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Contributions of natural sources to high PM_{10} and $PM_{2.5}$ events in the eastern Mediterranean

Mustafa Koçak[a], Nikos Mihalopoulos[b], Nilgün Kubilay[a,*]

[a]*Institute of Marine Sciences, Middle East Technical University, P.O. Box 28, 33731, Erdemli-Mersin, Turkey*
[b]*Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 2208, Gr-71003 Voutes, Heraklion, Greece*

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Abstract

In total 562 daily PM_{10} and $PM_{2.5}$ samples were collected from April 2001 to April 2002 at a rural site (Erdemli) located on the coast of the Eastern Mediterranean. The annual mean PM_{10} and $PM_{2.5}$ levels were 36.4 ± 27.8 and $9.7 \pm 5.9\,\mu g\,m^{-3}$, respectively. PM_{10} and $PM_{2.5}$ concentrations indicated orders of magnitude change from day to day ($PM_{10} = 2-326\,\mu g\,m^{-3}$; $PM_{2.5} = 0.5-28\,\mu g\,m^{-3}$). The highest levels of PM_{10} were observed during the transition period (March, April and May) due to mineral dust transported from North Africa and during winter due to sea spray generation. However, $PM_{2.5}$ levels exhibited higher concentrations during summer resulting from an enhanced production of secondary aerosols. The $PM_{2.5}/PM_{10}$ ratio (0.25) and categorization of air mass back trajectories indicated that PM_{10} at the study area is dominated by primary aerosol emissions (mineral dust particles from the Saharan Desert and sea salt particles from the Mediterranean Sea itself). During the whole sampling period 28 and 51 events exceeded the recommended maximum values of 50 and $15\,\mu g\,m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively. Source apportionment analysis indicated that PM_{10} exceedances originated as a consequence of natural events (mineral dust ~40%; sea salt ~50%) whereas $PM_{2.5}$ exceedances were accounted primarily by pollution events (in 90% of the cases).

Keywords: Air quality; PM_{10} and $PM_{2.5}$; Saharan dust; Eastern Mediterranean

1. Introduction

Atmospheric particulate matter (PM) can alter climate, biogeochemical cycles and chemistry of atmosphere and adversely affect public health (IPCC, 2001). Owing to the impacts on human health these aspects have been the subject of considerable research over the last few years. The major way aerosols enter the human body is via the respiratory system (Salma et al., 2002). Health effects of aerosols are determined by their size distribution, bulk chemical, microbiological concentration and composition (Griffin et al., 2001; Hetland et al., 2004). Recent epidemiological studies have shown positive and statistically significant correlations between elevated levels of PM and cardiopulmonary diseases and hence mortality (Salma et al., 2002). Although coarse ($d > 2.5\,\mu m$) PM has been shown to have a strong potential to

*Corresponding author.
E-mail address: kubilay@ims.metu.edu.tr (N. Kubilay).

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induce inflammatory mediators, the effect of PM_{10} may still largely be caused by fine ($d < 2.5\,\mu m$) particles due to their large number or greater surface area (Salma et al., 2002). In addition to particle size, chemical composition of PM is important. For example, mineral dust episodes may cause serious human respiratory health problems as dust particles may adsorb toxic chemical material and consist of minerals such as quartz, feldspar and palygorskite (Ichinose et al., 2005).

Legislation of the PM_{10} and $PM_{2.5}$ concentrations limit has been established by the European Commission for PM monitoring (European Community, EC/30/1999) and by the United States Environmental Protection Agency (EPA/600/P-99/002aF, October 2004), respectively. The daily PM_{10} value has been limited to $50\,\mu g\,m^{-3}$, which may only be exceeded 35 days/year in 2005 (Phase I) and 7 days/year in 2010 (Phase II). For $PM_{2.5}$ the daily and annual standards are proposed to be 65 and $15\,\mu g\,m^{-3}$, respectively. In addition, recently annual $PM_{2.5}$ value has been proposed by European Commission for $PM_{2.5}$ monitoring which may not exceed $25\,\mu g\,m^{-3}$ in 2015 (Council of the European Union, 2757th Council Meeting). Therefore, for PM_{10} and $PM_{2.5}$ values of 50 and $15\,\mu g\,m^{-3}$ will be applied as limit (threshold) levels, respectively, in this study.

Recent studies in Europe have shown that PM_{10} levels increase from natural to kerbside sites. Especially in urban and kerbside stations PM_{10} levels are above the EU annual PM_{10} ($20\,\mu g\,m^{-3}$) standard for 2010 (Van Dingenen et al., 2004; Putaud et al., 2004). A significant number of studies for different types of sites (background, rural, urban, etc.) have taken place around the Western Mediterranean (e.g. Artínano et al., 2001), focusing on the full chemical characterization of the PM (e.g. Querol et al., 2004) and the influence of dust events (e.g. Viana et al., 2002). However, studies for the Eastern Mediterranean are rather limited. To our knowledge the only study reporting the annual variability of PM_{10} and $PM_{2.5}$ levels in conjunction with chemical composition measurements on a long-term basis is that performed at the Negev Desert (Andreae et al., 2002).

The present study aims to determine the factors controlling PM_{10} and $PM_{2.5}$ levels and identify the origin and chemical composition of their exceedances in different environment in the Eastern Mediterranean compared to the Negev Desert, a coastal area during the period of April 2001–April 2002.

2. Material and methods

2.1. Site description and aerosol collection

Gent type PM_{10} stacked filter unit (SFU) sampler was used in order to collect atmospheric particles in two size ranges namely, coarse and fine at a rural site located on the coast of the Eastern Mediterranean, Erdemli (36° 33′ 54″ N and 34° 15′ 18″ E), Turkey (for more details see Kubilay and Saydam, 1995; Koçak et al., 2004a, b). The PM_{10} SFU sampler consists of two 47 mm diameter filter holders, placed in series. Upstream of the first holder is a pre-impaction stage which intercepts particles larger than 10 μm equivalent aerodynamic diameter (EAD). The sampler operates at a flow rate of $16\,L\,min^{-1}$. It collects particulates which have an EAD of less than 10 μm in separate coarse (2.5–10 μm EAD) and fine ($<2.5\,\mu m$ EAD) size fraction on two sequential 47 mm diameter Nuclepore filters. The first filter holder is loaded with an 8 μm pore size (Apiezon coated) Nuclepore polycarbonate filter and the second holder contains a 0.4 μm pore size Nuclepore filter (Hopke et al., 1997). The loading and unloading of the filters were done within a 100 laminar air flow cabinet (clean dust free) in order to minimize any possible contamination.

Sampling started in April 2001 and ended in April 2002. During this period a total of 562 aerosol filter samples were collected with a temporal resolution of 24 h. Sampling coverage during the whole period was found to be more than 70%. However, a two-month period (October–November 2001) was not sampled due to equipment failure.

2.2. Analytical measurements

After collection of aerosol filters $PM_{10-2.5}$ and $PM_{2.5}$ concentrations were determined gravimetrically. Filter samples were retrieved equilibrated and weighed. The difference in weights for each filter sample could be calculated and the mass of appropriate pairs of $PM_{10-2.5}$ and $PM_{2.5}$ samples can then be calculated under well stabilized temperature and relative humidity (20 °C and 50% RH; Hopke et al., 1997). Water soluble ions were measured by ion chromatography (IC) at Environmental Chemical Processes Laboratory (ECPL), University of Crete. For this purpose $10.88\,cm^2$ of the filter was extracted

by sonication for 45 min in 15 mL of ultra pure water and 100 μL chloroform was added as a biocide. The extraction efficiency is better than 98% for all water soluble ions of interest. A Dionex AS4A-SC separation column with an ASRS-I suppressor was used for the analysis of water soluble anions (Cl^-, Br^-, NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$). All the anions except methane sulfonate (MS^-) were determined with isocratic elution at 2.0 mL min^{-1} of $NaHCO_3/Na_2CO_3$ eluent. MS^- was analyzed applying an ASRS-I separation column and NaOH (from 0.1 to 3.5 mM) as eluent in gradient mode. A Dionex CS12-SC separation column with CSRS-I suppressor was used for the analysis of water soluble cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}). All cations were analyzed with isocratic elution at 1.0 mL min^{-1} of MS^- (20 mM; for more details see Bardouki et al., 2003). Concentrations of the elements (Fe, Ti, Ca, Mn, K, Cr, V, Zn, Cl, S) were obtained using 2 cm^2 of the filter sample applying Proton Induced X-ray Emission (PIXE) at ATOMKI (Institute of Nuclear Research of the Hungarian Academy of Sciences, Debrecen, Hungary). During the experiments the aerosol samples were irradiated by a 2 MeV proton beam, which was supplied by the 5 MV Van de Graaff Accelerator of ATOMKI (for more details see Borbely-Kiss et al., 1999). The accuracy of the IC measurements was tested by an inter-comparison using simulated rain water samples prepared by the World Meteorological Organisation (WMO) Precipitation Reference Laboratory (PRL). The accuracy of the PIXE measurements was tested in an inter-comparison using urban dust supplied by the International Atomic Energy Agency (IAEA). The urban dust material was collected from the air conditioning system of the Vienna General Hospital in Vienna, Austria (Bleise and Smopdis, 1999). In general, analytical recoveries yielded good recoveries (>85%) for all measured elements and water soluble ions. Blank contributions to the $PM_{10-2.5}$ sample water extracts accounted to less than 4% for all water soluble ions except K^+ (7.5%) and Br^- (8.5%). Blank contributions to the $PM_{2.5}$ filter samples amounted to less than 5% for all water soluble ions except Na^+ (7.8%), Ca^{2+} (8.6%) and K^+ (12.5%). In addition, blank contributions during PIXE analysis for all elements were less than 5% for both the coarse and fine fractions.

Black carbon (BC) content in 46 fine aerosol filter samples collected during winter and summer was determined by using a Smoke Stain Reflectometer (SSR).

3. Results and discussion

3.1. PM_{10} and $PM_{2.5}$ concentrations

Annual mean concentrations of PM_{10} and $PM_{2.5}$ at Erdemli were 36.4 ± 27.8 and $9.7 \pm 5.9\ \mu g\ m^{-3}$, respectively. PM_{10} and $PM_{2.5}$ concentrations showed considerable daily variability in agreement with the previous works conducted in the Mediterranean (Rodriguez et al., 2002; Shaka and Saliba, 2004; Kouyoumdjian and Saliba, 2005; Gerasopoulos et al., 2006, see Fig. 1a, b). Concentrations indicate order of magnitude change from day to day ($PM_{10} = 2-326\ \mu g\ m^{-3}$; $PM_{2.5} = 0.5-28\ \mu g\ m^{-3}$). In general, PM_{10} and $PM_{2.5}$ show lower concentrations (order of magnitude) during rain events since precipitation removes the particles from the atmosphere efficiently. PM_{10} indicates higher concentrations in spring and winter and were often associated with intense sporadic peaks of mineral dust (Alpert and Ziv, 1989; Kubilay and Saydam, 1995; Moulin et al., 1998; Kubilay et al., 2000; Koçak et al., 2004a) and enhanced sea spray generation, respectively (for more details see Section 3.2). On the other hand, $PM_{2.5}$ demonstrates higher concentrations mainly during summer. Table 1 presents the annual mean concentrations of PM_{10} and $PM_{2.5}$ (expressed as $\mu g\ m^{-3}$) for European and Mediterranean regions. PM_{10} and $PM_{2.5}$ values increase from rural to kerbside sites in Western Mediterranean whilst concentration of PM_{10} in Eastern Mediterranean is related tothe proximity of the site to arid regions (e.g. Saharan Desert and the Middle East).

Fig. 2 shows monthly arithmetic mean concentrations of PM_{10}. The seasonality of PM_{10} has been reported in rural, urban and industrialized sites of the Western Mediterranean (Rodriguez et al., 2002; Querol et al., 2004) and the highest monthly PM levels are recorded in summer. In contrast, PM_{10} did not indicate a clear seasonal variability at Erdemli. However, relative contributions of the fine fraction increased from winter to summer (Fig. 2). For example, in August the relative contribution of fine fraction accounted for 50% of the PM_{10} mass. This might be attributed to the enhancement of secondary aerosol (such as sulfate and organic compounds) generation during summer as observed not only for Erdemli (Kubilay et al., 2003) but also for whole Mediterranean region (Luria et al., 1996; Danalatos and Glavas, 1999; Erduran and Tuncel, 2001).

Fig. 3 illustrates the relationship between $PM_{2.5}$ and PM_{10} for continental Europe (Van Dingenen

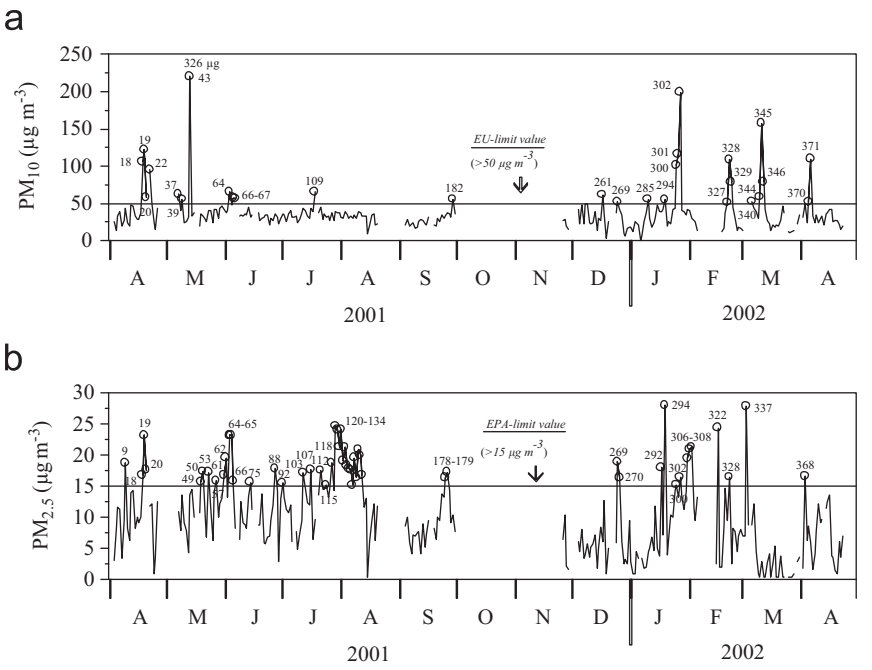

Fig. 1. Daily variability of the PM_{10} (a) and $PM_{2.5}$ (b) concentrations during April 2001 and April 2002, along with identified exceeded values. Numbers indicate Julian days.

Table 1
Annual arithmetic mean PM_{10} and $PM_{2.5}$ concentrations for different types of Mediterranean sites (natural, rural, urban, kerbside and arid)

Region	Sampling site	Category	Period	Mean-PM_{10} ($\mu g\,m^{-3}$)	Mean-$PM_{2.5}$ ($\mu g\,m^{-3}$)
Eastern Mediterranean	Finokalia[a]	Natural	2004–2005	35.5 ± 34.7	18.5 ± 13.3
	Erdemli[b]	Rural	2001–2002	36.4 ± 27.8	9.7 ± 5.9
	Sde Boker[c]	Arid	1995–1997	60.4	15.9
Western Mediterranean	Monagrega[d]	Rural	1999–2000	22	–
	Bemantes[e]	Rural	2001	18.9	13.5
	Tarragona[e]	Urban	2001	37.4	21.8
	Barcelona[f]	Urban	2001	36.8	22.5
	Madrid[e]	Kerbside	1999–2000	47.7	34.1

[a]Mihalopoulos et al. (unpublished data).
[b]This study.
[c]Andreae et al. (2002).
[d]Rodriguez et al. (2002).
[e]Querol et al. (2004).
[f]Viana et al. (2006).

et al., 2004), Western Mediterranean (Querol et al., 2004; Viana et al., 2006) and Eastern Mediterranean (Andreae et al., 2002; Mihalopoulos et al., unpublished data) sites. The $PM_{2.5}/PM_{10}$ ratios indicate great variability amongst the sites. The ratios range from ~0.25 to ~0.90. This may be attributed to the variability of the aerosol chemical composition which is affected by various sources (natural and anthropogenic) at each site. Therefore, it is not possible to suggest a common ratio for $PM_{2.5}/PM_{10}$ observed at the Mediterranean sampling sites. With the exception of the Erdemli and Sde Boker sites (Eastern Mediterranean), all stations show that more than half of their mass concentration originates from the $PM_{2.5}$ fraction. Hence, these stations are predominantly affected by secondary aerosol

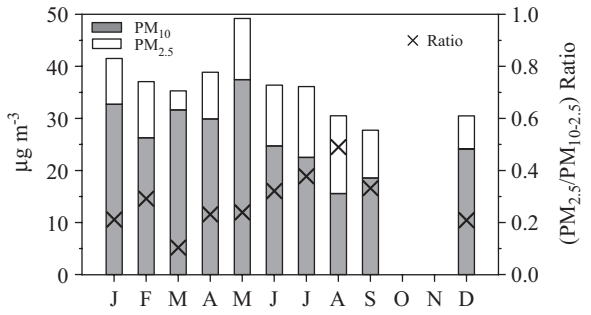

Fig. 2. Monthly mean concentrations of $PM_{10-2.5}$, $PM_{2.5}$ and $PM_{2.5}/PM_{10}$ ratio during the sampling period.

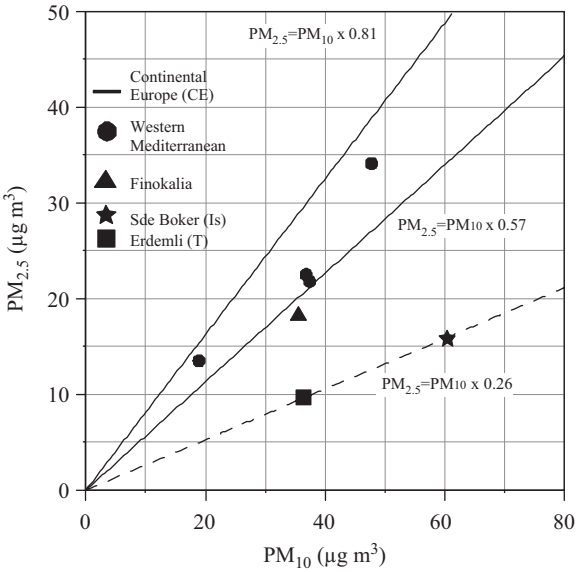

Fig. 3. Relationship between PM_{10} and $PM_{2.5}$ for Continental Europe (Putaud et al., 2004), Western (Rodriguez et al., 2002; Querol et al., 2004; Viana et al., 2006) and Eastern Mediterranean sites (Andreae et al., 2002 (Sde Boker); Mihalopoulos et al., unpublished data (Finokalia); this study (Erdemli)).

sources. Observed results for Erdemli are consistent with the findings made by Andreae et al. (2002) for another Eastern Mediterranean site (Sde Boker), i.e. that about 75% of PM_{10} mass originated from coarse particles. However, closer consideration of the $PM_{2.5}/PM_{10}$ ratios shows that this ratio at European and Western Mediterranean sites ranged from 0.6 to 0.80. On the contrary, a minimum of the $PM_{2.5}/PM_{10}$ ratio (0.26) is found for Erdemli and Sde Boker whilst this ratio for Finokalia is similar to the lower end ratios observed for continental Europe (Mihalopoulos et al., unpublished results).

3.2. *Origin of the exceeded* PM_{10} *and* $PM_{2.5}$ *levels in the area*

A number of studies have focused on the origin of exceeded PM_{10} levels in the Western Mediterranean region (Artínano et al., 2001; Rodriguez et al., 2002; Viana et al., 2002). These studies have shown that exceedances of the PM_{10} maximum value may not always be caused by anthropogenic sources. This can be illustrated by using Spain as an example (various rural, urban and industrial sites, including the Canary Islands), where the studies indicated differences in PM_{10} chemical compositions (Rodriguez et al., 2002; Viana et al., 2002; Alastuey et al., 2005). These authors have shown that PM_{10} concentrations are highly influenced by the occurrence of African dust events. For example, more than half of the exceedances of PM_{10} at rural sites were attributed to the dust events whereas approximately only 20% of the exceedances of PM_{10} at urban and industrialized sites originated from African dust transport. At Finokalia, during the dust events mineral dust contributed about 60–70% to the PM_{10} mass (Gerasopoulos et al., 2006). Therefore, at rural sites dust contributions might be considered to be an important contributor to the number of exceeded values of the EU daily limit value.

Air mass back trajectories are useful to determine possible sources of aerosols and have been extensively used in the literature (Kubilay and Saydam, 1995; Kubilay et al., 2000, 2003; Lelieveld et al., 2002). For the current study all daily air mass back trajectories for April 2001–April 2002 at Erdemli were categorized into seven different sectors at the pressure levels of 850 hPa. The classified sectors were as follows: (i) long fetch air masses from Europe (EL), (ii) short fetch air masses from Europe (ES), (iii) short fetch air masses from northwest Turkey (NWT), (iv) long fetch air masses from north Turkey (NT), (v) air masses from the Middle East and Arabian Peninsula (SE), (vi) air masses from Saharan Desert (SAH) and, (vii) maritime air masses from the Mediterranean Sea (MS).

The Kruskal–Wallis (K–W) test was applied to test for the presence of significant differences in PM_{10} and $PM_{2.5}$ concentrations categorized by sectors for dataset. Mean concentrations of PM_{10} and $PM_{2.5}$ in sampling site according to classified air masses trajectories are shown in Fig. 4. Although PM_{10} monthly mean concentrations did not indicate clear seasonality, application of the K–W test

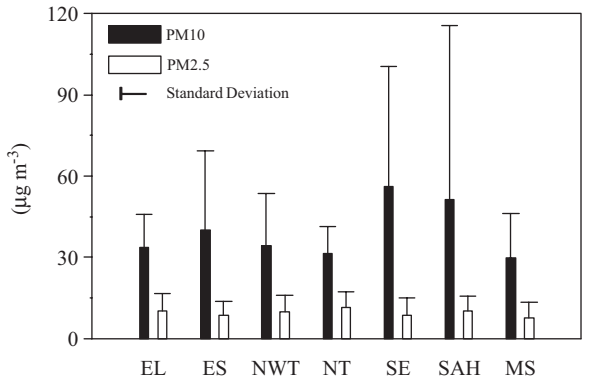

Fig. 4. Mean concentrations of PM_{10} and $PM_{2.5}$ as a function of the categorized three-day air mass back trajectory arriving at Erdemli. Dark and light grey colors show PM_{10} and $PM_{2.5}$ concentrations, respectively.

indicates that there was a significant difference in PM_{10} concentrations ($p<0.01$) whereas there was no statistically significant difference in the $PM_{2.5}$ concentrations. PM_{10} concentrations in SE and SAH were found to be statistically higher than those calculated for remaining sectors. These two categories are heavily affected by sea spray and crustal aerosol which are the main contributors to the Eastern Mediterranean aerosol. Therefore sea spray and crustal derived aerosols are expected to influence the PM_{10} levels in the Eastern Mediterranean in agreement with the conclusions made by Gerasopoulos et al. (2006).

3.3. *Chemical composition of the exceeded* PM_{10} *and* $PM_{2.5}$ *levels*

During the sampling period 28 events exceeded the legislative PM_{10} maximum value established by the European Commission for PM monitoring (Fig. 1a). For $PM_{2.5}$, 51 events were found to exceed the level of $15\,\mu g\,m^{-3}$ during the sampling period (Fig. 1b).

Air mass back trajectories and chemical composition were used to identify and categorize the origin (natural or anthropogenic) of the exceedances of the forthcoming EU daily limit values. Chemical composition was defined by four main classes: dust, sea salt, ionic mass and "unidentified", the latter accounting mainly for BC and OC.

Dust levels have been calculated using Fe or Ti as indicator of crustal material. The total amount of mineral dust was estimated using Fe concentrations assuming a relative ratio to upper crust of 3.089% (Wedepohl, 1995). The sea salt contribution was calculated from Na^+ concentrations assuming that Na^+ has pure marine origin. Finally, ionic mass is the sum of $nssSO_4^{2-}$; NO_3^-, $C_2O_4^{2-}$, NH_4^+, $nssK^+$ and $nssMg^{2+}$. Non-sea salt levels of the species were calculated using Na^+ as tracer and a standard seawater composition (Turekian, 1976).

3.3.1. PM_{10} *exceedances*

Fig. 5a shows variation in concentrations of PM_{10}, dust, sea salt and ionic mass for the 28 events exceeding $50\,\mu g\,m^{-3}$. For these exceedances, 25 events were characterized as natural (exceedance due to dust and sea salt) whereas 3 events were characterized as mixed since exceeded events were not dominated by one of the sources (natural or non-natural). Below we will discuss in detail one event from each category (dust, sea salt and mixed).

(a) *Dust events* ($n=11$): 34 dust days were identified by an abrupt increase in the concentrations of Fe and Ti, Mn, Ca during the study period. These dust days were characterized by 11 specific mineral dust events. Dust concentrations during these events ranged from 17 to $222\,\mu g\,m^{-3}$ in the PM_{10}. The lowest dust concentration accounts for 35% of the EU PM_{10} daily limit value, whereas the highest dust concentration is at least four times higher than that of the EU PM_{10} daily limit value. Such dust events have frequently been observed in the Mediterranean (Kubilay et al., 2000, 2003, 2005; Rodriguez et al., 2002; Koçak et al., 2004a). For example, dust concentrations during the intense dust events in eastern Spain fall in the range of $20-25\,\mu g\,m^{-3}$ (Rodriguez et al., 2002) whereas in the Canary Islands it exceeds $100\,\mu g\,m^{-3}$ (Viana et al., 2002).

As highlighted, 11 of the events of the exceeded PM_{10} values were caused by dust contributions during air masses originating from the Saharan Desert and accounted for 40% of the exceedances of the EU limit (Fig. 5a). A dust origin of these events was also confirmed by a strong correlation coefficient between PM_{10} and Fe ($p>0.01$; $r=0.95$). The highest PM_{10} concentration was observed on the 13th of May 2001 (case 7; Julian Day 43) with a value more than $320\,\mu g\,m^{-3}$. During this event mineral dust concentrations reached $222\,\mu g\,m^{-3}$ due to Saharan air mass transport (see Fig. 6a). On May 13th the back trajectories at all levels (except 1000 hPa) show air mass flow reaching Erdemli from the Northeastern Saharan. The TOMS image indicates a strong mineral desert dust episode

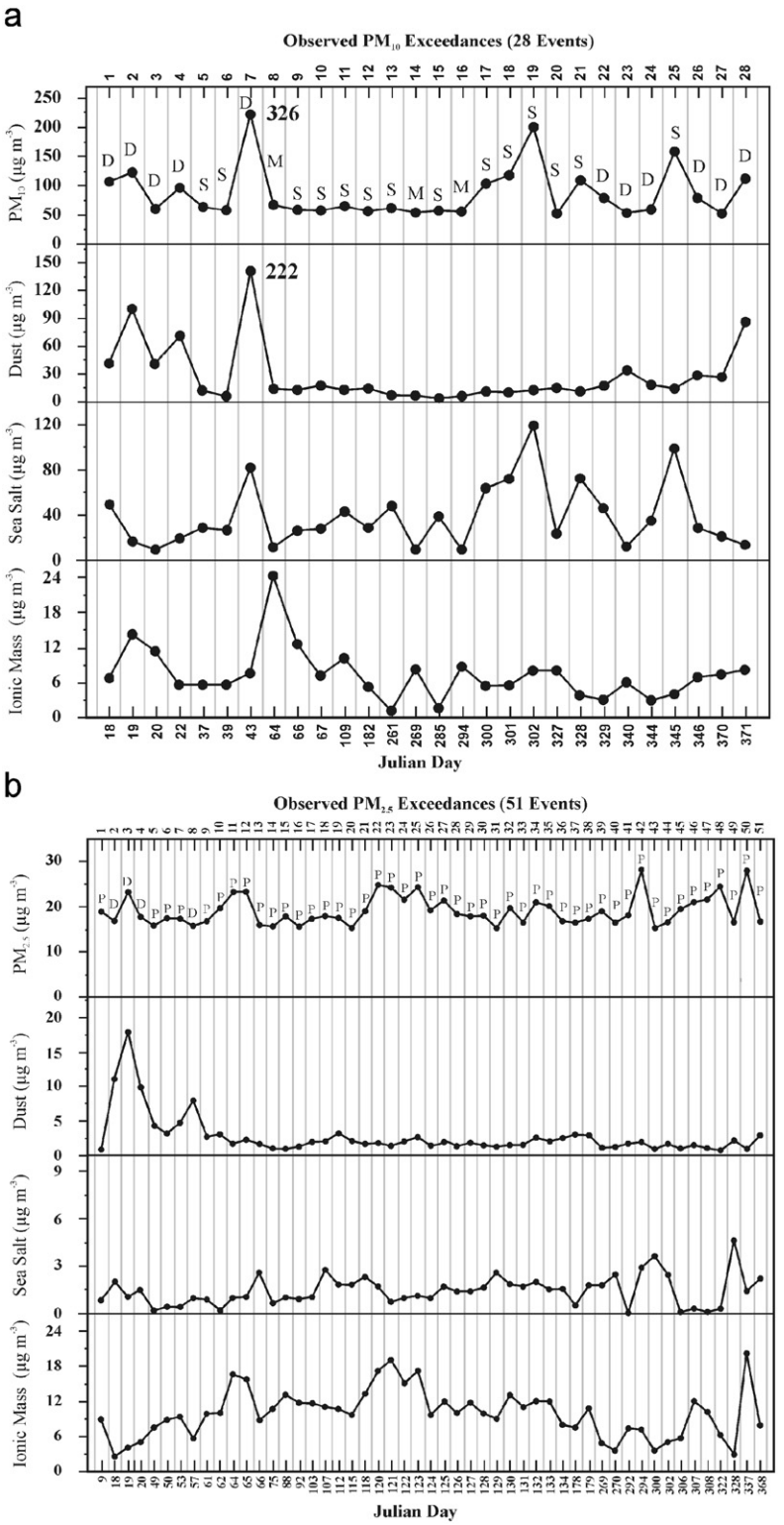

Fig. 5. (a) Variability in the concentrations of PM_{10}, dust, sea salt, and ionic mass for exceedances of the forthcoming EU limit values ($50\,\mu g\,m^{-3}$). D, S and M denote dust, sea salt and mix events. Numbers show Julian days. (b) Variability in the concentrations of $PM_{2.5}$, dust, sea salt and ionic mass for exceedances $15\,\mu g\,m^{-3}$. D and PS denote dust and pollution events. Numbers show Julian days.

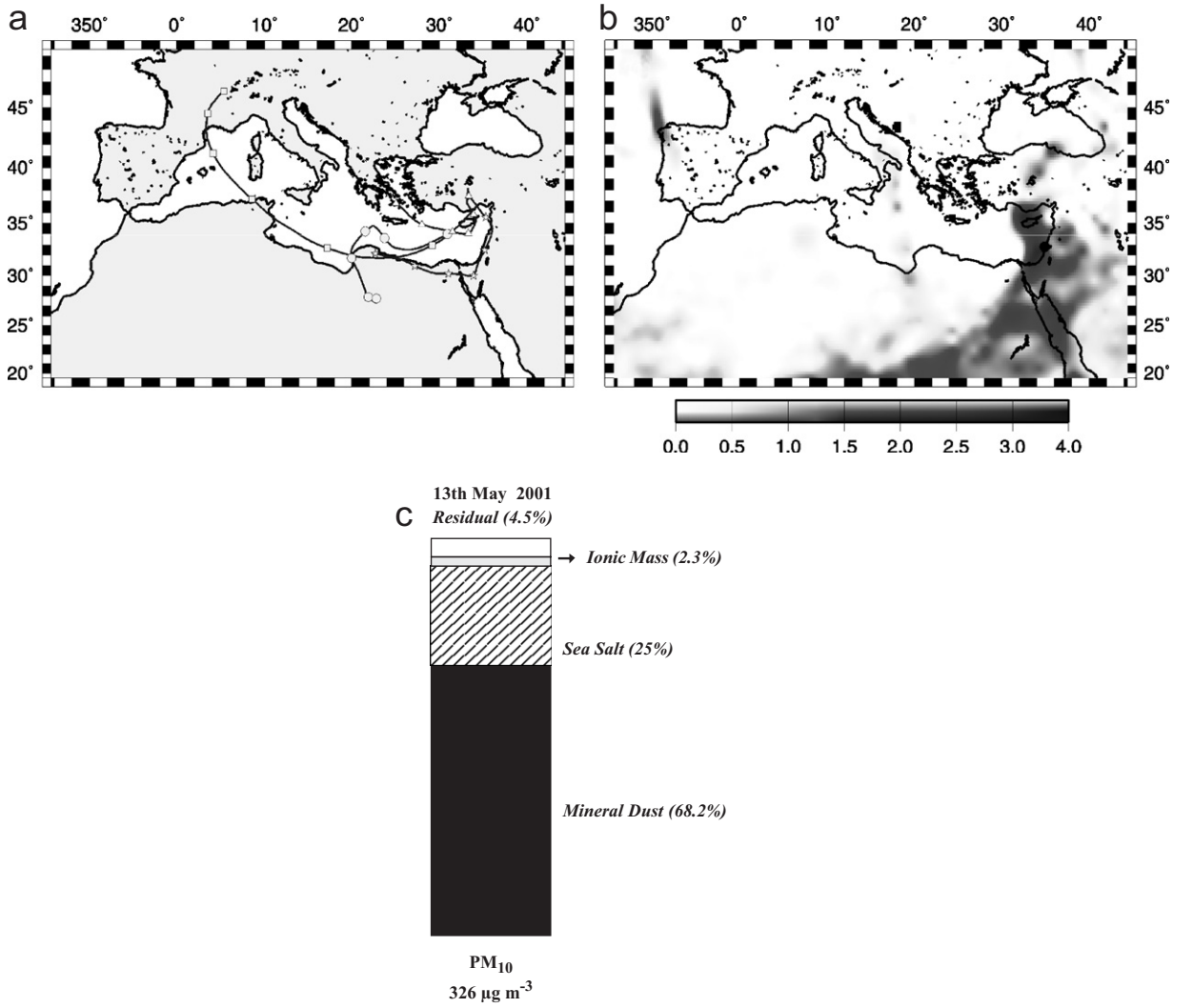

Fig. 6. Saharan dust transport observed on 13th of May 2001: (a) The three-day back trajectories showing the transport of air masses to the sampling site. The back trajectory pathway every 12 h is indicated by triangles for 1000 hPa, stars for 850 hPa, circles for 700 hPa and squares for 500 hPa. (b) TOMS Absorbing Aerosol Index. (c) Source apportionment analysis for PM_{10} during Saharan dust events for the 13th of May 2001.

particularly over the northern Saharan region and the Levantine basin (see Fig. 6b). The dust enriched air mass contributed largely to the increase in the PM_{10} level at Erdemli. The Saharan origin was also confirmed by the chemical composition of PM_{10} (see Fig. 6c). The source apportionment indicated that 68% of PM_{10} originated from mineral dust. Sea salt accounted for 25% of the PM_{10} levels whereas ionic mass contributed only 2%. Therefore, the dust enriched air mass contributed largely to the increase in the PM_{10} level at Erdemli.

Similar chemical compositions have been observed during Saharan dust events in the Mediterranean. Dust contribution accounted for 60–70% at Finokalia (Gerasopoulos et al., 2006), 52% of the PM_{10} mass at Barcelona (Artínano et al., 2001), for 75% of TSP mass at Izana and for 47% at Santa Cruz (Canary Islands, Alastuey et al., 2005).

(b) *Sea salt events* ($n = 14$): During the sampling period 50% (14 events) of the exceeded PM_{10} values were attributed to sea salt (see Fig. 5a). Sea salt concentrations during these events ranged from 23 to 118 $\mu g\,m^{-3}$ in PM_{10} mass. The lowest sea salt concentration (23 $\mu g\,m^{-3}$) accounted for 46% of the EU PM_{10} daily limit value (50 $\mu g\,m^{-3}$). The sea salt origin of these events was also supported by a

strong correlation between PM_{10} and Na^+ ($p > 0.01$; $r = 0.96$). For example, on the 17th of December 2001 (case 13; Julian Day 261) PM_{10} was observed to be around $60\,\mu g\,m^{-3}$ due to maritime air mass transport at 1000 and 850 hPa (Fig. 7a). During this event sea salt concentrations were found to be high ($47\,\mu g\,m^{-3}$) and the sea salt origin was also confirmed by the source apportionment analysis (see Fig. 7b). The source apportionment showed that sea salt accounted for 77.1% of the PM_{10} level while dust contribution explained for 10.4% of the PM_{10}. In addition, $nssSO_4^{2-}$ and NO_3^- together explained a small fraction (1.7%) of the PM_{10}.

(c) *Mixed events* ($n = 3$): Three of the exceeded values were not dominated by any one particular aerosol source. Therefore, it can be suggested that the mixing of aerosols originating from different sources (soil, sea spray, combustion and biogenic) resulted in PM_{10} mass concentrations exceeding the forthcoming EU daily limit values. For instance, on the 3rd of June 2001 (case 8; Julian Day 64) high concentration of $nssSO_4^{2-}$ ($15.2\,\mu g\,m^{-3}$) was detected. Nitrate concentrations were found to be around $5.5\,\mu g\,m^{-3}$. Source apportionment analysis denoted that sea salt and dust contributions together accounted for 36% of PM_{10} (see Fig. 8). Ionic mass explained 32% of PM_{10} mass. The chemical composition indicated that the PM_{10} mass was not dominated by one of the sources. However, the addition of contributions from different sources resulted in exceeded PM_{10} mass.

3.3.2. $PM_{2.5}$ *exceedances*

During the sampling period 10 common events were found for PM_{10} (see Fig. 5a) and $PM_{2.5}$ (see Fig. 5b) exceedances and only 4 events (8 %) of the

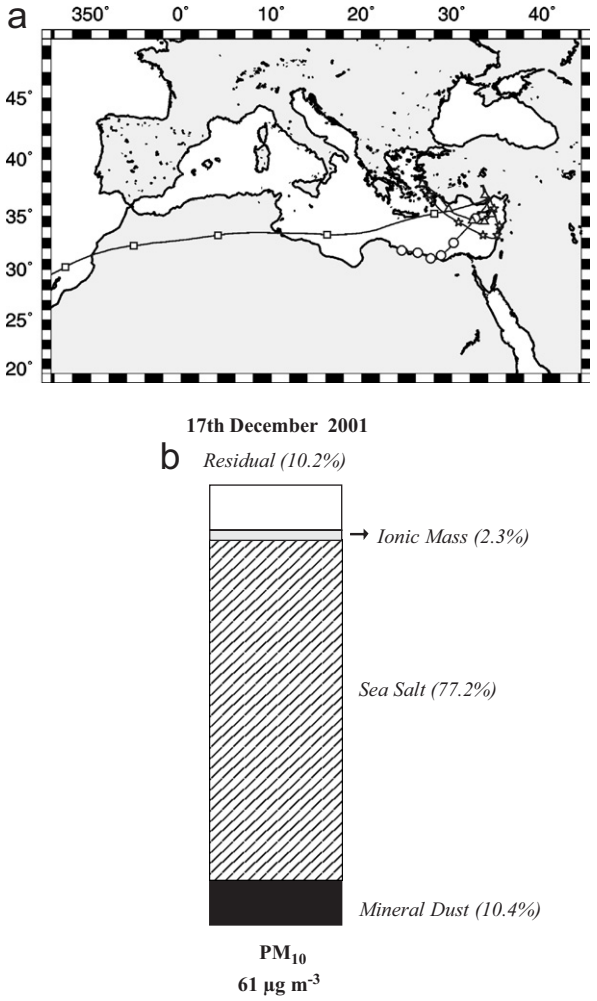

Fig. 7. (a) The three-day back trajectories showing the transport of air masses to the sampling site on 17th of December 2001. The back trajectory pathway every 12 h is indicated by triangles for 1000 hPa, stars for 850 hPa, circles for 700 hPa and squares for 500 hPa. (b) Source apportionment analysis for PM_{10} during the sea salt event on the 17th of December 2001.

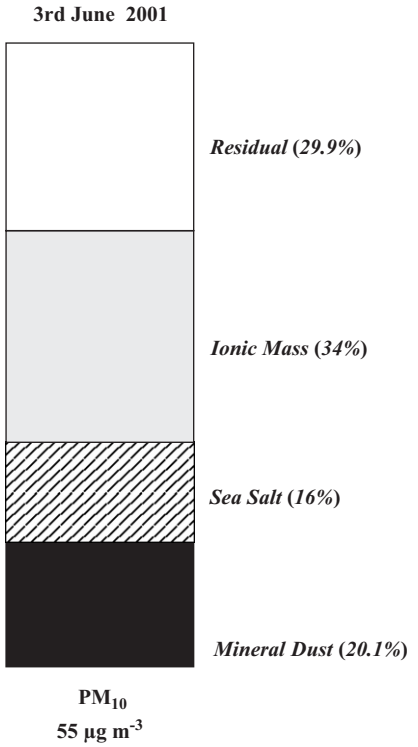

Fig. 8. Source apportionment analysis for PM_{10} during mix event on the 3rd of June 2001.

exceeded $PM_{2.5}$ values were characterized as natural in origin whereas more than 90% of the exceeded $PM_{2.5}$ values were attributed to pollution (due to ionic mass and carbonaceous mass).

(a) *Dust events* ($n = 4$): During these events dust concentrations ranged from 8 to 18 $\mu g\,m^{-3}$. The lowest dust level accounts for ~50% whereas the highest dust event is 1.2 times higher (see Fig. 5b) than that of the $PM_{2.5}$ threshold.

(b) *Pollution events* ($n = 47$): During the sampling period more than 90% ($n = 47$; see Fig. 5b) of the exceeded $PM_{2.5}$ values were categorized as pollution events. Among the 47 cases only two events (Julian Day 294 and 337, respectively) exceeded the value of 25 $\mu g\,m^{-3}$ established by the European Commission for $PM_{2.5}$ monitoring. Figs. 9a and b present the source apportionment for these two cases where in addition to dust, sea salt and ionic mass, BC has been also reported. Source apportionment for January 19 (case 42; Julian Day 294; see Figs. 5b and 9a) showed that BC was accounted for about 14% of the $PM_{2.5}$ whereas ionic mass explained 26% of the exceeded value. In addition mineral dust and sea salt together represented about 20% of the $PM_{2.5}$ level. On March 3 (case 50; Julian Day 337; see Figs. 5b and 9b), the source apportionment indicated that about 70% of the $PM_{2.5}$ originated from ionic mass. Mineral dust and sea salt together accounted for 8% whereas BC represented 3.1% of the $PM_{2.5}$. Residual fractions for these events might be attributed to particulate organic matter which is not measured during this study.

3.3.3. *Seasonal variability of the origin of* PM_{10} *and* $PM_{2.5}$ *exceedances*

The monthly number of exceedances of PM_{10} and $PM_{2.5}$ along with origin is given in Fig. 10a and b, respectively.

PM_{10}: During the winter, 10 events (36% of the annual exceedances) were observed and only one event induced by Saharan dust transport while 7 events (70% of the winter cases) were caused by sea salt. Two events were induced by the addition of contributions from different sources. About half (13 events) of the exceedances were observed in the transition period (March, April and May). During this period Saharan dust events dominated the number of the exceedances of the daily PM_{10} EU limit and accounted for 77% of the events. Sea salt accounted for only 23% of the exceedances in transition period. Five events (18% of the annual exceedances) were identified in summer and were dominated by sea salt.

$PM_{2.5}$: In winter 11 (21.5%) and summer 29 (57%) events were detected. All exceeded $PM_{2.5}$ values were induced by pollution events. In addition, 11 (21.5%) events of the exceedances were observed during transition period and 4 events

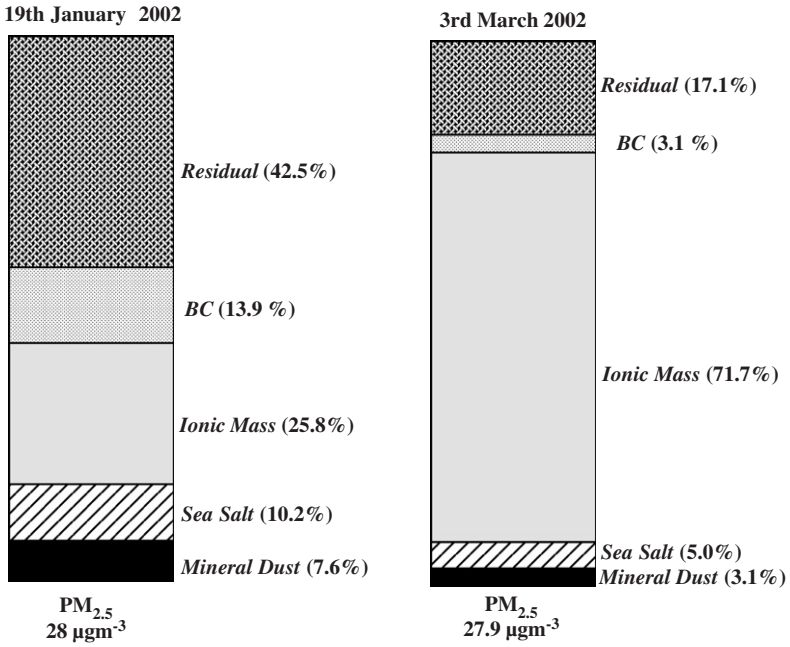

Fig. 9. Source apportionment analysis for $PM_{2.5}$ during pollution events on 19th January 2002 (a) and 3rd March 2002.

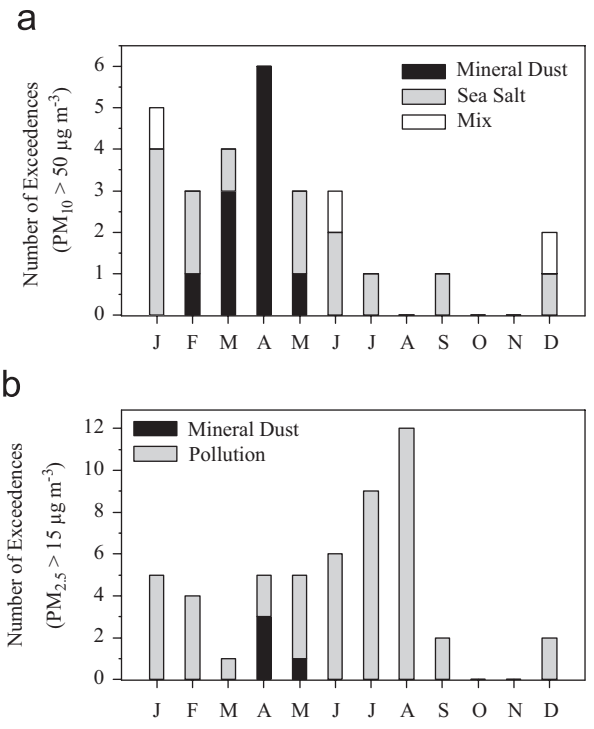

Fig. 10. Monthly number of exceedances of the daily PM_{10} (a) and $PM_{2.5}$ (b).

originated from mineral dust whereas 7 of $PM_{2.5}$ events were caused by pollution.

4. Conclusions

PM_{10} and $PM_{2.5}$ concentrations, factors controlling their levels and the origin and chemical composition of their exceedances have been identified at a rural site located on the coast of the Eastern Mediterranean. From these findings the following conclusions may be made:

- Annual mean concentrations of PM_{10} and $PM_{2.5}$ at Erdemli were 36.4 ± 27.8 and $9.7 \pm 5.9\ \mu g\ m^{-3}$, respectively, while concentrations indicated orders of magnitude change from day to day ($PM_{10} = 2-326\ \mu g\ m^{-3}$; $PM_{2.5} = 0.5-28\ \mu g\ m^{-3}$). PM_{10} exhibited higher concentrations particularly during transition period due to mineral dust transported from North Africa and during winter owing to sea spray generation. $PM_{2.5}$ shows higher concentration mainly during summer as a result of an enhanced production of secondary aerosols.
- In the Western Mediterranean there is a general trend that PM_{10} and $PM_{2.5}$ levels increase from rural to kerbside sites. In contrast PM_{10} values in the Eastern Mediterranean are related to the proximity of the site to arid regions (e.g. Saharan Desert and the Middle East).
- The $PM_{2.5}/PM_{10}$ ratio (~0.25) over the Levantine Basin is about two-to-four times lower than those of the Western Mediterranean. This would indicate that the Eastern Mediterranean is dominated by primary aerosol emissions whilst the Western Mediterranean is dominated by secondary aerosol emissions.
- During the whole sampling period 28 and 51 events exceeded the limit values of 50 and $15\ \mu g\ m^{-3}$ for PM_{10} and $PM_{2.5}$, respectively. Source apportionment analysis indicated that PM_{10} exceedances originated as a consequence of mainly mineral dust (~40%) and sea salt (~50%) events, whilst $PM_{2.5}$ exceedances resulted from pollution events (~90%) (ionic mass and carbonaceous aerosols). For dust induced PM_{10} exceedances dust concentrations range from 17 to $222\ \mu g\ m^{-3}$ and the lowest dust concentration accounted for 35% of the EU PM_{10} daily limit value. Only 8% of the exceeded $PM_{2.5}$ events were characterized as natural (mineral dust) in origin.

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