Defining the chemical character of aerosols from the atmosphere of the Mediterranean Sea and surrounding regions

Mediterranean atmosphere
Aerosols
Trace metals
"European background"
Saharan dust

Atmosphère méditerranéenne
Aérosols
Métaux-traces
«Composante européenne»
Poussière saharienne

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Received 31/08/92, in revised form 7/05/93, accepted 11/05/93.

ABSTRACT

Atmospherically-transported trace metals can play an important role in biogeochemical cycles in the Mediterranean Sea. However, although the magnitude of trace metal air to sea fluxes is initially dependent on the metal concentrations in the air, it is the "chemical character" of the aerosol which constrains the fate of the metals in sea water; for example, the solubility of trace metals is considerably greater from anthropogenic than from crustal components. To a first approximation the chemical composition of the Mediterranean particulate aerosol is controlled by the extent to which an anthropogenic-rich "background" material, having a mainly European origin, is perturbed by mixing with crustal components having a desert origin. These perturbations offer an environmentally meaningful index which can be used to define the "chemical character" of the Mediterranean particulate aerosol in terms of the manner in which trace metals are partitioned between the anthropogenic and crustal components.

This "chemical character" concept was assessed using: a) a total of 83 particulate aerosols collected on a W → E transect across the Mediterranean Sea and surrounding regions; and b) particulate aerosol populations from a number of adjacent coastal seas. The crustal component in the samples was assumed to have the composition of the average crust and trace metals in excess of their crustal metal:Al ratios were assigned to a European aerosol "background' component (EABC). It was found that the average Zn:Cu, Zn:Ni, Zn:Cr and Zn:Mn ratios in the EABC indicate that it has a composition which is generally similar to the average anthropogenic background emissions of trace metals over Europe.

The extent to which the EABC is affected by mixing with crustal material in the particulate aerosols was estimated using enrichment factors in which Al is employed as the source indicator; thus, $EF_{crust} = (C_{xp}/C_{Alp})/(C_{xc}/C_{Alc})$, in which C_{xp} and C_{Alp} are the concentrations of an element x and Al, respectively, in the aerosol, and C_{xc} and C_{Alc} are their concentrations in average crustal material. Elements which have EF_{crust} values < 10 in a particulate aerosol are assumed to

have a significant crustal source and are termed non-enriched elements (NEEs), and those which have $EF_{crust} > 10$ are assumed to have a significant non-crustal source and are termed anomalously enriched elements (AEEs).

For a particulate aerosol composed of crustal and anthropogenic components the EF_{crust} values of the AEEs will be reduced as the proportions of crustal material increase. When this is expressed in the form of an EF diagram, in which the EF_{crust} values of a trace metal in a particulate aerosol population are plotted against the concentrations of Al, the particulate aerosols from the atmosphere of the Mediterranean Sea and surrounding regions can be described in terms of the extent to which the EABC is mixed with, and diluted by, crust-rich components. Under certain conditions the "mixing relationship" is distorted by relatively large inputs of either: a) crust-rich components, or b) urban-rich material having a local origin. However, the overall "chemical character" of the aerosols can be assessed on the basis of the EF_{crust} values of the AEEs Cd, Pb, Zn, Cu, Ni and Cr.

Oceanologica Acta, 1993. **16**, 3, 231-246.

RÉSUMÉ

Caractère chimique des aérosols atmosphériques de la Mer Méditerranée et des régions voisines

Les métaux-traces transportés par l'atmosphère peuvent jouer un rôle important dans les cycles biogéochimiques de la Mer Méditerranée. Les flux de métaux-traces de l'atmosphère vers la mer dépendent essentiellement des concentrations de métaux dans l'air, mais c'est le «caractère chimique» de l'aérosol qui détermine le devenir des métaux dans l'eau de mer ; ainsi, la solubilité des métaux-traces est beaucoup plus grande dans la fraction anthropogénique que dans la fraction crustale. En première approximation, la composition chimique de l'aérosol particulaire méditerranéen est déterminée par le mélange de son constituant principal, d'origine anthropogénique essentiellement européenne, avec les constituants crustaux en provenance du désert. Cette perturbation est une caractéristique de l'environnement qui peut être utilisée pour définir le «caractère chimique» de l'aérosol particulaire méditerranéen, exprimé en termes de répartition de métaux-traces entre les fractions anthropogénique et crustale.

Le concept de «caractère chimique» a été établi en utilisant d'une part 83 aérosols particulaires, prélevés en Mer Méditerranée (radiale Ouest-Est) et dans les régions avoisinantes, et d'autre part des populations d'aérosols particulaires en provenance de plusieurs mers bordières adjacentes. La fraction crustale des échantillons est supposée avoir la composition moyenne de la matière crustale ; les métaux-traces en excès (valeurs déterminées par les rapports de leurs concentrations à celle de Al) sont attribués à la composante européenne de l'aérosol («EABC»). Les rapports Zn/Cu, Zn/Ni, Zn/Cr et Zn/Mn dans EABC indiquent que sa composition est généralement semblable à celle des émissions anthropogéniques de métaux-traces en Europe.

Le mélange de la matière crustale et de la composante EABC dans les aérosols particulaires est évalué par les facteurs d'enrichissement («EF») avec Al comme indicateur d'origine ; ainsi $EF_{croûte} = (C_{xp}/C_{Alp})/(C_{xc}/C_{Alc})$, où C_{xp} et C_{Alp} sont les concentrations des éléments x et Al dans l'aérosol, et C_{xc} et C_{Alc} sont les concentrations moyennes dans la matière crustale. Les éléments qui ont des valeurs $EF_{croûte}$ inférieures à 10 dans un aérosol particulaire sont supposés avoir une origine essentiellement crustale et sont des éléments non enrichis («NEE»), tandis que ceux pour lesquels les valeurs $EF_{croûte}$ sont supérieures à 10 sont supposés avoir une origine non crustale et sont appelés éléments artificiellement enrichis («AEE»).

Pour un aérosol particulaire ayant des constituants crustaux et anthropogéniques, les valeurs $EF_{croûte}$ des AEE diminuent lorsque la proportion de matière crustale augmente. Dans un diagramme où les valeurs $EF_{croûte}$ d'un métal-trace dans une population d'aérosol particulaire sont portées en fonction des concentrations de Al, les aérosols particulaires de l'atmosphère de la Méditerranée et des régions voisines peuvent être décrits en termes de mélange et de dilution de la composante

EABC avec les constituants majeurs de la croûte. Dans certaines conditions, la «relation de mélange» est modifiée par des apports relativement importants de constituants majeurs de la croûte ou de matière d'origine urbaine locale. Pourtant le «caractère chimique» global des aérosols peut être estimé par les valeurs $EF_{croûte}$ des éléments AEE Cd, Pb, Zn, Cu, Ni et Cr.

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INTRODUCTION

To gain a full understanding of the marine cycles of trace metals it is necessary to evaluate the relative importance of fluvial and atmospheric inputs to sea water. With respect to the atmospheric inputs the Mediterranean Sea is of special interest because it is bordered on its northern shore by industrialised regions, which act as a source for the supply of anthropogenic material to the atmosphere, and on its southern and eastern shores by arid and desert regions, which are sources for crustal material. Further, the meteorological regime over the Mediterranean Sea results in seasonal differences in the inputs of the anthropogenic-rich and crust-rich material. A considerable amount of work has been carried out on particulate and aqueous phases in the Mediterranean atmosphere. Topics covered include: a) the distribution of aerosols (*see e. g.* Chester *et al.*, 1977; Prospero, 1979; Prodi and Fea, 1979; Yaalon and Ganor, 1979; Ganor and Mamane, 1982); b) the relationship between aerosol deposition and sediments (*see e. g.* Chester *et al.*, 1977; Tomadin, 1981; Lenaz *et al.*, 1983; Tomadin *et al.*, 1983; Tomadin *et al.*, 1984; Correggiari *et al.*, 1989; Tomadin and Lenaz, 1989); c) the mineral, major element, trace metal, nutrient and organic composition of aerosols and rainwaters (*see e. g.*: Buat-Ménard and Arnold, 1978; Chester *et al.*, 1981; Arnold *et al.*, 1982; Chester *et al.*, 1984; Tomadin *et al.*, 1984; Mazzucotelli *et al.*, 1984; Loye-Pilot *et al.*, 1986; Dulac *et al.*, 1987; Guerzoni *et al.*, 1988; Lenaz *et al.*, 1988; Losno *et al.*, 1988; Bergametti *et al.*, 1989; Guerzoni *et al.*, 1989; Dulac *et al.*, 1989; Chester *et al.*, 1990; Guieu *et al.*, 1990; Sicre *et al.*, 1990; Chester *et al.*, 1991; Condé *et al.*, 1991; Simo *et al.*, 1990; 1991; Guerzoni *et al.*, 1991); d) atmospheric inputs of particulate and dissolved phases to the sea surface: (*see e. g.*; Migon *et al.*, 1989; Loye-Pilot *et al.*, 1989; Loye-Pilot, 1990; Guieu *et al.*, 1990; Alarcon and Cruzado, 1990; Guieu *et al.*, 1991; Migon *et al.*, 1991; Loye-Pilot *et al.*, 1991; Remoudaki *et al.*, 1991). One of the most significant findings to emerge from these studies is that the atmosphere is an important route by which trace metals are transported to the Mediterranean Sea (*see e. g.*: Martin *et al.*, 1989). Further, these atmospherically-transported trace metals can play an important role in some marine biogeochemical cycles (*see e. g.*: Boyle *et al.*, 1985; Hydes, 1985).

Particulate aerosols are deposited to the sea surface by "dry" (including gravitational) and "wet" (precipitation scavenging) processes, and the magnitude of the air to sea fluxes is dependent on the concentrations of the trace metals in the air. However, the information provided by concentration data alone is limited. This was recognised by Peirson *et al.* (1974) for particulate aerosols collected at a number of rural sites in the UK. The concentrations of particulate trace metals varied between the sites, but when the metals were normalised to their crustal concentrations it was found that there was a general particulate aerosol over the UK which had a variable trace metal concentration but an essentially uniform elemental composition ("chemical uniformity") in which anthropogenic-derived trace metals were enriched to the same extent relative to crustal material. The partitioning of trace metals between anthropogenic and crust-derived components in particulate aerosols is extremely important because it is one of the controls on the subsequent fate of the metals in the oceanic mixed layer. This was highlighted by Chester *et al.* (1992 *a*) who showed that in non-remote coastal aerosols Pb, Zn and Cu are considerably more soluble from anthropogenic-rich than from crust-rich components, but that Cd and Mn are significantly soluble from both components. Clearly, therefore, it is the manner in which a trace metal is partitioned between the components of particulate aerosols, *i. e.* its "chemical character", and not its concentration in the air, which constrains its fate in the marine environment.

The "chemical character" of a trace metal in a particulate aerosol is governed by a number of complex factors. One of these is the source which supplies the trace metal to the atmosphere. Because this has an important effect on the subsequent fate of the trace metal in sea water, and is therefore environmentally meaningful, "chemical character" in the context of the present paper is defined in terms of this source-related control. The globally-important sources of trace metals to the marine aerosol are: a) low temperature weathering of the Earth's surface (crustal source); b) a variety of mainly high temperature anthrogenic processes (anthropogenic source); and c) sea-salt generation (oceanic source). In addition, volcanic sources can supply trace metals to the Mediterranean atmosphere.

Larger particulate aerosols *e. g.* soil-sized material (> ~ 1.0 µm mass median diameter), are removed from the air during long-range transport and the composition of the bulk aerosol will change with distance from land-based sources. As a result, open-ocean particulate aerosols remote from the continents represent an integration of material from many sources (Maring and Duce, 1990). However, over non-remote seas two sources, *i. e.* anthropogenic and crustal, can dominate the particulate marine aerosol. For example, Dulac *et al.* (1986) concluded that over the Western Mediterranean volcanic activity and sea salt re-cycling from oceanic sources make a negligible contribution to trace metal concentrations in the bulk particulate aerosol. In this context, Chester *et al.* (1981) also suggested that, to a first approximation, the Mediterranean particulate aerosol can be considered to be composed of a mixture of two "end-mem-

ber" components; "background" anthropogenic-rich material, having a mainly European origin, upon which is superimposed "pulses" of dust from crust-rich desert sources.

Even over non-remote seas such as the Mediterranean, however, factors such as distance from the primary land-based sources and differences in the extent of precipitation scavenging result in the concentrations of trace metals varying from one location to another. For example, Bergametti *et al.* (1989) concluded that the two principal factors which control variations in the concentrations of trace metals in aerosols collected at Corsica in the Western Mediterranean are: a) precipitation scavenging, which affects both crustal and anthropogenic trace metal concentrations; and b) the input of Saharan dusts, which affects the crustal trace metal concentrations. Concentrations alone cannot, therefore, be used to fully characterise the Mediterranean aerosol collected at different sites. However, it was suggested above that the chemical composition of the Mediterranean aerosol is largely constrained by the extent to which an anthropogenic-rich "background" material is perturbed by mixing with crustal components having a desert origin. These perturbations therefore offer a potential index to define the "chemical character" of the Mediterranean particulate aerosol in terms of the manner in which trace metals are partitioned between the two principal components. This possibility is explored in the present paper using an extensive data base on the concentrations of particulate atmospheric trace metals over the Mediterranean Sea and surrounding regions.

COLLECTION AND ANALYTICAL TECHNIQUES

To assess the "chemical character" of the particulate aerosol in the atmosphere of the Mediterranean Sea and surrounding regions new data are combined with a number of data sets given in the literature.

The new data

A total of 83 particulate aerosol samples were collected along a W → E transect covering the North Atlantic westerlies/north east trades, the Western Mediterranean, the Tyrrhenian Sea, the Eastern Mediterranean, the Red Sea and the Arabian Sea regions. The samples were collected on board ship on a number of cruises using a high-volume (~ 2 m^3 min^{-1}) system incorporating 165 mm exposed diameter Whatman filters (for full details, *see e. g.* Chester *et al.*, 1991). Trace metals were determined using AA techniques, following the dissolution of the filters in redistilled HNO_3 and Aristar HF in PTFE beakers (for full details, *see e. g.* Chester *et al.*, 1991).

Data from previous studies

To compliment the Mediterranean transect results, data for particulate aerosols from a number of coastal margin and coastal sea sites in the surrounding regions are used in the present study; these sites are Cap Ferrat and Tour de Valet (southern France), Blanes (southeastern Spain), Corsica, the Black Sea, the North Sea and the Kiel Bight. With the exception of the Black Sea, the coastal margin and coastal sea aerosol populations were selected on the basis that samples had been taken over relatively long time periods covering at least several months.

The locations at which the Mediterranean transect, coastal margin and coastal sea samples were collected are illustrated in Figure 1.

RESULTS

For the purposes of the present study, the particulate aerosols have been assigned to a number of populations.

The total transect population (TT)

This includes all samples along the W → E transect for the Mediterranean Sea and surrounding regions.

Both the Eastern Mediterranean and the Red Sea receive inputs of atmospheric material from the same sources in the surrounding arid lands. In contrast, the Arabian Sea lies further to the east and the atmosphere receives both crustal material from the adjacent arid regions and anthropogenic material from distant European sources (Chester *et al.*, 1991). The Arabian Sea particulate aerosols were collected during the northeast monsoon regime, and it must be stressed that they will not be transported over the Mediterranean Sea. They are included in the present study simply to represent

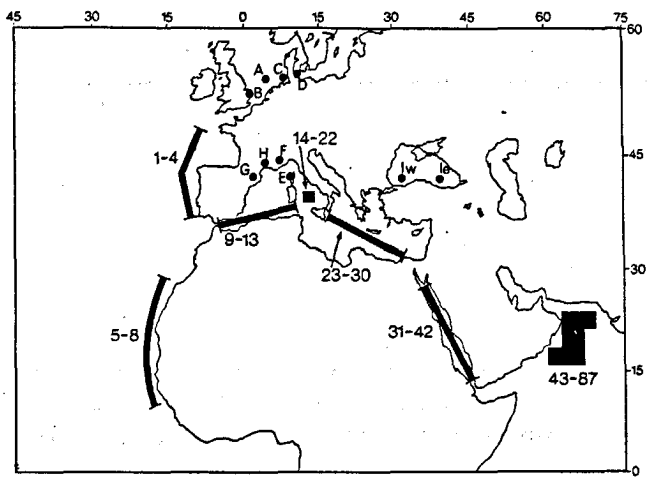


Figure 1

Locations of the particulate aerosol samples. Data sources: a) Mediterranean transect samples. 1-4, the North Atlantic westerlies (Murphy, 1985). 5-8, the North Atlantic trades (Murphy, 1985). 9-13, the Western Mediterranean (Sanders, 1983 and Saydam, 1981). 14-22, the Tyrrhenian Sea (Chester et al., 1984). 23-30, the Eastern Mediterranean (Sanders, 1983 and Saydam, 1981). 31-42, the Red Sea (Sanders, 1983). 43-87, the Arabian Sea (Sanders, 1983 and Berry, 1990); b) the coastal margin and coastal sea sites. A, the North Sea. Shipboard collection in southern North Sea (Chester and Bradshaw, 1991). B, Hemsby (Yaaqub, 1991). C, Helgoland (Kersten et al., 1989). D, Kiel Bight (Schneider, 1987). E, Corsica (Bergametti et al., 1989). F, Cap Ferrat (Chester et al., 1990). G, Blanes (Chester et al., 1991). H, Tour du Valet (Guieu, 1991). I, The Black Sea. Shipboard collection in Western (Iw) and Eastern (Ie) Black Sea..

Table 1

The average concentrations of particulate trace metals in the atmosphere over the Mediterranean Sea and surroundings regions (conc. units ng m^{-3}g air).

A: Mediterranean transect particulate aerosol populations [1].

Trace metal	Average concentration[2]					
	TT		MS		AS	
	A	G	A	G	A	G
Al	8177	1036	14773	936	2021	1139
Fe	5797	850	10092	707	1673	869
Mn	90.5	16	160	16	24	15
Ni	10	3.6	14	4.2	6.0	3.0
Cr	12	3.3	18	3.1	6.6	3.7
Cu	7.7	3.2	12	3.4	3.6	2.9
Zn	16.5	8.5	26	12	8.0	5.7
Pb	8.5	5.9	13.5	10.5	3.8	3.3
Cd	0.155	0.083	0.27	0.17	0.050	0.046

1, see text for definition of the aerosol populations.
2, A = arithmetic average; G = geometric average.

B: Coastal margins and coastal sea particulate aerosol populations.

Trace metal	Collection site*									
	A	B	C	D	E	F	G	H	I	J
Al	294.5	-	210	394	168	370	398	380	460	318
Fe	353	216	201	369	144	320	316	275	400	275
Mn	14.5	10	7.2	15	5.3	11	10	13	16	11
Ni	3.8	2.7	2.6	4.0	-	2.8	5.5	-	-	3.4
Cr	4.7	-	1.7	2.9	-	2.5	1.8	-	6.3	2.9
Cu	6.3	-	3.9	7.7	2.1	6.2	7.9	3.8	-	5.0
Zn	41	41	33	57	19	41	50	60	42	41
Pb	34.5	34	29	53	16	58	50	56	54	40
Cd	-	1.1	1.4	-	-	0.36	0.60	0.51	-	0.70

* see *Figure 1.*

A: North Sea (Chester and Bradshaw, 1991).
B: Hemsby, North Sea coastal site in SE England (Yaaqub et al., *1991).*
C: Helgoland, North Sea (Kersten et al., *1989).*
D: Kiel Bight (Schneider, 1987).
E: Corsica (Bergametti et al., *1989).*
F: Cap Ferrat, Mediterranean coastal site, South France (Chester et al., *1990).*
G: Blanes, Mediterranean coastal site, South Spain (Chester et al., *1991).*
H: Tour du Valet, Mediterranean coastal site, South France (Guieu, 1991).
I: Black Sea, average for Western Black Sea (west of ≈ 33°W, air masses from West and South) and Eastern Black Sea (east of ≈ 33°W, air masses from East and North; Tuncel, pers. comm.).
J: Geometric average for all coastal margin and coastal sea sites.

the composition of particulate aerosols derived from sources lying to the east of the Red Sea. For this reason, two particulate aerosol populations have been identified within the TT.

The Mediterranean Sea population (MS)

This is restricted to the North Atlantic westerlies/north east trades, Western Mediterranean, Tyrrhenian Sea, Eastern Mediterranean, and Red Sea aerosols, and represents material which can be directly transported into the atmosphere of the Mediterranean Sea.

The Arabian Sea population (AS)

This is confined to the Arabian Sea particulate aerosols and represents material from sources lying to the east of the Red Sea.

The coastal margin and coastal sea sites population (CMCS)

Average data for the various individual populations are listed in the appropriate tables in the text.

DISCUSSION

Concentrations of particulate trace metals in the atmosphere of the Mediterranean Sea and surrounding regions

Data for the concentrations of trace metals in the various particulate aerosol populations are given in Table 1. From the point of view of the present study two important trends can be identified on the basis of the average geometric concentration data; geometric averages are used for comparative purposes to avoid bias towards the higher concentration values, *e.g.* in the Red Sea samples. a) the CMCS aerosols contain 8.4 times more Cd, 6.8 times more Pb, 4.8 times more Zn and 1.6 times more Cu than the TT aerosols. However, the concentrations of Ni and Cr are about the same in the aerosols from the two populations, and the TT contains higher concentrations of Mn, Fe and Al; b) the MS aerosols contain 3.7 times more Cd, 3.2 times more Pb and 2.1 times more Zn than the AS aerosols. However, the concentrations of Al, Fe, Cu, Ni, Cr and Mn are about the same in aerosols from the two populations. It is apparent, therefore, that the average concentrations of Cd, Pb and Zn in the aerosol populations decrease in the order CMCS > MA > AS, whereas the average concentrations of Ni and Cr show little variation between aerosols in the three populations.

The manner in which the variations in the concentrations of the trace metals constrain the "chemical character" of the aerosols in the various populations is discussed in the following sections.

The composition of the anthropogenic and crustal components in the Mediterranean particulate aerosol

If it is assumed that, to a first approximation, the aerosol over the Mediterranean Sea and surrounding regions can be described in terms of a two-component system in which anthropogenic "background" is mixed with crustal material, then the composition of one component can be estimated if that of the other is known. It is usual to assume a uniform chemical composition for mineral dust, *i. e.* crustal material, in the atmosphere (*see e. g.*; Rahn, 1976); for example, Schneider (1987) assumed that the contribution to any trace metal in an aerosol from this source will form a constant ratio to Al which is the same as that in average crustal material. In the present paper, metal: Al ratios for average crustal material were taken from Taylor (1964). The ratios for each individual aerosol sample were then calculated and the "excess" for each trace metal over that of the crustal material was assumed to represent the anthropogenic "European aerosol background component" (EABC) transported over the Mediterranean Sea and surrounding regions.

If the trace metals in the EABC do in fact represent the European "background", their metal-metal ratios should be the same as those in the general anthropogenic atmospheric emissions from European sources, and following Schneider (1987) and Yaaqub *et al.* (1991) Zn:metal ratios are used here to test this. Pacyna *et al.* (1984) gave data on the anthropogenic emissions of trace metals to the atmosphere over Europe; these authors did not include Al and Fe, but data were provided on the other trace metals included in the present study. Following Schneider (1987) and Yaaqub *et al.* (1991), zinc was used as a reference element and zinc:metal ratios have been calculated for the average European emissions. In order to take account of spatial variations in emission strengths representative ratios have also been calculated for Western and Eastern European sources (*see* Tab. 2). Data for the average Zn:metal ratios in

Table 2

Average Zn:metal ratios in the estimated "European aerosol background component" (EABC) and European anthropogenic emissions.

Zn:metal ratio	EABC[1]								European emissions[2]		
	TT		MS		AS		CMCS		Total emissions	Western European emissions[3]	Eastern European emissions[4]
	A	R	A	R	A	R	A	R			
Zn:Pb	1.4	0.24 - 11	1.1	0.24 - 2.6	1.7	0.37 - 11	1.0	0.70 - 1.2	0.65	0.65	0.54
Zn:Cu	5.9	0.25 - 27	7.6	0.60 - 29	4.2	0.25 - 24	8.6	6.3 - 16	5.2	8.2	3.4
Zn:Ni	5.4	0.31 - 34	6.3	0.74 - 34	4.5	0.31 - 21	13	9.1 - 15	5.0	6.3	3.8
Zn:Cr	4.8[5]	0.44 - 37	7.5[5]	0.55 - 37	2.7	0.44 - 17	16.5	6.7 - 28	4.2	4.8	3.2
Zn:Mn	3.9	0.41 - 19	4.5	0.48 - 19	3.6	0.41 - 9.0	3.9	2.6 - 5.0	4.5	5.1	3.3
Zn:Cd	98	5.3 - 375	85	5.3 - 250	111	36 - 375	75	23.5 - 118	30	34	26

A: Arithmetic average of the ratios for individual samples.
R: Range.
1: For details of the calculations of EABC, and definition of the TT, MS, AS and CMCS aerosol populations (see *text*).
2: Data from Pacyna et al. *(1984).*
3: Data from Pacyna et al. *(1984). Representative Western European emissions are the average for France, UK, Germany, Spain and Italy.*
4: Data from Pacyna et al. *(1984). Representative Eastern European emissions are the average for the USSR, Poland, Turkey, Greece, Bulgaria and Rumania.*

the EABC for the TT, the MS, the AS and the CMCS particulate aerosol populations are also given in Table 2; for the present purpose, arithmetric average ratios are used in order to compare the data with those provided in the literature. There are relatively large ranges in the Zn:metal ratios, but these are not uncommon in Mediterranean particulate aerosol (for example, Dulac *et al.* (1987) reported Pb:Cd ratios in the range ~ 1.5 - ~ 230 for aerosols from the Western Mediterranean), and a number of trends can be identified from the average Zn:metal ratios listed in Table 2. These trends are summarised below.

The Zn:Pb ratio

The average Zn:Pb ratios are generally similar in the EABC for the TT (1.4), the MS (1.1), the AS (1.7) and the CMCS (1.0) populations. However, all these ratios are higher than those for the total European emissions (0.65), or for the Western (0.65) and Eastern (0.54) European emissions. On the basis of the present data for the TT, and the independent data for the CMCS sites, it is probable that a Zn:Pb ratio of ~ 1.0 - ~ 1.5 is representative of the EABC which is widely dispersed around Europe and the surrounding regions to form the "background" particulate aerosol.

The Zn:Cu ratio

The average Zn:Cu ratio in the EABC for the TT (5.9) is close to that of the average European background emission (5.2). Within the TT, the Zn:Cu ratio in the EABC for the MS (7.6) is close to that for Western European emissions (8.2), and that of the AS (4.2) is close to that for Eastern European emissions (3.4). The average Zn:Cu ratio for the EABC for the CMCS sites (8.6), which are mainly located around the west of the Mediterranean Sea, is similar to that for the Western Europe (8.2).

The Zn:Ni ratio

The average Zn:Ni in the EABC for the TT (5.4) is close to that of the average European background emission (5.0). Within the TT, the Zn:Ni ratio in the EABC for the MS (6.3) is close to that for emissions from the Western Europe (6.3), and that for the AS aerosols (4.5) is close to that for emissions from Eastern Europe (3.8). However, the average Zn:Ni ratio in the EABC for the CMCS sites (13) is considerably higher than those for either the average European background emission (5.0) or the emissions from Western Europe (6.3).

The Zn:Cr ratio

The average Zn:Cr ratio in the EABC for the TT (6.2) is higher than that for the average European background emission (4.2). However, the TT ratio is biased by four samples in the North Atlantic Westerlies and when these are omitted the average falls to 4.8, which is similar to that for the European background emission. The Zn:Cr ratio for EABC for the AS (2.7) is generally similar to that for the emissions from Eastern Europe (3.2); however, even after omission of the North Atlantic Westerlies samples, the average Zn:Cr ratio for the EABC for the MS (7.5) is higher than that for Western European emissions (4.2). Further, the average Zn:Cr ratio for the EABC for the CMCS sites (16.5) is even higher.

The Zn:Mn ratio

The average Zn:Mn ratio in the EABC for the TT (3.9) is somewhat lower than that for the average European background (4.5), but is still reasonably close to it. Within the TT, the average Zn:Mn ratio for the EABC for the MS (4.5) is reasonably close to that for emissions from Western Europe (5.1), and that for the AS aerosols (3.6) is close to that for emissions from Eastern Europe (3.3). The average Zn:Mn ratio for the EABC for the CMCS (3.9) is lower than the average for the Western Europe emissions (5.1).

The Zn:Cd ratio

The average Zn:Cd ratio in the EABC for the TT (98) is around three times higher than that for the European background emissions (30) and is also higher than those for emissions from both Western (34) and Eastern (26) Europe. However, the average Zn:Cd ratio in the EABC for the CMCS (75) is also higher than that for the European emissions (30), and the samples have a relatively large range (23.5-118) for Zn:Cd ratios in the coastal sea samples. The reason for the difference between Zn:Cd ratios in the European emissions and both the TT and the CMCS particulate aerosols is not known.

Two general conclusions can be drawn from the data for the Zn:metal ratios in the EABC for the various particulate aerosol populations.

a) The Zn:Cu, Zn:Ni and Zn:Cr ratios in the EABC for the CMCS sites are higher than those for the TT. It was shown above that the concentrations of Cd, Zn and Pb at the CMCS sites are higher, relative to those in the transect samples, than are those of Cu, Ni and Cr. It is apparent, therefore, that the atmosphere over the CMCS sites has suffered "local" urban pollution with respect to Cd, Zn and Pb and this is shown in the elevated Zn:Cu, Zn:Ni and Zn:Cr and Zn:Mn ratios in the EABC.

b) There is evidence that the EABC for the MS is most strongly influenced by emissions from Western Europe and that for the AS is most strongly influenced by emissions from Eastern Europe. However, the average Zn:Cu, Zn:Ni, Zn:Cr and Zn:Mn ratios in the EABC for the TT are generally similar to those in the average European background emissions. Further, although the average Zn:Pb ratio in the EABC for the TT aerosols is lower than that in the average European emissions, it is similar in the EABC for all the aerosol populations.

It is apparent, therefore, that there is a "background" component (the EABC) present in the atmosphere over the Mediterranean Sea and surrounding regions.

Variations in the trace metal composition of the EABC have

Table 3

Average EF_{crust}[1] values in the particulate aerosol populations.

Trace metal	Particulate aerosol populations[2]			
	TT	MS	AS	CMCS
Al	1.0	1.0	1.0	1.0
Fe	1.1	1.1	1.1	1.3
Mn	1.6	2.5	1.2	3.0
Ni	10	17	3.4	13
Cr	4.4	5.9	2.9	7.8
Cu	10	14.5	5.6	24
Zn	46.5	86	9.4	153
Pb	250	487	24.5	860
Cd	263	522	21	1092

1: For definition of EF_{crust}, see *text.*
2: For definition of aerosol populations, see *text.*

been identified but on average, with the exception of Cd, the composition approximates that expected from the average emission of trace metals over Europe. On the basis of the present data it is apparent, therefore, that the composition of particulate aerosols over the Mediterranean Sea and surrounding regions will be affected by the extent to which the EABC is mixed with: a) crustal material; and b) urban material of a local origin such as that identified at the CMCS sites. These "mixing relationships" are considered below.

The mixing relationship

The extent to which the EABC is affected by mixing with other material in the total particulate aerosol samples can be estimated using enrichment factors to indicate the degree to which an element is enriched, or

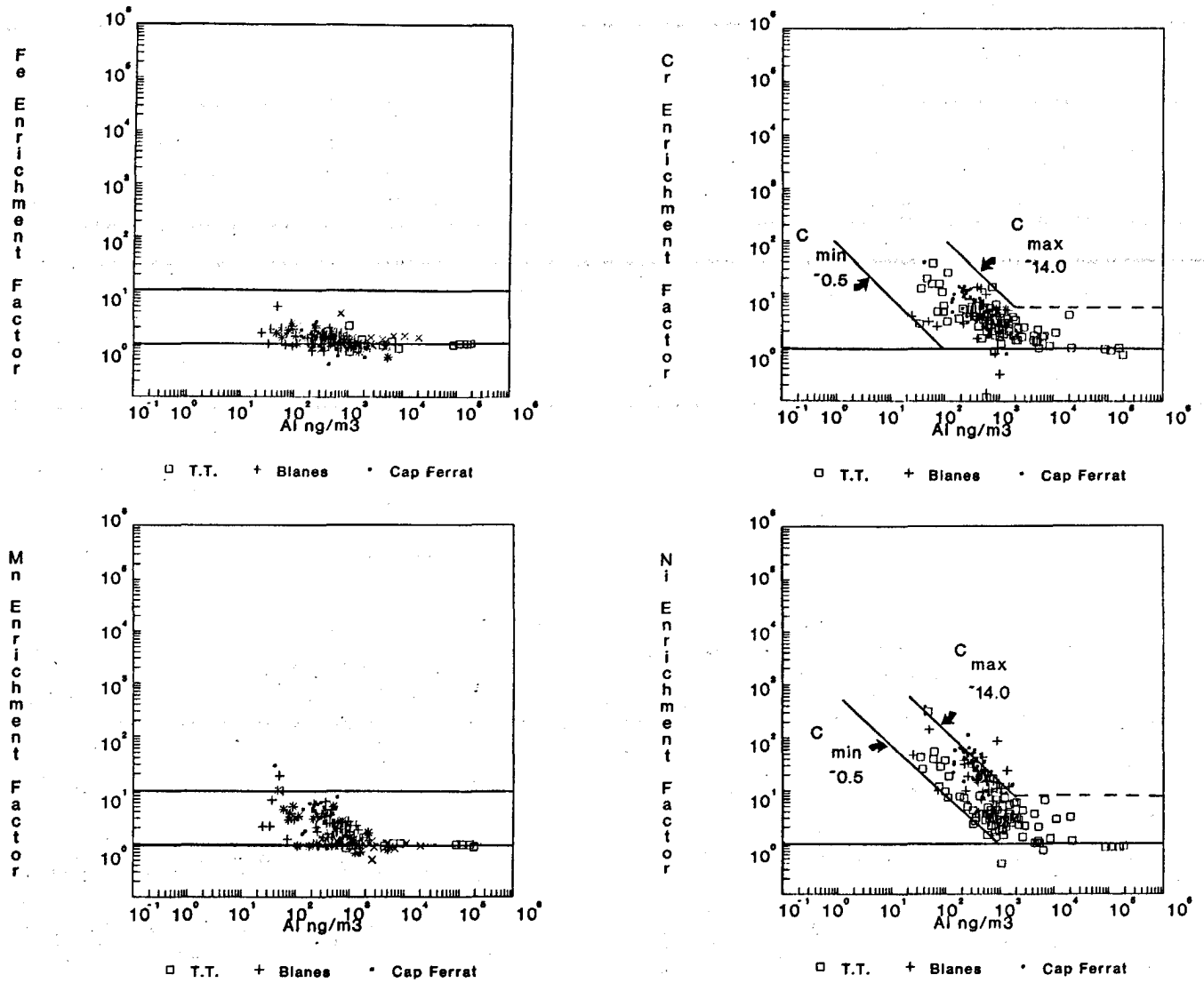


Figure 2

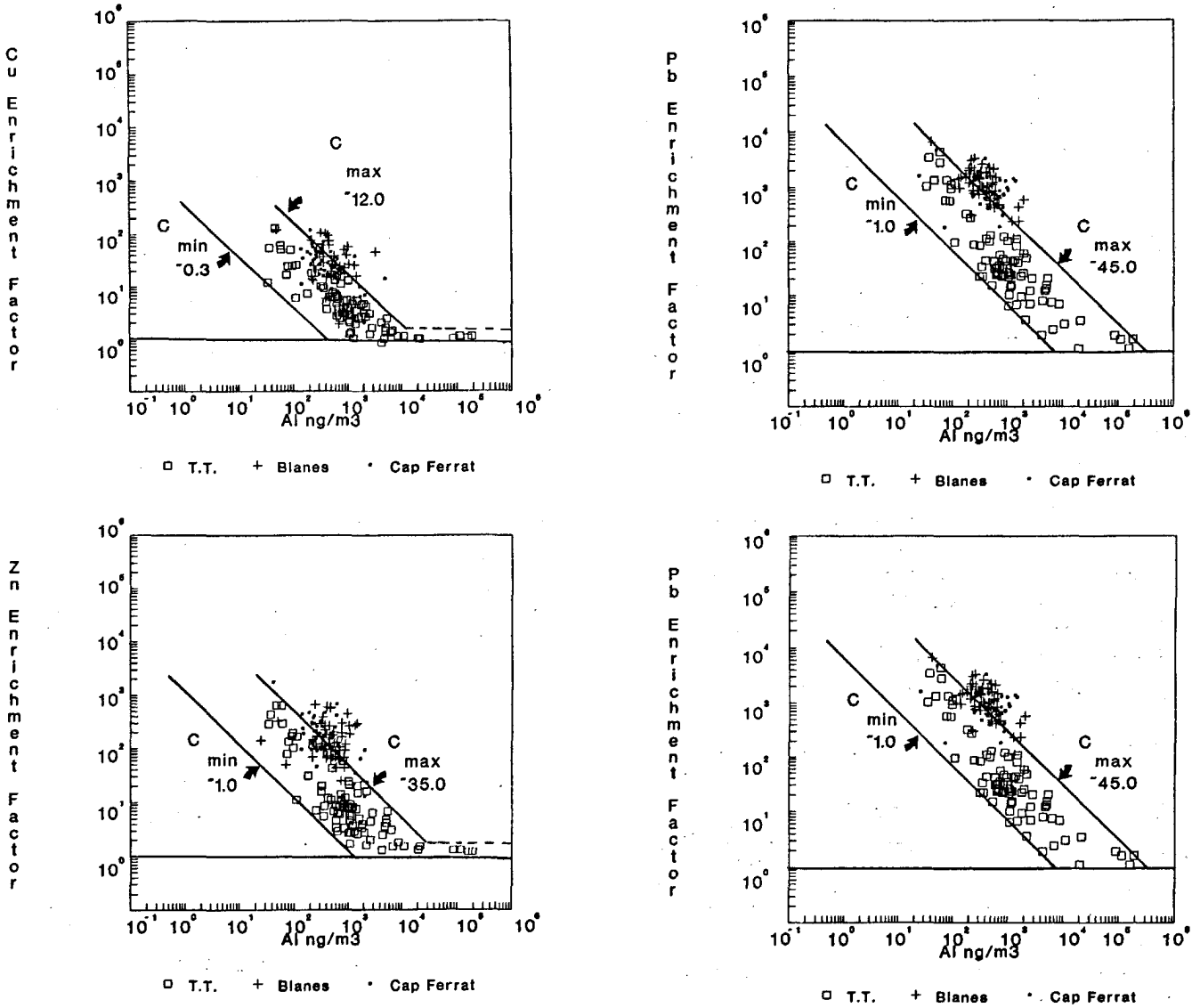
EF diagrams for trace metals in particulate aerosols from the Mediterranean transect (TT) and the coastal margin and coastal sea (CMCS*) sites. The 45° lines enclose the linear portions of the EF diagrams where the EF_{crust} values of the TT aerosols change in response to the extent in which the anthropogenic "background" material (high EF_{crust} values) is mixed with, and diluted by, crust-rich (low EF_{crust} values) components. This "mixing relationship" is constrained by C_{min} and C_{max} concentrations (see text for explanation) and can be perturbed (a) at the upper right hand corner when the C_{max} is exceeded*

depleted, relative to a specific source. For the crustal source, Al is normally used as the source indicator element, and the EF_{crust} value is calculated according to the equation

$$EF_{crust} = (C_{xp}/C_{Alp}) / (C_{xc}/C_{Alc})$$

in which C_{xp} and C_{Alp} are the concentrations of an element x and Al, respectively, in the aerosol, and C_{xc} and C_{Alc} are their concentrations in average crustal material. By convention, a "cut-off" EF_{crust} value of 10 is used to distinguish between two types of particulate trace metals in the atmosphere; this is a purely arbitrary value, but it is a useful parameter which offers a first order classification of trace metal sources. An average EF_{crust} value < 10 in the World Aerosol (*i. e.* aerosols from urban, rural and remote regions) is taken as an indication that elements have a significant crustal source, and these are termed non-enriched elements (NEE). An average EF_{crust} value of > 10 in the World Aerosol is considered to indicate that a significant proportion of an element has a significant non-crustal source, and these are referred to as anomalously enriched elements (AEE).

Average EF_{crust} data for the particulate aerosol populations, calculated using the crustal concentrations given by Taylor (1964), are listed in Table 3 and indicate that in the TT Population, Fe, Mn and Cr behave as NEEs and Ni, Cu, Zn, Pb and Cd behave as AEEs. However, the extent to which the AEEs are actually enriched varies, and under certain conditions they can behave as NEEs. Thus, in a particulate aerosol composed mainly of anthropogenic-rich and crust-rich material the EF_{crust} values of the AEEs will be reduced as the proportions of the crustal material increase, and it is this relationship which can be used to define the "chemical character" of the aerosol. Following Rahn (1976), the relationship can be expressed in the form of an EF diagram, in which the EF_{crust} values of a trace metal in a particulate aerosol population are plotted against the concentrations of Al, the crustal indicator, on a log-log-scale. On an EF diagram the NEEs plot in a broad horizontal field, limited by EF_{crust} values in the range ~ 1 to ~ 10, in which the EF_{crust} values themselves are independent of



in some aerosols from the Blanes and Cap Ferrat coastal sea sites which have suffered local anthropogenic pollution, and (b) at the lower right hand corner when the C_{max} is exceeded by some aerosols rich in crustal material. The dotted lines indicate the approximate boundaries of the field in which the "mixing relationship" is perturbed by crustal material; it should be noted that for some trace metals (e. g. Cu and Zn) the "mixing relationship" field extends to EF_{crust} values < 10 and approaches the crustal value of ≈ 1.0., and that for Pb and Cd the relationship is not significantly perturbed at the lower right hand corner of the EF diagrams - see text (see text for definition of aerosol populations).*

the atmospheric concentrations of Al; *i. e.* they are crust-controlled in all the aerosol samples. In contrast, the AEEs plot as part of a field in which the EF_{crust} values increase as the concentration of atmospheric Al decreases; *i. e.* the extent to which they are non-crust-controlled increases as they become less diluted by crustal components. The field has a hypotenuse along a line of constant concentration which forms an apparent lower limit of concentration.

Under certain conditions the AEE field can also be constrained by a line of maximum concentration (*see e. g.*; Chester *et al.*, 1981).

EF diagrams for Fe, Mn, Cr, Ni, Cu, Zn, Pb and Cd in the 87 particulate aerosols in the TT population are illustrated in Figure 2. To take account of the input of locally derived urban material, data for samples collected at two of the CMCS sites are also included on the plots; these sites are Cap Ferrat (n = 87) and Blanes (n = 47). Following Chester *et al.* (1981) the EF diagrams can be classified in the following manner.

Type 1

EF diagrams having a single field. These are displayed by the NEEs. Iron is the only trace metal to unambiguously display an EF diagram of this type for all the particulate aerosol samples. For the TT samples the EF_{crust} values for both Fe and Mn are all $< \sim 10$, and the data points for the various aerosols lie in horizontal fields between the EF_{crust} limits ~ 1 - ~ 10 in relatively narrow bands. When data for the two coastal sites are included on the EF diagrams, Fe retains the Type 1 form; however, for Mn there is evidence of a "mixing relationship" (*see* below) even at EF_{crust} values < 10, and 4 samples have EF_{crust} values > 10. Overall, however, both Fe and Mn are crust-controlled when crust-rich and anthropogenic-rich components are mixed together in the Mediterranean atmosphere.

Type 2

EF diagrams having two fields. This type of EF diagram incorporates a linear "mixing relationship" (Field 1), over which trace metals behave as AEEs. This is a relatively narrow region enclosed by lines at 45° to the axes, which represent minimum (C_{min}) and maximum (C_{max}) concentrations which constrain the limit of the field. For the purpose of assessing the effects of perturbations to the linear mixing relationship by crustal and urban inputs the positions of the C_{min} and the C_{max} concentration lines have been drawn simply by enclosing those samples in the TT which fall within 45° fields; *i. e.* the linear portions of the EF diagrams. Within this linear field the EF_{crust} values of the AEEs change in direct proportion to the extent to which high EF_{crust} anthropogenic background material (EABC) and low EF_{crust} crustal components are mixed together, with the anthropogenic-rich material predominating at the top left and the crustal material at the bottom right of the EF diagrams.

Type 2A EF diagrams

In these the "mixing relationship" is perturbed at the upper right hand corner (Field 2A) by some samples from the two coastal sites via admixture with locally derived urban-rich material which has raised the trace metal concentrations to a level higher than the C_{max} which defines the upper limit of the linear portion. This type of EF diagram is displayed by Pb and Cd.

Type 2B EF diagrams

In these the "mixing relationship" is perturbed at the lower right hand corner (Field 2B). This is a relatively narrow horizontal region similar to those shown by Fe and Mn, and indicates that the trace metals have a dual "chemical character"; *i. e.* over the "mixing relationship" they behave as AEEs, but they can become NEEs when there is sufficient crustal material present, as in some of the Red Sea aerosols, to perturb this relationship. When this happens the EF diagram is extended to the bottom right under the conditions of low EF_{crust} values at high atmospheric Al concentrations. This general type of EF diagram is displayed by Cr and possibly by Mn.

Type 3

EF diagrams having three fields. This type of EF diagram incorporates a linear "mixing relationship" (Field 1) which is perturbed by admixture with both urban-rich material at the upper right hand corner (Field 2A), and crust-rich material at the lower right hand corner (Field 2B). This general type of EF diagram is displayed by Zn, Cu and Ni.

The perturbations in the bottom right hand corner of the "mixing relationship" result from an increase in the input of crust-rich material; *i. e.* the concentrations of atmospheric Al increase and the AEEs behave as NEEs. However, the EF_{crust} of the AEEs, like those of the NEEs, are constrained by the crustal value of ≈ 1.0 so that although in the presence of such perturbations the linear portion of the EF diagrams is distorted to the lower right of the diagram, the EF_{crust} values themselves do not change since they cannot reach values significantly below the approximate crustal limit. In contrast, the perturbations at the upper right hand corner result from an increase in the input of urban-rich material which, in theory, should not be constrained by a maximum EF since the Al (crustal indicator) and the urban trace metals are derived from different sources. In reality, however, it can be seen from the Type 2A and Type 3 EF diagrams that the concentration-induced perturbations resulting from localised urban inputs occur over a relatively limited EF_{crust} range; *i .e.* the EF_{crust} values appear to be constrained by an apparent EF "end-member" maximum value for samples lying both inside and outside the mixing region. Thus, although the concentrations of the AEEs are higher in aerosols from the CMCS sites than those from the TT, and the Zn:metal ratios in the CMCS aerosols can differ from those in average European background emissions, the CMCS aerosol themselves appears to have similar AEE EF_{crust} values to some samples which plot inside the "mixing region" and which have lower atmospheric concentrations of the AEEs.

It is apparent, therefore, that although both the lower (crustal-generated) and upper (urban-generated) perturbations to the "mixing relationship" are the result of

increases in the concentrations of the trace metals to values above the C_{max} which constrains the relationship, the EF_{crust} values of the aerosols are generally similar to those which lie inside the "mixing field". The perturbations therefore simply arise because the mixing relationship has been affected by aerosols which have become dominated by either crustal or urban material. As a result, it may be concluded that the "chemical character" of the aerosol populations from the Mediterranean Sea and surrounding source regions can be defined by the EF_{crust} values of those trace metals which can behave as AEEs; *i. e.* on the basis of perturbations to the crust-rich/anthropogenic-rich "mixing relationship".

An EF_{crust} value of ~ 10 was used above as the "cut-off" to make the distinction between the NEEs and the AEEs. However, it is apparent from the EF diagram of some of the trace metals that the "mixing relationship" can extend below this "cut-off", indicating that the EF_{crust} values continue to be decreased by mixing with crustal material until they are ultimately constrained by the EF_{crust} value of $\approx$ 1.0. It is apparent, therefore, that the EF_{crust} of 10 makes only a crude distinction between the NEEs and the AEEs, and that in reality trace metals with an EF_{crust} value in the range $> \approx$ 1.0 - $< \approx$ 10 can still act as AEEs in so far as the EF_{crust} value itself can still be changed by admixture with crustal material. This is particularly evident for Mn, which exhibits evidence of a "mixing relationship" in the EF_{crust} range $> \approx$ 1.0 - $\approx$ 10. However, the "cut-off" EF_{crust} value of 10 is retained in the present study to distinguish between the NEEs and the trace metals which can act as AEEs because it is these metals which show the most clearly developed "mixing relationships". In this context, the AEEs used for the purpose of establishing the "chemical character" of the particulate aerosols are Cr, Ni, Cu, Zn, Pb and Cd.

Characterising the Mediterranean aerosol

Over the whole of the Mediterranean Sea material can be transported into the atmosphere from regions lying to the north, south, east and west, and the individual source strengths can vary over different regions of the sea. This can be illustrated with respect to data summarised by WMO (1985) in which air mass back trajectory data were used to establish the origins of air masses reaching both the Eastern and Western Mediterranean. The data reveal that the relative importance of the principal air masses differ for the two regions. For the Western Mediterranean the main air flows were as follows: 38 % of the air masses came in from western sector, which includes the North Atlantic Ocean and the Iberian Peninsula; 28 % were from the north and had crossed the European land mass; 13 % were from the south and would carry Saharan aerosols; and only ~ 1 % of the trajectories were from the east. The remaining ~ 20 % of the air flows could not be characterised on the basis of back trajectories. For the Eastern Mediterranean the main air flows were as follows: 39 % of the air masses were from the north and had crossed Greece, eastern Europe and the USSR; 28 % of the air masses came in from a west/northwest sector and had crossed parts of western Europe, including Italy, France, Spain and the UK; 16 % originated from the south, and would transport aerosols from the Sahara and North African deserts; and 17 % came from the east of the region, and had crossed the desert regions of the Middle East. It is apparent, therefore, that the main difference in the origin of the air masses over the Mediterranean Sea is that compared to the western region, the eastern region receives a significant percentage of the total air masses originating to the east.

The "mixing relationship" between crust-rich and anthropogenic-rich components can be perturbed by relatively large inputs of either crustal material from desert/arid source regions or by anthropogenic material from urban sources. However, it was shown above that EF_{crust} values can be used to characterise particulate aerosols even when these perturbations occur because the perturbations themselves appear to be constrained by real minimum (crustal) or apparent maximum (urban) "end-member" EFs. The "chemical character" of particulate aerosols from the atmosphere of the Mediterranean Sea and surrounding regions is evaluated below with respect to AEE EF_{crust} values for a series of aerosol "end-members". These "end-members" have been selected to represent the type of crust-dominated and anthropogenic-dominated particulate material derived from the various source regions surrounding the Mediterranean Sea.

The "end-member" particulate aerosols

Crustal "end-member"

- the most dust-rich Saharan "end-member" collected over the Tyrrhenian Sea,
- the > 3.5 μm mass median diameter-sized (crust-dominated) material for an aerosol sample collected by cascade impactor over the Eastern Mediterranean,
- and samples of the Red Sea aerosol collected under extreme dust storm conditions; *i. e.* at atmospheric Al concentrations > ~ 5 x 10^4 ng m^3 of air.

Anthropogenic "end-member"

- the European "end-member" collected over the Tyrrhenian Sea,
- the < 0.55 μm mass median diameter-sized (anthropogenic-dominated) material for a particulate aerosol sample collected by cascade impactor over the Eastern Mediterranean.

EF_{crust} data for the aerosol "end-members" are presented in the form of bar diagrams in Figure 3A.

Particulate aerosol populations from the CMCS sites

Bar diagrams showing the average EF_{crust} values for aerosols from the CMCS sites are illustrated in Figure 3B. From this figure it is apparent that there is an overall similarity in the "chemical character" of the particulate aerosols from the Cap Ferrat, Blanes, Tour du Valat and Corsica sites on the north coast of the Western Mediterranean; thus,

the AEEs Pb, Cd, Zn, Cu, Ni and Cr are all enriched, relative to crustal sources, to about the same extent in the four particulate aerosol populations and the values are more similar to those of the European "end-member" than to the Saharan "end-member".

Average EF_{crust} data for particulate aerosols from the other two Western European CMCS sites (the North Sea and the Kiel bight) and the Eastern European site (The Black Sea) are also generally similar to those for the Western Mediterranean northern coast sites.

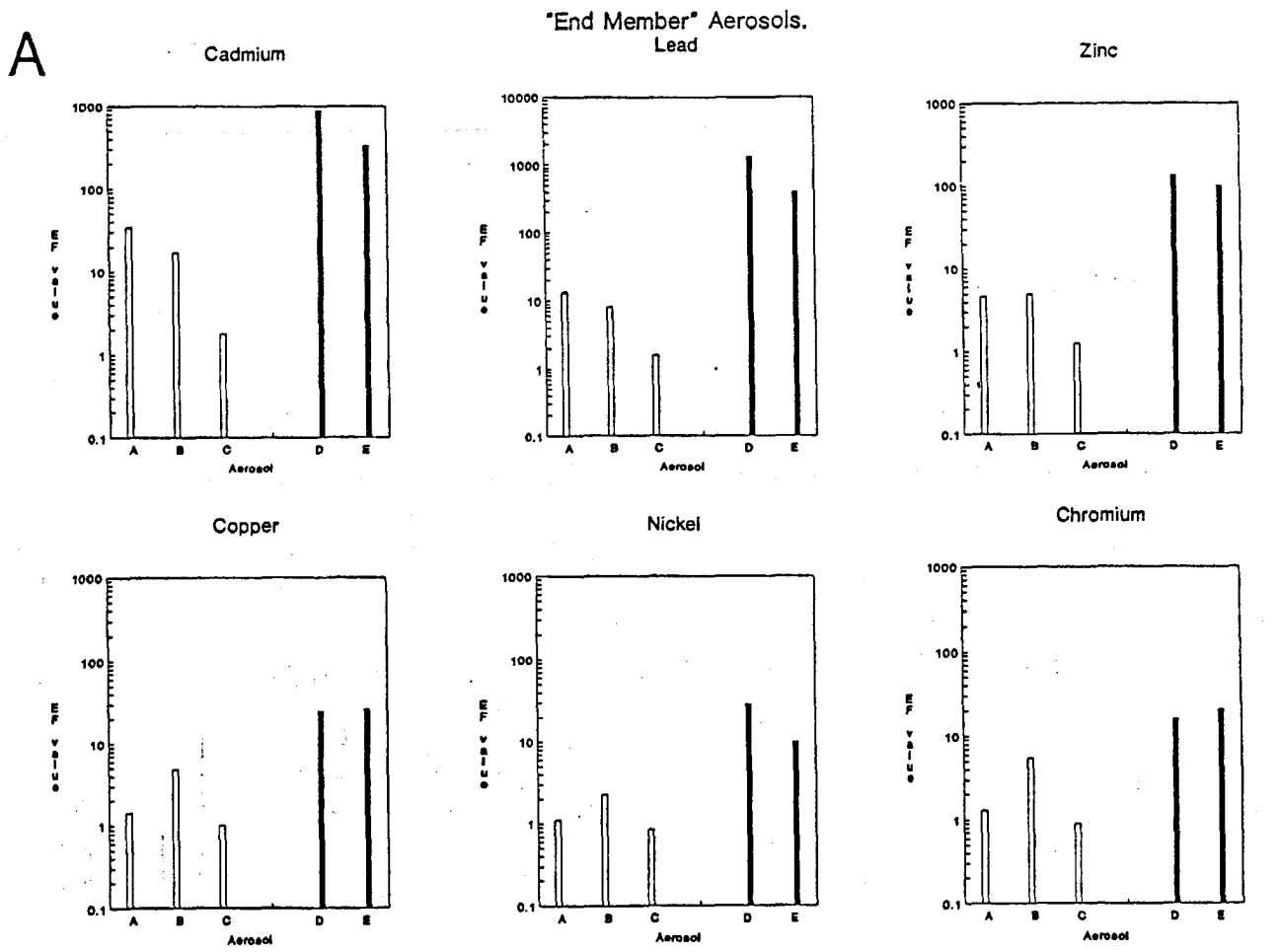
Thus, as Chester *et al.* (1992 *b*) suggested, the Western Mediterranean atmosphere over the north coast sites may be considered to be an extension of the Western European atmosphere which, at certain times, is perturbed by inputs of Saharan dusts. However, the southern coast of the Western Mediterranean is fringed by the North African desert belt, and particulate aerosols from this region may be perturbed by crustal material to much greater extent than those off the northern coast and will therefore have a different "chemical character".

Particulate aerosol populations from the eastern extremities of the Mediterranean Sea

The "chemical character" of aerosols collected over the Black Sea is similar to those from the northern coast Western Mediterranean sites, and to the anthropogenic fraction of the Eastern Mediterranean cascade impactor-collected particulate aerosol. Data are not yet available for long term particulate aerosol collections over the Eastern Mediterranean Sea itself. However, data for aerosols on the eastern extremity, *i. e.* the Red Sea and the Arabian Sea, have been provided in the present study, and bar diagrams showing the average EF_{crust} values for these aerosols are illustrated in Figure 3C. From this figure it can be seen that the "chemical character" of the Red Sea and Arabian Sea aerosols are very different from those of the "European" anthropogenic "end-members", and that their average EF_{crust} values lie much closer to those of the crustal "end-members" (*see* Fig. 3A); however, the average EF_{crust} values for both Pb and Cd are > 10 in both the Red Sea and the Arabian Sea aerosols.

Figure 3

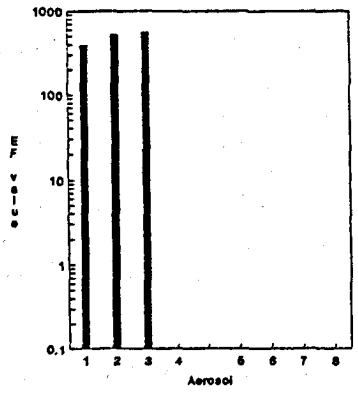
Bar diagrams illustrating the average EF_{values} of the AEEs in a series of "end-member" aerosols and aerosol populations from the atmosphere of the Mediterranean Sea and surrounding regions. For data sources, see text. 3A: "End-member" aerosols. Crustal source: A, Saharan "end-member" aerosol, Tyrrhenian Sea; B, > 3.5 μm mass median diameter-sized material from Eastern Mediterranean aerosol; C, Red Sea aerosol, dust-storm conditions. Anthropogenic source; D, European "end-member" aerosol, Tyrrhenian Sea; E, < 0.55 μm mass median diameter-sized material from Eastern Mediterranean aerosol. 3 B: Aerosol populations from Western Mediterranean northern coastal sites and other coastal seas; 1, Cap Ferrat; 2, Blanes; 3, Tour du Valet; 4, Corsica; 5, North Sea; 6, Kiel Bight; 7, Eastern Black Sea; 8, Western Black Sea. 3 C: Aerosol populations from the eastern and western extremities of the Mediterranean Sea; 9, Red Sea; 10, Arabian Sea; 11, North Atlantic westerlies; 12, North Atlantic trades; 13, Tropical North Atlantic.



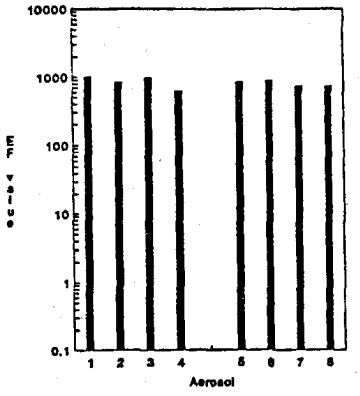
B

Aerosol Populations.

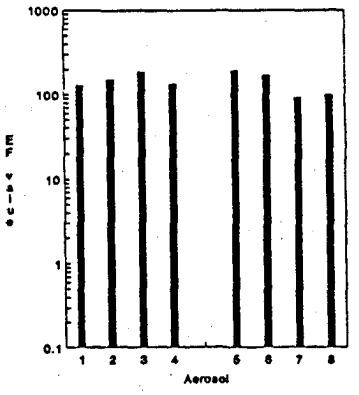
Cadmium



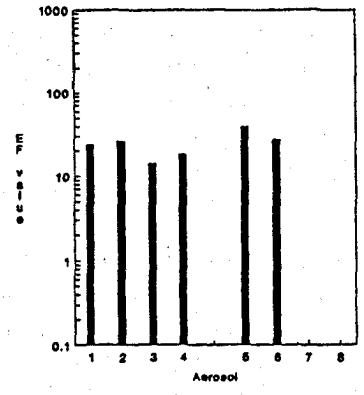
Lead



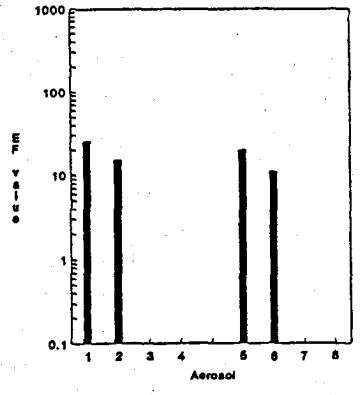
Zinc



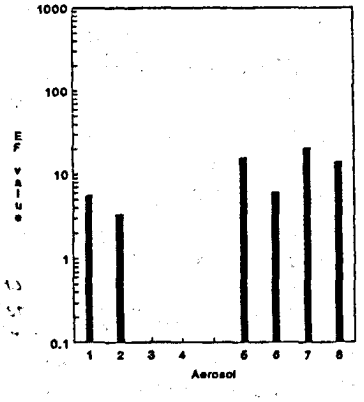
Copper



Nickel



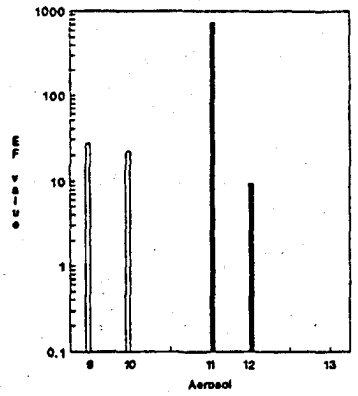
Chromium



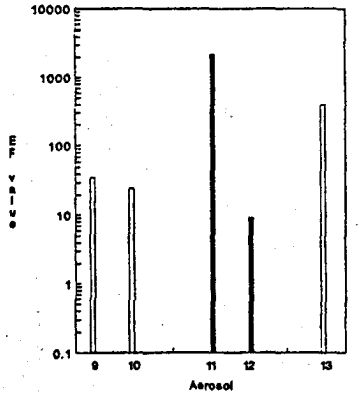
C

Aerosol Populations.

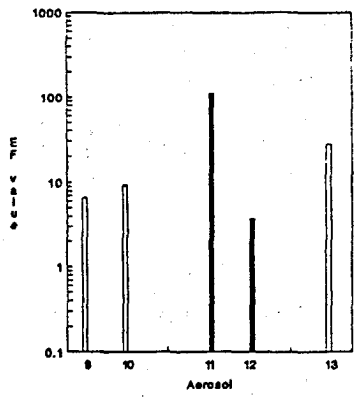
Cadmium



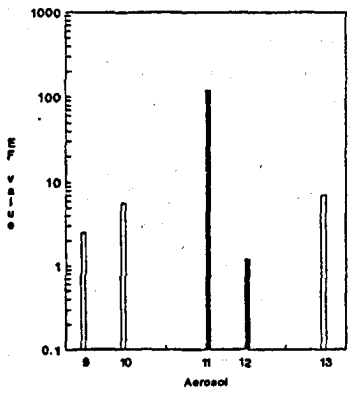
Lead



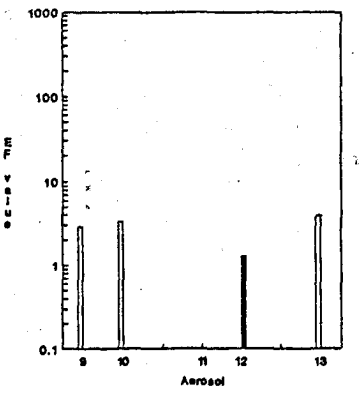
Zinc



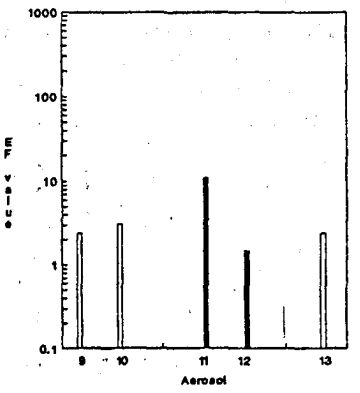
Copper



Nickel



Chromium



According to the data presented by WMO (1985), ~ 17 % of the air masses transported to the Eastern Mediterranean atmosphere are from the east; in contrast, < ~ 1 % of the air masses carried to the Western Mediterranean are from this source. It is apparent, therefore, that the bulk particulate aerosol over the Eastern Mediterranean will be significantly influenced by material brought in from the east, and since this is rich in crustal material it is probable that the extent to which the particulate aerosols in the Eastern Mediterranean, particularly off the southern coast, can be perturbed by crustal material from the surrounding desert regions will therefore be much greater than in the Western Mediterranean; however, long-term aerosol collections from the eastern region must be made in order to verify this.

Particulate aerosol populations from the western extremities of the Mediterranean Sea

The data for the Atlantic north east trades and westerlies used to construct the EF diagrams were selected from particulate aerosols collected close to the western end of the Mediterranean Sea; however, only four aerosols of this type from each population were available. EF_{crust}data for a set for ten particulate aerosols collected from the Atlantic north east trades off the coast of West Africa to the south of the Straits of Gibraltar (Murphy, 1985), and an Atlantic westerlies population (sixteen samples) collected north of 30°N (Duce and Hoffman, 1972) can be used to enlarge the original aerosol populations. Bar diagrams for the average EF_{crust} values for the Atlantic trades and westerlies particulate aerosol populations are plotted in Figure 3C. From this figure it can be seen that the values for the AEEs in the north east trades are all < 10; *i. e.* they are crust-controlled. In contrast, the values for the westerlies are similar to those of the European "end-member" material. In addition, average EF_{crust} data for particulate aerosols from the Tropical North Atlantic (Buat-Ménard and Chesselet, 1979) are plotted in Figure 3C, and it is apparent that these have a "chemical character" which lies between those of the trades and the westerlies; *i. e.* away from the coast of West Africa the admixture of other sources with the Saharan crustal material can change the "chemical character" of the particulate aerosols.

It may be concluded that particulate material brought into the Mediterranean atmosphere from both the western and eastern extremities can have a variable composition. From the western extremity the composition will depend on whether the aerosol components have been transported in the Atlantic trades or the westerlies; however, according to the air mass trajectory pathways identified by WMO (1985) air masses reaching the Mediterranean atmosphere from the west impinge on the Iberian Peninsula and will therefore tend to be more affected by anthropogenic than by crust-rich particulate aerosols. From the eastern extremity the chemical character of the aerosol will depend on whether the components originate from the desert and arid areas of the Middle East, or from the regions lying to the northeast of the Black Sea.

On the basis of their "chemical character" it would appear that there are a series of particulate aerosol populations found in the atmosphere over the non-remote Northern hemisphere extending from ≈ 55°N to the equator. The "chemical character" of the aerosols exhibit both latitudinal and longitudinal changes. With respect to latitude, the particulate aerosols are dominated by anthropogenic-derived components in the north, *e. g.* over Europe, and by crust-derived components in the south, *e. g.* over the North African deserts. With respect to longitude, they are dominated mainly by anthropogenic-derived components to the west and crust-derived components to the east.

The Mediterranean Sea is located at the intersection of the north/south and the east/west aerosol "divides", and the atmosphere over it can receive particulate aerosols transported in air masses crossing any of the source regions. However, from the present study it appears that the particulate aerosol over the Mediterranean Sea consists of a variety of individual populations which, on the basis of their "chemical characters", may simply be regarded as part of the series of aerosol populations in the non-remote Northern hemisphere. The "chemical character" of the individual Mediterranean particulate aerosol populations can be assessed on the basis of their AEE EF_{crust} values which vary with the extent to which anthropogenic-rich and crust-rich components are mixed together in the atmosphere. Variations in the predominance of either of these components depends on the aerosol source region crossed by air masses impinging on the Mediterranean atmosphere.

With respect to the Eastern Mediterranean, air masses from the south sector, which transport crust-rich material, account for 16 % of the total input and those from the east sector 17 %. Since the east sector includes air masses which have crossed the desert and arid lands of the Middle East, it can be expected that the aerosol over the Eastern Mediterranean will have a "chemical character" which is more strongly influenced by crust-rich components than that over the Western Mediterranean where the Saharan crust-rich input accounts for only 13 % of the total aerosol input reaching the region. This has a number of important environmental consequences for marine biogeochemical cycles in the Mediterranean; for example, considerably higher concentrations of atmospherically-deposited trace metals will enter the dissolved pool in the mixed layer of the Western, compared to the Eastern Mediterranean.

CONCLUSIONS

The "chemical character" of particulate aerosols form the atmosphere of the Mediterranean Sea and surrounding regions can be assessed on the basis of the average EF_{crust} values for trace metals which can behave as AEEs. Sources on the European mainland to the north supply particulate aerosols having an anthropogenic-dominated "chemical character" similar to that of other Western European aerosol populations. In contrast, aerosols from the Saharan region to the south have a crust-dominated "chemical character". To the east, air masses crossing the desert and arid regions of the Middle East also transport particulate aerosols having a crust-dominated "chemical character", but those impinging on areas to the northeast of the Black Sea

bring in aerosols of an anthropogenic-dominated type. To the west particulate aerosols in the Atlantic north east trades close to the coast of West Africa have a Saharan crust-dominated character; in contrast, the North Atlantic westerlies transport a particulate aerosol which has an anthropogenic-dominated "chemical character". However, air masses from all parts of this western sector may impinge on the European land mass, especially the Iberian peninsula, and so will tend to carry aerosols which will have an anthropogenic-dominated "chemical character" by the time they reach the atmosphere over the Mediterranean Sea.

In the atmosphere over the Mediterranean Sea and surrounding regions the particulate aerosol composition can therefore be considered to be constrained by the mixing of urban and crustal components. As a result, the aerosols consists of a variety of individual populations which, on the basis of their "chemical characters", may be regarded as being part of a series of aerosols in the non-remote Northern hemisphere troposphere.

Acknowledgements

Substantial parts of the study were funded by the Natural Environment Research Council, London (Grants GR4/80/AAPS/22, GR3/6040, GST/02/334/1), and the EROS-2000 Programme of the CEC.

REFERENCES

Alarcon M. and A. Crusado (1990). Particulate aerosol nutrient inputs into the North-Western Mediterranean Sea. in: *Water Pollution Reports*, 20, J.-M. Martin and H.Barth, editors. Commission of the European Communities, 635,644.

Arnold M., A. Seghaier, D. Martin, P. Buat-Ménard and R. Chesselet (1982). Géochimie de l'aérosol marin au-dessus de la Méditerranée occidentale. in: *Proceedings of VIth Journées d'Études sur les Pollutions marines en Méditerranée, Cannes, France*, 27-37.

Bergametti F , A.-L. Dutot, P. Buat-Ménard and E. Remoudaki (1989). Seasonal variability of the elemental composition of atmospheric aerosol particles over the northwestern Mediterranean. *Tellus*, **41 b**, 553-561.

Berry A.S. (1990). Solid state speciation and sea water solubility studies and trace metal chemistry of the Indian Ocean aerosol. *Ph. D. Thesis, University of Liverpool, U.K.*.

Boyle E.A., S.D. Chapnick, X.X. Bai and A. Spivack (1985). Trace metal enrichments in the Mediterranean Sea. *Earth planet. Sci. Letts*, **74**, 405-419.

Buat-Ménard P. and M. Arnold (1978). The heavy metal chemistry of atmospheric particulate matter emitted by Mount Etna volcano. *Geophys. Res. Letts*, **5**, 245-248.

Buat-Ménard P. and R. Chesselet (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. *Earth planet Sci. Letts*, **42**, 399-411.

Chester R. and G.F. Bradshaw (1991). Source control on the distribution of particulate trace metals in the North Sea atmosphere. *Mar. Pollut. Bull.*, **22**, 30-36.

Chester R., G.G. Baxter, A.K. Behairy, K.A. Connor, D. Cross, H. Elderfield and R.C. Padgham (1977). Soil-sized eolian dusts from the lower troposphere of the Eastern Mediterranean. *Mar. Geol.*, **24**, 201-217.

Chester R., A.C. Saydam and E.J. Sharples (1981). An approach to the assessment of local trace metal pollution in the Mediterranean marine atmosphere. *Mar. Pollut. Bull.*, **12**, 426-431.

Chester R., E.J. Sharples and G.S. Sanders (1984). Saharan dust incursion over the Tyrrhenian Sea. *Atmos. Environ.*, **18**, 929-935.

Chester R., M. Nimmo, K.J.T. Murphy and E. Nicholas (1990). Atmospheric trace metals transported to the Western Mediterranean; data from a station on Cap Ferrat, in: *Water Pollution Reports*, **20**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 597-612.

Chester R., A.S. Berry and K.J.T. Murphy (1991). The distributions of particulate atmospheric trace metals and mineral aerosols over the Indian Ocean. *Mar. Chem.*, **34**, 261-290.

Chester R., K.J.T. Murphy, F.J. Lin, A.S. Berry, G.A. Bradshaw and P.A. Corcoran (1992 *a*). Factors controlling the solubilities of trace metals from non-remote aerosols deposited to the sea surface by the "dry" deposition mode. *Mar. Chem.* (in press).

Chester R., M. Nimmo, M. Alarcon and P. Corcoran (1992 *b*). The chemical character of the Western Mediterranean aerosol, in: *Water Pollution Reports*, **28**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 495-504.

Condé A., M.-A. Sicre and A. Saliot (1991). A comparative study of hydrocarbons in coastal and marine aerosols over the Mediterranean Sea, in: *Water Pollution Reports*, **28**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 533-542.

Correggiari A., S. Guerzoni, R. Lenaz, G. Quarantotto and G. Rampazzo (1989). Dust deposition in the central Mediterranean (Tyrrhenian and Adriatic Seas): relationships with marine sediments and riverine input. *Terra Nova*, **1**, 549-558.

Duce R.A and G.L. Hoffman (1972). Trace metal measurements in the marine atmosphere and sea surface microlayer, in: *Baseline Studies of Pollutants in the Marine Environment*, NSF, Washington, 391-468.

Dulac F., P. Buat-Ménard, M. Arnold and U. Ezat (1987). Atmospheric input of trace metals to the Western Mediterranean Sea: 1: Factors controlling the variability of atmospheric concentrations. *J. geophys. Res.*, **92**, 8437-8453.

Dulac F., P. Buat-Ménard, U. Ezat, S. Melki and G. Bergametti (1989). Atmospheric input of trace metals to the Western Mediterranean: uncertainties in modelling dry deposition from cascade impactor data. *Tellus*, **41B**, 362-378.

Ganor E. and Y. Mamane (1982). Transport of Saharan dust across the Eastern Mediterranean. *Atmos. Environ.*,**15**, 57-64.

Guerzoni S., R. Lenaz and G. Quarantotto (1988). Field measurements at sea: atmospheric particulate trace metal "end-members" in the Mediterranean. *Air pollut. Res. Repts*, **14**, CEE, Brussels, 96-100.

Guerzoni S., A. Correggiari and S. Miserocchi (1989). Wind-blown particles from ships and land-based stations in the Mediterranean Sea: a review of trace metal studies. in: *Water Pollution Reports*, **13**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 377-384.

Guerzoni S., W. Landuzzi, R. Lenaz, G. Quarantotto, G. Cesari, G. Rampazzo and E. Molinaroli (1991). Mineral atmospheric particulates from south to NW Mediterranean: seasonal variations and characteristics, in: *Water Pollution Reports*, **28**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 483-493

Guieu C. (1991). Apports atmosphériques à la Méditerranée nord-occidentale. *Thèse de Doctorat, Université de Paris.*

Guieu C., J.-M. Martin and F. Elbaz-Poulichet (1990). Atmospheric input of trace metals (Cd, Co, Cu, Fe, Mn, Ni and Pb) to the Gulf of Lions, in: *Water Pollution Reports*, **20**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 613-621.

Guieu C., A.J. Thomas, J.-M. Martin and J.-C. Brun-Cottan (1991). Multielemental characterisation of the atmospheric input to the Gulf of Lions. Impact on the upper water layer chemistry, in: *Water Pollution Reports*, **28**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 505-518.

Hydes D.J. (1985). Dissolved aluminium in the Mediterranean Sea. *Terra Cognita*, **5**, 189.

Kersten M., M. Dicke, M. Kriews, K. Naumann, D. Schmidt, M. Scholz, M. Schwikowski and M. Steiger (1989). Distribution and fate of heavy metals in the North Sea, in: *Pollution of the North Sea. An Assessment*, W. Salomons, B.L. Bayne, E.K. Duursma and U. Forstner, editors. Springer-Verlag, Berlin, 330-347.

Lenaz R., V. Landuzzi and L. Tomadin (1983). Apporti eolici stagionali sul Mediterraneo Centrale. *Atti 5° Congresso A.I.O.L., Stresa, Italy, 19-22 Maggio 1982*, 559-578.

Lenaz R., V. Landuzzi and L. Tomadin (1988). Apports et concentrations de masse des poussières éoliennes sur le bassin oriental de la Méditerranée. *Memorie Soc. Geol. Ital.*, **36**, 189-200.

Losno R., G. Bergametti and P. Buat-Ménard (1988). Zinc partitioning in Mediterranean rainwater. *Geophys. Res. Letts*, **15**, 1389-1392.

Loye-Pilot M.-D. (1990). Atmospheric wet deposition of inorganic nitrogen to the North Western Mediterranean Basin, in: *Water Pollution Reports*, **20**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 623-634.

Loye-Pilot M.-D., J.-M. Martin and J. Morelli (1986). Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean. *Nature*, **321**, 427-428.

Loye-Pilot M.-D., J. Morelli and J.-M. Martin (1989). Atmospheric input of particulate matter and inorganic nitrogen to the North Western Mediterranean, in: *Water Pollution Reports*, **13**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 368-376.

Loye-Pilot M.-D., G. Cauwet, A. Spitzy and J.-M. Martin (1991). Preliminary results on atmospheric wet deposition of organic carbon and nitrogen in Corsica, in: *Water Pollution Reports*, **28**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 519-532.

Maring H.B. and R.A. Duce (1990). The impact of atmospheric aerosols on trace metal chemistry in open ocean surface sea water: 3: Lead. *J. geophys. Res.*, **95**, 5341-5347.

Martin J.-L, F. Elbaz-Poulichet, C. Guieu, M.-D. Loye-Pilot and G. Han (1989). River *versus* atmospheric input of material to the Mediterranean Sea: an overview. *Mar. Chem.*, **28**, 159-182.

Mazzucotelli A., V. Landuzzi, R. Lenaz, F. Oliveri, L. Tomadin and R. Vannucci (1984). Polveri in sospensione nella bassa atmosfera del Mare Tirreno e del Canale di Sicilia (Crociera Ban 80). *Memorie Soc. Geol. Ital.*, **27**, 311-321.

Migon C., G. Copin-Montégut, L. Élégant and J. Morelli (1989). Étude de l'apport atmosphérique en sels nutritifs au milieu côtier méditerranéen et implications biogéochimiques. *Oceanologica Acta*, **12**, 2, 187-191.

Migon C., J. Morelli, E. Nicolas and G. Copin-Montégut (1991). Evaluation of total atmospheric deposition of Pb, Cd, Cu and Zn to the Ligurian Sea. *Sci. total Environment*, **105**, 135-148.

Murphy K.J.T. (1985). Trace metal chemistry of the Atlantic aerosol. *Ph. D. Thesis, University of Liverpool, U.K.*.

Pacyna J.M., A. Semb and J.E. Hanssen (1984). Emissions and long-range transport of trace elements in Europe. *Tellus*, **36B**, 163-178.

Peirson D.H., P.A. Cawse and R.S. Cambray (1974). Chemical uniformity of airborne particulate material, and a maritime effect. *Nature*, **251**, 675-679.

Prodi F. and G. Fea (1979). A case of transport and deposition of Saharan dust over the Italian peninsula and southern Europe. *J. geophys. Res.*, **84C**, 6951-6960.

Prospero J.M. (1979). Mineral and sea salt aerosol concentration in various ocean regions. *J. geophys. Res.*, **84**, 725-731.

Rahn K.H. (1976). The chemical composition of the atmospheric aerosol. Technical Report, Graduate School of Oceanography, University of Rhode Island, Kingston, R.I., 265 pp.

Remoudaki E., G. Bergametti and R. Losno (1991). On the dynamic of the atmospheric input of copper and manganese into the Western Mediterranean Sea. *Atmos. Environ.*, **25A**, 733-744.

Sanders G. (1983). Metals in marine atmospheric particles. *Ph. D. Thesis, University of Liverpool, U.K.*

Saydam A.C. (1981). The elemental chemistry of Eastern Mediterranean atmospheric particulates. *Ph. D. Thesis, University of Liverpool, U.K.*

Schneider B. (1987). Source characterisation for atmospheric trace metals over Kiel Bight. *Atmos. Environ.*, **21**, 1275-1283.

Sicre M.-A., A. Conde, A. Lorre and A. Saliot (1990). Composition of the coastal aerosol and its variability over time: first assessment of the terrestrial component from the Cap Ferrat sampling station, in: *Water Pollution Reports*, **20**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 645-655.

Simo R., M. Colom-Altres, J.O. Grimalt and J. Albaiges (1990). Background levels of atmospheric hydrocarbons, sulphate and nitrate over the Western Mediterranean Sea, in: *Water Pollution Reports*, **20**, J.-M. Martin and H. Barth, editors. Commission of the European Communities, 657-666.

Simo R., M. Colom-Altes, J.O. Grimalt and J. Albaiges (1991). Background levels of atmospheric hydrocarbons, sulfate and nitrate over the Western Mediterranean. *Atmos. Environ.*, **25A**, 1463-1471.

Taylor S.R. (1964). Abundance of chemical elements in the continental crust: a new table. *Geochim. cosmochim Acta*, **28**, 1273-1285.

Tomadin L. (1981). Provenance and dispersal of clay minerals in recent sediments of the Central Mediterranean Sea, in: *Sedimentary basins of Mediterranean margins*, F.C. Wezel, editor. CNR Italian Project of Oceanography, Tecnoprint, Bologna, 313-324.

Tomadin L. and R. Lenaz (1989). Eolian dust over the Mediterranean and their contribution to the present sedimentation, in: *Paleoclimatology and paleometeorology: modern and past patterns of global atmospheric transport*, M. Leinen and M. Sarnthein, editors. Kluver, The Hague, 267-282.

Tomadin L., V. Landuzzi and R. Lenaz (1983). Influence of the aeolian supply to the sedimentation of the adriatic Sea. *Thalassia Jugosl.*, **19**, 377-382.

Tomadin L., R. Lenaz, V. Landuzzi, A. Mazzucotelli and R. Vannucci (1984). Wind-blown dusts over the Central Mediterranean. *Oceanologica Acta*, **7**, 1, 13-23.

World Meteorological Organization (1985). Atmospheric transport of contaminants into the Mediterranean region. GESAMP Report 26, 53 pp.

Yallon D.H. and E. Ganor (1979). East Mediterranean trajectories of dust-carrying storms from the Sahara and Sinai, in: *Saharan Dust Mobilization, transport, dispersion. Scope 14*, C. Morales, editor. John Wiley, New York, 187-193.

Yaaqub R.R., T.D. Davies, T.D. Jickells and J.M. Miller (1991). Trace elements in daily collected aerosols at a site in south east England. *Atmos. Environ.*, **A25**, 985-996.