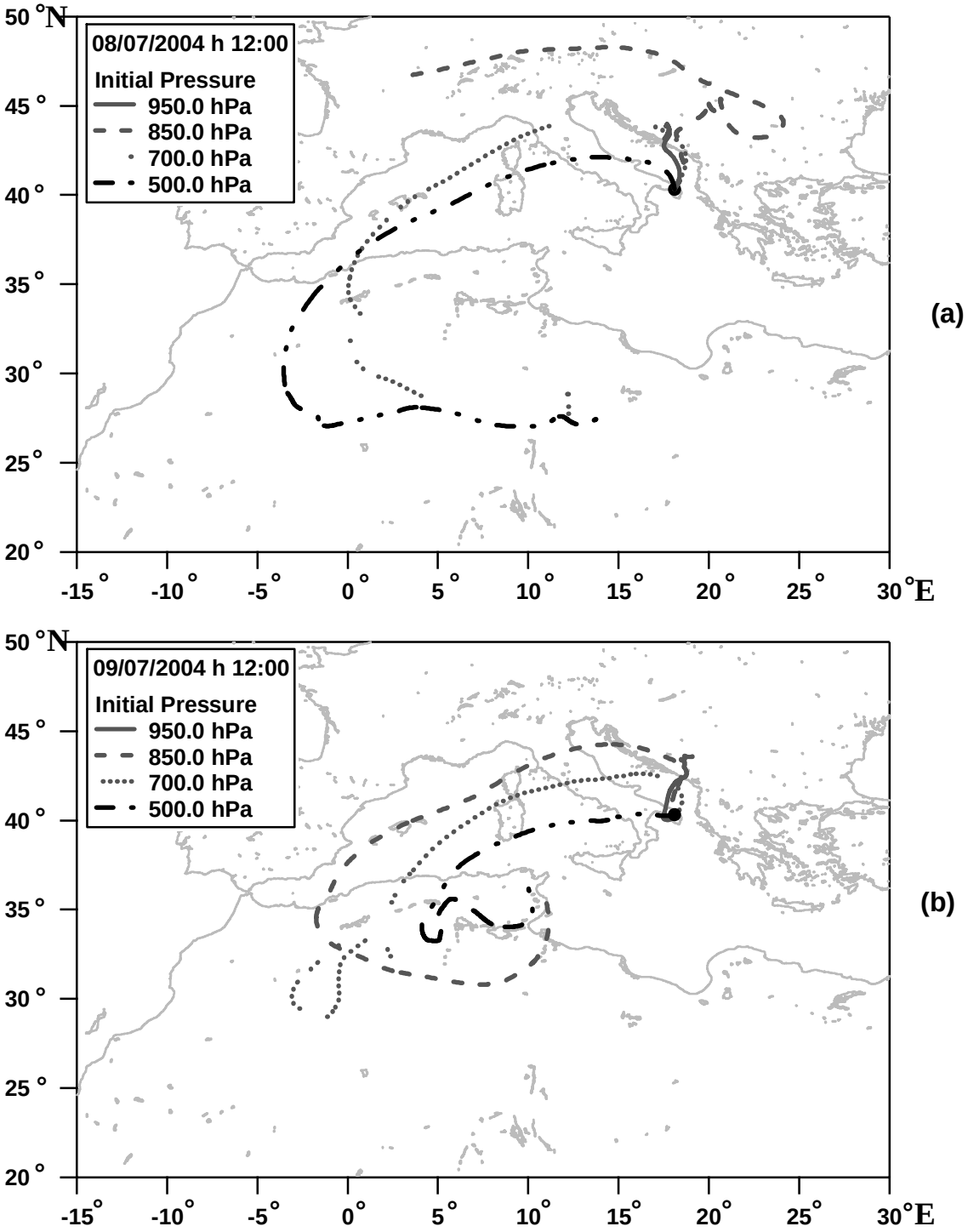

FIG. 2 - Seven-day analytical backtrajectories of (a) July 8 at 12:00 UTC and (b) July 9 at 12:00 UTC and for the 950, 850, 700, and 500 hPa pressure levels.

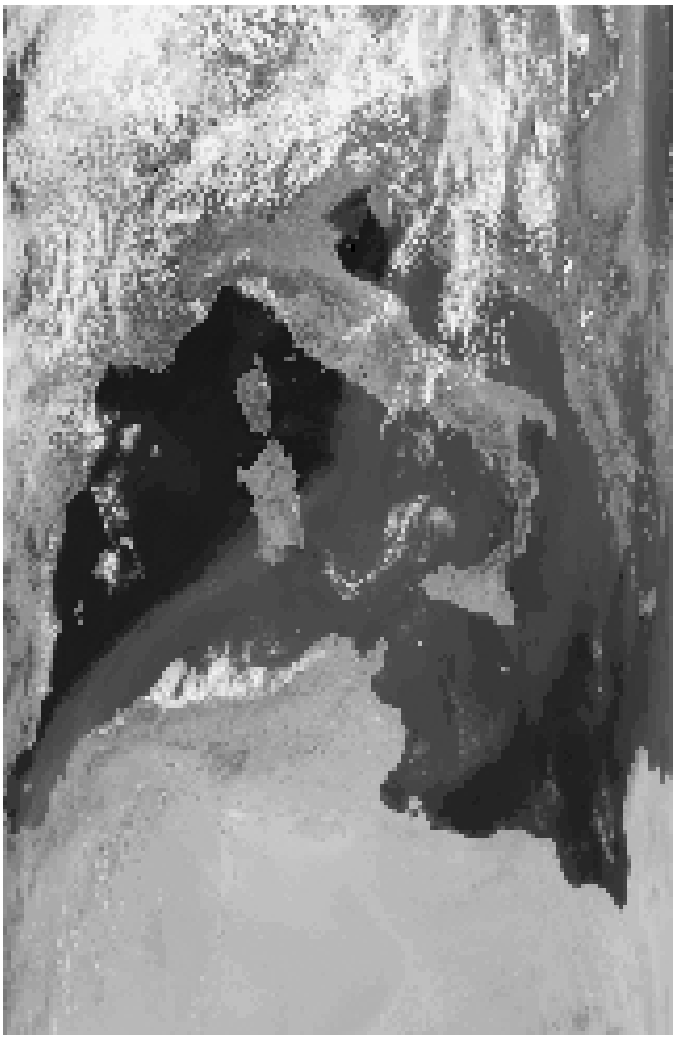

FIG. 3 - SeaWiFS true colour image relative to the African dust event of 9 July, 2004.

TABLE 1 - Mean, minimum (Min), and maximum (Max) mass concentrations (ng/m^3) of the investigated metals in 25 PTS samples. Sd is one standard deviation. *N* indicates the number of samples where the element has been observed**.**

Parameter	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**V**	**Zn**
N	25	4	21	25	25	25	14	11	25
Mean	547	0.4	6	18	541	13	16	9	30
Sd	362	0.1	3	14	289	7	7	5	15
Min	60	0.3	1	5	79	2	3	3	7
Max	1470	0.5	12	77	1120	28	35	20	75

TABLE 2 - Mean, minimum (Min), and maximum (Max) mass concentrations (ng/m^3) of the investigated metals in 20 PM10 samples. Sd is one standard deviation. *N* indicates the number of samples where the element has been observed.

Parameter	Al	Cd	Cr	Cu	Fe	Mn	Pb	V	Zn
N	20	2	20	20	20	20	14	12	20
Mean	396	0.8	27.4	16	582	11.1	11.1	9	28
Sd	245	0.2	22.7	11.4	280	4.8	5.1	4	11
Min	117	0.7	1.9	4.1	162	4.6	3.3	2	11
Max	984	0.9	69.2	53.4	1070	24.0	20.5	18	47

TABLE 3 - Mean, minimum (Min), and maximum (Max) mass concentrations (ng/m^3) of the investigated metals in 13 PM2.5 samples. Sd is one standard deviation. *N* indicates the number of samples where the element has been observed.

Parameter	Al	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
N	13	13	13	12	13	13	4	10	11	13
Mean	305	0.4	8.5	9	289	6.7	3.9	16	8.6	20.2
Sd	200	0.2	7.1	3	113	2.5	0.5	15	3.8	9.1
Min	120	0.2	0.9	3	180	2.5	3.3	6	2.0	7.1
Max	909	0.8	20.2	15	585	12.7	4.5	44	15.1	43.0

Figure 4 shows the mass concentration of (a) Al, (b) Fe, and (c) Mn retrieved in PTS (full dots), PM10 (open boxes) and PM2.5 (full triangles) samples versus the time of the year. PTS, PM10, and PM2.5 mass concentrations of Zn, Pb, and Cu as a function of the time of the year are given in Figure 5. Mass concentration mean values of Table 1, 2, and 3 have also been used to calculate the average relative percentage of Cd, Cr, Cu, Fe, Mn, V, Ni, Pb, and Zn heavy metals in PTS, PM10, and PM2.5 samples, respectively. Results are plotted in Figure 6.

Table 1, 2, and 3 show that Al and Fe are predominant metals in the investigated samples. The mass concentration of both elements is more than 20 times larger than that of other metals. Conversely, Cd and Ni are the heavy metal characterized by lower concentrations. Mass concentrations in the 0.2-0.9 ng/m^3 and 3.3-4.5 ng/m^3 range have been retrieved for Cd and Ni, respectively. Typical Cd and Ni concentrations of rural sites are in the 0.1-0.4 ng/m^3 and 0.4-2 ng/m^3 range, respectively. Conversely, for urban site affected by vehicular traffic, typical concentrations are in the 0.2-2.5 ng/m^3 range for Cd and in the 1.4-13 ng/m^3 range for Ni.[13] Mass concentrations as high as 20 and 50 ng/m^3 for Cd and Ni, respectively have instead been found in highly industrialised sites. It is worth noting that Cd and Ni concentrations reported in this paper, are closer to those typical of rural sites. These results further more show the rural characteristics of our monitoring site. Guide values provided by the World Health Organization[9] and limit values established by the European Council Directive 1999/30/CE for some heavy metals, are given in Table 4. It is worth noting that the data reported in Table 1, 2, and 3 reveal that Cd, Mn, Ni, Pb, and V mass concentrations are lower than guide and/or limit values of Table 4.

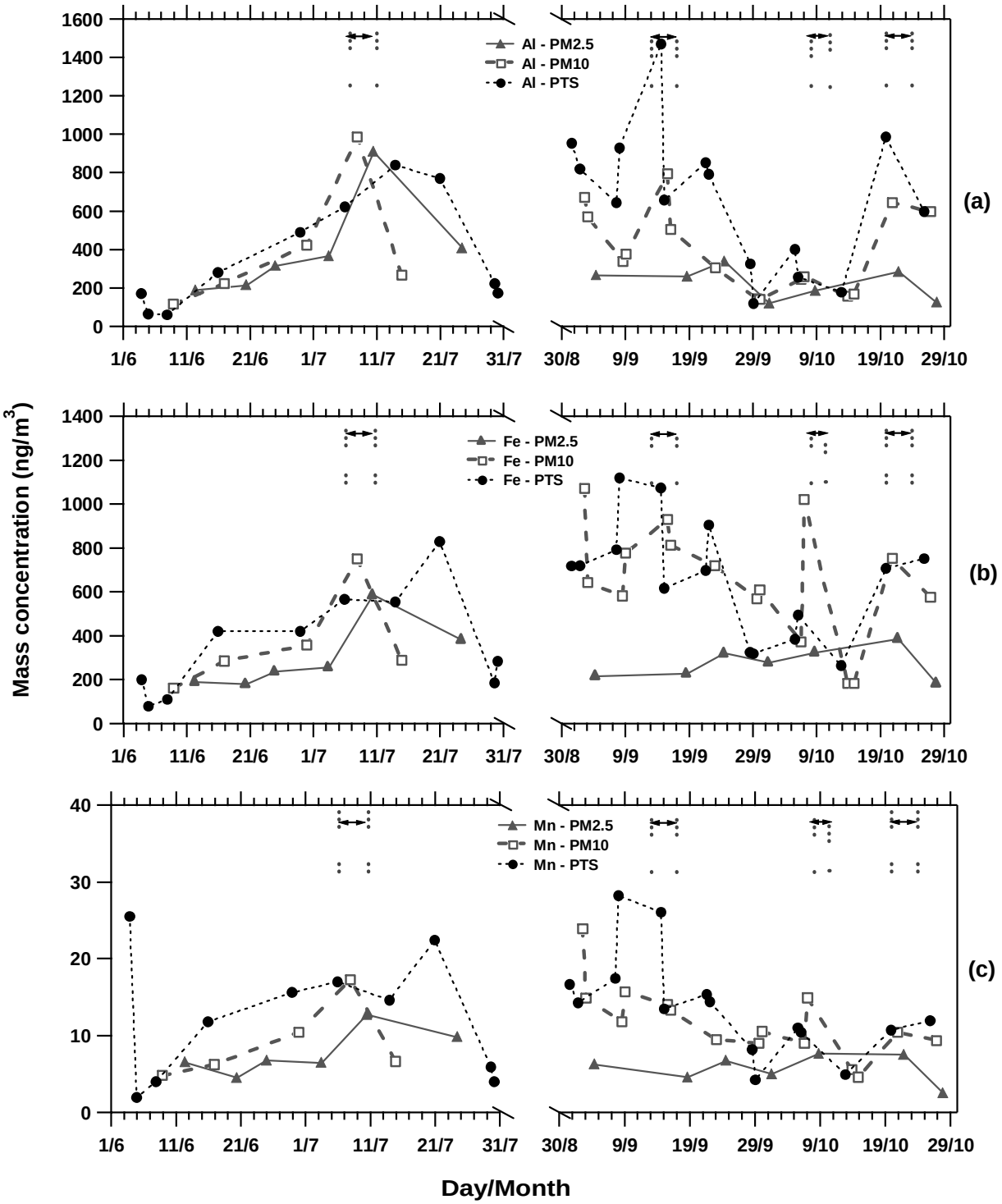

FIG. 4 - Temporal evolution of (a) Al, (b) Fe, and (c) Mn in PTS (●), PM10 (□), PM2.5 (▲) samples.

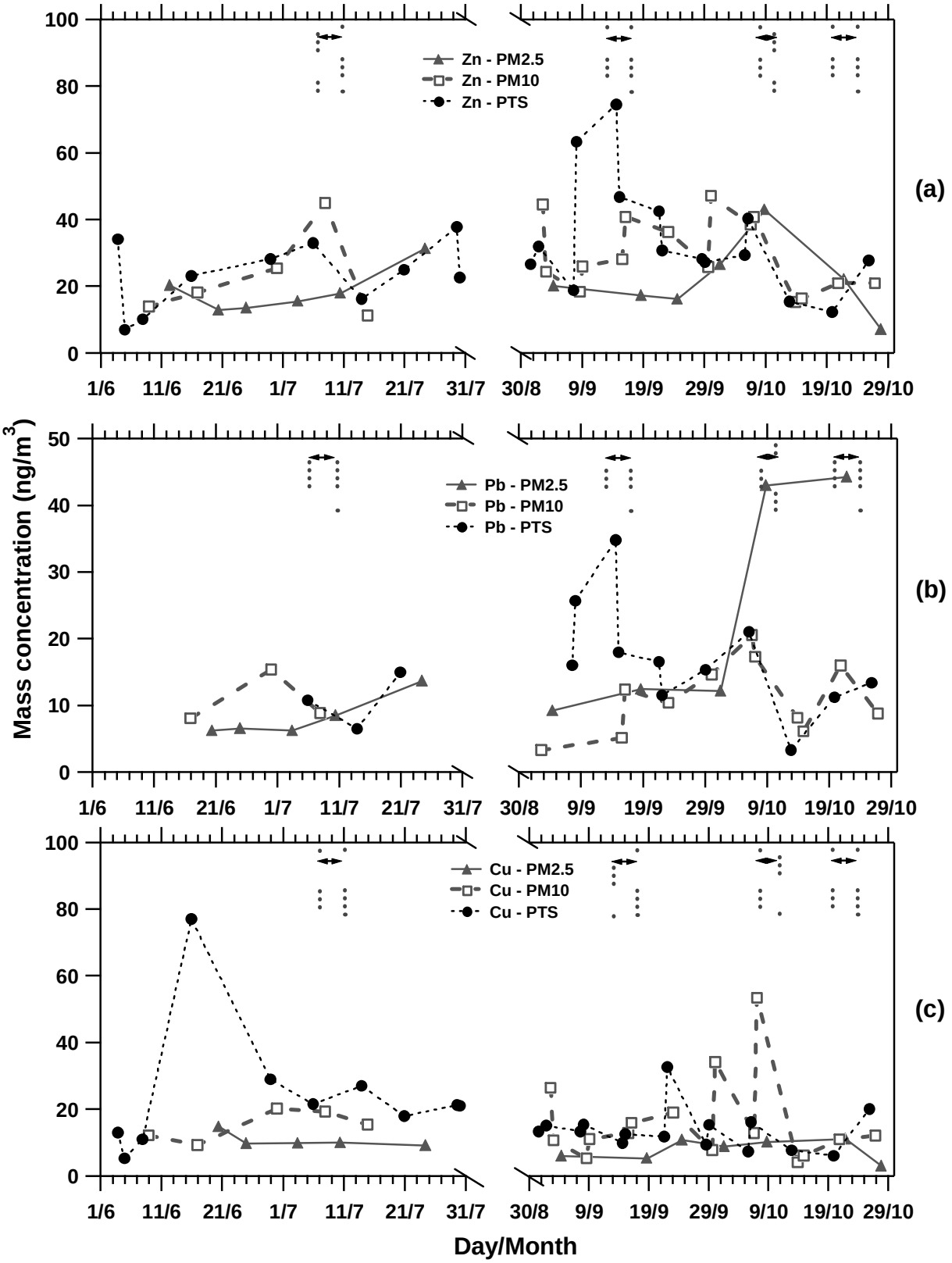

FIG. 5 - Temporal evolution of (a) Zn, (b) Pb, and (c) Cu in PTS (●), PM10 (□), PM2.5 (▲) samples.

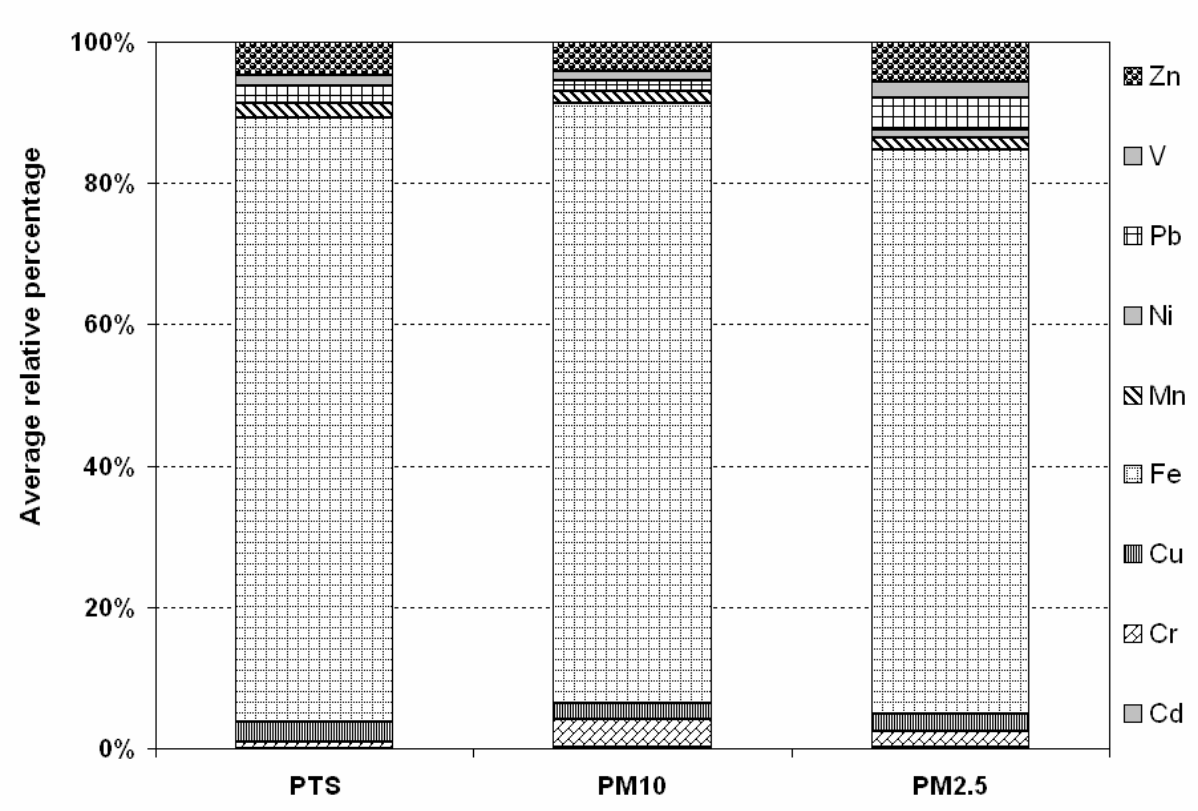

FIG. 6 - Average relative percentage of heavy metals in PTS, PM10, PM2.5 samples.

Tables 1, 2, and 3, and Fig. 6 reveal that heavy metal concentrations in PTS, PM10, and PM2.5 samples are almost similar. However, a more accurate analysis shows that the Fe average mass percentage that is of 85.4% and 84.9% in PTS and PM10 samples, respectively, reduces to 79.7% in PM2.5 samples. This result may indicate that iron was predominant in the coarse particle fraction[13], which generally characterizes particles with the aerodynamic diameter (*Da*) larger than 2.5 μm. Conversely, Fig. 6 indicates that Ni, Pb, V, and Zn were predominant in the fine particle fraction (particles with $Da \leq 2.5$ μm). Ni has only been detected in PM2.5 samples: its mass concentration was below the detection limit (< 2 ng/m^3) in PTS (Table 1) and PM10 (Table 2) samples.

TABLE 4 - Guide values provided by the World Health Organization (WHO) and limit values suggested by the European Council Directive 1999/30/CE.

Parameter	**Cd**	**Mn**	**Ni**	**Pb**	**V**[(a)]
WHO guide values	5 ng/m^3	0.15 μg/m^3	-	0.5 μg/m^3	1 μg/m^3
European limit values[(b)]	5 ng/m^3	-	20 ng/m^3	0.5 μg/m^3	-

[(a)] guide value is referred to the mean of 24-h; [(b)] annual mean of 24-h mean values revealed values established by the European Council Directive.

Natural Sources and Heavy Metals

Figure 4 reveals that the temporal evolution patterns of Al, Fe, and Mn mass concentrations are rather similar and appear to follow that of the PM mass concentration. These results may suggest either that Al, Fe, and Mn concentrations are quite correlated to PM mass concentrations and that the three metals have the same origin. Conversely, Figs. 5a, 5b, and 5c show that the temporal evolution pattern of Zn, Pb, and Cu mass concentrations are quite different from each other and from those of Figure 4. Mass concentrations of elements of different origin are expected to follow different temporal evolution patterns. In order to identify the role of potential sources of crustal and anthropogenic components, the enrichment factor (EF) technique has been used. Taylor's model (1964) is used to calculate EFs for crustal rock with Al as reference element.[14] The basic assumptions are that aluminium is entirely of crustal origin[15] and that the mean crustal composition represents the sampling area.[16] According to the suggested classification criteria[17], an EF value of <10 is taken as an indication that an element in an aerosol has a significant crustal source,[12] while EF values of > 50 are ascribed to an element of anthropogenic origin.[18] EF values for PTS, PM10, and PM2.5 samples are represented in Figs. 7a, 7b, and 7c, respectively, where symbols represent mean values, and error bars define maximum and minimum values. We observe from Figure 7 that EF values are rather similar in PTS, PM10, and PM2.5 samples. Moreover EFs indicate that Fe and Mn have a significant crustal origin and that the lower concentrations heavy metals Cd, Cu, Pb, and Zn are mainly of anthropogenic origin. EF values of V, Cr, and Ni suggest that a significant proportion of these last heavy metals has a non-crustal source.[12] These comments are further supported by the experimental results showing that Fe was predominant in the coarse particle fraction and that Ni, Pb, and V were predominant in the fine particle fraction. As it has been told, larger sized particles are often of natural origin while, small particles quite often are of anthropogenic origin.

Figure 4 shows that larger Al, Fe, and Mn mass concentrations have on average been observed during the advection of African dust particles. The significant increase of the Al mass concentration during African dust outbreaks, has been observed by several authors[12,19]. Al/Si ratios higher than 0.3 have always been considered indicative of the desert origin of the monitored particles by Guerzoni *et al*. (1997). Moreover, Dulac *et al.* (1987) have assumed that in the Mediterranean Sea, Al mass concentrations > 500 ng/m^3 represent the signature of desert-dust enriched PM concentrations. Figure 4a shows that during the dust events monitored at our site, Al concentrations > 500 ng/m^3 have been retrieved in the analyzed PTS and PM10 samples. The domination of coarse mode particles is a peculiar property desert-dust PM.[12] We have also found that in those samples Fe and Mn concentrations were > 600 ng/m^3 and > 10 ng/m^3. To better infer African dust signatures on heavy metal mass concentrations we have plotted in Figure 8 as function of the time of the year, Al/Fe and Al/Mn mass-ratios retrieved in PTS, PM10 and PM2.5 samples. Figure 8 suggests that Al/Fe and Al/Mn mass ratios reach on average larger peak values in desert-dust enriched PM samples.

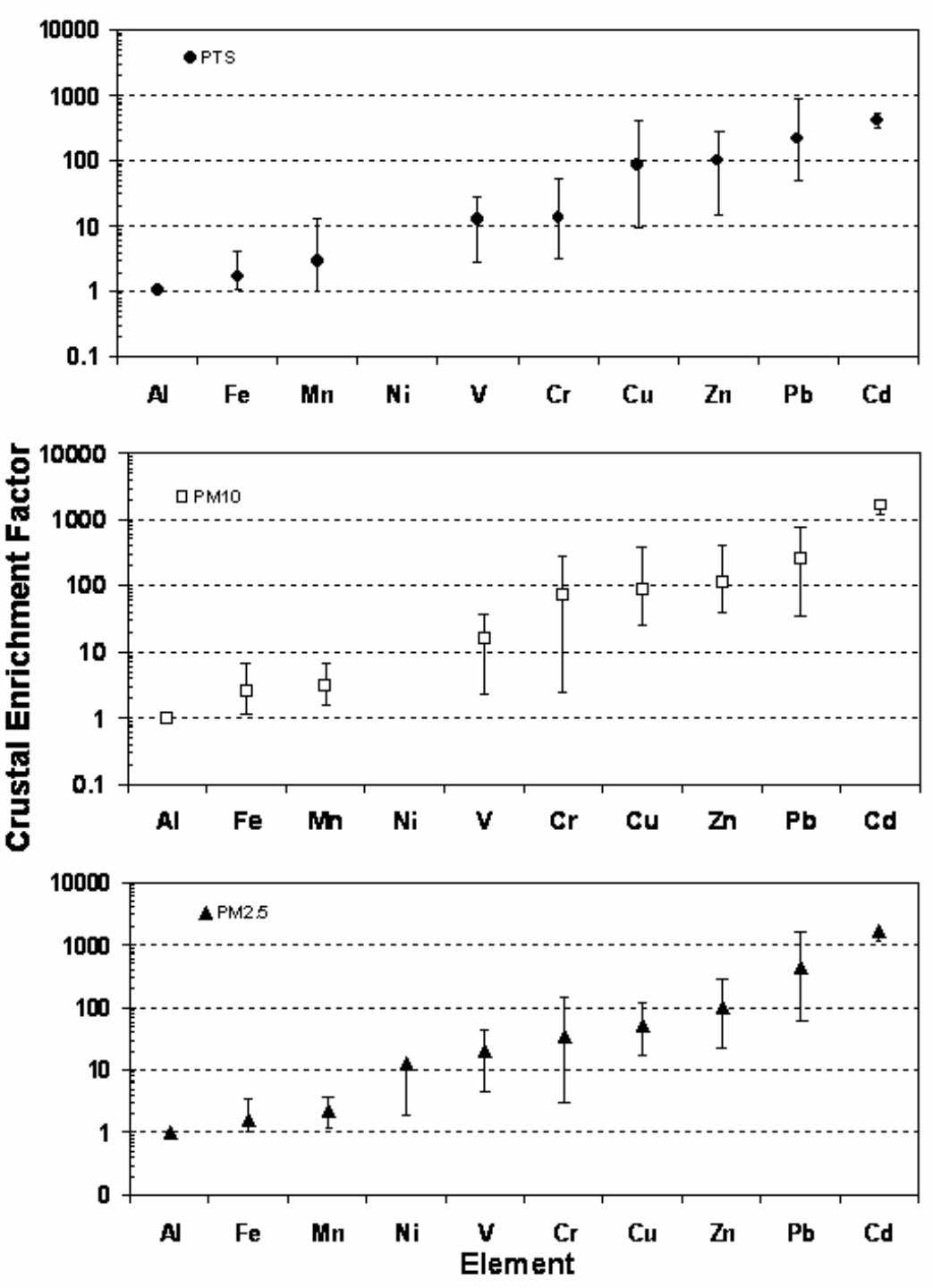

FIG. 7 - Crustal enrichment factors for (a) PTS, (b) PM10, and (c) PM2.5 samples: symbols represent mean values, and error bars define maximum and minimum values.

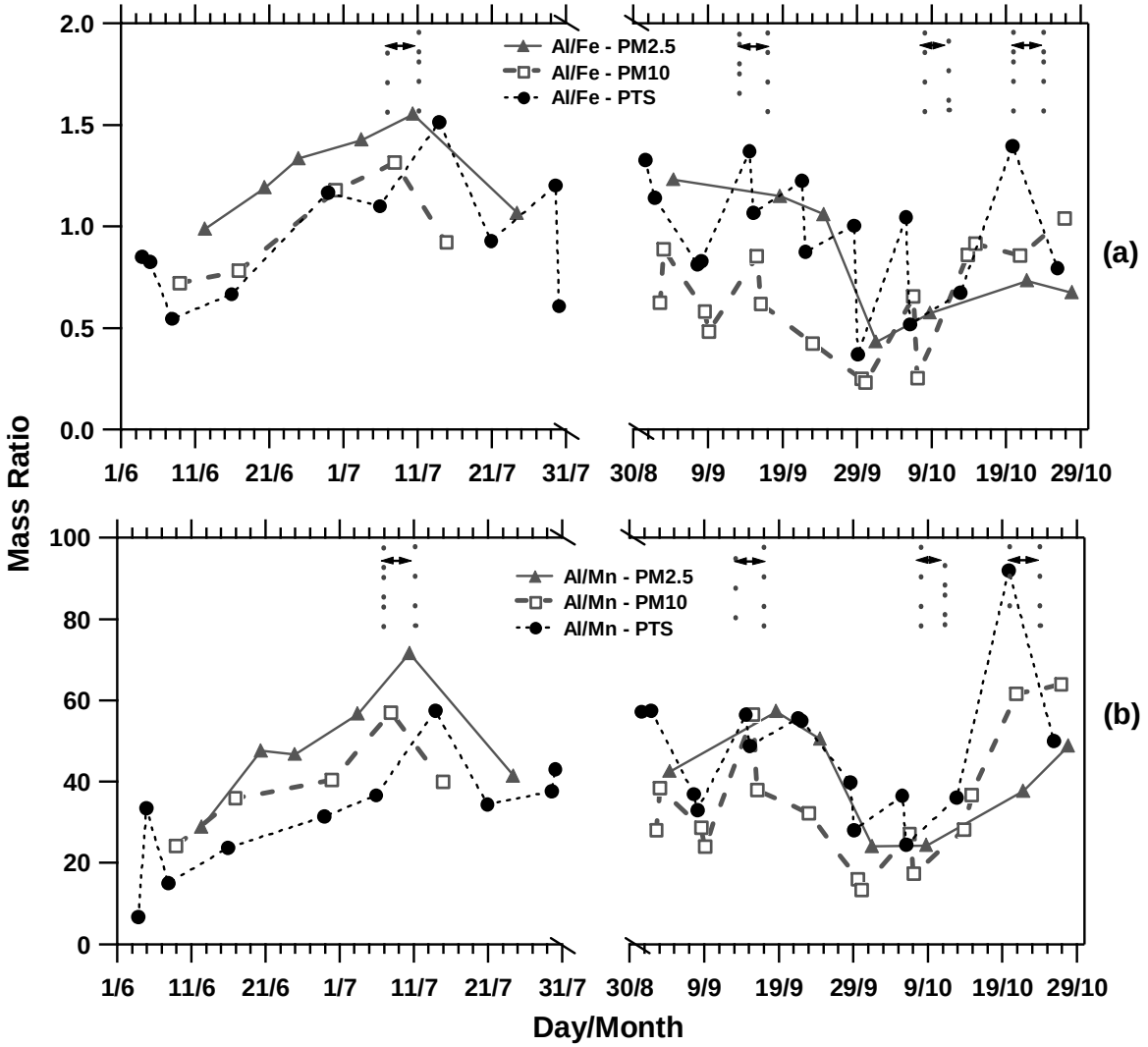

FIG. 8 - Mass ratios of (a) Al/Fe and (b) Al/Mn in PTS, PM10, and PM2.5 samples.

CONCLUSIONS

The mass concentration characterization of PTS, PM10, and PM2.5 samples collected at a rural site of south-east Italy and the investigation of the impact of African dust outbreaks on PM and metal mass concentrations, represent the main goals of this preliminary work. It is based on the analysis of 49, 43, and 19 samples of PTS, PM10, and PM2.5, respectively that have been collected from June to October, 2004 at the Physics Department of Lecce's University. It is shown that PM mass concentrations are characterized by a rather high variability range: mass concentrations varying in the 15-83 $\mu g/m^3$, 7-90 $\mu g/m^3$, and 17-63 $\mu g/m^3$ range have been observed in PTS, PM10, and PM2.5 samples, respectively. Moreover, PM10 mass concentrations exceeding the 24-hour limit value of 50 $\mu g/m^3$ have been monitored during dust events, even if additional high concentration PM10 peaks have also been monitored during sampling times free of African dust. Al, Cd, Cr, Cu, Fe, Mn, V, Ni, Pb, and Zn metal concentrations have been evaluated by an inductively coupled plasma atomic emission spectrometer. It has been found that Al and Fe were predominant metals in the investigated samples. The mass concentration of both elements was more than 20 times larger than that of other metals. EFs for crustal rock with Al as reference element

have indicated that Fe and Mn have a significant crustal origin and that Cd, Cu, Pb, and Zn are mainly of anthropogenic origin. EF values of V, Cr, and Ni have suggested that a significant proportion of these heavy metals has a non-crustal source. It is also shown that Cd, Mn, Ni, Pb, and V heavy metal mass concentrations never exceeded guide and/limit values recommended by the World Health Organization and the European Council Directives.

A significant increase of the Al mass concentration has been observed in samples collected during African dust outbreaks. In particular Al concentrations >500 ng/m^3 have been retrieved in PTS and PM10 samples. It is also shown that larger Al/Fe and Al/Mn mass ratios have been found in desert-dust enriched PM samples.

In conclusion, we believe that this paper contributes to the research activities devoted to the characterization of ground collected PM. In particular, the paper beside providing results on heavy metal concentrations sampled at a rural site, shows preliminary results on the impact of African dust outbreaks on metals and on PTS, PM10, and PM2.5 mass concentrations.

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