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Dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin: A refined assessment

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Abstract

The current work presents dry deposition fluxes of trace metals to the Southern and Northern Levantine Basin of the Eastern Mediterranean Sea. The dry depositional inputs were calculated taking into account (i) the spatial gradients in metal aerosol concentrations across the Levantine Basin (using concentrations from two location, Erdemli, Turkey and Tel Shikmona, Israel over a 3 year sampling period), (ii) the air mass origins, (iii) air mass temporal influence across the north and south Levantine basins and (iv) fine/coarse elemental aerosol size mass distributions allowing the use of new elemental settling velocities. Two distinct airflow sectors were defined at each site; North (N) and southwest (SW), having different temporal influences at each site (the temporal ratio of SW:N was 1.85 and 0.43 at Tel Shikmona and Erdemli, respectively). Temporal airflow weighted aerosol concentrations were then calculated for each site. The applied settling velocities calculated using size fractioned aerosol samples ($n = 227$) collected from Erdemli and from the literature, yielded higher (compared to previous work) settling velocities for Cu, Pb, and Zn being 1.1, 0.8 and 0.9 cm s^{-1}, respectively. Total dry deposition fluxes for the crustal elements (Al, Fe and Mn) were consistent with previous studies for the region; however, Cu, Pb, and Zn were much higher, in part, due to the larger adopted settling velocities. Using sequential leach data, the "exchangeable" as well as total elemental dry inputs were presented for both the north and south Levantine basins. Comparison with limited literature wet deposition would suggest that the dry deposition pathway is a more significant input for Cu, Pb, and possibly Al and Fe. The "exchangeable" dry atmospheric inputs of Pb, Cu and Cd to the southern basin were orders of magnitude greater than dissolved riverine inputs. A similar comparison could not be made for the northern basin owing to absence of riverine input data.
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1. Introduction

The importance of atmospheric inputs of chemical species to open and coastal marine systems has been highlighted by a number of recent studies (Jickells, 1995; Guerzoni et al., 1999a). Atmospheric inputs may have significant impacts on their distributions (Kremling, 1985) or may impact on biotic processes such as those of Fe atmospheric inputs to high nutrient low chlorophyll (HNLC) regions, enhancing primary productivity (Usser et al., 2004), or influencing phytoplankton community structure (Baker et al., 2003). Owing to this

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importance there have been many studies over the last decade which have attempted to define the atmospheric deposition of trace metals to open ocean and coastal seas. In particular, European coastal seas have been under intense study, extending from the N. Atlantic Ocean (Baker et al., 2003; Spokes et al., 2001), North Sea (Injuk et al., 1998; Rojas et al., 1993; Ottley and Harrison, 1993; Chester et al., 1994), Irish Sea (Chester et al., 2000), NW Mediterranean (Guerzoni et al., 1999b; Ridame et al., 1999; Migon et al., 1997; Guieu et al., 1991, 1997; Remoudaki et al., 1992), to the Eastern Mediterranean (Herut et al., 2001; Özsoy and Saydam, 2000, 2001; Kubilay et al., 2000; Al-Momani et al., 1998). These studies have considered dry or wet depositional fluxes or both. Reliable dry deposition fluxes require representative metal aerosol concentrations and the application of appropriate elemental settling velocities (e.g. Guerzoni et al., 1999b). Owing to the dynamic nature of the atmosphere, aerosol metal concentrations may vary over orders of magnitude at any one location during daily periods (Güllü et al., 1998; Dulac et al., 1987; Herut et al., 2001; Kubilay and Saydam, 1995; Koçak et al., 2004). Therefore to obtain reliable aerosol metal concentrations for dry deposition flux calculations, prolonged aerosol sampling periods are required, preferably spanning over several years (to take into account both seasonal and inter-annual variations). Hence, land-based coastal sampling locations offer the only practical solution. Many such sites have now been used (e.g. Kubilay and Saydam, 1995; Guieu et al., 1997; Migon et al., 1997; Herut et al., 2001). Encouragingly, it has been shown that shipboard aerosol metal concentrations are comparable to those collected at the coast from permanent land-based stations in the Mediterranean (Dulac et al., 1987). Additionally, networks of sampling sites would be advantageous in acquiring spatial trends within a coastal environment—although generally this opportunity is rarely available.

Despite the inherent difficulties in assessing atmospheric inputs, it is apparent from recent studies which have adopted land-based sampling stations, that the atmospheric input of trace metals are quantitatively significant. For example, estimates for the Western Mediterranean (Guerzoni et al., 1999a) suggest that the atmospheric inputs of various trace metals exceeds that of riverine sources (principally the Rhine and Ebro for the NW Mediterranean) for Cd, Pb, Cu and Zn (by the following factors Cd-9x; Pb-2x; Zn-8x).

A significant amount of information on atmospheric fluxes of trace metals to the Western Mediterranean is known; however, in comparison, there is still relatively little known about atmospheric fluxes to the Eastern Mediterranean, although a number of studies have defined the aerosol trace metal concentrations at a number of sites around the Levantine Basin (Kubilay and Saydam, 1995; Güllü et al., 1998; Koçak et al., 2004). Herut et al. (2001), Özsoy and Saydam (2001), Kubilay et al. (2000) and Al-Momani et al. (1998) all have presented deposition fluxes. Kubilay et al. (2000) emphasized the importance of dry deposition of mineral dust (estimated from aerosol Al measurements) on an annual basis at the northern Levantine (Erdemli, Turkey) which amounted to 56% of the total deposition. During the summer this contribution increased to 93%.

Therefore, the aim of the current study is to enhance our knowledge of dry deposition fluxes for a number of trace metals (Al, Fe, Mn, Cu, Pb, Zn, Cd) to the Levantine Basin of the Eastern Mediterranean. The extensive library of aerosol samples collected from two sampling sites, one located at Erdemli (typically daily sampling temporal resolution), Turkey, and the other located at Tel Shikmona, Haifa in Israel (one 3 day sample per week), will allow a refined dry deposition flux to be calculated by considering (i) the spatial gradients in metal aerosol concentrations across the Levantine Basin associated with air masses of contrasting origin influencing the two sites, (ii) air mass temporal influence over the Basin and (iii) elemental aerosol size mass distributions to calculate more realistic settling velocities. Hence the unique dataset produced, will provide novel information allowing an assessment of the importance of dry atmospheric inputs to the metal budgets for the Levantine Basin of the Eastern Mediterranean. Furthermore the potential ''exchangeable'' fraction of trace metal associated with the atmospheric dry deposition will be presented, based on sequential leach analysis of contrasting aerosol populations types (crustal and anthropic dominated). This will yield information on the fate of trace metal post-dry deposition.

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) Tel Shikmona (TS),

Israel (32°49′34″N and 34°57′24″E). For more details on sampling locations and collection methods see Kubilay and Saydam (1995), Herut et al. (2001) and Koçak et al. (2004). The sampling campaigns commenced during January 1999 and finished in December 2002. Over the sampling period a total of 844 and 106 aerosol samples were collected at Erdemli and TS, respectively. Aerosol samples collected at both Erdemli and TS underwent a total acid digestion; for further details of the analytical and sampling strategies procedures and their validation (using CRM's and inter-laboratory calibrations) see Koçak et al. (2004).

Air mass back trajectory analysis was applied to identify the sources of trace metals in 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 accuracy of the trajectories used in this work has been assessed by Kubilay et al. (2000) using mineral dust as a geochemical tracer.

Allocation of a particular sector was made using the criteria that the air mass should have a residence time in the sector for >55% of its total time, which is a similar criteria to that applied in previous works (e.g. Traub et al., 2003). Where an air mass from a continental source passed over the Eastern Mediterranean and the combined sum of the residence times exceeded 55% then it was allocated into the land mass sector. For the current study all daily air mass back trajectories for 1999–2002 at both Erdemli and TS were categorised into six different sectors at the four pressure levels 500, 700, 850, and 1000 hPa (see Fig. 1). This represents an extensive piece of data analysis, requiring the analysis of in excess of 2000 days of back trajectories, for the four different pressure levels. The defined air mass sectors were as follows: (1) Saharan (R1), (2) Western Europe (R2), (3) Eastern Europe (R3), (4) Arabian peninsular (R4), (5) Mediterranean Sea (R5) and (6) Turkey (R6). This allowed the general airflow characteristics at the two sites to be defined.

For elemental flux calculations (see later) a simpler classification was adopted: sectors 1, 4, 5 and sectors 2, 3, 6 were combined to yield southwest (SW) and north (N) airflow classifications, respectively. This was carried out for the 850 hPa pressure level back trajectories as this is accepted as the most representative level for the mixing layer (Kallos et al., 1998) and therefore would be the most reliable for assessing both long and short range transported material available for dry deposition. Using the elemental concentrations for the lowest pressure levels may underestimate the potential influence of Saharan derived material on predominantly crustally derived elements (e.g. Al, Fe and Mn); this material being mainly transported by the higher level air transport (see Kubilay et al., 2000; Traub et al., 2003).

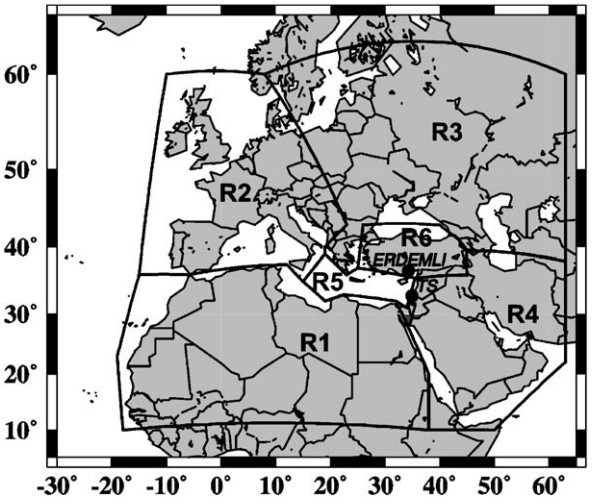

Fig. 1. Classification of 3-day back trajectories ending at Erdemli and TS. Major airflow sectors are indicated as R1 (Saharan), R2 (Western Europe), R3 (Eastern Europe), R4 (Arabian Peninsular), R5 (Mediterranean Sea) and R6 (Turkey).

3. Results and discussion

3.1. Airflow characteristics at the sampling sites

Table 1(a) and (b) presents a summary of the airflow characteristics at Erdemli and Tel Shikmona expressed as % influence of airflow from each of the defined six sectors for the four pressure levels based on daily air mass back trajectories (>2000 trajectories for each pressure level) covering the whole sampling period (1999–2002). Airflow at Erdemli (Table 1(a)) follows a number of clear trends. With increasing altitude, the % influence of distant sources (e.g. Saharan and Western European) increases whereas the % influence of local sources (e.g. Turkey) decreases. The % influence of Mediterranean airflow remains relatively constant throughout the air column. Contrasting source regions to the Mediterranean within its different

Table 1
Summary of airflow characteristics (given as % frequency) at (a) Erdemli and (b) TS for six air mass sectors at four pressure levels (1000, 850, 700, 500 hPa) over the sampling period

Pressure level (hPa)	Saharan (R1)	Western Europe (R2)	Eastern Europe (R3)	Arabian Peninsular (R4)	Mediterranean Sea (R5)	Turkey (R6)
(a) Erdemli						
1000	6	2	18	8	7	59
850	12	6	22	12	6	42
700	30	16	24	5	5	20
500	46	27	18	1	3	5
(b) TS						
1000	14	2	9	25	22	28
850	30	8	10	21	14	17
700	53	13	12	8	4	10
500	73	14	7	2	1	3

See Fig. 1 for the geographical coverage of the sectors.

atmospheric layers has also been shown by Lelieveld et al. (2002).

The airflow characteristics at TS (Table 1(b)) for the whole sampling period exhibits similar trends to that exhibited at Erdemli in that the % airflow contribution from distant sources (Saharan and Western European) increases at higher altitudes, whereas the importance of regional sources (Arabian peninsular and Turkey) decreases with altitude.

If we consider the pressure 850 hPa only, as this level will be adopted when calculating airflow influenced aerosol trace metal concentrations (as previously discussed), we can see that the influence of SW and N (as defined above) airflow sectors are different at the two sites (Fig. 2). Over the sampling period at Erdemli the northerly air masses predominates (1:2.3), whereas at TS the SW air mass dominates (1: 1.9).

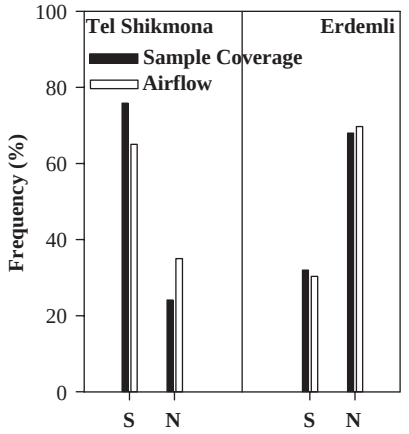

Fig. 2. Illustration of the % portion of the sample populations at each site for the North (N) and South (S) airflow categories.

3.2. Air sector aerosol trace metal concentrations

Trace metal aerosol concentrations (arithmetic and geometric means) are presented on Table 2 for both Erdemli and TS, representative for the whole of the sampling period for the respective N and SW air mass sectors at 850 hPa. Fig. 2 highlights the sample coverage for the two contrasting air mass types. It is apparent that the sample coverage for the N and SW air masses influencing Erdemli over the study period, owing to the adopted high resolution temporal sampling strategy, has virtually the same weighting as that observed in the airflow pattern. However, the TS aerosol sample library is bias by ~10% towards the northern air masses compared to the airflow pattern (see Fig. 2).

If we consider the trace metal concentrations for each of the two airflow sectors at both sites (Table 2(a)) the following general observations may be made:

(1) For the crustally derived trace metal concentrations (Al, Fe, Mn) at both sites the concentrations were greater in the SW sector than those calculated for the northerly airflow; the difference being statistically significant (at 95% confidence level). For example, the ratio of SW:N average concentrations of Al, Fe and Mn at TS (Erdemli) were 2.5 (2.0), 2.0 (1.9) and 1.8 (1.8), respectively. This of course is not

Table 2

(a) Summary of trace metal concentrations ($ng\,m^{-3}$) for N and SW airflow sectors influencing Erdemli and TS, between 1999 and 2002

	All-Samples—Tel Shikmona				All-Samples—Erdemli			
	SW		North		SW		North	
	Arithmetic mean ($\pm\sigma$)	Geom. mean	Arithmetic mean ($\pm\sigma$)	Geometric mean	Arithmetic mean ($\pm\sigma$)	Geometric mean	Arithmetic mean ($\pm\sigma$)	Geometric mean
Al	2367 (4971)	1143	565 (323)	475	1470 (1746)	912	548 (334)	437
Fe	1504 (2671)	891	497 (243)	439	949 (1059)	631	397 (249)	316
Mn	30.0 (48.3)	19.9	13.4 (13.6)	10.9	17.3 (17.6)	11.7	8.5 (4.9)	6.6
Zn	35.3 (27.6)	27.4	27.8 (41.2)	18.5	19.2 (13.3)	16.2	18.3 (34.5)	14.1
Cu	9.7 (10.0)	7.4	5.5 (2.7)	5.0	10.0 (8.0)	7.6	9.3 (6.3)	7.4
Pb	34.8 (23.2)	27.4	20.2 (10.8)	17.6	43.4 (56.0)	25.7	30.4 (28.5)	20.9
Cd	0.30 (0.25)	0.24	0.23 (0.11)	0.21	0.24 (0.46)	0.13	0.18 (0.23)	0.12

(b) Airflow weighted mean aerosol trace metal concentrations ($ng\,m^{-3}$) for both Erdemli and TS, between 1999 and 2002

	Tel Shikmona		Erdemli	
	W. Arithmetic mean	W. Geometric mean	W. Arithmetic mean	W. Geometric mean
Al	1736	909	827	581
Fe	1152	733	564	411
Mn	24.2	16.8	11.2	8.1
Zn	32.7	24.3	18.6	14.7
Cu	8.2	6.6	9.5	7.5
Pb	26.9	24.0	34.3	22.4
Cd	0.28	0.23	0.20	0.12

unexpected owing to the well-documented Saharan dust events (Koçak et al., 2004; Kubilay and Saydam, 1995) occurring mainly during the transitional period. The absolute difference in the SW air masses between the two sites is explained by the decay of crustal elemental concentrations by settling out during transport northwards across the Levantine Basin during transport. The decrease in the SW air masses between the two sites amounted to 20%, 29% and 41% for Al, Fe and Mn, respectively.

(2) The remaining elements considered in this study (Zn, Cu, Pb and Cd) at TS were all enhanced in the SW airflow. However, only excess Pb (i.e. non-crustally derived) concentrations indicated a statistical difference between the two airflows at TS. Excess Pb was calculated by subtraction of the fraction which is predicted to be derived from the crustal component of the aerosol population from the total Pb aerosol concentration. The crustal Pb fraction being determined from the aerosol Al concentration and the ratio of Pb/Al for Saharan dust. This ratio was taken from the analysis of material associated with an intense Saharan dust event (i.e. concentrations, expressed as $ng\,m^{-3}$ for Al-47000, and Pb-22) collected during a research cruise on board the research vessel R.V. *Aegaeo* positioned at the centre of the Levantine basin (at 33.42N and 32.83E on 13/5/01). The observed elemental/Al ratio (wt/wt) for Pb was 0.000468 and is consistent with that presented in the literature for Saharan dust end-member compositional data (Guieu et al., 2002). Enhancement of Pb in SW derived aerosol populations has been previously highlighted by Koçak et al. (2004) and Dulac et al. (1987) and may be explained by (i) anthropic sources located in N. Africa, (ii) Saharan dust acting as an impaction/condensation surface for fine anthropic aerosols and (iii) a combination of (i) and (ii). At Erdemli there was very little difference in these elemental concentrations between the contrasting air masses (again except for excess Pb, whose SW concentration was statistically higher). The possibility of local sources (regional mining activity) predominantly contributing to the Cu and Zn (and Cr) aerosol concentrations has been suggested (Koçak et al., 2004), which may explain the lower inter-sector variability in aerosol concentrations at Erdemli.

4. Trace metal dry deposition fluxes

Dry deposition fluxes were calculated using the equation:

$$F = C_{aero} \times V_d,$$

where F is the dry deposition flux, C_{aero} the trace metal geometric mean concentration taken from a prolonged sampling period and V_d is the elemental settling velocity. The deposition processes includes gravitational settling, impaction and diffusion (Duce et al., 1991), which are dependent upon wind speed, humidity, viscosity and surface roughness. A range of settling velocities have been applied to dry deposition flux calculations in the past, these being determined, by a number of approaches including mass-size distributions in the aerosol population, usually evaluated from cascade impactor data (Spokes et al., 2001; Ottley and Harrison, 1993; Dulac et al., 1989), mathematical modelling (Slinn and Slinn, 1980), the deployment of surrogate collectors (Sakata and Marumoto, 2004; Shahin et al., 2004; Chester et al., 1999; Hall et al., 1994; Morselli et al., 1999; Kaya and Tuncel, 1997) or the difference between total deposition and wet deposition measurements (Migon et al., 1997). All the methods adopted have their limitations. Using the approach adopted by Spokes et al. (2001), after Ottley and Harrison (1993), the elemental V_d's calculations for the current study were based on current best estimates, assuming that the V_d for fine particles is $0.1\,cm\,s^{-1}$ and the equivalent V_d of $2\,cm\,s^{-1}$ is appropriate for coarse particles (depositing to oceans regions less than 1000 km from land; Duce et al., 1991). Aerosol elemental size fraction data was available for Fe, Mn and Zn from samples collected daily at Erdemli during 2001. Separation of the coarse (2–10 μm) and fine particles ($< 2\,\mu m$) was achieved using a Gent PM10 stacked filter unit. Mean V_d's for Fe, Mn and Zn were calculated for samples which were categorized into the SW ($n = 73$) and N ($n = 154$) sectors, as well as for all collected samples. It is apparent from Table 3, that there is no difference between calculated V_d's for both airflow sectors. Therefore for flux calculations the mean value of V_d calculated from all size fractionated samples was adopted. However, when extreme Saharan dust events were identified ($n = 5$), calculated V_d's were higher as a result of a greater proportions of the element being present in the coarse fraction. Although no reliable Al coarse/fine data was available for Erdemli, we assume that the

Table 3
Elemental settling velocities ($cm\,s^{-1}$) calculated for the current study using elemental coarse/fine ratios determined from size fractionated samples associated with N and SW airflow sectors, collected from Erdemli during 2001, Crete (Smolik et al., 2003) and the Negev desert (Andreae et al., 2002)

Element	Using coarse/fine aerosol concentration data for all samples ($n = 227$)	Using coarse/fine aerosol concentration data for N sector ($n = 154$)	Using coarse/fine aerosol concentration data for SW sector ($n = 73$)	Using extreme Saharan events ($n = 5$)	Using data from Smolik et al. (2003)	Using data from Andreae et al. (2002)
Al	—	—	—	—	1.67±0.2	1.8
Fe	1.73±0.16	1.69±0.17	1.76±0.16	1.8±0.1	1.9±0.1	1.8
Mn	1.48±0.26	1.48±0.29	1.50±0.24	1.6±0.2	1.6±0.1	1.7
Cu	—	—	—	—	1.1±0.2	1.4
Zn	1.12±0.35	1.11±0.34	1.15±0.37	1.4±0.4	0.9±0.1	0.99
Pb	—	—	—	—	0.8±0.1	0.84

V_d is the same as that calculated for Fe. A similar approach was adopted for Pb and Cu using the size fractionated data presented in Smolik et al. (2003), although these were based on a very low sample number. As there was no size fractionated aerosol data for Cd, a V_d of $0.1\,cm\,s^{-1}$ was applied inline with literature suggested values (Duce et al., 1991). Unfortunately no size fractionated aerosol data exists for trace metals at Tel Shikmona; however, such data are available for the Negev desert aerosol covering a sampling period between January 1995 and November 1998 (Andreae et al., 2002). Therefore using the size fractionated mass concentration for Al, Fe, Mn Cu, Zn and Pb from Andreae et al. (2002) in the same way as described above, V_d's more appropriate for Tel Shikmona site are also presented on Table 3. Generally the V_d's are slightly higher than those calculated for the Erdemli site; however, this difference is probably within the errors associated with it's calculation. However, if we compare the settling velocities calculated for the predominantly anthropic derived elements for the current study, at both sites with those from the literature (Table 4), the current V_d's are higher, noteably compared to those over the North Sea; although the current values are more realistic for this region given that a significant proportion of these elements is observed associated with the coarse fraction (e.g. Pb 37%, Smolik et al., 2003; Zn 50%, current study). However, it is also likely that the calculated V_d for the crustal elements, although are close to the accepted values (Duce et al., 1991), of $2\,cm\,s^{-1}$, are underestimated owing to the presence of these elements in the larger coarse fraction, (i.e. $>10\,\mu m$ in size). This has been recently observed by Maenhaut et al. (1999) during the ARACHNE-96. They observed that the mineral elements in aerosol populations from the Negev desert, exhibited a unimodel size distribution, peaking at $6\,\mu m$, but significant contributions of particle $>10\,\mu m$ were clearly observed, being more pronounced during the day than during the night.

Dust settling velocities have recently been calculated using a surrogate collector at Tel Aviv (Ganor and Foner, 2001). It was shown that the V_d, during no dust episodes was $1.0\,cm\,s^{-1}$ increasing by a factor of 2 during the spring and autumn period. These observations would be consistent with the V_d calculated in the current study for the crustally derived elements. However, we accept that the settling velocities used in the current study will still be a source of uncertainty in the dry deposition calculations and further work is required to better define elemental V_d's.

The dry depositional flux for each site was calculated using aerosol trace metal concentrations in Table 2(a) and the settling velocities quoted in Table 4 presented for each airflow sector, using the equation

$$\text{Elemental dry depositional flux} = ([E]_N \times V_d \times R_N) + ([E]_{SW} \times V_d \times R_S),$$

where $[E]_N$ and $[E]_{SW}$ are the geometric mean aerosol elemental concentrations for the N and SW sectors, respectively; V_d the mean elemental settling velocities calculated at Erdemli, and for TS respectively; R_N and R_S are the temporal influence fraction for the N and SW airflow sectors, respectively, at each sampling locations (Fig. 2).

Table 4
Summary of elemental settling velocities ($cm\,s^{-1}$) applied in the literature for European coastal regions

Element	Ottley and Harrison (1993), North Sea	Injuk et al. (1998), North Sea	Rojas et al. (1993), North Sea	Dulac et al. (1989), Western Med.	Migon et al. (1997), Ligurian Sea	Remoudaki et al. (1992), Mediterranean Sea	Guerzoni et al. (1999a, b), Mediterranean	Wells (1999), English Channel	Current study, Eastern Med.	Spokes et al. (2001), N. Atlantic	Sakata and Marumoto (2004), Lake Michigan
Al	0.46	—	—	0.69–3.8	—	—	2	1.08	1.73–1.8	1.3	—
Fe	0.45	0.32–0.55	—	—	—	—	2		1.73–1.8	—	—
Mn	—	0.21–0.53	—	—	—	—	—	0.69	1.48–1.7	1.1–1.4	1–4.6
Cu	0.7	0.21–0.5	0.48	—	1.19	1.1	—	0.44	1.1–1.4	—	1.2–3
Zn	0.52	0.20–0.4	0.35	—	4.38	—	—	0.09	0.99–1.11	0.71–0.92	0.73–2.7
Pb	0.17	0.07–0.11	0.25	0.041	0.19	1.9	0.2	0.02	0.8	0.36–0.63	0.35–1.7
Cd	0.38	—	0.39	0.053	0.42	–	0.2	0.04	0.1	—	0.21–0.82

Dry depositional fluxes (presented as either mg $m^{-2}\,yr^{-1}$ or $\mu g\,m^{-2}\,yr^{-1}$) were calculated for each metal at each site and are presented in Table 5. Comparative dry deposition fluxes to the Western Mediterranean are also presented in Table 5. Calculated depositional fluxes for Al, Fe, Mn and Cd were within the same order of magnitude than those calculated by Herut et al. (2001) at TS. However, the dry deposition fluxes are several times greater than those observed for the north Western Mediterranean, which would be expected owing to the lower intensity of Saharan dust plumes (or lower rainfall around the eastern Mediterranean relative to the Western Mediterranean). Cu, Pb, and Zn fluxes for the current study are in excess of those previously calculated for both the Eastern (Herut et al., 2001) and Western (Chester et al., 1999; Migon et al., 1997) Sea and this is largely accounted by the revised significantly higher V_d's used in the current study (i.e. 0.8–1.4 $cm\,s^{-1}$ compared to 0.1 $cm\,s^{-1}$). A comparison was made (all except Fe and Mn) with total wet depositional fluxes (Table 5) of Al-Momani et al. (1998), representative of a sampling site near Antalya, Turkey. It is apparent from the comparison that the dry depositional fluxes are dominant for Al, Cu and Pb, contributing between 75% and 85% of the total atmospheric input. However, for Zn and Cd, using this comparison, the wet depositional pathway would be most significant. However, work carried out by Özsoy and Saydam (2000, 2001) would indicate that there is a high degree of variability in the total depositional inputs in this area, as they reported much higher wet depositional fluxes (at Erdemli) for Fe and Al. Therefore it is clear that more work is required to better define the spatial and temporal trace metal wet inputs to the Eastern Mediterranean.

5. Total atmospheric dry inputs

Using the elemental dry deposition fluxes from Table 5, the total dry input ($tons\,yr^{-1}$) to the Levantine Basin was calculated. Owing to the spatial difference in elemental fluxes at the TS and Erdemli, two input areas previously defined by Ludwing and Maybeck (2003) were adopted. These were the (i) southern Levantine basin (SLB; boarded by Lebanon, Israel, Egypt and Libya) having a surface area of 436,000 km^2 and the (ii) northern Levantine basin (NLB); boarded by Turkey, Cyprus, Syria and Lebanon, having a surface area of 111,000 km^2. The inputs to the SLB were calculated

Table 5
Comparison of trace metal dry deposition fluxes expressed as $\mu g\,m^{-2}yr^{-1}$ ($mg\,m^{-2}yr^{-1}$ for Al, Fe and Mn) to European coastal zones

Element	Chester et al. (1999), NW Mediterranean, total (dissolved)	Migon et al. (1997), Ligurian Sea	Chester et al. (1993), NW Mediterranean	Herut et al. (2001), Eastern Mediterranean	Eastern Mediterranean, TS, current study	Eastern Mediterranean, Erdemli, current study	Eastern Mediterranean (Antalya), wet deposition total (soluble), Al-Momani et al. (1998)	Eastern Mediterranean (Erdemli), wet deposition total, Özsoy and Saydam (2000, 2001)
Al	120 (1.2)	—	93.7	545	520	320	92 (11)	873
Fe	88 (8.8)	—	—	496	420	230	—	518
Mn	2.07 (0.4)	—	1.6	10	9.0	3.8	—	—
Cu	1190 (330)	1606	895	178	2900	2600	790 (300)	—
Pb	1850 (550)	2555	1410	1080	6360	5650	1600 (620)	—
Cd	—	32	49	8	7.2	3.8	7200 (690)	—
Zn	3200 (1500)	41610	—	2806	7580	5330	22,000 (19000)	—

using the depositional fluxes observed at TS whereas the dry atmospheric inputs to the NLB was achieved using the dry deposition fluxes calculated for Erdemli (Table 5). Comparison of the total metal dry inputs (Table 6) clearly highlights that they are much higher at the SLB than at the NLB owing to the (i) larger defined surface area (all elements), (ii) greater SW airflow temporal influence (crustal elements) and (iii) enhanced metal concentration in the SW sector (crustal elements).

The "exchangeable" fraction of the elemental inputs was then determined by multiplying the atmospheric total dry input by the characteristic elemental % exchangeable fraction for each metal. This component of the input is of importance as it indicates the potential pool of deposited metal that could subsequently be involved in marine biogeochemical cycling. The "exchangeable" fraction of the aerosol material was defined by applying a three-stage sequential leach scheme devised by Chester et al. (1989) on a wide range of mixed aerosol samples (further details will be available in Koçak et al., 2005) collected from Erdemli during the current sampling period. Samples ($n = 35$) analysed ranged from Saharan dominated to anthropogenically dominated aerosol populations. Clear elemental trends were established with Al and Fe being present mainly in the refractory phase (>90%) and those influenced by anthropogenic sources being dominating in the exchangeable phase, although for these metals the variability was comparatively high (12–64%, 19–85% and 40–100% for Zn, Pb and Cd, respectively). For the majority of elements considered greater % of "exchangeable" fractions were observed as the % anthropic contribution to the aerosol population increased. Using the weighted geometric mean concentrations from Table 3(a) at both sites, and the element/Al ratios for a Saharan end-member aerosol (see Koçak et al., 2005) the % anthropic contributions for the two sites were estimated to be between 90% and 99% for Pb, Cd, Zn and Cu, 51–63% for Mn and 18%–28% for Fe. Using these values the following range of % "exchangeable" fractions were estimated (using the data presented in Kocak et al., 2005) for Cu, Cd, Zn, Pb, Mn and Fe as 35–45%, 95–100%, 70%, 75–95%, 40–45% and 0.25–1%, respectively. The Al % "exchangeable" was calculated according to its mean aerosol concentrations; this amounted to between 3% and 6%. These % "exchangeable" ranges were then applied to the total dry flux inputs to yield the

Table 6
Trace metal atmospheric dry inputs (ton yr^{-1}) to the Northern Levantine Basin (NLB) and Southern Levantine Basin (SLB) (see text for method of calculation)

Element	NLB total	SLB total	NLB exchangable	SLB exchangable	Levantine Basin total	Levantine Basin exchangeable
Al	35,800	225,000	1100–2100	6900–13,500	260,800	8000–15,600
Fe	25,300	181,400	60–250	450–1800	206,700	510–2050
Mn	430	3930	170–190	1580–1770	4360	1750–1960
Zn	590	3330	420	2320	3920	2740
Cu	290	1270	100–130	450–570	1560	550–700
Pb	630	2770	470–600	2120–2630	3400	2590–3250
Cd	0.4	3.2	0.35–0.4	3.0–3.2	3.6	3.4–3.6

Table 7
Comparison of dissolved metal riverine and atmospheric exchangeable dry deposition (tons yr^{-1}) over the Southern Levantine Basin

Element	Riverine	Atmospheric
Pb	0.2	2120–2630
Cu	5.7	450–570
Cd	0.048	3.0–3.2

"exchangeable" atmospheric dry inputs to the NLB and the SLB and are presented on Table 6.

A comparison of some dissolved metal riverine inputs to the SLB is also made on Table 7. Concentrations of dissolved Pb, Cu Cd were available for the River Nile and corresponding freshwater inputs to the SLB (Ludwing and Maybeck, 2003), allowing the dissolved inputs to be calculated, although estuarine removal/addition could not be taken into account. For the NLB no riverine dissolved metals concentrations were available as well as sediment loadings. Therefore to develop a metal budget for the Levantine Basin there is an urgent need to expand our knowledge of riverine inputs; this requires (i) riverine sediment loadings, (ii) riverine dissolved and particulate trace metal concentrations and (iii) an understating of estuarine cycling (removal and addition processes) of trace metals.

However, comparisons of "exchangeable" atmospheric inputs to approximate dissolved riverine inputs to the SLB for Pb, Cu and Cd (Table 7) would clearly indicate that the atmospheric input is orders of magnitude greater in importance, owing to the low input of freshwater in this region. It should also be remembered that the current comparison underestimates the atmospheric input of "exchangeable" metal by omitting the wet inputs.

6. Conclusions

The current study has presented some "exchangeable" and total dry depositional fluxes of trace metals (Al, Fe, Mn, Cu, Zn, Cr, Pb and Cd) to both the SLB and the NLB of the Eastern Mediterranean Sea. The calculated fluxes were based on revised calculated elemental settling velocities, taking into account the typical element mass size fraction in the Eastern Mediterranean aerosol population influencing the NLB and SLB along with the temporal weighted aerosol concentrations representative of the two main air mass sectors. Total dry deposition fluxes were found to be dominant for Al, Cu and Pb whereas for Zn and Cd the wet depositional fluxes are likely to dominate, although there is relatively little wet depositional fluxes for the area and requires further study.

The total metal inputs were also presented, being adjusted to provide a measure of the "exchangeable" fraction which represents the upper amount of potentially soluble metal, post-deposition into the Eastern Mediterranean. This was achieved by using elemental % "exchangeable" fraction determined in a series of mixed filter samples using a three-stage sequential leach scheme (see Koçak et al., 2005 for further details), along with the typical anthropogenic % contribution to the aerosol population at each site. Comparison with riverine inputs to the SLB clearly indicated the dominating atmospheric inputs for Cu, Pb and Cd. However, to develop a more detailed and realistic trace metal budget of the Levantine Basin of the Eastern Mediterranean much more research is required to better define the riverine inputs to both the SLB and the NLB.

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