Sources and fluxes of atmospheric trace elements to the Gulf of Aqaba, Red Sea

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[1]   We present the first comprehensive investigation of the concentrations, fluxes and sources of aerosol trace elements over the Gulf of Aqaba. We found that the mean atmospheric concentrations of crustally derived elements such as Al, Fe and Mn (1081, 683, and 16.7 ng m^{-3}) are about $2-3$ times higher than those reported for the neighboring Mediterranean area. This is indicative of the dominance of the mineral dust component in aerosols over the Gulf. Anthropogenic impact was lower in comparison to the more heavily populated areas of the Mediterranean. During the majority of time (69%) the air masses over the Gulf originated from Europe or Mediterranean Sea areas delivering anthropogenic components such as Cu, Cd, Ni, Zn, and P. Airflows derived from North Africa in contrast contained the highest concentrations of Al, Fe, and Sr but generally lower Cu, Cd, Ni, Zn, and P. Relatively high Pb, Ni, and V were found in the local and Arabian airflows suggesting a greater influence of local emission of fuel burning. We used the data and the measured trace metal seawater concentrations to calculate residence times of dissolved trace elements in the upper 50 m surface water of the Gulf (with respect to atmospheric input) and found that the residence times for most elements are in the range of $5-37$ years while Cd and V residence times are longer.

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1. Introduction

[3]   Atmospheric deposition of trace elements to the ocean can significantly modify seawater chemistry and influence oceanic ecosystems [*Duce et al.*, 1991; *Jickells*, 1995; *Guerzoni et al.*, 1999]. In seawater, the maximum concentrations of dissolved Al, Mn, and Pb are often found at the surface as a consequence of significant atmospheric input of these elements [*Bruland*, 1983; *Patterson and Settle*, 1987]. Several elements that show surface depletion also have an atmospheric source, however, their distribution is predominantly controlled by rapid nutrient-like uptake in the upper ocean thus the surface enrichment is not marked [e.g., Fe and Cd, *Bruland*, 1983]. Atmospheric input of Fe has been identified as a factor that may control primary productivity in high nitrate low chlorophyll (HNLC) regions of the ocean

[*Martin*, 1990; *Young et al.*, 1991; *Martin et al.*, 1994; *Coale et al.*, 1996; *Boyd et al.*, 2000; *Tsuda et al.*, 2003]. Iron has also been suggested as a critical nutrient for nitrogen fixation in oligotrophic seas [*Paerl et al.*, 1994; *Falkowski*, 1997]. Mn [*de Baar et al.*, 1990] and Zn [*Bruland*, 1989] are also considered elements that may limit primary productivity in some situations and for which atmospheric deposition could be an important source.

[4]   Studies of trace element deposition from marine aerosols to seawater have been conducted in the open Atlantic and Pacific oceans [e.g., *Arimoto et al.*, 1995; *Chen and Siefert*, 2004] as well as in the Mediterranean Sea [*Ridame et al.*, 1999; *Migon et al.*, 1997; *Guieu et al.*, 1997; *Herut et al.*, 2001; *Kocak et al.*, 2005; *Bonnet and Guieu*, 2006]. Atmospheric fluxes of certain trace metals (Cd, Pb, Cu and Zn) to the ocean could exceed those of riverine sources [*Guerzoni et al.*, 1999; *Kocak et al.*, 2005]. Trace elements in atmospheric dry deposition can originate from both crustal and anthropogenic sources. Specifically, emissions of trace metals from pyrometallurgical industries, steel and iron manufacturing, and from biomass burning were found to be significant over the North Atlantic. These anthropogenic contributions were more evident in air masses transported from Europe and Africa than in those from North America [*Arimoto et al.*, 1995]. Similarly, over the southeastern Mediterranean Sea, significantly higher enrichment factors (relative to crustal sources) of Cd and Pb were observed in European-derived air masses compared

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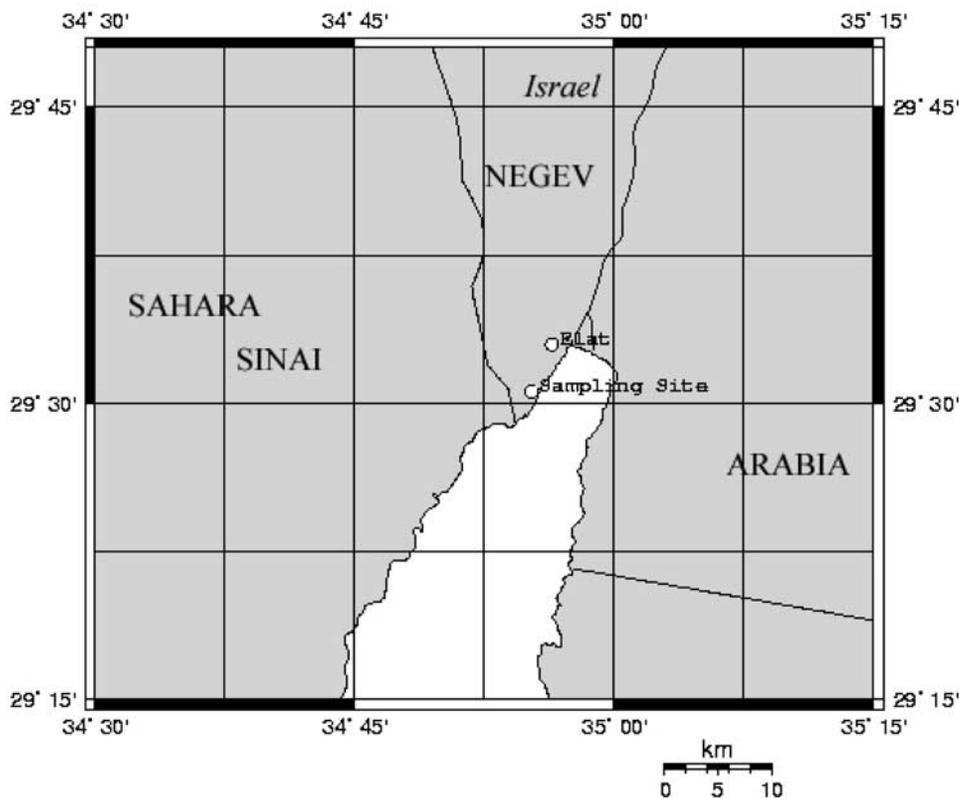[6]Steinitz Marine Biology Lab, Hebrew University, Eilat, Israel.

Figure 1. Aerosol sampling site at the northwest coast of the Gulf of Aqaba (29°31′N, 34°55′E) in Israel.

to those arriving from the North Africa-Arabian deserts [*Herut et al.*, 2001].

[5] No attempt has been made so far to determine the atmospheric fluxes of trace elements to the surface water in the Gulf of Aqaba (Figure 1). Such fluxes may be significant and are likely to impact the Gulf ecosystem. The Gulf of Aqaba represents a small scale, easy to access, regional analogue of larger oceanic oligotrophic systems. The Gulf is surrounded by arid lands (African, Arabian and local deserts) and receives negligible river discharge and atmospheric wet deposition [*Ganor and Foner*, 1996]. Therefore atmospheric aerosol deposition is a major (and possibly the only) external source of trace elements to this marine ecosystem. Importantly, this oligotrophic sea may be representative of other present-day or past dust-dominated oligotrophic systems and may also represent future global conditions of increased aridity and potentially also dust fluxes [*Tegen et al.*, 2004; *Woodward et al.*, 2005].

[6] In this study we monitored the concentrations of aerosol trace elements over the Gulf of Aqaba during a two-year period (20 August 2003 to 10 September 2005). Back trajectories of the air masses over the Gulf were calculated and categorized into six characteristic source sectors. Enrichment factors of elements (relative to average crust and to Sahara dust) were determined to identify potential sources of aerosol elements. Daily dry deposition fluxes of trace elements to the Gulf were estimated to illustrate temporal patterns and variability in the elemental deposition. In addition an annual average flux for each element was calculated. We also calculate the elements

residence times in the Gulf surface water with respect to their atmospheric fluxes. The central hypothesis of this study is that anthropogenic emissions from industrialized regions of Europe and the middle-east have a significant impact on the budget of some trace elements in the Gulf of Aqaba despite the dominance of mineral dust sources.

2. Methods

2.1. Aerosol Collection

[7] Aerosol samples were collected using a Total Suspended Particle High Volume Sampler (HVS) placed on a roof (about 10 m above the ground level) at the Interuniversity Institute of Marine Sciences (IUI) in Eilat, a few meters off the northwest coast of the Gulf of Aqaba (29°31′N, 34°55′E, Figure 1). The HVS was designed to have four filter holders connected to separate flowmeters, thus collecting four samples simultaneously. Two filter samples were used for pure water extraction and strong acid digestion to measure soluble and total chemical components, respectively. The other two were used for seawater dissolution, phytoplankton incubation experiments or other chemical analyses as needed. The airflow path of the HVS and the filter holders are made of all plastic to minimize trace metal contamination. Aerosol particles were collected on acid-cleaned 47-mm 0.4 μm pore size polycarbonate membrane filters (Isopore™). Polycarbonate filter (the thinnest filter type) was selected because it gives less error in aerosol-nitrate measurement due to its lower impact on nitrate evaporation and adsorption processes compared to

quartz and Teflon filters [*Chen et al.*, 2007]. The filters were weighted immediately before and after collection to quantify sampled aerosol mass. Filter samples were stored frozen in polystyrene Petri dishes inside plastic bags until analysis. Between 20 August 2003 and 28 November 2004 aerosol samples were taken at least once a week over a 24-h period with an airflow of $2.5-2.8$ m^3 h^{-1}. Between 29 November 2004 and 10 September 2005 aerosols were sampled continuously over a 72-h period with an airflow of $1.2-1.5$ m^3 h^{-1}. The short-duration (24 h) sampling allowed us to capture daily dust events, and the continuous sampling (3 day averages) was used to better represent the seasonal and annual aerosol concentrations over the Gulf. Detailed discussion of the benefits and limitations of the two sampling strategies is given by *Chen et al.* [2006].

2.2. Trace Element Analysis

[8] A strong-acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Thermo® Finnigan Element2) was applied to measure total elemental concentrations (Al, Ca, Fe, K, Na, Mg, Mn, Ni, Cu, Zn, V, Cr, Co, Cd, Pb, P) in the aerosol. The digestion procedure was done in Teflon vessels in batches which included 9 samples, one blank and one Standard Reference Material (SRM 2709 San Joaquin Soil, National Institute of Standards and Technology). 2 g of Optima nitric acid (VWR®) and 0.25 g of Optima hydrofluoric acid (VWR®) were added to each Teflon vessel. The samples were then digested in a MDS-2100 microwave digestion system (CEM®) and the temperature and pressure of the system were controlled. The heating program used was 30-min heating to 180°C followed by holding 180°C for 10 min. After cooling to room temperature, the digested solution was transferred to an acid-cleaned polyethylene container (Fisher Scientific®) and the liquid was dried under a laminar flow hood in a class 100 clean laboratory. The residue was dissolved in 30 g of 2% Optima nitric acid and stored at room temperature for ICP-MS analysis. Internal standards of Sc and Rh (SPEX CertiPrep®) were added to the digested samples before ICP-MS analysis of a suite of elements. The atmospheric concentrations of the analyzed trace elements were calculated using the mass of the extracted solution, the concentration of the element and the volume of the air (or the mass of aerosols) sampled. The filter and sample handling blanks were less than 8% of the measured minimum sample concentrations for each of the elements.

2.3. Back Trajectories

[9] Five-day isentropic air mass back trajectories (AMBTs) were calculated from the National Oceanic and Atmospheric Administration (NOAA) FNL database using the Hybrid Single-Particle Langrangian Integrated Trajectories (HY-SPLIT) program [*Draxler*, 2002]. Although the errors associated with these calculations increase as the model steps back in time, the AMBTs still provide useful information about the synoptic situation and general sources of the air mass sampled. Previous air back-trajectory studies demonstrated that in summer the eastern Mediterranean is connected at the lower troposphere with Europe, at the mid-troposphere with eastern North Africa and at the higher troposphere with the Asian monsoon [*Ziv et al.*, 2004].

AMBTs were calculated at 100, 700 and 2000 m height levels for each sampling day at the sampling site (29°31'N, 34°55'E, Figure 2 shows representative examples). The general aerosol sources were assigned to one of six air mass sectors according to the major residence (>60% of total time) of back trajectories at the 700 m level which was suggested as the most representative height for the mixing layer and thus the most reliable for assessing both long and short range transported material available for dry deposition [*Kallos et al.*, 1998]. The air mass sectors identified are (Figure 3): North Africa (Sahara desert, Z1), Arabian peninsular (Z2), Local region including Israel, Jordan, Syria, Iran and Iraq (Z3), Eastern Europe (Z4), Western Europe (Z5) and Mediterranean Sea (Z6).

2.4. Flux Estimate

[10] A particle deposition model [*Jacobson*, 2004] was used to calculate the dry deposition velocities for various sizes of aerosol particles collected for each sampling date. The dry deposition speed in this model is calculated as the sum of particle sedimentation speed in the air and its deposition against a series of resistances at the air-water interface, which vary with particle size and with meteorological and physical conditions in the troposphere [details by *Chen et al.*, 2006]. The meteorological inputs for the particle deposition model were obtained from the NOAA archived FNL METEOGRAM database, including surface pressure (HPA), surface temperature (K) and temperature (K) and wind speeds (cm s^{-1}) at reference height (10 m), for each sampling date. The model applied a dust particle density of 2.6 g cm^{-3} [*Chin et al.*, 2002] which is typical for mineral dust, since this component dominates the aerosols over the Gulf. The calculated aerosol deposition speeds were combined with the source analysis of each aerosol element to estimate the elemental deposition velocity. Dry deposition flux (Fd) of an aerosol element was calculated from the concentration of the element in air (Cel) and the average deposition velocity of the particles containing this element in the aerosols (V_{el}, equation (1)).

$$F_d = C_{el} \times V_{el} \tag{1}$$

The deposition fluxes of soluble fractions were calculated using the mean seawater solubilities for Al (3%), Fe (0.7%), Cu (49%), Ni (48%) and Zn (44%) measured directly from our aerosol samples [*Chen et al.*, 2006] and for other trace metals (Cd 85%, Co 20% and Pb 50%) we use values measured in Mediterranean aerosols [*Chester et al.*, 1996].

2.5. Trace Elements in Seawater

[11] Seawater samples were collected from the Israeli side of the Gulf on $19-20$ August 2003 and from both the Israeli and the Jordanian sides on $22-25$ March 2004, $17-22$ November 2004 and $5-9$ September 2005 [details by *Chase et al.*, 2006]. In August 2003 all samples were collected using acid-cleaned all-plastic GO-FLO bottles. In other periods surface samples were collected through acid-cleaned plastic tubing (C-flex) using a peristaltic pump while deep water samples were collected with GO-FLO bottles. Immediately after collection, seawater was filtered through in-line acid-cleaned 0.2 μm capsule filters with Supor membrane (Pall Acropak) and stored in acid-cleaned

a) March 10, 2005; 20 UTC
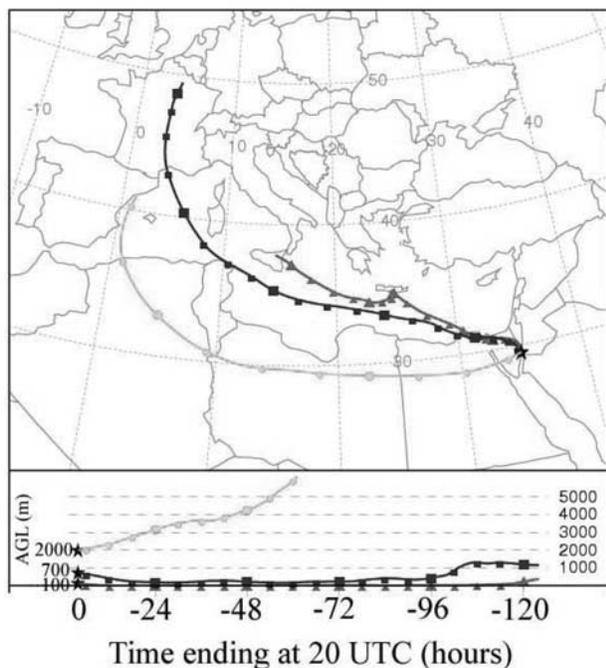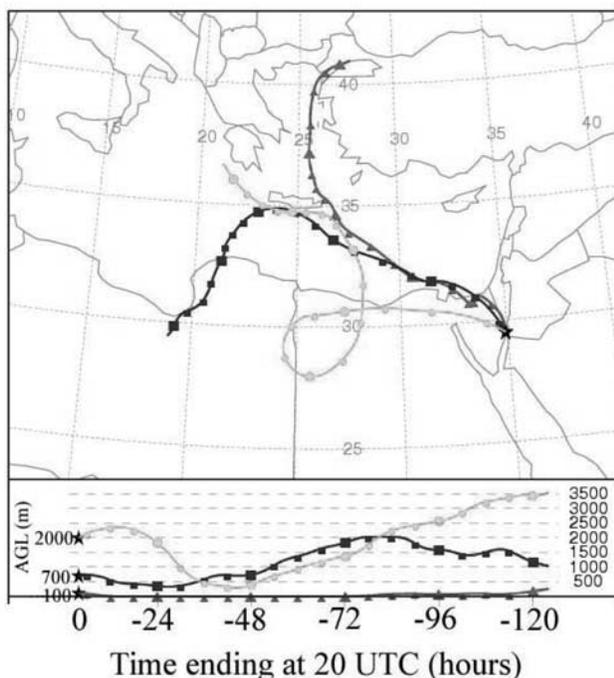

b) June 20, 2005; 20 UTC

Figure 2. Representative 5-day air mass backtrajectories assigned to the Mediterranean Sea sector, which may still be influenced by European anthropogenic (a) and African crustal (b) sources. The starting point is the northwest coast of the Gulf of Aqaba (29°31′N, 34°55′E) at altitudes 100, 700, and 2000 m.

low-density polyethylene bottles. Samples were acidified under class−100 conditions with 4 mL 6N ultrapure HCl per L and stored for at least 6 months prior to analysis. Trace metals (Fe, Co, Cu, Ni, Pb, Zn, Cd, and V) were pre-concentrated by ammonium pyrolidine dithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) organic extraction [*Bruland et al.*, 1985] and then run by ICP-MS. The analytical methodological blank was determined using acidified ultra-pure water, and the accuracy of the method was assessed by analyzing standard reference seawater (NASS-5, National Research Council, Canada). Samples for aluminum (Al) determinations were collected similarly into acid cleaned PMP bottles, shipped to the University of Hawaii, and determined using flow injection analysis [*Resing and Measures*, 1994]. Here we report Al data from November 2004 and September 2005, and other trace elements data from August 2003 and March 2004.

3. Results and Discussion

3.1. Aerosol Trace Elements

[12] Aerosol concentrations at the northwest coast of the Gulf of Aqaba ranged between 17 and 420 μg m^{-3} of air with an average and standard deviation of 54 ± 45 μg m^{-3} during the period of August 2003–September 2005 (Table 1). This average is slightly lower than the mean aerosol concentrations measured at the Israeli Mediterranean coast in Tel-Shikmona and Maagan Michael (around 70 μg m^{-3}, *Herut et al.*, 2001) but comparable to that observed over the southeastern Mediterranean Sea (57 μg m^{-3}, *Herut and Krom*, 1996). Trace element concentrations in the aerosol samples are summarized in Table 1 for the intermittent (20 August 2003–21 November 2004) and continuous (28 November 2004–10 September 2005) sampling periods, respectively. No statistically significant difference was found between the data collected during the two periods for most trace elements ($P > 0.05$, Table 1). Na showed higher concentrations during the second period (average of 1724 versus 1441 ng m^{-3}), probably a result of increased sea salt contribution to the aerosols during the second year due to either different meteorological conditions or longer exposure time to local sea spray (e.g., 3 days versus one day). The high Na concentrations could also be contributed to by dust particles coated with sulphates (e.g., Na$_2$SO$_4$, *Levin et al.*, 1996). The declined Cd concentrations (0.1 versus 0.2 ng m^{-3}) could be attributed to lower anthropogenic Cd emissions transported from Europe or the middle-east in 2005 relative to 2003 and 2004.

[13] The aerosols sampled at the Gulf contained significant amounts of Na and Al, ranging between 0.5−4 μg m^{-3} and 0.24−18 μg m^{-3} with mean values of 1.5 and 1.1 μg m^{-3}, respectively (Table 1). The Na is mostly derived from sea salt aerosols as supported by its significant correlation with Cl (r = 0.71, Figure 4b) and showed less temporal variability compared to the Al that represents the mineral dust component (Table 1) and thereby reflects the episodic nature of the dust events. Using the measured Al concentration and the average Na/Al ratio in the upper continental crust (0.36, *Taylor and McLennan*, 1985) and in Saharan dust (0.13, *Tomadin et al.*, 1984) the mineral dust contribution to the Na can be estimated. The remaining sea-salt
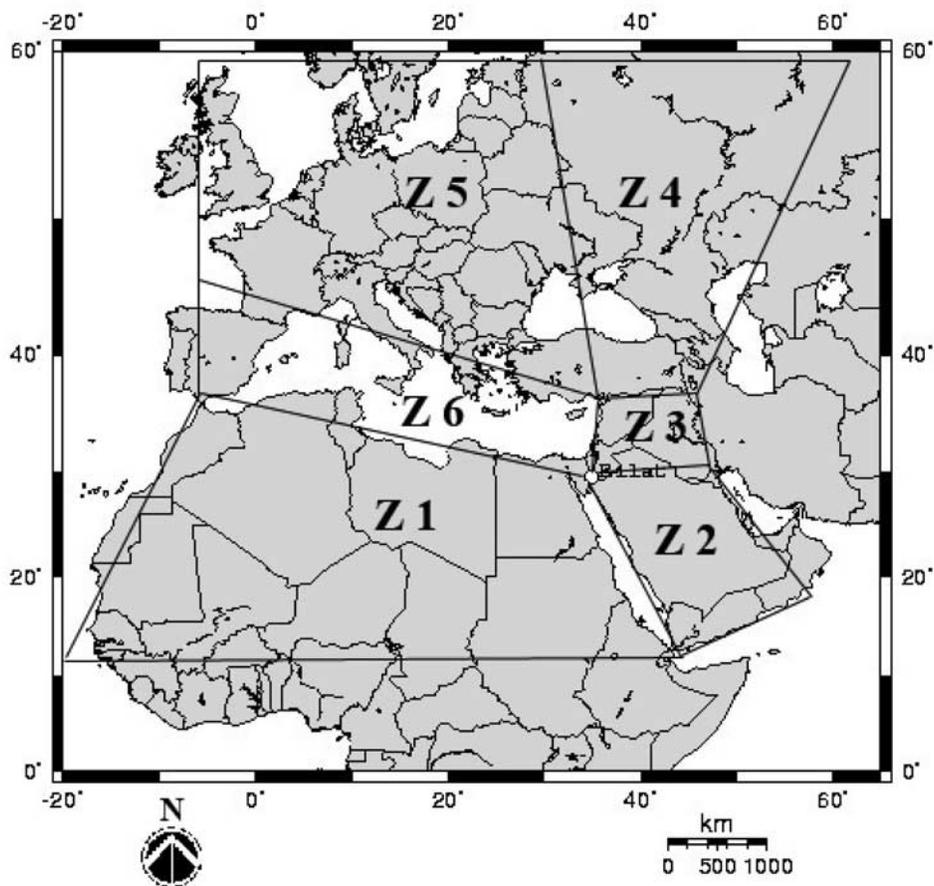
Figure 3. Classification of 700-m height level air mass back trajectories ending at Eilat, Israel. Major airflow sectors are indicated as Z1 (North Africa), Z2 (Arabian Peninsular), Z3 (Local region), Z4 (Western Europe), Z5 (Eastern Europe) and Z6 (Mediterranean Sea).

Table 1. Statistical Summary of Atmospheric Concentrations of Total Suspended Particles (TSP, μg m^{-3}) and Trace Elements (ng m^{-3}) Over the Gulf of Aqaba for the Intermittent (20 August 2003–21 November 2004) and Continuous (28 November 2004–10 September 2005) Sampling Periods Respectively and the Geometric Means for All the Samples

|	20 Aug 2003–21 Nov 2004 Intermittent Sampling (n = 60)			28 Nov 2004–10 Sep 2005 Continuous Sampling (n = 76)			All Samples
	Range	Average ± SD	Geomean	Range	Average ± SD	Geomean	Geomean
TSP	16.9–305	54.7 ± 40.7	46.7	19.2–420	52.9 ± 49.2	44.7	45.5
Al	242–14763	1413 ± 2024	892	346–17572	1799 ± 2263	1259	1081
Na	498–4123	1441 ± 678	1313	894–3892	1724 ± 522	1655	1494
Ca	730–34160	3784 ± 4561	2754	996–37943	4733 ± 4579	3839	3315
Fe	124–8123	847 ± 1121	558	184–12740	1146 ± 1570	801	683
K	121–4165	682 ± 636	507	262–4750	954 ± 796	753	633
Mg	127–5335	644 ± 712	488	308–6638	828 ± 823	673	584
P	13.4–983	167 ± 163	112	30.1–615	180 ± 106	153	133
Mn	4.0–144	20 ± 20	16	4.8–207	22.9 ± 25.4	17.7	16.7
Pb	0.9–34.9	8.5 ± 7.2	6.2	1.2–31.3	9.5 ± 6.4	7.8	7.0
V	0.7–28.6	6.0 ± 4.7	4.7	1.3–37.2	6.9 ± 4.6	6.0	5.4
Cr	0.6–23.3	3.7 ± 3.2	2.9	0.4–37.1	4.1 ± 4.5	3.1	3.0
Co	0.02–4.0	0.4 ± 0.6	0.3	0.07–4.0	0.5 ± 0.5	0.4	0.3
Cu	0.6–10.5	3.7 ± 2.1	3.2	1.0–10.1	3.9 ± 1.7	3.6	3.4
Cd	0.02–0.8	0.2 ± 0.1	0.1	0.01–0.3	0.1 ± 0.06	0.09	0.1
Ni	0.4–19.4	3.3 ± 3.0	2.5	0.6–20.5	3.5 ± 2.5	3.0	2.8
Zn	1.8–49.7	15.2 ± 10.2	12.3	5.0–43.2	18.5 ± 6.7	17.4	14.9
Sr	–	–	–	4.8–154	19.4 ± 18.8	15.7	15.7

(a)

(b)
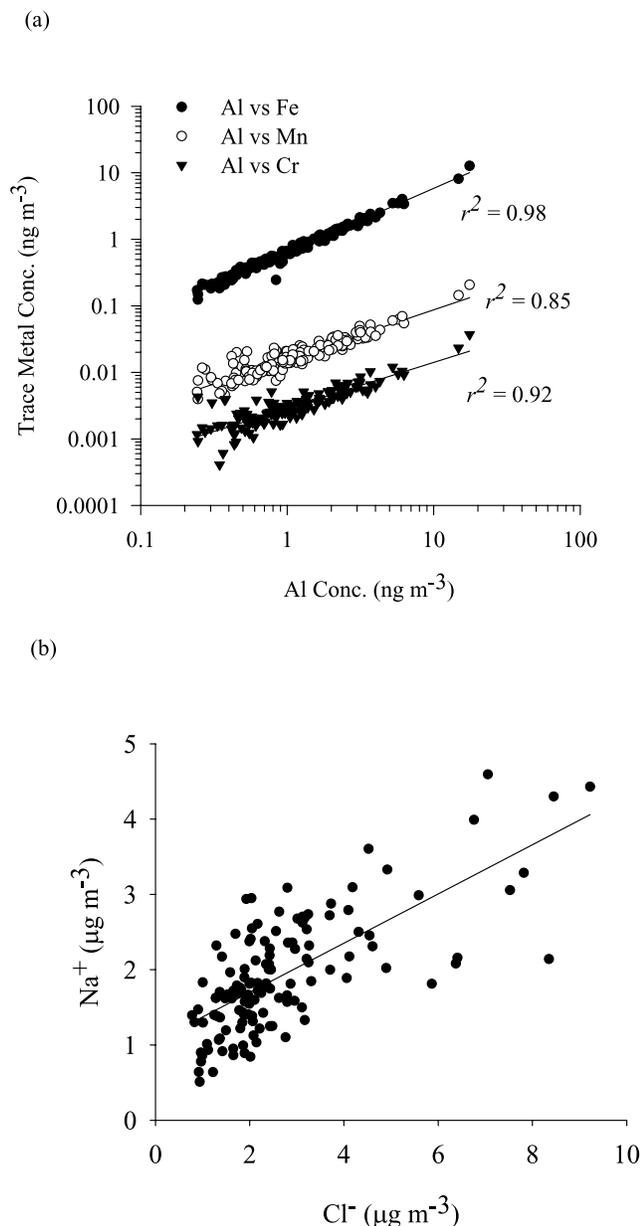
Figure 4. Linear relationships between particulate Al, Fe and Mn concentrations (a) and between Na and Cl (b) in the aerosol samples collected over the Gulf of Aqaba.

Na was calculated as 0.9 and 1.3 μg m^{-3}. From these values and using the major elemental composition of seawater (Na constitutes 30.6% of seawater salts by weight), sea salt contribution to bulk aerosol mass was calculated to be about 6–9% of the total aerosol mass (mean 46 μg m^{-3}, Table 1). This value is consistent with the minor sea salt influence on aerosols (2–5%) observed at the Israeli Mediterranean coast [Herut et al., 2001]. The contribution of mineral dust to total aerosol mass was around 30% (by weight) based on the Al content of average crustal material (8.04%, Taylor and McLennan, 1985) or 35% based on Saharan dust Al content (6.77%, Tomadin et al., 1984). Alternatively, using the Al content of the regional dust and loess deposits from the Negev

desert (~4.5%, Herut et al., 2001) or the Al content of air masses transported from North Africa determined in this study (3.8%, Table 3) we calculate that on average 40% of total aerosol mass was contributed by mineral dust (sea salt ~8%).

[14] Our measurements of aerosol elemental concentrations over the Gulf are generally comparable to or at least of the same order as those previously reported for the neighboring Mediterranean area (Table 2). The mean Al concentration over the Gulf (1081 ng m^{-3}) was slightly higher than those observed at the Israeli Mediterranean coast (827 ng m^{-3}, Herut et al., 2001) and Erdemli, Turkey (680 ng m^{-3}, Kubilay and Saydam, 1995) but over a factor of 2 higher than that over the western Mediterranean Sea (408 ng m^{-3}, Keyse, 1995). The elevated Al concentration in our samples suggests the relatively strong impact of mineral dust in this region [Duce et al., 1991], consistent with the proximity of surrounding arid regions. Higher concentrations compared to those of the western Mediterranean Sea (factor of 2–6) were also found for Fe, Mn and Cr at the Gulf (683, 16.7, and 3.0 ng m^{-3} compared to 278, 7.4, and 0.51 ng m^{-3}, Keyse, 1995). These concentrations however were comparable to those observed at the eastern Mediterranean coast (Table 2). Fe ($r^2 = 0.98$), Mn ($r^2 = 0.85$) and Cr ($r^2 = 0.92$) concentrations in our samples were significantly correlated with Al (Figure 4a) indicating that these metals, like Al, were predominantly contributed by a crustal source.

[15] Some trace elements such as Cu, Zn, Pb, and Cd in aerosols can be dominated by anthropogenic emissions [Duce et al., 1991]. The concentrations of these elements in aerosols over the Gulf are lower than those previously reported for the Mediterranean area as expected from the closer proximity of the latter site to Europe and other populated areas (Table 2). Specifically, the mean concentrations of aerosol Zn and Pb (14.9 and 7.0 ng m^{-3}) were about a factor of 5 lower than those observed at the Israeli Mediterranean coast (76 and 36.2 ng m^{-3}, Herut et al., 2001, Table 2), suggesting lower emissions of Zn and Pb through smelting operations or fuel burning [Fishman, 1999; Johansen and Hoffmann, 2003] at the Gulf compared to the Mediterranean coast. The lower Pb measured recently compared to previous work may also be due to the rapid phasing out of Pb in fuel. No significant relationships were found between Cu, Zn, Pb and Cd and Al, implying a noncrustal, anthropogenic, source for these metals.

3.2. Trace Elements in Airflow Sectors

[16] Air masses reaching the Gulf of Aqaba, based on the daily air mass backtrajectories calculated at 700-m height level, typically arrived from one of six sectors, Z1 to Z6 (Figure 3). It must be noted that airflows assigned to the Mediterranean Sea sector may still be influenced by European anthropogenic and/or African crustal sources before their circulation over the Mediterranean Sea (e.g., prior to the last 3 days before arrival at the Gulf, Figure 1). Aerosol samples associated with the airflows from Z1, Z2, and Z3 were found to be more "dusty" with a mean aerosol load (66 μg m^{-3}) almost a factor of 2 higher than that of samples originating from the other three sectors (average 39 μg m^{-3}, Table 3). These "dusty" samples accounted for less than one third of sampling days, and during the majority of time (69%) the air masses over the Gulf were dominated by

Table 2. Particulate Trace Metal Concentrations (ng m^{-3}) and Their Enrichment Factor (EF) Values in the Air Over the Gulf of Aqaba and its Neighboring Mediterranean Sites

| | Gulf of Aqaba[a] | | Israeli Med. Coast[b] | | | Turkey Erdemli[c] | | Western Med. Sea[d] | |
| | | | Tel Shikmona | | MM[e] | | | | |
	Conc.	EF	Conc.	EF	Conc.	Conc.	EF	Conc.	EF
Al	1081	1	865	1	788	680	1	480	1
Fe	683	1.5	787	2.3	685	685	2.5	278	0.85
Mn	16.7	2.0	15.7	2.4	18.1	12.6	2.5	7.4	1.3
Cr	3.0	6.2	2.4	6.4	4.0	10.8	29[f]	0.51	0.89
Cu	3.4	11	5.7	21	7.2	–	–	–	–
Zn	14.9	17	89[g]	117	63	19	31	21	52
Pb	7.0	28	34.2	159	38.2	30	176	14	194
Cd	0.1	97	0.24	228	0.23	0.19	228	0.3	260

[a]Present study.
[b] *Herut et al.* [2001].
[c] *Kubilay and Saydam* [1995].
[d]*Keyse* [1995].
[e] Location is called Maagan Michael.
[f]High Cr concentration in Erdemli is attributed to contamination by local ophiolitic rocks [*Kubilay and Saydam*, 1995].
[g]*Migon et al.* [1997].

European and Mediterranean Sea sources (sectors Z4-Z6). The relatively higher aerosol loads transported from sectors 1–3 (below called dusty sectors) are most likely due to the high percentage of desert area in these sectors.

[17] The mean concentrations of crustally derived trace elements (Al and Fe) in airflows transported from the dusty sectors were significantly higher than those from other sectors (Z4, Z5 and Z6, Table 3). Specifically, the aerosols of Z1 contained the highest Al, Fe, and Sr (mean 33.7, 23.0, and 0.4 mg g^{-1} respectively), about 50–60% higher than the values observed in airflows from eastern Europe (Z4). Concentrations of Pb, Cu, Cd, Ni, Zn, V, and P were found to be the lowest in Z1 sector aerosols, suggesting dominant mineral dust and relatively low anthropogenic influence on this sector (Table 3). The mean concentrations of Cu, Cd, and Zn were similar in airflows from all other five sectors, while Pb, V, and Ni were significantly higher in the airflows

of local and Arabian origins (253, 169, and 89.1 μg g^{-1}) than those from the European and Mediterranean Sea (176, 133, and 69.6 μg g^{-1}, Table 3). Such difference suggests that anthropogenic emission of certain trace element could vary with the industrial and human activities in different regions. Cu and Cd pollutants in the air generally come from nonferrous industrial and vehicle emissions, respectively [*Venkataraman et al.*, 2002; *Bilos et al.*, 2001]. Zn may reach the atmosphere through smelting and incinerating operations [*Huang et al.*, 2001]. Non-crustal Pb, V and Ni are often associated with the burning of fossil fuel [*Rahn and Lowenthal*, 1984; *Yatin et al.*, 2000; *Venkataraman et al.*, 2002]. The higher Pb, V and Ni related to the local and Arabian sectors suggest that emission of fuel burning pollutants may be mostly derived from the local area rather than the European source. Alternatively, this may be due to the loss of large particles and associated trace elements

Table 3. Geometric Mean Concentrations of Trace Elements (mg g^{-1} for Al, Na, Ca, Fe, K and Mg; μg g^{-1} for P, Mn, Pb, V, Cr, Co, Cu, Cd, Ni, Zn and Sr) in Aerosols Normalized by the Aerosol Masses and the Total Suspended Particulate Concentrations (μg m^{-3}) Over the Gulf for Each of the Six Defined Aerosol Source Sectors

	North Africa (Z1) n = 19	Arabian Peninsular (Z2) n = 6	Local Region (Z3) n = 17	Eastern Europe (Z4) n = 10	Western Europe (Z5) n = 37	Mediterra. Sea (Z6) n = 47
	μg m^{-3}					
TSP	68.0	62.6	66.8	41.2	39.8	36.8
	mg g^{-1}					
Al	37.7	34.5	33.6	21.9	24.9	24.6
Na	23.5	27.0	22.1	49.3	44.7	48.3
Ca	82.1	81.0	89.8	85.5	86.4	81.0
Fe	23.0	21.4	21.4	14.1	15.6	15.7
K	16.3	25.5	20.2	14.3	14.3	15.4
Mg	16.2	15.3	15.8	13.8	14.1	14.6
	μg g^{-1}					
P	2148	3693	4306	3666	3365	3630
Mn	430	553	489	426	398	404
Pb	134	251	255	176	193	159
V	121	169	169	133	128	137
Cr	72.7	83.5	94.9	83.5	76.6	71.2
Co	9.9	10.4	10.7	6.2	7.7	7.2
Cu	52.0	108	95.6	97.4	89.2	93.9
Cd	1.2	2.7	3.2	3.8	3.1	3.1
Ni	58.1	82.7	95.5	70.9	70.8	67.0
Zn	255	453	373	374	425	397
Sr	400	382	320	353	343	345

Table 4. Element to Al Ratios in the Upper Continental Crust, Sahara Dust (Over Italy), Sahara Sand (Sudan) and Negev Loess (Israel) and the Calculated Enrichment Factors Based on Average Upper Crust (EF$_{crust}$) and Sahara Dust (EF$_{sahara}$) for Trace Elements in Aerosols Over the Gulf of Aqaba

	Element/Al ratios					
	Upper Crust, *Taylor and McLennan* [1985]	Sahara Dust, *Tomadin et al.* [1984]	Sahara Sand, *Eltayeb et al.* [2001]	Negev Loess, *Herut et al.* [1999]	EF$_{crust}$	EF$_{sahara}$
Al	1	1	1	1	1	1
Fe	0.44	0.55	0.79	1.3	1.47	1.16
K	0.35	0.40	0.18	0.65	1.57	1.37
Mg	0.17	0.34	0.079[a]	0.55	3.15	1.51
Na	0.36	0.13	0.19[a]	0.25	4.13	11.7
Ca	0.37	1.29	0.67	1.8	8.86	2.57
P	0.012×10^{-4}	0.027	0.017	0.030	10.3	4.84
Mn	75	131	120	–	1.97	1.13
Sr	44	277	40	–	3.1	0.49
Cr	4.4	29	8.4	–	6.23	0.93
V	7.5	3.0	–	–	6.88	17.4
Co	1.2	4.7	–	–	2.44	0.64
Cu	3.1	18	3.4	–	10.5	1.85
Ni	2.5	30	–	–	11.2	0.94
Zn	8.8	–	26	–	16.7	–
Pb	2.5	–	3.4[b]	–	28.0	–
Cd	0.012	–	–	–	97.3	–

[a]Harmatten dust (south Sahara) measured by *Wilke et al.* [1984].
[b]Sahara soil measured by *Guieu et al.* [2002].

during long-range transport of air masses from Europe to the Gulf (however this would need to be verified by a time series sampling of the same air mass). P mean concentration (4.3 mg g^{-1}) was the highest in airflows originating from the local region (Z3), which may be a consequence of the local P-ore ports in Eilat and Aqaba or the relatively high concentration of P in regional crustal material such as Negev loess [*Herut et al.*, 1999, Table 4].

3.3. Enrichment Factor Analysis

[18] Enrichment factors relative to crustal and Sahara dust compositions (equation (2)) were estimated by normalizing the trace element abundance to Al in the samples [e.g., *Chester et al.*, 1993; *Huang et al.*, 2001; *Bilos et al.*, 2001].

$$EF_{crust/Sahara} = \frac{(El/Al)_{air}}{(El/Al)_{crust/Sahara}} \qquad (2)$$

Where $(El/Al)_{air}$ is the concentration ratio of the trace element to Al in collected aerosol samples and $(El/Al)_{crust/Sahara}$ is their average ratio in the upper continental crust or the Saharan source [*Taylor and McLennan*, 1985; *Tomadin et al.*, 1984]. Average upper crust contains lower element/Al ratios for most elements compared to the ratios in the regional natural dust (e.g., Saharan and Negev dust, Table 4). Therefore the enrichment factor values calculated in this study when normalized to average crust (EF$_{crust}$) probably overestimate the anthropogenic imprint of trace elements, but the data are useful for comparison to previous studies which typically use average upper crust as a reference. The EF$_{Sahara}$ may be more representative (Table 4) since dust storms from North Africa are the most common in Israel [*Ganor et al.*, 1991].

[19] Figure 5 shows the enrichment factors relative to average upper crust calculated for 17 different aerosol elements for all 136 samples collected over the Gulf. High EF$_{crust}$ values (medians >10, Figure 4) were observed for Cd,

Cu, Pb, Ni, Zn and P suggesting substantial contribution from non-crustal source. Cd was the most enriched element in the Gulf aerosols suggesting its dominant anthropogenic origin. Relatively low EF$_{crust}$ values (medians <10, Figure 4) were calculated for the remaining 11 aerosol elements, particularly for Mn, Co, K and Fe (median <3) indicating the strong impact of a crustal source on these elements. Our calculated EF$_{crust}$ for aerosol Cu, Zn, Pb and Cd over the Gulf were significantly lower than those previously reported for different Mediterranean sites [*Herut et al.*, 2001; *Kubilay and Saydam*, 1995; *Keyse*, 1995; Table 2], further indicating that non-crustal sources had less influence on air mass over the Gulf compared to the Mediterranean area. Similar EF$_{crust}$ of crustally derived elements Fe, Mn, and Cr were found
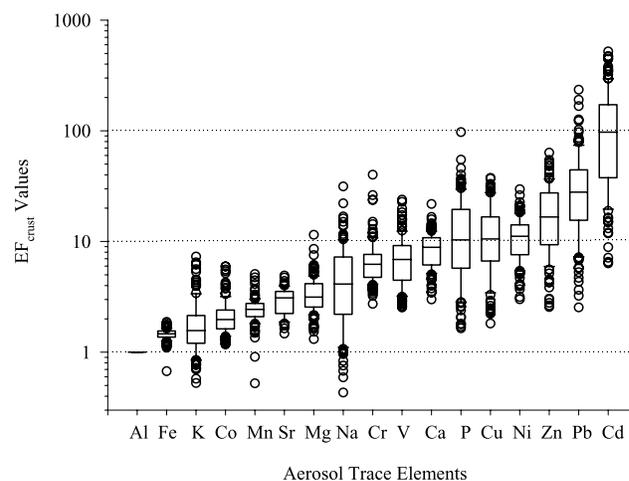

Figure 5. Box plots of EF$_{crust}$ values for various trace elements in aerosols over the Gulf of Aqaba. The bottom and the top of each box are located at the 25 and 75 percentiles. The central horizontal line is drawn at the sample median.

Table 5. Estimates of Dry Deposition Velocities (cm s^{-1}) and Fluxes (μg m^{-2} d^{-1}) of Aerosol Trace Elements Over the Gulf of Aqaba

		Velocities (cm s^{-1})		Fluxes (μg m^{-2} d^{-1})	
		Range	Geomean	Range	Geomean
EF$_{crust}$ > 10	Cd			0.0004 – 0.2	0.03
	Pb			0.04 – 10.4	2.18
	Zn			0.07 – 22	4.61
	Ni			0.01 – 12.4	0.86
	Cu	0.01 – 0.77	0.36	0.02 – 6.7	1.05
EF$_{crust}$ < 10	P			12.1 – 831	116
	Ca			725 – 34,237	2870
	V			0.63 – 28.8	4.67
	Cr			0.36 – 28.7	2.63
	Na			399 – 4,275	1294
	Mg			115 – 5,347	506
	Sr			4.2 – 119	13.4
	Mn			3.8 – 160	14.5
	Co			0.02 – 4.0	0.28
	K			116 – 4,174	548
	Fe	0.8 – 1.2	1.0	119 – 9,851	591
	Al			234 – 14,796	936

between the Gulf (this study) and the southeastern Mediterranean (i.e., Israeli coast and Erdemli, Table 2). This is not surprising because of the geographic proximity of these regions and the impact of crustal dust from the same general source. The different EF$_{crust}$ values of Fe, Mn and Cr observed between the Gulf and the western Mediterranean Sea [*Keyse*, 1995, Table 2] suggest influences of distinct crustal sources on these two regions.

[20] The calculated EF$_{sahara}$ are generally lower than the EF$_{crust}$ for most elements in aerosols as a result of the lower Al content (higher element/Al ratio) in Saharan dust compared to the average upper crust (Table 4). The most notable difference is the decrease of EF$_{sahara}$ values of Ca and P by a factor of 2 – 3 from enriched (EF$_{crust}$, ~10) to non-enriched (EF$_{sahara}$ < 5) levels. High P/Al ratio in Sahara dust is probably due to abundant phosphorite deposits in the area [*Cook and McElhinny*, 1979; *Notholt et al.*, 1989]. High Ca/Al ratio was also observed in the particles settling in Israel following dust storms [*Ganor et al.*, 1991] and in aerosols from Syria [*Cornille*, 1990] as a result of the wide distribution of calcite and dolomite in the region [*Eltayeb et al.*, 2001]. Cu and Ni, which are typically associated with anthropogenic sources (see discussion above), also fall into the group of non-enriched elements based on their EF$_{sahara}$ values (Table 4). This may be due to anthropogenic contamination of the Saharan reference sample that was collected over Italy and the central Mediterranean [*Tomadin et al.*, 1984]. It may be more accurate to determine enrichment factors relative to the Sahara soil directly rather than to air born aerosols, however this approach also has its limitation. The EF$_{sahara}$ of Na (11.7) and V (17.4) were about a factor of 3 higher than their EF$_{crust}$ values (Table 4), consistent with the sea salt contribution (8%) and the impact of burning of heavy oil on aerosols over the Gulf, respectively.

3.4. Deposition Velocities of Trace Elements

[21] Dry deposition velocity varies with aerosol particle size and is also dependent on meteorological conditions such as wind speed, air column stability and humidity [*Jacobson*, 2004]. A number of approaches have been used to estimate the deposition velocities of aerosols, including

evaluation of mass-size distributions in the aerosol population by cascade impactors [*Spokes et al.*, 2001; *Ottley and Herrison*, 1993; *Dulac et al.*, 1989], mathematical modeling [*Slinn and Slinn*, 1980] and 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]. The deposition velocity in this study was calculated using a particle deposition model [*Jacobson*, 2004] which calculates the deposition speeds for different sizes of particles according to the meteorological and physical conditions of each sampling date. Very similar velocities (difference around 10%) were found for all particles smaller than 5 μm collected on the same sampling date. Thus we used the model calculation for a 0.75 μm particle (mean velocity of 0.36 cm s^{-1}) to represent the deposition velocities of fine fraction aerosols (<2 μm). For particles with an aerodynamic diameter greater than 5 μm, the deposition velocities increased dramatically with size [*Chen et al.*, 2006]. Although aerosols were sampled with no size resolution (e.g., TSP), the size distributions of aerosols were analyzed separately using a GT – 321 particle monitor (Met One Instruments$^{®}$). It was found that about 60% of the total aerosol mass was contributed by particles with an aerodynamic diameter greater than 5 μm, and the particles between 2 – 5 μm and <2 μm accounted for the remaining 35% and 5% mass respectively. Previous studies used a mean deposition velocity of 2 cm s^{-1} for the flux calculation for coarse particles in coastal regions [e.g., *Duce et al.*, 1991; *Guerzoni et al.*, 1999]. In our case, coarse fraction sampled over the Gulf contained a significant percentage (~35%) of smaller than 5 μm particles that had relatively low deposition speed (around 0.5 cm s^{-1}). Therefore we used the model calculation for a 10 μm particle (mean deposition velocity of 1.0 cm s^{-1}) to represent the coarse particle deposition speeds. This is lower than values published previously in the literature but more relevant to this specific site. The velocity estimate for coarse fraction aerosols in our study has an uncertainty of up to a factor of 2 [see *Chen et al.*, 2007 for more details].

[22] Deposition velocities of 0.75 and 10 μm particles were used for calculating dry fluxes of anthropogenically (EF > 10) and crustally (EF < 10) derived elements, respectively. Anthropogenic aerosols normally fall into the fine particle fraction (<2 μm) while crustal dust and sea salts are often present within the coarse size range [*Duce et al.*, 1991]. High temporal variability was found for element deposition velocities due to the changes of meteorological conditions [*Chen et al.*, 2006], however, our mean velocities (0.36 and 1 cm s^{-1}) are in the same order of magnitude as those used for dry flux calculations by previous studies [e.g., *Ottley and Herrison*, 1993; *Rojas et al.*, 1993; *Kocak et al.*, 2005; *Spokes et al.*, 2001]. Specifically, our data (Table 5) are comparable to the deposition velocities for many aerosol elements calculated using the direct measurements of their dry deposition fluxes and atmospheric concentrations at Cap Ferrat, Mediterranean (0.30 – 0.86 cm s^{-1}, *Chester et al.* [1999]). The simple assignment of elements to the fine or coarse fractions may cause an uncertainty of up to a factor of 3 for flux estimation, however when compared to using a fixed deposition velocity results are very similar
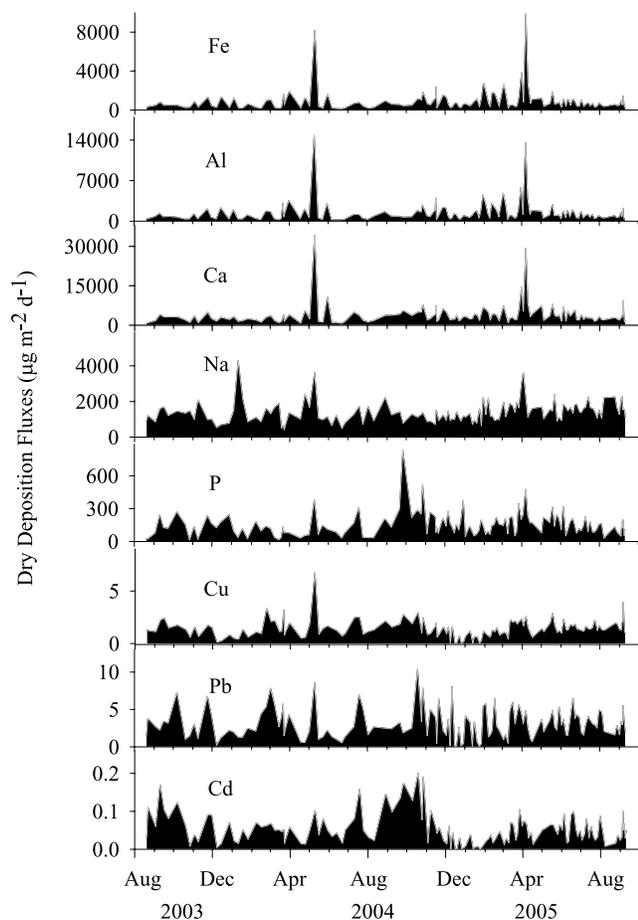
Figure 6. Temporal changes of dry deposition fluxes of representative aerosol elements showing different source contributions over the Gulf of Aqaba.

suggesting that the estimates are representative and comparable to previously reported data.

3.5. Atmospheric Fluxes of Trace Elements

[23] The dry deposition fluxes represent the total atmospheric inputs of trace elements to the Gulf of Aqaba due to the extremely dry climate in this region throughout the year (e.g., no wet deposition). Deposition fluxes of trace elements estimated for each sampling date in this study can provide unique information on temporal patterns and ranges in the daily fluxes of aerosol elements (Table 5) in addition to annually averaged values (Table 6). The deposition fluxes of measured aerosol elements showed no clear seasonal trend; however two spike fluxes on 10 May 2004 and 9 April 2005 were observed for most aerosol elements especially for those derived predominantly from crustal sources (Figure 6). These high fluxes were due to dust storms resulting in large contributions of mineral dust to the aerosols as winds moved vertically and lifted large quantities of soil dust from the Sinai and local deserts (shown by trajectories). These two springtime spikes were apparent in all crustally derived elements (e.g., Al, Fe, and Ca) but became less and less significant for elements that show a non-crustal source (e.g., Na, P, and Cu) until finally, for the anthropogenically derived elements (e.g., Cd, Figure 6) the

peaks disappeared into the background of the daily flux variation. Such features can provide useful information regarding crustal source identification of trace elements in the aerosol. Likewise, relatively higher fluxes in July and October, compared to other months, were observed for the elements derived mainly from anthropogenic emissions (e.g., Pb and Cd, Figure 6), thus providing a reference for anthropogenic source identification. The distribution of P fluxes was unique as it demonstrated both a moderate springtime crustal spikes and the anthropogenic features, suggesting important contributions of both sources to aerosol P over the Gulf (Figure 6). The daily fluxes of trace elements varied up to two orders of magnitude (e.g., Cd, Ni, Cr, etc., Table 5) suggesting the potential importance of individual dust events (Table 5).

[24] The mean atmospheric fluxes of crustally derived elements (e.g., Al, Fe, and Mn) over the Gulf were higher than those measured for the northwestern Mediterranean site [*Chester et al.*, 1999], but comparable to or lower than those estimated for the eastern Mediterranean coast [*Herut et al.*, 2001; *Kocak et al.*, 2005; Table 6]. For elements dominated by anthropogenic sources (Cu, Zn, Pb, and Cd, Table 6), the estimated fluxes over the Gulf are about a factor of 2–4 lower than those measured directly for the northwestern Mediterranean (except Zn flux reported by *Migon et al.* [1997]). This is not surprising because air masses in the northwestern Mediterranean have a lower desert dust component and larger anthropogenic sources compared to the Gulf and the eastern Mediterranean. Our estimated mean fluxes of Cu, Zn, and Pb are about 3–8 times lower than those reported by *Kocak et al.* [2005] but comparable to those estimated by *Herut et al.* [2001] for the eastern Mediterranean coast. The discrepancy between the two previously reported values is most likely due to the different deposition velocities applied by Kocak et al. (0.8–1.4 cm s^{-1}, 2005) and Herut et al. (0.1 cm s^{-1}, 2001) for dry flux calculation respectively. The relatively higher Cd flux estimated over the Gulf compared to the eastern Mediterranean may also be partly explained by the higher deposition velocities (mean 0.36 cm s^{-1}) used in our flux calculation compared to Herut et al. (0.1 cm s^{-1}).

[25] Atmospheric aerosol deposition is an important external source of trace elements to the Gulf of Aqaba. In this system wet deposition and riverine inputs are negligible and the only water source to the Gulf is surface Red Seawater that enters in the upper 70 m of the water column at the Straits of Tiran [*Reiss and Hottinger*, 1984] and can not account for the high trace metal concentrations observed here [*Morley et al.*, 1993]. Accordingly, dry atmospheric deposition may influence the concentrations and distribution of dissolved elements in the water column of the Gulf and may particularly be important in the surface layer during stratification. Moreover, a single dust event may add orders of magnitude higher amounts of trace elements to the Gulf over a short timescale compared to the background deposition flux and could trigger short-term alteration of water chemistry and ecosystem structure [*Jickells*, 1995; *Guerzoni et al.*, 1999]. A significant addition of nutrient elements such as P and micronutrients such as Fe and Zn [*Chen*, 2004; *Chen et al.*, 2007; *Chase et al.*, 2006; *Bruland*, 1989] through aerosol deposition to the Gulf may affect carbon production in this oligotrophic system.

Table 6. Comparison of Trace Element Dry Deposition Fluxes (mg m^{-2} yr^{-1}) Between the Gulf of Aqaba and the Mediterranean Coastal Sites

	Gulf of Aqaba, Current Study	NW Med. Chester et al. [1999]	NW Med. Migon et al. [1997]	Eastern Med. Herut et al. [2001]	Eastern Med. Kocak et al. [2005] Tel Shikmona	Eastern Med. Kocak et al. [2005] Erdemli
Al	342	120	–	521	520	320
Fe	216	88	–	464	420	230
Co	0.1	0.024	0.095	–	–	–
Mn	5.28	2.07	–	10.5	9.0	3.8
Cr	0.96	0.38	–	0.10	–	–
Cu	0.38	1.19	1.61	0.20	2.9	2.6
Ni	0.31	0.33	0.66	–	–	–
Zn	1.68	3.2	41.6	2.39	7.58	5.33
Pb	0.80	1.85	2.56	1.31	6.36	5.65
Cd	0.012	–	0.033	0.008	0.007	0.004

3.6. Residence Times of Trace Elements in the Gulf Surface Water

[26] Trace metal concentrations in 0–50 m surface seawater were measured during the two important hydrographic conditions in the Gulf, the deep mixing (starting in November and increasing in intensity through March and early April) and the stratified period (starting in April and intensifying through November). The residence time of dissolved trace elements in the up 50 m of the Gulf with respect to atmospheric deposition was therefore estimated by dividing the average dissolved trace element inventory by the mean atmospheric flux of the element (Table 7). Such an estimate will inherit the uncertainties associated with the calculation of trace element deposition rate and the measured element solubility in seawater. Residence times of less than 15 years are found for most trace elements in the Gulf surface, while Cd and V demonstrate relatively longer residence times of over 100 years (Table 7). The long residence time estimated for V is consistent with its low-particle reactivity and conservative behavior in seawater, as V exists mostly in seawater as the unreactive oxyanion, vanadate [*Bruland*, 1983]. The estimated residence time 4.9 years for dissolved Fe is about a factor of 3–10 longer than those calculated previously for the surface layer of the North Pacific (0.5 years, *Boyle et al.*, 2005), in the upper 100 m Sargasso Sea (0.7 years, *Jickells*, 1999) and in 0–50 m water column of the Gulf of Aqaba (0.4–1.5 years, *Chase et al.*, 2006). The longer residence time estimated in this study is mainly due to the lower aerosol Fe solubility (0.7%) used for the calculation of atmospheric flux of dissolved Fe compared to previous studies (~30–40%, *Boyle et al.*, 2005; 2%, *Chase et al.*, 2006). The relatively higher dissolved Fe inventory in the Gulf surface water

(up to 6 nmol L^{-1}, *Chase et al.*, 2006) also contributes to the longer residence time calculated. A greater degree of solubilization of aerosol Fe over the North Pacific compared to the Gulf is expected, because of the long transit times (7–14 days to Midway) and atmospheric chemical reactions of aerosols during transport [*Hand et al.*, 2004]. Our estimates of residence times for other trace elements such as dissolved Al, Pb, and Co (5.0, 10 and 13 years, Table 7) in the Gulf surface are comparable or slightly longer than those reported for other oligotrophic surface oceans, for instance, the dissolved Al and Pb in the eastern Indian Ocean (~2 years, *Obata et al.*, 2004), dissolved Pb in the central North Pacific (~2 years, *Nozaki et al.*, 1976) and dissolved Al (5 years, *Measures and Brown*, 1996; *Jickells*, 1999) and Co (7.6 years, *Saito and Moffett*, 2002) in the North Atlantic.

4. Conclusions

[27] Our results indicate that aerosol trace element deposition has an impact on the surface water chemistry of the Gulf and thus may affect the primary production in the surface water by supplying important macro and micro-nutrients or possibly high levels of toxic elements. The study shows that even in an area dominated by mineral dust deposition and surrounded by deserts a significant contribution of anthropogenic air emissions to the levels of various trace elements in aerosols is detected. About 50% of total suspended particles in the air are found to be associated with an anthropogenic sources and a number of trace elements (e.g., Cu, Zn, Pb, Cd, V, and Ni) are found to be mainly derived from anthropogenic emissions. The residence times of trace elements in the Gulf surface (5–37 years) are generally longer than those reported in other oligotrophic surface oceans with respect to the dust input, consistent with the higher dry deposition rates and trace metal concentration in this area. The estimated residence times of a few years for most trace elements suggest the importance of atmospheric trace elements fluxes to the Gulf ecosystem and the episodic nature of some of these deposition events may indicate that specific short term events may have an even larger impact on this system.

Table 7. Average of the 0–50 m Trace Metal Concentrations Measured in the Stratified Summer (August 2003- All But Al, September 2005- Al), Well-Mixed Winter (March 2004- All But Al, November 2004- Al) and Residence Times of Dissolved Trace Metals in the Up 50 m Gulf Surface

	Al	Co	Cu	Ni	Pb	Zn	Fe	Cd	V
0–50 m Ave. Conc. (nmol L^{-1})	38.3	0.09	1.9	1.9	0.39	2.8	2.6	0.6	26.9
Residence time (years)	5.0	13.1	32.3	37.1	10.2	12.6	4.9	339	160

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