Aerosol
Molybdenum
Source for aerosol
Enrichment factor
Atlantic Ocean

Aérosol
Molybdène
Source d'aérosol
Facteur d'enrichissement
Océan Atlantique

The distribution of particulate Mo in the Atlantic aerosol

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ABSTRACT

The distribution of Mo has been determined in the Atlantic aerosol. Samples collected on a north-south transect show that the concentrations of Mo exhibit a well-defined latitudinal dependence; ranging from a maximum of ~ 10 ng m^{-3} of air close to the UK coast to ~ 10 pg m^{-3} of air in the open-ocean South Atlantic westerlies. Average Mo EF$_{crust}$ values are > 50 for most of the Atlantic aerosol but fall to an average of ~ 5 in samples from the north east trades, and the distribution of the element can be described in terms of the dilution of Mo-rich background" phases with Mo-poor crustal material. Mo EF$_{sea}$ values range from ~ 0.5 to ~ 900; the highest average being found in the UK coastal aerosol (116), and the lowest in samples from the South Atlantic westerlies (1.4). There is a tendency in the Atlantic aerosol towards a minimum Mo EF$_{sea}$ value of ~ 1.0, thus leading to the conclusion that the bulk sea water Mo concentration is the constraining factor on Mo: Na ratios in some sea-salt generated particles; however, sea-salts are only a significant source for Mo in a relatively small number of samples. The global oceanic Mo source strength is estimated to be in the range ≈ 3.6 to $\approx 36 \times 10^8$ g.yr^{-1}, which is similar to the crustal source strength ($\approx 10 \times 10^8$ g.yr^{-1}). Natural low temperature generated particles are important contributors to Mo in the Atlantic aerosol in some regions, together accounting for $\sim 47\%$ of the total Mo in the north east trades and $\sim 62\%$ in the South Atlantic westerlies. In other Atlantic aerosol populations, however, the excess" Mo (*i.e.*that not accounted for by crustal and oceanic sources) is dominant, and has its highest concentrations in the North Atlantic relatively close to anthropogenic sources. It is concluded that pollutant emissions are the principal control on the distribution of the excess" Mo in the Atlantic aerosol, and that the oceans act as a sink for atmospheric Mo.

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RÉSUMÉ

Répartition du molybdène particulaire dans l'aérosol atlantique

La répartition du molybdène a été déterminée dans l'aérosol atlantique. Les échantillons prélevés sur une section nord-sud mettent en évidence une relation entre les concentrations et la latitude, les valeurs mesurées allant d'un maximum voisin de 1 ng.m^{-3} d'air vers la côte des États-Unis, à environ 10 pg.m^{-3} d'air dans les vents d'ouest de l'Atlantique Sud. Les valeurs moyennes du facteur d'enrichissement des particules par rapport à une référence crustale dépassent 50 pour l'aérosol atlantique, et descendent à 5 dans les alizés du nord-est; les concentrations en Mo observées peuvent être expliquées par un effet de dilution dû à une composante crustale pauvre en Mo. Les valeurs du facteur d'enrichissement des particules par rapport à l'eau de mer vont de 0,5 à 900, la plus forte moyenne étant trouvée vers la côte des États-Unis, et la plus faible dans les vents d'ouest de l'Atlantique Sud. L'aérosol atlantique a un facteur d'enrichissement minimal par rapport à l'eau de mer d'environ 1,0, indiquant que la concentration globale de Mo dans l'eau de mer est le facteur limitant pour les rapports Mo/Na dans les particules provenant du sel marin; cependant les sels marins ne sont une source notable de Mo que dans un petit nombre d'échantillons. L'intensité globale de la source océanique de Mo est estimée entre 3,6 et 36 × 10^8 g.an^{-1}, du même ordre que celle de la source crustale (10 × 10^8 g.an^{-1}). Les particules naturelles

formées à basse température jouent un rôle important pour le Mo dans l'aérosol atlantique de certaines régions, représentant environ 47% du Mo total dans les alizés du nord-est et environ 62% dans les vents d'ouest de l'Atlantique Sud. Dans d'autres populations d'aérosols atlantiques, le Mo en excès (c'est-à-dire ni crustal ni océanique) est dominant, avec sa plus forte concentration dans l'Atlantique Nord, à proximité des sources anthropogéniques. En conclusion, les émissions de polluants constituent le principal contrôle de la répartition du Mo en excès dans l'aérosol atlantique, et les océans constituent un puits du Mo atmosphérique.

INTRODUCTION

For some elements in the world aerosol the combined source strengths from both natural and anthropogenic volatilization (*i.e.* high temperature) processes exceed those from low temperature processes by a large factor; *e.g.* for As, this factor is ~120 (Walsh *et al.*, 1979). Under certain conditions, however, low temperature particle generation can yield significant amounts of material to the atmosphere and when this occurs its magnitude must be assessed for the estimation of elemental budgets. This is especially important in relation to the marine atmosphere, for which the sea surface itself can act as a particle source.

Crustal weathering and sea-salt production are two of the major natural processes for the direct, low temperature, generation of atmospheric particulate material from the earth's surface to the marine aerosol. However, the supply of crustal material to the marine atmosphere differs significantly from that of sea-salt production in one important respect. That is, the generation of crustal material depends mainly on geological and weathering conditions on the surrounding land masses and, as such, it is latitudinally dependent. In contrast, although the magnitude of sea-salt production is controlled to a large extent by local sea state conditions, the sea surface is a potential particle reservoir at all latitudes. In general, therefore the importance of oceanic, relative to crustal, particle sources should increase in those marine areas which are more remote from the major continental supply regions. However, this effect may be difficult to identify for some trace metals since their surface water distributions, and potentially therefore their sea-salt concentrations, can vary from one marine area to another, thus necessitating a detailed knowledge of their local concentrations.

From this point of view, Mo is unique among the trace metals in sea water since, according to Bruland (1983), it has a conservative distribution in the oceans; *i.e.* it shows a constant concentration relative to salinity as a result of its low reactivity in sea water. Because of this conservative behaviour it is of interest to assess the effect of sea-salt generation on the distribution of Mo in the marine aerosol and to compare its magnitude to that arising from crustal weathering, the other major low temperature particle source. However, little is known about either the concentration, or the distribution, of Mo in the marine aerosol and in order to acquire a basic data set the element was determined in a series of 52 aerosols collected on an Atlantic Ocean

transect from ~55°N to ~65°S. In many ways such an Atlantic transect is ideal" for the study of variations in the concentrations of major aerosol components since it passes through a number of particle catchment regions and a variety of wind systems. In the present transect these included: UK coastal waters and the North Atlantic westerlies, with catchments in the Northern European pollution belt"; the north east trades, with catchments in the North African desert belt; and the South Atlantic westerlies, which were sampled in open-ocean areas relatively remote from the land masses. On the basis of samples collected on this transect the distribution of Mo in the Atlantic aerosol is described, and is related to crustal and sea-salt sources in the contrasting catchment regions.

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 sample locations are illustrated in Figure 1.

Particulate samples were taken using a high volume filter system which incorporated Whatman 41 filters (165 mm exposed diameter). The system was based on a heavy duty centrifugal pump connected to two clear 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. The filter rig was mounted ~6 m beyond the bows of the ship, and air flow rates (typically, 2 m^3 min^{-1}) were measured using an orifice-type flow meter. The filters, two of which were exposed during each collection, were sealed in plastic bags before and after exposure. None of the data reported in the present investigation were obtained under sampling conditions in which following winds occurred.

In the analytical procedure all sample handling was carried out in a clean-air cabinet and the filters were dissolved in redistilled HNO$_3$ and Aristar HF in PTFE beakers. The digests were stored in polystyrene vials. A number of blank filters were taken through the shipboard handling procedures, without actual exposure to the atmosphere in the rig, and blanks from the same batch as those used for the collections were run through the analytical techniques. After appropriate correction was made for filter blanks (signal to blank ratio was typically >10:1), the elemental concentrations for each individual collection were calculated as

Figure 1

Aerosol sample locations on the Atlantic transect. The start and finish of each collection period is indicated by the perpendicular lines.
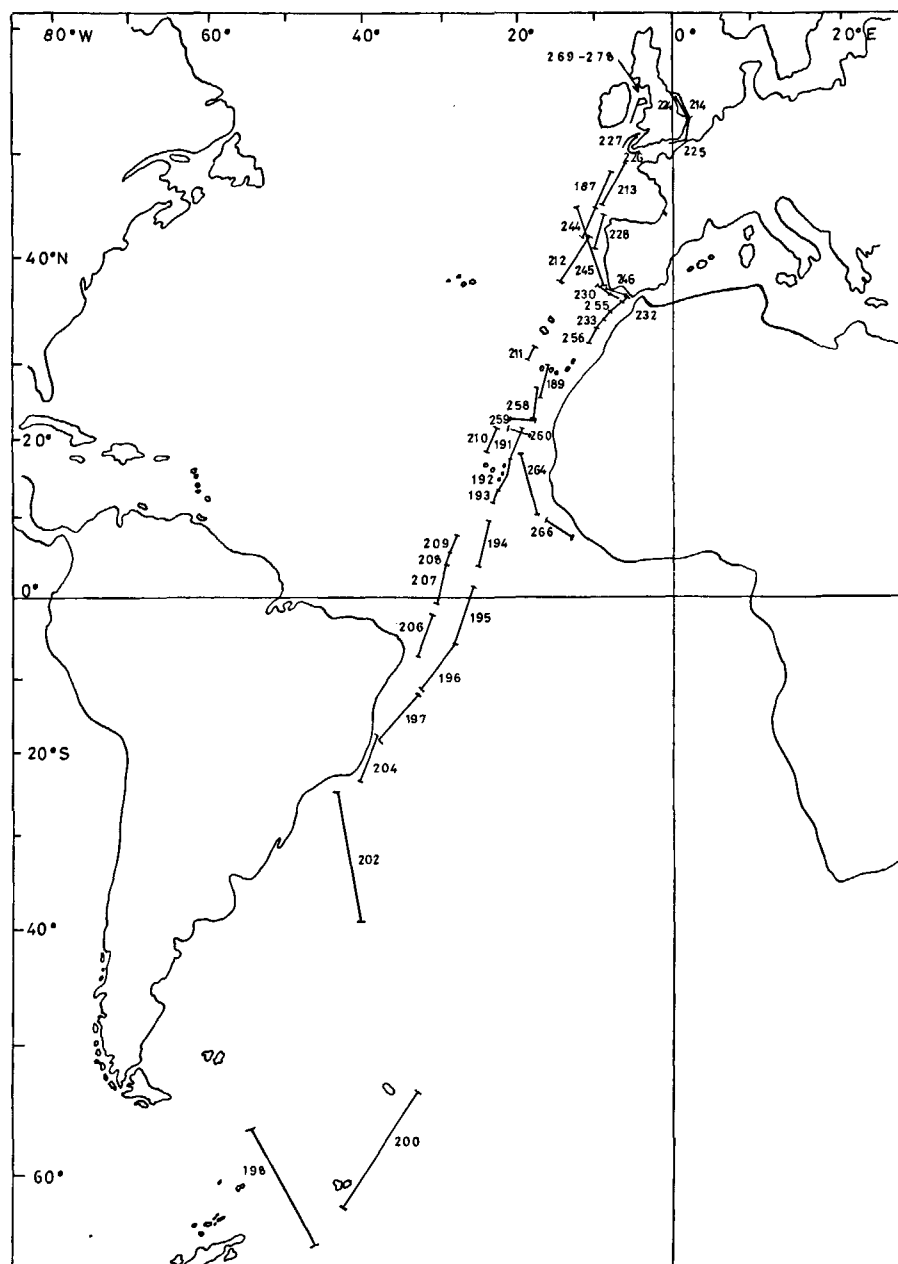
the means of the two exposed filters; average agreement between Mo concentrations for filter pairs was 11% for the data set. Mo was determined by an atomic absorption technique using graphite furnace atomization; Al was determined by an atomic absorption technique employing the flame mode; Na was determined by flame photometry. Replicate determinations on sub-samples of a mesh-collected atmospheric particulate, for which sufficient sample was available, showed that the analytical techniques had coefficients of variation of 3.4% for Mo, 2.4% for Al and 3.6% for Na.

RESULTS AND DISCUSSION

Concentrations of Mo in the Atlantic aerosol

The concentrations of Mo in the Atlantic aerosol samples studied range between 9 pg and 1 ng m^{-3} of air,

and there are well-defined latitudinal variations within the overall distribution pattern. In Table 1, the Mo concentration data, together with those for Al and Na, are arranged in terms of a number of arbitary collection regions, and it is apparent that the highest concentrations of Mo are found in the UK coastal aerosol and the lowest in samples from the South Atlantic westerlies. Although the authors were unable to find any data in the literature for the concentration of Mo over marine areas, Rahn (1976) has compiled a data set for urban samples, and from this it appears that Mo concentrations in urban aerosols are in the range ~2 to ~20 ng m^{-3} of air; and at a remote European site (The Jungfraujoch, Switzerland) Mo had a range of <0.1 to 0.8 ng m^{-3} of air, with an average of 0.3 ng m^{-3} of air (Dams, De Jonge, 1976). From this sparse data it is apparent that Mo concentrations in the UK coastal aerosol (range; 0.08 to 1.0 ng m^{-3} of air) are lower than those found for the urban environment. However, the average concentration for the UK

Table 1
Concentration of Mo, Al and Na in the Atlantic aerosol.

Oceanic region	Aerosol sample	Mo (pg m^{-3} of air)	Al (ng m^{-3} of air)	Na
North Atlantic;	214	136	132	19 375
UK coastal waters,	224	1 000	575	1 209
winds variable	225	444	438	1 343
	226	134	445	3 585
	227	249	162	3 546
	269	383	596	628
	270	338	475	883
	271	92	217	1 166
	272	177	360	632
	273	181	196	206
	274	199	472	2 583
	275	138	158	3 992
	276	78	33	2 257
	277	122	53	1 572
	278	199	82	3 465
Geometric average;		203	217	1 746
North Atlantic;	187	172	59	2 321
Eastern margin,	188	130	37	834
westerlies	211*	93	159	7 925
	212	47	30	6 520
	213	51	34	3 349
	228	31	21	28 573
	244	47	37	5 831
	245	50	96	1 577
	256	48	46	3 977
Geometric average		64	47	4 130
North Atlantic;	189	304	743	28 390
eastern margin,	230	128	508	2 847
Straits of Gibraltar	231	352	1 881	5 223
	232	207	723	12 718
	246	467	1 458	1 972
	255	75	760	798
Geometric average;		215	910	4 517
North Atlantic;	191	118	1 062	7 615
eastern margin,	192	141	4 353	10 124
north east trades	193	154	6 345	2 951
	207	90	3 079	4 003
	208	685	45 439	8 886
	209	1 200	57 730	63 838
	210	58	58	2 433
	233	160	418	87 420
	258	104	288	6 104
	259	73	367	4 015
	260	93	254	8 914
	264	21	67	10 002
	266	39	1 083	4 240
Geometric average;		119	1 204	8 385
South Atlantic;	194	80	49	2 951
south east trades	195	124	63	3 079
	196	154	20	3 709
	197*	16	4	12 937
	204*	44	13	25 639
	206	32	499	2 521
Geometric average;		57	34	5 517
South Atlantic;	198*	23	1.5	11 798
westerlies	200	10	2.2	22 339
	202	9	5.4	3 075
Geometric average;		13	2.6	9 323

* Values based on single filter collection.

coastal waters (0.2 ng m^{-3} of air) is similar to the value of 0.38 ng m^{-3} of air reported by Hamilton (1974) at Sutton (UK), an aerosol which Rahn (1976) classified as being semi-marine" in character; the similarity is to be expected because the UK coastal aerosol will have been strongly influenced by continental sources.

Variations in the concentrations of Mo in the Atlantic aerosol are extremely important because they control the atmospheric fluxes of the element to the sea surface. However, absolute atmospheric concentrations themselves yield little information on the sources of an element in an aerosol population. Because the total particulate trace metal concentrations in aerosols vary over such relatively large ranges, both spatially and temporally, many authors have used an enrichment factor (EF), rather than an absolute concentration, in an attempt to identify potential elemental sources. In order to assess the enrichments of an element relative to crustal and marine sources the excess" fraction is defined with respect to the equations:

$$EF_{crust} = (E/Al)_{air}/(E/Al)_{crust}, \text{ and}$$
$$EF_{sea} = (E/Na)_{air}/(E/Na)_{sea\ water};$$

in which $(E/Al)_{air}$ and $(E/Na)_{air}$ are the concentrations of an element, and either Al or Na, in the aerosol, and $(E/Al)_{crust}$ and $(E/Na)_{sea\ water}$ are their concentrations in average crustal material and bulk sea water, respectively. In this approach, Al is employed as a crustal indicator element, and Na as a sea water indicator element. EF values close to unity are taken as an indication that an element has a mainly crustal, or oceanic source, and those >10 are considered to indicate that a substantial portion of the element has a non-crustal, or a non-oceanic, origin.

Variations in the distribution of Al and Na in the Atlantic aerosol

In order to fully understand variations in the Mo crustal and oceanic EFs it is necessary to identify any trends in the distributions of the indicator elements themselves.

The Atlantic aerosol provides a classical example of the factors which control the distribution of crustal material over the oceans. The concentrations of Al, the crustal material indicator element, in the Atlantic aerosol are extremely latitudinally dependent and clearly reflect variations in the supply of crustal material from the surrounding land masses. That is, the highest concentrations are found at low latitudes in the north east trades off West Africa, and the lowest in the remote South Atlantic westerlies (*see* also: Krishnaswami, Sarin, 1976; Chester, 1982).

Al concentrations in the UK coastal and North Atlantic westerlies aerosols range between 21 and 575 ng m^{-3} of air, with the highest values being found close to the UK mainland where the continental influence is the strongest. Few data are available in the literature for atmospheric Al concentrations over this region of the Atlantic, but the value of 155 ng m^{-3} of air reported for a gas platform in the North Sea (Cambray *et al.*, 1975) is within the range found in the present work. The atmospheric concentrations of Al increase around the Straits of Gibraltar (range; 508 to 1 881 ng Al m^{-3} of air) where the North African deserts begin to influence the aerosol, and reach their maximum values in the north east trades off West

Africa. Al concentrations in these winds are extremely variable (range; 58 to 57, 730 ng m^{-3} of air. Such variability is not unexpected in the north east trades aerosol collected relatively close to West Africa where sporadic dust storm outbreaks can occur. For example, mineral aerosol concentrations at Sal Island, off the coast of West Africa, during Saharan air out-breaks varied over the range $\gtrsim$10 to $\gtrsim$180 µg m^{-3} of air during July, August and September, 1974 (Savoie, Propero, 1977). Hoffman *et al.* (1974) gave data on the concentrations of Fe on a transect from Dakar to Bermuda and by assuming an Al/Fe ratio of 1.6 for aerosols in this region (Buat-Menard, Chesselet, 1979) the equivalent Al concentrations for samples from the coast to ~25°W are ≈60,000 to $\gtrsim$100 ng Al M^{-3} of air; these are in the same range as those found for the present investigation. Few data are available for the concentration of Al in the south east trades of the Atlantic. Prospero (1979) reported an average of 0.69 µg m^{-3} of air for the mineral aerosol over the tropical and central South Atlantic, which is equivalent to ~58 ng Al m^{-3} of air. Six samples in the present study are placed in the general south east trade system on the basis of prevailing winds. However, only two of these (samples 194 and 195) are open-ocean samples and they have an average Al concentration of 56 ng m^{-3} of air, which is similar to the estimated from Prospero's data. The three samples collected in the South Atlantic westerlies have an average 3.1 ng Al m^{-3} of air, and the range of concentrations (1.5 to 5.4 ng m^{-3} of air) is extremely low for the marine aerosol. Duce *et al.* (1983) reported a range of Al concentrations in the marine aerosol at Enewetak in the North Pacific of 1.3 to 150 ng m^{-3} of air, and concentrations as low as 8 ng m^{-3} of air have been found over the Atlantic north of 30°N (Duce *et al.*, 1975). Preliminary results from SEAREX suggest that Al concentrations during both the dry and wet season at Samoa, a remote site in the South Pacific, are $\gtrsim$1.0 ng m^{-3} of air (Duce *et al.*, 1982). Clearly, therefore, Al concentrations in the range $\gtrsim$1.0 to 10 ng m^{-3} of air are found over some marine regions, and the average for the South Atlantic westerlies (3.1 ng m^{-3} of air) is a factor of ~3.8 higher than the average found further south at the South Pole (0.82 ng m^{-3} of air; Maenhaut *et al.*, 1979). None-the-less, from the very limited number of samples available, the atmospheric Al concentrations given in the present work cannot be regarded as being typical for the South Atlantic westerlies; they are however useful in so far as they provide data which may be compared to that from other regions of the Atlantic which have a much higher input of crustal solids.

For a number of regions in the Atlantic Ocean lying between ~60°N and ~35°S, Prospero (1979) reported arithmetic average sea-salt concentrations of between 6.71 and 11.3 µg m^{-3} of air, and at a Na concentration of 36% these are equivalent to a range of Na concentrations of ~2400 to ~4000 ng m^{-3} of air. However, the concentration of Na in the marine aerosol is extremely variable, depending among other factors on wind speed, and for the same data set individual samples range from ~100 to ~17000 ng Na m^{-3} of air; the highest values being found in the middle and high latitudes of the South Atlantic as a consequence of the strong wind regimes (Prospero, 1979). Other evidence for the variability of sea-salt concentrations has been provided by Buat-Menard *et al.* (1974). These authors measured the sea-salt associated Na over the tropical and equatorial Atlantic and found a range of 590 to 58,800 ng Na m^{-3} of air; however, concentrations 10^4 ng Na m^{-3} of air were rare, and were only recorded in winds which ranged up to, or were greater than, ~15 m sec^{-1}. It is apparent, therefore, that although they are relatively rare, concentrations of $\gtrsim 10^4$ ng Na m^{-3} of air can be found in the marine aerosol at high wind speeds. The highest concentration found in the present investigation was 87,400 ng Na m^{-3} of air; this is an extremely high value and although there was no evidence to confirm it, bow spray contamination of this sample must be suspected. If this sample is excluded, the range of Na concentrations is 206 to 63,839 ng m^{-3} of air, which is close to that reported by Buat-Menard *et al.* (1974), and it should be noted that the present values include Na from crustal, in addition to marine sources.

It may be concluded, therefore, that the concentrations of both Al and Na vary widely in the marine aerosol. These variations are reflected in the samples collected on the north-south Atlantic transect which may therefore be regarded as a representative sample of the marine aerosol since it includes order of magnitude variations in the inputs of both crust-derived and ocean-derived components.

Crustal sources for Mo in the Atlantic aerosol

Average EF$_{crust}$ values for Mo in aerosols from the various regions of the Atlantic are given in Table 2. The average Mo EF$_{crust}$ values vary considerably, but for most of the populations they are $\gtrsim$50; *i.e.* crustal material is not the principal source of Mo for most of the Atlantic aerosol. However, the Mo EF$_{crust}$ values fall considerably in samples from the Straits of Gibraltar (average; 13) and the north east trades (average; 5.4). In the aerosol from the north east trades there is a large range of Mo EF$_{crust}$ values, but for some samples they approach unity. It is apparent, therefore, that under certain conditions crustal material can become the dominant source of Mo in the aerosol, and because most atmospheric particulates over marine areas contain at least some crustal solids this material may be considered to act as a diluent on non-crustal Mo-containing components. It was shown above that the

Table 2
Average Mo EF$_{crust}$ values for Atlantic aerosol populations.

Aerosol population	Geometric average Mo EF$_{crust}$
UK coastal	51
North Atlantic westerlies	74
Straits of Gibraltar	13
North east trades	5.4
South east trades	93
South Atlantic westerlies	~270

concentration of Al, the crustal indicator element, varies considerably in the Atlantic aerosol, and in an attempt to assess its dilution effect on other atmospheric components on an ocean-wide basis it may be treated as an end-member" in a two component (*i.e.* crustal and non-crustal) model. For this purpose, the Mo data for the whole Atlantic aerosol is presented in the form of an enrichment factor diagram in Figure 2. Rahn (1976) developed the concept of such diagrams, in which the relationship between the EF_{crust} values of an element and the atmospheric concentrations of Al is expressed graphically on a logarithmic basis. This approach has the advantage over the use of EFs alone, since the EFs themselves are related directly to the actual amounts of crustal material (Al) present in the aerosol. This is particularly important in assessing the effects of crustal material on an aerosol population such as that of the whole Atlantic, in which there are large variations in the amount of crustal solids present. On an EF diagram lines of constant concentration appear inclined at 45° counterwise from the vertical (Rahn *et al.*, 1979).
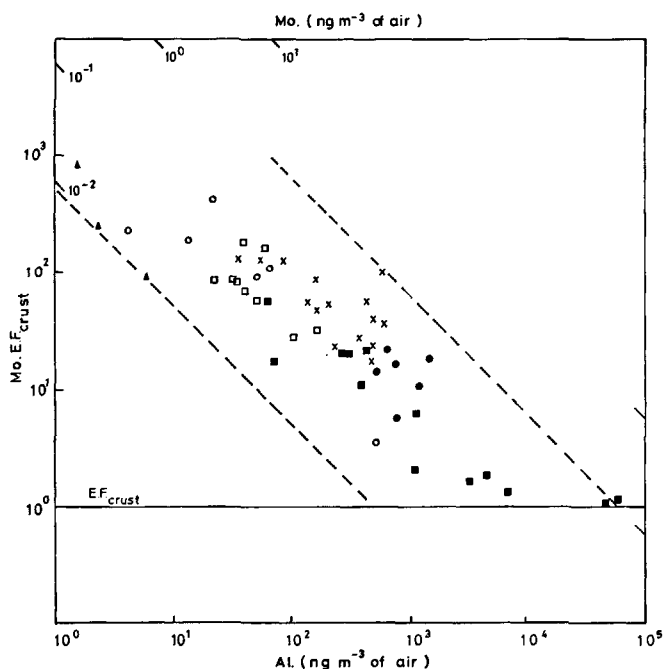

Figure 2

Mo EF$_{crust}$ diagram for the Atlantic aerosol. UK coastal (×), North Atlantic westerlies (□), Straits of Gibraltar (●), north east trades (■), south east trades (○), South Atlantic westerlies (▲). The 45° broken lines enclose the field in which the distribution of Mo is generally controlled by the dilution of Mo-rich background" phases with Mo-poor crustal material.

It can be seen from the EF diagram that in the Atlantic aerosol Mo behaves in an enriched manner; *i.e.* the EF_{crust} values increase as the atmospheric concentrations of Al decrease. Further, the relationship between the Mo EF_{crust} values and atmospheric Al follows a general inverse linear trend, and one of the most important conclusions that can be drawn from the present data is that as a consequence of this trend there is a reasonably well-defined field for Mo in the Atlantic

aerosol. The field is constrained by apparent minimum and maximum concentration lines.

Crustal material is a ubiquitous component of the marine atmosphere and the use of an EF diagram to interpret the Mo data reveals that for the Atlantic aerosol the distribution of the element can be described in terms of the mixing of this crustal material with non-crustal components within a limited field. The non-enriched crustal material dilutes the Mo-enriched non-crustal components with the result that the Mo EF_{crust} values are progressively lowered as the proportion of crustal material increases. However, it is only in the north east trades that there are sufficient quantities of crustal solids present to dominate the atmospheric population. For these aerosols, the mixing/dilution relationship between crustal and non-crustal components, which for most of the Atlantic aerosol results in an inverse linear trend on the EF diagram, is perturbed and the Mo field is extended horizontally to the right.

Oceanic sources for Mo in the Atlantic aerosol

Over many marine areas the concentrations of sea-salt particles in the atmosphere exceed those having a crustal origin by a factor of at least two; however, an exception to this is found in the Atlantic north east trades, in which crustal material can be present at higher concentrations in the aerosol than are sea-salts (Prospero, 1979). According to Berg and Winchester (1978) the bursting of bubbles produced by the trapping of air in surface waters by breaking waves, and sea spray arising from the direct shearing of droplets from wave crests, are the main processes involved in the formation of sea-salt. Buat-Menard (1983) has pointed out that the source region for sea surface generated aerosols is a very thin layer at the air/sea interface, *i.e.* the oceanic micro-layer, together with dissolved and particulate material scavenged by rising bubbles. There is now considerable evidence that the chemistry of this micro-layer is very different from the sea water immediately beneath it, and that in particular a number of trace metals are enhanced in the layer relative to bulk sea water (*see e.g.*; Hunter, 1980). For these metals, therefore, bulk sea water itself will not be the constraining factor on the composition of the sea surface-generated particles. Elements which are known to be concentrated in the micro-layer include Cu, Pb and Zn (Szekielda *et al.*, 1972), and recent data reported by Duce *et al.* (1983) showed that in the marine aerosol collected at Enewetak, a site in the tropical North Pacific, the average EF_{sea} values for these elements were: Cu, 2.7×10^3; Pb, 26×10^3; Zn, $\sim 100 \times 10^3$. However, these sea water enrichments do not, in themselves, of course mean that the elements have been fractionated at the air/sea interface.

Mo is the most abundant transition metal in sea water, with a concentration of ~ 10.6 µg l^{-1} (Bruland, 1983), and since it is a conservative element it can be assumed that over most oceanic regions there are only relatively small variations in its sea water concentrations (*see e.g.*: Sugawara, Okabe, 1966; Head, Burton, 1970; Morris, 1975). The bulk sea water concentration of 10.6 µg l^{-1}

Table 3

Average Mo EF$_{sea}$ values for Atlantic aerosol populations.

Aerosol population	Geometric average Mo EF$_{sea}$
UK coastal	116
North Atlantic westerlies	20
Straits of Gibraltar	63
North east trades	13
South east trades	9.5
South Atlantic westerlies	∼ 1.4

was therefore used in the calculation of Mo EF$_{sea}$ values in an initial attempt to estimate the magnitude of the oceanic source for this element in the Atlantic aerosol. For all the data there is a large range of Mo EF$_{sea}$ values, from ∼0.5 to ∼900, but a general pattern emerges when they are considered in terms of the individual collection regions. In Table 3, geometric average Mo EF$_{sea}$ values are listed for the various wind systems, and it is apparent that the highest values are found for the UK coastal samples and those collected around the Straits of Gibraltar. The lowest Mo EF$_{sea}$ values are those for the 3 samples from the South Atlantic westerlies, which average, ∼1.4. To elucidate the factors controlling the relationship between Mo and Na in the aerosol the data is presented in Figure 3 in the form of an element v element plot in which the crustal components of both Mo and Na have been subtracted. Mo EF values of 1 and 10 are superimposed onto the figure as 45° lines. An interesting trend emerges when the data is displayed in this manner, and it is apparent that when correction is made for crustal components there is a tendency towards a minimum Mo EF$_{sea}$ value in the Atlantic aerosol. This minimum Mo EF$_{sea}$ is ≈1.0 and leads to the conclusion that at the low end of the Mo concentration range bulk sea water can be the constraining factor on the aerosol EF$_{sea}$ values. In this respect, Mo differs from most trace metals in the marine atmosphere (*see e.g.;* Duce *et al.*, 1983). The minimum Mo Ef$_{sea}$ value is only found for a few samples and most of the aerosols (75%) have Mo EF$_{sea}$ values ≳10, which is probably the result of the presence of Mo from other, *i.e.* non-oceanic, sources. For example, the highest Mo EF$_{sea}$ values are found in UK coastal aerosols, which are closest of any of the samples studied to major pollutant emissions. The generation of sea-salts via the micro-layer is an extremely complex process and involves both dissolved and particulate material. It may well be that atmospherically-deposited Mo-rich particulates, possibly of a pollutant origin, may be resuspended into the aerosol. However, it is apparent from Figure 3 that aerosol samples having Mo EF$_{sea}$ values in the range ∼1.0 to ∼10 are found in a variety of marine locations. The Na concentrations for most of these samples are ≳10^4 ng m^{-3} of air, which are relatively high for most oceanic aerosols, and the presence of bow spray in the filters cannot be fully discounted. However, for other trace metals even these relatively large injections of sea-salts into the atmosphere do not result in aerosol EF$_{sea}$ values which approach unity with respect to bulk sea water. For example, in the sample set which has Mo EF$_{sea}$ values in the range ∼1.0 to ∼10, the mini-

mum EF$_{sea}$ value for Cu was ∼800, for Pb ∼6 000 and for Zn ∼1 700 (Chester *et al.*, 1984). On the basis of the present data it is suggested, therefore, that the injection of relatively large amounts of sea-salts into the marine atmosphere can result in the total aerosols having correspondingly low Mo EF$_{sea}$ values when other sources do not predominate; a situation which is analogous to that resulting from the injection of large amounts of crustal material, which leads to the aerosols having low Mo EF$_{crust}$ values—*see* above.

From the treatment presented above it is apparent that on the evidence of Mo EF$_{sea}$ values, sea-salts generated from the ocean surface can be a major source for Mo in some samples of the Atlantic aerosol. However, this happens only rarely, and does not imply that the sea is a significant source for Mo in most aerosol samples; but simply that EF$_{sea}$ values ≳10 can be found under some conditions. The injection of sea-salts into the atmosphere depends largely on meteorological conditions but does not have the same well-defined latitudinal distribution that controls the concentration of crustal material in the marine aerosol.

Global crustal and oceanic Mo source strengths

According to Lantzy and Mackenzie (1979) the Mo global source strength from continental weathering is ≈10 × 10^8 g.yr^{-1}. As far as the authors are aware no such estimate is available for the global oceanic source strength of Mo, but one can be made on the basis of the present data.

There are a number of estimates in the literature for the annual sea-salt production rate, the values most commonly used being 10^{15} g.yr^{-1} (Erikson, 1959) and 10^{16} g.yr^{-1} (Blanchard, 1963), and both are employed in the present work to calculate a minimum and a maximum oceanic Mo source strength. To estimate the
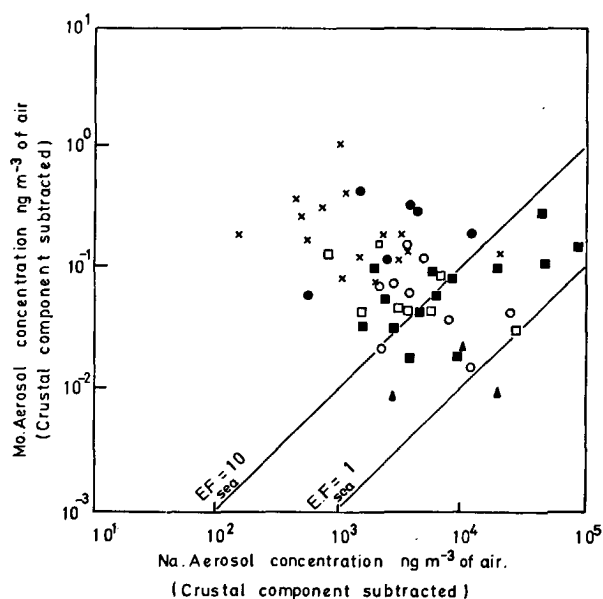

Figure 3

Mo v Na plot in the Atlantic aerosol. Concentrations are on a non-crustal and the 45° lines are for Mo EF$_{sea}$ values of 1 and 10-see text. UK coastal (×), North Atlantic westerlies (□), Straits of Gibraltar (●), north east trades (■), south east trades (○), South Atlantic westerlies (▲).

source strength two assumptions are made. 1) According to a number of workers, $\gtrsim 90\%$ of the sea-salt aerosol mass is located in particles in the size range ~ 1-~ 20 μm (see e.g.; Berg and Winchester, 1978), with $\gtrsim 75\%$ of the mass of Na being on particles $\gtrsim 3$ μm mass median diameter. In the absence of particle size data for Mo in the marine aerosol, it has been assumed that the Mo recycled from the sea surface has the same size distribution as that of sea-salt, although this may not in fact be the case. 2) It is assumed on the basis of the discussion given above that the sea surface generated salts have the same Mo:Na ratio as bulk sea water. Taking an average value of 36% Na in sea-salt, the minimum and maximum estimated oceanic Mo source strengths are ≈ 3.6 and $\approx 36 \times 10^8$ g.yr^{-1}. On a global basis, therefore, the oceanic source strength for Mo appears to be of the same order of magnitude as that for crustal weathering; however, it must be remembered that apart from those generated in coastal regions, most sea-salts are recycled directly over oceanic regions, whereas crustal weathering products are partitioned between land and marine areas. Although crustal and oceanic source strengths for Mo are roughly comparable, both are an order of magnitude less than the anthropogenic source strength for this element estimated by Lantzy and Mackenzie (1979), i.e. $\approx 510 \times 10^8$ g.yr^{-1}. However, within this global pattern, crustal and oceanic contributions to the total Mo in the atmosphere will vary and the Atlantic aerosol, with its variety of particle catchment regions, provides an example of this. The crustal and oceanic contributions to the total Mo in the Atlantic aerosol samples have been calculated on the basis of the ratios of the element to Al in the crust, and to Na in bulk sea water, and the results are given in Table 4. It can be seen from the data in this table that the highest crustal contributions of Mo are found in the aerosols from the north east trades, for which the average is $\sim 34\%$ of the total Mo, and the lowest in those from the South Atlantic westerlies, which have an average crustal contribution of only $\sim 5\%$. In contrast, the highest sea-salt contribution is for the South Atlantic westerlies (average $\sim 62\%$) and the lowest in the UK coastal aerosol (average $\sim 2\%$). This highlights the combined importance of these two natural low temperature particle sources for Mo in the aerosol over some regions of the Atlantic; in the north east trades (crustal + sea-salt) Mo is on average $\sim 47\%$ of the total, and in the south Atlantic westerlies these two components make up $\sim 62\%$ of the total Mo.

Table 4

Average source contributions to the total Mo in Atlantic aerosol populations.

Aerosol population	Crustal contribution (% total Mo)	Oceanic contribution (% total Mo)	"Excess" fraction contribution (% total Mo)
UK coastal	2.5	2	95.5
North Atlantic westerlies	2.0	16	82
Straits of Gibraltar	9	2	89
North east trades	34	13	53
South east trades	5	24	71
South Atlantic westerlies	0.5	62	37.5

The excess" Mo in the Atlantic aerosol, i.e. that which is not accounted for by direct crustal weathering or sea-salt generation, can originate from a number of sources; these include volcanic activity, rock volatilization, release from plant surfaces, forest fires and anthropogenic emissions. No specific indicator elements are available for these sources, but since the highest concentrations of excess" Mo are found in Northern Hemisphere samples relatively close to anthropogenic sources it may be concluded that pollutant emissions have a major control on the distribution of this fraction of the total Mo. Along the eastern margins of the North Atlantic between $\sim 55°N$ and $\sim 35°N$, the excess" Mo makes up $\gtrsim 80\%$ of the total Mo in the aerosol, and if the excess" Mo is assumed to be largely anthropogenic in origin, the partitioning of the element among the aerosol components is in general agreement with the data given by Lantzy and Mackenzie (1979) from which it can be estimated that $\sim 97\%$ of the total Mo released into the world atmosphere has an anthropogenic origin. It may be concluded, therefore, that on a global scale the oceans are a sink for atmospheric Mo.

In order to assess the status of the atmosphere in the transport of Mo to the oceans on a global scale, a knowledge of the atmospheric flux for the element to the World Ocean is required. The present data is restricted to the Atlantic aerosol and a large number of assumptions must be made to relate them to other oceanic areas. In the model adopted in the present paper, the following Mo aerosol concentrations have been assumed: a) the North Atlantic aerosol; ~ 0.15 ng Mo m^{-3} of air (present study); b) the North Pacific and northern Indian Ocean. The marine regions are influenced to a much smaller extent than the North Atlantic by anthropogenic inputs. For example, Walsh et al. (1979 a) reported that the mean concentration of As at Bermuda was ~ 0.16 ng m^{-3} of air, whereas at Hawaii it was ~ 0.07 ng m^{-3} of air. As an order of magnitude estimate therefore the North Pacific and northern Indian Ocean aerosols have been assigned a mean concentration which is one half of that for the North Atlantic, i.e. ~ 0.07 ng Mo m^{-3} of air; c) all the Southern Hemisphere oceanic regions have been assumed to have the same aerosol concentration of Mo as that of the South Atlantic westerlies (present study) i.e. ~ 0.01 ng m^{-3} of air; however, this is likely to be an overstimate. Using the oceanic areas, tropospheric scale height (3 900 m) and removal factor (40 removals per year) given by Walsh et al. (1979 b), and applying the concentrations given above, an atmospheric flux of $\approx 26 \times 10^8$ g Mo yr^{-1} was calculated for the World Ocean. The total, i.e. dissolved + particulate, river flux for Mo to the World Ocean appears to be in the range ≈ 640 to $\approx 700 \times 10^8$ g yr^{-1} (see e.g.: Lantzy, Mackenzie, 1979; Martin, Whitfield, 1983). There are a large number of uncertainties inherent in comparing atmospheric and riverine fluxes of trace metals to the oceans. For example, most river particulate material is trapped in the estuarine environment at present. However, it is apparent from the present very crude estimate that on a whole-ocean basis, even when sea surface recycling is neglected, the direct atmospheric input of Mo is $\gtrsim 5\%$ of that of the river input.

CONCLUSIONS

The general conclusions which can be drawn from the present investigation are summarized below,

1) The concentrations of Mo in the Atlantic aerosol exhibit a well-defined latitudinal dependence; ranging from a maximum of ~ 1 ng m^{-3} of air close to the UK coast to ~ 10 pg m^{-3} of air in open-ocean South Atlantic westerlies.

2) Average Mo EF$_{crust}$ values in most of the Atlantic aerosol populations are $\gtrsim 50$, but fall to ~ 5 in the north east trades. Crustal material is therefore an important end-member" component for Mo in the marine atmosphere and the distribution of the element in the Atlantic aerosol can be described in terms of the dilution of Mo-rich background" phases with Mo-poor, crust-derived material. This relationship can be expressed in the form of an EF diagram in which there is an inverse linear trend between the Mo EF$_{crust}$ values and the atmospheric concentrations of Al.

3) Mo EF$_{sea}$ values in the Atlantic aerosol range from ~ 0.5 to ~ 900, with the highest average being found in the UK coastal aerosol (116) and the lowest in samples from the South Atlantic westerlies (1.4).

4) A Mo v Na plot reveals a tendency in the Atlantic aerosol towards a minimum Mo EF$_{sea}$ value of ≈ 1.0 which is found for samples from a variety of locations. This leads to the conclusion that under certain, fairly rare, conditions the bulk sea water Mo concentration can be the constraining factor on the Mo:Na ratios in the marine aerosol.

5) The global oceanic Mo source strength is estimated to be in the range ≈ 3.6-$\approx 36 \times 10^8$ g.yr^{-1}, which is similar to the crustal source strength ($\approx 10 \times 10^8$ g.yr^{-1}). The highest crustal contributions to the total aerosol Mo are found in samples from the north east trades ($\sim 34\%$ of the total Mo), and the highest oceanic contributions in particulates from the South Atlantic westerlies ($\sim 62\%$) of the total Mo).

6) Natural low temperature generated particulates from crustal and oceanic sources are important contributors to Mo in the Atlantic aerosol, together accounting for $\sim 47\%$ of the total Mo in the north east trades and $\sim 62\%$ in the South Atlantic westerlies. However, in the other Atlantic aerosol populations sampled the excess" Mo (i.e. that which is not accounted for by crustal and oceanic sources) is dominant, and has its highest concentrations in the North Atlantic close to anthropogenic sources. It may be concluded that pollutant emissions are the major control on the distribution of the excess" Mo fraction in the Atlantic aerosol, and that the oceans are a sink for atmospheric Mo.

REFERENCES

Berg W. W., Winchester J. W., 1978. Aerosol chemistry of the marine atmosphere, in: *Chemical oceanography*, edited by J. P. Riley and R. Chester, Academic Press, Vol. 7, 173-231.

Blanchard D. C., 1963. Electrification of the atmosphere by particles from bubbles in the sea, in: *Progress in oceanography*, edited by M. Sears, Pergamon Press, Vol. 1, 71-202.

Bruland K. W., 1983. Trace elements in sea water, in: *Chemical oceanography*, edited by J. P. Riley and R. Chester, Academic Press, Vol. 8, 157-220.

Buat-Menard P., 1983. Particle geochemistry in the atmosphere and oceans, in: *Air-sea exchange of gases and particles*, edited by P. S. Liss and W. G. N. Slinn, Reidel Publishing Company, 455-532.

Buat-Menard P., Chesselet R., 1979. Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter, *Earth. Planetary Sci. Lett.*, 42, 399-411.

Buat-Menard P., Morelli J., Chesselet R., 1974. Water-soluble elements in atmospheric particulate matter over tropical and equatorial Atlantic, *J. Rech. Atmos.*, 8, 661-673.

Cambray R. S., Jefferies D. F., Topping G., 1975. An estimate of the input of atmospheric trace elements into the North Sea and the Clyde Sea (1972-1973), United Kingdom Atomic Energy Authority Harwell, Report AERE-R7733, 20 p.

Chester R., 1982. Particulate aluminium fluxes in the Eastern Atlantic, *Mar. Chem.*, 11, 1-16.

Chester R., Sharples E. J., Murphy K., 1984. Oceanic sources of trace metals in the Atlantic aerosol (in prep.).

Dams R., de Jonge J., 1976. Chemical composition of Swiss aerosol from the Jungfraujoch, *Atmoz. Environ.*, 10, 1079-1084.

Duce R. A., Hoffman G. L., Zoller W. M., 1975. Atmospheric trace metals at remote northern and southern hemisphere sites: pollution or natural?, *Science*, 197, 551-557.

Duce R. A., Ray B., Williams J., Hewitt A., 1982. SEAREX Research Notes, *SEAREX New.*, 5, 7-8.

Duce R. A., Arimoto R., Ray B. J., Unni C. K., Harder P. J., 1983. Atmospheric trace elements at Enewetak Atoll: 1, concentrations, sources, and temporal variability, *J. Geophys. Res.*, 88, 5321-5342.

Eriksson E., 1959. The yearly circulation of chloride and sulfate in nature. Meterological, geochemical, pedological implications. Part 1, *Tellus*, 11, 317-403.

Hamilton E. I., 1974. The chemical elemental and human morbidity, *Sci. Total Environ.*, 3, 3-85.

Head P. C., Burton J. D., 1970. Molybdenum in some ocean and estuarine waters, *J. Mar. Biol. Assoc. UK*, 50, 439-448.

Hoffman E. J., Hoffman G. L., Duce R. A., 1974. Chemical fractionation of alkali and alkaline earth metals in atmospheric particulate matter over the North Atlantic, *J. Rech. Atmos.*, **8**, 675-688.

Hunter K. A., 1980. Process affecting particulate trace metals in the sea surface microlayer, *Mar. Chem.*, **9**, 49-70.

Krishnaswami S., Sarin M. M., 1976. Atlantic surface particulates: composition, settling rates and dissolution in the deep sea, *Earth Planetary Sci. Lett.*, **32**, 430-440.

Lantzy R. J., Mackenzie F. T., 1979. Atmospheric trace metals: global cycles and assessment of man's impact, *Geochim. Cosmochim. Acta*, **43**, 511-525.

Maenhaut W., Zoller W. M., Duce R. A., Hoffman G. L., 1979. Concentration and size distribution of particulate trace elements in the South Polar atmosphere, *J. Geophys. Res.*, **84**, 2421-2431.

Martin J. M., Whitfield M., 1983. The significance of the river input of chemical elements to the ocean, in: *Trace metals in sea water*, edited by Wong, Boyle, Bruland, Burton and Goldberg, Plenum Publishing Corporation, 265-296.

Morris A. W., 1975. Dissolved molybdenum and vanadium in the northeast Atlantic Ocean, *Deep-Sea Res.*, **22**, 49-54.

Prospero J. M., 1979. Mineral and sea salt aerosol concentrations in various oceanic regions, *J. Geophys. Res.*, **84**, 725-731.

Rahn K. A., 1976. The chemical composition of the atmospheric aerosol, Tech. Rep., Graduate School of Oceanography, University of Rhode Island, Kingston, R.I.

Rahn K. A., Borys R. D., Shaw G. E., Shutz L., Jaenicke R., 1979. Long-range impact of desert aerosol on atmospheric chemistry: two examples, in: *Saharan dust*, edited by Morales, John Wiley, 243-266.

Savoie D. L., Prospero J. M., 1977. Aerosol concentration statistics for the tropical North Atlantic, *J. Geophys. Res.*, **82**, 5954-5963.

Sugawara K., Okabe S., 1966. Molybdenum and vanadium determination of Umitaka-Maru" samples from her 1962-1963 and 1963-1964 cruises of the International Indian Ocean Expedition, *J. Tokyo Univ. Fish.*, **8**, 165-171.

Szekielda K. M., Kupferman S. L., Klemas V., Polis D. F., 1972. Element enrichment in organic films and foam associated with aquatic frontal systems, *J. Geophys. Res.*, **77**, 5278-5282.

Walsh P. R., Duce R. A., Fasching J. L., 1979 a. Tropospheric arsenic over marine and continental regions, *J. Geophys. Res.*, **84**, 1710-1718.

Walsh P. R., Duce R. A., Fasching J. L., 1979 b. Considerations of the enrichment sources and flux of arsenic in the troposphere, *J. Geophys. Res.*, **84**, 1719-1726.