ELSEVIER

Atmospheric Environment 38 (2004) 2133–2144

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Spatio-temporal aerosol trace metal concentrations and sources in the Levantine Basin of the Eastern Mediterranean

M. Koçak[a], M. Nimmo[b,*], N. Kubilay[a], B. Herut[c]

[a] *Institute of Marine Sciences, Middle East Technical University, Erdemli, Mersin, Turkey*
[b] *Plymouth Environmental Research Centre, School of Environmental Sciences, University of Plymouth, UK*
[c] *Israel Oceanographic and Limnological Research, National Institute of Oceanography, Haifa, Israel*

Received 24 June 2003; accepted 19 January 2004

Abstract

The current study considers the spatial and temporal variability in aerosol trace metal concentrations (Al, Fe, Mn, Cr, Cu, Pb, Cd, Zn) in the Levantine Basin of the Eastern Mediterranean, utilising an extensive sample library ($n = 621$) collected between 1999 and 2001, at two coastal sites located at the northern, Erdemli (Turkey) and southeastern, Tel Shikmona (TS, Israel), region of the Basin. A critical evaluation of the datasets from the two locations was presented. Enhanced concentrations of Al ($1.7\times$), Fe ($1.8\times$), Mn ($2.1\times$) were detected at the more southerly sampling station, during common dust events, owing to the greater proximity of desert dust sources (NE Africa and Saudi Peninsula); leading to a gradual decline in crustal inputs northwards across the basin. An insignificant Pb gradient was noticed across the Levantine Basin, which has exhibited a decadal decrease (40%). Cr was enriched in the north by a factor of three accounted by local sources. Cu was also enriched, to a lower extent, by about a factor of two. Seasonal variations of the crustal elements (Al, Fe, Mn) at Erdemli were detected (transitional > summer > winter) owing to both, a greater frequency and intensity of dust events during the transitional period and a greater washout effect during winter. It is likely that similar variations occur at TS as both sites experienced similar dust and rainfall events. It was observed at Erdemli that all elements (except Pb and Cd) exhibit their lowest concentrations in the winter period due to a greater washout effect. The lack of seasonal difference between winter and summer for Pb and Cd may have been due to the relatively high emission intensities of regional sources rapidly regenerating aerosol concentrations and their association with fine particles which are less efficiently scavenged during rain events. During the summer, Zn derived from local transportation and agricultural activities, was more pronounced, leading to an enhancement of around 10% in its concentration.

Keywords: Eastern Mediterranean; Levantine Basin; Marine aerosol; Trace metals

1. Introduction

Owing to the important influence of atmospheric derived trace metals on marine biogeochemical processes, numerous research studies have been carried out over the last two decades to better understand and quantify atmospheric inputs of trace metals to the marine environment (Jickells, 1995, and references therein). These studies have considered a whole range of marine systems extending from European coastal zones such as the Irish Sea, the North Sea, the Western Mediterranean and the Black Sea (Chester et al., 1993, and references therein; Guieu et al., 1997) to open ocean environments such as the Northern Pacific (Duce et al., 1983). Studies have used either land-based stations (covering annual sampling periods) (Bergametti et al., 1989; Kubilay and Saydam, 1995;

*Corresponding author.
E-mail addresses: kubilay@ims.metu.edu.tr (M. Koçak), m.nimmo@plymouth.ac.uk (M. Nimmo), barak@ocean.org.il (B. Herut).

1352-2310/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.atmosenv.2004.01.020

Güllü et al., 1998; Remoudaki et al., 1991a,b) or transient sampling studies on research cruises or ships of opportunity (e.g. Dulac et al., 1987; Kubilay et al., 1995; Guieu et al., 2002).

The atmospheric concentrations of trace elements in the Eastern Mediterranean aerosol have been defined in previous studies along with calculations of their subsequent inputs (Kubilay and Saydam, 1995; Güllü et al., 1998; Kubilay et al., 2000; Herut et al., 2001; Herut, 2001). These studies have clearly shown that the Eastern Mediterranean marine aerosol is strongly impacted by sporadic intense Saharan desert pulses occurring primarily during transition periods in March, April, May and October. During these periods the concentrations of crustally derived trace metals such as Al, Fe and Mn may reach concentrations in excess of the background concentrations by up to one or two orders of magnitude. Remoudaki et al. (1991b) have shown that sporadic but intense Saharan dust transport events are responsible for the highest atmospheric concentrations and variability of Mn at a remote site in the western Mediterranean. The unique contribution of the current study is to define the spatial and temporal variability of the aerosol trace metal composition influencing the Levantine Basin of the Eastern Mediterranean, using contemporaneously collected aerosol samples (over a 3-year period) across the Basin. One site was located on the NE edge of the Basin (Erdemli, SE Turkey) whilst the other was located on the SE edge of the Basin (Tel Shikmona (TS), Israel). This approach is used to identify the contrasting impacts of (i) aerosol sources and (ii) meteorological processes. From such knowledge and understanding a more refined calculation of atmospheric inputs of trace metals to the basin may be evaluated.

2. Methodology

Bulk aerosol filter samples were collected from two different rural sites located on the coastline of the Eastern Mediterranean, (i) Erdemli (36°33′54″N and 34°15′18″E), Turkey, (ii) TS (32°49′34″N and 34°57′24″E), Israel. For more details on sampling locations and collection see Kubilay and Saydam (1995) and Herut et al. (2001). The sampling campaigns commenced during January 1999 and finished in December 2001. Over the sampling period a total of 556 and 75 aerosol samples were collected at Erdemli and TS, respectively. Temporal resolution of the sampling at Erdemli station was daily (except from July to December, 2000, owing to equipment failure). For some weekends and holidays multi-day samples were taken. At TS the sampling was carried out every weekend, covering typically a 3-day per week period. The percentage of sampling coverage per month at each site over the whole sampling period is highlighted in Fig. 1. The representative nature of the sampling coverage is discussed in the results and discussion section. Aerosol samples collected at both Erdemli and TS underwent a total acid digestion, for further details please see Kubilay and Saydam (1995) and Herut et al. (2001).

After total dissolution, digest solutions samples were analysed for trace elements by one of Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) or Flame Atomic Absorption Spectroscopy (FAAS). The quality of the trace metals measurements, carried out at both laboratories, was evaluated on the basis of the analyses of National Research Council Certified Reference Material (BCSS-1). Analytical recoveries were

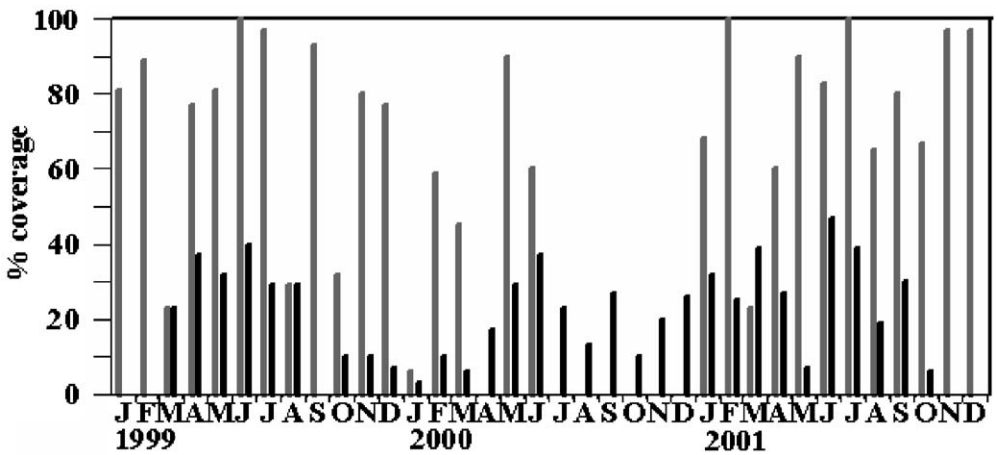

Fig. 1. Percent coverage of the months when aerosol samples were collected at Erdemli (gray bars) and TS (black bars) throughout the sampling period.

good, being >95% for Al, Fe, Mn, Pb, whereas for Zn, Cu, Cr the recoveries were slightly lower, being >85%. To further verify the comparability of the measurements made by the different laboratories, an inter-laboratory comparison was carried out, whereby 13 aerosol samples from the IOLR library, covering the full range of aerosol trace metal concentrations encountered, underwent separate total acid digestion and then the digest solutions were each analysed by the two different research groups. For all the elements analysed by both groups, after applying a Wilcoxon test to the sample populations, there was no statistically significant difference between the two laboratories (at the 95% confidence level). Operational blank contributions to sample digests amounted to <5% for all trace elements except for Zn (9%); Cr (9%) and Cu (11%). The analytical precision of repeat measurements ($\times 3$) was <2% for Al, Fe, Mn, Pb and < 5% for Zn, Cd, and Cu, with analytical detection limits being <5% of the average aerosol digest solution concentration (except for Cu and Cd which were approximately 13%).

Air mass back trajectory analysis was applied to identify sources of the Eastern Mediterranean marine aerosol. The operational trajectory model developed by the European Centre for Medium-Range Weather forecasts (ECMWF) in Reading, UK, was applied to three-dimensional wind fields acquired from the archives of ECMWF. The aerosol index (AI), the distribution of UV absorbing aerosol defined as the difference between the 331 and 360 nm radiances from the Earth Probe/Total Ozone Mapping Spectrometer (EP/TOMS) (Herman et al., 1997; Torres et al., 2002), was also utilized to judge mineral aerosol transport to the stations.

3. Results and discussion

3.1. Air flow climatology at the sampling sites

Climatically, the Mediterranean region is characterized by generally warm winter temperatures, (November through February) dominated by rainfall and dry summers (June through September). The transitional seasons, spring and autumn are of very different lengths. The relatively long spring season (March through May) is noted for periods of unsettled winter-type weather associated with an increased occurrence of North African cyclones; the rest of this period is very similar to that in the summer. Autumn usually lasts only 1 month (October) and is characterized by an abrupt change from summer to the unsettled weather of winter (Brody and Nestor, 1980; Milliman et al., 1992).

Three day back trajectories were calculated daily at 12 00 UT for Erdemli and TS for 1000, 850, 700 and 500 hPa and classified into airflow sectors of origin according to the criteria applied by Dayan (1986) for Israel. Major airflow sectors are as follows (see Fig. 2):

(1) northwest sector including western Europe; (2) north-northeast sector including eastern Europe and Former Soviet Union States; (3) southeast sector including the Arabian peninsula; (4a) southwest sector including the west of North Africa; (4b) southern sector including the east of North Africa. Trajectories were assigned to a particular sector if they resided over it more that 50% of their travel time to the site. Trajectories were unclassified when they did not meet this criteria. The percent contribution of each sector to the air masses arriving at TS and Erdemli is given in Fig. 3. The contribution of each sector at TS for trajectories arriving at 850 hPa is compared with the air mass sector frequency averages over Israel (for a 5-year period) carried out by Dayan (1986). It is clear from this comparison that the air masses sampled and their associated relative proportions at TS for the current study are generally representative of the air masses influencing this area (within $\pm$ 5% for each defined air mass sector, except for sector 3). At Erdemli this classification was performed for the trajectories arriving at 850 hPa as well as 500 hPa. This comparison between different pressures re-emphasizes findings from previous studies that during dust events in the Mediterranean region, African air is generally found at upper levels over air from other source regions in the boundary layer

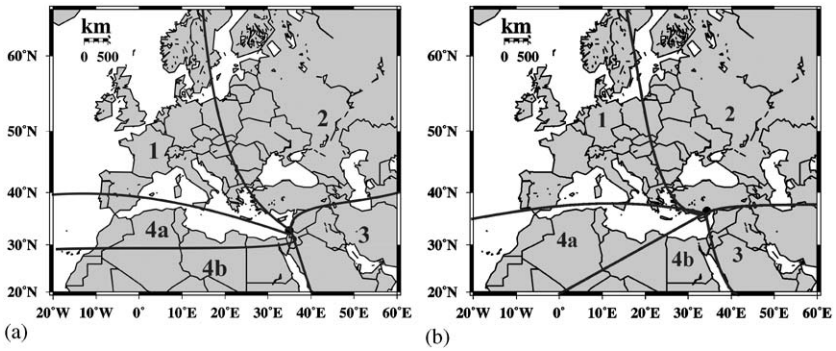

Fig. 2. Classification of 3-day back trajectories ending at (a) TS and (b) Erdemli. Major airflow sectors are indicated.

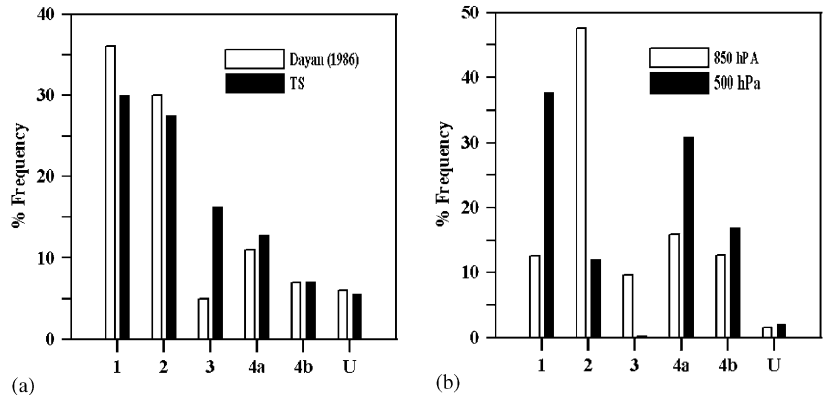

Fig. 3. Percent contribution of source regions identified in Fig. 2 to the air mass flow at (a) TS and (b) Erdemli.

Table 1
(a) The trace metal aerosol composition at Erdemli and at Tel Shikmona between 1999 and 2001. (b) The trace metal aerosol composition associated with contemporaneously collected samples at Erdemli and Tel Shikmona

	Tel Shikmona (Israel)				Erdemli (Turkey)			
	Arithmetic mean ($\pm\sigma$)	Median	Geometric mean (σ_g)	Min–Max	Arithmetic mean ($\pm\sigma$)	Median	Geometric mean (σ_g)	Min–Max
(a) *At Erdemli and at Tel Shikmona between 1999 and 2001*								
Al	2138 (5091)	810	952 (2.79)	199–36,950	814 (897)	632	567 (2.39)	15–8278
Fe	1265 (2654)	620	724 (2.40)	168–22,031	555 (524)	447	407 (2.27)	8–5601
Mn	26.1 (47.8)	15.6	16.7 (2.18)	3.3–394	11.0 (8.8)	9.9	7.9 (2.63)	0.1–92
Zn	30.8 (28.1)	25.7	22.4 (2.27)	3.8–165	20.4 (35.1)	16.9	15.9 (1.86)	0.7–744
Cu	7.3 (5.1)	5.8	5.9 (1.93)	0.6–31	10.9 (7.6)	9.2	8.9 (1.86)	1.0–65
Cr	3.6 (5.8)	2.2	2.3 (2.37)	0.2–46	5.7 (5.0)	4.2	3.9 (2.57)	0.1–39
Cd	0.27 (0.23)	0.22	0.22 (1.88)	0.05–1.38	0.21 (0.19)	0.18	0.17 (2.06)	0.01–2.36
Pb	32.1 (22.9)	25.9	24.9 (2.14)	4.7–119	34.4 (43.7)	21.9	21.5 (2.63)	0.3–586

	Tel Shikmona (Israel)			Erdemli (Turkey)		
	Arithmetic mean ($\pm\sigma$)	Geometric mean (σ_g)	Min–Max	Arithmetic mean ($\pm\sigma$)	Geometric mean (σ_g)	Min–Max
(b) *With contemporaneously collected samples at Erdemli and Tel Shikmona*						
Al	2320 (6151)	828 (2.9)	199–36,950	1100 (902)	852 (2.0)	130–4010
Fe	1351 (3198)	680 (2.5)	168–22,030	725 (523)	594 (1.9)	145–2399
Mn	27.2 (57.8)	15.4 (2.3)	3.3–394	13.9 (7.9)	12.2 (1.7)	3.4–40.8
Zn	28.8 (26.7)	19.8 (2.4)	3.8–133	19.6 (6.5)	18.5 (1.4)	7.3–41.6
Cu	7.0 (5.9)	5.4 (2.1)	0.6–31.6	11.7 (6.3)	10.4 (1.6)	4.4–37.2
Cr	3.7 (7.0)	2.0 (2.6)	0.2–46.2	7.9 (5.8)	6.3 (1.9)	1.7–32
Cd	0.29 (0.21)	0.23 (1.93)	0.05–1.19	0.23 (0.15)	0.19 (1.83)	0.03–0.79
Pb	29.1 (19.1)	22.7 (2.1)	4.7–74.9	41.7 (38.4)	29.9 (2.3)	5.1–174.2

due to the frontal situations bringing dust to the north (Martin et al., 1990; Kubilay et al., 2000).

3.2. Datasets characteristics

A summary of the total trace elemental concentrations observed in the Eastern Mediterranean aerosol at the different sampling sites is presented in Table 1. The concentration range of each element is very wide resulting in high standard deviations from the mean concentrations. Such high standard deviations are not unusual for the dataset belonging to aerosol data obtained in the Mediterranean atmosphere (Dulac et al., 1987; Bergametti et al., 1989; Kubilay and

Saydam, 1995; Güllü et al., 1998). Geometric means will be used in subsequent discussions owing to the lognormality of the two datasets. The log-normality of the dataset was verified by applying the Kolmogorov–Smirnov test at the 95% confidence level. Fig. 4, for example, illustrates the lognormal distribution of the aerosol population for two selected elements Al and Pb which are representative of contrasting sized and sourced aerosol particles.

Before discussing the environmental implications of the presented dataset, evaluation of the representative nature of the two aerosol datasets is considered. As was highlighted in the experimental section the two sites had a common sampling coverage of nearly 3 years. However, the temporal coverage within this 3-year period was different at each site. The adopted sampling strategy at Erdemli was of a higher temporal resolution than that at TS. Therefore the impact of these on the representative nature of the dataset will be evaluated. The more restricted TS sampling coverage may have lead to the omission of important events (such as Saharan dust events) which would have had an impact on the representative nature, particularly for the crustal elemental aerosol concentrations (Dulac et al., 1987; Kubilay et al., 2000). However the representative nature, in terms of air mass influence, of the TS population was good and was clearly highlighted earlier, by comparison of air mass frequencies over the sampling period with those observations made by Dayan (1986). The extent to which Saharan events had been missed at Erdemli owing to malfunction of sampling equipment was evaluated by comparing the TOMS AI with the time series of aerosol Al (proxy for mineral dust) measurements and air mass back trajectories (see Figs. 5a and b). In making this comparison, it should be remembered that the aerosol Al concentration is collected over 1–3 days period. In contrast the TOMS AI value is obtained from an instantaneous satellite measurement made during the overpass, which occurs at about 1130 UT. The criterion for TOMS detection (AI, $\geqslant 0.5$) of African dust event adapted by Chiapello et al. (1999) has been accepted and complemented by air mass back trajectories. By this way we have identified 72 events throughout the 3-year period at Erdemli (indicated by stars on Fig. 5a). Since in winter time the cloud cover precluded the use of remote sensing data (TOMS AI) the dust events are identified by aerosol Al concentration peaks and back trajectories. As can be seen both from Figs. 5a and b during the summer of 2000, intense dust transport events were detected at both sites. However taking into account the missed sampling period, 85% coverage of Saharan dust events at Erdemli was achieved over the 3-year sampling period, which would seem to be a reasonable coverage.

A comparison was also made of the aerosol concentrations in samples collected from both sites only during the same sampling dates. Hence, the Erdemli dataset was reduced to give a TS type sample set (by taking the mean trace metal concentration of three daily samples equivalent to each of the TS sample, covering a 3-day period) and the TS dataset was reduced omitting samples associated with the 6-month period in 2000 when there was no sample collection at Erdemli.

The elemental concentrations for the reduced datasets are presented in Table 1(b). It is apparent that some crustal elements show higher levels at TS whilst Cr and Cu exhibit higher levels at Erdemli. These and other differences are discussed hereafter. The higher level of desert derived elements at TS is supported both by its significantly higher AI and aerosol Al levels (during dust storms) compared to those of Erdemli (see Figs. 5a and b). However, while the TS reduced and whole datasets indicated no statistical differences between elemental concentrations, it is apparent that at Erdemli a significantly different concentration is calculated for all elements except Cu and Cr. The observed bias may be explained by the reduced set being composed of samples collected during predominantly dry days, implying that

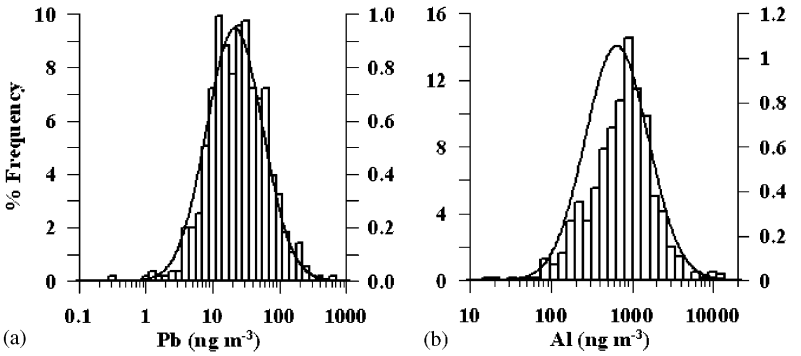

Fig. 4. Population frequency histograms of the log-transformed atmospheric concentrations of the elements and their expected normal distributions at Erdemli. (a) Pb; (b) Al.

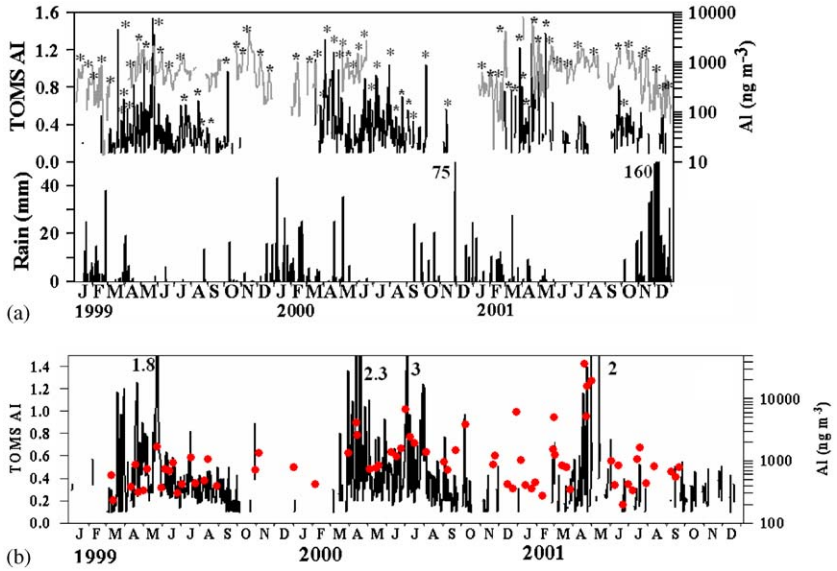

Fig. 5. Time series of (a) daily aerosol Al concentrations (gray line) and TOMS aerosol index (black line) at Erdemli. Daily local precipitation rate is indicated at the bottom; (b) 3-day integrated aerosol Al concentrations (dots) and TOMS aerosol index (black line) at TS.

the reduced Erdemli dataset is not as representative as the whole elemental aerosol dataset. The TS reduced dataset and the whole dataset indicated no statistical differences between elements, however both are bias towards dry periods, similar to the reduced Erdemli dataset. Although the two reduced datasets may not be wholly representative of the annual aerosol trace metal concentration, the datasets do present a unique opportunity to evaluate the spatial differences between similar types of dataset for the two locations.

3.3. Spatial variations in aerosol trace metal concentrations

Considering the discussion above regarding the representative nature of the datasets at both sites, a comparison of spatial difference will only be considered between the samples collected at both sites during the same sampling periods (Table 1b). Fe, Mn, Zn, Pb and Cd aerosol geometric mean concentrations observed at TS are all higher than those detected at Erdemli. By applying the Wilcoxon signed–rank test, used for nonparametric populations, it was shown that for a number of these elements (Fe, Mn,) the differences observed between the two locations were statistically significant at the 95% confidence interval. The regional difference was apparent for those elements, which have predominantly a crustal source. Although, interestingly, Al displays a much greater arithmetic mean concentration at TS (2.1x) in comparison to Erdemli; whereas its geometric mean was similar (Table 1b), and there was no significant difference between the geometric means for the two sites, using the Wilcoxon test. This apparent contradiction might be explained by Al being present in relatively higher concentrations in local crustal material at Erdemli than that observed at TS, which would ultimately lead to slightly enhanced Al geometric mean concentrations in the Erdemli aerosol if only local crustal material inputs are prevailing. However, the arithmetic mean, being higher than that at Erdemli, is likely to be more strongly influenced by episodic Saharan dust pulses.

Therefore, investigations into any spatial differences in the crustal elemental concentrations during individual common Saharan events was then considered. The choice of common events was based on air mass back trajectory analyses for both sites. Of all the dust events occurring over the 3-year period at the two sites, eleven were identified as being common. Table 2 presents the respective elemental concentrations for the two sites. This comparison clearly exhibits much higher concentration of Al ($1.7\times$), Fe ($1.6\times$) and Mn ($1.9\times$) at TS compared to Erdemli. Clearly this spatial difference arises from progressive decay of dust plumes during their transport South–North over the Levantine Basin. It is also clear that during Saharan dust events the crustal elemental concentrations on average are between 3.0 (Mn) and 3.6 (Al) times higher than those determined over the whole sampling period (Erdemli). The spatial variability between the two sites for crustal

Table 2
Elemental concentrations (ng m^{-3}), as geometric means, for common Saharan dust events at Tel Shikmona and Erdemli

Element	Common dust events (Tel Shikmona)	Common dust events (Erdemli)	Tel Shikmona/ Erdemli ratio
Al	3400	2019	1.7
Fe	2171	1316	1.6
Mn	45	24	1.9
Zn	34 (25)	21 (19)	1.6
Cu	10 (7.3)	14.3 (12.9)	0.7
Cr	6.3	10	0.6
Cd	0.38 (0.34)	0.24 (0.22)	1.6
Pb	42 (37)	35 (33)	1.2

Values in parentheses represent concentrations corrected for crustal contributions.

elements during Saharan dust events is additionally exemplified by a specific event occurring over the Laventine Basin during April 2001. Fig. 6 indicates the TOMS AI distribution over the region on 17 April 2001 together with air mass back trajectories arriving to the sampling sites and aerosol Al concentrations measured at two sites. As can be seen from Fig. 6, both TOMS AI and Al concentration levels are most enhanced at TS relative to Erdemli during extreme dust events due to proximity of the former site to the desert regions.

The overall concentrations of Cd, Pb and Zn Table 1b, derived principally from anthropogenic sources, are enhanced at TS for Cd and Zn but enhanced at Erdemli for Pb. However, the inter-site difference is statistically insignificant for these elements. It is also noticeable, comparing the Pb concentrations for the whole Erdemli dataset to historic values (Kubilay and Saydam, 1995), that there has been a detected decline, amounting to 40% during the last decade. The decadal decrease in Pb concentrations is likely to be due to the diminished emissions from vehicular transport. For example, Hassanien et al. (2001) indicated that urban Pb concentrations in Cairo have decreased by 40% between 1994 and 1997. Furthermore, it is apparent that diminished aerosol Pb concentrations have been observed in other European coastal atmospheres: (Ligurian Sea, 25–30% and North Sea, 50%, decrease, respectively), (Migon and Nicolas, 1998; Ridame et al., 1999; Lammel et al., 2002; Flament et al., 2002). Compared to the Western Mediterranean (Migon and Nicolas, 1998) a higher Pb concentration in the Eastern Mediterranean aerosol would be expected, based on recent European emission inventories of Pb. According to Pirrone et al. (1999) on a regional scale North Africa and Middle Eastern nations represent the major contributors of Pb (nearly 75%) to the Mediterranean atmosphere (in 1998).

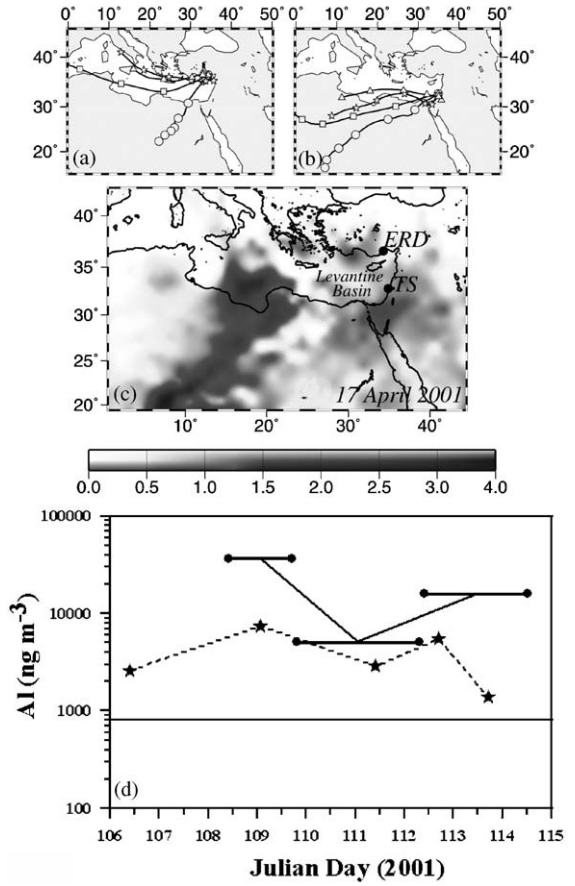

Fig. 6. Three day back trajectories illustrating the transport of air masses on the 18 April 2001 to Erdemli (a) and TS (b). The back trajectory pathway every 12 h is indicated by triangles for 1000 hPa, stars for 850 hPa, circles for 700 hPa and squares for 500 hPa. Regional aerosol index distribution is highlighted in (c) and on (d) the time series of aerosol Al concentrations at TS (unbroken line) and Erdemli (dashed line) during 16–24 April 2001 (Julian day 107–115) are presented. Geometric mean of aerosol Al concentration (813 ng m^{-3}) in the transitional season at Erdemli is indicated on the diagram as a continuous line.

Enhanced Cr and Cu aerosol concentrations were observed at Erdemli in the reduced datasets and are statistically higher than those observed at TS (enhancement factors of 3.1 and 1.9, respectively). Elevated Cr levels in the eastern Mediterranean have previously been explained by the presence of ophiolitic rock outcrops that are enriched in Cr (Kubilay and Saydam, 1995; Güllü et al., 1998; Ċağatay et al., 2002) above that found in the average crust. In addition, extensive regional past and present mining for Cr has taken place (see URL site of the General Directorate of Mineral Research and Exploration (MTA), www.mta.gov.tr/madenler/turmaden/ic.asp).

Local crustal inputs as a potential source for the enhanced Cr concentration in the aerosol was investigated by categorising samples into "local" and "non-local" groupings depending upon their air mass influence. Those defined as "local" were those whose air masses did not extend too far beyond the mainland of Turkey (see Fig. 7a), and "non-local" air masses were those which extended beyond mainland Turkey (see Fig. 7b). The "local" air mass categories had an enhanced mean Cr concentration of 8.7 ng m^{-3}, whereas "non-local" air masses had a comparatively lower mean Cr concentration of 3.5 ng m^{-3}, indicating the importance of local sources for Cr inputs to the Eastern Mediterranean marine aerosol.

The enhancement of Cu at Erdemli may be attributed to local and regional anthropogenic sources which include (i) application of fungicides and herbicides and (ii) mining of ore along with their processing in the Black Sea region. For both sources it is known there is an association between Cu and Zn. The possibility of local agricultural Cu sources is supported by previous workers (Alva et al., 2000) who observed enhanced Cu concentrations in soils where there has been long term citrus production (compared to that in soils under natural vegetation). As Erdemli is surrounded by an area rich in citrus plantations therefore an agricultural source for Cu is possible.

3.4. Temporal variability in aerosol trace metal concentrations

To serve as an example of the typical daily variability in the concentrations of aerosol trace metals, the temporal variability of the Al aerosol concentrations during the 3-year period from January 1999 up to the end of 2001 at Erdemli and TS sites are shown in Figs. 5a and b. As is has been observed in previous studies (e.g. Bergametti et al., 1989; Kubilay and Saydam, 1995; Güllü et al., 1998; Remoudaki et al., 1991a,b), short-term temporal variability in trace metal aerosol concentrations is great, ranging up to three orders of magnitude.

The seasonality of aerosol trace metals at Erdemli sampling site was tested statistically by applying the Wilcoxon test at the 95% confidence level. Seasonality was not considered for the samples from TS owing to the lower resolution of sample collection (see Table 3). Within the annual period three seasons were defined; Winter, Transitional and Summer seasons. Al and Fe exhibited statistically significant decreasing concentrations in their mean values (taken over 1999 & 2001) in the order of Transitional > Summer > Winter. Enhanced concentrations of the crustally derived trace metal observed during the Transitional period arise owing to a higher number of Saharan dust episodes occurring during this season. Taking into account only intense dust events (Al > 2000 ng m^{-3}) it was apparent that 74% of dust events occurred during the transitional period (whereas winter and summer accounted for 22% and 4%, respectively). Such dust events have also been observed previously for the Eastern (Kubilay and Saydam, 1995; Kubilay et al., 2000; Herut et al., 2001; Herut, 2001) and Western Mediterranean (Martin et al., 1990; Guieu et al., 1997) marine atmosphere.

The difference in the Al, Fe and Mn concentrations between the Winter and Summer seasons is likely to be accounted by enhanced removal/scavenging by rainfall and diminished re-suspension of local crustal material, as well as the comparative lack of Saharan dust pulse incursions during this period. This is exemplified by Fig. 8, which highlights the lower monthly aerosol metal concentrations corresponding to periods of enhanced monthly rainfall. As a comparison the data for 1992 is also included (Kubilay and Saydam, 1995) in Fig. 8. It is apparent that the aerosol trace metal levels are strongly affected (exponentially) by scavenging processes during these wet months, for both crustal and some anthropogenically derived elements (Cu, Cr, and Zn). During this process the most significant removal takes place in monthly precipitation up to 200 mm (Fig. 9).

Exceptions to this were Pb and Cd which exhibited no statistical difference in their aerosol concentrations between summer and winter seasons (Table 3). As these elements are typically associated with fine aerosol

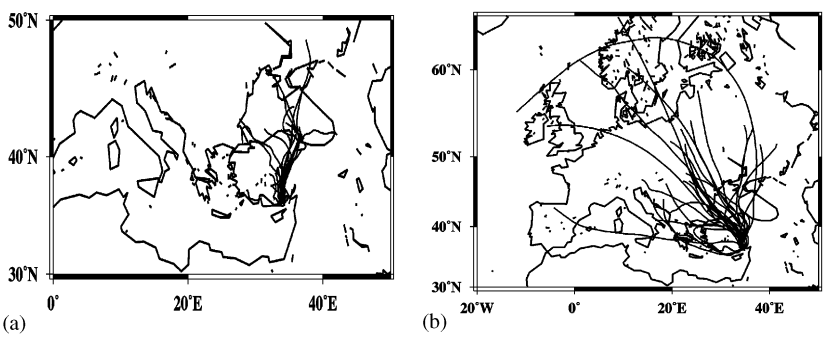

Fig. 7. (a) Local trajectories arriving at Erdemli and (b) long range transported airflow pattern.

Table 3
Seasonal variations in aerosol concentrations (ng m^{-3}) observed at Erdemli

	Winter		Transitional seasons		Summer	
	Arithmetic mean ($\pm\sigma$)	Geometric mean (σ_g)	Arithmetic mean ($\pm\sigma$)	Geometric mean (σ_g)	Arithmetic mean ($\pm\sigma$)	Geometric mean (σ_g)
Al	484 (556)	316 (2.54)	1188 (1396)	813 (2.27)	830 (388)	759 (1.56)
Fe	377 (404)	251 (2.51)	751 (778)	537 (2.25)	568 (238)	525 (1.53)
Mn	7.6 (8.0)	4.5 (3.34)	13.8 (11.9)	10.2 (2.30)	12.0 (4.6)	11.2 (1.50)
Cr	4.2 (3.9)	2.6 (3.01)	7.5 (6.1)	5.6 (2.20)	5.7 (4.5)	4.5 (2.09)
Cu	8.8 (6.5)	7.1 (1.95)	13.1 (9.6)	10.7 (1.83)	11.1 (6.1)	9.8 (1.64)
Zn	17.6 (18.2)	13.2 (2.04)	23.5 (58.2)	16.6 (1.95)	20.8 (18.9)	18.2 (1.49)
Cd	0.20 (0.21)	0.15 (2.30)	0.24 (0.18)	0.19 (1.91)	0.20 (0.16)	0.16 (1.45)
Pb	30.3 (33.6)	19.1 (2.75)	47.6 (63.1)	30.2 (2.59)	27.6 (28.4)	18.6 (2.39)

Number of samples utilised are 194, 161 and 201 for winter, transitional seasons and summer, respectively.

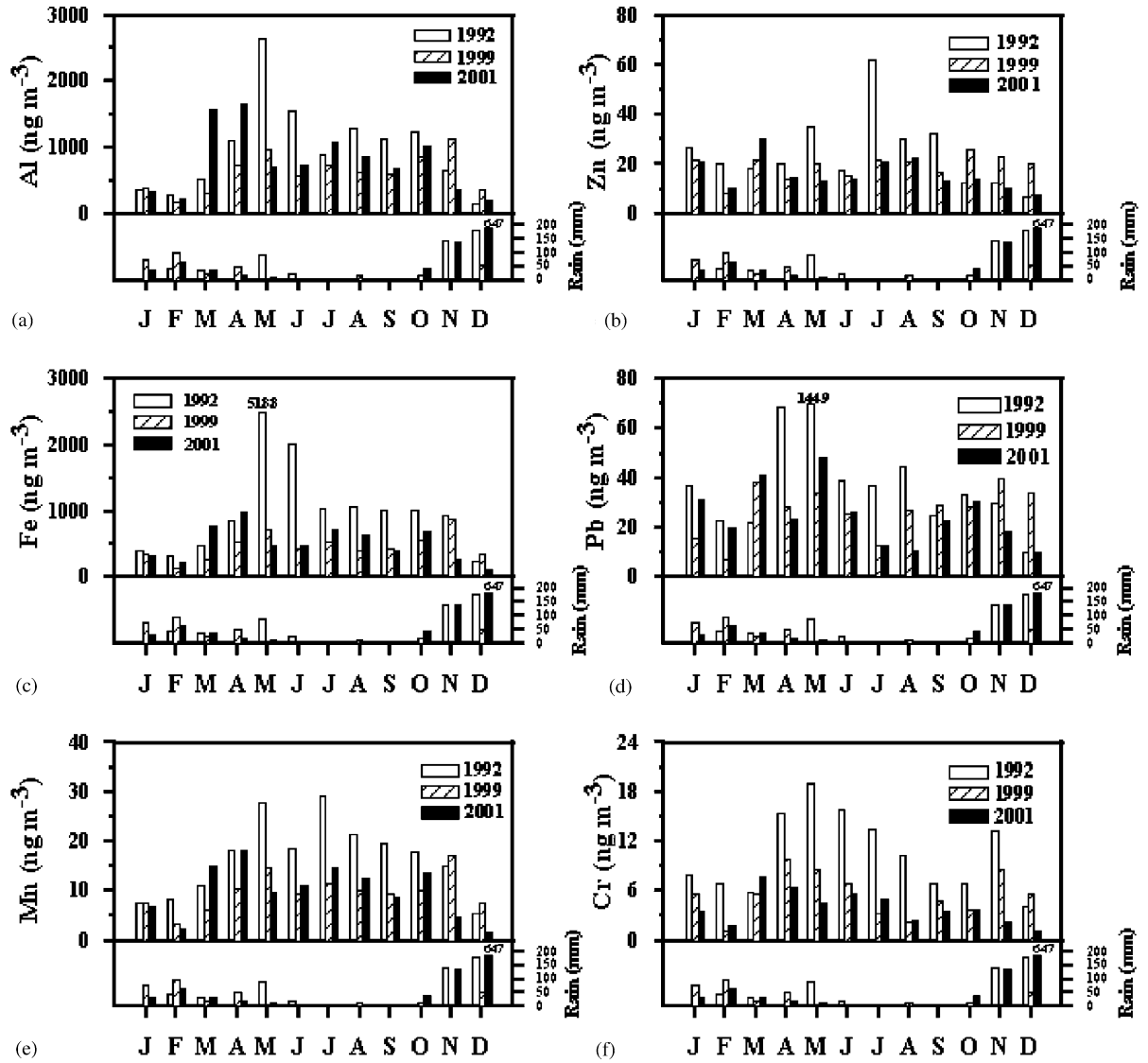

Fig. 8. Monthly mean concentrations and rainfall amounts of aerosol trace metal concentrations detected at Erdemli for the years 1992, 1999 and 2001.

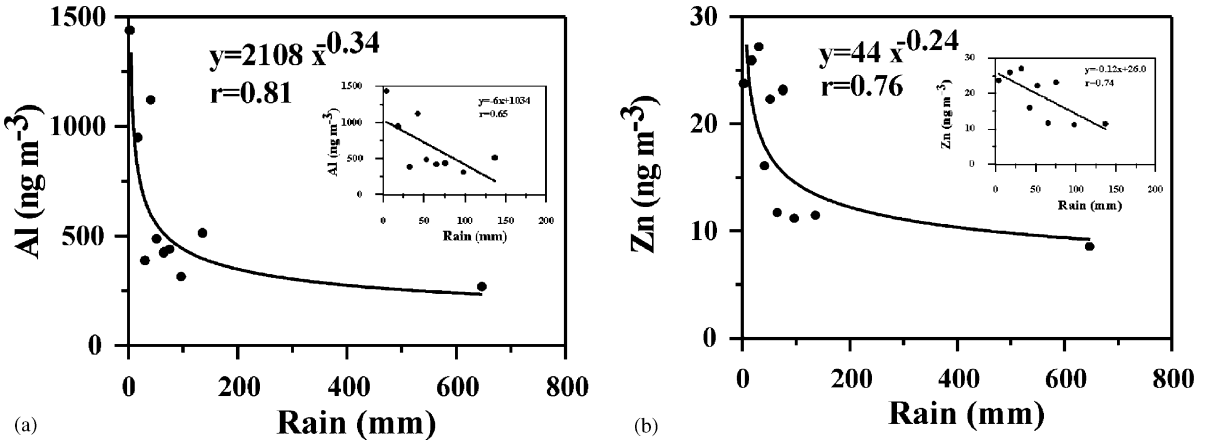

Fig. 9. Examples of the relationship between monthly aerosol concentrations (ng m^{-3}) and rainfall amount (mm) for (a) Al and (b) Zn. Each diagram has an insert which illustrates a statistically significant (95% confidence level) linear relationship for monthly rainfall < 200 mm.

particulates directly injected into the atmosphere via high temperature processes, are less efficiently scavenged compared to crustally originated elements and hence are less likely to exhibit winter/summer seasonal trends. Scavenging ratios have previously been used to measure the efficiency of rainwater scavenging of elements from aerosols (Chester et al., 1997; Kane et al., 1994). From these studies it is clear that elements (e.g. Pb) associated with finer anthropic derived aerosol material had much lower scavenging ratios (Pb—77–131; Chester et al., 1997; Kane et al., 1994) compared to scavenging ratios calculated for elements associated with crustal derived elements (Al—467; Co—706), indicating the possible fractionation of aerosol population during rain events, with a greater proportion of aerosol Pb escaping deposition, allowing greater dispersion in the atmosphere. However, the significant lower levels recorded during wet days as compared to dry days in the Winter season follow the washout dynamics suggested by Remoudaki et al. (1991a, b). Thus the observed lack of seasonally for Pb and Cd may be accounted by rapid injection and hence re-loading, post rain event, from local sources. As stated previously it was not possible to assess seasonal differences at TS, however it is likely that absolute aerosol concentrations will be impacted in a similar manner to those for Erdemli as both site experienced similar rainfalls during the sampling periods.

Pb and Cd (total Cd exhibited no significant seasonal difference) had elevated concentrations during the transitional season compared to those observed during summer and winter. It is speculated that this enhancement during the transitional period is due to (i) association and transport by high dust concentrations and/or (ii) contribution from land based sources in the south and southeastern region of the Mediterranean Basin. A similar enhancement of anthropogenic elements during high dust events has been observed by Güllü et al. (1996).

Cu and Cr both exhibited significant differences (approx. 20%) between the transitional and summer period. As discussed above this area is influenced by local sources and generally experiences higher Cu and Cr concentrations. However, the processe(s) leading to this difference is still unknown. The difference between the transitional and summer in Zn (approximately 10% higher in the summer) may possibly be accounted by enhanced local traffic and agricultural activities.

4. Conclusions

The current study has produced a unique and extensive dataset of temporal and spatial trace metal aerosol concentrations in the atmosphere of the Levantine Basin. From these finding the following conclusions may be made;

(1) There is a general increasing gradient of the crustal material load from north to south across the Levantine Basin, especially during Saharan dust events, with enhanced concentrations of Al (1.7), Fe (1.6) and Mn (1.9) observed at TS compared to Erdemli.
(2) Cr was enriched at Erdemli, to the North of the Levantine Basin, accounted by local sources, with Cu also being enriched, but to a lower extent (by a factor of 1.6).
(3) At an annual scale, no significant gradient of Pb concentrations was observed across the Levantine

Basin, which has exhibited a decrease over the last decade. However there are daily and seasonal variations as highlighted by the detailed (daily) time series carried out at Erdemli.

(4) At Erdemli, crustally derived elements exhibit seasonal trends in their concentrations (transitional > summer > winter) owing to a greater frequency and intensity of dust events during the transitional period.

(5) It was observed at Erdemli that all elements (except Pb and Cd) exhibit their lowest cocentrations in the winter period due to a greater washout effect and/or rapid air mass recharge.

Acknowledgements

This study was funded in part by Middle East Technical University (AFP-2001-07-01-01) and NATO (through a linkage grant of EST.CLG.977811). In addition the authors would like to thank Emin Özsoy for making available the ECMWF trajectory analysis through collaboration with the Turkish State Meteorological Office and the assistance of UNEP/MAP within the frame of MED POL Phase III and project 18.635. We thank the NASA/GSFC/TOMS group for the use of aerosol index data. The authors would also like to thank two anonymous reviewers for helpful comments.

References

Alva, A.K., Huang, B., Paramasivam, S., 2000. Soil pH affects copper fractionation and phytotoxicity. Soil Science Society American Journal 64, 955–962.

Bergametti, G., Dutot, A.L., Buat-Menard, P., Losno, R., Remoudaki, E., 1989. Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean. Tellus 41B, 353–361.

Brody, L.R., Nestor, M.J.R., 1980. Handbook for forecasters in the Mediterranean, Part 2. Regional forecasting aids for the Mediterranean basin. Naval Environmental Prediction Research Facility, Technical Report TR 80-10, Monterey, CA, pp. VII-1; VII-13.

Çağatay, N., Yiğitbaş, E., Güney, A., 2002. Sources and distribution of chromate mineral concentrations in alluvial and coastal sands in the region of Mersin and Tarsus. Report of the Faculty of Mine, Technical University of Istanbul, p. 33 (in Turkish).

Chester, R., Nimmo, M., Alarcon, M., Saydam, C., Murphy, K.J.T., Sanders, G.S., Corcoran, P., 1993. Defining the chemical character of aerosols from the atmosphere of the Mediterranean Sea and surrounding regions. Oceanologica Acta 16, 231–246.

Chester, R., Nimmo, M., Corcoran, P.A., 1997. Rain water–aerosol trace metal relationships at Cap Ferrat: a coastal site in the Western Mediterranean. Marine Chemistry 58, 293–312.

Chiapello, I., Prospero, J.M., Herman, J.R., Hsu, N.C., 1999. Detection of mineral dust over the north Atlantic Ocean and Africa with the Nimbus 7 TOMS. Journal of Geophysical Research 104, 9277–9291.

Dayan, U., 1986. Climatology of back trajectories from Israel based on synoptic analysis. Journal of Climate and Applied Meteorology 25, 591–595.

Duce, R.A., Arimoto, R., Ray, B.J., Unni, C.K., Harder, P.J., 1983. Atmospheric trace metals at the Enewatak Atoll. I Concentrations, sources and temporal variability. Journal of Geophysical Research 88, 5321–5342.

Dulac, F., Buat-Menard, P., Arnold, M., Ezat, U., Martin, D., 1987. Atmospheric input of trace metals to the western Mediterranean sea: 1. Factors controlling the variability of atmospheric concentrations. Journal of Geophysical Research 92, 8437–8453.

Flament, P., Bertho, M.L., Deboudt, K., Veron, A., Puskaric, E., 2002. European signatures for lead in atmospheric aerosols: a sources apportionment based upon Pb-206/Pb-207 ratios. The Science of the Total Environment 296 (1–3), 35–57.

Guieu, C., Chester, R., Nimmo, M., Martin, J.M., Guerzoni, S., Nicolas, E., Mateu, J., Keyse, S., 1997. Atmospheric input of dissolved and particulate metals to the northeastern Mediterranean. Deep-Sea Research II 44, 655–674.

Guieu, C., Bozec, Y., Blain, S., Ridame, C., Sarthou, G., Leblond, N., 2002a. Impact of high Saharan dust inputs on dissolved iron concentrations in the Mediterranean Sea. Geophysical Research Letters 29, 1911 (10.1029/2001GL014454).

Güllü, H.G., Ölmez, Ỳ., Tuncel, G., 1996. Chemical concentrations and element size distributions of aerosols in the eastern Mediterranean during strong dust storms. In: Guerzoni, S., Chester, R. (Eds.), The Impact of Desert Dust Across the Mediterranean. Kluwer Academic Publishers, Dordrecht, pp. 207–216.

Güllü, H.G., Ölmez, Ỳ., Aygün, S., Tuncel, G., 1998. Atmospheric trace element concentrations over the eastern mediterranean sea: factors affecting temporal variability. Journal of Geophysical Research 103, 21943–21954.

Hassanien, M.A., Riewerts, J., Shakour, A.A., Bitto, A., 2001. Seasonal and annual variations in air concentrations of Pb, Cd, and PAHs in Cairo, Egypt. International Journal of Environmental Health Research 11, 13–27.

Herman, J.R., Bhartia, P.K., Torres, O., Hsu, C., Seftor, C., Celarier, 1997. Global distribution of UV- absorbing aerosols from Nimbus 7/TOMS data. Journal of Geophysical Research 102, 16911–16922.

Herut, B., 2001. Levels of aerosol trace metals along the Mediterranean coast of Israel (1996–97). Fresenius Environmental Bulletin 10, 89–93.

Herut, B., Nimmo, M., Medway, A., Chester, R., Krom, M., 2001. Dry deposition of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes. Atmospheric Environment 35, 803–813.

Jickells, T., 1995. Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects. Marine Chemistry 48, 199–214.

Kane, M.M., Jickells, T.D., Davies, T.D., 1994. Atmospheric scavenging processes over the North Sea. Atmospheric Environment 28, 2523–2530.

Kubilay, N., Saydam, C., 1995. Trace elements in atmospheric particulates over the Eastern Mediterranean: concentrations, sources and temporal variability. Atmospheric Environment 29, 2289–2300.

Kubilay, N., Yemenicioglu, S., Saydam, C., 1995. Airborne material collections and their chemical composition over the Black Sea. Marine Pollution Bulletin 30, 475–483.

Kubilay, N., Nickovic, S., Moulin, C., Dulac, F., 2000. An illustration of the transport of mineral dust onto the eastern Mediterranean. Atmospheric Environment 34, 1293–1303.

Lammel, G., Rohrl, A., Schreiber, H., 2002. Atmospheric lead and Bromine in Germany—post abatement levels, variabilities and trends. Environmental Science and Pollution Research 9, 397–404.

Martin, D., Bergametti, G., Strauss, B., 1990. On the use of the synoptic vertical velocity in trajectory model: validation by geochemical tracers. Atmospheric Environment 24A, 2059–2069.

Migon, C., Nicolas, E., 1998. Effects of antipollution policy on anthropogenic lead transfers in the Ligurian Sea. Marine Pollution Bulletin 36, 775–779.

Milliman, J.D., Jeftic, L., Sestini, G., 1992. The Mediterranean sea and climate change—an overview. In: Jeftic, L., Milliman, J.D., Sestini, G. (Eds.), Climatic Change and Mediterranean, pp. 1–14. UNEP, Great Britain.

Pirrone, N., Costa, P., Pacyna, J.M., 1999. Past, current and projected atmospheric emissions of trace elements in the mediterranean region. Water Science and Technology 39 (12), 1–7.

Remoudaki, E., Bergametti, G., Buat-Menard, P., 1991a. Temporal variability of atmospheric lead concentrations and fluxes over the northwestern Mediterranean Sea. Journal of Geophysical Research 96, 1043–1055.

Remoudaki, E., Bergametti, G., Losno, R., 1991b. On the dynamic of the atmospheric input of copper and manganese into the western Mediterranean Sea. Atmospheric Environment 25, 733–744.

Ridame, C., Guieu, C., Loye-Pilot, M.D., 1999. Trend in total atmospheric deposition fluxes of aluminum, iron and trace metals in the northwestern Mediterranean over the past decade (1985–1997). Journal of Geophysical Research 104 (10), 127–130.

Torres, O., Bhartia, B.K., Herman, J.R., Sinyuk, A., Ginoux, P., Holben, B., 2002. A long term record of aerosol optical depth from TOMS observations and comparison to AERONET measurements. Journal of Atmospheric Science 59, 398–413.