The potential for biological mobilization of trace elements from aeolian dust in the ocean and its importance in the case of iron

R. M. Moore[a], J. E. Milley[b], A. Chatt[b]
[a] Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, B3H 4J1, Canada.
[b] Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J1, Canada.

ABSTRACT

In order to determine whether particulate material, atmospherically supplied to the ocean surface, may be significantly leached not only by direct interaction with sea water but also as a result of zooplankton grazing, samples of atmospheric dust were leached at pH values between 5.4 and 8.0. The elements Cu, As and V showed significant increases in the proportion leached as the pH was lowered. Iron was found to be leached to an extent of ca. 10%, but with no significant pH effect. A comparison of the crustal concentrations of a number of elements with their sea water concentrations suggests that Fe is among the most likely to have an appreciable atmospheric contribution to its supply to surface ocean waters. An estimate of the atmospheric flux of this element in a leachable form supports the idea that this source is the main contributor to the requirements of the biota. Since the efficiencies with which phytoplankton can grow at low Fe concentrations vary between species it follows that the meteorological factors that govern the rate of transport of atmospheric dust to the ocean areas could affect plankton ecology and productivity.

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RÉSUMÉ

Potentiel de mobilisation biologique dans l'océan des éléments-trace d'origine atmosphérique et son importance dans le cas du fer

Des échantillons de poussière atmosphérique ont été traités à des valeurs de pH comprises entre 5,4 et 8,0, afin de déterminer si le matériel particulaire fourni par l'atmosphère à la surface des océans, peut être solubilisé de manière significative, non seulement par interactions directes avec l'eau de mer, mais aussi par le broutage du zooplancton. La proportion de Cu, As, V libérée est en augmentation significative lorsque le pH diminue. Environ 10% du fer peuvent être libérés, sans effet marqué du pH. La comparaison des concentrations d'un certain nombre d'éléments à terre et dans l'eau de mer, suggère que le fer atmosphérique a probablement la contribution la plus appréciable. L'évaluation du flux atmosphérique de cet élément sous forme libérée confirme l'apport de cette source aux besoins du biotope. La croissance du phytoplancton étant variable d'une espèce à l'autre aux faibles concentrations en fer, il s'ensuit que les facteurs météorologiques qui règlent le transport de la poussière atmosphérique vers les zones océaniques peuvent affecter l'écologie et la productivité du plancton.

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INTRODUCTION

A number of studies in the past have addressed the question of whether airborne particulate matter makes a significant contribution to the concentration of dissolved trace elements in sea water (Walsh, Duce, 1976; Hodge et al., 1978; Crecelius, 1980; Hardy, Crecelius, 1981). These studies have suggested that a number of elements such as Cd, Cu, Zn, Mn and V will rather readily dissolve from atmospheric particulates while others, eg. Al, are apparently not significantly leached; in the case of Fe estimates are variable, 1-8% (Hodge et al., 1978; Hardy, Crecelius, 1981).

Such studies have not directly considered the question of whether particulate matter added from the atmosphere might make a significant contribution to the trace metal flux through marine organisms. It has become quite clear that inorganic detritus added at or near the surface is consumed by micro-zooplankton as might be expected if such particle-feeders are selective chiefly according to the size of particles rather than their composition.

Thus Deuser et al. (1981) have shown how the downward flux of aluminosilicates in both large and small particles in the deep ocean is correlated to surface productivity. So the transport to the sediments of inorganic particles added from the atmosphere, or introduced from coastal waters, depends on harvesting by zooplankton and the incorporation of micron-size particles into larger rapidly sinking ones. These conclusions are similarly supported by particle flux experiments reported by Honjo (1982). Syvitski and Lewis (1980) describe mineralogical alterations of particles that result from their ingestion by zooplankton.

It follows that simple measurements of the solubility of the components of atmospheric particulates in sea water are unlikely to be a good index of the tendency for these elements to become involved in biological cycles and perhaps to be released to the dissolved state. It is to be expected that the harsher chemical environment present within an organism gut would mobilize a higher proportion of some elements than mere exposure to sea water.

The fate of elements after release inside an organism is a problem which cannot be dealt with here, though it may be presumed that the material is either excreted in the dissolved form or incorporated into the organism. The excreted elements potentially can follow similar pathways to those of the more abundant nutrient species such as ammonia and forms of phosphorus: that is, they can become available to the phytoplankton. Of special interest in this respect is the element iron, the supply of which has frequently been referred to as a possible limiting factor on primary production in the open ocean.

This work is concerned primarily with the question of whether there is dissolution of a number of elements from atmospherically derived particulate matter when it is ingested by microzooplankton. The problem has been limited to the more tractable form of establishing the effect of lowered pH on element mobility. This means that effects of digestive enzymes or complexing ligands present in the gut are not taken into account: furthermore, subsequent mobilization of elements due to formation of a reducing micro-environment within fecal pellets is also not accounted for.

An estimate of the likely pH that particles would encounter was made from a consideration of the optimum pH at which zooplankton digestive enzymes operate (van Weel, 1970): these experiments have used a pH range 5-8.

It is necessary that the leaching medium should have some buffer capacity so that the selected pH can be maintained for the duration of the leaching period. At the same time it was considered necessary to avoid using solutions which might affect element solubility through complexation (for instance carboxylic acid groups that would complex with transition metal ions, or phosphate which might inhibit the solution of iron). For these reasons a sea water medium was chosen, in which the pH was adjusted by bubbling with a CO_2-air mixture; the gas space above the liquid would tend to hold the pH constant. The pH of the solution was measured on a small decanted volume immediately before the particulate matter was introduced. Six pH values were used ranging from pH 8.11 for unadjusted sea water to pH 5.39.

AEROSOL SAMPLING

Atmospheric particulate matter was collected on dried, preweighed 0.45 μm Nuclepore[R] filters by means of a high volume sampler. The collection site was situated some 50 m above ground level at a maritime environment in Halifax, Nova Scotia. The filter was installed in a Perspex holder in a covered shelter and the air was drawn through the filter at 17 m^3/h, over a 5-day period in June 1982. During this time there was no precipitation and an onshore wind from the E or ESE prevailed at speeds ranging from 11-33 km/h. The meteorological data indicated that the sample was probably taken from a single air mass.

The air-filter was subdivided into equal portions one of which was used for each leaching, and one for measuring the initial composition of the material by neutron activation analysis (NAA).

For each leaching experiment a portion of the Nuclepore filter with its coating of particulates was introduced to a Teflon bottle containing 100 ml of filtered sea water having a predetermined pH. The samples were shaken for two hours and the particulates, now dislodged from the Nuclepore filter, were collected on preweighed Millipore filters (0.45 μm pore size, 25 mm diameter), washed rapidly with a small volume (1 ml) of Super Q water, to remove NaCl, dried, reweighed and packaged for neutron activation analysis.

NEUTRON ACTIVATION ANALYSIS

All samples were irradiated at the Dalhousie University Slowpoke-2 Reactor Facility using a thermal neutron flux of 5×10^{11} neutrons cm^{-2} $sec.^{-1}$ in an inner pneumatic site. The stability, homogeneity and reproducibility of the neutron flux of this reactor has been previously reported (Ryan et al., 1978). The gamma ray spectrum of the irradiated sample was recorded, after suitable decay times, using a 60 cm^3 Canberra Ge (Li) detector. This had a resolution of 1.9 keV at the 1 332 keV gamma-ray of ^{60}Co and was used in conjunction with a tracer Northern TN-11 multichannel pulse height analyser. Standards were prepared from 1 000 ppm Alfa-Ventron atomic absorption standard solutions, aliquots of which were deposited on Whatman filter paper or Nuclepore polycarbonate membranes, evaporated to dryness and sealed for irradiation in polyethylene envelopes. Further details of the method are given by De Silva (1981).

RESULTS

The most practical way to describe the changes in elemental composition of the particulates after leaching is to refer each metal to the quantity of Al present in the sample. In support of this procedure is the fact that Al is readily measured by NAA at the relatively high levels in which it occurs in the particulates, furthermore it may be assumed that the fraction of the Al that is present in clay mineral lattices will not dissolve significantly under conditions as mild as those used in this study (Hydes, Liss, 1976). Nevertheless, to the extent that any Al is leached from the samples, the degree of leaching of other elements will be correspondingly under-estimated: this remains an important question which needs further study. While in principle this problem could be solved by analysis of the leaching medium for dissolved Al, in practise it was found that the analytical method of choice, fluorimetric measurement of an Al-lumogallion complex (Hydes, Liss, 1976), showed a strong interference which was attributed to the presence of relatively high concentrations of metals from the particulates.

In Table 1 are shown the ratios of various elements to Al in atmospheric particulates before and after leaching: these are given as ratios of the activity of the element concerned to that of Al (both corrected for blanks and background) at standard times after irradiation. This is the most direct way of expressing the results and avoids the errors that would be introduced when each element is determined in terms of mass by comparison with standards.

The results confirm that a number of elements are leached to a considerable extent from atmospheric particulates even at pH 8; the elements include Mn, V, Cu, As, Sb and Co. The elements La, Sm, Ce and Sc do not show any significant leaching at pH 8 nor at lower pH. Iron was leached to an extent of ca. 10% at pH 8 but there was no increase as the pH was lowered. Three elements, Cu, V and As showed a significant increase in the extent of leaching as the pH was reduced from 8 to 5.4 with Cu increasing from 30% leached at pH 8 to 50% at pH 5.4, V increasing from 80 to 85% and As from 78 to 90%. While Co appears to be leached to an extent of about 50%, results are rendered uncertain by that fact that the blank is similar to the quantity of Co present in the particulates.

Hodge et al. (1978) and Crecelius (1980) have looked at the solubilities of atmospheric particulates in sea water: the main concern of these two studies was simple dissolution of elements from the particulates, but possible enhancement of leaching by lowered pH or other effects of consumption by organisms was not considered. The technique used by Hodge et al. for measuring the quantity of elements leached into sea water was, for Fe, Zn, Cu, Ni, Mn, Cr and Al, flame atomic absorption which is of relatively low sensitivity particularly when used on samples in a sea water matrix. For this reason the estimates of the solubility of the elements Fe and Al are especially liable to error. Both this work and that of Crecelius on marine aerosols point to a rather higher solubility of Fe (3-13%) compared with the 1% or less reported by Hodge et al. (1978) which may be a consequence of their inadequate analytical sensitivity. The reason for the higher solubility of V found in this study (80%) compared with that reported by Hodge et al. (30%) is likely to be linked to the large component of this element originating in oil burning: Walsh and Duce (1976) have reported a high solubility for V from particulates when enriched above crustal levels by pollution.

The high solubility of As, 80% at pH 8, is somewhat greater than reported by Crecelius (1980) who gives a figure of 50%. The results for antimony are in good agreement, this study indicating about 50% solubility and Crecelius giving figures in the range 30-40%. Both studies indicate essentially no leaching of La.

Table 1

Neutron activation results: ratio of activity (counts per minute) for each element relative to aluminium in samples leached at various pH values.

pH	Mn $\times 10^4$	Fe $\times 10^5$	V $\times 10$	Cu $\times 10^4$	As $\times 10^4$	Sb $\times 10^4$	Sc $\times 10^5$	La $\times 10^3$	Ce $\times 10^5$	Sm $\times 10^3$	Co $\times 10^5$
5.39	140	112	13	281	149	105	226	145	949	573	19
5.60	150	110	13	328	144	67	246	120	917	468	15
6.16	146	113	15	358	285	132	229	176	1 088	591	26
6.40	152	108	15	391	299	93	226	157	1 030	571	16
7.99	158	107	17	412	309	84	226	150	967	553	9
Unleached	307	125	85	587	1 408	221	234	168	1 000	584	44

DISCUSSION

The leachability of Fe from atmospheric particulates suggests that this source might make a significant contribution to the Fe uptake by marine organisms. An indication of the potential importance of atmospheric supply of trace elements is revealed by the ratio of the concentration of the element in atmospheric particulates to its concentration in sea water. For most elements it is a reasonable approximation to use the crustal abundance rather than atmospheric concentrations, though some elements such as Se, Pb, Sb, Cd, Cu are enriched in atmospheric particulates, possibly by such natural processes as volcanism or biological mobilization (Duce et al., 1975), the effect being observed even in regions distant from anthropogenic sources.

Table 2 lists ratios (R1) of crustal abundance to sea water abundance for a range of trace elements. A number of these elements occur at higher concentrations in atmospheric aerosols than in crustal material, for this reason a ratio is also given for atmospherically-derived material (R2), but it should be noted that, except in the case of Cd, the data used are from Chester and Stoner (1974) who record considerably lower enrichment factors for elements in aerosols than do other workers, for example Duce et al. (1975); consequently the values of R2 could be significantly higher than those listed in Table 2. It is seen that the ratios span about six orders of magnitude and that Fe and Al are by far the most depleted elements in sea water relative to their crustal and atmospheric abundances. For this reason, and because much interest has been shown in the supply of Fe to the biota, an attempt will be made

Figure
Steady-state model of metal fluxes through surface layer of ocean. Subscripts s and ss denote surface and subsurface waters.

here to estimate the importance of atmospherically derived Fe to the requirements of biota in regions of the open ocean far removed from river sources of the element.

A simple model is presented to compare the flux of leachable Fe deposited from the atmosphere (F_A) with both the advective or mixing flux of "dissolved" Fe (F_W) and the downward flux of Fe associated with biogenic debris (F_B). The model will also be applied to a number of other trace elements. Some of these terms need defining: "dissolved" Fe will include colloidal forms and particles smaller than 0.45 μm; biogenic debris refers to organic matter and the hard parts of organisms which comprise the downward organic flux, most of which is carried in large particles; it does not include the Fe which is still integrally associated with lithogenous minerals even though this will be present in fecal pellets which apparently provide its main mode of transport to the sediments (Deuser et al., 1981; Honjo, 1982). This distinction is important since the model is concerned with Fe necessary for the proper nutrition of organisms which is cycled through the biota. The term "advective source" will be used to represent a temporally and spatially averaged supply of Fe from subsurface waters that may be enriched in the element. This supply results from a combination of the local upwelling and vertical mixing.

The quantities which are being compared here (F_A, F_W, F_B) are undoubtedly all quite variable, the first on account of meteorological conditions and geographic location, the second due to the variability of vertical mixing or advection and of dissolved Fe concentrations, and the last due to variable biological productivity. The last two quantities are likely to show some correlation since the productivity depends on the upward vertical flux of phosphorus. It is therefore advantageous to normalize the dissolved metal flux (upwards) and the particulate biogenic metal flux (downwards) to the corresponding phosphorus fluxes.

The two-box model is illustrated in the Figure. A steady state is assumed in the surface box so that the supplies of metal and phosphorus equal the quantities removed:

Table 2
Abundance of metals in crust and in atmospheric particulates, their sea water concentrations and molar ratios of these two quantities.

Metal	Crustal abundance (a, b)	Av. conc. in atmos. particles (a, c)	Sea water conc. nmolar	R1	R2	Ref. for sea water conc.
Fe	5.6%	5.2%	1	1×10^9	0.9×10^9	d
Al	8.2%		20	150×10^6	150×10^6	e, f
V	135 ppm	163 ppm	25	100×10^3	130×10^3	g
Cr	100 ppm	119 ppm	3	600×10^3	800×10^3	h
Mn	950 ppm	1 340 ppm	1	17×10^6	24×10^6	i
Co	25 ppm	10 ppm	.1	4.2×10^6	1.7×10^6	j
Ni	75 ppm	96 ppm	10	127×10^3	160×10^3	k
Cu	55 ppm	168 ppm	2	430×10^3	1.3×10^6	k
Zn	70 ppm	780 ppm	10	100×10^3	1.2×10^6	k
Cd	0.11 ppm	80 ppm	1	1×10^3	0.7×10^6	k
Pb	14 ppm	588 ppm	.01	6.8×10^6	280×10^6	m

R1 is ratio of concentration in crust to sea water.
R2 is ratio of concentration of metal in atmospheric particulate to sea water.
a) Chester and Stoner (1974).
b) Bowen (1979).
c) Duce et al. (1975).
d) Gordon et al. (1982).
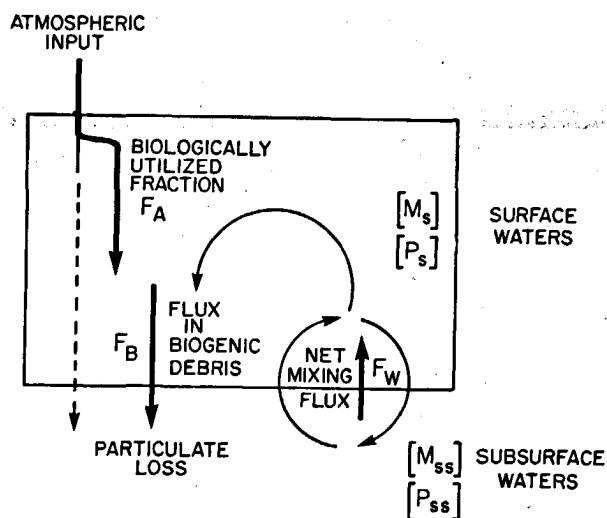e) Hydes (1979), f. Moore (1981).
g) Morris (1975).
h) Murray et al. (1983).
i) Landing and Bruland (1980).
j) Knauer et al. (1982).
k) Bruland (1980).
l) Schaule and Patterson (1981).

$$P_{removed} = P_{supplied}, \tag{1}$$

$$M_{removed} = M_{supplied}. \tag{2}$$

If the atmospheric supply of P is neglected, an assumption that is justified below, equation (1) is equivalent to:

$$P_{partic. \, flux} = P_{mixing \, flux} \tag{3}$$

and (2):

$$M_{partic. \, flux} = M_{mixing \, flux} + F_A. \tag{4}$$

Where F_A is the atmospheric supply of metal that is utilized by organisms.

The ratio of upward fluxes of metal and phosphorus due to mixing is given by:

$$\frac{(M_{mixing \, flux})}{(P_{mixing \, flux})} = \frac{(M_{ss} - M_s)}{(P_{ss} - P_s)}. \tag{5}$$

Where M_s and M_{ss} are the metal concentrations in surface and subsurface waters, and P_s, P_{ss} are the corresponding phosphorus concentrations. When $P_s \ll P_{ss}$, and $M_s \ll M_{ss}$ this becomes:

$$\frac{M_{mixing \, flux}}{P_{mixing \, flux}} = \frac{M_{ss}}{P_{ss}} = R_{ss}. \tag{6}$$

The ratio of metal to P in subsurface waters will be referred to as R_{ss}, and the ratio in biogenic debris as R_D.

So

$$M_{mixing \, flux} = P_{mixing \, flux} \times R_{ss} \tag{7}$$

and

$$M_{partic. \, flux} = P_{partic. \, flux} \times R_D. \tag{8}$$

Equation (4) becomes:

$$P_{partic. \, flux} \times R_D = P_{mixing \, flux} \times R_{ss} + F_A.$$

But from (3):

$$P_{mixing \, flux} = P_{partic. \, flux}.$$

So

$$F_A = P_{partic.} (R_D - R_{ss}).$$

In the case of no significant flux of atmospherically derived metal through the biota $F_A = 0$ and $R_D = R_{ss}$; but if the atmosphere is a significant source then R_D must exceed R_{ss}. This will be used as a test for the significance of atmospheric supply.

A conservative estimate of R_D (ratio of metal to phosphorus in biogenic debris) can be made from plankton analyses. It is likely to be a minimum value because organic debris lost from the surface box quickly becomes depleted in phosphorus, and so far there is little indication that any metal except Cd may be recycled as rapidly as as phosphorus (Bruland et al., 1978).

Table 3

Molar metal to phosphorus ratios (R_D) for plankton samples from the data of Martin and Knauer (1973). Subdivision of phytoplankton samples collected in Monterey Bay into three groups is on a chemical basis: group I, Ti not detected; group II, Ti detected; group III, Sr concentrators present: a detailed discussion of these groupings is given by Martin and Knauer.

	(M/P × 10³)				
	Fe	Cu	Zn	Cd	Mn
Group I	12	0.16	0.9	0.04	0.34
II	84	0.36	5.8	0.06	0.75
III	13	0.72	1.1	0.11	0.43
Euphausids (Monterey Bay)	6.1	0.91	3.9	0.09	0.24
Microplankton (Hawaii)	110	2.8	37	0.04	0.85

Table 4

Molar ratios of metal to phosphorus in subsurface (ca. 300 m) ocean water Rss.

	Metal nmol 1^{-1}	P μmol 1^{-1}	(M/P × 10³)	Source
Fe	1.5	0.8	1.9	Moore (1981)
Cu	1.3	1.6	0.8	Bruland (1980)
Zn	1.9	1.6	1.2	Bruland (1980)
Cd	0.5	1.6	0.3	Bruland (1980)
Mn	0.34	0.8	0.4	Landing and Bruland (1980)

Estimates of R_D (Tab. 3) have been made from plankton analyses reported by Martin and Knauer (1973); the Redfield value of 106 was assumed for the molar C/P ratio in phytoplankton and a figure of 124 was used for the zooplankton samples (Beers, 1966). Values of Rss, the molar ratio of metal to phosphorus in subsurface waters which provide the non-atmospheric metal supply to surface dwelling organisms are listed in Table 4. Ideally the values of R_D and Rss should apply to the same geographic location, but reliable metal analyses for both plankton and water remain too scarce to permit this. The data of Martin and Knauer were chosen as the best available, and further selection was made amongst them so as to avoid samples that might have been contaminated. It should be possible to draw more definite conclusions from this model as more data on trace metal concentrations become available.

A comparison of the ratios R_D and Rss for Cd show that R_D is considerably less than R_{ss} so that no atmospheric supply of this element is required.

For Cu the two quantities are more similar so that the water supply approximately balances the estimated particulate removal. An exception is the microplankton sample from Hawaii which has a relatively high metal concentration: if this value of R_D were representative of the particulate debris being transported out of the surface waters, an additional supply of metal would be required. There have been some suggestions that Cu does have a significant atmospheric source, the indications being an elevated concentration in the surface waters of the ocean. This effect has been reported by Boyle et al. (1977) who found a correlation between surface enrichment of Cu and surface Pb-210 levels.

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Such an observation is strongly indicative of an atmospheric source for the Cu. Bruland (1980), also in a survey of the N. Pacific, did not observe such an enrichment of copper and was led to attribute the earlier results to sampling problems. However, the temporal variability that would be anticipated for an atmospheric supply of Cu could also account for the different results of these workers.

In the case of Zn there is greater variability among the estimates of R_D, with the ratio derived for microplankton from Hawaii being the highest. There is little evidence for this element having a significant atmospheric input, the oceanic profiles normally show a marked depletion at the surface (Bruland, 1980), but Bruland did observe a single elevated concentration in a surface sample which he suggested was due to input with rain. Data for the Western North Atlantic (Bruland, Franks, 1983) show no indication of enrichment with Zn in surface waters.

For Mn the mean value for R_D of 0.5 (Tab. 3) is close to the R_{ss} of 0.4, it should be noted that in the case of this element surface ocean waters do, in some areas, have an additional input of reduced Mn from coastal sediments. This is not taken into account in the model, and as a result, any excess of R_D over R_{ss} need not indicate an atmospheric source.

For Fe alone the value of R_D consistently exceeds Rss by a factor ranging from 3 to 60, this suggests that a significant contribution to the biogenic flux may be contributed by atmospheric deposition.

It should be noted that in the model it was for simplicity assumed, when estimating the ratio of metal to phosphorus in the flux from vertical mixing and advection, that the metal was depleted in surface relative to subsurface waters. If this is not the case for an element it simply means that use of M_{ss}/P_{ss} as an index of $(M/P)_{mix}$ is an overestimate, so that the importance of atmospheric supply is under-estimated.

Another simplification of the model is its neglect of the atmospheric flux of phosphorus to surface waters. The condition for this to be justified is that the ratio of leachable metal to phosphorus in atmospheric dust be greater than the concentration ratio in subsurface waters, which means, from the data in Table 4, having a molar ratio greater than *ca.* 10^{-3}. Using values from Graham and Duce (1979) for the phosphorus content of soil particles (0.1%) and its solubility from terrigenous particles (8%), it follows that metals such as Fe, Mn, Zn, Cu, and Cd must have a leachable fraction greater than *ca.* 0.1 ppm in atmospheric dust for the model to be valid. A consideration of the metal abundances in atmospheric particles (Tab. 2) and leachabilities shows that for these elements the simplification is appropriate.

Estimates can be made of the atmospheric supply of particulate Fe to the surface waters of the ocean, and then, using the measurements of leachability determined in this work, the quantity available to the biota can be determined. Such estimates will be made and compared with the supply from the water column:

the latter quantity is at present very much harder to determine both because of the scarcity of data on Fe in sea water and because of the uncertainty of vertical mixing coefficients and upwelling velocities.

When considering the atmospheric supply of any element it is important to recognize the great variability that results from such factors as the geographic distribution of arid regions, wind direction and strength, and the efficiency of washout by precipitation. To these natural factors must be added some uncertainty in deposition velocities, estimates of which may vary by at least an order of magnitude.

Chester and Stoner (1974) give values for the Fe content of atmospheric particulates ranging from 3-10%; a figure of 5% appears to be a reliable average which is close to the crustal abundance of the metal, 5.6% (Krauskopf, 1967). As one would expect, atmospheric loadings of particulate Fe show great variability ranging from 3 ng m^{-3} reported by Duce et al. (1975) for a North Atlantic sample, through a minimum of 10 ng m^{-3} derived from the data of Aston et al. (1973) for the China Sea, to 290 ng m^{-3} reported by Duce et al. (1976) for a sample collected in Bermuda. Duce et al. (1976) also give time-averaged figures for Fe loadings in Bermuda of 100 ng m^{-3}.

To determine fluxes into the ocean, these figures must be combined with deposition velocities variously estimated as 0.3 cm sec.$^{-1}$ (Cambray et al., 1975) and 3 cm sec.$^{-1}$ (Sehmel, Sutter, 1974). Fluxes of Fe calculated from these figures range from 0.3 to 95 mg m^{-2} year, the latter figure being derived from the Bermuda iron-loadings. Buat-Menard and Chesselet (1979) have estimated a North Atlantic Fe flux of 32 mg m^{-2} year^{-1}. These figures represent averages over a year and it may be assumed that the flux can be very much higher over short periods as shown by the data of Duce et al. (1976). Applying a figure of 10% as the leachable fraction gives an estimate of up to 10 mg Fe m^{-2} year^{-1} available to the biota. If we assume an Fe concentration in the subsurface waters of 1.5 nmoles l^{-1}, we find that the leachable atmospheric supply each year is equivalent to the Fe content of a 120 m column of subsurface water.

This should be compared with the addition that can be made by vertical advection and diffusion. Wind driven vertical advection is temporally and spatially variable with values in the North Atlantic from 20 to 50°N ranging between approximately -60 m and $+30$ m/year. Negative values apply in the Sargasso Sea, and they become progressively more positive with increase in latitude (Leetmaa, Bunker, 1978).

A vertical diffusive mixing flux is estimated from the product of K_v, the coefficient of vertical eddy diffusivity, taken as 10^{-4} m^2 sec.$^{-1}$ and an Fe concentration gradient. The latter is given a value corresponding to a decrease from the subsurface concentration, Fe$_{ss}$, to a hypothetical zero at the surface (to obtain a maximum flux estimate) with the gradient occurring over 500 m.

Vertical diffusive flux $= K_v \cdot Fe_{ss}/500$ moles m^{-2} yr^{-1} (here Fe_{ss} is concentration in moles m^{-3}) $= 6 \cdot Fe_{ss}$ moles m^{-2} yr^{-1},

which is the equivalent of a 6 m column of subsurface water per year.

Combined vertical advection and diffusion may therefore provide a dissolved Fe flux equivalent to about 40 m of subsurface water per year, but as indicated above, the supply is very much less in the downwelling waters of the Sargasso Sea.

This result indicates that even over a twelve month period the utilizable atmospheric Fe flux could considerably exceed the supply to the surface by mixing processes. It must be stressed that the pulsed nature of atmospheric dust additions, dependent on meteorological conditions, will certainly result in at least periodic, if not continuous, predominance of atmospheric over mixing supply.

The literature dealing with the importance of Fe to phytoplankton is extensive and the following section attempts only a brief summary. Harvey (1933) demonstrated that the addition of Fe in a quantity of 1 μg l^{-1} to sea water already enriched in nitrate, phosphate and silicate, doubled the growth rate of the diatom *Nitzschia closterium*. Cooper (1935) has discussed the Fe requirements of phytoplankton: based on samples collected in the English Channel off Plymouth, he states that phytoplankton require several times more Fe than phosphorus (wt/wt). While this observation is at variance with the data recorded in Table 3, it may be valid and a consequence of the coastal origin of Cooper's samples. Harvey (1937) showed that the diatoms *Nitzschia closterium* and *Lauderia borealis* need very much less Fe than reported by Cooper; he showed that diatoms can utilize colloidal or particulate Fe and he suggests that the cells have the ability to use Fe that adsorbs on their surface. Goldberg (1952) has confirmed the observation that particulate and/or colloidal Fe can be utilized as a nutrient by diatoms, but he reports data in agreement with Cooper's high estimates of the Fe/P ratio in growing diatoms. A number of workers (Ryther, Kramer, 1961; Lewin, Chen, 1971) have found variations in the facility of various phytoplankton species to satisfy their requirement for Fe under the same conditions. Fedorov (1973) has referred to the possibility of Fe supply being among the factors controlling phytoplankton diversity and several workers (Kim, Martin, 1974) have looked specifically for a connection between Fe supply and dinoflagellate blooms. Of more concern here is the effect of Fe on open ocean phytoplankton which are less abundantly supplied with river-borne iron. Menzel and Ryther (1961) have reported experimental results that suggest Fe is a limiting nutrient for phytoplankton growth in the Sargasso Sea. Trick *et al.* (1983) have identified an extracellular siderophore produced by a marine dinoflagellate that is presumed to enhance the availability of Fe by rendering it soluble. This mechanism could be independent of the one described above involving the mediation of zooplankton, but it would also provide a means of maintaining Fe in a useable form after it had been mobilized and excreted by zooplankton.

While the flux calculations given above point to the potential importance to the biota of the atmospheric flux of Fe there is little direct evidence to demonstrate that marine organisms do indeed utilize atmospherically supplied trace elements. However, a study made of the distribution of bomb-produced Fe-55 in atmospheric dust, sea water and marine organisms provides good support for the arguments given here. Weimer *et al.* (1978) observed that Fe-55 specific activities in marine organisms including euphausids and salmon were frequently higher than the specific activities measured in atmospheric dust and sea water. The first of these observations is explained by the occurrence of the Fe-55 on dust particles predominantly as a surface coating which is relatively leachable. This was confirmed in the laboratory by the use of a dilute acid leaching solution. They have almost certainly under-estimated the specific activity of Fe-55 in sea water since their stable Fe concentrations (30-200 nmolar) are up to two orders of magnitude greater than recent measurements. Then, since they observed that sea water itself could leach 30-97% of the Fe-55 from air filters, specific activities in the water would exceed those in the particulate source. Their statement that virtually all Fe-55 enters the ocean as an atmospheric aerosol was supported by the observation that the concentrations of Fe-55 in salmon from the NE Pacific decreased with a half time of *ca.* 1 year, closely matching the decrease in supply from the stratospheric reservoir. These observations provide good evidence for the importance of atmospheric rather than riverine flux to the biota in the open ocean.

Since it has been shown that the atmosphere can be a significant source of mobile Fe it follows that the vicissitudes of dust deposition could be a controlling factor in phytoplankton ecology and perhaps also productivity in the open ocean.

CONCLUSIONS

For the elements Cu, V and As it appears that the lower pH values that atmospheric particles would encounter within marine micro-organisms may increase the proportion which is leached.

A 10% leachable fraction of Fe in atmospheric dust would cause the atmospheric supply of this element to the surface dwelling oceanic biota to exceed the mixing supply even on an annual basis and certainly on shorter time scales. The atmosphere may, therefore, provide the main source of Fe for the biota in the open ocean.

If phytoplankton species do complete for available Fe as studies have suggested, the irregularities of atmospheric supply could significantly affect phytoplankton ecology in the open ocean.

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