THE DISTRIBUTION OF NATURAL AND NON-CRUSTAL FERRIMAGNETIC MINERALS IN SOIL-SIZED PARTICULATES FROM THE MEDITERRANEAN ATMOSPHERE

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Abstract. Magnetic susceptibility (χ) values have been measured in 38 soil-sized atmospheric particulates from the Mediterranean Sea and surrounding regions, and have been used to assess the factors which control the distribution of ferrimagnetic minerals in the Mediterranean aerosol. Soil-sized components generated from the North African desert belt have χ values in the range ~ 25 to $\sim 65\ 10^{-6}$ G $Oe^{-1}\ cm^{-3}\ g^{-1}$, whereas those originating in deserts lying to the east of the Mediterranean have higher values which can range up to $\sim 200\ 10^{-6}$ G $Oe^{-1}\ cm^{-3}\ g^{-1}$. In addition to natural ferrimagnetic components there is a supply of χ-contributing material to the Mediterranean atmosphere from non-soil sources, which are probably dominated by industrial and domestic combustion processes; values in samples in which the non-soil material is an important source of ferrimagnetic material range up to $\lesssim 700\ 10^{-6}$ G $Oe^{-1}\ cm^{-3}\ g^{-1}$. The χ values in samples from an east-west Mediterranean transect vary between 25 to 734 10^{-6} G $Oe^{-1}\ cm^{-3}\ g^{-1}$. The ferrimagnetic mineral content of the aerosol is controlled by the extent to which the non-soil material is mixed with, and diluted by, crustal components, and there is a general inverse linear trend between the χ values and the concentrations of crustal material in the Mediterranean atmosphere. Over the Mediterranean the large-scale mixing of populations derived from different catchments can mask the relationship between the concentration of a specific component and its distance from a source, and χ values provide a useful indicator for tracking the extent of material transport and for estimating the degree of inter-population mixing in the Mediterranean atmosphere.

1. Introduction

According to some authors the black magnetic spherules found in various environmental samples (e.g. sediments, ice deposits) are predominantly natural, originating for example from cosmic sources or from terrestrial volcanic activity. However, Del Monte *et al.* (1975) carried out a detailed study of a number of types of magnetic particulates and concluded that volcanic sources do not make any contribution to the black magnetic spherules found in the atmosphere. There is little doubt that some of the spherules are extra-terrestrial in origin and have been identified in some host materials (e.g. deep-sea sediments) which were deposited prior to the onset of industrial contamination. The accretion rate of these cosmic spherules to the Earth's surface, however, is spasmodic

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and according to Parkin *et al.* (1967) can, in fact, approach zero. Magnetic particles can also be produced by man's activities. Oldfield *et al.* (1978) measured the atmospheric fallout rates of these anthropogenic particles in peat sections and provided evidence which they suggested conclusively supports the conclusions of Doyle *et al.* (1976) that the dominant source of ferrimagnetic minerals in the present-day atmosphere is magnetic spherules which originate in industrial and domestic combustion processes. The concentration of ferrimagnetic minerals, i.e. mainly pollutant magnetic spherules, in a sample can be estimated from measurements of specific magnetic susceptibility (χ) and saturation isothermal remanent magnetization (SIRM). Values of both of these parameters have been used to assess the magnitude of industrial pollution in peat bogs (Oldfield *et al.*, 1978), lake deposits (Oldfield *et al.*, 1981), and coastal sediments (Scoullos *et al.*, 1979).

The atmosphere is an important pathway by which pollutants are transferred to the oceans following their transport from the land areas, and because ferrimagnetic minerals have a significant anthropogenic contribution their distribution in the marine aerosol offers a potentially attractive insight into the extent to which such pollutant transport occurs. For example, Parkin *et al.* (1970) reported the presence of black magnetic fly ash spherules in soil-size atmospheric particulates taken on a transect across the North Atlantic. According to these authors, the presence of this type of spherule is a certain indication of 'city' pollution, i.e. the burning of coal. This is in contrast to the presence in the atmosphere of carbon, either as crumbs (from diesel engines) or cokey balls (from oil burning), both of which could come from passing ships as well as from cities. Parkin *et al.* (1970) were able to show that the concentrations of the spherules decreased away from the North American and European mainlands and reached their lowest values in mid-ocean areas; a distribution they related to pollution from urban and industrial regions. However, these authors based their conclusions on data obtained from the visual identification of the spherules in their atmospheric samples, and little information is available on the actual magnetic characteristics of the marine aerosol. The present work was therefore undertaken in order to provide some basic data on this important aspect of marine atmospheric particulates. In the investigation, χ has been measured in a series of soil-sized particulates from the lower atmosphere over the Mediterranean Sea and surrounding regions, and the data have been used to assess the factors which control the distribution of ferrimagnetic minerals in the Mediterranean aerosol.

2. Methods of Collection and Analysis

The atmospheric particulates were sampled by means of nylon meshes on board the *RRS Shackelton*. The technique, which results in the collection of soil-sized (i.e. > 0.5 μm diameter) particles, has been described extensively elsewhere (see e.g.: Chester *et al.*, 1972; Chester and Stoner, 1974). Two 1 m^2 meshes were exposed during each collection and were immediately sealed in plastic bags on being taken down. The particulates were subsequently removed by washing the mesh fabric in 'metal-free' water

in the laboratories at Liverpool. After settling, the water was decanted and the particulates were dried at ~ 40 °C in an oven.

Measurements of χ were made using a low-field susceptibility bridge circuit similar to that described by Molyneux and Thompson (1973). The technique, which is non-destructive, requires a minimum of ~ 0.1 g of sample and has a reproducibility of $\pm 5\%$.

3. Results and Discussion

Specific χ is a measure of the magnetisability of a sample and mainly reflects the concentration of ferrimagnetic minerals (e.g. magnetic and maghemite) in it. χ is not a precise expression of the ferrimagnetic content of a sample since it is affected by the grain size and shape of the magnetic particles, their spontaneous magnetization, internal stress and other non-intrinsic parameters (Thompson *et al.*, 1975). However, only when ferrimagnetic minerals are sparse, or absent, can the presence of haematite contribute significantly to χ. Therefore, χ may generally be regarded as being proportional to the concentration of ferrimagnetic minerals present in a sample (see e.g., Thompson *et al.*, 1975). For this reason, χ has been used to estimate the ferrimagnetic content of various environmental materials (see e.g., Scoullos *et al.*, 1979). Because the main χ-contributing component is magnetic spherules having an anthropogenic origin (Doyle *et al.*, 1976), χ has also been used to assess the degree of pollution these materials have suffered from combustion processes.

In an attempt to evaluate the factors which control the concentration of ferrimagnetic (i.e. χ-contributing) minerals in marine atmospheric particulates, a sample suite from a specific region having more than one aerosol catchment area was chosen. The Mediterranean Sea provides an excellent example of such a region. It is bordered in the north by nations having a variety of economies, ranging from industrial and semi-industrial to agricultural, and in the south by the North African desert belt. Further, Chester *et al.* (1977) were able to show that atmospheric particulates in the Eastern Mediterranean consist of at least two individual populations; one originating on the European mainland, and one in the deserts of North Africa and the Middle East.

The principal catchment regions for crustal components transported to, and within, the Mediterranean atmosphere are the desert regions of North Africa, the Middle East and Arabia; together with the arid lands of southern Europe. In the present investigation χ values have been measured in 38 samples of soil-sized atmospheric particulates collected on a east-west transect of the Mediterranean Sea, and from those marine regions to the east and west via which material might be expected to be transported into the Mediterranean atmosphere. No attempt was made to further size fractionate the particulates since the purpose of the present investigation was to examine the usefulness of χ values as a diagnostic tool in the soil-sized aerosol as sampled directly. The magnetic, and some chemical, data for the samples are listed in Table I, and sample locations are illustrated in Figure 1.

χ values in the samples range from 25 to 734 10^{-6} G Oe^{-1} cm^{-3} g^{-1}, and in Table I they are listed according to collection region. Aluminium is often used as a crustal

TABLE I

χ values and Al concentrations in soil-sized atmospheric particulates from the Mediterranean Sea and surrounding regions

Collection region	Sample No.	χ 10^{-6} G Oe^{-1} cm^{-3} g^{-1}	Al (ppm)	χ/Al × 10^5	Atmospheric Al loading; ng m^{-3} of air
North Atlantic	JL49	64	87000	74	3810
North east trades	JL48	28	86000	32	7940
	JL46	25	68000	37	1380
	JL45	56	88000	64	2983
	JL44	62	103000	60	3986
	JL43	50	91000	55	2366
Mediterranean	C8	39	74000	1560	
Sea	C11	62	80000	–	
	C13	50	86000	–	
	C23	47	97000	1700	
Red Sea	129	113	71490	160	1702
	64	99	54470	190	394
	130	133	64290	210	801
	131	198	68018	290	1053
	63	99	62450	160	518
	132	106	71187	150	527
	62	72	69420	100	1828
	61	60	62746	96	583
	60	92	65037	140	241
	59	77	66180	120	4348
Mediterranean;	133	734	53279	1380	15
east/west	134	701	49778	1410	13
transect	34	651	58910	1100	35
	33	631	58000	1090	15
	35	445	55850	800	16
	36	386	82580	470	38
	41	321	64260	500	75
	32	306	79720	390	130
	43	215	85875	250	1202
	31	170	54160	320	76
	37	97	69560	140	44
	42	96	80017	120	480
	44	72	93177	78	1005
	135	68	59000	120	1271
	38	64	71070	90	1285
	39	54	66760	81	1349
	40	44	74470	59	2803
	136	44	56000	74	2820

indicator element and Al loadings in the marine atmosphere range over several orders of magnitude, i.e. from <1 to $>10^3$ ng m^{-3} of air; the highest loadings being found adjacent to the major desert regions. For the marine aerosel, therefore, Al loadings $>10^3$ ng m^{-3} of air may be taken as an indication that desert (or arid land) derived

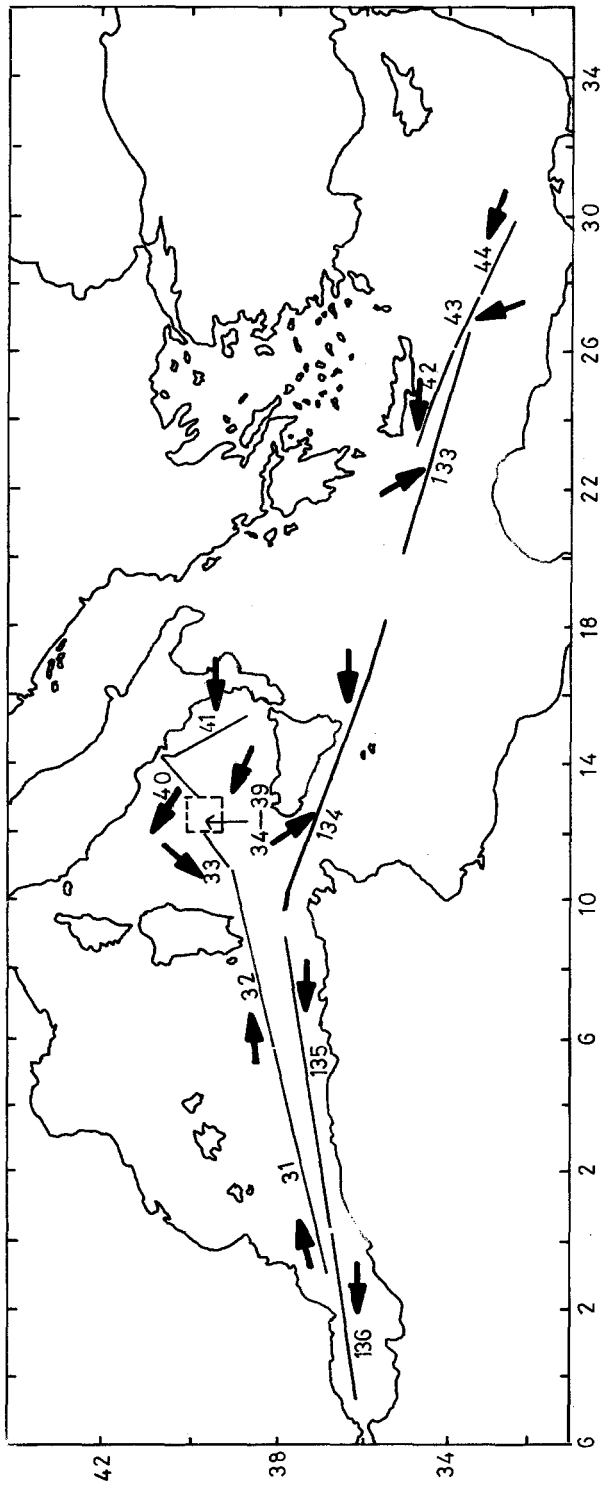
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Fig. 1a.

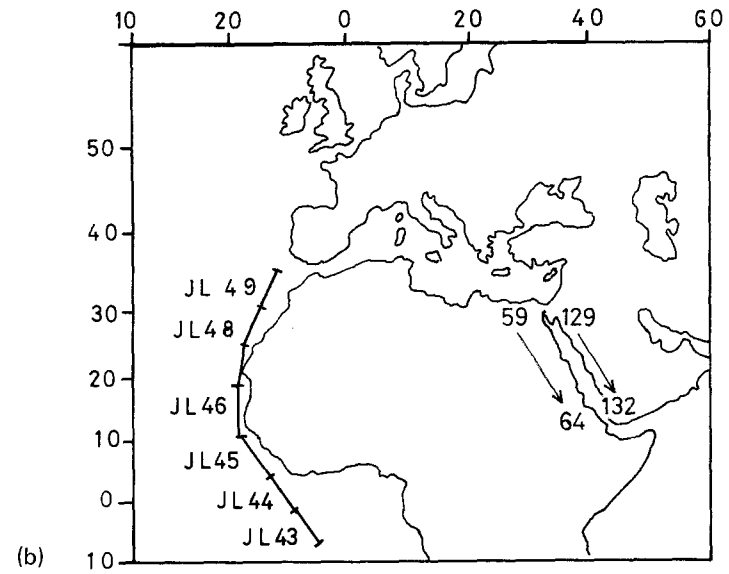

Fig. 1. Location of the soil-sized atmospheric particulate sample. (a) The Mediterranean transect. The solid lines show the ship's track during the collection of each sample, and the arrows indicate the dominant prevailing wind. (b) The Atlantic north east trades and Red Sea samples. For the Red Sea samples the arrows indicate the Red Sea transects from which the samples 59 to 64 and 129 to 132 were taken on separate cruises.

Red Sea atmospheric particulates (see Table I), although these have Al loadings $< 10^3$ ng m^{-3} of air. It may be concluded therefore that natural, i.e., crust-derived, components can contribute to the χ values of atmospheric particulates. Further, the magnitude of the natural contribution may vary from one catchment region to another, in response to variations in the extent to which the lithospheric 'background' input is derived from secondary ferrimagnetic minerals formed as a result of the magnetic 'enhancement' processes described by Le Borgne (1955) and Mullins (1977). More data, especially for particle size relationships, is obviously required before these inter-catchment differences in χ-contributing components can be established with certainty; however it is clear that before attempting to use χ values as an indicator of 'city' pollution, account must be taken of the contribution made to them by natural material from appropriate catchment regions.

χ values for the soil-sized atmospheric samples collected on the east-west Mediterranean transect vary considerably, ranging from 44 to 734 10^{-6} G Oe^{-1} cm^{-3} g^{-1}. With one exception (Sample 43) the six samples from the transect which have Al loadings $> 10^3$ ng m^{-3} of air have χ values lying between 44 and 72 10^{-6} G Oe^{-1} cm^{-3} g^{-1}, which are reasonably similar to those found for particulates originating from the North African desert belt, i.e. $\sim$25 to $\sim$65 10^{-6} G Oe^{-1} cm^{-3} g^{-1}. However, Sample 43 has a χ value of 215 10^{-6} G Oe^{-1} cm^{-3} g^{-1}, which is considerably higher than any of

those for North African desert samples, but is only slightly outside the range found for particulates originating from the deserts lying to the east of the Mediterranean (i.e. 72 to 198 10^{-6} G Oe^{-1} cm^{-3} g^{-1}). On the basis of their χ values, therefore, it would appear that samples in the east-west Mediterranean transect which are dominated by desert-derived components (i.e. those having Al loadings $> 10^3$ ng m^{-3} of air) contain crustal material originating largely from the North African desert reservoir. Sample 43 is an exception to this, and probably contains ferrimagnetic minerals from desert catchments lying to the east of the Mediterranean.

When the transect samples are considered in terms of location (see Figure 1) it is apparent that there are no discernible spatial patterns in the distribution of their χ values. For example, samples 34 and 39 were both collected in the same general region, but the former has an order of magnitude higher χ value than the latter. Over the Mediterranean, therefore, there is no apparent relationship between the χ value of a soil-sized atmospheric particulate and its distance from a specific anthropogenic source. Such a relationship was proposed by Parkin *et al.* (1970), who reported a decrease in the proportion of fly-ash spherules in soil-sized atmospheric particulates over the North Atlantic eastwards from the American mainland. However, for the Mediterranean aerosol, in which particulates can originate from a variety of catchments, other explanations must be sought to describe the distribution of the ferrimagnetic minerals. One such explanation is that the composition of the Mediterranean aerosol is controlled by the mixing of materials from different catchments, and this is considered below.

In Table I the transect samples are ranked on the basis of decreasing χ values, and it can be seen that relative to Al certain of them are enriched in χ-contributing material. χ/Al ratios in the samples vary over three orders of magnitude and largely reflect variations in χ, i.e. that they are independent of location. It is also apparent from the data in Table I that there is a relationship between χ, and χ/Al ratios, and the soil-sized atmospheric particulate Al loadings in the Mediterranean aerosol, and that in general the highest χ values are associated with the lowest Al loadings. This implies that the greater the concentration of crustal material in the atmosphere, the smaller the concentration of ferrimagnetic minerals. This relationship is illustrated in Figure 2, which demonstrates that there is an overall inverse linear trend between the χ/Al ratios in the solids and the concentration of Al in the atmosphere. Since both χ values, and χ/Al ratios, can vary in surface deposits from the catchment regions supplying components to the Mediterranean atmosphere the relationship will only hold for samples having crustal material from similar sources, and for this reason Sample 43 (see above) is omitted from Figure 2. Although there is considerable scatter in the data plotted in Figure 2, some of which may result from the non-quantitative collection efficiency of the meshes yielding underestimates of the atmospheric Al loadings, it is suggested that the most probable explanation for the type of co-variance found is that over the Mediterranean there is a supply of non-crustal χ-contributing material which is diluted as it is mixed with crustal components in the atmosphere. Much of this non-soil χ-contributing material probably originates from industrial and domestic combustion processes in Western Europe and is transported by winds which have crossed this catchment region.

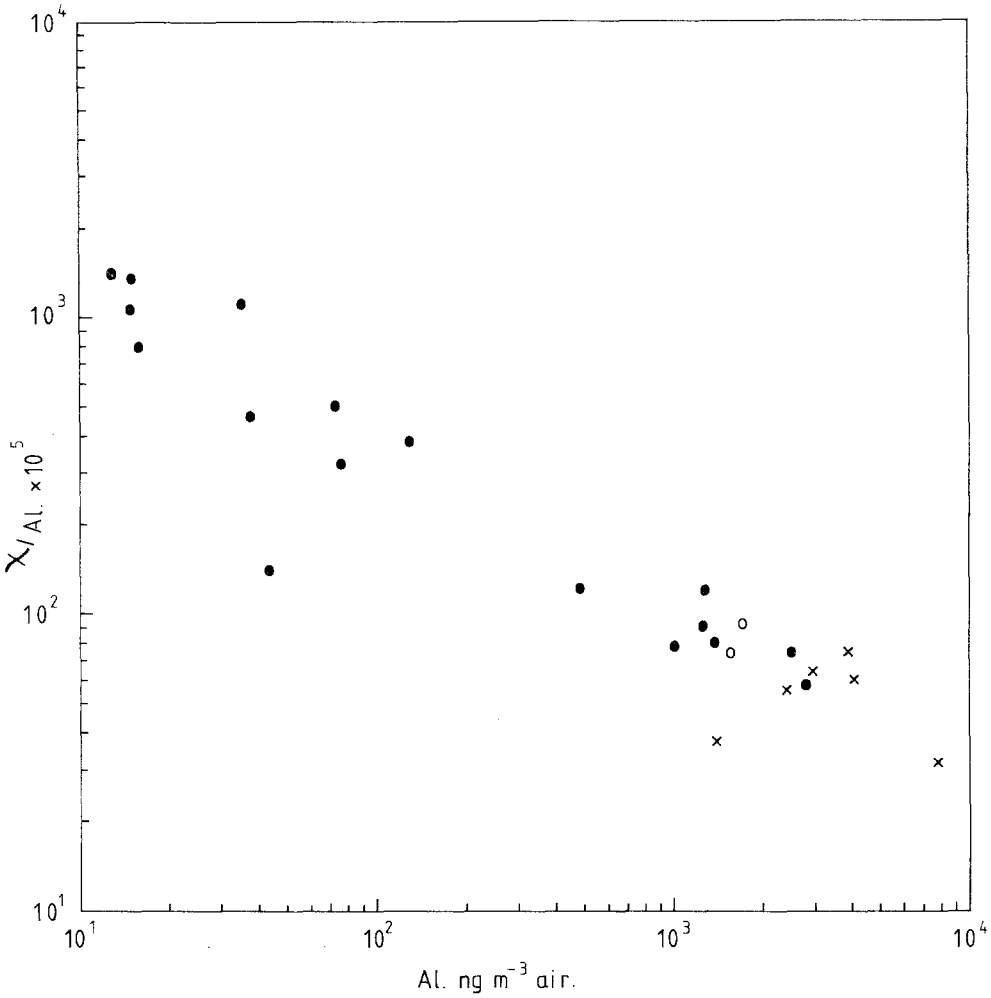

Fig. 2. χ/Al ratios for the soil-sized particulates; as a function of atmospheric Al loadings. Mediterranean transect samples (●), other Mediterranean samples (C8, C23; ○), Atlantic north east trade samples (×).

Both the crustal and the non-crustal components in the Mediterranean aerosol will have their highest concentrations closest to the sources of their injection into the atmosphere, and the degree to which they are mixed will depend on the ageing of the individual aerosol populations in which they predominate. The Mediterranean Sea has a number of different aerosol catchment regions, with contrasting types on its northern and southern shores. However, in terms of atmospheric transport distances, the Mediterranean is relatively very narrow and this can result in the large-scale mixing of components from more than one catchment. This kind of mixing offers an explanation for the order of magnitude differences in χ values found in samples collected in the same general region; for example, those between samples 34 and 39 cited above. Both were

taken in the region lying between Sicily and the Italian mainland, but Sample 34 has a χ value of 651 10^{-6} G Oe^{-1} cm^{-3} g^{-1}, whereas Sample 39 has a value of only 54 10^{-6} G Oe^{-1} cm^{-3} g^{-1}. However, the difference can be explained by the fact that the Al loading for Sample 34 is relatively small (35 ng m^{-3} of air) compared to that of Sample 39 (1346 ng m^{-3} of air); that is, during the collection period for Sample 39 there was an injection of desert-derived crustal components to the region which resulted in the dilution of the non-soil χ-contributing material. In contrast, non-soil components, originating on the European landmass, dominated the ferrimagnetic material in Sample 34.

It is apparent therefore that over the Mediterranean the large-scale mixing of different aerosol populations can mask the relationship between the concentration of a specific component (e.g. a pollutant) and its distance from a source. Further, the present investigation has shown that the determination of χ values in soil-sized atmospheric particulates can yield important information on the characterization of individual aerosol populations, and on the extent to which inter-population mixing has occurred.

4. Conclusions

(1) Natural, soil-derived, components which supply crustal solids to the Mediterranean aerosol contain χ-contributing material, and the magnitude of the contribution made by such material to the ferrimagnetic mineral content of the soil-sized aerosol can vary from one catchment to another. Soil-sized components generated from the North African desert belt, one of the principal reservoirs for the supply of crustal solids to large areas of the Mediterranean, appear to have χ values in the range ~ 25 to ~ 65 10^{-6} G Oe^{-1} cm^{-3} g^{-1}. In contrast, those originating in deserts lying to the east of the Mediterranean have higher χ values, which range up to ~ 200 10^{-6} G Oe^{-1} cm^{-1} g^{-1}.

(2) In addition to natural ferrimagnetic components, there is a supply of non-crustal χ-contributing material to the Mediterranean atmosphere which is derived from sources other than the generation of uncontaminated soils. For samples in which this non-soil material is an important contributor of ferrimagnetic minerals, χ values range up to $\lesssim 700$ 10^{-6} G Oe^{-1} cm^{-3} g^{-1}. The present data cannot be used to show unequivocally that the non-soil χ-contributing material originates from industrial and domestic combustion processes, but the proportion of non-crustal ferrimagnetic material in a sample from the Mediterranean aerosol can be estimated from the measured χ values, or the χ/Al ratios, in the collected solids by reference to the χ values in the appropriate soil-derived components.

(3) The ferrimagnetic mineral content of the Mediterranean aerosol is controlled by the extent to which the non-crustal material is mixed with, and diluted by, crustal components, and there is a general inverse linear trend between the χ values and the concentrations of crustal material in the atmosphere over the Mediterranean.

(4) The Mediterranean Sea has contrasting aerosol catchment regions on its northern and southern boundaries, and because of its relatively narrow width large-scale mixing

between populations derived from these catchments occurs. This mixing can mask relationships between the concentration of a specific component in the aerosol and its distance from a source. Ferrimagnetic material, estimated on the basis of χ values, provides a useful indicator both for tracking the extent of material transport and for estimating the degree of inter-population mixing in the Mediterranean atmosphere.

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