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Advection patterns and composition of TSP and PM2.5 samples over south-east Italy

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24-hour Total Suspended Particulate (TSP) matter and PM2.5 samples have simultaneously been collected at a suburban site of South-East Italy (40.4° N; 18.1° E) to investigate the dependence of TSP and PM2.5 mass concentrations on long-range transported air masses, and to infer how concentration and composition of sampled particles were dependent on particulate matter (PM) cut-off diameter. The PM chemical composition is quite dependent on particle size and as a consequence, can allow inferring aerosol types and corresponding sources.
Ion chromatography (IC) and Organic Carbon/Elemental Carbon (OC/EC) analyses have been performed on some PM2.5 and TSP randomly selected samples, in order to determine mass concentrations of main ionic species and of EC and OC, respectively. In accordance with TSP and PM2.5 mass concentrations and PM2.5/TSP ratios, ion chromatography and OC/EC analyses have revealed that both ionic species and OC/EC concentrations significantly varied from sample to sample, as a consequence of the significant dependence of aerosol properties on regional sources and pathways of the air masses advected over the monitoring site.

1. Introduction

Studies performed in the Mediterranean basin suggest that both anthropogenic and natural sources significantly affect the composition of atmospheric particles (Koçak et al., 1997), mainly by means of long-range transport processes from the different regions around the basin: Europe, Africa, Asia, and the Atlantic Ocean.
The anthropogenic components mainly present in the fine fraction, consist of nitrates, sulphates, and carbonaceous particles, especially originated from urban and industrial sources of European countries. Conversely, air masses coming from Sahara desert are predominantly responsible for the transport of coarse type mineral and crustal aerosols. Long-range transported polluted air masses from the Atlantic Ocean and from the Mediterranean itself may instead cause the advection of marine aerosols.
A main objective of this study is to investigate either how TSP and PM2.5 mass concentrations vary with the time of the year and how mass concentrations and the chemical composition of TSP and PM2.5 samples are affected by source regions of the air masses advected over the monitoring site. Therefore, the current study reports some results on 24-h TSP and PM2.5 samples simultaneously collected at a suburban site of South-East Italy, during March-December 2007. The simultaneity of measurements has

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allowed us investigating how the contribution of fine- and coarse-mode particles and hence, of natural and anthropogenic particles, varies with the time of the year.
Analytical back trajectories provide information on the aerosol origin observed at a particular location and on the dynamical patterns governing the air mass transport (Kazadzis et al, 2007). In our study, 7–day analytical back trajectories have been used to characterize main advection patterns over the monitoring site. The used trajectories are based on the trajectory Code 613.3 developed at NASA/Goddard - The Atmospheric Chemistry and Dynamics Branch (http://croc.gsfc.nasa.gov/aeronet/index.html) and are provided for distinct arrival pressure levels and for two arrival times (12:00 and 24:00 UTC) on a day-by-day basis.
In order to asses the relative contribution of natural and anthropogenic sources to the ground collected PM, IC and OC/EC analyses have been performed on some randomly selected TSP and PM2.5 samples, respectively. This work reports in particular results on the IC and OC/EC analyses performed on two couples of TSP and PM2.5 samples, which have simultaneously been collected during a pollution event from East Europe occurred on 15 March 2007 and a Saharan dust event occurred on 25 June 2007.

2. Experimental

2.1 Sampling site and device

The monitoring site (40.4° N; 18.1° E) of this study, located in the middle of a narrow peninsula (~ 35 km from coast to coast) in the central-east Mediterranean basin, is away from large sources of local pollution and as a consequence it is well suited to infer the effects on the ground-collected PM, of long-range transported air masses coming from the various surrounding geographical regions. In particular, the PM sampling has been made at the top of the Physics Department building (University of Salento), at about 10 m from ground. The Physics Department is located in a rural area ~6 km away from the town of Lecce.
A low volume (2.3m^3/h) HYDRA-FAI dual sampler has been used to perform 24-h simultaneous samplings of TSP and PM2.5 between March and December 2007. The sampled PM has been deposited on 47-mm-diameter quartz fibre filters, conditioned before and after sampling (25°C during 48 h and 50% humidity). Particulate matter concentrations have been determined by the gravimetric method.

2.2 Chemical analysis

Ion chromatography analyses have been performed to determine mass concentrations of the main ionic species (F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) in some selected TSP and PM2.5 samples. Anions analyses were carried out by means an Ion Pac AS14A (Dionex) culumn using 8 mM Na2CO3/1mM NaHCO3 as eluent at 1mL/min flow rate and, for the detection, a conductivity system equipped with a ASRS-ULTRA suppression mode (Dionex). Cations determination was performed by means of a CS12A (Dionex) column using 20 mM MSA (Methanesulphonic Acid) as eluent at 1mL/min flow rate and, for the detection, a conductivity system equipped with a CSRS-ULTRA suppression mode (Dionex). The extraction procedure is reported in Fermo et al., 2006a.

2.3 EC/OC analysis

Beside the chemical analyses, EC and OC mass concentrations have been determined in the considered TSP and PM2.5 samples, by the thermal/optical transmittance (TOT) technique by means of an OC/EC Sunset Analyzer. More details on the methodology can be found in Birch and Cary, 1996. The technique detection limit is 0.15 μgC/cm^2 and the precision is 5% (Fermo et al., 2006b).

3. Results

Results on the evolution with time of TSP and PM2.5 mass concentrations are at first presented in this section. Then, results on IC and OC/EC analyses performed on two couples of TSP and PM2.5 samples are presented and discussed.

3.1 Results on TSP and PM2.5 mass concentrations

Mass concentrations by the gravimetric method of TSP and PM2.5 samples, collected from March to December 2007 are shown in figs. 1a and 1b, respectively.

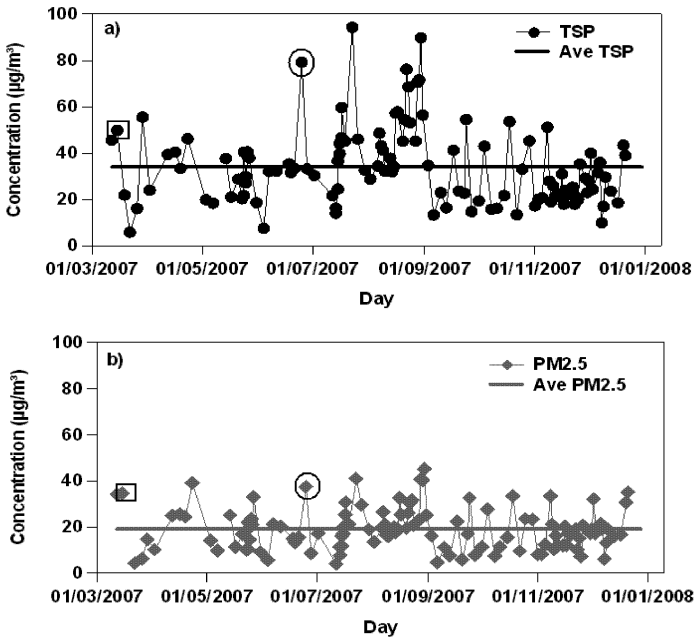

Figure 1 –Mass concentrations of (a) TSP and (b) PM2.5 ground collected samples as a function of the sampliung day. Horizontal lines represent average mass concentrantion values. Square and circle markers indicate the East-European pollution event occurred on March 15, 2007 and the Saharan dust event occurred on June 25, 2007, respectively.

We observe from fig.1 that both TSP and PM2.5 mass concentrations significantly vary day by day. Changes in air mass transport arriving from different source regions toward the sampling point have mainly been considered responsible for these results. Figure 1 highlights that TSP and PM2.5 mass concentrations take larger values on July and

August. Conversely, November and December are the months during which TSP and PM2.5 mass concentrations take smaller values.

Figure 1a shows that TSP mass concentrations vary within the 6 – 94 μg/m^3 range and are characterized by a mean value ± 1 SD of 34 ± 17 μg/m^3. The TSP mass concentrations higher than 80μg/m^3 that have been monitored on 25 June and 30 August are due to dust events, in accordance with analytical back trajectories and satellite images (MODIS - http://modis.gsfc.nasa.gov/).

Figure 1b reports the temporal trend of PM2.5 mass concentrations, which, within the sampling period, vary between 4 and 45 μg/m^3, with a mean value of 19 ± 9 μg/m^3. It is important to highlight that the dust events occurred in July and August, have also affected PM2.5 mass concentrations, which reached the highest values: about 40 - 45 μg/m^3.

The mass ratio among the two PM fractions (PM2.5/TSP), shown in fig.2, varies between 0.2 and 0.9 with an average value of 0.6. It is evident that PM2.5 particles represent a substantial fraction of the total suspended particulate matter.

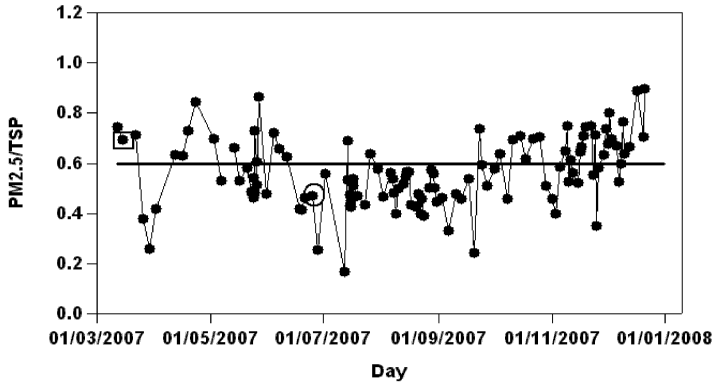

Figure 2- PM2.5/TSP mass ratios as a function of the sampling day. Horizontal line represents the average value. Square and circle markers indicate the East-European pollution event occurred on March 15, 2007, and the Saharan dust event occurred on June 25, 2007, respectively.

Like the temporal series of TSP and PM2.5 mass concentrations, also the PM2.5/TSP mass ratios showed significant daily variations. A slight seasonal dependence is also revealed by fig. 2. In particular, the smaller PM2.5/TSP mass ratios recorded from June to September indicate that mass concentrations due to coarse-mode particles were larger during summer. This result can probably to be ascribed to dust events, which are more frequent in summertime.

3.2 Results on IC and OC/EC analyses of two couples of TSP and PM2.5 samples

The results on the composition of TSP and PM2.5 samples collected during March 15, 2007, and June, 25, 2007 are presented and discussed in this section. TSP and PM2.5 mass concentrations referring to both sampling days are marked in figs. 1a and 1b by a square and a circle, respectively. Figure 3a shows the pathways of the 950, 850, 700,

and 500 hPa analytical back trajectories that reached the monitoring site on 15 March. Pressure levels of each back trajectory as a function of time are shown on fig. 3b. We can observe from fig. 3 that all back trajectories travelled over Eastern Europe before reaching the monitoring site. As a consequence, they can be responsible for the advection over the monitoring site of anthropogenic polluted air masses. Figures 3c and 3d report the 7-days back trajectories and corresponding pressure levels, respectively for the air masses arrived at the sampling site on 25 June, after spending most of travelling time over northwestern Africa.

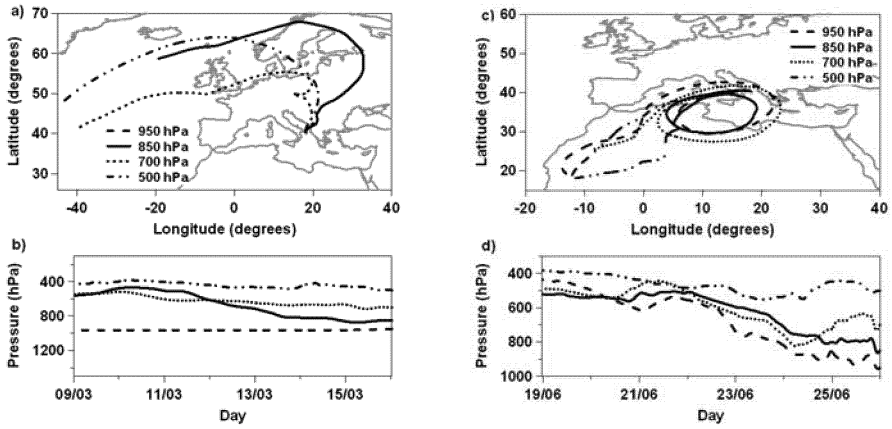

Figure 3 - (a) 7-days analytical back trajectories for the air masses reaching the sampling site on March, 15, 2007. (b) Pressure levels of each back trajectory as a function of time. (c) 7-days analytical back trajectories for the air masses reaching the sampling site on June, 25, 2007. (d) Pressure levels of each back trajectory as a function of time.

TSP and PM2.5 mass concentrations of the main ionic species and organic and elemental carbon referring to the two sampling days are reported in Table 1. Beside the compositional results Table 1 gives also the total sampled mass (S-M), the total analyzed mass (A-M) and the analyzed mass percentage (A-M)/(S-M). It is worth observing from Table 1, that on March 15, 89% and 62% of the total sampled PM2.5 and TSP, respectively has been analyzed. Conversely, on June 25, IC and OC/EC analyses have allowed characterizing only 42% and 36% of the total PM2.5 and TSP sampled mass, respectively. This last result shows that more than 55% of the PM collected during the dust event, was made of particles, such as alumino-silicate particles, that could not be analyzed by the techniques used in this study.

Figures 4 and 5 report mass percentages of investigated species in TSP and PM2.5 samples collected on March 15, and June 25, respectively. We can observe from Table 1 and both figures that compositional properties of the sampled PM are quite dependent on advection patterns. Mass percentages of coarse ionic species (Ca^{2+}, Mg^{2+} and Na^{+}) are higher in dust event samples; whereas mass percentages of fine components (NH_4^{+}, SO_4^{2-}, NO_3^{-} and EC) are larger in anthropogenic polluted samples. Moreover, for each day, it can be seen that Ca^{2+}, Mg^{2+} and Na^{+} mass percentages decrease with particulate

matter cut-off diameter. Conversely, mass percentages of NH_4^+, SO_4^{2-}, NO_3^- and EC reach higher values in the fine fraction.

Table 1- Mass concentrations (μg/m^3) of the analyzed species in TSP and PM2.5 samples collected on 25 June, 2007 and 15 March, 2007. A-M is the total analyzed mass, S-M is the total sampled mass and (A-M)/(S-M) is the ratio between the analyzed and the sampled mass. Uncertainties for ions and for OC and EC are of 5% .

	25/06/2007		15/03/2007	
	TSP	**PM2.5**	**TSP**	**PM2.5**
F^-	0.1	0.005	0.004	0.1
Cl^-	0.4		0.7	
NO_2^-	0.002	0.01	0.03	0.04
NO_3^-	0.4	0.1	1.7	1.0
SO_4^{2-}	6.4	4.7	8.5	8.6
Na^+	1.3	0.4	0.5	0.2
NH_4^+	0.7	1.0	3.9	4.4
K^+	0.5	0.5	0.7	0.7
Mg^{2+}	0.9	0.2	0.2	0.04
Ca^{2+}	6.8	2.2	1.8	0.3
OC	9.8	5.6	10.4	9.6
EC	1.3	0.8	2.5	2.2
A-M	28.7	15.6	30.9	27.3
S-M	79.2	37.3	49.9	30.6
(A-M)/(S-M) %	36	42	62	89

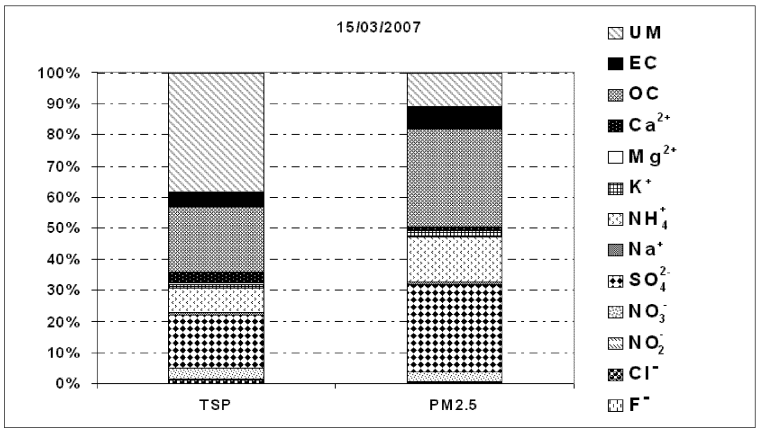

Figure 4 – Mass concentration percentages of all investigated species and undefined mass (UM) in the TSP and PM2.5 sample collected during the pollution event occurred on 15 March 2007.

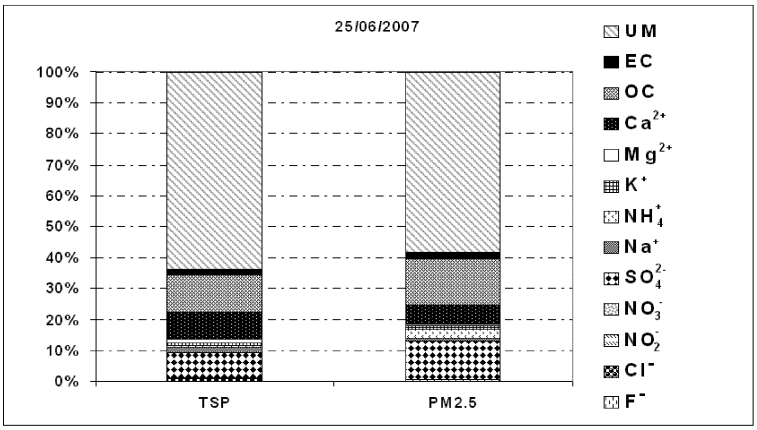

Figure 5 – Mass concentration percentages of all investigated species and undefined mass (UM) in the TSP and PM2.5 sample collected during the dust event occurred on 25 June 2007.

Nitrates are found both in TSP and PM2.5 samples; however mass concentrations reach higher values in TSP samples. This result, also observed in other studies (Henning et al., 2003, Putaud et al., 2004., Marenco et al., 2004), could be ascribed to the adsorption of HNO_3. Chlorine depletion reactions due to HNO_3–sea salt particle reactions (Perrone et al., 2006), are responsible for the lack in Cl^- ions in the PM2.5 samples of both sampling days. In addition, artefacts during sampling leading to ammonium volatilization processes, as a consequence of the interaction of ammonium particulate with alkaline particulate matter, might partially be responsible for the minor presence of ammonium particulate in TSP samples.

4. Conclusions

The current work reports mass concentrations of 24-h TSP and PM2.5 samples simultaneously collected from March to December 2007, at a suburban site of South-East Italy. Daily variations characterized both the TSP and PM2.5 temporal trend, however no marked seasonal dependence was found. Unlike the TSP and PM2.5 evolution with time, the PM2.5/TSP mass ratio was characterized by lower values between June and September. These last results indicate that mass concentrations due to coarse-mode particles dominated in summertime may be as a consequence of a larger contribution of dust events.

Ion Chromatography and Organic/Elemental Carbon analyses were performed to characterize the composition of some selected samples. The study of this paper focuses on IC and OC/EC results referring to two couples of TSP and PM2.5 samples simultaneously collected during different advection patterns: a pollution advection event from East Europe occurred on 15 March, 2007 and a Saharan dust event occurred on 25 June, 2007. Compositional analyses have shown that coarse type species such as Ca^{2+}, Mg^{2+} and Na^+ were larger in dusty samples. However, their mass concentrations decrease with PM cut-off diameter. It is worth noting, that in dusty samples the

analyzed anthropogenic species (SO_4^{2-}, NH_4^+, NO_3^-, NO_2^-, EC, OC) were 24% and 33% of the total TSP and PM2.5 sampled mass, respectively. During the East-Europe advection pattern, 54% and 85% of the total TSP and PM2.5 sampled mass, respectively was made of analyzed anthropogenic species. Finally, it is worth noting that on 15 March, IC and OC/EC analyses have allowed characterizing 89% and 62% of the total PM2.5 and TSP sampled mass, respectively. Conversely, on 25 June, only 42% and 36% of the total PM2.5 and TSP sampled mass, respectively was characterized. During the dust event, more than 55% of the collected PM could not be analyzed by the thechniques used in this study. The significant effect of dust particles on PM2.5 mass concentration and composition has also been observed.

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