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SAHARAN DUST INCURSION OVER THE TYRRHENIAN SEA

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Abstract—The Tyrrhenian Sea aerosol was sampled by both mesh and filter techniques. Geostrophic back trajectories were used to identify potential aerosol catchment regions, and it was shown that the atmosphere over the Tyrrhenian Sea received incursions of Saharan dust during the collection period in the autumn of 1979. Mineralogical and chemical parameters were used to characterize this desert-derived material and it was shown that it exerts an important influence on the composition of the local aerosol. On the basis of the present data, it was concluded that the northward movement of Saharan dust across, the Mediterranean can result in the transport of relatively large amounts of crustal material to the southern European coast and so should be included in estimates of Saharan dust production.

INTRODUCTION

Ganor and Mamane (1982) have recently pointed out that although the movement of Saharan dust across the west coast of Africa via the NE trades has been extensively documented, its transport to other regions is less well known. The authors concluded that such transport should be included in estimates of the production of natural dust from the Sahara, and provided evidence for the movement of Saharan-derived eolian material to the eastern Mediterranean. Previously, Chester *et al.* (1977) had shown that soil-sized aerosols over the eastern Mediterranean consist of at least two individual populations; one originating on the European mainland and Mediterranean islands, and one in the desert regions of North Africa and the Middle East. It is apparent, therefore, that the Sahara Desert is an important source of aerosol components over the eastern Mediterranean. There is also evidence for the northward movement of Saharan dust across the Central Mediterranean. For example, the 'Sirocco' can transport desert-derived dust from North Africa across the Mediterranean to Malta and Sicily where, on termination of the winds by the passage of cold fronts, the dust burden is deposited in the so-called 'red rains'. Examples of the northward movement of Saharan dust have been identified (see e.g. Prodi and Fea, 1979; and references therein; Arnold *et al.*, 1982), but the phenomenon has not been studied in nearly as much detail as transport within the NE trades (see e.g. Ganor and Mamane, 1982; Fig. 4). Further, relatively little compositional data is available which may be used to characterize the desert-derived components and so identify actual incidents of the incursion of the dust over the southern European coast of the Mediterranean. In an attempt to investigate such incursions of Saharan dust, a series of aerosol collections were made during the autum of 1979 over the Tyrrhenian Sea. In the present paper geostrophic back trajectories have been used to identify catchment regions for the components in the Tyrrhenian Sea aerosol, and a number of mineralogical, magnetic and chemical parameters have been employed to characterize the components with a view to identifying those originating in the Saharan region.

SAMPLING AND ANALYSIS

Aerosol collection techniques

The aerosol was collected on board *R.R.S. Shackleton* during the autumn of 1979. One set of collections was made on terylene meshes suspended above the bows of the ship. Two meshes were exposed for each collection and were immediately sealed in plastic bags on being taken down. The aerosols were subsequently removed from the meshes by washing in 'metal-free' water in the laboratories at Liverpool. A second set of collections was made using a high volume filter system positioned ahead of the ship's bows. The system was constructed at Liverpool and was based on a heavy duty centrifugal pump connected to two plastic filter holders in such a manner that no metal parts were in contact with the sampled air prior to its passing through the filters (type; Whatman 41). Air flow rates were measured using an oriface type flow meter, and typical sampling rates were $\sim 2\,\mathrm{m}^{-3}$ air min^{-1} through 'clean' filters, with a face velocity of $\sim 80\,\mathrm{cm\,s}^{-1}$. The filters, two of which were exposed during each collection period, were sealed in plastic bags before and after exposure. The locations of the samples used in the present investigation are illustrated in Fig. 1, and are listed in Table 1.

Clay mineral analysis

The determination of the clay minerals was carried out on the mesh-collected samples using X-ray diffraction. Quantitative estimates were made by measuring areas under

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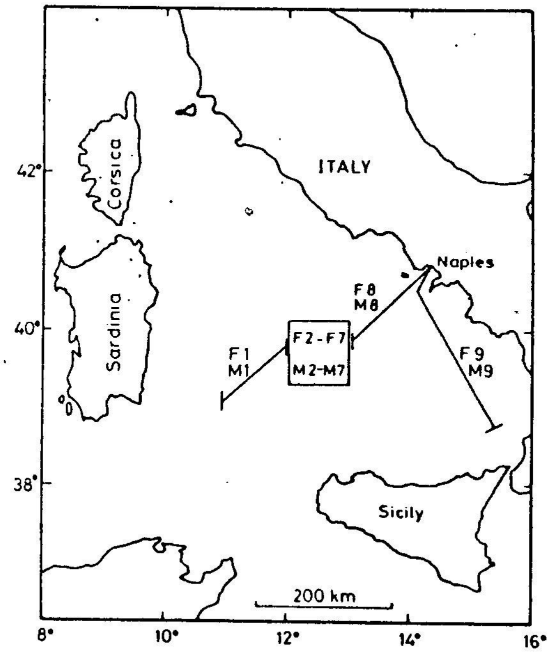

Fig. 1. Location of the aerosol samples. Prefix F indicates filter-collected samples and prefix M indicates mesh-collected samples. Sample pairs F2/M2–F7/M7 were collected within the general area of the square at the individual locations given in Table 1. The remaining sample pairs were taken along the tracks indicated.

the relevant peaks on the diffractograms, using oriented samples.

Ferrimagnetic mineral analysis

Measurements of magnetic susceptibility (χ) were made on the mesh-collected samples using a low-field susceptibility bridge circuit similar to that described by Molyneux and Thompson (1973). The technique has a reproducibility of ±5%.

Elemental analysis

Elemental analysis was carried out on the filter-collected samples. In the analytical procedure, the filters were dissolved in redistilled HNO_3 and Aristar HF in PTFE beakers, and the digests stored in polystyrene vials. The elements were then determined in the digests by an atomic absorption technique using either a flame or flameless mode, as necessary. Appropriate correction was made for filter blanks and the elemental concentrations for each individual collection were calculated as the means of the two exposed filters. Replicate determinations on a mesh-collected sample, for which sufficient material was available to test the analytical procedure, showed that the atomic absorption technique had the following co-efficients of variation: Fe, 6%, Mn, 7%, Cd, 9%; Pb, 5%; Zn, 5%; Cu, 4%; Cr, 5%; Ni, 9% and Al, 2%.

AEROSOL TRANSPORT PATHS

In an attempt to identify the potential source areas of the aerosols, geostrophic back trajectories were reconstructed for the air parcels from which the samples were collected. For each sampling period 12-h geostrophic back trajectories were plotted, at surface level only, from Northern Hemisphere synoptic charts using the method outlined by Petterson (1956); the times and locations of the deployment and retrival of the mesh and the high-volume filters were essentially the same, and the estimated trajectories apply to both sample sets. The reconstructed geostrophic back trajectories are illustrated in Fig. 2, and on the basis of these wind tracks the sample pairs, i.e. mesh and high-volume filters, can be placed into two general populations.

Population A includes sample pairs F1/M1, F2/M2, F3/M3, F4/M4 and F9/M9. These samples were collected from winds having predominantly easterly trajectories which ran along the length of part of the Mediterranean and which, for some samples, impinged on southern Europe during the period of the reconstructed trajectories. No back trajectory data was available for Sample F9/M9; however, during the collection the winds were predominantly easterly.

Population B includes sample pairs F5/M5, F6/M6, F7/M7 and F8/M8. Trajectories for these samples were all predominantly southerly and indicate that the winds had crossed part of the North African mainland.

It is evident from the air parcel trajectory data, therefore, that during the collection period some of the samples, i.e. those of Population B, were taken from winds which had crossed part of the Sahara Desert. Once this had been established a number of para-

Table 1. Locations and times of atmospheric particulate collections

		Collection	Start	Collection	Finish
Mesh sample No.	Filter sample No.	Location	Date	Location	Date
M1	F1	39 07′N, 10 53′E	7 10 79	39 47′N, 11 59′E	8 10 79
M2	F2	39 47′N, 11 59′E	8 10 79	39 26′N, 12 19′E	9 10 79
M3	F3	39 26′N, 12 19′E	9 10 79	40 09′N, 12 59′E	10 10 79
M4	F4	40 09′N, 12 59′E	10 10 79	39 26′N, 12 33′E	11 10 79
M5	F5	39 52′N, 12 44′E	13 10 79	39 42′N, 12 11′E	14 10 79
M6	F6	39 42′N, 12 11′E	14 10 79	39 41′N, 12 44′E	15 10 79
M7	F7	39 41′N, 12 44′E	15 10 79	39 48′N, 12 44′E	16 10 79
M8	F8	39 48′N, 12 44′E	16 10 79	40 37′N, 13 29′E	17 10 79
M9	F9	38 00′N, 14 15′E	24 10 79	38 37′N, 15 27′E	25 10 79

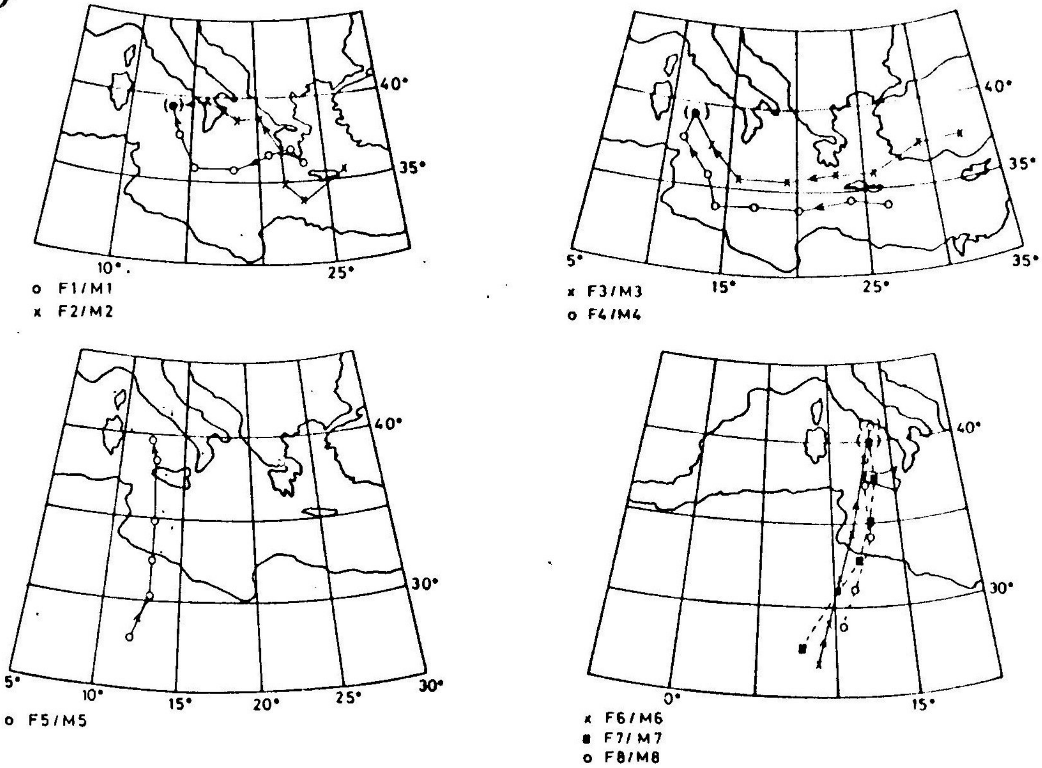

Fig. 2. The identification of sample catchment areas by geostrophic back trajectories. Marker points are at 12-h intervals back-tracked from the end of each collection period. Maximum collection periods were ~ 24 h.

meters were used in an attempt to characterize the Saharan dust, and to investigate the effect it has on the Tyrrhenian Sea aerosol.

THE CHARACTERIZATION OF SAHARAN DUST IN THE TYRRHENIAN SEA AEROSOL

(1) *The clay mineralogy of the soil-sized aerosols*

The collection characteristics of the meshes employed in the present investigation have been discussed in detail by Delany *et al.* (1967), Goldberg (1971), Parkin *et al.* (1972) and Chester and Stoner (1974), and it may be concluded that mesh-collected particles are primarily derived from the uplift of soils and so represent the soil-sized fraction of the aerosol. The meshes have only a low efficiency for the collection of particles less than about 1 μm in size, but have the advantage that they collect relatively large amounts of sample which can be easily removed for subsequent analysis. In the present works the meshes were therefore used to collect the volumes of sample required for the mineralogical and magnetic analyses.

The clay mineralogy of eolian soil-sized dusts has been used as a parameter for the identification of potential aerosol source areas by several authors (see e.g. Delany *et al.*, 1967; Chester *et al.*, 1972). For example, Chester *et al.* (1972) demonstrated that the clay mineralogies of a series of aerosols from the eastern Atlantic varied latitudinally, and reflected the weathering characteristics of the source soils on the adjacent land masses.

The concentrations of the four principal clay minerals, i.e. illite, montmorillonite, chlorite and kaolinite, in the soil-size Tyrrhenian Sea aerosols are given in Table 2, in which the samples are classified into the two populations deliniated on the basis of the geostrophic back trajectories. These populations were distinguished in terms of their aerosol catchment regions, and it is evident from the data in Table 2 that the differences between them are reflected in the gross clay mineralogy of the soil-sized samples. Population A samples, which originate on the northern boundary of the Mediterranean, are characterized by having relatively high concentrations of illite (average; 67%) and roughly similar proportions of kaolinite (average; 15%) and chlorite (average; 18%). Population B samples, which contain material derived from the Sahara also have relatively high concentrations of illite (average; 56%) but differ from those of Population A in that their concentrations of kaolinite (average; 35%) considerably exceed those of chlorite (average; 7%). The higher concentrations of kaolinite in the Population B samples are entirely consistent with their proposed Saharan origin. Evidence for this has been provided by Chester *et al.* (1977) who investigated the clay mineralogy of a series of soil-sized aerosols from the eastern Mediterranean. On the basis of clay

Table 2. Clay mineralogy of the soil-sized atmospheric particulate

Sample population†	Sample No.	Illite (%)	Chlorite (%)	Kaolinite (%)	Montmorillonite (%)
A	M2	64	18	18	N.D.
	M3	72	19	9	N.D.
	M4	70	15	15	N.D.
	M9	61	20	19	N.D.
Average		67	18	15	
B	M5	62	12	26	N.D.
	M6	69	4	25	~ 2
	M7	59	8	31	~ 2
	M8	34	4	59	~ 3
Average		56	7	35	~ 2
Mediterranean 'southeastern' eolian population‡		40	8	50	5

* The individual clay mineral %ages are expressed in terms of a 100% clay mineral sample; i.e. (illite + chlorite + kaolinite + montmorillonite) = 100%. N.D., not detected.

† See text for population classification; no data for Sample M1.

‡ Data from Chester *et al.* (1977).

mineralogy, these authors were able to distinguish a 'southeastern' eolian assembledge which originated in the deserts of North Africa and the Middle East. The kaolinite content (average, ~ 50%) of this population was twice as high as that of a 'northeastern' eolian assembledge, which contained material derived from the soils of southern Europe.

For comparison with the present samples the average clay mineral composition of the 'southeastern' assembledge is given in Table 2. Of the various samples in Population B, M8 has the highest associated Al loading (see Table 4) and so may be regarded as representing the maximum influx of Saharan material to the atmosphere over the Tyrrhenian Sea during the present collection period, and it can be seen from Table 2, that its clay mineral composition is reasonably similar to that of the average for the 'southeastern' assembledge.

It may be concluded, therefore, that there are differences in the gross clay mineralogies of the soil-sized aerosols . . . of Populations A and B. Aerosols which originate from the soils of the southern European landmass, and the northern Mediterranean islands, have illite as their principal clay mineral and roughly equal proportions of kaolinite and chlorite. These aerosols probably form the normal assembledge present over the Tyrrhenian Sea at most times of the year. However, the present investigation has shown that the clay mineral composition of the total soil-sized aerosol can be modified by the injection of relatively kaolinite-rich, soil-derived material from the North African deserts. In the desert-derived 'end member' samples, such as M8, kaolinite exceeds illite and becomes the predominant clay mineral, and it may be regarded as an indicator for soil-sized material transported across the Mediterranean towards the European mainland. The proportion of kaolinite in the soil-sized aerosols over the Tyrrhenian Sea depends on the extent to which the local atmosphere has received injections of Saharan dust, and this is discussed below in terms of variations in the concentrations of atmospheric Al.

(2) *The ferrimagnetic mineralogy of the soil-sized aerosols*

According to Doyle *et al.* (1976) and Oldfield *et al.* (1978) the dominant source of ferrimagnetic minerals in the present-day atmosphere is magnetic spherules generated in industrial and domestic combustion processes. The concentration of ferrimagnetic minerals in a sample can be estimated from measurements of specific susceptibility (χ) and such measurements have been used to assess the magnitude of industrial pollution in such diverse materials as peat bog deposits (Oldfield *et al.*, 1978) and coastal sediments (Scoullos *et al.*, 1979). In a recent paper, Chester *et al.* (1984a) gave data on the magnetic susceptibility (χ) of a series of soil-sized aerosols from the Mediterranean atmosphere. They concluded that in addition to non-crustal sources, natural soil-derived material yielded ferrimagnetic, i.e. χ-contributing, material to the atmosphere. Their data showed that soil-sized components originating from the deserts of North Africa contained ferrimagnetic minerals which have χ values in the range ~ 25 to $\sim 65 \times 10^{-6}\,\mathrm{GOe^{-1}\,cm^{-3}\,g^{-1}}$, whereas aerosols from southern Europe were dominated by non-soil ferrimagnetic components having χ values which are in the range of about 100 to more than about $700 \times 10^{-6}\,\mathrm{GOe^{-1}\,cm^{-3}\,g^{-1}}$. As part of a general survey of the distribution of χ values in soil-sized aerosols from the atmosphere of the Mediterranean Sea and surrounding regions, the authors gave data for the samples from the Tyrrhenian Sea and these are listed in Table 3.

On the basis of their χ values, there is a very clear distinction between the samples of Populations A

Table 3. χ values for the soil-sized atmospheric particulate*

Sample population†	Sample No.	χ (10^{-6} G Oe^{-1} cm^{-3} g^{-1})
A	M1	631
	M2	651
	M3	445
	M4	386
	M9	321
Average		487
B	M5	97
	M6	64
	M7	54
	M8	44
Average		65

* Data from Chester *et al.* (1984).
† See text for population classification.

and B. The soil-sized aerosols of Population A have χ values ranging between 321 and 651×10^{-6} GOe^{-1}cm^{-3}g^{-1}, with an average of 487 $\times 10^{-6}$ GOe^{-1}cm^{-3}g^{-1}; values which are typical for soil-derived material originating in southern Europe. In contrast, samples in Population B have values in the range 44–97 $\times 10^{-6}$ GOe^{-1}cm^{-3}g^{-1}, with an average of 65×10^{-6} GOe^{-1}cm^{-3}g^{-1}. Three of the four Population B samples have χ values between 44 and 64×10^{-6} GOe^{-1}cm^{-3}g^{-1}; these lie within the range found for North African desert-derived material, and so provide further evidence for the injection of Saharan dust into the atmosphere over the Tyrrhenian Sea. It should be noted that Sample M8, which had the highest concentration of kaolinite, also had the lowest χ value of any of the samples.

(3) *The elemental chemistry of the total aerosol samples*

The high volume filter system collects the full spectrum of particles in the atmosphere and the concentrations, and enrichment factors, for a number of elements in the total aerosol samples are given in Table 4.

Under most conditions particulate Al in the atmosphere is associated almost exclusively with alumino-silicates, and for this reason is often employed as an indicator of the amount of crustal material in an aerosol population. The atmospheric concentration of Al in the Tyrrhenian Sea samples ranges between 80 and 5072 ng m^{-3} of air, with a distinct difference between the two populations; Population A having an average of 112 ng Al m^{-3} of air, and Population B an average of 2000 ng Al m^{-3} of air. Within all samples there is also a general tendency for the highest concentrations of soil-sized kaolinite (an indicator for Saharan dust) to be associated with the highest total aerosol Al concentrations. Clearly, therefore, the elevated Population B Al concentrations in the Tyrrhenian Sea atmosphere are a result of the transport of crustal material to the region from the Sahara. The range of atmospheric Al concentrations (~250 to ~5000 ng m^{-3} of air) associated with the Saharan dust incursions of Population B lies within the same orders of magnitude of that usually found for the NE trades off West Africa (see e.g. Chester *et al.*, 1979), and although it may vary considerably on a seasonal basis it is apparent that the northward transport of desert-derived material across the Mediterranean represents an important pathway in the dispersion of dust from the Saharan reservoir.

The concentrations of the other elements in the aerosol also show considerable variation both within, and between, the two populations, and in order to interpret the compositional differences in terms of crustal and non-crustal elemental sources, enrichment factors have been used; for a discussion of the use of enrichment factors—see Berg and Winchester (1978). The enrichment factors given in Table 4 employ Al as a crustal reference element and have been calculated using the following equation; $EF_x = (C_{xp}/C_{Alp})/(C_{xc}/C_{Alc})$, 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. Enrichment factors close to unity are taken as an indication that an element has a mainly crustal origin, and those which are greater than about 10 are considered to indicate that a substantial portion of an element has a non-crustal source.

In terms of their enrichment factors the elements in the Tyrrhenian Sea aerosol can be divided into three general groups: (1) the non-enriched elements, which have enrichment factors generally less than about 10, i.e. Fe, Mn and Cr; (2) the intermediate elements which have enrichment factors between about 10 and 100, i.e. Ni, Cu and (3) the enriched elements which have enrichment factors which can exceed 100, i.e. Zn, Pb, Cd. It can be seen from the data in Table 4 that the enriched and non-enriched elements behave differently in the two populations. The non-enriched elements have generally low enrichment factors in all samples. In contrast, there are considerable variations in the enrichment factors of the enriched elements (Zn, Pb, Cd) even between samples which have relatively small variations in the concentrations of atmospheric Al.

Table 4. Elemental concentrations and enrichment factors in the total aerosol (filter-collected samples)

Population*	sample	Al		Fe		Mn		Cr		Ni		Cu		Zn		Pb		Cd	
	No.	Conc	Ef	Conc	Ef	Conc	Ef	Conc	Ef	Conc	Ef	Conc	Ef	Conc	Ef	Conc	Ef	Conc	Ef
A	F1	80	1.0	99	1.8	3.4	3.7	1.5	16	2.1	29	1.4	25	9.0	133	16	1333	0.17	886
	F2	97	1.0	127	1.9	3.4	3.0	0.71	6.1	0.85	9.7	1.7	25	8.4	102	16	1100	0.11	473
	F3	75	1.0	81	1.6	2.4	2.8	0.42	4.7	0.84	12	0.86	17	5.0	79	6.4	569	0.08	445
	F4	90	1.0	149	2.4	5.2	5.0	1.2	11	—	—	3.2	51	13	170	7.5	556	0.26	1203
	F9	216	1.0	128	0.87	7.2	2.9	1.4	5.4	1.4	7.2	2.6	18	21	115	8.9	275	1.6	3087
Average		112	1.0	117	1.7	4.3	3.5	1.0	8.6	1.3	15	2.0	28	12	120	11	767	0.44	1219
B	F5	249	1.0	175	1.0	2.8	1.0	1.1	3.7	1.1	4.9	3.0	18	1.5	7.1	3.2	86	0.07	117
	F6	1396	1.0	865	0.91	15	0.93	5.9	3.5	3.9	3.1	1.8	1.9	9.0	7.6	9.0	43	0.39	116
	F7	1283	1.0	709	0.81	10	0.67	4.4	2.9	2.3	2.0	0.90	1.0	3.1	2.9	7.7	40	0.35	114
	F8	5072	1.0	3247	0.94	46	0.78	8.2	1.3	5.1	1.1	4.9	1.4	20	4.7	9.6	13	0.41	34
Average		2000	1.0	1249	0.92	18.5	0.84	4.9	2.9	3.1	2.8	2.7	5.6	8.4	5.6	7.4	46	0.31	96

* See text for population classification.
† Concentrations in ng m^{-3} of air.

However, on average, the enrichment factors for these elements are considerably higher in Population A particulates; thus allowing a clear distinction to be made between the two sample populations. Sample F8 was collected from winds which had crossed parts of the Sahara and its equivalent mesh-collected sample has the highest concentration of kaolinite and the lowest χ value of any soil-sized aerosol. This sample also has the highest total aerosol atmospheric Al concentration and may therefore be regarded as containing the greatest proportion of Saharan dust of all the Tyrrhenian Sea aerosols, and it is significant that it also has the lowest enrichment factors for the enriched elements Pb and Cd. It may be concluded therefore that Saharan dust injected into the atmosphere over the Tyrrhenian Sea has relatively low enrichment factors for all elements, and that as its concentration increases it has the diluting effect of reducing the enrichment factors within the total aerosol. However, for some elements, e.g. Pb, Cd, the enrichment factors in the desert-derived aerosols are still, on average, > 10, suggesting that there is an independent, non-crustal, concentration of the enriched elements over the Mediterranean Sea and surrounding areas (see also; Chester *et al.*, 1981). This is probably analogous to the minimum concentration ($C_{\min}$) concept which has been developed by several authors (see e.g. Rahn, 1976; Adams and Van Crean, 1980; Chester *et al.*, 1984b. The present data set is too small to permit individual elemental $C_{\min}$ values to be established with any degree of certainty and although such values should be taken into account in assessing total concentrations, the actual variations in the elemental composition of the aerosol can be described in terms of two principal components. These are: (1) a 'southern European' component, consisting of crustal material which is enriched in some non-crustal elements, e.g. Pb, Cd, Zn, supplied mainly from anthropogenic sources on the European mainland, and (2) a 'Saharan' component consisting of crustal material which has not been significantly enriched in non-crustal elements. Over the Tyrrhenian Sea; the composition of the aerosol is controlled by the mixing of these two components, superimposed on the presence of any $C_{\min}$ concentrations present in the atmosphere. The varying proportions of the two components are dependent on the aerosol catchment regions crossed by the prevailing winds. Air parcels which have included part of southern Europe in their catchments, or which have received material from this region, transport material with enhanced concentrations of the enriched, non-crustal, elements which therefore have relatively high enrichment factors. In contrast, air parcels which have impinged on the North African deserts transport material impoverished in non-crustal elements, and this is reflected in their generally low enrichment factors for all elements. However, the distinction between the two components will obviously not always be clear cut since the aerosols are mixed assembledges.

CONCLUSIONS

The present investigation has identified incidents of a northward transport of Saharan dust to the European Mediterranean coast, and it has been clearly established that this dust exerts an important influence on the composition of the total aerosol in the region of the Tyrrhenian Sea. This supports the conclusion drawn by Ganor and Mamane (1982) that such northward transport should be included in estimates of Saharan dust production. On the basis of the data for the Tyrrhenian Sea atmosphere it is apparent that Saharan dust can be identified in a multi-component, aerosol, and it is suggested that long-time studies should be made to establish the magnitude of the northward transported Saharan dust flux.

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