Trace elements in daily collected PM1 samples and source identification

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Ground-based observations of fine aerosol particles (PM1) have been carried out in Tito Scalo (Basilicata region, Southern Italy), from April 2006 to March 2007 by means of a low-volume gravimetric sampler. The aerosol samples have been analysed using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Atomic Absorption Spectrophotometer (AAS) techniques to determine the concentrations of 14 trace elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Ti and Zn). In the investigated period, PM1 values range from 0.3 μg m^{-3} to 55 μg m^{-3} with a mean value of 8 μg m^{-3}. Al, Ca, Fe, K, Mg, Na and Ti, generally considered crustal elements, are characterised by higher concentrations in the warm season (April–September) than in the cold season (October–March). On the contrary, for Cd, Cr, Cu, Mn, Ni, Pb and Zn, typical anthropogenic elements, we observe an increase in the cold season or no significant differences between warm and cold seasons. Cluster analysis (CA) Principal component analysis (PCA) and allow us to identify four source profiles for trace elements: an anthropogenic/industrial profile, an anthropogenic/traffic profile, a natural/crustal profile and a natural/marine profile. Finally, we investigate the long range transport contribution on PM1 levels and chemical composition combining concentration data, analytical back trajectories and cluster analysis. The preliminary results point out a defined relationship among natural elements when air masses come from North Africa or cross the sea for a long time.

1. Introduction

In recent years, fine aerosol particles (e.g. PM2.5 and PM1) have been found to have impact on human health, on ecosystems and on atmospheric processes including cloud formation, visibility, solar radiation and precipitation (Cattani et al., 2006; WHO, 2003). Due to the importance of the fine aerosol particles impacts, the number of studies regarding this fraction have increased recently, focusing the determination of atmospheric levels, elemental composition and source apportionment. In particular, it is

important to identify the source characteristics of aerosol particles not only for the development of air quality control strategies and for the improvement of emission sources, but also to better understand the different phenomena, such as long range air mass transport. In fact this phenomenon may affected significantly the levels and the chemical composition of particulate matter measured at ground level (Ragosta et al., 2008; Querol et al., 2007).
In this context, daily PM_1 samples were collected in the industrial area of Tito Scalo (40° 36' N; 15° 44' E, 760 m a.s.l., Basilicata region, Southern Italy) from April 2006 to March 2007 and each sample was analysed for its content of 14 trace elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Ti and Zn). Explorative analysis and multivariate statistical techniques are applied to point out the correlation structure among particulate and trace element concentrations, to highlight source profiles and to investigate the contribution of long range transport to PM1 concentrations and chemical composition.

2. Experimental procedures

PM1 levels are measured by means of a TCR Tecora low-volume gravimetric sampler (16.7 l min^{-1} flow rate), equipped with PM1 cut-off inlet and cellulose filters (Gelman filters, Ø=47 mm). The gravimetric determination of the mass is carried out using a Mettler Toledo MX5 analytical microbalance with a precision of 0.001 mg and a sensitivity of ± 0.0001%. After the sampling, each filter is treated with 3 ml of HNO3 and a drop of HF. Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn and Ti are determined by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Atomic Absorption Spectrophotometer (AAS). In order to test the extraction procedure, six samples of reference material (Urban Particulate Matter SRM 1648 from NIST National Institute of Standards and Technology) are analyzed. The recovery percentages for all elements are within the range of 100±15 %.

3. Results and discussion

3.1 Explorative statistical analysis

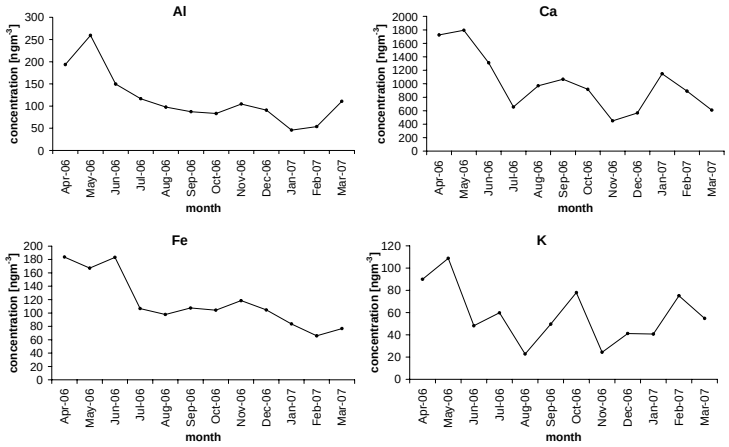
Descriptive statistics of PM1 and trace element concentrations measured in Tito Scalo from April 2006 to March 2007 are presented in Table 1. PM1 values range from 0.3 µg m^{-3} to 55 µg m^{-3} with a mean value of 8 µg m^{-3}. This mean value is lower than values measured in other background areas and/or urban sites (Vecchi et al., 2008; Ariola et al., 2006; Giugliano et al., 2005; Lin et al., 2004; Querol et al., 2001). Moreover, the PM1 concentrations measured in Tito Scalo show a lognormal distribution with positive skewness values. We also observe a large standard deviation indicating a quite high dispersion of the values around the mean. This is probably due to the different sources such as industrial emissions, traffic emissions, long range transport that influence the PM1 concentrations in the study area. Regarding trace elements, we measure mean values higher than or comparable with those measured in other sites (Vecchi et al., 2008; Ariola et al., 2006). Furthermore, skewness values indicate that Cd and Cr are the only elements characterised by a normal frequency distribution. All the other elements

are positively skewed towards the lower concentrations as confirmed by median concentrations lower than mean concentrations.

Table 1: Explorative statistical parameters of PM1 and trace element daily concentration distribution. PM1 concentrations are expressed in μg m^{-3} and trace element concentrations in ng m^{-3}. Legend: N = number of observations, m = mean value, md = median, SD = standard deviation, min= minimum value, max=maximum value, S = skewness.

Element	N	m	SD	md	min	max	S
Al	327	114	103	85	1.2	971	3
Ca	327	996	902	737	43.2	8379	3
Cd	327	4	1	4	1.3	6	0.3
Cr	327	38	9	38	11.8	83	0.4
Cu	327	4	3	3	0.01	24	3
Fe	327	115	75	93	40.6	628	3
K	327	58	52	44	0.2	394	2
Mg	327	29	18	24	9.3	148	3
Mn	327	3	2	2	0.1	11	1
Na	327	111	65	95	4.3	319	1
Ni	327	6	6	5	1.2	56	5
Pb	327	12	18	6	0.6	135	3
Ti	327	6	4	4	1.0	26	2
Zn	327	6	5	4	0.6	35	2
PM_1	327	8	7	6	0.3	55	3

Figure 1 shows the monthly mean value profiles of the 14 trace elements concentrations. Al, Ca, Fe, K, Mg, Na and Ti, generally considered crustal elements, show the similar patterns. We observe higher concentrations in the warm season (April–September) than in the cold season (October–March) (Figure 2).



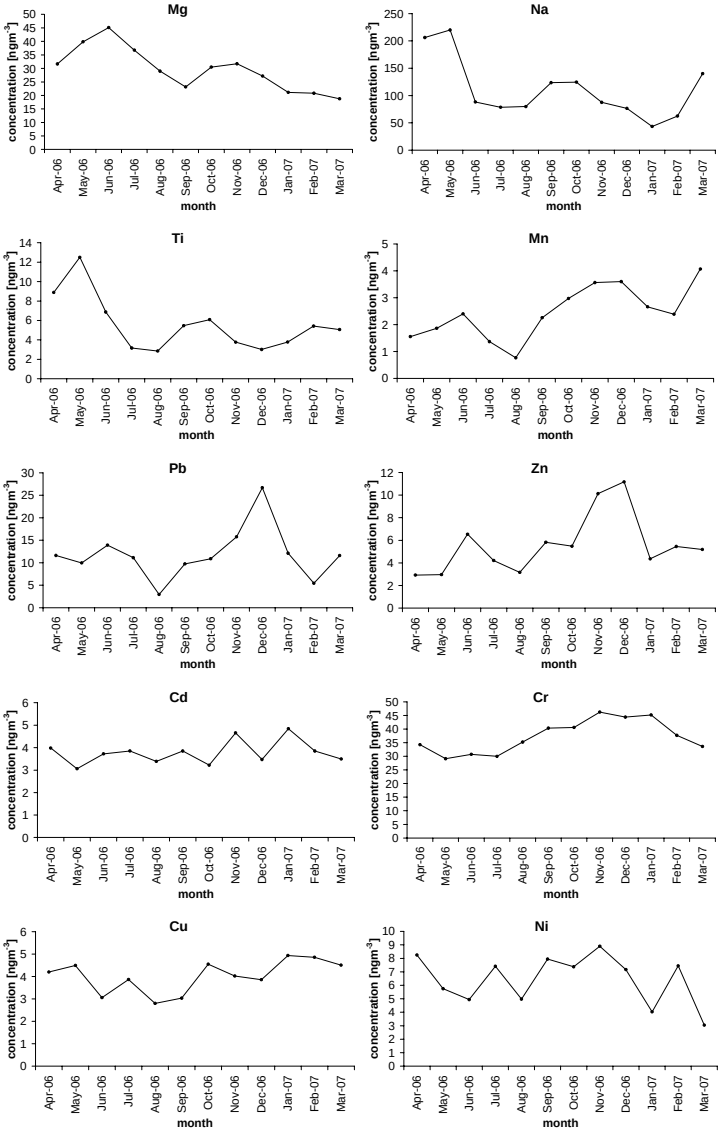


Figure 1: Monthly mean value profiles of trace elements concentrations

In particular, in the warm season, we measure a positive percentage increase for Al (35%), Ca (28%), Fe (24%), K (15%), Mg (17%), Na (24%) and Ti (22%). The higher concentrations of crustal elements measured in the warm season could be due to the contribution to PM1 levels and chemical composition of desert dust transport events which frequently occur in this period (Escudero et al., 2007; Gobbi et al., 2007). On the contrary, regarding Cd, Cr, Cu, Mn, Ni, Pb and Zn, typical anthropogenic elements, we observe an increase in the cold season or no significant differences between warm and cold seasons. These results are in agreement to the local anthropogenic sources and activities located in the monitored site.

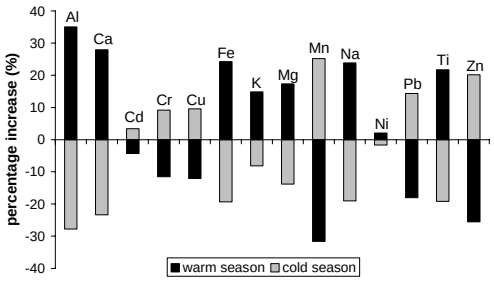


Figure 2: Percentage increase of trace element mean concentrations registered during warm and cold seasons compared to trace element mean concentrations registered during the whole period

3.2 Multivariate statistical analysis

In order to point out the relationships among the observed variables and to identify the source profiles of trace elements in PM1, we apply a combination of Cluster Analysis (CA) and Principal Component Analysis (PCA) (Quiterio et al., 2004; Ragosta et al., 2002). Regarding CA, we apply a hierarchical clustering algorithm to the correlation matrix using the furthest neighbour method as the criterion for forming clusters. The results point out three sub-groups of variables (Figure 3). The first cluster is composed by Pb, Zn, Mn and Cu with marker couple (Pb, Zn). These elements are typically related to anthropic emissions such as industrial and/or traffic ones. The second cluster is composed by Cd, Cr and Ni with the marker couple (Cd, Cr) and it is related to industrial emissions. The third cluster is composed by Al, Mg, Fe, Na, Ti, K and Ca. All these elements are mainly of natural origin.

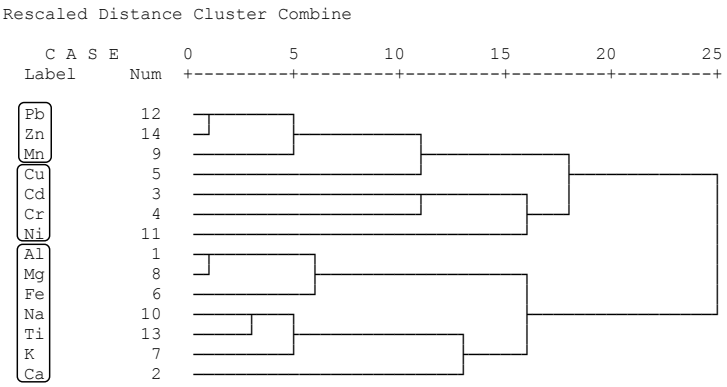


Figure 3: Dendrogram for PM1 and trace elements by furthest neighbour hierarchical clustering method.

Table 2: Rotated component matrix. Loadings, percentage of explained variance (P%), cumulative percentage of explained variance (CP%) and communality (h^2) are reported.

	PC_1	PC_2	PC_3	PC_4	h^2
Al	0.88				0.84
Ca			0.52		0.33
Cd				0.70	0.57
Cr				0.64	0.48
Cu		0.51			0.58
Fe	0.75				0.61
K			0.79		0.73
Mg	0.83				0.74
Mn		0.81			0.70
Na			0.55		0.65
Ni				0.58	0.61
Pb		0.87			0.77
Ti	0.71				0.77
Zn		0.87			0.76
P%	20	18	15	12	
CP%	20	39	53	65	

Regarding PCA, each variable is normalized to unit variance and all the principal factors with eigenvalues > 1 are retained. We point out five significant PCs that explain 68% of the data variance. Table 2 shows loadings with a VARIMAX normalized rotation. The first component explains 20% of data variance and it is characterized by Al (0.88), Fe (0.75), Mg (0.83) and Ti (0.71). It describes the natural sources contribution to PM1 composition such as soil and resuspended dust. The second component, that explains 18% of data variance, is characterized by Cu (0.51), Mn (0.81), Pb (0.87) and Zn (0.87) which are elements mainly related to industrial and motor vehicle emissions. In fact Pb and Zn are often identified as tracers of traffic. The third component explains 15% of data variance and includes Ca (0.52), K (0.79) and Na (0.55) which are elements that could be related to natural/marine emissions. The fourth component, explaining 12% of data variance, consists of Cd (0.70), Cr (0.64) and Ni (0.58). These elements are mainly related to anthropogenic emissions such as industrial emissions. In the last column of Table 2, we also report the communality values (h^2). For all the variable, except Ca, the communality values are higher than 0.4 indicating that these variables account for an acceptable proportion of variance and are well defined by the solution. In conclusion, we may identify four different source profiles. The first profile, classified as natural/crustal profile, contains elements typical of soil dust and crustal material (Al, Fe, Mg, Ti). The second profile, characterized by Cu, Mn, Pb and Zn, may be classified as anthropogenic/traffic source profile. The third profile, characterised by Ca, K and Na may be classified as natural/marine source profile. The fourth profile, containing elements typical of industrial processes (Cd, Cr, Ni), may be classified as anthropogenic/industrial profile. Finally, the increase of natural element concentrations in the warm season and the identification of an atypical marine profile for a mountainous area, suggest us the investigation of the potential contribution of

long-range transport on PM1 and trace element concentrations measured during this field survey. For each sampling day, we calculate 4-day backward trajectories using HYbrid Single-Particle Langrangian Integrated Trajectory model (HYSPLIT4). Subsequently, we classify the back trajectories in homogeneous sub-groups by k-means clustering procedure and we analyse the PM1 and trace elements concentrations associated with each trajectory cluster by means of CA. The preliminary results point out a defined relationship among natural/crustal and natural/marine elements when air masses come from North Africa or cross the sea for a long time.

4. Conclusions

In this study we present and discuss data collected in a one-year field survey, aimed to evaluate PM1 daily concentrations and its content of 14 trace elements (Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Ti and Zn) in an area of Southern Italy. We measure PM1 mean concentration lower than values measured in other background areas and/or urban sites and trace element mean values higher than or comparable with values measured in other sites. Moreover, in the warm season (April-September), we observe a percentage increase of Al, Ca, Fe, K, Mg, Na compared with the cold season that could be due to the contribution to PM1 chemical composition of desert dust transport events which frequently occur in this period. Regarding Cd, Cr, Cu Mn, Ni, Pb and Zn, typical anthropogenic elements, we observe an increase in the cold season or no significant differences between warm and cold seasons. These results are in agreement to the local anthropogenic sources and activities present in the monitored site. Cluster analysis (CA) and Principal component analysis (PCA) allow us to identify four source profiles: an anthropogenic/industrial profile, an anthropogenic/traffic profile, a natural/crustal profile and a natural/marine profile. Therefore, because the results highlight an influence of desert dust and sea salt on PM1 levels and chemical composition measured in a mountainous site, we combine concentration data, analytical back trajectories and cluster analysis to identify the contribution of the long range transport. The preliminary study points out a defined relationship among natural elements when air masses come from North Africa or cross the sea for a long time.
Actually, there are few studies on PM1 concentration and its trace elemental composition, so the results of this work represent an important contribution to the knowledge of fine aerosol composition and to understand the different phenomena that affect the behaviour of aerosol particles in the atmosphere.

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