The spatial and temporal trace metal concentrations (Al, Fe, Mn, Cr, Cu, Pb, Cd, Zn) in the Eastern Mediterranean aerosol

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Abstract- Aerosol samples collected from different sites (Erdemli, Eastern Turkey & Tel Shikmona, Israel) around the Eastern Mediterranean basin during the same period (1999 – 2001) were analysed for a suite of trace metals (Al, Fe, Mn, Cr, Cu, Pb, Cd, Zn). Spatial and temporal variations were investigated. Statistical differences were observed between the two sites for the crustally derived elements Al, Fe, Mn, Cr, and the anthropogenically derived Zn, with all elements except Cr & Cu being enhanced at Tel Shikmona. These observations being consistent with the closer proximity of Tel Shikmona to dessert sources to the south and southeast. The contrary behaviour of Cr being due to the contribution to aerosol populations of local natural ophiolitic minerals. Temporal variability was assessed at Erdemli on an Inter-annual basis. The only significant difference was calculated for Cr, Cu and Zn which all had lower concentrations compared to 1999 and 2000. This is thought to due to the higher number of Saharan desert pulses during 2001 being measured, effectively lowering the impact of local derived material enriched in Cr, during the sampling period.Separate desert dust events experienced simultaneously at both sites, again indicated spatial differences, with enhanced concentrations of Al, Fe, Mn, by factors 1.6, 1.5, and 1.8 respectively being observed at Tel Shikmona. During these common dust events EFcrust values for all considered elements (except Cr and Cu) were the similar at both sites indicating that the general chemical character of the dust events were similar at each site. However Cr and Cu EFcrust were higher at Erdemli, suggesting a significant contribution of local natural / anthropic material.

Keywords- aerosol, trace metals, Eastern Mediterranean

Introduction

It is now accepted that the input of trace metals to the sea surface from the atmosphere is quantitatively significant. Indeed, it has been established that for coastal seas bordered by industrial nations atmospheric inputs of elements such as Pb, Cd and Zn may be in excess of those from other sources. This has been found for the North Sea (Chester et al., 1993), the Irish Sea (Fones, 1996) and the Western Mediterranean Sea (Chester et al., 1990). Additionally the inputs of trace elements to the sea surface extend over open ocean systems, via long-range transport. Such inputs have been recently postulated to be a potential source of nutrients to high nutrient low productivity regions, hence potentially stimulating primary productivity (e.g. Fe in the Southern Ocean). Atmospheric inputs of trace elements have also been shown to influence the distribution of trace metals in the open ocean sea surface, classical examples being those for Pb and Al. These elements in certain regions exhibit surface maximum in their dissolved concentrations.

Owing to the important influence of atmospheric derived trace metals on marine biogeochemical processes, numerous research studies have been carried out over the last two decades to better understand and quantify atmospheric inputs of trace metals to the marine environment. These studies have considered a whole range of marine systems extending from European coastal zones such as the Irish Sea (Chester et al., 2000; Fones, 1996), the North Sea (Chester et al., 1993), the English Channel (Wells, 1999) and the Western Mediterranean (Chester et al., 1990; Guieu et al., 1997) to open ocean environments such as the Northern Pacific (Duce et al., 1983). Studies have used either land-based stations (covering annual sampling periods) [Chester et al., 1990] or transient sampling studies on research cruises or ships of opportunity (Kubilay et al., 1994).

Dry deposition of trace metals is influenced by the ambient aerosol trace metal concentrations. Therefore to calculate the atmospheric fluxes it is necessary to define aerosol trace metal concentrations and to understand the factors that influence the variability of aerosol trace metals. Such factors are (i) aerosol source type, (ii) source emission strength, (iii) source proximity, (iv) air mass transport and (v) removal and chemical transformations during transport.

The current study focuses upon the processes influencing the trace metal concentrations in the Eastern Mediterranean Sea. The atmospheric concentrations of trace elements in the Eastern Mediterranean aerosol and their subsequent inputs have been considered in recent studies (Kubilay and Saydam, 1995; Kubilay et al., 1997; Herut et al., 2001). These studies have clearly shown that the Eastern Mediterranean marine aerosol is strongly impacted by sporadic intense dessert pulses occurring primarily during transition periods in April, May, September and November. During these periods the concentrations of crustally derived trace metal such as Al, Fe and Mn may reach concentrations in excess of the background concentrations by upto two orders of magnitude.

The current study's aim was, therefore, to further define the aerosol trace metal concentrations in the Eastern Mediterranean marine atmosphere and to evaluate the processes impacting upon their variability. The project takes advantage of a library of contemporaneously collected aerosol samples from different sites (one at Erdemli, Eastern Turkish coast and the others at Tel Shikmona, Israel). This sample base provides a unique opportunity to define spatial and temporal variations in the trace metal concentrations around the Eastern Mediterranean basin. In addition the extensive set of samples will allow the monitoring of selected simultaneous dust events influencing the Eastern Basin. From such knowledge and understanding refined inputs of trace metals to the basin may be evaluated.

Sampling and Analytical Methodologies

Aerosol sample were collected from two contrasting sites (See Fig. 1) situated around the Eastern Mediterranean basin, (Erdemli, East Southern Turkey, (ii) Tel Shikmona, Israel. Aerosol Samples were collected using high volume samplers with flow rates around ($1m^3\ min^{-1}$) on Whatman 41 cellulose acetate fibrous filters. Samples were collected over the period February 1999 – December 2001. Temporal resolution of sampling varied from daily (Erdemli, 1999 and 2001; January – June, 2000) and every weekend (Tel Shikmona, covering a three day period) .

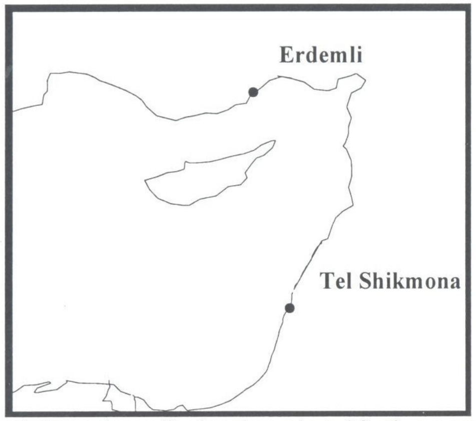

Fig. 1. Aerosol sampling locations adopted for the present study.

After collection aerosol samples underwent a total acid digest using a mixture of concentrated HF and HNO_3 at IMS/METU & UOP (for samples collected at Erdemli) and at IOLR (for samples collected at Tel Shikmona). Running a CRM (BCSS-1), along with the samples, the accuracy and precision of the digestion process was assessed. After total dissolution, digest solutions (samples collected at Erdemli) were analysed for trace elements at the University of Plymouth either by ICP-AES (Al, Fe, Mn, Ca, Mg, Zn, Cu) or ICP-MS (Ti, Cr, Co, Ni, Cd, Sb, Pb, Na, K); samples collected from Tel Shikmona were analysed for elements by GFFAAS & FAAS. To verify the comparability of the measurements made by the different laboratories, an inter- laboratory comparison was carried out. 13 aerosol samples, ranging in trace metal concentration, from the IOLR library, were digested and analysed by the two different groups. For all the common elements (Al, Fe, Mn, Cr, Cu, Cd, Pb, Zn), applying a t-test to the sample populations, there was no statistically significant difference between the two laboratories. Analytical recoveries, as determined by CRM analysis, yielded % recoveries >95% for Al, Fe, Mn, Pb, whereas for Zn, Cu, Cr the recoveries were slightly lower, being >85%.

Operational blank contributions to sample digests amounted to < 5% for all trace elements except for Zn (9%); Cr (9%); Cu (11%). The analytical precision of repeat measurements was <2% for Al, Fe, Mn, Pb and < 5% for Zn, Cd, and Cu, with analytical detection limits being <5% of the average aerosol digest solution concentration (except for Cu and Cd which were approx 13%).

Results and Discussion

Spatial variations

A summary of the trace elemental concentrations observed in the Eastern Mediterranean aerosol at the different sampling sites is presented in Table 1. The data is summarised in terms of the arithmetic and geometric means, although the geometric mean is a more representative indicator of concentrations (owing to the lognormal distributions of sample populations), and is commonly used in the literature. Considering the data in Table 1 it is clear that there are generally higher aerosol trace metal concentrations observed at Tel Shikmona compared to those detected at Erdemli, this is particularly true for those elements which have a predominantly crustal natural source. This group includes the elements Al, Fe, and Mn (all have EF crust <10; see later). Indeed for these elements their concentrations are enhanced by factors of 1.7, 1.8 and 2.1 (for Al, Fe and Mn respectively). Applying the Mann-Whitney test (used for nonparametric populations) it was shown that the difference observed between the two locations was statistically significant at the 95% confidence interval. This enhancement may be explained by the closer proximity of the Tel Shikmona site to crustal dessert sources, to the south and southeast. However an element, which exhibits contrasting behaviour, is Cr, although generally cited as a crustally derived element [Chester et al., 1990] the concentration of Cr at Tel Shikmona is statistically lower than that detected at Erdemli ($2.27 ngm^{-3}$ compared to $3.94\ ngm^{-3}$). This is most likely to be due to the geological character of the local environment around Erdemli. The crust is enriched with ophiolitic minerals, leading to an enhancement of Cr in local crustal material.

Table 1 The trace metal concentrations (ng m^{-3}) in the Eastern Mediterranean aerosol (Sampling period 1999-2001)

	Tel Shikmona	Erdemli
	Geometric mean ; (Arithmetic mean ± St dev): range	**Geometric mean ; (Arithmetic mean ± St. dev): range**
Al	952 ; (2138 ± 5091)	567 ; (813 ± 897) ; 14.4 – 8278
Fe	724; (1265 ± 2633)	406; (554 ± 524); 7.8 – 5601
Mn	16.7; (26.1 ± 47.8)	7.91; (16.9 ± 8.82); 0.03-92.7
Cr	2.27; (3.61 ± 5.86)	3.94; (5.68 ± 5.02); 0.02-39
Cu	5.94; (7.3 ± 5.13)	8.97; (10.8 ± 7.5); 1.0-65.6
Pb	24.9; (32.1 ± 22.8)	21.5; (34.4 ± 43.7); 0.3-586
Cd	0.22; (0.27 ± 0.25)	0.17; (0.21 ± 0.19) ;0.01-2.36
Zn	22.3; (30.7± 28)	15.9; (20.4 ± 35.1); 0.7-743

Similar to the crustal elements the overall concentrations of those elements derived principally from anthropic sources (Cd, Pb & Zn) are enhanced at Tel Shikmona, although the inter-site difference is only statistically significant for Zn. Similar trends in trace metal concentration between the two sampling sites have been presented previously (Herut et al., 2001), except that absolute aerosol concentrations at both sites for Pb appears to have decreased, this is likely due to diminished emissions of this element to the atmosphere.

The determination of elemental sources has been defined historically with the application of the EFcrust (crustal enrichment factor). For crustal sources, Al is normally used as the source indicator element and the earth's crust as the source material. The EF_{crust} value is then calculated according to the equation:

$$EF_{crust} = (Cxp/CAlp)/(Cxc/CAlc)$$

Where (Cxp and CAlp) are the concentrations of a trace metal x and Al, respectively, in the aerosol, and (Cxc and CAlc) are their concentrations in average crustal material. By convention, an arbitrary average EF_{crust} value of <10 is taken as an indication that an element in an aerosol has a predominantly crustal source, In contrast, EF_{crust} > 10 is considered to indicate that a significant proportion of an element has a non-crustal source. Table 2 highlights the EF_{crust} values for the current study As predicted the elements, Fe, Mn and Cr all have EF_{crust} <10 and are therefore classified as non-enriched elements, having a predominantly crustal natural source to the atmosphere. Cr clearly has a slightly higher EF_{crust} at Erdemli, which is in agreement with the concept of a local enriched natural material. The remaining elements Pb, Cd and Zn are enriched elements (EF_{crust} > 10) and are hence assumed to have non-crustal sources. Higher EF_{crust} were detected at Erdemli, being likely due to the lower influence of the overall aerosol population of Saharan dust incursions compared to Tel Shikmona, diluting to a lower degree the anthropic derived material.

Table 2. EF_{crust} values at Erdemli and Tel Shikmona

	Tel Shikmona	Erdemli
	Geometric mean;(Arithmetic mean ± St dev): range	Geometric mean; (Arithmetic mean ± St dev): range
Fe	1.2; (1.6 ± 0.6)	1.2; (1.2 ± 0.6)
Mn	1.4; (1.6 ± 0.7)	1.2; (1.6 ± 0.7)
Cr	1.9; (2.2 ± 1.1)	5.1; (8.3 ± 9.7)
Cu	9.3 (13.2±11)	23.7 (34.3 ±51.5)
Pb	174; (288 ± 279)	254; (460 ± 669)
Cd	94; (142 ± 134)	122; (186 ± 269)
Zn	26; (43± 57)	33; (49 ± 109)

Temporal Variability

As the samples considered in the current study were collected over a three-year sampling period, any temporal variability was investigated. For the current study only the sample database for Erdemli was considered in this comparison (n=550).

Applying a Mann- Whitney test between the trace metal datasets for each of the years 1999, 2000, and 2001 at the 95% confidence limit; the following significant difference in concentrations were found. Interestingly there were no statistical differences between sampling periods for Al even though it was clear that during the year 2001 there was a high frequency of intense dessert dust episodes (see later). Cr had statistically lower concentrations during 2001 compared to both 1999 and 2000, this may be explained by a greater contribution during this year to the crustal aerosol component from distant source rather than the more Cr enriched local crustal material. Cu and Zn similarly exhibited statistically significant difference (i.e. concentration in 2001 < 1999 & 2000). No difference was observed for Pb and Cd concentration between the considered years. Table 3 highlights the elemental annual concentrations.

Table 3. Geometric annual trace metal concentrations at Erdemli (expressed in ngm^{-3})

	Al	Fe	Mn	Cr	Pb	Cu	Cd	Zn
All data	567	406	7.91	3.94	21.5	8.97	0.17	15.9
1999	577	443	9.4	5	22.8	12.8	0.18	18.2
2000	487	328	6.6	4.4	20.1	10.2	0.15	18.7
2001	582	404	7.3	3.2	21	6.8	0.16	13.9

Episodic dessert pulses

The seasonal occurrence of dessert pulses has a great influence on the Eastern Mediterranean aerosol trace metal chemistry and the subsequent atmospheric inputs (see above). Additionally, for example in 1992, 30 % of the annual dust input was associated with only two dessert pulse events. Therefore the current library of samples presents a unique opportunity to investigate simultaneous dessert events over a wide graphical area. From such a comparison it might be possible to establish the changes in the chemical nature of the aerosol populations. The sample set from Tel Shikmona and Erdemli were scrutinised, and all potential (first criteria being Al >1000 ngm^{-3}) simultaneous dessert events were identified. As some of the samples may not necessarily be common episodes a further criteria was applied. The samples were then categorised based on their air mass trajectories. From this classification it was noted that 11 common dust event were clearly apparent over the sampling period with most occurring during 2001 (n=8). The trace metal concentrations and EF_{crust} for these populations at the different sites are presented on Table 4.

From the comparison during the common dust events the concentrations of trace metals are enhanced in particular for the crustal derived elements - regional differences amounting to on average; 1.7, 1.6, 1.9 x greater at Tel Shikmona for Al, Fe and Mn respectively. It is clear that the chemical character of the aerosol population at the two sites, as described by the EF_{crust} are very similar for all elements except that Cr which has a slightly higher values at Erdemli. This has previously been explained. The noted similarity in chemical character for the other elements is consistent with a common source of the aerosol material at the two sites.

Table 4. Geometric mean concentrations (expressed as ngm^{-3}) and EF_{crust} in "common" dust events, Tel Shikmona & Erdemli

	Tel Shikmona	Erdemli	EF_{crust}	Tel Shikmona	Erdemli
Al	3400	2019			
Fe	2171	1316	Fe	1.06	0.9
Mn	45	24	Mn	1.14	1.02
Zn	34	21	Zn	11	12.6
Cu	10.7	14.3	Cu	4.7	11
Cr	6.3	10	Cr	1.5	4.1
Cd	0.38	0.24	Cd	47	48
Pb	42	34	Pb	81	111

Summary and Conclusions

The current study has presented preliminary results and interpretations of the spatial and temporal variations of trace metal aerosol concentrations in the Eastern Mediterranean marine atmosphere. These may be summarized as follows:

- Spatial statistical differences were detected at contrasting sites for (all samples) Al, Fe, Mn, Cr and Zn (Erdemli < Tel Shikmona); no difference was detected for Pb & Cd
- Annual temporal variations observed for Cr, Cu, and Zn at Erdemli.
- Lower concentrations of anthropically derived elements (Pb & Zn) at the sampling sites compared with previous sampling periods indicating lower emission source strengths.
- Both sites were subject to intense desert dust pulses - notably during 2001. Common events were categorized. Similar elemental chemical character (EF_{crust}) at both sites was established indication of a common source of material, with regional variations in elemental concentrations (lower concentrations being detected at Erdemli).

This knowledge and understanding of the spatial, temporal, air mass aerosol elemental variability will be used to calculate weighted mean refined inputs. These calculations may be extended to other elements (Sb, Ti, Ni, Co, Mg, Na, Ca, K), for which data is now available for samples collected from Erdemli.

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