Hydraulics Research
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HEAVY METAL TRANSPORT BY PHYTOPLANKTON IN TIDAL WATERS

A literature review

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ABSTRACT

The ability to model the association of heavy metals and phytoplankton within an estuarine system would further improve the understanding of the heavy metal budgets of such systems and the environmental effect. This review, carried out by an environmental scientist and a mathematical modeller at Hydraulics Research, Wallingford with specialist advice from two marine biologists, was undertaken to acquire a greater understanding of the biological processes involved and to identify the main characteristics which would need to be modelled.

The phytoplankton biomass is the smallest of the three heavy metal "reservoirs", sediment and water being the other two. Seasonal variations in the species composition and size of the phytoplankton population are such that phytoplankton accumulation and transport of heavy metals is only of importance during the spring and summer when blooms are evident.

It is apparent from the literature that the mechanism of heavy metal uptake by phytoplankton is a two stage process with adsorption onto the cell wall followed by absorption. However, the uptake takes place rapidly and it is concluded that it is reasonable to assume that the uptake is instantaneous.

The chemical speciation of metals influences the phytoplankton uptake by affecting the biological availability of the metals. It has been suggested (Driver (1986)) that the complex processes can be simplified by assuming that the dissolved metal concentration is representative of that which is biologically available. All published experimental work reviewed refers to the total dissolved metal concentration.

Data produced by Davies (1979, 1980) from laboratory experiments on zinc and copper association with natural phytoplankton populations were adequately described by a Langmuir adsorption isotherm. Equivalent data on the more toxic metals cadmium and mercury is not at present available but it is felt that initially zinc or copper could be used for preliminary model development. It is considered inadvisable to develop a species specific model since the comparison of numerous laboratory studies indicated that distinguishing between diatoms and dinoflagellates represented the greatest refinement necessary.

It is concluded that the contribution of phytoplankton to the heavy metal budget of an estuarine system requires further study especially in view of the accumulation of heavy metals along the food chain. Consideration of the whole ecosystem is thought impractical at this stage but an understanding of the effect of phytoplankton is a necessary first step. The mathematical modelling of the uptake and transport of heavy metals by phytoplankton is considered feasible.

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1 INTRODUCTION

Heavy metals enter estuaries and coastal waters by various routes including fresh water and sewage discharges, the disposal of sewage sludge, industrial discharges, mining activities and subsequent metal refining, precipitation and from the sea. The potential dangers in the uncontrolled discharge of effluents containing high levels of heavy metals to the estuarine and marine environments were demonstrated by the mercury poisoning which occurred at Minamata in Japan (46). In order to remove or minimise such dangers it is necessary to gain a knowledge of the source of heavy metal inputs and to understand the processes which govern the transport and accumulation of metals in the marine environment.

The control of Pollution Act 1974 placed the responsibility for the control of polluting discharges to the estuarine environment upon the Water Authorities in England and Wales. If controls are to be set to limit the ultimate concentrations of heavy metals in the estuarine and coastal waters it is necessary to be able to predict the transport and accumulation of metals. Figure 1 illustrates some of the metal pathways in aquatic ecosystems.

Phytoplankton are known to accumulate certain heavy metals. Transport of phytoplankton by tidal and residual currents in surface waters and the settling of detrital material must therefore be considered in any realistic prediction on heavy metal transport.

The work described in this report fell into two categories. Firstly, a literature review was undertaken of the processes of uptake and concentration of heavy metals by phytoplankton. Secondly, the means by which the concentration and transport of heavy metals by phytoplankton could be incorporated into a mathematical model were investigated, with particular reference to Liverpool Bay.

An experienced biologist, Dr P Driver of W S Atkins and Partners, acted as a specialist adviser in the study and help was also given by Dr A Davies of the Marine Biological Association at Plymouth. The references are listed in alphabetical order.

2 HEAVY METALS IN THE MARINE ENVIRONMENT

2.1 The fate of heavy metals within the estuarine environment

Heavy metals vary from many contaminants in that they are normal constituents of the marine environment, and therefore traces at least are always found in marine organisms. Probably the most important feature which distinguishes the heavy metals from other toxic pollutants is that they are not biodegradable, and having entered the environment their potential toxicity is controlled to a great extent by biological and geochemical factors (Jarvis (21)).

The fate of heavy metals such as lead, zinc, cadmium and mercury in the estuarine environment is of extreme importance due to their impact on the ecosystem (Meyerson et al (33)). This is especially true in urban estuaries where the inputs are non point in nature and include municipal and industrial discharges, urban runoff, atmospheric contributions and the presence of harbour facilities with heavy ship traffic. The metals in such an environment can be accommodated in three basic reservoirs: water, sediment and biota. The importance of the biota reservoir is quite evident as organisms in the estuary can be adversely affected and human health hazards can arise through consumption of the contaminated organisms.

The potential hazardous effects of lead accumulation by phytoplankton has been emphasised by Schulz-Baldes and Lewin (45), stating that even if lead is not appreciably toxic at present environmental levels, its uptake by phytoplankton may be of great ecological importance, since such organisms may not only play a role in the geochemical distribution of lead, but also, by serving as food, transport the lead to higher trophic levels.

The biota reservoir however, is small compared to the water, which in turn is much smaller than the sediment reservoir. Even so, despite the phytoplankton representing a small reservoir for metals in relative terms, the dismissal of their influence on the heavy metal budget of an estuarine system could lead to significant errors. For example, cells of the common diatom Skeletonema costatum have been found to have areas in the range 240-400 μm^2, Davies (9), hence a million cells would have a total surface area exceeding $2 cm^2$. A million diatoms per litre of sea water is by no means unusual with considerably greater numbers occurring during spring blooms. Hence Davies (9) stated that it was not surprising that the adsorption onto the outside of cells represented an important aspect of metal uptake by phytoplankton.

Having identified the need to understand the potential accumulation of heavy metals by phytoplankton, it would be advantageous to be able to incorporate their effect within a mathematical model with the aim of being able to predict the effect of changes in the disposal of heavy metals on the estuarine and coastal environment.

2.2 Liverpool Bay

Liverpool Bay represents an example of a system whereby the management and control of polluting loads could be benefited by the ability to predict the environmental effect of altering the metals input to the Bay.

Quantities of domestic and industrial sludge, liquid wastes and spoil enter Liverpool Bay from rivers, coastal outfalls and ships. All these discharges, including Manchester and Salfords sludge disposal operations have continued for many years and constitute a continual load to the bay [DoE (13)]. The Liverpool Bay working group reported in 1972 (16) that the waters of the bay were rich and generally supported algae typical of a fairly muddy open sea estuary. From observations undertaken in 1971 [DoE (14)], it was concluded that when conditions are suitable, high standing crops of phytoplankton are produced in Liverpool Bay, which by accumulating heavy metals could considerably influence their distribution.

2.3 Biological availability of metals

As a general rule the organic constituents of sewage sludge bind metals into a form that renders them biologically unavailable [Waldichuk (49)]. This may occur through chelation of the metals by organic compounds or by simple adsorption. A high organic content in the sediments usually ensures that metals are quite firmly fixed on the suspended sediments and are not freely available to the marine biota in the water column.

The availability of heavy metals for bioaccumulation (and their toxicity) is also influenced by chemical speciation [Nelson and Donkin (35)]. It is known, for example, that alkyl species of mercury are more toxic to biota than inorganic forms.

The speciation of individual metals depends upon ambient conditions, the interactions of which are complex.

Taking Liverpool Bay as an example, the amount of biologically available metal present at any one time will therefore depend upon a wide range of factors related to the nature of the sludge and suspended sediments, and to the physico-chemical conditions of the sea water (pH, temperature, salinity, etc). It would be very difficult to take account of all of these factors and therefore the relationship between total metal inputs to the Bay and the amounts of metal biologically available cannot be reliably calculated. It is therefore assumed that for the purposes of the development of a phytoplankton and heavy metal model that published dissolved metal concentrations may be taken to represent those biologically available (Driver (16)).

2.4 Concentration of heavy metals in British Coastal Waters

The problems associated with metal accumulation by phytoplankton will obviously be more evident in areas experiencing long term inputs of metals. A detailed knowledge of metal levels in coastal areas and the open ocean is thus required if realistic concentration factors for phytoplankton are to be calculated. Table 1 summaries dissolved metal concentrations in British Coastal Waters and Figure 2 illustrates the distribution of cadmium in Liverpool Bay, Cardigan Bay and the Bristol Channel.

The significantly higher levels of metal concentrations in solution at shoreline sites compared to offshore sites is clearly illustrated by the data for the East and West Irish Sea and Conway Bay. For example, comparison between the West and East Irish Sea is 3.0 and 4.2 for zinc and 0.59 and 0.66ppb for copper, indicating the influence of metals discharged into Liverpool Bay. Similar differences may also be identified between the local and offshore water of Conway, 3.0 and 0.7 for copper and 8.8 and 5.8ppb for zinc. Reductions of metal concentration with increasing salinity highlights the considerable input of metals from rivers and coastal outfalls. Ratios between coastal and offshore waters of 8:1 for zinc, 6:1 for manganese and 3:1 for cadmium have been quoted for Liverpool Bay (DOE (13)). (Ratios for copper, iron and nickel were less than twice those concentrations offshore).

The presence of a physical discontinuity marking the boundary between coastal and offshore water in Liverpool Bay tends to retain pollutants in the near shore waters. Such concentration of nutrients entering the coastal waters promotes the growth of dense blooms of the dinoflagellates, _Phaeocystis_ and _Gyrodinium aureolum_ in the late spring and summer respectively (DOE (13)). Therefore the presence of such blooms of phytoplankton in regions of metal pollution inevitably provide ideal conditions for considerable metal accumulation.

The sludge disposal that takes place in Liverpool Bay contributes to the metal concentration in the Bay, thus again providing metal for potential accumulation in areas of phytoplankton production.

Table 2 illustrates the generally higher standing crops of phytoplankton in the coastal areas of central Liverpool Bay, also identifying the _Phaeocystis_ and _Gyrodinium aureolum_ blooms in late spring and summer. The Marine Science Laboratory has shown that much larger quantities of plant pigments are present below

5m depth - and therefore the figures quoted in Table 2 should be considered conservative, representing surface samples. The succession of phytoplankton species in Liverpool Bay is identified in Table 3. During winter, phytoplankton are scarce in Liverpool Bay, with a standing crop of approximately 0.2g/m^3 of chlorophyll a and production is close to zero. During this period the role of phytoplankton in the cycling of metals would be negligible and it therefore does not seem unreasonable that in modelling of Liverpool Bay metals cycling in mid-winter conditions, phytoplankton be ignored.

3 HEAVY METAL ASSOCIATION WITH PHYTOPLANKTON

3.1 Concentration factors of metals by phytoplankton

Detailed laboratory experiments have been undertaken by a number of investigators in an attempt to understand the mechanism of uptake of the metals by the phytoplankton (Davies (9,10,11,12,) Meinhard-Baldes Schulz and Lewin (45), Romeo and Barelli (18)). Two mechanisms of uptake are generally known to occur, adsorption onto the external surface of the cell walls and absorption whereby the phytoplankton take up metals from solution through their cell walls against a concentration gradient. The combined effect results in considerable accumulation of heavy metals by the phytoplankton, as shown by the concentration factors in Table 4a. It should be noted that such figures should really be more correctly termed 'concentration ratios', for example, the factors/ratios calculated by Bowen (4) were based on data for elements in the open ocean provided by Goldberg in 1963, with data for the same elements in dry plankton produced by Vinogradova and Kovalsky in 1962 from the Black Sea. Likewise Lowman

(9) derived his concentration factors also from the data of Vinogradova and Kovalsky. Typical concentration ratios although not as useful as direct concentration factors, do however provide an insight into the extent of the problem of metal concentration.

Further examples of concentration factors (Jennet et al (22)) are shown in Fig 4(b). There are great differences in the concentration factors for different heavy metals. The ability of planktonic algae to accumulate metals is generally in the order: mercury; lead; cadmium (Jennet et al), or: mercury; silver; zinc; cadmium (Fisher et al (17)).

Some difference in accumulation of metals by diatoms and flagellates have been observed - the necessity to distinguish between these types of phytoplankton within a mathematical model is discussed later.

In order to understand the significance of such metal concentrations to the mass balance of metals within a system, a rough estimate of the quantity of a sample metal (Cu) contained in the phytoplankton, in solution and on suspended sediments in Liverpool Bay has been made by Driver (15). The following assumptions have been made:

Size of Liverpool Bay	2500km^2 x 25m deep
Concentration of dissolved Cu	1.5mg/m^3
Mass of Cu on suspended solids	100mg/kg
Suspended sediment load	50ppm (summer max)
Density of algal cells	1.6 million cells/litre (August bloom conditions)
Shape of individual cells	50 x 3μ rod
Cu conc. factor for algae	17,000

The above assumptions resulted in the following mass distribution of Cu in Liverpool Bay.

Cu in solution	900 tonnes
Cu on suspended solids	300 tonnes
Cu in phytoplankton cells	10 tonnes

Although the mass of metals held in the biota is small compared to the amounts held in solution and adsorbed onto suspended matter, it is being continuously recycled as the algae grow, die, settle and decay.

Its incorporation within a mathematical model of heavy metal transport would therefore be advantageous.

The work of Knauer and Martin (25) provides an insight into the relevance of phytoplankton in metals cycling. They analysed metal concentrations (Cd, Cu, Mn, Pb and Sn) in surface water and in mixed phytoplankton from Monterey Bay over a period of one year.

Generally, metal levels in the near shore surface water appeared to be more dependent on hydrological fluctuations than on biological factors, with the exception of cadmium whose concentrations in sea water decreased during the peak of algal productivity whilst increasing in the phytoplankton. The system is described in more detail below.

During the period of intense upwelling productivity was relatively low, an average of 8mg $C/m^3/hr$. The effects of phytoplankton on dissolved metal concentration were therefore secondary, and dissolved metal concentrations were in fact at their annual highest. During the period of low upwelling, ie, stability of the water column and higher surface temperature, productivity reached high peaks of 60mg $C/m^3/hr$. If phytoplankton were to influence sea water metal concentrations, the effect would be expected during this period. In fact, only cadmium decreased significantly (although decreasing trends for copper, lead and zinc were observed during a later productivity peak). Data collected on metal concentrations in sea water and phytoplankton during the period of high productivity enabled estimates to be made of the magnitude of the influence of phytoplankton.

If an average of 55mg C/m^3/hr were fixed during the 30 day period of high productivity, and if this rate persisted for 6 hours per day, then about 10mg C/l would be fixed during the period. Average levels of cadmium in the phytoplankton during this period were 2 µg/g (dry weight). If it is assumed that the average carbon content of diatoms is 20% (dry weight), then the phytoplankton contain an average of 0.01 µg/ Cd/mg C. Therefore during the period of high productivity, 0.1 µg Cd was removed by the phytoplankton from each litre of surface water. If the average Cd concentration of 0.14 µg/litre during the period of low productivity is assumed to be the concentration immediately preceding the onset of high productivity, then the uptake of Cd during the 30 day period can be calculated by subtraction of the lowest Cd value (0.06 µg/l) measured at the end of the the high productivity period. The result (0.08 µg Cd/l) is in good agreement with the 0.1 µg/ Cd/l uptake previously calculated for the phytoplankton and it can therefore be safely assumed that the decrease in dissolved cadmium was due to phytoplankton uptake. (Similar calculations showed that 0.14, 0.4 and 0.85 µg/l of Cu, Mn and Zn could be taken up by the phytoplankton. These amounts are not great enough to produce marked changes in sea water concentration, similar to those found for Cd).

3.2 Mechanisms of metal uptake

Theory

In order to be able to predict the amount of a metal associated with a phytoplankton population, a detailed understanding of the uptake processes is required. It should be appreciated, however, that it may not be necessary to incorporate every stage within the final model in order to gain a realistic prediction.

Laboratory experiments have been reported, with various species of phytoplankton, attempting to identify the generally accepted theory of a two-stage metal uptake process involving adsorption and absorption. Davies (9) provided a tentative description of these processes as follows.

"The physico-chemical nature of the surfaces of phytoplankton may be considered as consisting of a mosaic of interspersed cationic and anionic exchange sites, provided by carboxylic, sulphydryl, phosphatidic, amino and other groups, the net charge on the surface being related to the degree to which the sites are occupied by protons and the other ions present in sea water, ie, being a function of the pH and salinity. The initial uptake of a positively charged heavy metal ion can then be envisaged as occurring by the displacement of the cations already occupying the binding sites, the amount of metal finally bound onto the surface at equilibrium being determined by the relative affinities of the sites for the metal and sea water cations and also the concentrations of each remaining in solution; in accord with the principles of ion-exchange. The metal once bound on to the surface, would be suitably placed for being transported, actively or passively, through the diffusion barrier presented by the cell membrane in the cytoplasm".

Experimental support of the two-stage process theory

Schulz-Baldes and Lewin (45) were able to produce a greater understanding of the mechanism and permanance of lead uptake by two marine phytoplankton organisms, from the results of laboratory experiments on cultures of the organisms. They clearly demonstrated that lead ions are first clearly bound to the cell surfaces, and only later penetrate to deeper sites, where they may be expected to exert their main biological effects. Their experiments involved the exposure of cultures of the diatom, Phaedactylum tricornutum and the green flagellate, Platymonas subcordiformis to varying lead concentrations, along with varying additions of EDTA in an attempt to identify the strength and permanence of the bonds between the metal and the algal cell. [EDTA - ethylenediaminetetra acetic acid is a chemical that promotes chelation (chemical association) of metal ions, the complexes of which are not significantly adsorbed on the surface of solids, and hence represents competition for the algal cells for the bonding of the remaining free metal ions. If present in high enough concentrations, it may promote desorption of metal from the phytoplankton, and therefore may be used experimentally to identify the permanence and strength of metal: algal bonds.]

The first phase of uptake (that of adsorption), was completed within minutes after addition of the lead. The relationship between the amount of lead adsorbed and that in solution, after one hour of exposure when the cells may be considered to be in equilibrium with the surrounding medium is illustrated in Figure 3. There appears to be no difference between the diatom and dinoflagellate, in both cases the amount of lead adsorbed being directly related to the concentration of lead in solution. By converting the concentration of lead in solution to mg/l thus both scales representing ppm, the concentration of lead per dry weight of algae is approximately 2.0 x 10^4 times greater than the concentration in the surrounding medium, representing a concentration factor of the same order of magnitude as quoted in Table 4a.

The limited number of binding sites of the diatom was illustrated by exposing the cells to high concentrations of dissolved lead and then determining the amount of lead taken up. Despite differences in cell numbers and lead concentrations, Schulz-Baldes and Lewin (45) claimed a maximum concentration of adsorbed lead of about 12,000 ppm, suggesting the presence of a limited number of binding sites.

The extent of absorption of the metal by the phytoplankton was shown to be related to the length of exposure of the phytoplankton to the free ions. When pre-treated cells were exposed to high concentrations of EDTA (10^{-2}m) much of the adsorbed lead was removed. However, the longer the lead pretreatment period, the less readily the metal was removed from the cells. Such an increase with time of the residual lead burden after EDTA extraction identifies the greater strength of the association between absorbed metal and the algae, the metal having been translocated to within the cell wall, the plasma membrane and eventually to the cytoplasm.

The uptake of metals depends on many different factors, for example, species composition, diversity of the culture conditions and chemical state of the metal in the culture medium. Numerous experiments have been performed, illustrating the effect of chemical chelators, which have been shown to reduce metal accumulation by Phaedactylum tricornutum and Nannochloris atomas by Cossa and by Sunda and Guillard (1976) respectively (Ref 9). However, less work has been performed identifying the effect of natural chelators such as humic acids. Even so, it is generally acknowledged that the chemical form of a metal does influence its uptake, free ions being readily adsorbed. For example, during experiments on the adsorption of Zn by the diatom Phaedactylum tricornutum, Bernhard and Zattera (50) showed that Zn^{65} added in the ionic form was more readily adsorped than some of the Zn already present, which appeared to have been firmly bound, probably in the organic form.

Laboratory experiments performed with cultures of Cricosphaera elongata by Hardstedt - Romeo and Barelli (18), identified an increase in the concentrations of cadmium and copper accumulated with increasing concentrations of metals in the medium, as well as a reduction in the amounts of metals accumulated in the presence of natural phytoplankton exudates. This latter phenomenon was considered to be due to a change in the chemical form of the metal ions initially added. As only a small percentage of the metal introduced into the culture medium was taken up by the cells this indicated the presence of an upper limit. The metal uptake was explained to be initiated by an ion exchange type of reaction, the amount of metal finally bound on to the surface of the cell at equilibrium being determined by the relative affinities of the binding sites for metals, and the sea water cations, and also the concentration of each remaining in solution. Thus, by increasing the metal concentration the equilibrium among the metal itself, other cations and organic ligands may be affected.

The decreasing uptake of cadmium and copper in the presence of organic substances liberated by the phytoplankton into the culture medium could be regarded as a indication that the potential accumulation by phytoplankton of metals may not be as great as feared.

Time to reach equilibrium conditions

Controlled Experimental Ecosystem (CEE) studies were undertaken in Saanich Inlet, Vancouver Island, Canada by Wallace et al (50). The experiments to study the biochemical fate of mercury, showed that as the primary productivity increased the mercury half life decreased. The kinetics of adsorption and complexation of mercury by organic matter in the CEE were not specifically analysed. Even so, a probable upper limit to the time required to reach equilibrium by particulate matter was suggested of the order of an hour. The maximum uptake of mercury by plankton was considered to be of a similar order of magnitude.

The actual rate of metal uptake will vary according to species and ambient conditions. Fisher et al (17) found that maximum concentrations were generally reached within 24 hours, and under most circumstances metal level per cell did not change appreciably beyond 12 hours. In the case of cadmium, accumulation was completed in 4 hours. Jennet, Smith and Hassett (22) reported the removal of lead and mercury from solution within 3 hours by various types of phytoplanktonic algae.

Equilibrium between phytoplankton and its surrounding media may be considered to take place therefore from between a few minutes up to a number of hours. With respect to the modelling of metals within an aquatic system, it does not seem an unreasonable assumption to consider that metal uptake by phytoplankton is instantaneous and thus all phytoplankton are in equilibrium with surrounding sea water (Davies - informal discussion).

3.3 Adsorption of zinc and copper to phytoplankton assemblages

A series of laboratory experiments using natural phytoplankton assemblages from the English Channel in 1979 and 1980, undertaken by Davies and Sleep (10, 11) were aimed mainly at identifying the possible inhibitory and therefore toxic effects of heavy metals (zinc and copper being used as examples) on phytoplankton production.

Although the final results are not of direct application for the modelling of metal accumulation, the experimental procedure identified quite detailed information of the relationship between the metal concentrations in solution and the amount adsorbed by the phytoplankton.

Equilibrium values of copper and zinc adsorbed on to natural assemblages of phytoplankton were identified by Davies and Sleep (10, 11) from laboratory experiments. The results indicated that the metal: chlorophyll a ratios (being a measure of phytoplankton quality), could be related to the metal concentrations in the water by an equation of the same form as the Langmuir adsorption isotherm.

$$z = \frac{z_{max} \cdot C}{(k+c)}$$

where

z	is metal/chlorophyll a ratio (μg metal/μg Chl a)
z_{max}	is the maximum metal/chlorophyll a ratio (μg metal/μg Chl a)
c	is the metal concentration in solution ($\mu g/l$)
k	is the metal concentration in water when phytoplankton cells reach half saturation (μg metal/l)

It may thus be possible to employ the above equation to describe the concentration of metal adsorbed onto natural populations of phytoplankton elsewhere, if the metal concentration in solution, c, is known, using the constants produced from experimental study. A great deal of emphasis shall be placed on the results produced by Davies and Sleep (10,11), as there appeared to be a lack of reliable data from other sources. Although all the results for zinc and copper will be discussed, it is appreciated that other metals may react differently, but as this report represents only the initial stages of the development of model techniques for heavy metals and phytoplankton interaction, the consideration of these two metals may be considered adequate. Davies (10, 11) performed his experiments using natural assemblages of phytoplankton obtained from the English Channel (50°15'N, 4°13'W) in July 1978, and November and December 1979, for zinc and copper respectively. The dates and species composition of the sea water samples are summarised in Table 4.

The relationship between the carbon fixation rates of the phytoplankton assemblages and the metal concentrations in solution are shown in Figures 4a and 5a. In both cases a reduction in production occurred. The effect of copper was a lot more severe with a greater reduction occurring with lower concentrations of metal. A ten percent variation in results due to experimental procedure was estimated and hence any reduction in production more than 10% of the mean control value was considered to be the result of metal inhibition.

The relationship between the metal adsorbed by the phytoplankton assemblages and the metal concentrations in solution in equilibrium with the phytoplankton are shown in Figures 4b and 5b. The curves drawn represent the best fit of the Langmuir adsorption isotherm. The experiments were conducted at constant temperatures, 14°C for zinc and 12°C for copper, the temperatures representing the average temperature of the water sample at the time of collection.

The values of the constants z_{max} and c obtained from adsorption isotherms established for several samples are given below:

	z_{max} $\left(\frac{\mu g\ \text{metal}}{\mu g\ \text{chlorophyll}\ \underline{a}}\right)$	k (µg metal/l)
Copper		
Sample a	0.39	12.4
b	0.39	13.6
zinc		
Sample a	0.42	14.7
b	0.28	11.4
c	0.40	19.4

The above constants suggest that the maximal metal binding capacity is proportional to the chlorophyll *a* content rather than species composition. The species composition used for the zinc and copper experiments were different, but there was very little variation between the z_{max} and k values. The zinc and copper possess similar affinities for binding sites as shown by the small variation between the half saturation values.

Ranges of zinc and copper concentrations recorded in British Coastal waters have been summarised in Table 1. The ranges of copper and zinc concentrations, 0-20 µg/l and 0-80 µg/l respectively, exposed to the phytoplankton by Davies and Sleep (10, 11) cover the ranges tabulated and are within the same order of magnitude and therefore it could not be unreasonable to assume that the same Langmuir adsorption isotherm, could realistically be applied to other areas.

The half saturation values produced for zinc and copper generally occur at concentrations slightly greater than the mean concentration quoted in Table 1, the concentrations of copper being significantly less than the k values. This indicates that the maximum potential accumulation by phytoplankton is significantly higher than may be experienced at typical concentrations of metals in British coastal waters.

A linear relationship between the carbon fixation rates (productivity) and the amount of metal adsorbed onto the phytoplankton is shown in Figures 4c and 5c. Again the greater toxicity of copper is obvious. For both copper and zinc, the linear relationship highlights the dependence of carbon fixation rate inhibition on the amount of metal adsorbed, as opposed to the metal concentration in solution as suggested by other authors, Riley and Roth (41) and Mandelli (30). However, if equilibrium is assumed to be instantaneous the two hypotheses are not necessarily inconsistent.

3.4 Variation between different species of phytoplankton

Most experiments undertaken using phytoplankton use cultures of one species alone. The choice of species being biased towards those that may survive in laboratory conditions for the greatest length of time. Phaedactylum tricornutum is one such species, hence its presence in most experiments, Schultz-Baldes and Lewin (45), Cossa (from 9), Bernhard and Zattera (from 50). Davies and Sleep (10, 11) used natural assemblages of phytoplankton to reproduce natural conditions, and therefore their results are likely to be more realistic. Their two sets of experiments used water samples containing totally different combinations of species, thus the consistency of their results and therefore the lack of dependence upon the nature of the phytoplankton suggest that the maximal metal binding capacity is proportional to the chlorophyll a content.

The results produced by Schultz-Baldes and Lewin (45) shown in Figure 3, identify a similar consistency between the amount of lead accumulated by two species even though one was a diatom and the other a dinoflagellate. However, other experimental work has indicated that flagellates have a greater than average affinity for metals than other species. For example, Jennet et al (22) showed Chlamydomonas to be superior to other phytoplankton species tested in its ability to take up lead, Table 7 highlights such differences. Wolter et al (52) and Mandelli (30) have also noted such differences for cadmium and copper respectively. It has been suggested by Hessler (19) that the flagella of Platymonas subcordiformis provides the sites for a significant fraction of its lead uptake. This would provide an explanation for the apparently greater ability of flagellates to accumulate metals. The evidence for greater than average metal uptake by flagellates is of particular relevance to Liverpool Bay where annual blooms of the dinoflagellates Phaeocystis pouchetii and Gyrodinium aureolum occur in early summer and autumn respectively. The dinoflagellate Noctiluca miliaris also accumulates in bloom patches and streaks at the surface of Liverpool Bay during mid-summer calms.

These examples suggest that it perhaps is not necessary, and would be unreasonable, to attempt the development of a model that is species specific. Separation into the two main groups, diatoms and dinoflagellates, could be considered the greatest refinement necessary in order to obtain a realistic model. Such an approach could account for seasonal variations due to the spring and summer dinoflagellate blooms.

3.5 Metal toxicity - inhibition of production

The minimal levels of copper and zinc in solution at which carbon fixation inhibition occurs are 1 to 2.5 μg/l and 10 to 15 μg/l respectively (Figs 4a and 5a). Copper is considerably more toxic than zinc.

There should be an awareness of the potential toxicity of metals on phytoplankton and hence the inhibition of productivity. It may be argued that in areas of chronic long term exposure to sub-lethal concentrations, development of metal tolerance by phytoplankton assemblages may occur, thus leading to a reduction in the effective toxicity of the metals. Thomas et al (12) identified that a phytoplankton population in mercury containing enclosures rapidly developed tolerance towards the metal which presumably accounted for the eventual resurgence of growth in the polluted water. Evans (26) identified that the Mersey region was associated with algal blooms and reduced species diversities, thus suggested that the flora may be under stress. Table 7 provides an indication of the possible effects of heavy metal concentrations of 10 µg/l on the productivity of phytoplankton populations, mercury representing the most toxic metal.

It is not necessary to provide a detailed description of the varying toxicities of metals in this report, however, it is important for there to be an awareness of the potential effects as reduction in productivity will inevitably lead to reduced phytoplankton blooms, and hence reduced accumulation. A reduction in phytoplankton blooms would also have an effect on higher levels of the ecosystem. It should also be considered that toxicity of a metal is related to cell numbers and the amount of metal adsorbed to them, and therefore if cell numbers increase, even with an increase in metal concentration, this may not necessarily represent an increase in toxicity.

Elevated levels of dissolved organic matter

The presence of elevated levels of dissolved organic matter may also reduce the metal toxicity as complexation reduces the biological availability. This point could be of significant importance when considering regions such as Liverpool Bay, where areas of elevated organic matter resulting from sewage sludge disposal may reduce the effective toxicity of the metals present to the phytoplankton, and also may promote desorption of metals from phytoplankton transported from waters of lower organic matter content.

4 TRANSPORT OF PHYTOPLANKTON BY TIDAL AND RESIDUAL CURRENTS

It is necessary to relate the accumulation of heavy metals by phytoplankton to overall metal transport and cycling in an estuarine system. Such biological mobilisation may result from the biochemical uptake of the metal by an organism followed by its release into the water column on the death and decay of an organism, after the physical movement of the organism out of the system by tidal and residual currents.

Biochemical processes only transfer heavy metals from one phase to another. Their significance is to the relative mobility of different phases which can affect rates of metal transport through biological and physical interactions. So although chemical processes are not directly responsible for, they are vital, to the mechanism of heavy metal transportation in the estuarine environment (Turner and Burt (48)).

The distribution of cadmium in the surface waters of Liverpool Bay, Cardigan Bay and the Bristol Channel is shown in Figure 2. The Bristol Channel in particular shows that water movements along the channel are responsible for the 'streaming', along the northern part of the channel. Whilst some of the phytoplankton, flagellates, are capable of limited locomotion, they generally drift with the currents. If phytoplankton are accumulated within surface waters one could reasonably expect that they be transported with the surface currents along with their accumulated metals. Such strong seaward surface flow of an estuarine system may tend to disperse pollutants rapidly (Parsons et al (38)) and hence such water movements should represent an important part of a heavy metal and phytoplankton model.

It is important to obtain an accurate understanding of water mass movements involved before biological phenomena such as phytoplankton growth, and hence possible metal accumulation, can be realistically inferred (Riaux and Douville (40)). Cloern and Cheng (7) from a study in the Northern San Fransico Bay, California, noted that inorganic particulate distribution was totally governed by water movement transport phenomena, however, as algae cells grow, divide, decompose or are consumed, the distribution, abundance and size composition of phytoplankton in partially mixed estuaries are determined by the kinetics of the biological processes in addition to the same transport mechanisms that affect suspended solids.

Vertical mixing initiated by wind may stimulate an increased productivity of a phytoplankton population and an associated increase in metal accumulation (Jones (24)), particularly if combined with long residence times Toner (47) . The factors promoting such increases in productivity need to be investigated. Vertical mixing sustains phytoplankton in the water column, thus retarding settling of cells to the bottom. Upwelling of nutrient rich water promotes additional phytoplankton growth and, by circulating phytoplankton vertically through various levels of the euphotic area, ensures that they receive both sufficient energy for the light phase of photosynthesis and the near darkness required by some for metabolism.

It can be concluded that in order for the concentration of metals accumulated by phytoplankton to be of any predictive value, it is essential that any model should incorporate a realistic approximation of the transport phenomena associated with estuarine circulation.

5 SUMMARY AND CONCLUSIONS

Experimental evidence supports the existence of a two-stage uptake of metals by phytoplankton with adsorption onto the cell wall followed by absorption. There is a maximum amount of metal that can be adsorbed by a cell which is due to the limited number of binding sites. Uptake of metals occurs quite quickly with phytoplankton reaching equilibrium with their surrounding media in a few hours.

The amount of metal taken up by assemblages of phytoplankton in different dissolved metal concentrations can be obtained using the Langmuir adsorption isotherm if the necessary constants are known. Data for copper and zinc is available for the natural assemblages of phytoplankton found in British coastal waters from work by Davies and Sleep (11,10).

Heavy metals can be toxic to phytoplankton, reducing productivity, which could have an important effect on the coastal environment and indirectly affecting metal accumulation. Concentrations of metals are generally higher in nearshore waters where the elevated nutrient concentrations tend to support higher standing crops of phytoplankton. The effect of toxicity cannot therefore be ignored.

If predictions are to be made of the effect of sludge disposal or other inputs of metals on the estuarine and coastal environment, it is advisable to at least consider the role of phytoplankton. It is impractical to develop a mathematical model that is species specific at this stage. Initially a division between diatoms and dinoflagellates would probably suffice. There is a large seasonal variation in the species composition and magnitude of the phytoplankton population. During the winter there are negligible standing crops of phytoplankton and it is therefore only necessary to consider the role of phytoplankton during spring and summer.

It is thought practical to develop a basic mathematical model of the uptake of metals by phytoplankton and the resultant transport, death, settlement and decay. Liverpool Bay represents an almost ideal site to test such a model since relatively large amounts of metals are introduced into the system annually and extensive algal blooms during spring and summer give a significant potential biotic reservoir.

6 ACKNOWLEDGEMENTS

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TABLE 1

Dissolved metal concentrations in British waters

(ppb)

Metal Location		Ag	Cd	Cu	Fe	Mn	Ni	Pb	Zn	Reference
W. Irish Sea-Mean		-	-	1.3	0.1	0.5	0.5	-	7.1	
1969	Range	-	-	0.7 -2.8	0.1 -0.6	0.3 -0.8	0.3 -1.2	-	3.0 -20.0	
1970	M	-	0.11	0.59	0.09	0.53	0.38	0.19	3.0	39
	R	-	<0.01-0.52	0.18-3.75	0.03-0.6	0.15-2.6	0.22-0.55	<0.05-1.2	0.8-9.0	
E.Irish Sea -	M	-	-	1.3	0.5	0.6	0.7	-	6.5	
1969	R	-	-	0.8 -1.9	0.1 -1.1	0.2 -2.2	0.3 -1.4	-	1.8 -14.8	39
1970	M	-	0.04	0.66	0.18	1.95	0.71	0.11	4.2	
	R	-	<0.01-0.62	0.28-0.98	0.06-1.9	0.22-14.6	0.32-22.9	<0.05-1.0	2.3 -7.5	
Liverpool		-	-	1.45	-	-	-	-	11.86	2
Bay 1972		-	-	0.9 -3.03	-	-	-	-	2.3 -47.6	
1976 July		-	0.15	0.85	2.25	1.6	0.95	-	9.05	
		-	0.1 -0.5	0.40-2.0	1.4 -4.4	0.4 - 6.9	0.4 -1.5	-	2.8 -23.5	
Sept		-	0.15	1.0	2.65	1.46	0.86	-	9.14	16
		-	0.1 -0.3	0.4 -3.3	1.8 -6.3	0.3 -3.0	0.4 -1.3	-	4.6 -15.5	
Oct		-	0.35	1.0	1.4	0.71	1.45	-	17.88	
		-	0.2 -1.0	0.5 -2.3	0.7 -3.1	0.3 -2.2	0.6 -2.6	-	9.2 -40.1	
Conway (local)		-	0.76	3.0	-	-	3.7	3.6	8.8	39
Conway (ofshore)		-	0.2	0.7	-	-	0.7	0.1	5.8	
English	M	-	-	1.3	0.7	0.4	0.7	-	6.4	39
Channel 1969	R	-	-	1.1 -1.6	0.2 -2.3	0.3 -0.5	0.5 -1.3	-	4.3 -9.0	
1970	M	-	0.06	0.46	0.3	0.32	0.38	0.17	2.0	
	R	-	0.01-0.38	0.23-1.29	0.06-1.3	0.10-0.49	0.22-0.95	0.05-1.1	1.2 -3.8	
NE Atlantic	M	-	0.04	0.26	-	0.06	0.43	-	3.0	39
1970	R	-	0.01-0.41	0.05-0.80	-	0.03-0.09	0.29-0.66	-	1.4 -7.0	
Bristol	M	-	1.13	2.07	-	-	-	1.18	9.98	2
Channel	R	-	0.28-4.20	1.02-4.74	-	-	-	0.35-5.06	3.57-21.42	

TABLE 2

Quantities of plant pigments (chloroghyll + phaeophytic pigments)
(µg|1)

		Central Liverpool Bay (surface waters)		Coastal Water of Liverpool Bay 1976	
		1975	1976	Lancashire Coast Water	North Wales Coast Water
May	Mean	2.8	-	8.8	14.0
	Max	6.2	-	11.1	34.4
June	Mean	1.7	5.7	2.4	7.9
	Max	7.7	13.5	3.7	*23.3* *Phaeocystis*
July	Mean	-	1.1	3.7	2.2
	Max	-	2.0	6.3	3.0
Aug	Mean	3.6	-	5.4	11.7
	Max	10.7	-	11.3	21.1
Sept	Mean	3.2	3.3	28.0	49.2
	Max	14.9	25.8	*108.8* *Gyrodinium aureolum* bloom	66.4
Oct	Mean	30.5	-		
	Max	*104.0* Bloom of *Gyrodinium aureolum*	-		

TABLE 3

Phytoplankton Species in Liverpool Bay

Source: LWSF(26)

Seasonal succession of algae in the eastern Irish Sea, as exemplified by the succesion in Heysham Channel

Spring outburst - commenced March

Biddulphia aurita
Skeletonema costatum
Navicula pelagica Filamentous algae
Asterionella japonica
A Kariana
Thalassiosira rotala

After spring outburst in late May

Phaeocystis colonial flagellate
Nitzschia delicatissima

Summer succession

Rhizosolenia delicatula
Leptocylindrus danicus diatoms
L minimum
Chaetoceros spp

Noctiluca scintillans (hot calm-red tide dinoflagellate)

Late summer flora

A japonica
C debile
C sociale
L danicus
G aureolum (red dinoflagellate)

N closterium => ubiquitous - never abundant, but was observed throughout the year

Autumn

G aureolum

Nov - Feb - sparse winter flora

Coscinodiscus spp *Thalassiothrix nitzshiodes*
Biddulphia spp and typical spring dintoms.

TABLE 4a

Concentration factors of metals by phytoplankton

Metal	Conc in open ocean ppm	Conc in phytoplankton (diatoms) ppm	Concentration Factor	(asuming organism contains 75% water)
Ag	0.0003	0.25	210	
Cd	0.00011	0.4	910	
Cu	0.003	200	17000	
Fe	0.01	3500	87000	45000
Pb	0.00003	5	41000	40000
Zn	0.01	2600	65000	26000
	Goldberge (1963)	Vinogradova & Kovalsky (1962)	Bowen (1966)	Lowman (1971)

TABLE 4b

Metal Concentration Factors

Organism	Type	Habitat	Type of	Concentration	Basin	Researcher
			ARSENIC			
Phytoplankton	Assorted	Lake Michigan	Ecological	1.5×10^3	Wet	Copeland & Ayers (1972)
			CADMIUM			
Prasinecladus subsala	green flagellated	Lab culture (Marine)	Stable isotope	6.7×10^3	Dry	Kerfoot & Jacobs (1976)
Phaeodactylum tricornutum & *Chaeotoceras* spp	Diatoms	Marine	Stable isotope	4×10^3	Dry	Kerfoot & Jacobs (1976)
			COPPER			
Phytoplankton	Assorted	Lake Michigan	Ecological	1.2×10^3	Dry	Copeland & Ayers (1972)
Phytoplankton	Assorted	Monterey Bay	Ecological	2.8×10^3	Dry	Martin & Knauer (1972)
Scenedesmus	green colonial	Lab culture	Stable isotope	$3.7\text{-}4.0 \times 10^3$	Dry	Stokes (1975)
			LEAD			
Phaeodactylum tricornutum	Diatom	Lab culture (Marine)	Stable isotope	2×10^3	Dry	Schulz-Baldes & Lewin (1976)
Platymonas subcordiformis	green flagellated	Lab culture (Marine)	Stable isotope	1×10^3	Dry	Schulz-Baldes & Lewin (1976)
			MERCURY			
Phytoplankton	Assorted	Lake Michigan	Ecological	5.9×10^3	Wet	Copeland & Ayers (1972)
Phytoplankton	Assorted	Monterey Bay	Ecological	2.2×10^2	Wet	Knauer & Martin (1972)
Phaeodactylum tricornutum	Diatom	Lab culture (Marine)	Radio isotope	1.3×10^4	Wet	Hannan etal (1973)
			NICKEL			
Phytoplankton	Assorted	Monterey Bay	Ecological	5.7×10^2	Dry	Knauer & Martin (1972)
			ZINC			
Phytoplankton	Assorted	Monterey Bay	Ecological	5.5×10^3	Dry	Martin & Knauer (1972)

TABLE 5

Details of the phytoplankton in the sea water samples
used for zinc and copper experiments

	Sampling Station (50° 15N, 4° 13'W)	
Sample	A (Zinc)	B (Copper)
Date	10 July 78	19 Nov 1979
Temp (°C)	14	12.2
Metal conc in sea water (μg/l)	0.4	<1
<u>Phytoplankton</u>		
Chlorophyll <u>a</u> (μg/l)	2.1	1.8
Composition	100% diatoms	60% diatoms 40% dinoflagellates

TABLE 6

Concentration factors determined by JENNET et al (22)

MERCURY

Organism	Type	Culture Age	Conc Factor (Wet)
Navicula pelliculosa	Diatom	Young	$3.5 - 6.8 \times 10^3$
Chlamydomonas	green flagellated	Young	$9.1 \times 10^3 - 1.6 \times 10^4$

CADMIUM

Organism	Type	Culture Age	Conc Factor (Wet)
Navicula pelliculosa	Diatom	Young	$3.6 - 4.9 \times 10^3$
		Old	70 - 320
Chlamydomonas	green flagellated	Young	5.5×10^3

LEAD

Organism	Type	Culture Age	Conc Factor (Wet)
Chlamydomonas	green flagellated	Young	$1.7 - 2.0 \times 10^4$

Young = 11 days Old = 44 days

TABLE 7

Inhibition of Primary Production of phytoplankton populations taken from different sea areas by metals at a concentration of 10µg|1.

Metal	Source of phytoplankton	Productivity (% of control)	Reference
Mercury	Monterey Bay, California	12	Knauer & Martin (1972)
	W Caspian Sea	28	Patin et al (1974)
	Estuary, S Carolina	76	Zingmark & Miller (1975)
	Sargasso Sea	49	Zingmark & Miller (1975)
	Gulf Stream	55	Zingmark & Miller (1975)
	Red Sea	28	Ibragim & Patin (1976)
	E Mediterranean Sea	50	Ibragim & Patin (1976)
Copper	W Caspian Sea	46	Patin et al (1974)
	Red Sea	56	Ibragim & Patin (1976)
	E Mediterranean Sea	54	Ibragim & Patin (1976)
Cadmium	W Caspian Sea	79	Patin et al (1974)
	Red Sea	65	Ibragim & Patin (1976)
	E Mediterranean Sea	82	Ibragim & Patin (1976)
Lead	Red Sea	86	Ibragim & Patin (1976)
	E Mediterranean Sea	92	Ibragim & Patin (1976)
Zinc	W Caspian Sea	115	Patin et al (1974)

Source: Davies from 9

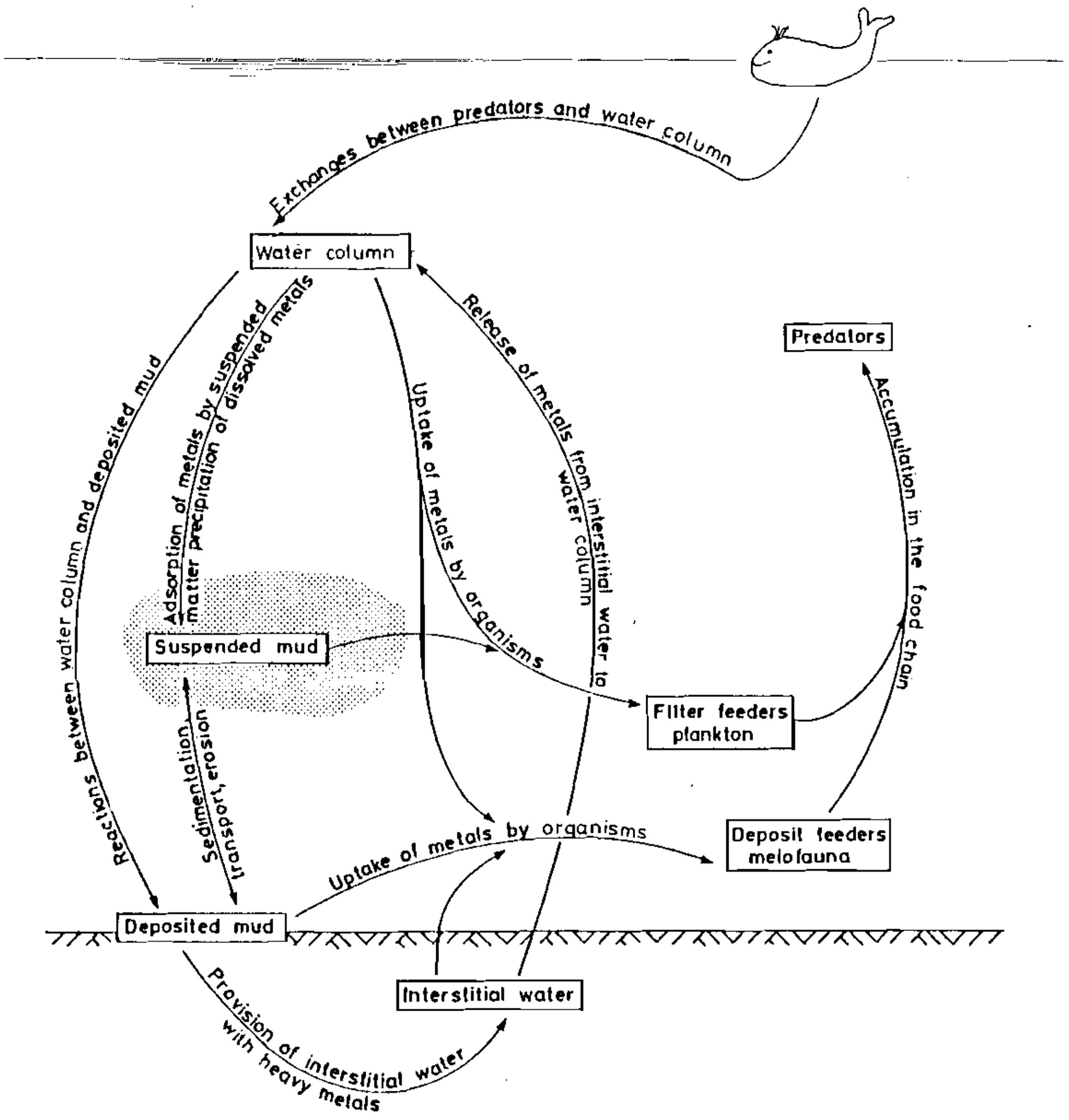


Fig 1 Pathways of metals in aquatic ecosystems, adapted from Salomons & van Driel (1980)

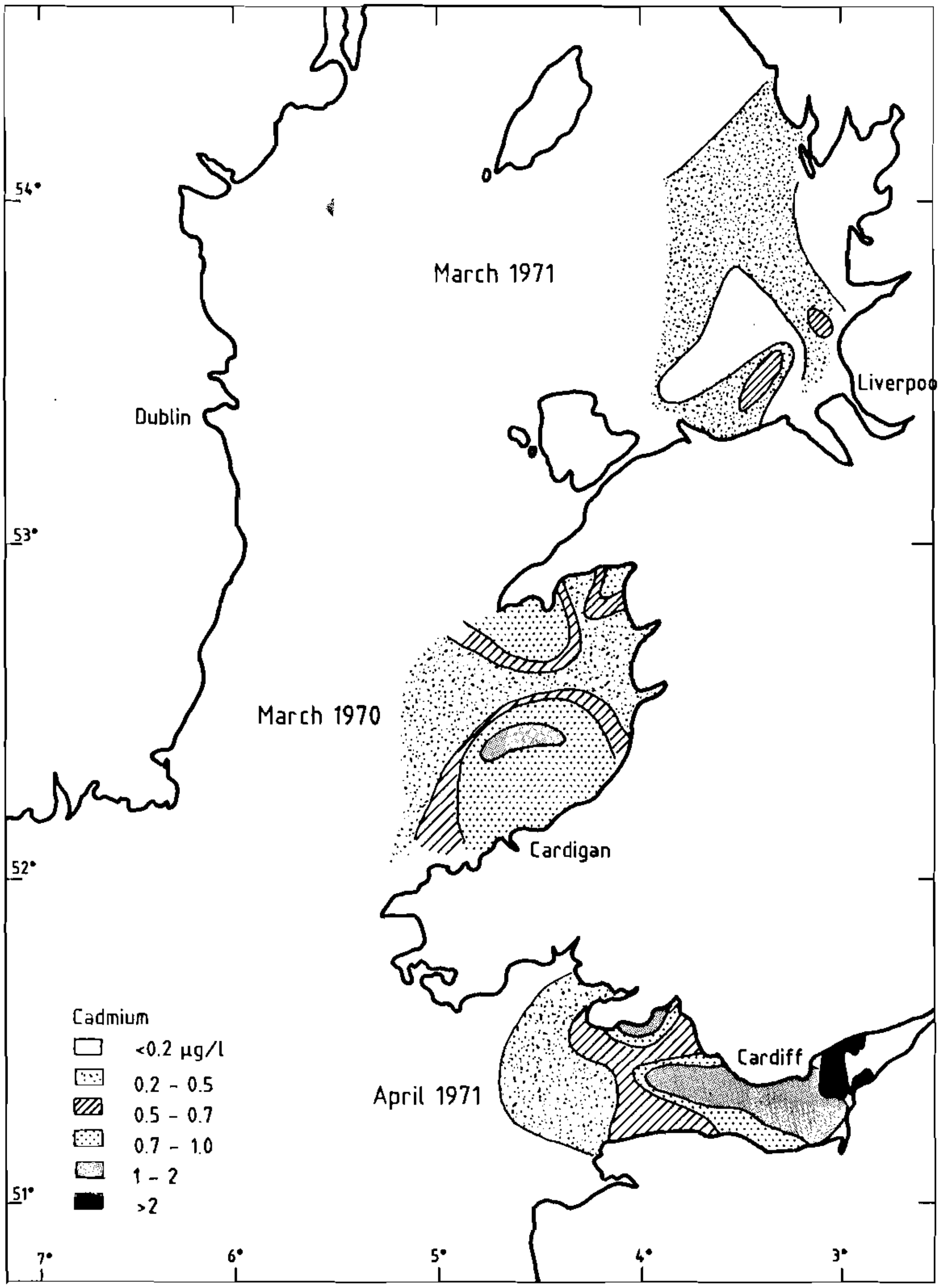


Fig 2 The distibution of cadmium in Liverpool Bay, Cardigan Bay and the Bristol Channel surface waters. Source : Abdullah & Royle (1972)

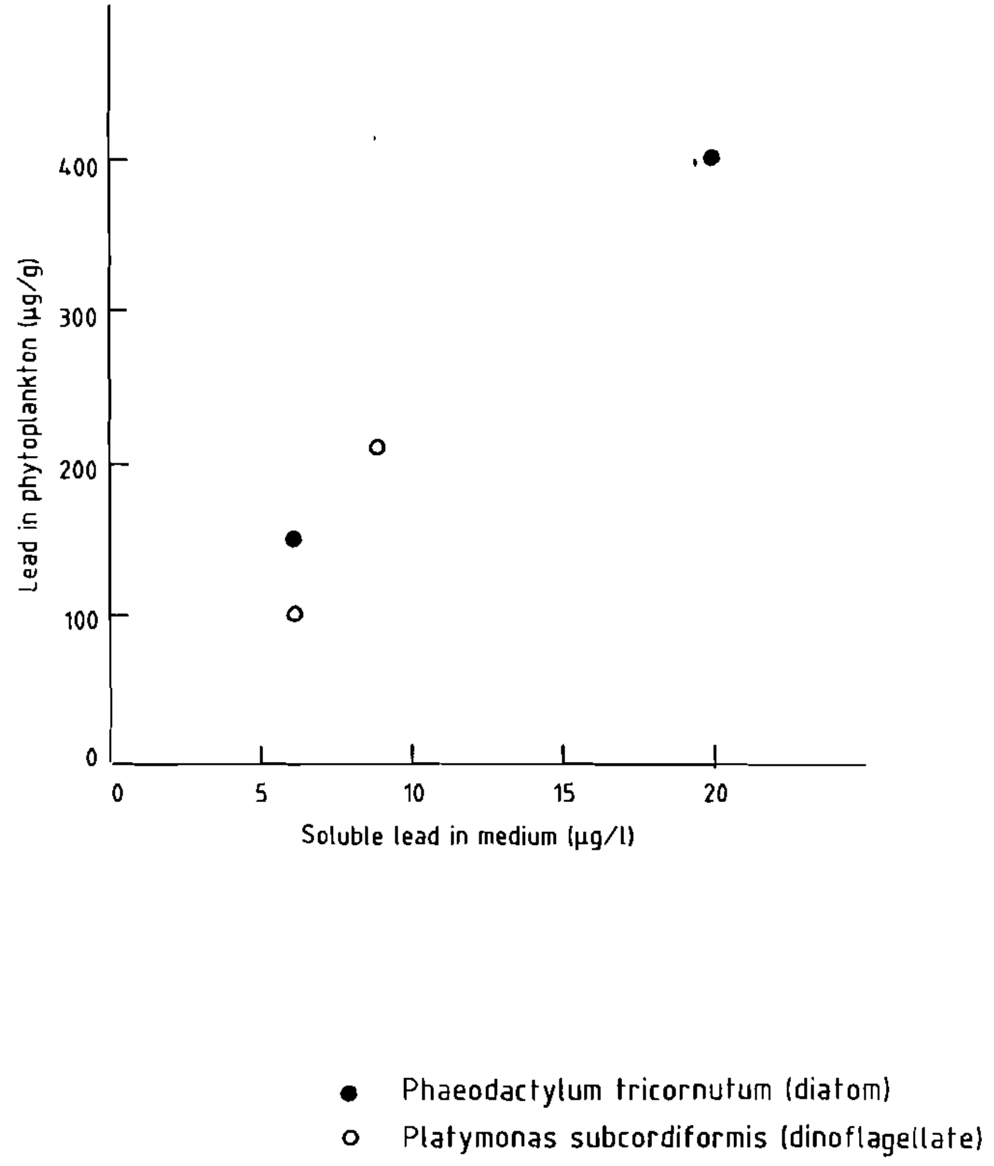
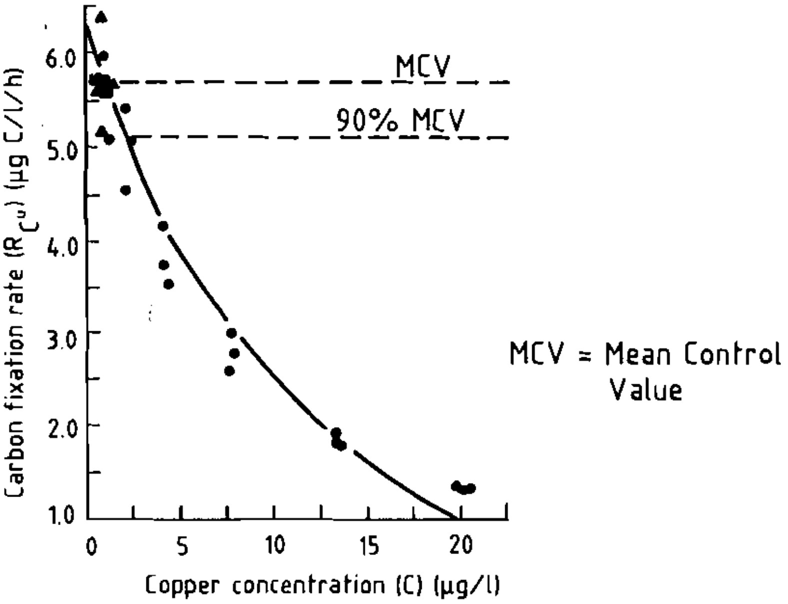
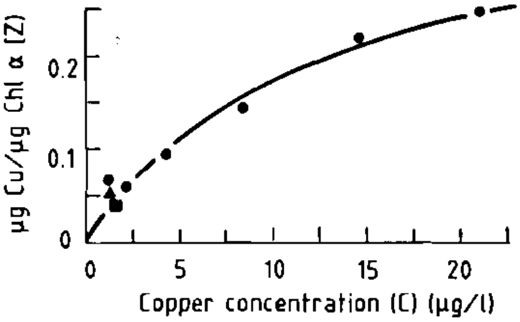


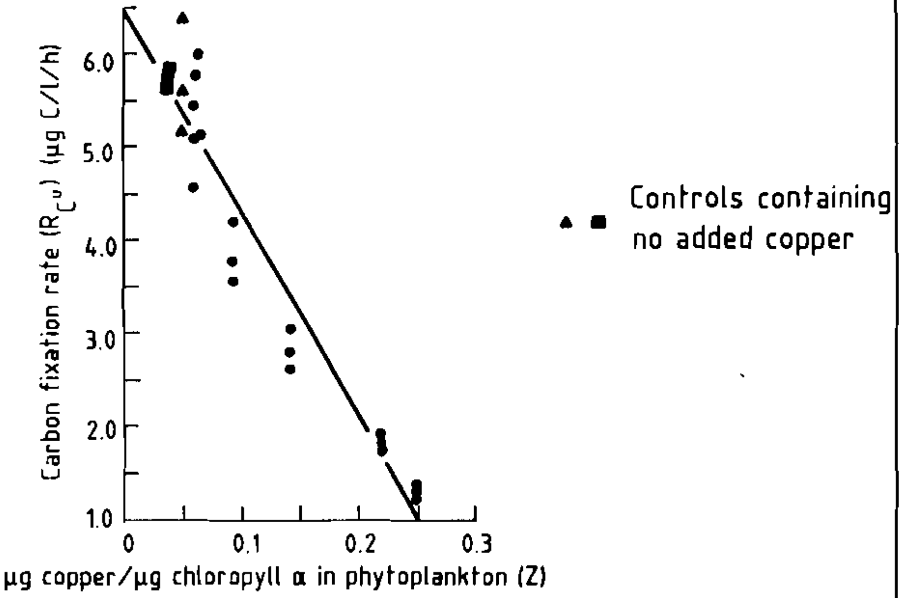
Fig 3 Lead adsorbed to phytoplankton after one hour of exposure from Baldes & Lewin (1976)



(a) The effect of copper on carbon fixation rates

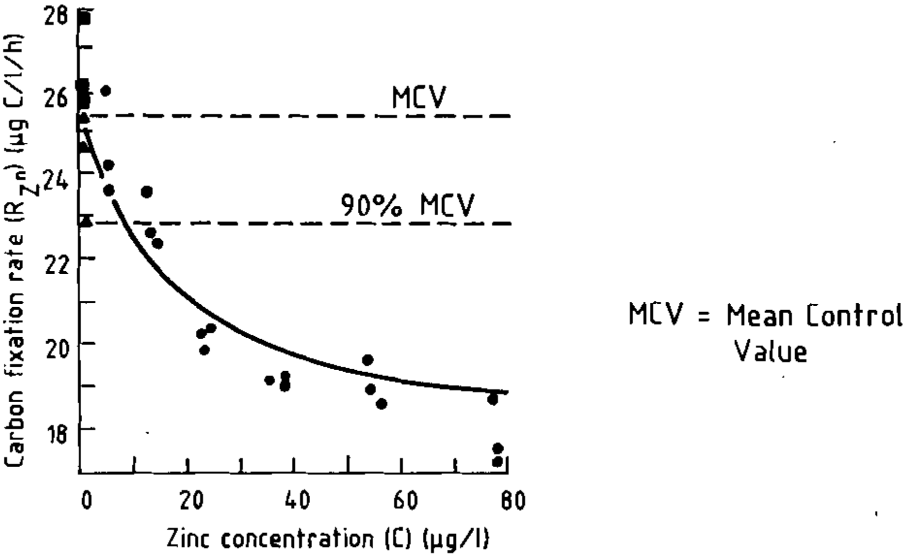


(b) The relationship between copper and its adsorption to phytoplankton

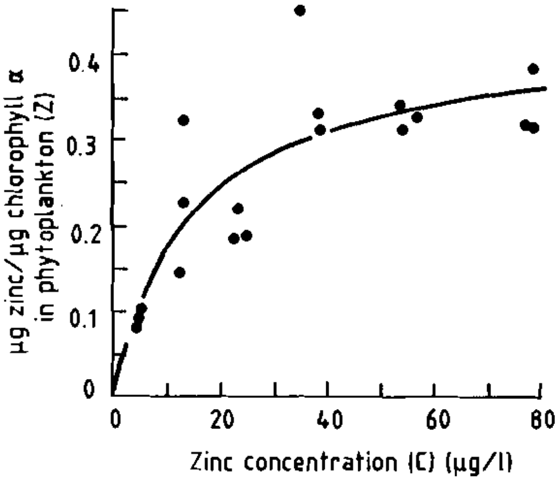


(c) Carbon fixation v/s adsorbed copper

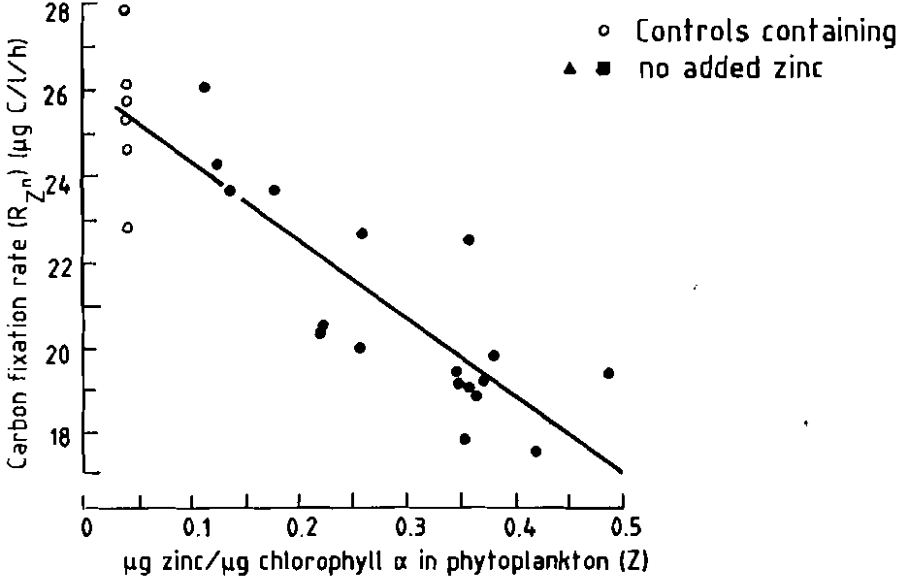
Fig 4 The effects of increasing copper concentrations on a natural phytoplankton assemblage from Davies & Sleep (1980)



(a) The effect of zinc on carbon fixation rates



(b) The relationship between zinc and its adsorption to phytoplankton



(c) Carbon fixation v/s adsorbed zinc

Fig 5 The effects of increasing zinc concentrations on a natural phytoplankton assemblage from Davies & Sleep (1979)