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The significance of atmospheric inputs of soluble and particulate major and trace metals to the eastern Mediterranean seawater

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ABSTRACT

Atmospheric deposition (wet and dry) of major and trace metals (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) was monitored at a remote location in the eastern Mediterranean Sea from January 2005 through December 2006. A comparison of atmospheric deposition fluxes with sediment traps data (simultaneously collected) highlighted the significance of atmospheric inputs to the biogeochemical cycling of trace elements.

V, Cr, Fe and Pb were mainly associated with the particulate form (64–98%), whilst for Mn, Zn, Cu and Cd the soluble fraction represents 60–70% of the total input. The solubility of all studied metals in both wet and dry deposition was found to decrease with increasing pH values and increasing dust mass.

Cr, Mn and Cu fluxes were higher during the dry season compared to those measured during the wet season. For the remaining metals the opposite trend is valid, whilst Fe and Zn are removed from the atmosphere almost equally by wet and dry deposition.

Atmospheric deposition of major and trace metals in the eastern Mediterranean Sea was sufficient to balance metals in the water column, indicating the predominant role of atmospheric deposition as an external source of trace elements in the area.

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1. Introduction

The atmosphere is a significant route by which both natural and anthropogenic compounds are transported from land-based sources to coastal and offshore waters (e.g., Duce et al., 1991a,b; Jickells, 1995). This is of particular interest, especially for oligotrophic oceanic areas and semi-enclosed seas, such as the Mediterranean, due to the relative proximity of land-based sources and densely populated shores.

Riverine inputs, to the Mediterranean are limited (Guieu et al., 1997) and localized and will not affect offshore sites such as the Cretan or the Levantine sea (Statham and Hart, 2005). Therefore, atmospheric transport and deposition of major and trace metals to the Mediterranean Sea could be of significant importance. The Mediterranean Sea on its northern shore is bordered by industrialized European countries, which act as a continuous source of anthropogenic derived constituents on the atmosphere, and on the southern shores by the arid and desert regions of north African (Sahara) and Arabian Desert belts, which act as sources of crustal material in the form of non-continuous dust 'pulses' (Martin et al., 1989; Chester et al., 1993, 1999; Guerzoni et al., 1999a). The chemical signature of these two sources, anthropogenic and crustal, is very different particularly regarding their trace metal content. Metals associated with the aerosols can reach the sea surface by dry and wet deposition (in-cloud or below-cloud scavenging). After contact with the seawater the solubility of metals may change as a result of pH changes. During dry deposition aerosols are delivered directly to the sea surface and major and trace metals can solubilize to different extents.

Thus atmospheric deposition may play an important role in the supply of bioavailable nutrients to surface waters and hence marine biological productivity (Duce, 1986; Duce et al., 1991a,b; Young et al., 1991). Therefore a comparison between dry and wet deposition fluxes of metals would be noteworthy regarding the bioavailability and toxicity of the metals in the marine system.

The aim of the current study, therefore is to present a detailed data set on the atmospheric deposition of major and trace metals (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) to the eastern Mediterranean monitored over a two year period (January 2005–December 2006). To our knowledge this is the first time that the relative contribution of both pathways is addressed in a rural area in the eastern Mediterranean as the majority of the published works has focused either on wet (Al-Momani et al., 1998; Kaya and Tuncel, 1997) or dry deposition (Chen et al., 2008; Koçak et al., 2005; Herut et al., 2001). This data set enables the establishment of a reliable quantitative budget of the atmospheric input to the eastern Mediterranean in which both the wet and dry, major and trace metal

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fractions, soluble and particulate, have been identified. Moreover the factors controlling soluble and total metal deposition such as the pH and dust content will be considered. The significance of atmospheric deposition of metals on seawater productivity (e.g. Fe and Mn) in the eastern Mediterranean will be examined by comparing the atmospheric deposition of elements entering the eastern Mediterranean with sediment traps data. Such a comparison will help to quantify the importance of atmospheric inputs as an external source of these elements to Mediterranean waters.

2. Experimental

2.1. Sampling site

Wet and dry deposition samples were collected at Finokalia (35°20′ N, 25°40′E), a remote coastal site in the northeast part of Crete Island, Greece, in the eastern Mediterranean. Finokalia station is situated 70 km northeast of Heraklion, the biggest city of the island and is located at a central position in the Mediterranean Basin. Consequently, the data from this site could be considered representative of the open eastern Mediterranean Sea. Apart from the main sampling site at Finokalia, wet deposition samples were also collected at a secondary station situated at the University of Crete, 6 km south of Heraklion (35°20′N, 25°07′E). Further description of the site and the prevailing meteorology can be found in Arsene et al. (2007). The sediment traps were moored for seven years (1999–2005) in the southern Cretan Sea (along 45°06′E, 500 m and 1715 m depth, Kouvarakis et al., 2001).

2.2. Sampling and analytical techniques

2.2.1. Atmospheric deposition samples

At both locations, Finokalia and Heraklion, wet deposition samples were collected, on an event basis, using wet-only collectors (Van Essen) consisting only of plastic parts, with a lid activated by the rain sensor. Samples were immediately filtered and frozen at the cessation of the event (see below).

In parallel to the wet deposition samples, bulk deposition samples were collected at Finokalia station. Bulk deposition was estimated based on the collection of particles on a flat surface covered by multiple layers of glass beads which can trap larger particles, thus avoiding resuspension. The glass beads were positioned on a funnel installed 3 m above the ground as described by Kouvarakis et al. (2001). The glass bead system was exposed to the atmosphere for 1 to 2 weeks at a time and in the absence of rain it was washed with ultrapure water (500 ml) and treated in the same manner as a rainwater sample. Dry deposition refers to bulk samples not affected by wet deposition, using the bulk deposition collector as discussed above. More details on sample collection can be found in Theodosi et al. (in press).

Wet and bulk deposition samples were filtered immediately after collection, through a pre weighed nitrocellulose filter (Millipore, 0.45 μm) and the pH was immediately determined. A 0.74 N nitric acid solution was used to acidify the samples and then the samples were stored in the freezer until analysis, which was performed within a month. The crustal mass was estimated by pre- and post-weighted cellulose filters.

During the sampling period (January 2005–December 2006) 38 wet-only precipitation samples (*RF*) were collected at Finokalia. In total 49 bulk deposition samples were collected at Finokalia station, out of which 28 can be considered as dry deposition samples as they have not been affected by wet deposition. During the months of May, June and October with a single rain event, the dry deposition was calculated as the difference between bulk and wet deposition.

2.2.2. Aerosol samples

A comparison of dry deposition fluxes using the glass bead collector and those estimated using aerosol concentrations in the fine and coarse fractions was carried out. Aerosol samples were collected at Finokalia station during July 2004–July 2006 using a virtual impactor (VI; Loo and Cork, 1988) modified to separate particles into two size fractions: fine (aerodynamic particle diameter $D_a < 1.3$ μm) and coarse particles ($D_a > 1.3$ μm). The inlet preceding the VI has a cut-off size of 10 μm and the average sampling time for the VIs was two days (from 1 to 3 days).

Polytetrafluoroethylene (PTFE) filters (Millipore Fluoropore; pore size 3.0 μm; diameter 47 mm) were used in the VI sampler (henceforth PTFE-VI). More details on sample collection can be found in Koulouri et al. (2008).

2.2.3. Sediment traps samples

In the southern Cretan Sea, sediment traps were deployed during a seven year period (1999–2005). The sediment trap samplers were moored in the southern Cretan sea at two depths (500 m and 1715 m depth) and the samples were collected, on a two-week basis, using two time-series sediment traps (Technicap PPS3/3) (Markaki, 2008). Each collector consists of 12 cylinders positioned in a circular orientation, with each cylinder having a collection surface of 0.125 m^2.

Immediately after collection every sample was divided into aliquots. The 1/8th or the 1/16th of the sediment trap sample was filtered through a pre-weighted nitrocellulose filter (0.45 μm) for sediment mass determination. The filtered material was then acid digested for total metal detection using ICP-MS.

2.2.4. Analysis

An acid microwave digestion procedure followed by Inductively Coupled Plasma Mass Spectrometry (*ICP-MS, Thermo Electron X Series*) was applied to measure particulate elemental concentrations (V, Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb) in both wet and dry depositions as well as in trap samples. The digestion procedure was performed in Teflon vessels (DAP—60 K, 60 ml/40 bar) with the use of concentrated nitric acid (puriss. p.a., Fluka Prod. No. 84380). The samples were then digested in a Microwave digestion system (*Berghof MWS-2*), where the temperature, pressure and time of the procedure were controlled. The heating program used was 30 min heating at 180 °C and 999 W of microwave power. This first step was repeated and then it was followed by heating at 100 °C and 800 W of microwave power for 20 min. After cooling to room temperature, the digested solution was transferred to an acid-cleaned polyethylene container and stored in the freezer for ICP-MS analysis.

Indium (*In, CPI International, S4400-1000241*) was added as an internal standard to the samples before ICP-MS analysis and calibration curves were performed for each analytical batch using standard certified solutions by CPI International ($r^2 = 0.9999$). The detection limits, defined as three times the standard deviation of the blank value, were (in μg L^{-1}): V = 0.08, Cr = 0.03, Mn = 0.09, Fe = 2.35, Ni = 0.41, Cu = 0.39, Zn = 0.76, Cd = 0.02 and Pb = 0.03. The overall accuracy for both, digestion and analysis, as well as the selection of the isotope for each metal, were verified by three certified marine sediments reference materials (MESS-3, GBW 07313 and BCSS-1) and through intercomparisons with other analytical techniques (ICP-AES, ICP-MS, XRF and GF-AAS) applied by collaborating laboratories. Metal recoveries obtained with the use of certified reference materials and verified with measurements of dry deposition samples by collaborating laboratories were found to be excellent, ranging from 90.0 to 104.1% for all studied elements.

3. Results and discussion

3.1. Major and trace metal wet deposition fluxes

3.1.1. Temporal variability of wet deposition fluxes

Table 1 summarizes the annual wet deposition fluxes for both soluble and total fractions of V, Cr, Mn, Fe, Ni, Zn, Cd and Pb. Total wet

Table 1
Total annual major and trace metal wet deposition fluxes (in mg m^{-2} $year^{-1}$, soluble in parenthesis) for Finokalia station, comparison with literature data from other Mediterranean sites and the years of the sampling period.

Metal	Location					
	NW Med.	NW Med.	Eastern Med.	Eastern Med.	Finokalia Eastern Med.	
					2005	2006
V	–	–	–	0.34 (0.21)	–	0.96 (0.38)
Cr	–	0.50	–	0.31 (0.16)	–	0.87 (0.08)
Mn	–	3.25	–	–	2.7 (2.1)	2.8 (1.1)
Fe	–	168	–	4.00 (0.68)	134 (7.6)	260 (3.1)
Ni	0.36 (0.19)	0.48	–	0.28 (0.20)	0.32 (0.24)	0.80 (0.30)
Cu	1.46 (1.11)	1.27	0.79 (0.30)	0.52 (0.45)	0.36 (0.31)	0.98 (0.60)
Zn	–	0.46	22 (19)	3.40 (2.84)	3.6 (3.2)	3.7 (1.7)
Cd	–	0.16–0.65	7.2 (0.69)	1.50 (0.00)	0.031 (0.028)	0.045 (0.018)
Pb	1.91 (1.24)	1.41	1.6 (0.62)	2.2 (0.87)	0.79 (0.48)	0.93 (0.33)
Sampling period	8 months	3 stations, 21 months	24 months	20 months	24 months	
Reference	Chester et al. (1999)	Guieu et al. (1997)[a]	Al-Momani et al. (1998)	Kaya and Tuncel (1997)	This study	

[a] Wet deposition fluxes have been calculated from total deposition fluxes (Table 4) using the %wet deposition (Table 7).

deposition is defined as the sum of soluble and particulate fluxes. Monthly fluxes have been also estimated to assess the temporal variability of the measured elements over the eastern Mediterranean. Selected representative elements of 'mixed', crustal and anthropogenic origin, respectively, are depicted in Fig. 1a to f. Metal deposition presents a clear seasonal pattern. From November to April rainfall is the main pathway of the atmospheric input of major and trace metals to the sea surface, whereas dry deposition dominates from May to October (see Section 3.2, dry deposition).

Elements of crustal origin such as Fe present a peak value during spring (March and April) due to mineral dust transportation from the arid areas of northern Africa, and the Arabian Peninsula. Mn exhibits in addition a second maximum during the dry season. Given its 'mixed' origin (crustal and anthropogenic), this summer maximum could be attributed to air masses transport from industrialized areas of eastern Europe, enhanced during that period. However as during the whole sampling period Mn was significantly correlated to Fe, it is believed that Mn is mainly crustal in origin in our area.

Finally Pb by presenting two maxima during the wet and dry period resembles to Mn. To determine the prevailing source of atmospheric Pb in the area, the Enrichment Factor was calculated (using Fe as crustal marker; Chester et al., 1990). For our Pb data the low Enrichment Factor (<10) indicates significant contribution from a crustal source. Indeed Ridame et al. (1999) demonstrated that Saharan dust is a potential source of natural Pb to the Mediterranean Sea.

As expected, partitioning between the particulate and soluble forms in wet deposition samples varies among the various metals (Fig. 1). Elements originating from crustal sources such as Fe are mainly deposited in the particulate form. For Mn, Cu, Zn and Cd the soluble fraction varies from 58 to 68% of the wet deposition, whereas for V and Pb the soluble fraction is 40 and 47%, respectively.

3.1.2. Comparison of wet deposition fluxes with literature data

Table 1 compares the annual wet deposition fluxes (mg m^{-2} $year^{-1}$) for both soluble and total fraction of the metals obtained during the current study with the limited wet deposition fluxes data available in the literature.

Despite the different sampling periods covered by previous studies and the possibility of interannual variation, the total and soluble wet deposition atmospheric fluxes of elements such as V, Cr, Mn, Ni and Cu are in good agreement with those reported for the north western and eastern Mediterranean (Guieu et al., 1997; Chester et al., 1999; Kaya and Tuncel, 1997).

Wet deposition fluxes of Zn, Cd and Pb, dominated by anthropogenic sources show a notable site by site variability. The total wet deposition Zn flux was 6 times lower than values reported by Al-Momani et al. (1998) collected at a rural site in the eastern Basin. For the case of Cd wet depositional fluxes are lower by a factor of 37 to 180 in comparison to those reported by Kaya and Tuncel (1997) and Al-Momani et al. (1998) (1.50 and 7.2 mg m^{-2} $year^{-1}$, respectively) for the eastern Mediterranean. Moreover the values are more in the range of the values presented by Guieu et al. (1997) in the north western Mediterranean, 0.16–0.65 mg m^{-2} $year^{-1}$. Therefore these metal fluxes are not representative of a long-range transport to the Mediterranean, but more likely as a result of a local/regional contamination. The lower wet deposition fluxes observed for metals such as Cd and Pb, are likely to be due to a combination of factors including a reduction in their source emissions and the occurrence of local sources (Ridame et al., 1999).

3.1.3. Solubility of major and trace metals in wet deposition samples

Solubility is defined as the percentage of the soluble metal concentration divided by its total (soluble plus particulate) concentration (Baker et al., 2006). Metal dissolution can be influenced by a number of parameters: chemical, biotic and physical processes such as pH, presence of dissolved organic complexing ligands, particle size, concentration, bacteria, phytoplankton, and temperature (Chester et al., 1990, 1993; Lim et al., 1994; Bonnet and Guieu, 2004). Evaluation of the metal soluble and particulate fraction is essential since soluble and particulate metals will have different fates in the oceans, especially with respect to bioavailability.

Mean solubilities of all metals estimated during the studied period were compared with solubilities reported in the literature for north western and eastern Mediterranean regions (Table 2). For all measured metals the solubility compares favourably with those reported for other Mediterranean coastal sites (Guieu et al., 1997; Lim et al., 1994; Table 2). The impact of factors such as pH and dust content on major and trace metal solubility will be examined in the following sections.

3.1.3.1. Major and trace metals solubility as a function of rainwater pH. The pH of rainwater appears to be one of the dominant parameters controlling the phase distribution of metals in deposition samples (Lim et al., 1994). Additional data from wet deposition samples collected at Heraklion during the same sampling period as in Finokalia have been included to serve as a comparison for the observations in wet deposition at Finokalia. Figs. 2 and 3 present the solubility of selected metals as a function of pH for the two sampling sites in the Levantin basin. These figures demonstrate that for both stations the soluble fraction for all studied metals is usually higher than 60–80% (especially for Mn, Ni, Cu and Cd) in the low pH range (3.5–6.5) whilst this decreases considerably at higher pH values.

In particular, both at Heraklion and Finokalia the maximum metal solubility lies between pH 4 and 6 (Figs. 2 and 3), characteristic of anthropogenically influenced rainwater (Loye-Pilot and Morelli, 1988). Whilst the minimum values are observed at pH values close to 8, characteristic of Saharan-influenced rain (Mahowald et al., 2005).

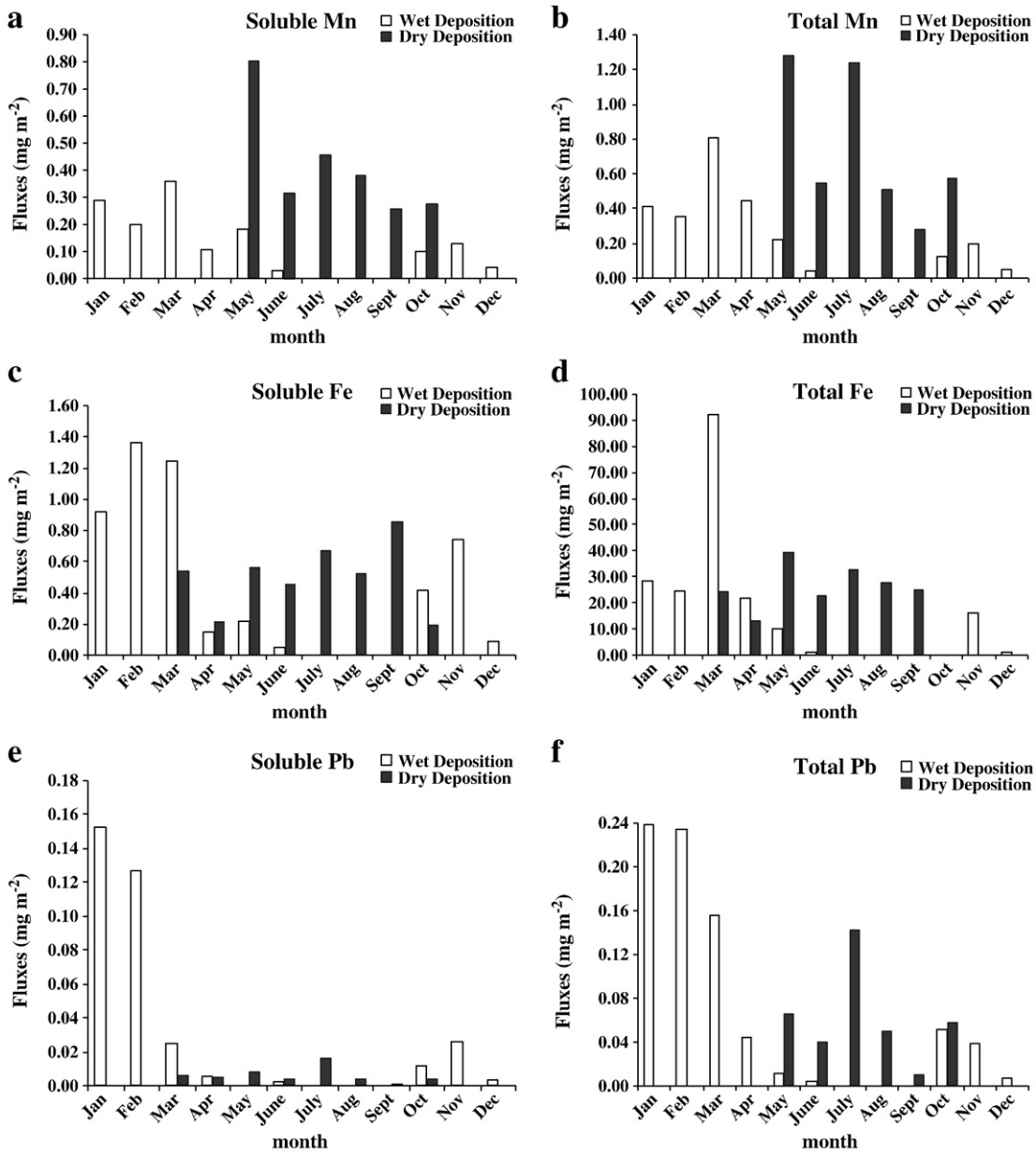

Fig. 1. Temporal variability of monthly averaged fluxes of soluble and total inputs of Mn (a, b) Fe (c, d) and Pb (e, f) in wet and dry deposition samples collected at Finokalia during the sampling period January 2005–December 2006.

Table 2
Estimated average (volume weight mean in parenthesis) solubilities for wet deposition samples of all major and trace metals at Finokalia and comparison with solubilities from the Mediterranean.

Metal	% Solubilities wet deposition			
	Location			
	Finokalia station Eastern Med.	NW Med.		Western Med.
		Tour du Valat	Cap Ferrat	Corsica
V	70 ± 29 (50)	–	–	–
Cr	44 ± 36 (11)	–	–	–
Mn	69 ± 26 (56)	63 ± 28	60	–
Fe	18 ± 23 (2.3)	11 ± 16	–	–
Ni	59 ± 26 (49)	58 ± 36	54	–
Cu	68 ± 28 (64)	71 ± 21	82	48 ± 32
Zn	62 ± 31 (64)	68 ± 30	–	72 ± 30
Cd	72 ± 30 (68)	75 ± 26	92	
Pb	47 ± 36 (50)	52 ± 30	65	53 ± 37
Reference	This study	Guieu et al. (1991, 1997)		Lim et al. (1994)

Moreover solubilities of Cr, Fe, Zn, Cd and Pb can vary up to one or two orders of magnitude. For instance the solubility of Cd decreases from 92% to 3% for a pH variation between 4 and 8, respectively. Regarding the variation in solubility as a function of pH, the studied metals are divided into two groups. For elements such as Fe and Pb the inflection point of their pH/solubilities curves occurs at pH between 5 and 6, whereas for elements such as V, Cr, Ni and Cd the inflection point occurs at pH higher than 6. This is clearly seen in Fig. 2 (a–f) where the solubility of metals as a function of pH is presented. The behavior of elements such as Fe presenting an early infection point at pH around 5 could be explained by considering its solid state speciation (e.g. content in insoluble forms like hematite). Elements such as V, Ni, Zn and Cd associated with anthropogenic sources, illustrate distinct behavior with relatively higher inflection points. Pb was expected to demonstrate similar behavior as Zn and Cd, however it behaves similar to Fe denoting significant contribution from crustal sources (see Section 3.1.3.2).

The pH dependence of solubility for Cu, Zn and Pb determined during this study is comparable with results reported in literature by Lim et al.

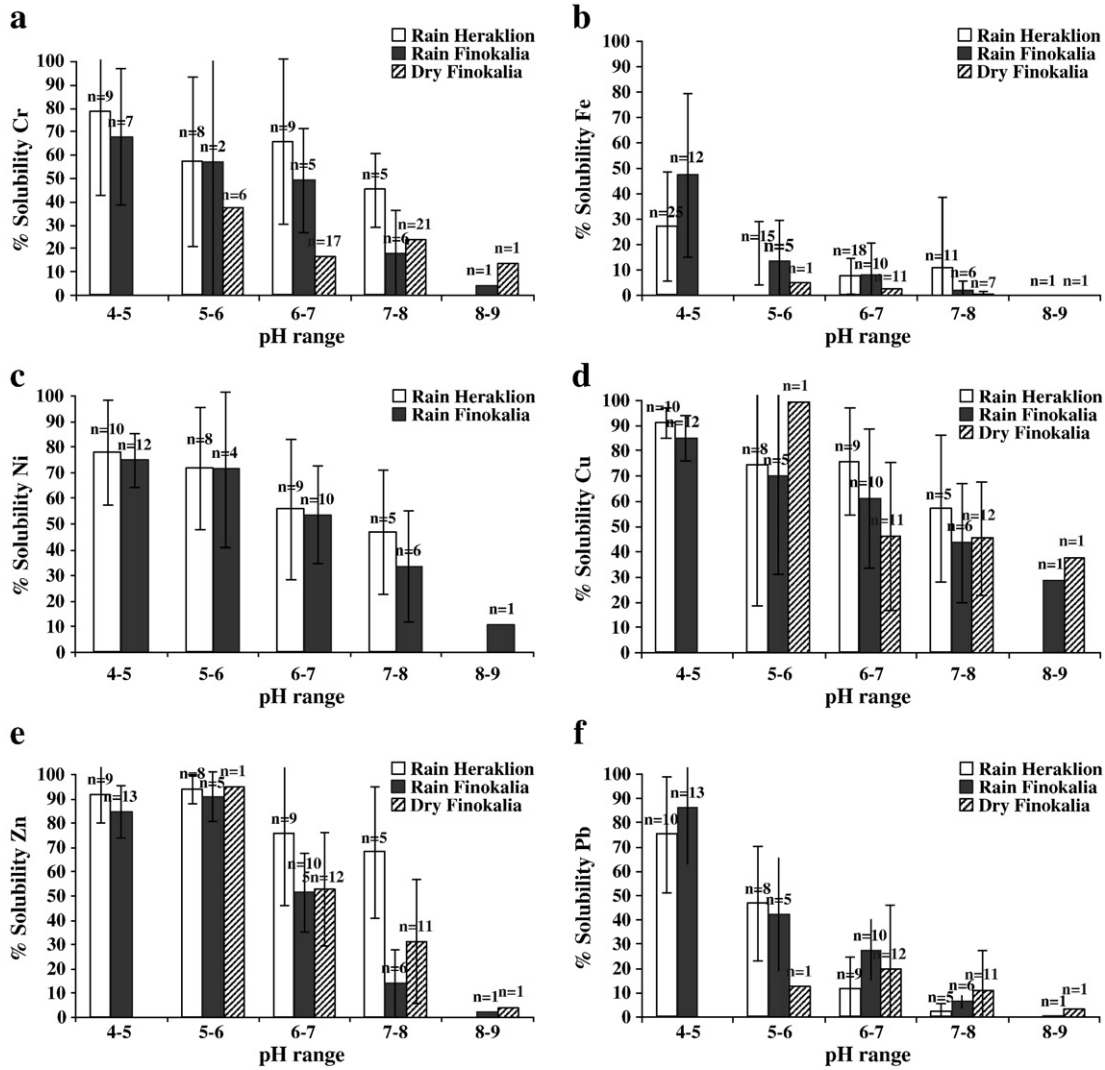

Fig. 2. Variation of solubility as a function of pH for various elements: (a) Cr, (b) Fe, (c) Ni, (d) Cu, (e) Zn and (f) Pb.

(1994). For Zn similar observations as in Figs. 2e and 3d have been reported in western Mediterranean rainwater samples ($n = 11$) by Losno et al. (1988), where the majority of the Zn is soluble in the samples with pH lower than 5.5. In contrast an abrupt decrease in zinc solubility has been observed for higher pH values.

3.1.3.2. Major and trace metals solubility as a function of dust load. In addition to pH, metals partitioning in deposition samples are affected by the abundance of crustal material since elements in soil can be in forms of hydroxides, oxyhydroxides, silicates, sulfides, etc., which are less soluble than oxides commonly found in anthropogenic emissions (Chester et al., 1993). Thus the amount of crustal material present is expected to influence the solubility of metals.

Fig. 4 (a–f) depicts the solubility of selected metals as a function of dust load (mg m^{-2}) in rainwater. All studied elements are more soluble when the dust load present decreases. During high dust loadings the source is likely to be more crustal in nature and hence the associated metals are likely to have a lower "exchangeable" phase association. It is also clear that high dust loads will lead to a greater "particle effect" which will also lead to a lower observed metal solubility (Herut et al., 2001; Koçak et al., 2005). This could be substantial for elements such as Pb, for which the dust load ranges from 0 to 70 mg m^{-2} and leads to solubility of $74 \pm 23\%$, whereas for dust load greater than 500 mg m^{-2} the solubility decreases to 0.3%.

3.2. Major and trace metal dry deposition fluxes

3.2.1. Validation of dry deposition fluxes

Dry atmospheric deposition flux (DF_x) can been calculated by a number of methods: (i) by collecting fine and coarse aerosols using the virtual impactor (Bergametti, 1987), (ii) from theoretical models (Dulac et al., 1989), (iii) by collecting material on surrogate surfaces (Dolske and Gatz, 1985; Baeyens et al., 1990) and (iv) by subtracting wet deposition from the total deposition (Migon et al., 1997). There have been very few studies over the last decade that have attempted to estimate the dry deposition of metals in the Mediterranean Sea: in the western Basin by Guieu et al. (1997) and Chester et al. (1999) and in the eastern Basin only one has been reported by Muezzinoglu and Cizmecioglu (2006) at an urban site for a series of heavy metals based on a 9 month sampling period.

At the Finokalia sampling station, dry deposition of major and trace metals has been estimated in two ways: i) by collecting aerosol samples in the two fractions (fine and coarse) and ii) by using a glass bead collector.

Dry deposition of a metal x (DF_x) is calculated as the product of the following equation.

$$DF_x = C_x \cdot V_d \quad (1)$$

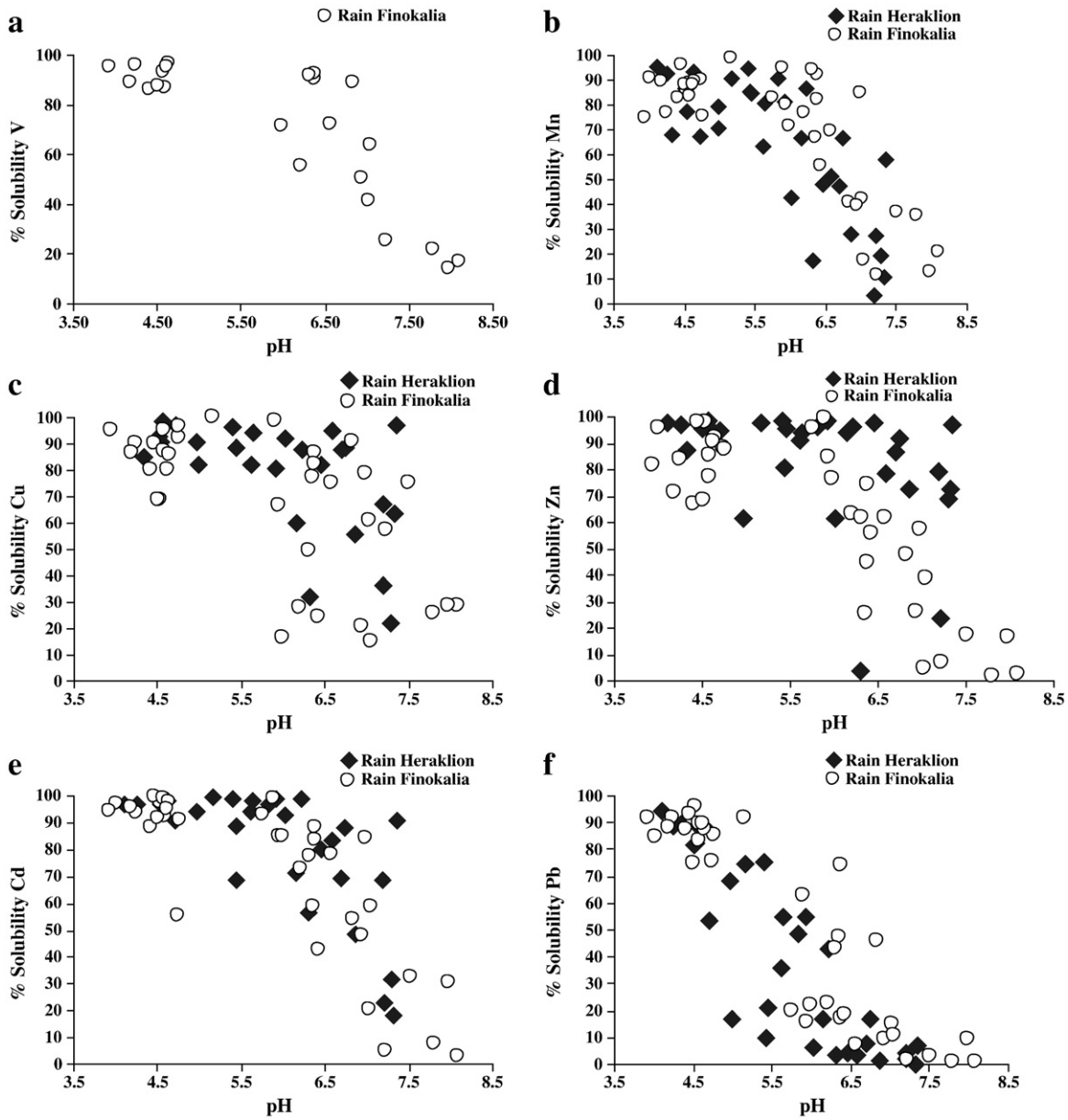

Fig. 3. Variation of solubility as a function of pH for: (a) V, (b) Mn, (c) Cu, (d) Zn, (e) Cd and (f) Pb.

The mean deposition velocities values adopted here are 2 cm s^{-1} for the coarse particles and 0.1 cm s^{-1} for the fine (Duce et al., 1991a, b; Koçak et al., 2005). Using these dry deposition velocities and metal concentrations in atmospheric aerosols (fine plus coarse concentrations) collected at Finokalia station during the 2005–2006 period the DF_x was calculated.

These calculated DF_x fluxes are compared in Table 3 with those measured using the glass bead collector. For the majority of metals (V, Cr, Mn, Fe, Cu, Zn and Pb) the observed and calculated dry deposition fluxes agree within a factor of 2 to 3 which is reasonable given the uncertainty existing in V_d estimation. For these metals, the adopted average depositional velocities (Duce et al., 1991a,b) are apparently appropriate to predict dry deposition fluxes. In contrast, Cd shows the largest discrepancy, as the calculated dry deposition flux is by a factor of 5 higher than the measured one (3 if the geometric mean value is used), probably indicating that the deposition velocities used for Cd are inadequate. Note that Cd is of anthropogenic origin and primarily associated with submicrometer particles (<1 μm) (Guerzoni et al., 1999b).

The dry deposition fluxes presented hereafter refer to the measured fluxes by the glass bead collector as they cover a longer sampling period and correspond to measurements carried out in parallel with wet deposition collection.

3.2.2. Temporal variability of measured dry deposition fluxes

The measured dry deposition fluxes of soluble and total metals for the eastern Mediterranean are given in Fig. 1a to f as monthly averaged trace element fluxes at Finokalia during the whole sampling period, January 2005–December 2006. It is clearly shown that dry deposition is the main mechanism of atmospheric inputs, both soluble and total, into the oceans during summer and autumn (Kouvarakis et al., 2001; Markaki et al., 2003).

Table 4 compares the dry deposition fluxes measured at Finokalia with those reported in the literature. Note that the majority of published dry deposition fluxes derived indirectly (Eq. (1)). The measured dry deposition fluxes of crustal elements (e.g. Fe) reported during this work compare well with those calculated for the eastern Mediterranean coast (Koçak et al., 2005, in the case of Erdemli) or for

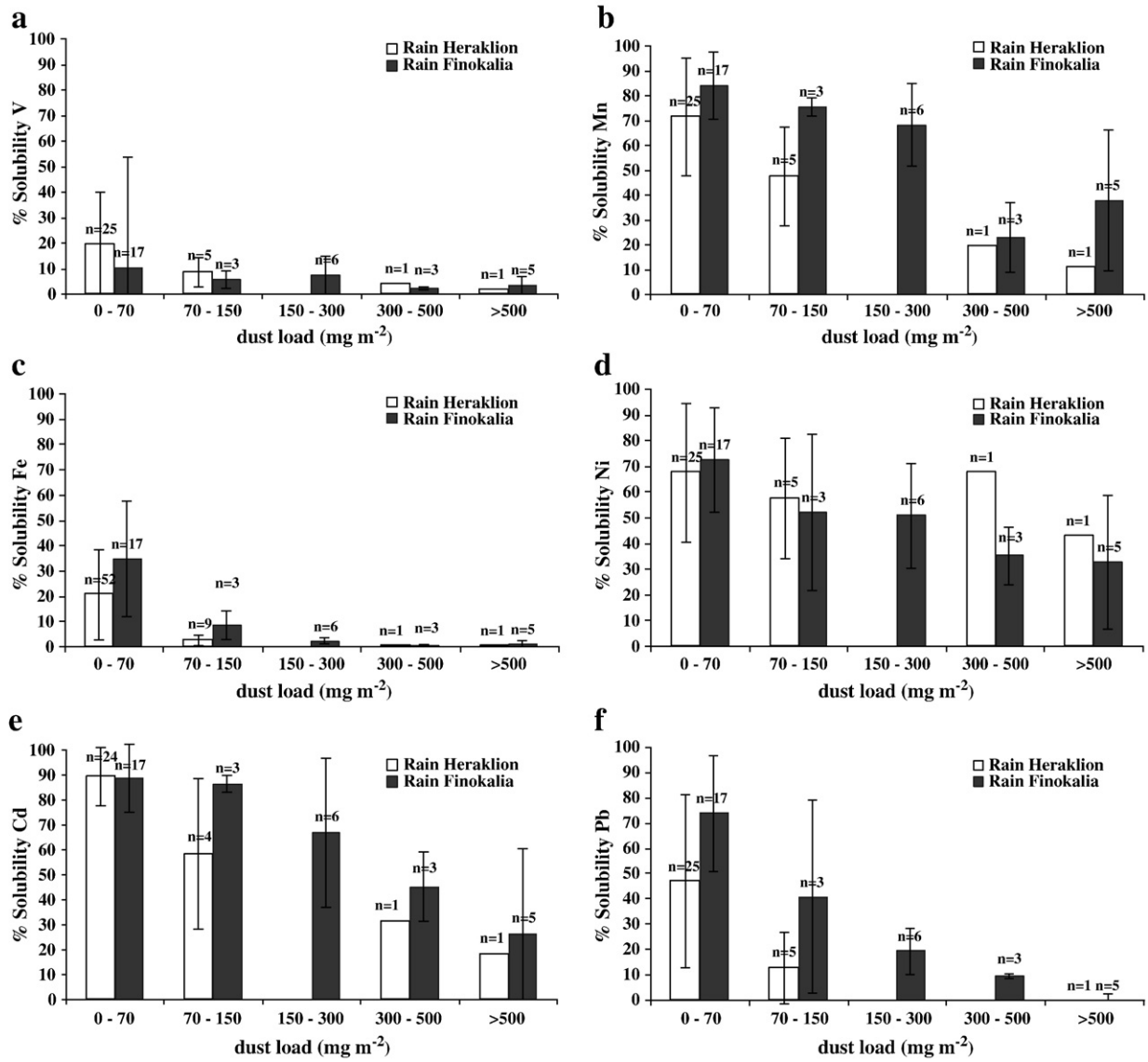

Fig. 4. Variation of solubility as a function of dust load for various elements: (a) V, (b) Mn, (c) Fe, (d) Ni, (e) Cd and (f) Pb.

Aqaba (Chen et al., 2008). Comparison of dry deposition fluxes for crustal elements (Fe and as mentioned earlier Mn) suggested that the eastern Mediterranean receives 2 to 4 times higher aerosol dry deposition than the western Mediterranean. An important Fe interannual variability can be also seen from our results due to variability in dust loadings (10 versus 14.1 g m^{-2} year^{-1} during 2005 and 2006, respectively). Significant interannual variability can also be seen from our results for Fe due to the correlation between dust and TFe observed, indicating the importance of mineral dust in cycling of Fe over the eastern Mediterranean (Theodosi et al., in press).

For elements dominated by anthropogenic sources (e.g. Cu, Zn, Cd and Pb), the values measured at Finokalia are either in agreement (Cu, Zn and Cd) or lower (Pb) than those reported for the eastern Mediterranean. This difference could be because of the high number of crustal events in those sampling sites during their study period or to interannual variability. Moreover it could be due to either the deposition velocities applied by Koçak et al. (2005) (0.8–1.4 cm s^{-1}) and Herut et al. (2001) (0.1 cm s^{-1}) for the dry flux calculation and/or the difference in source regions (see Section 3.1.2). The relatively low value reported here for Pb, 3 to 16 times lower than reported in the literature, could be attributed to the restrictions in the use of Pb additives in gasoline, which have resulted in a decrease in the European atmospheric lead emissions (Ridame et al., 1999).

Table 3
Measured and calculated dry deposition fluxes at Finokalia sampling site.

mg m^{-2} month^{-1}	Dry deposition	
	Calculated	Measured
V	0.10 ± 0.08 (0.07)	0.07 ± 0.01 (0.06)
Cr	0.15 ± 0.05 (0.14)	0.19 ± 0.26
Mn	0.23 ± 0.18 (0.14)	0.88 ± 0.44 (0.77)
Fe	10 ± 8 (6)	22 ± 3 (25)
Cu	0.07 ± 0.02 (0.07)	0.19 ± 0.09 (0.18)
Zn	1.2 ± 0.54 (1.1)	0.75 ± 0.48 (0.64)
Cd	0.020 ± 0.019 (0.013)	0.004 ± 0.002 (0.003)
Pb	0.16 ± 0.06 (0.15)	0.06 ± 0.05 (0.05)

Both measured and calculated values are presented as average ± standard deviation (geometric mean).

3.2.3. Solubility of major and trace metals in dry deposition

Mean solubilities for trace metals determined in dry deposition samples collected at Finokalia are given in Table 5. Since dry deposition samples derive from washing the particles collected on the glass beads with ultrapure water (pH = 5.5), the solubility will

Table 4
Total annual major and trace metal dry deposition fluxes (in mg m^{-2} $year^{-1}$, soluble in parenthesis) for Finokalia station and comparison with literature data from other Mediterranean sites.

Metal	Location							
	NW Med.	NW Med.	Gulf of Aqaba	Eastern Med.		Eastern Med.	Finokalia Eastern Med	
				Tel Shikm.	Erdemli		2005	2006
	Measured values	Calculated values	Calculated values	Calculated values		Calculated values	Measured values	
V	–	–	–	–	–	–	–	0.39 (0.05)
Cr	0.38	–	0.96	–	–	0.10	–	6.8 (0.54)
Mn	2.07 (0.4)	–	5.28	9	3.8	10	4.8 (4.2)	7.1 (3.7)
Fe	88 (8.8)	–	216	420	230	496	132 (4.1)	256 (2.4)
Cu	1.19 (0.33)	1.61	0.38	2.9	2.6	0.178	2.0 (1.9)	1.3 (0.44)
Zn	3.2 (1.5)	41.6	1.68	7.58	5.33	2.806	3.3 (3.0)	4.4 (1.3)
Cd	–	0.033	0.012	0.007	0.004	0.008	0.017 (0.015)	0.034 (0.015)
Pb	1.85 (0.55)	2.56	0.8	6.36	5.65	1.08	0.21 (0.05)	0.60 (0.05)
Reference	Chester et al. (1999)	Migon et al. (1997)	Chen et al. (2008)	Koçak et al. (2005)		Herut et al. (2001)	This study	

depend on the amount of water used (500 ml) and consequently the solubility values reported are considered to be a lower limit. However, they can provide important information as the pH of dry deposition samples is closer to that of seawater compared to that of the wet deposition samples.

For all trace elements solubility decreases with increasing pH as it has been observed for wet deposition samples (Figs. 2 and 3). In addition similar values have been observed between the two deposition modes for similar pH ranges. Indeed solubility of metals of crustal origin, such as Fe, decreases from 10% for pH greater than 5 to 2.9 and 0.8% respectively for pH between 7 and 8. In the case of Cd and Pb lower solubilities are observed compared to previous studies. For Pb, solubility is less than 20% for pH greater than 6 and decreases down to 7% for pH greater than 7. Similar relationship between solubility and pH has been noted for Mn, Cu, Zn and Cd with values comparable to those for rainwater samples. In addition to pH, similar behavior to wet deposition samples has been observed with dust load in dry deposition samples. The presence of high dust load decreases metal solubility.

Solid state speciation of aerosols can explain the increase in solubility with decreasing pH and decreasing aerosol dust, i.e. with increasing anthropogenic influence for all presented major and trace metals. Indeed Koçak et al. (2007) by applying the solid state speciation scheme proposed by Chester et al. (1994) to eastern Mediterranean aerosols, reported for Zn, Cd, Pb, and to lesser extent Fe, an increase in their percent exchangeable fraction (the most mobile) with a corresponding increase in anthropogenic influence (or a decrease in crustal contributions). In addition, "atmospheric processing" i.e. potential surface evaporation and condensation reactions taking place during transport within anthropogenically influenced air masses, might modify the solid phase association at the particle surface, leading to an enhanced solubility (Spokes and Jickells, 1996).

Table 5
Estimated average (volume weight mean) solubilities for dry deposition samples of all major and trace metals at Finokalia and comparison with solubilities from north western Mediterranean and Gulf of Aqaba.

Metal	Location		
	% Solubilities dry deposition		
	Finokalia station Eastern Med.	NW Med.	Gulf of Aqaba[a]
V	12 ± 6 (11)	–	–
Cr	19 ± 35 (11)	–	–
Mn	56 ± 27 (54)	20	–
Fe	2 ± 2 (2)	10	0.7
Cu	52 ± 26 (41)	28 ± 8	49
Zn	48 ± 29 (44)	47 ± 7	44
Cd	57 ± 24 (54)	–	85
Pb	14 ± 13 (11)	30 ± 5	50
Reference	This study	Chester et al. (1990, 1999)	Chen et al. (2008)

[a] Mean seawater solubilities.

3.3. Total atmospheric deposition in the eastern Mediterranean environment

3.3.1. Wet versus dry deposition fluxes

Based on the two year observations, a budget of the atmospheric inputs of both major and trace metals in the eastern Mediterranean can be established. The relative contribution of the wet and dry deposition as well as the soluble and particulate fractions has been quantified (Table 6).

For most of the metals, dry deposition appears to be the predominant removal pathway. Mn and Cu are essentially deposited by dry deposition, which represents 69% and 70% of the total atmospheric inputs, respectively. In contrast, Fe and Zn are removed from the atmosphere almost equally by wet and dry deposition. Finally 59–71% of V, Cd and Pb are deposited to the sea surface mainly through wet deposition, where V and Pb mainly occur in the insoluble form (68% and 64% of the total atmospheric deposition, respectively) and Cd in the soluble 60%. Mn, Cu and Zn are mainly in soluble forms in the total atmospheric deposition (61–70%).

The soluble fraction for most of the studied metals (V, Zn, Cd and Pb) has a higher contribution to wet deposition compared to dry deposition due to the lower pH of the latter.

A comparison between the atmospheric fluxes of metals calculated at Finokalia with other Mediterranean coastal sites is presented in Table 7. With few exceptions such as Cd and Pb for which depositions are about 2–4 times lower than those measured by Guieu et al. (1997) and Chester et al. (1999), good agreement exists for the deposition of the other metals between the two Mediterranean basins.

Table 6
Relative contribution of soluble and particulate fractions of metals in total atmospheric deposition (Finokalia station, 2005–2006).

	Wet deposition		Dry deposition		Total deposition	
	% Soluble	% Particulate	% Soluble	% Particulate	% Soluble	% Particulate
V	28	43	4	25	32	68
Cr	1	10	7	82	8	92
Mn	18	13	46	23	64	36
Fe	1	49	1	49	2	98
Cu	20	9	50	21	70	30
Zn	32	16	29	23	61	39
Cd	36	23	24	17	60	40
Pb	32	36	4	28	36	64

Table 7
Total atmospheric deposition fluxes of major and trace metals (sum of wet and dry deposition, in mg m^{-2} $year^{-1}$ and soluble in parenthesis) at Finokalia station, comparison with literature data.

Metal	Location					
	NW Med.	NW Med.	Whole Med.	Western Med.	Finokalia Eastern Med	
					2005	2006
V	–	–	–	–	–	1.4 (0.43)
Cr	2.5	–	–	–	–	7.7 (0.62)
Mn	5.7	–	–	–	7.5 (6.3)	9.9 (4.8)
Fe	840	–	619	788	266 (12)	516 (5.5)
Cu	2.7	2.65	–	–	2.4 (2.2)	2.3 (1.0)
Zn	2	–	9.6	12.1	6.9 (6.3)	8.1 (3.0)
Cd	0.31–1.3	–	0.036	0.04	0.047 (0.043)	0.079 (0.033)
Pb	3.2	3.76	1.43	1.45	1.0 (0.53)	1.5 (0.38)
Sampling period	3 stations, 21 months	144 days	12 months	12 months	24 months	
Reference	Guieu et al. (1997)	Chester et al. (1999)	Guieu et al. (2010)	Guieu et al. (2010)	This study	

4. Atmospheric versus vertical fluxes through the seawater column

Once metals (from various sources) are deposited to sea surface they will be either assimilated by marine biota or transferred directly through the water column. The latter will be collected by sediment traps. Thus by comparing influx (atmospheric deposition) with the outflow from the marine upper layer, an estimation of the importance of atmospheric deposition can be obtained.

Sediment traps can provide reliable estimates of the outflow of metals from the euphotic zone. Although a similar approach has been successfully used for nutrients such as nitrogen (Kouvarakis et al., 2001) no data exists on major or trace metals in the eastern Mediterranean. There is only one study, performed in the western Basin by Migon et al. (2002) based on a limited data set (six month sediment trap sampling).

The atmospheric deposition estimates of major and trace metals derived during the current study are compared (Table 8) with results from sediment traps data. The values presented here refer to sediment traps moored at 1715 m since no significant difference was reported between the sediment traps deployed at different depths (Markaki, 2008).

As the sediment trap samples collected during 2005 cover only a six month period (January to June), Table 8 includes the 2005 sediment trap data and the mean values obtained during the whole sampling period (1999–2005, Markaki, 2008). Total atmospheric deposition fluxes during the same periods (January to June 2005) and the average for the two year period of our study (2005–2006) are also included in Table 8.

The average total atmospheric depositions of Cr, Cu and Cd are equal or even higher to the fluxes derived from sediment trap deployment. Thus atmospheric deposition entirely dominates the total external input of those elements in the Mediterranean. The same was also valid for Cr and Cd when the fluxes of the common period (January 05–June 05) are considered. For the whole sampling period for V, Mn, Fe, Zn, and Pb atmospheric deposition supplies 67–79% of the fluxes measured in the water column of the Cretan Sea. Taking into consideration the 6-month common period, Zn and Pb are exclusively attributed to the atmosphere, whilst for Mn, Fe and Cu 54–74% of the fluxes in the seawater of the Cretan Sea are provided by wet and dry atmospheric deposition.

Therefore for the majority of the metals the atmosphere delivers more than half of the amount collected in the sediment traps, indicating the predominant role of atmospheric deposition as an external source of trace elements in the area. Hence, atmospheric deposition is sufficient to balance major and trace metals, in both particulate and soluble forms, to the seawater of the eastern Mediterranean.

Table 8
Major and trace metals atmospheric fluxes during 2005–2006 (mg m^{-2} $year^{-1}$) and fluxes in the water column of the Cretan Sea (mg m^{-2} $year^{-1}$) at 1715 m depth during 2005 and 1999–2005.

Metal	Sediment trap fluxes		Total atmospheric deposition 2005–6 months	Total atmospheric deposition 2005–2006
	1715 m, 1999–2005	1715 m, 2005–6 months		
V	2.1	1.2	–	1.4
Cr	7.5	1.7	2.9	7.7
Mn	11	6.8	5.0	8.7
Fe	511	287	157	391
Cu	2.5	1.1	0.59	2.3
Zn	10	3.7	4.0	7.5
Cd	0.04	0.003	0.030	0.063
Pb	1.7	1.0	0.91	1.3

5. Conclusion

A detailed data set on atmospheric deposition of major and trace metals (V, Cr, Mn, Fe, Ni, Zn, Cd and Pb) to the eastern Mediterranean, covering a two year period is reported in this work. The major findings of this study can be summarized as follows:

- Partitioning of atmospheric deposition between soluble and insoluble fractions demonstrated that V, Cr, Fe and Pb are mainly in the particulate form (64–98%). For Mn, Zn, Cu and Cd, the soluble fraction represents 60–70% of the total atmospheric input.
- Mean solubility for all metals in both wet and dry deposition appears to be related to pH and dust mass. More precisely solubility decreases with increasing pH values and increasing dust mass.
- Monthly deposition fluxes as well as the relative contribution of wet versus dry deposition modes have been estimated for all studied metals. Cr, Mn and Cu are removed from the eastern Mediterranean atmosphere by dry deposition, whilst Fe and Zn almost equally by wet and dry deposition whereas the rest of the studied metals via wet deposition.
- Finally by comparing atmospheric deposition fluxes of metals with data from sediment trap collectors, the significant role of the atmosphere as an external source of major and trace metals to the eastern Mediterranean seawater has been demonstrated.

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References

Al-Momani, I.F., Aygun, S., Tuncel, G., 1998. Wet deposition of major ions and trace elements in the eastern Mediterranean basin. Journal of Geophysical Research 103 (D7), 8287–8299.

Arsene, C., Bougiatioti, A., Kanakidou, M., Bonsang, B., Mihalopoulos, N., 2007. Tropospheric OH and Cl levels deduced from non-methane hydrocarbon measurements in a marine site. Atmospheric Chemistry and Physics 7, 4661–4673.

Baeyens, W., Dehairs, F., Dedeurwaerder, H., 1990. Wet and dry deposition fluxes above the North Sea. Atmospheric Environment 24A, 1693–1703.

Baker, A.R., Jickells, T.D., Witt, M., Linge, K.L., 2006. Trends in the solubility of iron, aluminium, manganese and phosphorus in aerosol collected over the Atlantic Ocean. Marine Chemistry 98, 43–58.

Bergametti, G. (1987). Apports de matiere par voie atmosphtrique a la Mediterranee Occidentale. Ph.D. thesis, Universite de Paris 7, 296 pp.

Bonnet, S., Guieu, C., 2004. Dissolution of atmospheric iron in seawater. Geophysical Research Letters 31, L03303. doi:10.1029/2003GL018423.

Chen, Y., Paytan, A., Chase, Z., Measures, C., Beck, A.J., Sanudo-Wilhelmy, S.A., Post, A.F., 2008. Sources and fluxes of atmospheric trace elements to the Gulf of Aqaba, Red Sea. Journal of Geophysical Research 113, D05306. doi:10.1029/2007JD009110.

Chester, R., Nimmo, M., Murphy, K. J. T., and Nicholas, E. (1990). Atmospheric trace metals transported to the Western Mediterranean: Data from a station on Cap Ferrat, EROS 2000 2nd workshop. Water Pollution Research Report, 20, pp. 597–612, March 90, Blanes, Spain.

Chester, R., Murphy, K.J.T., Lin, F.J., Berry, A.S., Bradshaw, G.A., Corcoran, P.A., 1993. Factors controlling the solubilities of trace metals from non-remote aerosols deposited to the sea surface by the 'dry' deposition mode. Marine Chemistry 42, 107–126.

Chester, R., Bradshaw, G.F., Corcoran, P.A., 1994. Trace metal chemistry of the North Sea particulate aerosol; concentrations, sources and sea water fates. Atmospheric Environment 28 (17), 2,873–2,883.

Chester, R., Nimmo, M., Preston, M.R., 1999. The trace metal chemistry of atmospheric dry deposition samples collected at Cap Ferrat: a coastal site in the Western Mediterranean. Marine Chemistry 68, 15–30.

Dolske, D.A., Gatz, D.F., 1985. A field intercomparison of methods for the measurement of particle and gas dry deposition. Journal of Geophysical Research 90, 2076–2084.

Duce, R.A., 1986. The impact of atmospheric nitrogen, phosphorus and iron species on marine biological productivity. In: Buat-Menard, P. (Ed.), The Role of Air–Sea Exchange in Geochemical Cycling: NATO AS1 Series, Series C, vol. 185, pp. 497–529.

Spokes, L.J., Jickells, T.D., 1996. Factors controlling the solubility of aerosol trace metals in the atmosphere and on mixing into seawater. Aquatic Geochemistry 1, 355–374.

Duce, R.A., Liss, P.S., Merrill, J.T., Atlas, E.L., Baut-Menard, P., Hicks, B.B., Miller, J.M., Prospero, J.M., Arimoto, R., Church, T.M., Ellis, W.G., Galloway, J.N., Hansen, L., Jickells, T.D., Knap, A.H., Reinhardt, K.H., Schneider, B., Soudine, A., Tokos, J.J., Tsunogai, S., Wollast, R., Zhou, M., 1991a. The atmospheric input of trace species to the world ocean. Global Biogeochemical Cycles 5, 193–259.

Duce, R.A., Tindale, N.W., Duce, R.A., Tindale, N.W., 1991b. Atmospheric transport of iron and its deposition in the ocean. Limnology and Oceanography 36, 1715–1726.

Dulac, F., Buat-Menard, P., Ezat, U., Melki, S., Bergametti, G., 1989. Atmospheric input of trace metals to the western Mediterranean: uncertainties in modeling dry deposition from cascade impactor data. Tellus 41B, 362–378.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loye-Pilot, M.-D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., Ziveri, P., 1999a. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Progress in Oceanography 44, 147–190.

Guerzoni, S., Molinaroli, E., Rossini, P., Rampazzo, G., Quarantotto, G., De Falco, G., Cristini, S., 1999b. Role of desert aerosol in metal fluxes in the Mediterranean Area. Chemosphere 39 (2), 229–246.

Guieu, C., Martin, J.M., Thomas, A.J., Elbaz-Poulichet, F., 1991. Atmospheric versus river input of metals to the Gulf of Lions: total concentrations, partitioning and fluxes. Marine Pollution Bulletin 22, 176–183.

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 north western Mediterranean. Deep-Sea Research II 44 (3–4), 665–674.

Guieu, C., Loÿe-Pilot, M.-D., Benyaya, L., Dufour, A., 2010. Spatial variability of atmospheric fluxes of metals (Al, Fe, Cd, Zn and Pb) and phosphorus over the whole Mediterranean from a one-year monitoring experiment: Biogeochemical implications. Marine Chemistry 120, 165–179.

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

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

Kaya, G., Tuncel, G., 1997. Trace element and major ion composition of wet and dry deposition in Ankara, Turkey. Atmospheric Environment 31, 3985–3998.

Koçak, M., Kubilay, N., Herut, B., Nimmo, M., 2005. Dry atmospheric fluxes of trace metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin: a refined assessment. Atmospheric Environment 39, 7330–7341.

Koçak, M., Kubilay, N., Herut, B., Nimmo, M., 2007. Trace metal solid state speciation in aerosols of the Northern Levantine Basin, East Mediterranean. Journal of Atmospheric Chemistry 56, 239–257.

Koulouri, E., Saarikoski, S., Theodosi, C., Markaki, Z., Gerasopoulos, E., Kouvarakis, G., Mäkelä, T., Hillamo, R., Mihalopoulos, N., 2008. Chemical composition and sources of fine and coarse aerosol particles in the Eastern Mediterranean. Atmospheric Environment 42, 6542–6550.

Kouvarakis, G., Mihalopoulos, N., Tselepides, T., Stavrakakis, S., 2001. On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea. Global Biogeochemal Cycles 15, 805–818.

Lim, B., Jickells, T.D., Colin, J.L., Losno, R., 1994. Solubilities of Al, Pb, Cu and Zn in rain sampled in the marine environment over the North Atlantic Ocean and Mediterranean Sea. Global Biogeochemical Cycles 8, 349–362.

Loo, B.W., Cork, C.P., 1988. Development of high efficiency virtual impactor. Aerosol Science and Technology 9, 167–170.

Losno, R., Bergametti, G., Buat-Ménard, P., 1988. Zinc partitioning in Mediterranean rainwater. Geophysical Research Letters 15, 1389–1392.

Loye-Pilot, M.-D., Morelli, J., 1988. Fluctuations of ionic composition of precipitations collected in Corsica related to changes in the origins of incoming aerosols. Journal of Aerosol Science 19, 577–585.

Mahowald, N., Baker, A., Bergametti, G., Brooks, N., Duce, R., Jickells, T., Kubilay, N., Prospero, J., Tegen, 2005. Atmospheric global dust cycle and iron inputs to the ocean. Global Biogeochemical Cycles 19 (4), GB4025. doi:10.1029/2004GB002402.

Markaki, Z., Role of atmospheric deposition of nutrients in seawater productivity in SE Mediterranean. PhD thesis, University of Crete, Greece, 215p, 2008.

Markaki, Z., Oikonomou, K., Koçak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., Mihalopoulos, N., 2003. Atmospheric deposition of inorganic phosphorus in the Levantine Basin, Eastern Mediterranean: spatial and temporal variability and its role in seawater productivity. Limnology Oceanography 48 (4), 1557–1568.

Martin, J.H., Elbaz-Poulichet, F., Guieu, C., Loye-Pilot, M.D., Han, G., 1989. River versus atmospheric input of material to the Mediterranean: an overview. Marine Chemistry 28, 159–182.

Migon, C., Journal, B., Nicolas, E., 1997. Measurement of trace metal wet, dry and total atmospheric fluxes over the Ligurian Sea. Atmospheric Environment 6, 889–896.

Migon, C., Sandronia, V., Marty, J.C., Gasser, B., Miquel, J.C., 2002. Transfer of atmospheric matter through the euphotic layer in the northwestern Mediterranean: seasonal pattern and driving forces. Deep-Sea Research II 49, 2125–2141.

Muezzinoglu, A., Cizmecioglu, S.C., 2006. Deposition of heavy metals in a Mediterranean climate area. Atmospheric Research 81, 1–16.

Ridame, C., Guieu, C., Loye-Pilot, M.-D., 1999. Trend in the total atmospheric deposition fluxes of aluminium, iron and trace metals in the north western Mediterranean over the past decade (1985–1997). Journal of Geophysical Research 104 (D23), 30127–30138.

Statham, P.J., Hart, V., 2005. Dissolved iron in the Cretan Sea (Mediterranean). Limnolology Oceanography 118–124.

Theodosi, C., Markaki, Z., Mihalopoulos, N., in press. Iron speciation, solubility and temporal variability in wet and dry deposition in the Eastern Mediterranean. Marine Chemistry. doi:10.1016/j.marchem.2008.05.004.

Young, R.W., Carder, K.L., Betzer, P.R., Costello, D.K., Duce, R.A., DiTullio, G.R., Tindale, N.W., Laws, E.A., Uematsu, M., Merril, J.T., Feely, R.A., 1991. Atmospheric iron inputs and primary productivity: phytoplankton responses in the North Pacific. Global Biogeochemical Cycles 5, 119–134.