

THE ATMOSPHERIC DISTRIBUTION OF LEAD OVER A NUMBER OF MARINE REGIONS

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ABSTRACT

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A data base of 111 filter-collected marine atmospheric particulates is used to describe the distribution of lead over the North and South Atlantic, the Mediterranean Sea, the Red Sea, the Gulf of Aden and the northern and central Arabian Sea. The distribution of atmospheric Pb is assessed in terms of enrichment factor diagrams, and it is shown that over the marine regions studied in both the Northern and Southern Hemispheres the distribution of Pb in the atmosphere is controlled by the mixing of a background component, or components, with crustal material within certain concentration limits. For the Northern Hemisphere samples used in the investigation there is a reasonably well-defined Pb concentration minimum of $\sim 0.6 \text{ ng m}^{-3}$ of air; however, this will be severely decreased in more remote Northern Hemisphere marine regions. Geometric average Pb atmospheric concentrations vary from one marine region to another, ranging from $\sim 0.98 \text{ ng m}^{-3}$ of air for the South Atlantic westerlies to $\sim 15 \text{ ng m}^{-3}$ of air in the North Atlantic westerlies; although the latter reduces to $\sim 7 \text{ ng m}^{-3}$ of air when 'polluted' samples are excluded. Lead sea-surface deposition fluxes are calculated on the basis of two deposition velocities (0.25 and 1 cm s^{-1}), the largest flux ($220 \text{ ng Pb cm}^{-2} \text{ yr}^{-1}$) being found for the westerlies over the eastern margins of the North Atlantic. The distribution of lead over the North Atlantic is assessed in terms of the global lead budget and it is estimated that a maximum of $\sim 24\%$ of the total 'natural' lead injected annually into the World atmosphere, and $\sim 3.5\%$ of the anthropogenic lead injected annually into the Northern Hemisphere atmosphere, are deposited over the North Atlantic sea surface.

INTRODUCTION

In recent years a great deal of research has been carried out into the elemental composition of atmospheric particulates from marine regions. Because particulate elemental concentrations in the marine atmosphere vary considerably, both spatially and temporally, various authors have used an enrichment factor (EF) to assess the origin, and the degree of enhancement, of an element in the particulates. The most commonly employed EF uses Al as a reference element for crustal material and is calculated according to the equation:

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$$EF_x = (C_{xp}/C_{Alp})/(C_{xc}/C_{Alc}),$$

in which C_{xp} and C_{Alp} are the concentrations of an element x and Al respectively, in the particulate, 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 ≥ 10 are considered to indicate that a substantial portion of an element has a non-crustal origin. One of the major findings which has emerged from the study of marine atmospheric particulates is that, relative to crustal material, they are enriched in some elements, but not in others.

Following Rahn (1976), the relationship between aluminium and other elements in atmospheric particulates can be expressed logarithmically in the form of an EF diagram, in which the EF_x is plotted against the concentration of aluminium in the air. In this type of diagram enriched elements fall in a triangular field in which the EF 's increase as the concentration of aluminium decreases. In contrast, non-enriched elements have EF 's which plot in a broad horizontal field with only a small vertical range, i.e. the EF 's are largely independent of variations in the concentration of aluminium. On the basis of their EF diagrams in continental, and semi-marine and marine atmospheric particulates, Rahn (1976) classified a series of elements into three broad groups. *Non-enriched*, including Na, Mg, K, Ca, Si, Ti; *intermediate*, including Fe, Mn, Ga, V, Cr, Co; and *enriched*, including Ni, Cu, Se, Cd, Sn, Sb, Hg, Pb.

According to Berg and Winchester (1978), aerosol composition in the marine atmosphere resembles that expected from the mixing of finely divided materials from large-scale sources. Sources which have been proposed to account for the enrichment of elements in marine atmospheric particulates include aerosol generation at the sea surface (Duce et al., 1976), volatilization from the earth's surface (Goldberg, 1976), release of metal-rich particulates from vegetation (Beauford et al., 1977), volcanism (Lepel et al., 1978), and a number of anthropogenic processes which include the burning of fossil fuel and general industrial activity. The relative importance of a number of these sources has been assessed by Lantzy and Mackenzie (1979), who concluded that the EF 's of many trace metals are of the same order of magnitude at high latitudes in both the Northern and Southern Hemispheres, and are larger at high latitude than at low latitude.

One of the problems in assessing the factors which control the distribution of particulate elements over marine regions has been a lack of sufficient data on which to base overall conclusions. Over the past few years atmospheric particulates have been collected from various oceanic regions in a programme carried out by the Oceanography Department at Liverpool. In the present paper, 111 samples are used as a data base to describe the distribution of particulate lead in the marine atmosphere, mainly in the Northern Hemisphere.

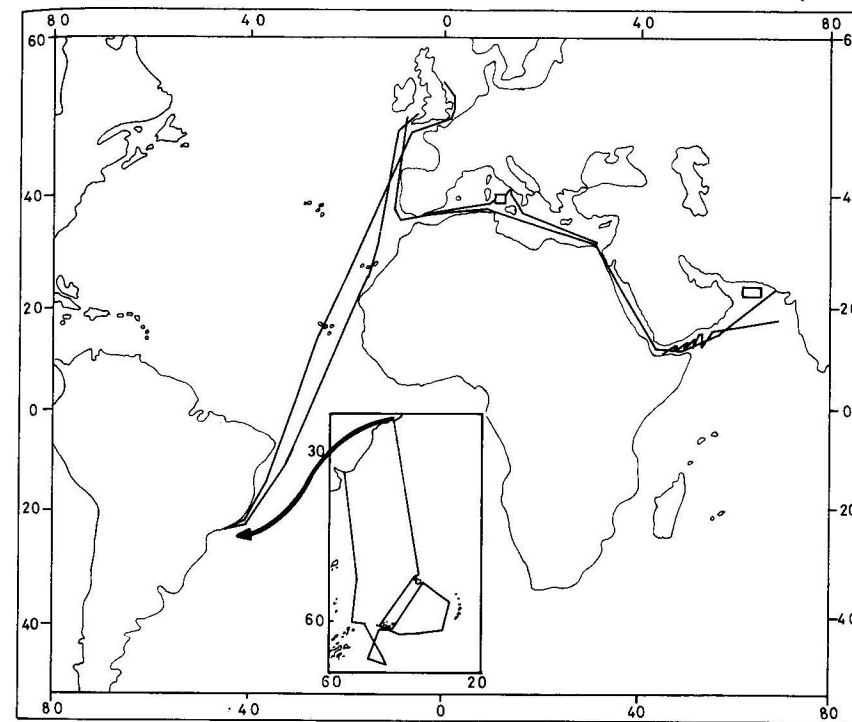


Fig. 1. Collection of atmospheric particulates made on board R.R.S. Shackleton, (1979–1981). The ship's track over which sampling was carried out is indicated by the solid lines. Individual samples are not shown.

METHODS OF COLLECTION AND ANALYSIS

The atmospheric samples were collected on board R.R.S. Shackleton during a number of cruises over the period 1979–1981; the ship's tracks are illustrated in Fig. 1. Samples were taken using a high-volume filter system which was positioned ~ 6 m ahead of the ship's bows at ~ 7 m above the sea surface. The system incorporated Whatman 41 filters, two of which were exposed during each collection. The filters were mounted in clear plastic holders and before and after exposure were sealed in plastic bags. All analyses were carried out in the laboratories at Liverpool and sample handling on board ship was minimised.

In the analytical procedure the Whatman 41 filters were dissolved in redistilled HNO_3 and Aristar HF in PTFE beakers and the digests stored in polystyrene bottles. Lead and aluminium 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 mean of the two exposed filters. Replicate determinations on sub-

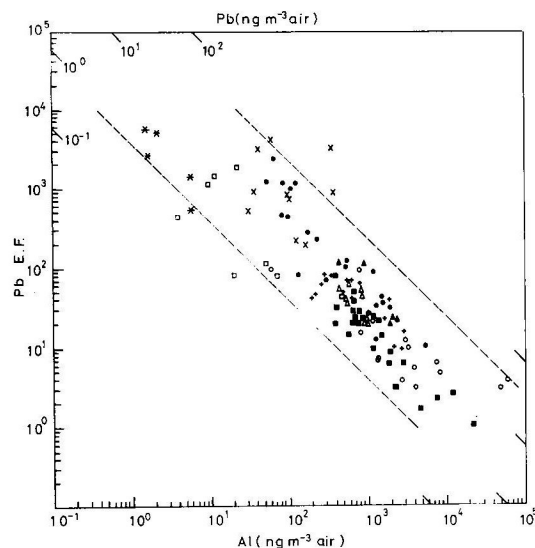


Fig. 2. Pb enrichment factor diagram for the marine atmospheric particulates. North Atlantic westerlies (\times), Atlantic north east trades (\circ), South Atlantic westerlies ($*$), Atlantic south east trades (\square), Mediterranean Sea (\bullet), Red Sea (\blacktriangle), northern Arabian Sea (\blacksquare), central Arabian Sea (\triangle), Gulf of Aden ($+$). The 45° broken lines enclose the field in which the distribution of Pb in the particulates is controlled to the same general extent by the dilution of a background material by crustal solids. The left hand broken line, which indicates the particulate Pb concentration minimum (see text), is drawn largely on the basis of the Northern Hemisphere samples.

samples of a mesh-collected atmospheric particulate, for which sufficient sample was available, showed that the atomic absorption technique had a coefficient of variation of 5% for Pb and <10% for Al.

RESULTS AND DISCUSSION

The marine atmospheric *EF* diagram for particulate Pb is illustrated in Fig. 2, and incorporates data from eight individual populations; i.e. those from the Arabian Sea, the Gulf of Aden, the Red Sea, the Mediterranean Sea, the North and South Atlantic westerlies and the Atlantic north east and south east trades. A number of important points emerge from a study of this diagram; these are discussed below.

Rahn (1976) was able to identify a well-defined 'marine' region in the *EF* diagrams of some elements, evidenced by high enrichments in remote marine and semi-marine areas. Sodium was one of the elements which most clearly showed such a 'marine' region; a Na *EF* diagram for a series of samples collected from the North and South Atlantic during the present work is illustrated in Fig. 3a. It is apparent from this figure that over marine regions Na acts as an enriched element, i.e. the *EF*'s increase as the concentration

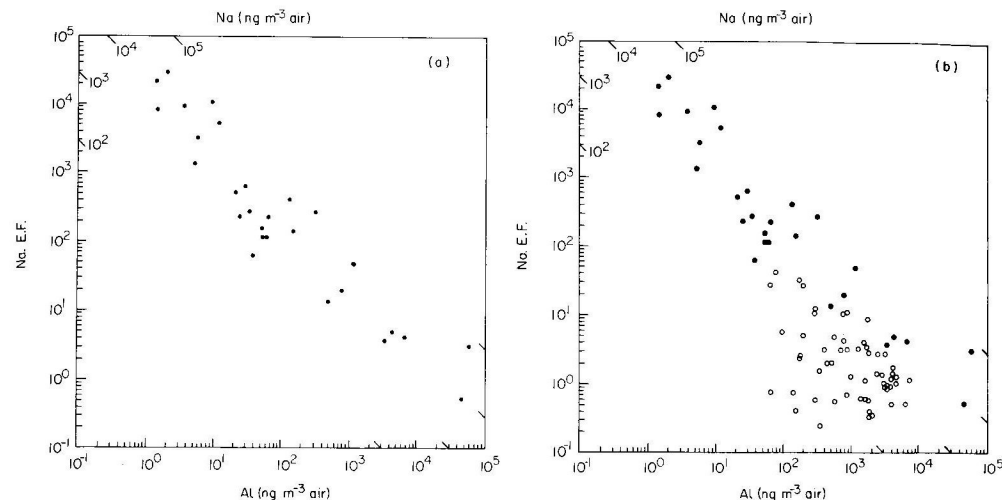


Fig. 3. Na enrichment factor diagram. (a) Na *EF* diagram for a series of particulates from the North and South Atlantic marine atmosphere. (b) Na *EF* diagram for the North and South Atlantic marine atmospheric particulates (solid circles), together with a series of semi-marine and continental samples (open circles; data from Rahn, 1976).

of Al decreases, and that the relationship between Na and Al follows an inverse linear trend. In addition to marine samples, Rahn (1976) included a series of semi-marine and continental samples in his Na *EF* diagram and a number of these are included with the present data in Fig. 3b, from which it can be seen that the continental samples have Na *EF*'s which are generally <10 at all Al concentrations. Thus, for Na there is a well-defined 'marine' region in the *EF* diagram, and it is clear that that is the result of the element having a largely oceanic source in the marine atmosphere, resulting from processes such as the injection of sea salt into the air.

From the *EF* diagram for Pb (Fig. 2) a linear inverse trend in the relationship between this element and Al in the oceanic atmosphere is apparent; i.e. the greater the concentration of Al, the smaller the Pb *EF*. The form of this relationship implies that over these marine regions there is a 'background' component, or components, in which the particulates have relatively high Pb *EF*'s, which is mixed with, and diluted by, crustal components. This relationship is similar to that found for a single marine atmospheric population, that from the Eastern Mediterranean, by Chester et al. (1981); it is important since it is now shown to operate over other adjacent regions of the World Ocean. The present investigation included relatively few data from the Southern Hemisphere. However, those that are available show that, despite concentration differences (see below), the distribution of Pb in both the North and South Atlantic aerosols is controlled by a similar mixing/dilution relationship. This confirms the suggestion made by Berg and

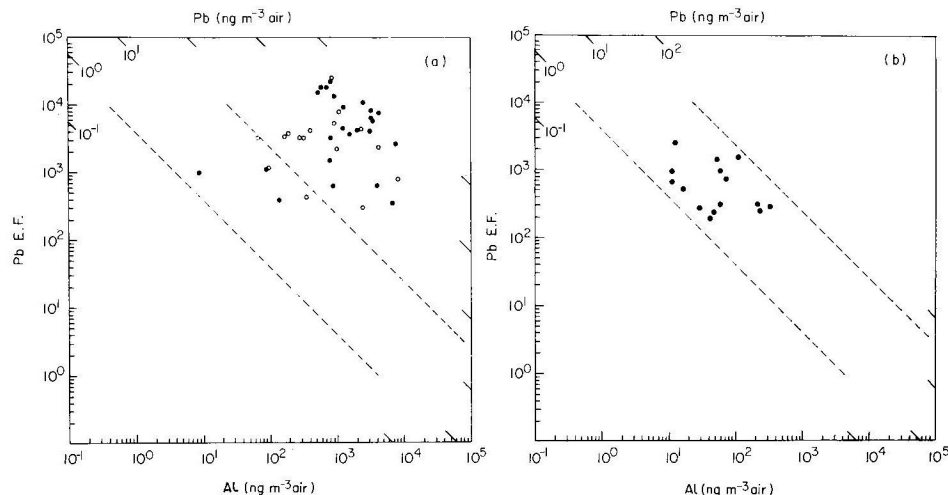


Fig. 4. Pb enrichment factor diagram for some non-marine atmospheric particulates. (a) Pb *EF* diagram for some continental non-marine (●) and semi-marine (○) atmospheric particulates (data from Rahn, 1976); 45° broken lines enclose the 'marine' field (see Fig. 2). (b) Pb *EF* diagram for a series of remote continental samples collected at Jungfrauoch, Switzerland (data from Dams and De Jonge, 1976); broken lines enclose the 'marine' field (see Fig. 2).

Winchester (1978) that aerosols in the marine atmosphere have a composition resulting from the mixing of materials from various sources.

It may be concluded from the present data, therefore, that there is a 'marine' region in the *EF* diagram for Pb in the aerosols studied, at least to the extent that the various atmospheric particulates plot within a limited field, and that the Pb *EF*'s are highest in remote, i.e. low-Al, areas. However, the *EF* diagram for Pb differs significantly from that of Na in one important respect, i.e. when data points for continental samples are included they do not group in such a way as definitely to identify a 'marine' region which can be distinguished, as could that for Na, on the basis of high *EF*'s alone. This is illustrated in Fig. 4a, in which a set of non-marine data points are plotted onto a Pb *EF* diagram for which the 'marine' field is delineated. In this *EF* diagram many of the non-marine data points group towards the upper right-hand corner, under the constraints of relatively high *EF*'s at relatively high Al concentrations. In contrast, the Na non-marine data points tend to group at the lower right hand corner of the *EF* diagram, under the constraints of relatively low *EF*'s at relatively high Al concentrations (see Fig. 3b). Another feature of Fig. 4a is that of the non-marine data set, which consists of 41 samples, only five fall inside the 'marine' field and of these four are from the same investigation. It would seem therefore that there is a portion of the Pb *EF* diagram which appears generally to characterise the Northern Hemisphere marine samples studied here. However, the addition of further data points from a remote continental region shows that the field is not in

fact restricted to marine samples. This is illustrated in Fig. 4b in which samples from Jungfrauoch, a mountain site 3750 m above sea level in Switzerland (Dams and De Jonge, 1976), are plotted. These points all fall within the 'marine' Pb field in which the principal control of the Pb *EF*'s is the mixing of crustal material and 'background' component(s), a process which is confined within the same concentration limits in both the marine and the remote continental populations, thus leading to the common field in the Pb *EF* diagram. The 'background' component(s) itself contains pollutant material, but the important point is that the principal control on the distribution of Pb in the atmospheric particulates is apparently the same over both the marine areas studied here and remote European continental regions. That is, over these regions any pollutant Pb in the atmospheric samples has, with certain exceptions detailed below, been incorporated into the general mixing/dilution relationship.

Rahn (1976) pointed out the *EF* diagrams of the enriched elements had a strong tendency to assume a triangular shape, with the data points falling along lines of equal concentration. Further, where sufficient data points were available, there was a reasonably well-defined lower limit of concentration. One of the outstanding features of the marine atmosphere Pb *EF* drawn from the present data is this tendency towards a minimum Pb concentration, particularly for the Northern Hemisphere samples (see Fig. 2). For Pb, the concentration minimum for the Northern Hemisphere samples studied appears to be $\sim 0.6 \mu\text{g m}^{-3}$ of air. The reason for the appearance of this concentration minimum on the Pb *EF* diagram is not clear, but it seems to be a real feature and has important implications, particularly with regard to the existence of a Pb background concentration.

The concept of elemental atmospheric minimum concentrations has been considered by Adams et al. (1980). These authors proposed that elements which are anomalously enriched in the atmosphere have two general sources in the aerosol: a large particle source associated with dispersion processes, and a sub-micron particle source which is responsible for a concentration minimum which is assumed to be constant at a given sampling site. They used a mathematical approach to calculate the minimum concentration (C_{\min}) for two data sets, one from Western Europe and one from South America, both being land sites. They found that for some elements, e.g. Cu, Zn, the C_{\min} values were higher at the European site, but that for others, e.g. Se, As, the highest values were found for the South American location, although there is a greater anthropogenic influence on the European aerosol. For Cu and Zn, the *EF*'s in the dispersed aerosol fraction were also higher over the European site; this the authors related to an enrichment in the coarse particle material due to pollution over Western Europe. From this work, it may be concluded that for some elements anthropogenic influences can affect both the large and small sized aerosol fractions. On the basis of their study, Adams et al. (1980) concluded that the mean concentrations, or the *EF*'s, of enriched atmospheric elements as obtained at different remote

locations cannot be compared without making the assumption that the large-particle aerosol generation rate and the scavenging history are identical. The reason for this is that unless this assumption is made, differences in both concentrations and EF 's may be due as much to variations of the reference element used as to differences in the concentrations of the enriched elements, and that minimum concentrations offer a better approach to characterize remote aerosols.

Adams et al. (1980) showed that C_{\min} can have different values at different sites. The present data suggest that there is a tendency for Pb to have the same C_{\min} at all the marine sites studied in the Northern Hemisphere. However, it should be noted that the C_{\min} for the present paper was read from the EF diagram, which may be considerably less accurate than the mathematical approach adopted by Adams et al. (1980) when attempting to reveal small differences between individual sites. None-the-less, the present data indicate that there is a C_{\min} for Pb which is the same for all the Northern Hemisphere samples investigated. The existence of this minimum background Pb concentration offers an explanation for the patterns in the latitudinal distribution of EF 's found by a number of workers. For example, Lantzy and Mackenzie (1979) reported that EF 's for many trace metals are larger at high than at low latitudes. For the Atlantic aerosol this can be explained in terms of the presence of a C_{\min} which is reasonably constant at all latitudes if the concentration of the material with which it is mixed varies. A large part of this latter material is composed of crustal solids and these are generated at a much greater rate at low than at high latitudes. This can be illustrated with reference to the crustal indicator element Al. For example, the average atmospheric concentrations of Al in the Atlantic north-east trades ($\gtrsim 10^3 \text{ ng m}^{-3}$ of air) are at least an order of magnitude higher than those in the North Atlantic westerlies ($\lesssim 10^2 \text{ ng m}^{-3}$ of air), and if the concentration of non-crustal Pb remained constant this would result in higher EF 's at higher latitudes. In practice, of course, the non-crustal Pb concentrations do not remain constant since there are sources for the element which, although they may contribute to the C_{\min} , do not yield the same concentrations at all locations. One such source is that resulting from anthropogenic activity which, according to Adams et al. (1980), may affect both the large and the small-sized aerosols. Because of this, there will be a spread of values in the elemental EF diagrams which characterise a specific population. This is apparent from the Pb marine EF diagram (Fig. 2). In this figure, the marine mixing region is illustrated and is shown to extend over a range of EF 's for a particular atmospheric Al concentration, the EF 's lying between that for the C_{\min} and that for a higher concentration; thus the marine mixing region forms a band across the EF diagram. The extent to which this band extends vertically is discussed below.

In addition to the C_{\min} and the crustal component there are materials from other sources which contribute to the marine aerosol; one of these results from anthropogenic activity. The effect of this material on the form

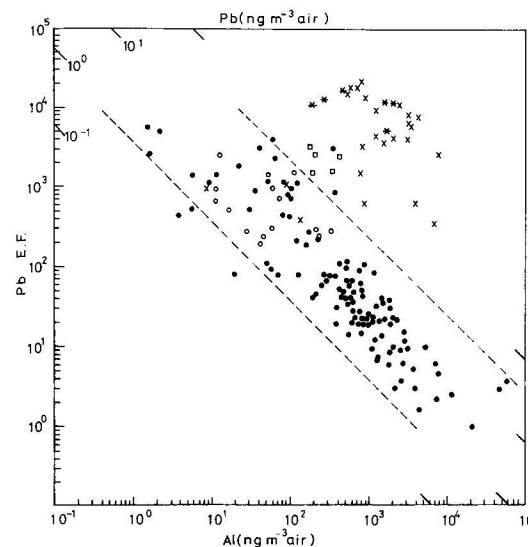


Fig. 5. Composite Pb enrichment factor diagram. Marine samples (present data, ●); samples collected at Jungfrau, Switzerland (Dams and De Jonge, 1976; ○); non-marine samples (Rahn, 1976; ×); polluted samples, Ghent, Belgium (Demynck et al., 1976; *); U.K. non-urban particulates (Cawse, 1978; □). Broken lines enclose the 'marine and remote European continental' field (see text).

of elemental EF diagrams was discussed by Chester et al. (1981), who suggested that these diagrams could be used to identify marine atmospheric particulates which have suffered 'local' pollution. This was based on data for a series of samples from the Eastern Mediterranean, but was only a prediction since none of these samples showed evidence of such 'local' pollution. However, when the various data points from the present survey are included in a composite Pb EF diagram (see Fig. 5), it can be seen that three of the marine samples plot to the right of the 'marine and remote European continental' field. It is suggested that these samples have suffered 'local' Pb pollution, i.e. they contain at least one other component in addition to those found in other marine aerosols. Further, it is significant that all three samples were collected from the North Atlantic westerlies close to the European coast, i.e. they are non-remote marine and tend to behave like non-remote continental samples. It is apparent, therefore, that this type of composite Pb EF diagram can be used to identify 'local' Pb pollution in specific aerosol populations. However, great caution must be used when applying this type of EF diagram on a global scale. One reason for this is that the left-hand side of the 'marine and remote European continental' region is defined by the C_{\min} , and according to Adams et al. (1980) this can vary from site to site. It may be, therefore, that any independently defined region in the EF diagram of enriched elements, such as the 'marine and remote European continental' field in the Pb diagram, is restricted to

individual, or to a number of inter-related specific, populations and may overlap with others on a global plot. For example, data are emerging from the SEAREX Programme to show that Pb concentrations in the North Pacific easterlies at Eniwetok are $\sim 0.2 \text{ ng m}^{-3}$ of air (Settle and Patterson, 1982) and are perhaps even an order of magnitude lower at Samoa (Patterson and Settle, 1982). It is apparent, therefore, that the Pb C_{\min} values vary from location to location, depending largely on how remote a particular site is from the major sources of Pb. For smaller C_{\min} values the hypotenuse of the triangular field of an enriched element EF diagram will be pushed further to the left, until a true C_{\min} is perhaps reached in very remote areas.

As a consequence of the lowering of the C_{\min} , the EF for any specific atmospheric Al concentration will decrease and as a result the enriched elements in truly remote aerosols may have relatively low enrichment factors. Eniwetok is a remote location in the North Pacific and it is to be expected that particle concentrations in the aerosol there will be considerably smaller than those in the Northern Hemisphere aerosols sampled in the present work, all of which were considerably closer to the land masses. However, even though the present collections spanned a variety of oceanic locations, it is apparent that for those in the Northern Hemisphere the distribution of Pb in the aerosols is controlled by a mixing/dilution relationship that is confined to a relatively broad concentration band, the lower limit of which appears to be constrained by a C_{\min} characteristic of some, but not all, of the aerosol populations. This is simply a result of the overall 'similarity' of some of the sampling regions, and the Pb C_{\min} is obviously considerably lower in the North and South Pacific aerosols. That is, there is probably a set of Pb C_{\min} gradations in the Marine Aerosol, extending from those close to urban Pb sources to those in truly remote locations. As a result, there should be an inverse linear relationship between the EF 's of the enriched elements and the atmospheric concentrations of Al at all sites. On EF diagrams this relationship will appear in the form of a field constrained to the left by the C_{\min} appropriate to that site. The vertical extent of the field at any specific atmospheric Al concentration will be dependent, among other factors, on the remoteness of the site. For sites relatively close to urban Pb sources, the right-hand side of the field will tend to merge with that for continental aerosols, as was the case for Pb in the North Atlantic westerlies sampled close to the European mainland. The more remote a site, the more the field will be separated from that occupied by the continental particulates; these remote fields may also have a much narrower vertical extent as a consequence of relatively small variations in elemental concentrations.

Although there is a strong tendency towards an overall Pb C_{\min} in the Northern Hemisphere aerosols studied here, both the C_{\min} and the average concentrations for the element in the individual populations vary greatly. The geometric average atmospheric Pb loadings for the various aerosol populations are given in Table I, from which it can be seen that in the Northern Hemisphere they range from 2.6 ng m^{-3} of air over the northern

TABLE I

Average atmospheric Pb concentrations over some oceanic regions (ng m^{-3} of air)

Oceanic region		Wind system	No. of samples	Range	Geometric average
Atlantic	North Atlantic	Westerlies (eastern margin)	12	2.6–203	15 ^a
		North east trades	17	1.3–38	4.3
	South Atlantic	South east trades	8	0.27–7.5	1.3
		Westerlies	5	0.44–1.4	0.98
Indian	Northern Arabian Sea	Variable	23	1.2–5.5	2.6
	Central Arabian Sea	Variable	9	2.6–7.2	4.2
Mediterranean Sea		Variable	21	1.7–25	8.3
Gulf of Aden		Variable	14	1.7–15	4.3
Red Sea		Variable	5	6.3–16	8.8

^a Non-polluted geometric average for North Atlantic westerlies is $\sim 7 \text{ ng Pb m}^{-3}$ of air (see text).

Arabian Sea to 15 ng m^{-3} of air in the eastern Atlantic westerlies. Differences such as these are important since they control the fluxes of Pb to the sea surface. However, there are inherent difficulties in calculating these fluxes. The input of atmospheric trace metals to the sea surface is controlled by their concentrations in the air and their deposition velocities. The total deposition velocity occurs by a combination of dry deposition and rain-out, and the magnitude of each of these will vary from one oceanic area to another.

The estimation of the input of atmospheric trace metals to sea and land surfaces has been discussed by various authors (see Chester, 1982), but there is no general agreement on the best method of calculating the resulting fluxes. For this reason, sea-surface fluxes for Pb given in the present paper have been calculated using two sets of deposition data in order to provide maximum and minimum estimates. A survey of the relevant literature showed that the atmospheric deposition rates applied to a Pb range from 0.25 cm s^{-1} (Cambray et al., 1975; dry deposition) to 1.0 cm s^{-1} (Buat-Menard and Chesselet, 1979; total deposition); the results of applying these two extremes to the calculation of Pb deposition fluxes to the sea surface using the present data are listed in Table II. The values in this table show that the deposition of Pb from the atmosphere to the sea surface varies by an order of magnitude in the Northern Hemisphere, being greatest in the westerlies over the eastern North Atlantic and smallest over the northern Arabian Sea. Data for the North Atlantic westerlies were obtained from aerosol samples collected from the eastern margins of the ocean, relatively close to the European mainland. The highest Pb concentration (203 ng m^{-3}

TABLE II

Estimated Pb fluxes in the sea surface over some oceanic regions ($\text{ng cm}^{-2} \text{ yr}^{-1}$)

Oceanic Region	Wind system	Pb fluxes ^a	
		Model 1	Model 2
North Atlantic	Westerlies (eastern margin)	220	56
	North east trades	140	35
South Atlantic	South east trades	40	10
	Westerlies	30	7.5
Northern Arabian Sea	Variable	80	20
Central Arabian Sea	Variable	130	32.5
Mediterranean Sea	Variable	260	65
Gulf of Aden	Variable	140	35
Red Sea	Variable	280	70

^a These are an estimate of the 'minimum' and 'maximum' fluxes; Model 1 is calculated on the basis of a Pb deposition velocity of 1.0 cm s^{-1} , and Model 2 on the basis of 0.25 cm^{-1} (see text).

of air) was found for a sample taken in the English Channel/North Sea and is similar to the concentrations reported for non-urban U.K. atmospheric particulates ($16\text{--}340 \text{ ng Pb kg}^{-1}$ of air; Cawse, 1978) and the yearly average on a North Sea gas platform ($120 \text{ ng Pb kg}^{-1}$ of air; Cambray et al., 1975). Clearly, the English Channel/North Sea aerosol is little different from those found in U.K. non-urban regions on the adjacent land mass, and cannot be considered relevant in the calculation of open-ocean deposition fluxes since it has obviously been affected by local Pb sources. It was shown above that samples which have suffered such local pollution can be tentatively identified from the appropriate Pb EF diagram, and the geometric average Pb concentration for the North Atlantic westerlies when such samples are excluded is $\sim 7 \text{ ng m}^{-3}$ of air and it is this value which has been used for the calculation of the Pb deposition fluxes (see Table II). From the limited data available it would appear that the atmospheric Pb flux from the South Atlantic westerlies is an order of magnitude smaller than that from their Northern Hemisphere counterparts. Atmospheric Pb patterns of this kind are consistent with the distribution of the element in the oceanic water column, which is strongly affected by the input of atmospheric Pb (see, e.g., Bruland, 1983).

Recently, Settle and Patterson (1982) used experimentally verified parameters for the calculation of the deposition flux of Pb to the sea surface. Using four different methods they estimated that the deposition of Pb to the sea surface from the North Atlantic westerlies lay in the range 55 to

$275 \text{ ng cm}^{-2} \text{ yr}^{-1}$, with an average of $170 \text{ ng cm}^{-2} \text{ yr}^{-1}$. For the North Atlantic westerlies at 23°N , 66°W , they reported a Pb concentration of 2.4 ng m^{-3} of air and calculated the deposition flux to be $55 \text{ ng cm}^{-1} \text{ yr}^{-1}$. The Pb deposition flux from the North Atlantic westerlies given in the present paper, i.e. $220 \text{ ng cm}^{-2} \text{ yr}^{-1}$ at a deposition velocity of 1 cm s^{-1} , was calculated using much less sophisticated parameters than those employed by Settle and Patterson (1982), but does not seem unreasonable for samples collected relatively close to land in the eastern Atlantic margins where the input of Pb from anthropogenic emissions would be expected to be relatively high.

From the present data the geometric average Pb concentration over marine regions in the Northern Hemisphere is 5.2 ng m^{-3} of air. However, this does not include aerosols from the North Pacific Ocean, which recent data have shown to have Pb concentrations an order of magnitude lower than this figure (see above) and so cannot be considered to apply to the whole Northern Hemisphere marine atmosphere. Nonetheless, the present data does permit the distribution of Pb over some specific oceanic regions to be assessed in terms of the global atmospheric Pb budget. This can be illustrated with respect to the North Atlantic.

According to Lantzy and Mackenzie (1979) the 'natural' emissions of Pb (i.e. those from the continental dust flux, the volcanic dust flux and the volcanic gas flux) to the global atmosphere total $\sim 59 \times 10^8 \text{ g yr}^{-1}$. The geometric average Pb concentration over the North Atlantic is 7 ng m^{-3} of air and the geometric average Al concentration is 750 ng m^{-3} of air. On the basis of the Pb/Al ratios in the particulates and in the average crustal material the concentration of 'crustal' Pb is $\sim 0.15 \text{ ng m}^{-3}$ of air. Assuming the maximum deposition velocity of 1 cm s^{-1} for the 'crustal' Pb from a 5000 m high column of air which has a volume of $\sim 0.15 \times 10^{18} \text{ m}^{-3}$ over the North Atlantic between the equator and $\sim 60^\circ\text{N}$, the amount of 'crustal' Pb over the North Atlantic is $\sim 14 \times 10^8 \text{ g yr}^{-1}$. That is, using the maximum estimate $\sim 24\%$ of the total 'natural' Pb injected annually into the world atmosphere falls out over the North Atlantic sea surface.

Lantzy and Mackenzie (1979) also estimated that the anthropogenic Pb emissions (i.e. those from industrial activity and the burning of fossil fuel) into the world atmosphere total $\sim 20\,300 \times 10^8 \text{ g yr}^{-1}$. According to Robinson and Robbins (1971) this anthropogenic material is distributed 90% to the Northern Hemisphere and 10% to the Southern Hemisphere, which would result in the injection of $\sim 18\,270 \times 10^8 \text{ g Pb yr}^{-1}$ into the atmosphere of the Northern Hemisphere. The geometric average 'non-crustal' Pb over the North Atlantic is $\sim 6.85 \text{ ng m}^{-3}$ of air, and using the parameters given above this leads to $\sim 627 \times 10^8 \text{ g 'non-crustal' Pb yr}^{-1}$ in the North Atlantic marine atmosphere. That is, using the maximum estimate $\sim 3.5\%$ of the total anthropogenic Pb injected annually into the atmosphere of the Northern Hemisphere is deposited over the North Atlantic sea surface.

CONCLUSIONS

The conclusions which can be drawn from the present study may be summarised as follows.

(1) Over the marine regions studied of both the Northern and Southern Hemispheres the distribution of particulate Pb in the atmosphere is controlled by the mixing of a background component, or components, with crustal material. Over most of the regions studied the relationship between Pb and Al (the crustal indicator element) is an inverse linear one, and the samples plot within a restricted region in the Pb *EF* diagram.

(2) Although most marine atmospheric samples plot within the restricted region on the Pb *EF* diagram, this region is not confined to marine samples alone, but rather includes samples from any 'remote' area in which the aerosol composition is controlled by the mixing of background component(s) which have a similar C_{\min} and crustal material. This is illustrated by the inclusion in the Pb *EF* diagram of a data set from a remote European location which plots within the 'marine' region. It is apparent, therefore, that there is not a specific 'marine region' within the Pb *EF* diagram.

(3) An important feature of the Pb *EF* diagram is that over the Northern Hemisphere marine regions studied there is a minimum concentration of Pb, which is $\sim 0.6 \text{ ng m}^{-3}$ of air. The existence of this minimum concentration is reflected in the fact that the *EF*'s for Pb are greater at higher than at lower latitudes, since the dilution with crustal material is much less at the lower latitudes.

(4) The Pb *EF* factor diagram can be used to identify 'local' pollution over the marine areas studied. Of the 111 atmospheric samples which form the data base for the present study, only three fall to the right-hand side of the 'marine and remote European' region on the *EF* diagram. These three samples, all of which are from the North Atlantic westerlies off the European mainland, have Pb *EF*'s which are relatively high for their respective Al concentrations; it is suggested that the 'excess' Pb is a result of local pollution.

(5) Geometric average atmospheric Pb concentrations have been calculated for a number of marine regions. In the Northern Hemisphere these range from 2.6 ng m^{-3} of air over the Arabian Sea to 15 ng m^{-3} of air in the Atlantic westerlies off Europe. Average atmospheric Pb concentrations in the Southern Hemisphere appear, from the limited data collected, to be considerably lower than those over northern regions; for example, the North Atlantic westerlies have an order of magnitude more Pb than their South Atlantic counterparts.

(6) Pb sea-surface deposition fluxes have been calculated on the basis of two extreme deposition velocities (0.25 and 1.0 cm s^{-1}) and these range from between 56 and $220 \text{ ng cm}^{-2} \text{ yr}^{-1}$ for the North Atlantic westerlies to between 7.5 and $30 \text{ ng cm}^{-2} \text{ yr}^{-1}$ for the South Atlantic westerlies, for the two deposition velocities, respectively.

(7) The distribution of Pb over the North Atlantic has been assessed in terms of the global atmospheric Pb budget. It was estimated that a maximum of $\sim 24\%$ of the total 'natural' Pb injected annually into the world atmosphere, and $\sim 3.5\%$ of the anthropogenic Pb injected annually into the Northern Hemisphere, are deposited over the North Atlantic sea surface.

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Short Note

ABSTRACT

The correct values of the Huckel equation

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