J Atmos Chem (2007) 56:239–257
DOI 10.1007/s10874-006-9053-7

Trace Metal Solid State Speciation in Aerosols of the Northern Levantine Basin, East Mediterranean

Mustafa Koçak · Nilgun Kubilay · Barak Herut · Malcolm Nimmo

Received: 27 July 2006 / Accepted: 2 November 2006 /

Abstract An established three stage sequential leach scheme was applied to a series of selected high volume aerosol samples (n=35) collected from the Turkish Eastern Mediterranean coastline (Erdemli). Samples were selected according to their air mass back trajectory history to reflect the contrasting mixtures of aerosol material present in the Eastern Mediterranean marine aerosol. Two populations were adopted, those samples which were classed as "anthropogenic" and those which were "Saharan" dominated aerosol populations. Applying the three stage leach it was possible to define the proportion for each of the considered metals (Al, Fe, Cu, Pb, Cd, Zn and Mn) present in the (a) "exchangeable" (b) "carbonate / oxide" and (c) "refractory" phases, representing novel solid state aerosol speciation data for this marine system. Clear trends were established, conforming with data from previous studies with mainly crustal derived metals (Al and Fe) being present in the refractory phases (Al>88%; Fe>84%) and those influenced by anthropogenic sources being dominating in the exchangeable phase, although for these metals the variability was comparatively high (12–64%; 19–85%; 40–100% for Zn, Pb and Cd, respectively). For the majority, greater exchangeable fractions were present the lower the crustal source contribution to the aerosol population, whereas the "refractory" fraction exhibited contrasting behaviour. This was illustrated by the novel application of the mixing diagram, presenting each of the three speciation stages against the corresponding percent anthropogenic contribution to each collected sample. Zn, Pb and Cd all illustrated progressive decrease in the percent exchangeable with increasing crustal contribution to the

M. Koçak · N. Kubilay
Institute of Marine Sciences, Middle East Technical University, Erdemli, Mersin, Turkey

N. Kubilay
e-mail: kubilay@ims.metu.edu.tr

B. Herut
Israel Oceanographic and Limnological Research, National Institute of Oceanography, Haifa, Israel
e-mail: barak@ocean.org.il

M. Nimmo (✉)
School of Earth, Ocean and Environmental Sciences, University of Plymouth, Plymouth, UK
e-mail: mnimmo@plymouth.ac.uk

aerosol population. The percent exchangeable was discussed in terms of its use to represent the upper limit of the bioavailable fraction of metal associated with the aerosol, post deposition. The mixing diagram approach enabled the prediction of the residual fractions for Cd, Pb and Zn (41±4%; 62±4% and 82±5%, respectively,) in Saharan end-member material.

Key words aerosol · trace metals · speciation · Levantine Basin

1 Introduction

The importance of wet and dry atmospheric inputs of trace metals to marine systems has been emphasised in previous work (e.g. Jickells 1995; Guieu et al. 1997; Herut et al. 2001). Both inputs are influenced by the aerosol metal loadings which vary spatially and seasonally depending on dominating aerosol source types, emission strengths and physical and chemical modifications to the aerosol population during atmospheric transport. Recent studies have discussed the influence of these factors on Eastern Mediterranean marine aerosols (Kubilay and Saydam 1995; Herut 2001; Herut et al. 2001; Koçak et al. 2004, 2005). The impact of such atmospheric inputs on marine biogeochemical cycles is determined by the quantity of total atmospheric inputs and the degree to which the aerosol associated trace metals undergo dissolution in both rainwater (during wet deposition events) and seawater, post dry deposition. Studies have been carried out to define aerosol trace metal solubility / bioavailability in a variety of aqueous media (e.g. Chester et al. 1994, 2000; Lim et al. 1994; Fernandez et al. 2000, Fernandez Espinosa et al. 2002; Dabek-Zlotorzynska et al. 2002, 2003, 2005; Voutsa and Samara 2002; Chen and Siefert 2003; Bonnet and Guieu 2004; Hand et al. 2004; Desboeufs et al. 2005; Heal et al. 2005; Al-Masri et al. 2006; Baker et al. 2006a,b). The processes which influence seawater and rainwater dissolution of trace metals from aerosol material are varied and act simultaneously in a complex manner. Chemical, biotic and physical factors such as pH, presence of dissolved organic complexing ligands, particle concentrations, bacteria, phytoplankton, and temperature may influence the extent of metal dissolution. In addition, the trace metal solid state speciation of aerosol material from contrasting sources will markedly control the potential availability of trace metals for seawater/rainwater dissolution (Chester et al. 1989, 1994). Solid state speciation has, in the past, been defined by applying operational sequential leach schemes to aerosol material. Different schemes have been applied depending on the environmental application of the generated data (Chester et al. 1989; Zatka et al. 1992; Spokes et al. 1994; Fernandez et al. 2000, Fernandez Espinosa et al. 2002; Fuchtjohann et al. 2000; Slejkovec et al. 2000; Dabek-Zlotorzynska et al. 2003; Profumo et al. 2003; Al-Masri et al. 2006). One of the first schemes applied to aerosol collected on filter material was proposed by Chester et al. (1989). This approach was able to separate aerosol associated trace metals into three contrasting solid phases; i.e. (a) "exchangeable" (b) "oxide-associated and carbonate" and (c) "refractory". The importance of the exchangeable fraction in predicting the potential impact of trace metal inputs to marine systems has been exemplified by Chester et al. (1994), who defined a relationship between the seawater solubility of trace metals and the exchangeable fraction. The exchangeable fraction generally represents the upper limit of the soluble or bioavialable fraction of the aerosol associated trace metals. Hence carrying out solid state speciation studies of aerosol populations yields essential information on the potential reactivity of the associated metals with seawater, post-deposition or during wet deposition events, and hence their impact on marine biogeochemical cycles.

Therefore the current study describes the application of an established operational three stage sequential leach scheme of Chester et al. (1989) on aerosol populations sampled from the Eastern Mediterranean coast of Turkey (Erdemli), producing an important and unique dataset. Processes that may affect the metal speciation during aerosol transport are also considered. Aerosol sampling has been carried out at this site for the last decade (Kubilay and Saydam 1995; Koçak et al. 2004, 2005) allowing us to define the spectrum of solid state speciation signals of the eastern Mediterranean in aerosol populations with a varying mixture of Saharan / anthropogenic sourced material.

2 Methodology

Bulk aerosol filter samples (Whatman 41) were collected using a high volume sampler positioned at the top of a specially designed sampling tower, 20m asl, located at a rural site on the coastline of the Eastern Mediterranean, (Erdemli; 36° 33′ 54″ N and 34° 15′ 18″ E), Turkey. Samples were collected from January 1999 to December 2002, during which time a total of 835 aerosol filter samples were collected. Care was always taken in the handling of samples in order to minimise contamination (see Koçak et al. 2004). A selection of aerosol samples (n=35) were chosen according to; (a) the sample's potential source area described using air mass back trajectories and (b) their Al and Pb concentrations, ensuring that the sequential leach solution uncertainties were well above the analytical blanks (i.e. typically <5% contribution to the leach solutions; see below) and detection limits. Three categories of the selected aerosol samples were defined; (a) "Saharan" (b) "anthropogenic" and (c) "mixed". These then underwent a three stage sequential leach scheme (after Chester et al. 1989). Air mass source was defined using the operational trajectory model developed by the European Centre for Medium-Range Weather forecasts (ECMWF) in Reading U.K, which was applied to three-dimensional wind fields acquired from the archives of ECMWF.

The first stage of the sequential leach scheme consisted of taking a portion of the filter sample and shaking at a constant rate for 15 min with 25 mL of 1 M ammonium acetate (BDH-AnalaR; adjusted to pH 7 using Aristar NH_4OH and /or HNO_3). This was then centrifuged for 15 min at 3,000 rpm and the first stage leach was decanted off and stored in a "sterilin" container to await analysis. Then 25 mL of 25% acetic acid (Romil-Ultra pure) and 1 M hydroxylamine hydrochloride (BDH Analar) was added and then shaken for 6 h, again at a constant rate. Following centrifugation the acetic acid and hydroxylamine hydrochloride solution was decanted off and retained for analysis. The final stage involved a total HNO_3/HF digestion (see Koçak et al. 2004) of the remaining aerosol material, to yield the fraction of trace metal associated with the refractory solid phase. Carry over between stages was corrected by weighing the amount of leach solution remaining after centrifugation and decanting procedures between the three stages.

After each stage leach solutions were analysed for trace elements by one of ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry; all Stages Al and Fe), ICP-MS (Inductively Coupled Plasma Mass Spectrometry; Stages 1 and 3 Cu, Pb, Zn, Cd, Mn; Stage 2 Pb, Zn, Mn), GFAAS (Graphite Furnace Atomic Absorption Spectrometry; Stage 2 Cu and Cd). The accuracy for the analyses and procedures was tested by summation of the metal concentrations for each sample of all the three stages to yield the "total" concentration for each sample processed through the sequential leach scheme. These were then compared with total metal concentrations determined on a separate portion of the same filter which had undergone only a total acid digest, i.e. concentrated HNO_3 / HF. The analytical accuracy of the total digest method has already been defined as $<\pm 5\%$ using BCSS-1 (see for example Koçak et al. 2004, 2005). For all total and sequential leach "total" elemental concentrations (except for Cd), after applying a regression line to compare the sample populations, there was no statistically significant difference between the slope, intercept and correlation coefficients compared with their predicted standard deviations at the $p>0.05$. Figure 1, for example, shows the regression lines for the two elements (Fe and Pb) which are characteristic of the two contrasting aerosol sources. This also indicated that the accuracy of the approach was acceptable for all sample types encountered with potentially very different chemical compositions (crustal versus anthropogenic dominated aerosol material). This assessment is not possible when the accuracy is determined using only a single CRM (normally an urban derived aerosol).

Therefore, considering the potential analytical and procedural errors associated with the application of the sequential leach scheme and the errors associated with using different filter sections in making this comparison, the speciation data presented in the current study is of a high analytical quality. Operational blank contributions to sample leach solutions were low, amounting to < 5% for all trace elements for all stages, except for Mn and Zn for stage 2 (7% and 15 %, respectively); Zn and Cd for stage 3 (17% and 47%, respectively).

3 Results and Discussion

3.1 Overview

Table 1a and b present a statistical summary of the solid state speciation signal for the two categories of Eastern Mediterranean marine aerosol populations ; i.e. those aerosol samples whose origin, based on air mass trajectories, was (a) "Saharan" ($n=16$) and (b) "anthropogenic" ($n=14$) sources. The air mass back trajectories, at different pressure levels, for each of the categories are presented in Figs. 2a ("anthropogenic") and b ("Saharan").

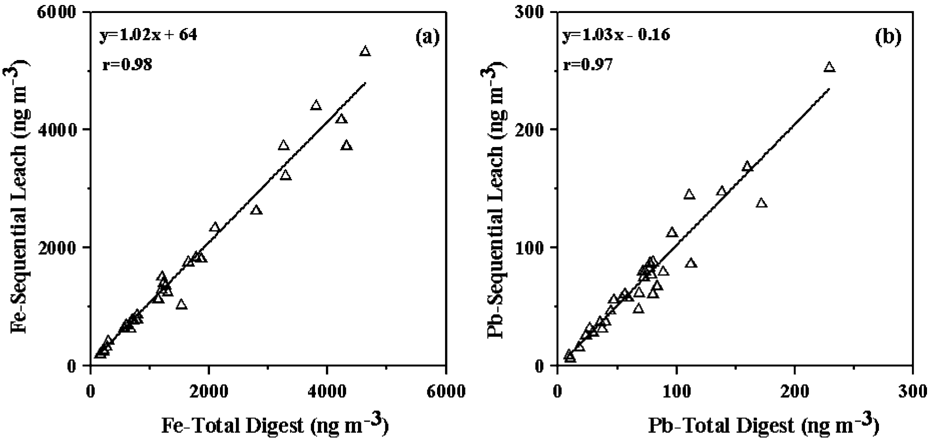


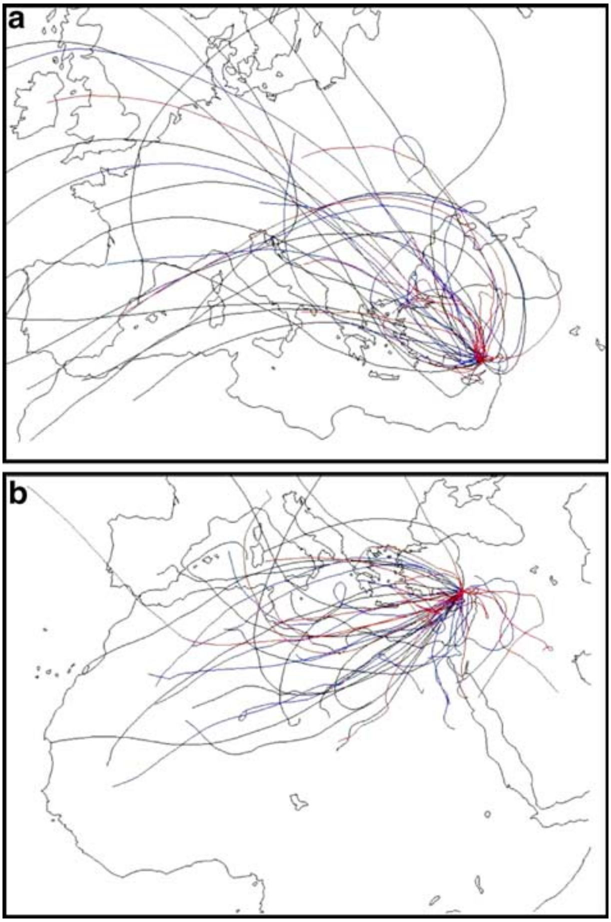
Fig. 1 Plot of total Pb and Fe concentrations (ng m^{-3}) against the equivalent sum of the concentrations derived from a three sage sequential leach

Table 1 Statistical summary of the trace metal aerosol solid state speciation (expressed as a % wt. of extracted metal / wt of total metal) signatures for (a) “Saharan” (n=16) (b) “anthropogenic” (n=14) samples collected from the Eastern Mediterranean aerosol

(a)	Mean (1 S.D.)			Range			EF$_{crust}$* Geometric Mean	Crustal Cont.% (±SD)
Element	Stage-1	Stage-2	Stage-3	Stage-1	Stage-2	Stage-3		
Al	1.0(0.5)	4.0(2.2)	95.0(2.3)	0.4–2.4	1.2–10.5	88–97	1.0	100
Fe	0.9(0.6)	2.9(1.6)	96.2(2.2)	0.3–2.8	1.1–7.7	90–97	1.5	68 (10)
Mn	35.3(4.9)	19.3(3.7)	45.4(6.2)	26.4–41.2	12.1–25.2	38–61	1.3	75 (13)
Zn	38.5(14.9)	28.2 (6.4)	33.3 (14.1)	12.4–63.6	15.6–43.2	17–64	3.4	30 (22)
Cu	35.7 (3.4)	16.8 (10.3)	47.5 (13.1)	28.2–43.4	5.2–40.3	23–67	5.3	19 (16)
Pb	60.7 (19.7)	30.0 (12.9)	9.3(8.3)	19.3–86.1	11.8–54.4	2–30	19.4	5 (14)
Cd	78.4 (15.7)	10.4 (8.8)	11.2 (8.3)	39.7–91.4	0.0–36.5	1–34.	w4.1	25 (17)
(b)	Mean (1 S.D.)			Range			EF$_{crust}$ Geometric Mean	Crustal Cont.% (±SD)
Al	3.9(1.2)	3.1(1.2)	92.9(1.7)	0.8–5.7	1.5–6.4	88–96	1.0	100
Fe	2.6(1.1)	7.2(3.2)	90.2(3.2)	0.7–4.6	4.0–12.1	84–93	1.9	54 (8)
Mn	52.9(4.1)	6.1(6.4)	41.4(4.7)	45.6–59.9	0.0–15.7	34–50	2.0	51 (7)
Zn	65.6(8.6)	24.9(6.6)	9.5(4.9)	53.6–87.7	11.3–33.7	1–17	12.2	8 (3)
Cu	37.0(4.4)	19.8(11.2)	43.2(11.9)	27.1–43.7	1.9–40.9	22–62	21.7	5 (4)
Pb	84.9(10.5)	12.8(11.2)	2.3(1.5)	53.0–94.8	2.7–47.0	0–5	215.0	0.5 (0.3)
Cd	91.7(7.7)	5.1(5.3)	3.3(3.5)	76.8–100	0.0–16.4	0–11	35.2	3 (3)

*Calculation of the Saharan contribution and EF$_{crust}$ are discussed further in the text

Fig. 2 Back trajectories for all samples in the (all pressure levels included i.e. 500 hPa; 700 hPa; 850 hPa) (a) Anthropogenic-Dominated Population (b) Saharan-Dominated Population



A summary of the elemental crustal enrichment factor (EF_{crust}) data are also presented in Table 1a and b for each aerosol population category. The crustal enrichment factor has been used extensively in the past to define aerosol elemental sources (e.g. Chester et al. 1996; Herut et al. 2001). The choice of element:Al ratio, used in the calculation of the EF_{crust}, is not trivial. Ideally an elemental:Al ratio as close to the precursor crustal material should be used. Often this is not available, hence the use in previous studies (Chester et al. 1994) of compiled global elemental:Al ratios (Taylor and McLennan 1985; Wedepohl 1995 and Rudnick and Gao 2003). For the current study the ratios were taken from the analysis of material associated with an intense Saharan dust event collected on board the R V Aegaeo (central Levantine basin; 33.42°N and 32.83° E on 13/5/01). The observed elemental:Al ratios (wt/wt) for Pb and Zn (0.00046 and 0.0012) are similar to those ratios calculated from literature regional crustal end-member compositional data (i.e., 0.00034 for Pb from Guieu et al. (2002) for Saharan dust and 0.002 for Zn from Andreae et al. (2002) in the coarse fraction during a Negev dust storm). No such comparable ratios exist for Cd in Saharan dust. For Fe a ratio of 0.59 was applied, this value being consistent with that presented in the literature (e.g. 0.63 as presented by Guieu et al. 2002). These values, along with

Table 2 Comparison of the Eastern Mediterranean trace metal solid state speciation (expressed as a % wt. of extracted metal / wt of total metal), signature with other (a) European aerosols and speciation / extraction techniques

Element	Current Study Eastern Med. "Saharan"	Current Study Eastern Med."Anthropic"	North Sea[1]	Saharan Crust[2]	LUAP[2] (Liverpool Urban Aerosol particulate)	Urban, Spain[3]	Urban, Greece[4]
Al	S1-1.0±0.5	S1-3.9±1.2	S1-5	S1-0.05 ± 0.015	S1-5.6±4.8	–	–
	S2 -4.0±2.2	S2 -3.1±1.2	S2-13.5	S2-14.4±2	S2-12.1±5.8		
	S3-95.0±2.3	S3-92.9±1.7	S3-81.5	S3-85.6±2	S3-82.3±7.2		
Fe	S1-0.9±0.6	S1-2.6±1.1	S1-6.5	S1-0.03±0.003	S1-9.9±6.2	S1-4	–
	S2-2.9±1.6	S2-7.2±3.2	S2-11	S2-9.5±2	S2-31.9±11.8	S2-16	
	S3-96.2±2.2	S3-90.2±3.2	S3-82.5	S3-90.5±2	S3-58.2±12.2	S3-26	
						S4-55	
Mn	S1-35.3±10.0	S1-52.9±4.1	S1-56	S1-22.8±1.1	S1-44.2±13.2	S1-33	S1-75
	S2-19.3±3.7	S2-6.1±6.4	S2-7	S2-34.2±2.6	S2-22.7±12.3	S2-23	
	S3-45.4±6.2	S3-41.4±4.7	S3-37	S3-43±2.7	S3-33.1±13.7	S3-34	
						S4-9.	
Zn	S1-38.5±14.9	S1-65.6±8.6	S1-77	S1-0.2±0.35	S1-77.9±9.8	–	S1-93
	S2-28.2±6.4	S2-24.9±6.6	S2-12	S2-8.4±3.7	S2-8.8±6.1		
	S3 -33.3±14.1	S3-9.5±4.9	S3-11	S3-91.4±3.8	S3-13.2±8.6		
Cu	S1-35.7±3.4	S1-37.0±4.4	S1-45	S1-3.7±1.9	S1-52±15.2	S1-27	S1-90
	S2-16.8±10.3	S2-19.8± 11.2	S2-27	S2-20.6±3.4	S2-28.7±14	S2-10	
	S3-47.5±13.1	S3-43.2± 11.9	S3-27	S3-75.7±5	S3-19.3±10.7	S3-43	
						S4-21	
Pb	S1–60.7±19.7	S1-84.9± 10.5	S1-77	S1-5.7±5.1	S1-81.5±6.9	S1-4	S1-61
	S2-30.0±12.9	S2-12.8± 11.2	S2-15.5	S2-28.8±5.7	S2-11.1±6.7	S2-33	
	S3-9.3±8.3	S3-2.3±1.5	S3-7	S3-65.5±6.2	S3-7.4±4	S3-35	

Table 2 (continued)

Element	Current Study Eastern Med. “Saharan”	Current Study Eastern Med.“Anthropic”	North Sea[1]	Saharan Crust[2]	LUAP[2] (Liverpool Urban Aerosol particulate)	Urban, Spain[3]	Urban, Greece[4]
						S4-28	
Cd	S1-78.4±15.7 S2-10.4±8.8 S3-11.2±8.3	S1-91.7±7.7 S2-5.1±5.3 S3-3.3±3.5	–	–	–	S1-25 S2-21 S3-31 S4-24	S1-90

For current study and those of [1] Chester et al. (1994) and [2] Chester et al. (1989), S1=“exchangeable”, S2=“carbonate and oxide,” S3=“ residual”, [3] Fernandez Espinosa et al. (2002), S1 =“exchangeable,” S2=“carbonate /oxide/ reducible,” S3=“ organic/oxidisable and sulphidic,” S4 = “residual”. Voutsa and Samara (2002), S1=“labile” individual elemental and aluminium aerosol concentrations, were used to calculate the % crustal / anthropic contributions for each sample in the same manner as described previously in Herut et al. (2001). The elemental:Al ratios adopted in the current study, however will be subject to error owing to the potential variation of elemental ratios of Saharan dust from different source regions. Such difference have been recently highlighted by Chiapello et al. (1997) for a number of major elements in Saharan dust of contrasting origins influencing Sal Island (Cape Verde).

Table 2 compares the contrasting solid state speciation signatures for the Eastern Mediterranean aerosol populations to those determined for other European aerosol populations using a similar three stage sequential leach approach (e.g. North Sea, Chester et al. 1994; LUAP-Liverpool Urban Aerosol Particulate and Saharan derived mesh collected dust, Chester et al. 1989) and with other documented sequential leach schemes (e.g. Fernandez Espinosa et al. 2002; Voutsa and Samara 2002). Considering the general trends in the Eastern Mediterranean dataset (Table 1a and b) and comparison with the literature (Table 2), it is apparent that metals exhibit contrasting solid state speciation signatures.

3.2 Al and Fe

Al and Fe are present predominantly (> 84% of their total concentrations) in the refractory fraction (Stage-3) with only 0.5–5% being found in the exchangeable fraction (Stage-1). This is consistent with literature values (see Table 2) for the refractory fraction in European aerosol material of 81–86% for Al and 83–91% for Fe (Chester et al. 1989, 1994; Fernandez Espinosa et al. 2002).

Owing to the role played by atmospheric deposition of Fe in stimulating primary productivity in HNLC regions of the world' oceans, there have been a number of recent studies (e.g. Zhu et al. 1992; Chen and Siefert 2003; Bonnet and Guieu 2004; Hand et al. 2004; Desboeufs et al. 2005; Baker et al. 2006a,b) focussed on defining the "solubility" of aerosol associated Fe. Some of these studies have considered "end-member" aerosol populations in controlled laboratory simulations (e.g. Bonnet and Guieu 2004; Desboeufs et al. 2005) whilst others have used mixed, typically filter collected, aerosol populations (e.g. Chen and Siefert 2003; Hand et al. 2004; Baker et al. 2006a,b). Some of these recent findings are summarised on Table 3, but for a more detailed critical summary see Mahowald et al. (2005). Comparison of these values with those from the current study is difficult owing to the contrasting experimental approaches. However, from the summary, it can be concluded that the extent of "soluble" Fe is generally lower for crustally derived aerosols and lowest in systems that apply extraction solutions buffered at higher pH (8.2, seawater; Bonnet and Guieu 2004; Chen et al. 2006; compared to ca 4.7 ; Baker et al. 2006a,b), although the literature does report a wide range of values. Clearly the observed range of % Fe in the exchangeable and % oxide / carbonate fractions for the current study (0.3–4.6%; 1.1–12.1%, respectively) for both "Saharan" and "anthropogenic" aerosol types of the Eastern Mediterranean atmosphere are within the range of values observed in these recent studies (Table 3).

3.3 Cd, Pb and Zn

Elements whose solid state speciation signal is dominated by the exchangeable phase in both the anthropogenic and Saharan aerosol populations are Cd, Pb and Zn. For example, the average % of this phase contributing to "anthropogenic" aerosol influenced populations

Table 3 The solubility of Fe in contrasting populations using different extraction approaches

Reference	Summary of employed method	Location of sample collection	Types of aerosol sample	% fraction contributing to the total Fe (range)
Baker et al. (2006a)	1 M ammonium acetate pH=4.7 for 1–2 h	Atlantic Ocean	North Atlantic/Remote	median=7.8 (4.0-19)
			Saharan	median=1.7 (1.4-4.1)
Baker et al. (2006b)	1 M ammonium acetate pH=4.7 for 1-2 h	Atlantic Ocean	Saharan	Median=1.2 (0.5-2.5)
Chen et al. (2006)	Water	Gulf of Aqaba	Crustal	Water ; mean=5 (0.5-19)
	Sargasso Sea			Seawater; mean=0.7 (0.003-2)
Sedwick et al. (2005)	Estimated by comparing increase in the dFe inventory of the surface mixed layer with total eolian Fedeposition	Bermuda–Atlantic	Open ocean	3-30
Desboeufs et al. (2005)	Aqueous solution, pH=4.7 for 120 min	Cape Verde	Loess	0.04
			Urban	3
Hand et al. (2004)	Fe(II) measurement after aerosol extraction with 0.5 mM formate-acetate buffer, pH=4.5	Atlantic and Pacific Oceans	Open Ocean	Fine mode; $x = 4 \pm 9(0 - 45)$
				Coarse mode; $x = 2 \pm 10(0 - 8)$
Bonnet and Guieu (2004)	Seawater pH=8		Saharan	0.001-1.6
			Anthropogenic	0.2-2.2
Current study	“exchangeable”	Eastern Mediterranean	Anthropogenic	2.6
			Saharan	0.9
	“oxide/carbonate”		Anthropogenic	7.2
			Saharan	2.9

was 92% (Cd), 85% (Pb) and 66% (Zn). The average exchangeable fraction for Cd was higher than that observed for Pb, despite the fact that Pb is more enriched by anthropogenic sources than Cd in the aerosol populations. The chemical form in which the element is present affects its potential dissolution from the source material. From the literature, Cd in MSW (municipal solid waste) fly ash is mostly present as water-soluble species such as $CdCl_2$ and $CdSO_4$ (Pinzani et al. 2002). In contrast Pb is will be generally present as; $PbCO_3$, $PbSO_4$, or PbO which are derived from emission sources including waste incineration (Sobonska et al. 1999) and smelters, and are comparably less soluble.

Previous studies (Chester et al. 1989, 1994; Guerzoni et al. 1999; Fernandez Espinosa et al. 2002; Voutsa and Samara 2002; see Table 2) have also reported high average % exchangeable or soluble phase associations for Zn, Pb and Cd. Although there is a significant degree of variability for these elements (e.g. Pb and Zn have quoted ranges of 5%–97% and <1% to 80%, respectively; Chester et al. 1994), this variability being detected in samples collected from the current sampling site (Table 1a).

3.4 Cu and Mn

Elements that had no overall dominating solid phase association were Mn and Cu. Cu and Mn which were generally equally distributed between the exchangeable (44% and 36%, respectively,) and refractory (44% for both elements) phases.

3.5 Differences in the speciation signal between the different populations

Table 4 indicates statistically significant differences in elemental solid phase associations between the Saharan and anthropogenic aerosol populations. For Zn, Pb, and Cd, enhancement of their mean exchangeable fractions was observed for the anthropogenic populations (enhanced by 11% for Zn; 24% for Pb; 13% for Cd) with a corresponding decrease in their refractory fraction (29%-Pb; 10%-Zn; 7%-Cd) in comparison with the "Saharan" aerosol populations (these differences were statistically significant at the 95% confidence level). Such differences have been observed in previous studies and were attributed to the predominant mechanism by which the metals are incorporated in the two contrasting populations (i.e. anthropogenic populations via high temperature/condensation reactions; crustal dominated populations via low temperature weathering processes).

Interestingly, Cu exhibited no statistical difference between the two populations for all of the exchangeable stages (Table 4) which is in contrast to previous studies such as those carried out by Chester et al. (1989, 1994), who observed dual behaviour. They showed that

Table 4 Summary of the statistical difference (using Mann Whitney test and confidence level 95%) for corresponding Stages (numerical subscript) between the two aerosol population types. Saharan dominated aerosol populations (subscript S) and anthropogenically dominated aerosol population (subscript A)

	STAGE-1	STAGE-2	STAGE-3
Al	$Stg_{1S}<Stg_{1A}$	$Stg_{2S}<Stg_{2A}$	$Stg_{3S}>Stg_{3A}$
Fe	$Stg_{1S}<Stg_{1A}$	$Stg_{2S}<Stg_{2A}$	$Stg_{3S}>Stg_{3A}$
Mn	$Stg_{1S}<Stg_{1A}$	$Stg_{2S}>Stg_{2A}$	$Stg_{3S}\approx Stg_{3A}$
Zn	$Stg_{1S}<Stg_{1A}$	$Stg_{2S}\approx Stg_{2A}$	$Stg_{3S}>Stg_{3A}$
Cu	$Stg_{1S}\approx Stg_{1A}$	$Stg_{2S}\approx Stg_{2A}$	$Stg_{3S}\approx Stg_{3A}$
Pb	$Stg_{1S}<Stg_{1A}$	$Stg_{2S}>Stg_{2A}$	$Stg_{3S}>Stg_{3A}$

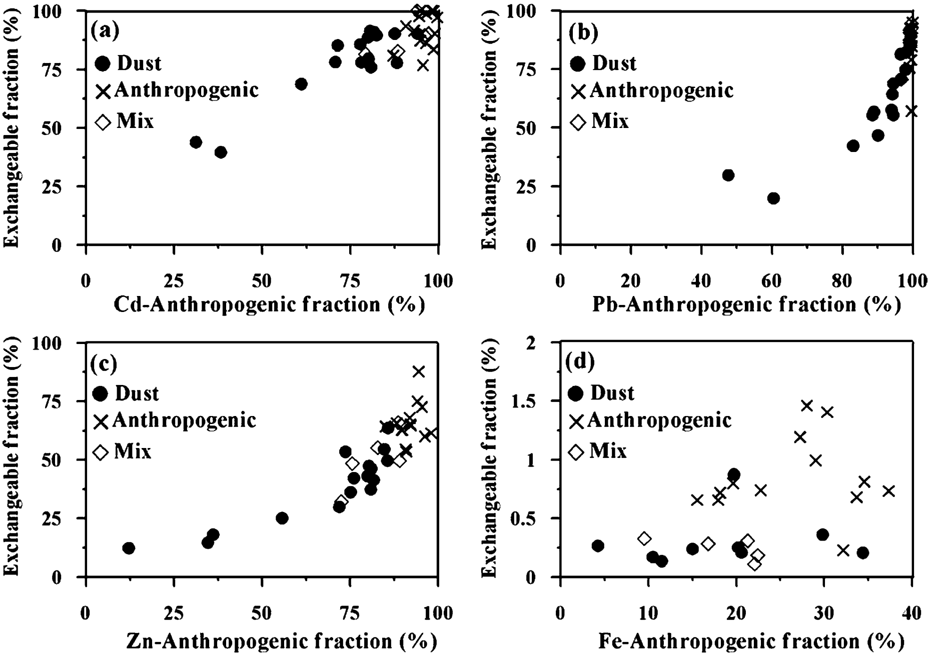


Fig. 3 (a–d). Plots of the % exchangeable fraction of trace metal against the % anthropic contribution. (*closed circle*=anthropic dominated aerosol populations : *open triangles*="Saharan" populations; *crosses*= mixed populations)

the Cu solid state speciation signal was dominated by the exchangeable fraction in anthropogenic aerosols but conversely was dominated by the refractory phase in crustal dominated aerosol populations. The uniqueness of the uniformity of the exchangeable Cu fraction observed in the current study may be due to the dominant contribution made to aerosol Cu from regional / local sources. This has previous been suggested by Koçak et al. (2004) for the Erdemli sampling site. Iron and Al, exhibited relatively smaller differences in their speciation signal for the two populations, but these differences were statistically significant (p=0.05) with higher exchangeable and oxide / carbonate fractions in the anthropogenic populations.

Samples within the two defined aerosol populations will in effect represent a spectrum of mixing proportions of the contrasting anthropogenic and crustal sources, rather than being pure aerosol populations. Hence the elemental solid state speciation characteristics of any aerosol population will be dependent upon the relative mixing of the two major sources or end-members. If this is the case then a mixing diagram approach can be used to investigate aerosol chemical interactions during atmospheric transport which may modify the solid state speciation signal during aerosol transport from source to sink (Chester et al. 1995). Therefore to investigate the full range of aerosol mixtures the elemental % solid phase fractions for all samples were plotted against % anthropogenic contribution or Al concentrations (for Al). The % elemental anthropogenic contribution for each element was determined from the following equation:

$$\% \text{ anthropogenic contribution} = \{(C_{xa} - [C_{Ala} * (C_{xc}/C_{Alc})])/C_{xa}\} * 100 \qquad (1)$$

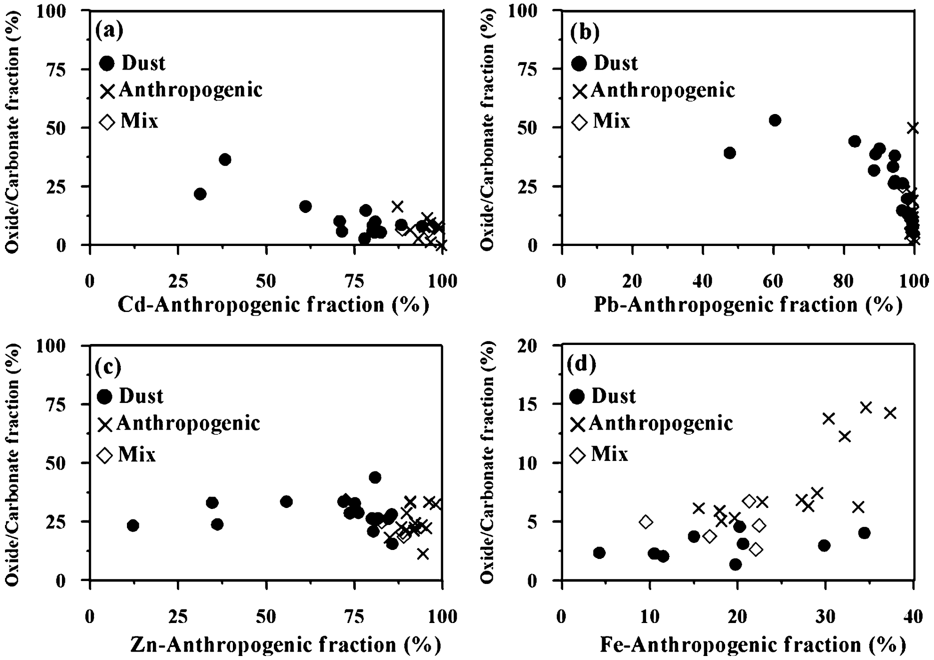


Fig. 4 (a–d). Plots of the % oxide / carbonate fraction of trace metal against the % anthropic contribution.(*closed circle*=anthropic dominated aerosol populations: *open triangles*="Saharan" populations; *crosses*=mixed populations)

where (C_{xa} and C_{Ala}) are the concentrations of a trace metal x and Al, respectively, in the individual aerosol samples, and C_{xc} and C_{Alc} are their comparable concentrations in crustal material (see earlier).

Hence a plot of each of the three stages against the % anthropogenic contribution for all samples would indicate any changes in the solid state speciation with different degrees of mixing between the non-crustal and crustal aerosol sources. Such plots are presented in Fig. 3a–d (Cd, Pb, Zn, Fe; % exchangeable fraction); Fig. 4a–d (% oxide / carbonate fraction); Fig. 5a–d (% residual fraction).

Figure 3a–c shows clear trends for Cd, Pb and Zn with enhanced % exchangeable fractions with increasing proportions of anthropogenic contributions to the aerosol population. The maximum % exchangeable fraction being > 90% for Pb and Cd and > 60% for Zn, occurring at > 99%; 90% and 90% anthropogenic contributions, respectively, to the aerosol population. Although it was clear that there was a significant degree of variation of the exchangeable fraction for both Pb and Zn between a relatively small range (90–100%) of anthropic contributions; this amounted to 47–92% and 53–87%, respectively, with a relatively lower range of 70–100% being observed for Cd, indicative of a more homogeneous speciation signal for Cd derived from multiple anthropogenic sources.

Interestingly, both Cd and Pb illustrated statistically significant linear relationships ($P<0.01$) between the exchangeable and oxide / carbonate solid phases. No such relationship was observed for Zn. A linear relationship between Stage 1 and 2 may be a result of one or a combination of the following, (a) different amounts of exchangeable and oxide / carbonate phases present in the anthropogenic (i.e. a higher % exchangeable phase exists in anthropogenic end-members compared to that in crustal material and the opposite

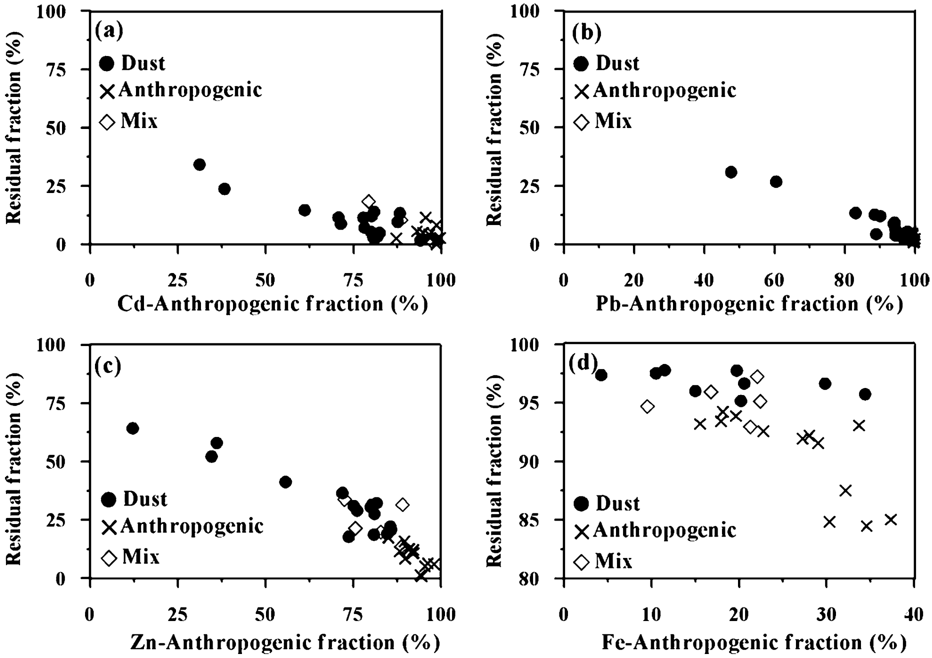


Fig. 5 (a–d). Plots of the % residual fraction of trace metal against the % anthropic contribution. (*closed circle*= anthropic dominated aerosol populations : *open triangles*="Saharan" populations ; *crosses*=mixed populations)

is the case for the oxide / carbonate phase; see Chester et al. 1989 and Table 2) and crustal material leading to an inverse relationship upon different degrees of their mixing and or (b) chemical transfer of Pb and Cd between the two phases during aerosol mixing. The latter process may occur during condensation and evaporation cycles at an aerosol surface during transport. In principle the exchangeable phase associated metal may be mobilised into the particle surface aqueous film and subsequently re-adsorb onto adsorptive sites on the aerosol particle surface (such as oxide surfaces, mineral lattices) or form complexes of lower solubility in the aqueous film. Such a phase shift for Pb has been reported by Chester et al. (1995). Recently Falkovich et al. (2004) observed the interaction of mineral dust originating from the Sahara with semi-volatile organic compounds (along Israel's coastal plain), and identified as specific tracers for urban air pollution. This suggests that dust may provide surfaces for uptake of anthropogenic material, which would then lead to potential chemical interaction and modifications during transport of the combined aerosol material. For Cd, dilution of the speciation signal with aerosol mixing is most likely owing to the more linear behaviour of the mixing line in Fig. 3a. However, for Pb, curvature in the response was apparent at anthropogenic contributions <90% (Fig. 3b) – which might be due to phase transfer with aerosol interactions as discussed above. However, owing to the high variability of the % exchangeable Pb signal in the anthropogenic "end-member" the apparent curvature may also be due, in part, to the anthropogenic "end-members" having different % exchangeable. In addition, it should be acknowledged that the current sample data are limited in that the samples do not extend to a 100% Saharan "end-member," with maximum crustal aerosol contributions for example for Pb and Cd being only 25% and <15%, respectively, hence a complete mixing line cannot be produced out for the current data set.

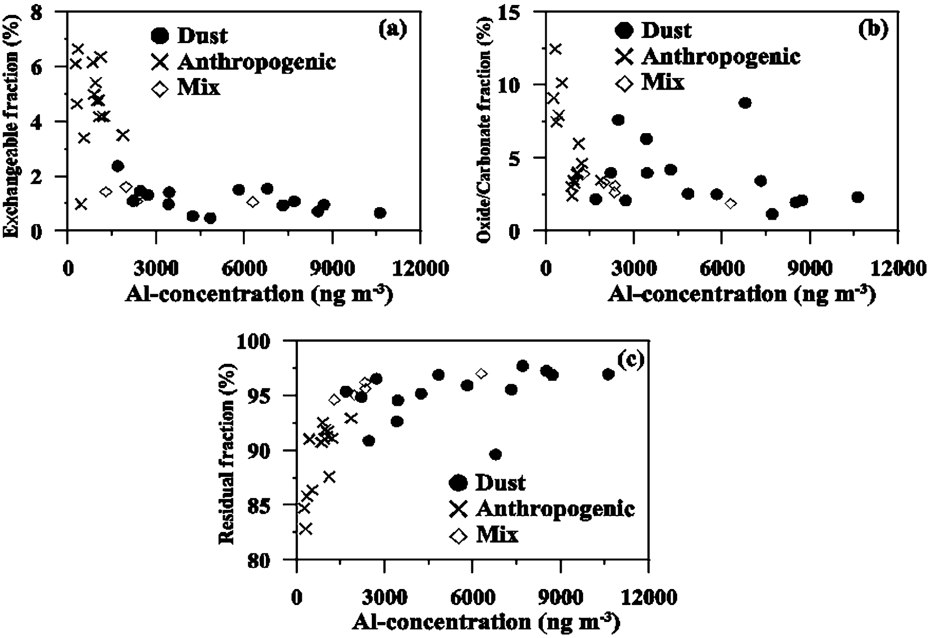


Fig. 6 Plots of the % (a) exchangeable, (b) oxide / carbonate, (c) residual, fractions of the total aerosol Al against Al concentrations. (*closed circle*=anthropic dominated aerosol populations : *open triangles*="Saharan" populations ; *crosses*=mixed populations)

The behaviour of residual Pb, Cd and Zn with % anthropogenic contributions are linear ($P < 0.01$), indicating that the major control of this solid phase for these elements is the extent to which the crustally sourced aerosol material is mixed / diluted with anthropogenic derived aerosol material. From regression equations it is predicted that when the percent anthropogenic contribution is zero, the residual fraction for Cd, Pb and Zn would be 41± 4%; 62±4 and 82±5%, respectively. The values for Pb and Zn compare favourably with those observed by Chester et al. (1989) for the residual fraction of an end-member Saharan dust of 66±6 % and 91±4%, respectively (Table 2).

In contrast, for Fe it was apparent that there was no clear relationship between % exchangeable fraction with percent anthropogenic contribution, which ranged from ca 0.1% to 1.5%. Results of stages 2 and 3 are presented in Figs. 4d and 5d respectively against the % anthropogenic contribution. When one considers the oxide / carbonate and refractory phases against anthropogenic contributions again there was little variation in the crustal dominated population during mixing, whereas for the anthropogenic dominated population there was an enhancement of the oxide / carbonates phase with a corresponding decrease in the residual phase with increasing anthropogenic influence of the aerosol population. This is particularly noticeable at >30% anthropogenic contributions. This may indicate (a) a different speciation signal for Fe associated with an increasing contribution to the aerosol population from different anthropogenic activities and / or (b) modification of the Fe between phases during cloud evaporation/condensation. Spokes et al. (1994) suggested previously that the solubility of Fe is modified during evaporation/condensation reactions owing to rapid changes in the micro pH climate of the aerosol material. The Al is predominantly present in the refractory phase. As Al is assumed to be derived from crustal sources, the different solid phases were plotted against the Al concentrations, rather than % anthropogenic contributions (Figs. 6a–c). At the low range of Al concentrations the "refractory" solid phase (Fig. 6c) exhibited a relatively lower refractory % (in the non-Saharan samples; ranging from 82 to 92%). Inverse trends for both the oxide / carbonate were apparent (Fig. 6b). This change may be accounted for by slightly dissimilar speciation signals in local crustal material compared with Saharan dust. At lower Al concentrations, local crustal material would have a progressively greater oxide /carbonate and refractory phase.

4 Conclusions

The study has clearly highlighted the contrasting metal solid state speciation signals for the Eastern Mediterranean aerosol, in agreement with previous studies carried out at other European marine systems.

(a) Al and Fe were predominantly incorporated into the resistant refractory solid phase (Al >88%; Fe> 84%).
(b) Pb, Cd and Zn were predominantly present in the exchangeable phase (e.g. the mean values for anthropogenic aerosols were 85%, 92% and 66%, respectively).
(c) It was also apparent that in the two different aerosol populations "Saharan" and anthropogenic Pb, Zn, Cd, and to lesser extent Al, Fe, exhibited contrasting behaviour with a decrease in their percent exchangeable fraction with a corresponding increase in crustal contributions and an increasing importance of their percent refractory solid phase. Mixing diagrams supported the above inferences and allowed prediction of the Saharan end-member residual fraction for Pb, Zn and Cd. However clear interpretation of such diagrams was limited owing to (a) variations in the anthropogenic "end-member" signals, particularly for Pb and Zn, (b) an incomplete set of samples covering the whole range of percent anthropogenic contributions and (c) precursor crustal material of different origins having different element:Al ratios.

Defining the trends in the trace metal solid state speciation characteristics of the Eastern Mediterranean aerosol, in particular the exchangeable fraction, will allow a better understanding of the dry atmospheric inputs of the potentially soluble metal fraction to the Levantine Basin, and subsequently their marine biogeochemistry. However, the operationality of the applied sequential leach technique has to be stressed. The degree to which the various metal fractions are removed from the solid aerosol phases during each step is dependent on the applied experimental approach. Consistency within sample determinations allows trends to be established between aerosol sample batches (Baker et al. 2006b). However different approaches have been adopted (e.g. Fernandez Espinosa et al. 2002; Voutsa and Samara 2002) depending upon the scientific context within which the data is to be applied. This has been the case more recently for various studies carried out to define the "solubility" of Fe associated with the marine aerosol (e.g. Chen and Siefert 2003; Bonnet and Guieu 2004; Hand et al. 2004; Desboeufs et al. 2005; Baker et al. 2006a,b), leading to non-comparable datasets. Therefore there is an urgent need to assess the relative efficiencies of the different extraction stages of these techniques to facilitate more informed comparisons. In addition, it is crucial to show how a metal's aerosol solid state speciation relates to its actual seawater solubility. A limited number of previous studies have attempted to do this (Chester et al. 1993, 1994) and these suggest that the exchangeable fraction represents an upper limit of their seawater solubilities.

Acknowledgements This study was funded in part by the Middle East Technical University (AFP-2001-07-01-01) and NATO (through a linkage grant of EST.CLG.977811). We would like to thank Emin Özsoy for making available the ECMWF trajectory analysis through collaboration with the Turkish State Meteorological Office and in addition acknowledgement is made for the use of ECMWF's computing and archive facilities. The assistance of MEDPOL III and project 18.635 is also acknowledged. The authors would like to thank the anonymous reviewers for their helpful comments.

References

Al-Masri, M.S., Al-Kharfan, K., Al-Shamali, K.: Speciation of Pb, Cu and Zn determined by sequential extraction for identification of air pollution sources in Syria. Atmos. Environ. **40**, 753–761 (2006)

Andreae, T.W., Andreae, M.O., Ichoku, C., Maenhaut, W., Cafmayer, J., Karnieli, A., Orlovsky, L.: Light scattering by dust and anthropogenic aerosol at a remote site in the Negev Desert, Israel. J. Geophys. Res. **107**(D2) (2002), doi: http://dx.doi.org/10.1029/2001JD900252

Baker, A.R., French, M., Linge, K.L.: Trends in aerosol nutrient solubility along a west-east transect of the Saharan dust plume. Geophys. Res. Lett. **33**, LO7805 (2006a) doi: http://dx.doi.org/10.1029/2005GL024764

Baker, A.R., Jickells T.D., Witt M., Linge K.L.: Trends in the solubility of iron, aluminium, manganese and phosphorous in aerosol collected over the Atlantic Ocean. Mar. Chem. **98**, 43–58 (2006b)

Bonnet, S., Guieu, C.: Dissolution of atmospheric iron in seawater. Geophys. Res. Lett. **31** (2004) doi: http://dx.doi.org/10.1029/2003GL018423

Chen, Y., Siefert, R.A.L.: Determination of various types of labile atmospheric iron over remote oceans. J. Geophys. Res. **108**(D24) (2003) doi: http://dx.doi.org/10.1029/2003JD003515

Chen, Y., Street, J., Paytan, A.: Comparison between pure water and seawater soluble nutrient concentrations of aerosols from the Gulf of Aquaba. Mar. Chem. **101**, 141–152 (2006)

Chester, R., Lin, F.J., Murphy, K.J.T.: A three stage sequential leaching scheme for the characterisation of the sources and environmental mobility of trace metals in the marine aerosol. Environ. Technol. Lett. **10**, 887–900 (1989)

Chester, R., Murphy, K.J.T., Lin, F.J., Berry, A.S., Bradshaw, G.A., Corcoran, P.A.: Factors controlling the solubilities of trace metals from non-remote aerosol deposited to the sea surface by the dry deposition mode. Mar. Chem. **42**, 107–126 (1993)

Chester, R., Bradshaw, G.F., Corcoran, P.A.: Trace metal chemistry of the North Sea particulate aerosol; concentrations, sources and seawater fates. Atmos. Environ. **28**(17), 2873–2883 (1994)

Chester, R., Keyse, S., Nimmo, M.: In: Martin J-M, Barth H. (eds.) Factors controlling the solubility of Pb in rainwater; the solid state speciation of Pb in scavenged aerosols. Water Poll. Res. Report **32**, 287–298 (1995)

Chester, R., Nimmo, M., Keyses, S.: The influence of Saharan and middle eastern desert-derived dust on the trace metal composition of Mediterranean aerosols and rainwaters: an overview. In: Guerzoni, S., Chester, R. (eds.) The impact of desert dust across the Mediterranean, pp. 253–273. Kluwer, The Netherlands (1996)

Chester, R., Nimmo, M., Fones, G.R., Keyse, S., Zhang, J.: The solubility of Pb in coastal marine rainwaters: pH-dependent relationships. Atmos. Environ. **34**, 3875–3887 (2000)

Chiapello I., Bergametti G., Chatenet B., Bousquet P., Dulac B., Santos Soares E.: Origins of African dust transported over the northeastern tropical Atlantic. J. Geophys. Res. **102**(D12), 13,701–13,709 (1997)

Dabek-Zlotorzynska, E., Aranda-Rodriguez, R., Buykx, S.E.J.: Development and validation of capillary electrophoresis for the determination of selected metal ions in airborne particulate matter after sequential extraction. Anal. and Bioanal. Chem. **372**, 467–472 (2002)

Dabek-Zlotorzynska, E., Kelly, M., Chen, H., Chakrabarti, C.L.: Evaluation of capillary electrophoresis combined with a BCR sequential extraction for determining distribution of Fe, Zn, Cu, Mn, and Cd in airborne particulate matter. Anal. Chim. Acta **498**, 175–187 (2003)

Dabek-Zlotorzynska, E., Kelly, M., Chen, H., Chakrabarti, C.L.: Application of capillary electrophoresis combined with a modified BCR sequential extraction for estimating the distribution of selected trace metals in PM2.5 fractions of urban airborne particulate matter. Chemosphere **58**, 1365–1376 (2005)

Desboeufs, K.V., Sofikitis, A., Losno, R., Colin, J.L., Ausset, P.: Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter. Chemosphere **50**, 195–203 (2005)

Falkovich, A.H., Schkolnik, G., Ganor, E., Rudich, Y.: Adsorption of organic compounds pertinent to urban environments onto mineral dust particles. J. Geophys. Res. **109**, D02208 (2004) doi: http://dx.doi.org/10.1029/2003JD003919

Fernandez, A.J., Ternero, M., Barragan, F.J., Jimenez, J.C.: An approach to characterization of sources of urban airborne particles through heavy metal speciation. Chemosphere **2**, 123–136 (2000)

Fernandez Espinosa A.J., Ternero M., Barragan F.J., Jimenez J.C.: A chemical speciation of trace metals for fine urban particles. Atmos. Environ. **36**, 773–780 (2002)

Fuchtjohann, L., Jakubowski, N., Galdthe, D., Barnowski, C., Klockow, D., Broekaert, J.A.C.: Determination of soluble and insoluble nickel compounds in airborne particulate matter by graphite furnace atomic absorption spectrometry and inductively coupled plasma spectrometry. Fresenius' J. Anal. Chem. **366**, 142–145 (2000)

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

Guieu, C., Chester, R., Nimmo, M., Martin, J.M., Guerzoni, S., Nicolas, E., Mateu, J., Keyse, S.: Atmospheric input of dissolved and particulate metals to the North Western Mediterranean. Deep-Sea Res. II **44**, 665–674 (1997)

Guieu, C., Loye-Pilot, M-D., Ridame, C., Thomas C.: Chemical characterization of the Saharan dust end-member: some biogeochemical implications for the western Mediterranean Sea. J. Geophys. Res. **107** (D15) (2002) doi: http://dx.doi.org/10.1029/2001JD000582.

Hand, J.H., Mahowald, N.M., Chen, Y., Siefert, R.L., Luo, C., Subrmaniam, A., Fung, I.: Estimates of atmospheric processed soluble iron form observation and a global mineral aerosol model: biogeochemical implications. J. Geophys. Res. **109**, D17205 (2004) doi: http://dx.doi.org/10.1029/2004JD004574

Heal, M.R., Hibbs, L.R., Agius, R.M., Beverrlan, I.J.: Total and water-soluble trace metal content of urban background PM_{10}, $PM_{2.5}$, and black smoke in Edinburgh, UK. Atmos. Environ. **39**, 1417–1430 (2005)

Herut, B.: Levels of aerosol trace metals along the Mediterranean coast of Israel (1997). Fresenius Environ. Bull. **10**, 89–93 (2001)

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

Jickells, T.D.: Atmospheric inputs of metals and nutrients to the oceans: their magnitude and effects. Mar. Chem. **48**, 199–214 (1995)

Koçak, M., Nimmo, M., Kubilay, N., Herut, B.: Spatio-temporal aerosol trace metal concentrations and sources in the Levantine Basin of the Eastern Mediterranean. Atmos. Environ. **38**, 2133–2144 (2004)

Koçak, M., Kubilay, N., Herut, B., Nimmo, M.: Total and leachable atmospheric particulate fluxes of heavy metals (Al, Fe, Mn, Pb, Cd, Zn, Cu) over the Levantine Basin; a refined assessment. Atmos. Environ. **39**, 7330–7341 (2005)

Kubilay, N., Saydam, C.: Trace elements in atmospheric particulates over the Eastern Mediterranean: concentration, sources and temporal variability. Atmos. Environ. **29**, 2289–2300 (1995)

Lim, B., Jickells, T.D., Colin, J.L., Losno, R.: The solubilities of Al, Pb, Cu and Zn in rain sampled in the marine environment over the North Atlantic Ocean and Mediterranean Sea. Glob. Biogeochem. Cycles **8**, 349–362 (1994)

Mahowald, N.M., Baker, A., Bergametti, G., Brooks, N., Duce, R.A., Jickells, T.D., Kubilay, N., Propsero, J.M., Tegen: Atmospheric global dust cycle and iron inouts to the Ocean. Global Biogeochem. Cycles **19**, GB4025 (2005) doi: http://dx.doi.org/10.1029/2004GB002402

Pinzani, M.C.C., Somogyi, A., Siminovici, A.S., Ansell, S., Steenari, B.M., Lindovist, O.: Direct determination of Cadmium speciation in municipal solid waste fly ash by synchrotron radiation induced μ-X-ray fluorescence and μ-X-ray absorption spectroscopy. Environ. Sci. Technol. **36**, 3165–3169 (2002)

Profumo, A., Spini, G., Cucca, L., Pesavento M.: Determination of inorganic nickel compounds in the particulate matter of emissions and workplace air by selective sequential extraction. Talanta **61**, 465–472 (2003)

Rudnick, R.L., Gao, S.: Composition of the continental crust. Treatise in Geochem. **3**, 1–46 (2003)

Sedwick, P.N., Church, T.M., Bowie, A.R., Marsay, C.M., Ussher, S.J., Achilles, K.M., Lethaby, P.J., Johnson, R.J., Sarin, M.M., McGillicuddy, D.J.: Iron in the Sargasso Sea (Bermuda Atlantic Time-series Study region) during summer: Eolian imprint, spatiotemporal variability, and ecological implications. Global Biogeochem. Cycles 19(4) (2005)

Slejkovec, Z., Salma, I., van Eletren, J.T., Zemplen-Papp, E.: Speciation of arsenic in coarse and fine urban aerosols using sequential extraction combined with liquid chromatography and atomic fluorescence detection. Fresenius' J. Anal. Chem. **366**, 830–834 (2000)

Sobonska, S., Riqo, N., Laboudigue, A., Bremard, C., Laureyns, J., Merlin, J.C., Wignacourt, P.: Microchemical investigation of dust emitted by a lead smelter. Environ. Sci. Technol. **33**, 1334–1339 (1999)

Spokes, L.J., Jickells T.D., Lim B.: Solubilisation of aerosol trace metals by cloud processing: a Laboratory study. Geochim. Cosmochim. Acta **58**, 3281–3287 (1994)

Taylor, S.R., McLennan, S.M.: The continental crust; Its composition and evolution. Blackwell, Oxford, UK (1985)

Voutsa, D., Samara, C.: Labile and bioaccessible fractions of heavy metals in the airborne particulate matter from urban and industrial areas. Atmos. Environ. **36**, 3583–3590 (2002)

Wedepohl, H.: The composition of the continental crust. Geochim. Cosmochim. Acta **59**, 1217–1239 (1995)

Zatka, V.J., Warner J.S., Maskery D.: Chemical speciation of nickel in airborne dusts: analytical methods and results of an interlaboratory test program. Environ. Sci. Technol. **26**, 138–144 (1992)

Zhu, X.R., Prospero, J.M., Millero, F.J., Savoie, D.L., Brass, G.W.: The solubility of ferric ion(do you mean iron?) in marine aerosol solutions at ambient relative humidities. Mar. Chem. **38**, 91–107 (1992)