International Council
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C.M. 1974/E31
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THE MOVEMENT OF HEAVY METALS IN A MARINE ECOSYSTEM

by

G. Topping

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Summary

This paper examines the question of trace metal variations in seawater and phytoplankton activity. Calculations of the rates of metal removal by phytoplankton are made for the open ocean and coastal waters. The results suggest that present day surveys of trace metals in seawater, with their inherent deficiencies regarding sampling and analyses, have little hope of relating trace metal levels in seawater to phytoplankton activity.

Introduction

Most publications dealing with trace metal studies in marine systems inevitably refer to the importance of phytoplankton in the cycling of metals in the sea. Many trace metals in marine waters are known to be concentrated by phytoplankton (Riley and Roth, 1971) and one might assume that this mechanism could represent a significant removal of metal from sea water. Surprisingly few attempts have been made however to estimate this uptake and when attempts have been made they have invariably been based on a single element for a particular area of the sea (Chow and Patterson, 1966 (lead) and Spencer and Brewer, 1969 (copper)). Attempts have also been made to relate trace metal levels in sea water directly with phytoplankton activity but these have met with little success (Menzel and Spaeth, 1962 (iron) and Alexander and Corcoran, 1965 (copper)). Despite this lack of success some workers in this field (Dutton et al., 1974) continue to refer to the possibility of phytoplankton affecting the spatial distribution of metals in the sea. Considering the amount of work presently devoted to trace metal studies in relation to pollution and food chain studies the subject of trace metals and phytoplankton activity deserves further study.

Under what conditions would there be significant removal of trace metals from sea water by phytoplankton? Can present-day surveys, concerned with trace metal distribution in the sea, possibly hope to relate differences in trace metal content of sea water to phytoplankton or are the differences observed largely dependent on other factors (i.e. sampling, inputs or other loss mechanisms). This paper examines these questions by calculating the removal of metal from sea water by phytoplankton under the wide range of conditions observed in the sea. Use is made of existing data on trace metal levels in sea water, concentration factors for phytoplankton and the relevant primary productivity and hydrographic data. In keeping with trace metal studies conducted by this laboratory these calculations will be confined to the toxic heavy metals copper, cadmium and lead.

Data used in calculations

Concentration factors for marine phytoplankton

Concentration factors (C.F.) are defined as the ratio of the element in or associated with an organism to the concentration in the medium under equilibrium conditions.

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Concentration factors for marine phytoplankton

Concentration factors (C.F.) are defined as the ratio of the element in or associated with an organism to the concentration in the medium under equilibrium conditions.

$$C\ F = \frac{\text{Concentration of metal in plankton (ug/gm dry wt)}}{\text{Concentration of metal in sea water (ug/ml)}}$$

Laboratory experiments have indicated that the accumulation of metal by plankton is largely dictated by surface adsorption and ion exchange processes (Glooschenko, 1969 and Gutknecht, 1964). Field measurements of metals in phytoplankton are therefore made difficult by the presence of detritus which also accumulates metals and which may be collected in the same sampling net. Recent studies by Riley and Roth (1971) in which they compared levels of metals in cultured phytoplankton and phytoplankton collected from the Irish Sea showed that the latter plankton had an enormously high value of lead which they associated with inorganic suspended material collected in the plankton haul. The most reliable information on the uptake of metals by phytoplankton is usually derived from the use of radioisotopes and a recent review by Rice et al. (1973) gives concentration factors of 3×10^4 for copper, 4×10^4 for lead and 1×10^4 for cadmium.

Primary Production

The world's seas may be subdivided into three distinct areas with regard to primary productivity; these are the open oceans, coastal waters areas, and the upwelling zones. Ryther (1969) has given the mean primary productivity (gm $C/m^2/yr$) for these areas as 50, 100 and 300 respectively. The high production at a given position in an upwelling zone results from the continual (or sporadic) movement of upwelled water offshore. The production in any parcel of moving water may be no higher than that of the water in a coastal area. Because of this fact subsequent treatment of metal removal by phytoplankton in this paper will be confined to the two general areas known as the open ocean and the coastal zones.

Strickland (1965) has suggested that the depth of the euphotic zones for the open oceans and coastal water areas are 100 and 10 respectively. By combining these data and assuming a uniform production over the year for both areas it is possible to calculate the production of plant life per unit volume of water in a known water column. The relevant data for concentration factors may then be used to assess the % removal of any one metal from this volume of water.

Trace Metal Values for Sea Water

Naturally occurring concentrations of trace metals in the sea are still not well defined despite the large amount of work done to date in this field. The most recent survey concerned with the trace metal levels in surface waters in the Atlantic and Indian Oceans (Chester and Stoner, 1974) has gone a long way to establish baseline levels in coastal waters and open ocean areas. Average values for copper and cadmium in these two regions are 0.9 and 0.8 ug Cu/litre and 0.09 and 0.07 ug Cd/litre respectively and average values for lead have been quoted by Chow and Patterson (1966) as 0.03 and 0.07 ug/litre.

Calculation of metal removal from sea water by phytoplankton

Let primary productivity ($gC/m^2/yr$) = P (1 gm C=2 gm dry wt)

metal level in sea water (ug/litre) = M

concentration factor = CF

$\therefore$ Metal accumulated by phytoplankton/m^2/yr = $\frac{2\ P \times CF \times M}{10^3}$ /ug

Amount of metal in a water column 1 m^2 and of height H metres = MH 10^3 /ug

% of metal taken up by phytoplankton from this water column in one year $= \frac{2\ P \times CF}{10^4 H}$

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$$\therefore \%\text{ of metal taken up by phytoplankton from this water column in one year} = \frac{2\,P \times CF}{10^4\,H}$$

N.B. Metal concentration M is not really necessary in this calculation.

Using the above equation and the relevant data for P, CF and H, calculations were made of the daily, monthly and yearly rate of metal removal from sea water for the two areas in question. The results of these calculations are presented in Table 1.

Results and Discussion

(a) Removal of metal from sea water

Open Ocean

The annual removal of these metals from the upper layers of the ocean by phytoplankton assimilation is extremely small. In terms of the entire water column of the ocean, which averages 3,800 m (Riley and Chester, 1972) these amounts of metal represent <0.1% of the entire water column's content of metals.

Coastal Waters

Assuming an average water depth of 50 m for coastal waters the % removal of metal annually by phytoplankton assimilation ranges from 4% for Cadmium to 16% for Lead. In an area like the North Sea (average depth of 50 m) this fraction of the metal removed by plankton could scarcely account for the fluctuations in trace metal content of sea water observed between winter and summer.

(b) Trace metal variations in relation to phytoplankton activity

Trace metal intercalibration exercises for sea water samples have indicated that most analytical techniques have coefficients of variation of $\nless$ 10%. In one exercise (Brewer and Spencer, 1970) the coefficients of variations for these three metals for a number of laboratories were observed to fall in the ranges, 24% - 79% for cadmium, 1% - 34% for copper and 2% - 36% for lead. The mean coefficients for copper and lead were given as 20.4% and 29.2% respectively. It should be borne in mind however that these figures do not include an error associated with the sampling part of any trace metal programme as they were based on the analysis of a subsample of sea water collected in a large sampling container. The coefficients of variations obtained by laboratories with known expertise however are usually lower than these mean values and fall in the range 10% - 15%. The error associated with sampling has rarely been quantified but for the sake of discussion an additional error of 10%, for this part of any trace metal study, would not be too unrealistic.

Bearing the above data in mind a preliminary examination of the results in Table 1 would indicate that the daily removal of metals by phytoplankton from the open ocean and coastal waters would not be detected by the differences in the trace metal levels in sea water from day to day. Likewise monthly observations on water collected from these areas would show little difference from month to month. In terms of the annual variations, or winter and summer observations, the coastal waters area is the one area in which differences could be observed. This assessment is based on the assumption that the water in these areas does not interact in any way with either (a) surface water which has not been exposed to phytoplankton activity or (b) water below the euphotic zone which has been brought up to the surface by vertical mixing. Either of these mechanisms will cause an apparent reduction in the % of metal removed by the phytoplankton, e.g. if the bottom waters in the North Sea should

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One may conclude from these calculations and observations that present-day surveys of trace metals in sea water, with their inherent deficiencies regarding sampling and analysis, have little hope of relating trace metal levels to phytoplankton activity in the open sea. In theory the coastal water programmes appear a little more hopeful on the basis of winter and summer observations, providing that one can time one's programmes to start at the beginning of the spring bloom and end just before winter overturn, and that vertical mixing is ignored. In practice, however, the problems of contamination during sampling, deficiencies in analyses and inputs from the atmosphere and runoff (Topping, 1974) will probably be large enough to camouflage any changes in levels caused by phytoplankton activity.

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Table 1

% Uptake of metal from sea water by Phytoplankton

Metal	OPEN OCEAN * (Water Column $1m^2$ x 100m)			COASTAL WATERS ** (Water Column $1m^2$ x 10m)		
	Daily	Monthly	Annually	Daily	Monthly	Annually
Cadmium	0.003	0.08	1	0.05	1.7	20
Copper	0.008	0.25	3	0.16	5.0	60
Lead	0.01	0.33	4	0.22	6.7	80

* Based on annual production rate of $50gC/m^2/yr$ and euphotic zone of 0-100m

** Based on annual production rate of $100gC/m^2/yr$ and euphotic zone of 0-10m