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A CRITICAL REVIEW OF CADMIUM IN THE MARINE ENVIRONMENT

by

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PREFACE

The initial concern for the effects of elevated concentrations of cadmium in the environment arose out of an endemic disease noted in the people of the Jintsu River Basin, Japan, who lived in the vicinity of metal mines and smelters. The symptoms of what is now known as Itai-Itai (Ouch-Ouch) disease, so called because of the pain produced in the bone, were noted as early as 1935. Although the disease was thought to be related to the mining activities, no scientific evidence was forthcoming to substantiate its connection with cadmium until 1961, the proof being produced through the efforts of Hagino, Kobayashi and Yoshiaka (1). One hundred people died of Itai-Itai disease and 57 more were confirmed to have contracted the disease. There was a similar number of suspected cases and a further 280 were kept under observation. Other than this one epidemic, there has been only one other recorded incident of cadmium poisoning arising directly from the environment in which three people were affected (2). Several cases have been reported from industry, involving workers in smelting and processing plants and the alkaline battery industry.

Many reviews have been written on cadmium but they have tended to concentrate on the effects of cadmium on man, a concise summary of which is presented in Appendix 4.

This report focuses attention on the marine environment and examines in detail the aquatic chemistry and transport of the metal, its global distribution in saline waters, the effects of marine disposal of cadmium-containing wastes, the fluxes and cycles of cadmium to, in and from the oceans, the residence time of cadmium in the oceans, and the biochemical and physiological effects of cadmium on marine organisms.

Many gaps in our knowledge which are fundamental to the understanding of the behaviour of cadmium in the marine environment have been identified and the research requirements are summarised in the last chapter.

CHAPTER 1

BACKGROUND INFORMATION AND REPORT SUMMARY

1.1 PHYSICAL PROPERTIES

The metal cadmium is in Group 2B of the periodic table, the same Group as zinc and mercury. It has an atomic number of 48, atomic weight of 112.4, melting point of 320.9°C and a relatively low boiling point of 767°C. The main oxidation state is 2 and the divalent ion, resulting from the loss of the outer 5_s^2 electrons (leaving a full 4d shell), has a radius of 0.097 nm.

1.2 AQUATIC CHEMISTRY

1.2.1 Dissolved speciation

In freshwater, cadmium is present predominantly as the Cd^{2+} ion, the $Cd(OH)_2^0$ complex and organic complexes, depending on the pH and the concentration of soluble organic material. Cadmium may begin to precipitate as the carbonate at about pH 6.

As salinity increases, the degree of complexation with chloride ions increases, until in 100% seawater cadmium exists almost entirely as $CdCl_2^0$ and $CdCl^+$ complexes. There is no evidence for the organic chelation of cadmium in seawater.

In anoxic conditions, cadmium may be present as the soluble bisulphide complex.

1.2.2 Particulate association

The adsorption of cadmium onto particulate material increases with increasing pH but decreases with increasing ionic strength. The latter effect is the most influential, mainly because cadmium has the lowest selectivity coefficient relative to other heavy and alkali metals. In seawater, therefore, cadmium uptake by particulates is negligible. The only inorganic components to show appreciable adsorption of cadmium in freshwater, and particularly in seawater, are hydrous manganese oxides.

In freshwater cadmium-organic particulate interactions are dependent upon the concentration of organic matter. The most influential cadmium-particulate association in seawater is with faecal pellets, by biological uptake and concentration rather than by adsorption (see below).

1.2.3 Remobilization from sediments

The observed desorption of cadmium from sediments by resuspension in seawater is greater than for any other heavy metals.

The controlling factor in remobilization is redox potential, which regulates the solubility of manganese, which in turn regulates cadmium availability. Manganese, and hence cadmium, are mobilized under anoxic conditions, and coprecipitated under oxic conditions.

1.3 GEOCHEMICAL ABUNDANCE AND ENVIRONMENTAL DISTRIBUTION

1.3.1 Crustal materials

The abundance of cadmium in common rocks and minerals is given in Table 1. The mean continental abundance is given as 0.15μg g^{-1}, that of soil, 0.06μg g^{-1} and oceanic sediments, 0.5μg g^{-1}. High concentrations are found in phosphorites (10-500μg g^{-1}) and the principal economic ore is sphalerite (ZnS) with a cadmium content of 0.02 to 1.8% by weight.

1.3.2 Saline waters

The background concentration of cadmium in all waters (including freshwater) is 0.01μg l^{-1}. From the collected data, a gradient in the range of values quoted is apparent in the order: estuaries and enclosed bays > bays and coastal waters > seas and oceans (0.2 to 0.01μg l^{-1} for max. to min. of normal range). A similar pattern is observed for sediments, which show a 10^4 accumulation factor compared to overlying waters.

Excessively elevated levels, i.e. up to 5×10^4 above background concentrations, are nearly always due to industrial activities; natural mineralization is rarely responsible.

In deep ocean waters, the dissolved cadmium concentration increases from 0.01μg l^{-1} at the surface to about 0.1μg l^{-1} at 1000 to 2000 m and bears a direct relationship to the dissolved phosphate concentration (see 1.4.2 below).

Table 1 Abundance of cadmium in common rocks and minerals ($\mu g\ g^{-1}$) (compilation from (2, 3, 4)

Igneous:-	
Granite	0.12 (0.2)
Granodiorite	0.07
Pitchstone and Obsidian	0.17 (0.25)
Andesite	0.017
Syenite	0.16
Basalt	0.22
Gabbro	0.11
Average	0.2
Metamorphic:-	
Eclogite	0.11
Garnet schist	1.0
Gneiss	0.14
Sphalerite (ZnS) (major Cd ore)	0.02-1.8%
Sedimentary:-	
Bituminous shale	0.8
Bentonite	1.4
Marlstone	2.6
Shale and Claystone	1.0-1.4
Limestone	0.035-0.1
Phosphorites	10-500
Super phosphate	7-170
Coal	0.04-10.0
Oil	0.07-16.0
Peat	4.0
Manganese nodules	3-21.2

1.4 CADMIUM FLUXES AND OCEANIC RESIDENCE TIME

1.4.1 General

The contribution of atmospheric inputs to the dissolved cadmium content of seawater may be as important as the dissolved cadmium influx from rivers (2.64 × 10^9g v 3.25 × 10^9g respectively).

The only major inorganic input to sediments is thought to be by coprecipitation with hydrous manganese oxides but the estimated mass flux of about 5 × 10^8g yr^{-1} to sediments by this mechanism is an order of magnitude lower than that supplied by the vertical flux of faecal pellets.

1.4.2 The importance of faecal pellet fluxes and the relationship to productivity

The output of cadmium to sediments in faecal pellets is estimated to be at 6.5 × 10^9g yr^{-1}, which emphasises the importance of biological activity in the global transport of the metal. The maximum cadmium concentration in oceanic sediments of 60µg g^{-1} (<2 µm fraction) was recorded in an area of exceptionally high organic productivity.

The depletion of cadmium (and phosphate) in surface waters with respect to deep water is explained by planktonic uptake. As the faecal pellets from grazing zooplankton settle through the water column, the encapsulating membrane dissolves, allowing cadmium and phosphate to be leached from the material, thus giving rise to the profiles mentioned above. On upwelling, the dissolved cadmium and phosphate return to the surface waters. Not all the cadmium is regenerated and thus some may accumulate in sediments.

The close relationship of the cadmium and dissolved phosphate by total reservoir masses, fluxes and residence times (1.74 × 10^5 yr and 1.8 × 10^5 yr respectively) help to substantiate the postulated mechanism.

1.4.3 The effect of man's activities

Man's current contribution to the oceanic input of cadmium is estimated to be ≃50% of the total input of 7.6 × 10^9 g yr^{-1}. Most of the seawater - leachable cadmium from the atmospheric input is thought to be derived from anthropogenic sources and is equivalent to a third of the total input. It is estimated that by the year 2000 man will have introduced nearly 250,000 tonnes of cadmium to the oceans.

The slow dissipation of cadmium from manufactured products is indicated as the major contributor to the cadmium influx. The industrial losses plus the accumulative dissipation figures at present equal the annual production figures; ≈ 25% of the total losses find their way to the oceans. Because there is a time-lag between production and the disposal of the product, the peak of cadmium input into the oceans will not arise until two or three centuries hence, unless strict controls are imposed on incineration and smelting processes.

1.5 MARINE DISPOSAL OF CADMIUM-CONTAINING WASTES

There is circumstantial evidence for elevated dissolved cadmium levels in surface waters and the water column around dumpsites. An increased concentration may result from dissolved cadmium within the waste, e.g. acid wastes, or by leaching of cadmium from the solids, e.g. dredged wastes, both in water column and in the sediments.

In choosing disposal sites careful consideration should be given to water circulation, the productivity of the area and the synergistic effects on biota of the many other toxicants supplied to the area.

As a direct input of cadmium to the marine environment, surprisingly little is known of the mass cadmium input from this source (possibly many hundreds of tonnes each year) or of the leaching - retention properties of the wastes with respect to cadmium.

1.6 PHYSIOLOGICAL AND BIOCHEMICAL EFFECTS ON MARINE BIOTA

Bacteria may be important in both the precipitation of cadmium to sediments under anoxic conditions and the remobilization of cadmium from oxic sediments. Of direct importance to man is the possible selection of plasmid-mediated multi-drug multi-metal resistant pathogens through the exposure of organisms to high metal concentrations. Resistant organisms tend to accumulate cadmium in the cell wall and cell membrane, either by active enzyme immobilization of the metal transport or by accommodation. This effect may be significant in the accumulation of cadmium in their predators.

Phytoplankton are highly tolerant to cadmium. Uptake is primarily by adsorption onto the cell surface. The presence of inorganic phosphate was shown to somehow limit cadmium uptake; on phosphate depletion in the media cadmium uptake was rapid which suggests absorption into the cell by some form of anion transport mechanism. The only sublethal effect measured to date is the depression of photosynthesis by the uncoupling of the photosystem II electron transport chain.

Of the higher marine organisms, molluscs concentrate cadmium to the greatest extent and hence they may prove useful as pollution indicators.

Most marine animals concentrate cadmium in the liver (or digestive glands), kidney and gills. Food chain amplification is not evident on the basis of whole animal analysis, but may be found if specific organs are taken as monitors.

The internal complexation and concentration of cadmium in kidney and liver tissue is often due to the binding by metallothionein, a low molecular weight protein.

The increase in oxygen consumption in the presence of cadmium is indicative of increased enzyme activity and the decrease in oxygen consumption may be due to gill membrane inhibition of oxygen uptake or inhibition of enzyme systems.

CHAPTER 2

THE CHEMISTRY OF THE AQUATIC TRANSPORT OF CADMIUM

This chapter is divided into three parts. The first examines dissolved speciation, the second adsorption onto particulates and the third reports the desorption and remobilization of cadmium from sediments. The transport of any metal through the aquatic ecosystem is a complex process as illustrated in part by Figure 1. It is controlled by, among other factors, the pH, redox potential (Eh), chlorinity, ionic strength, dissolved and particulate organic material, iron and manganese hydrous oxides and the biota.

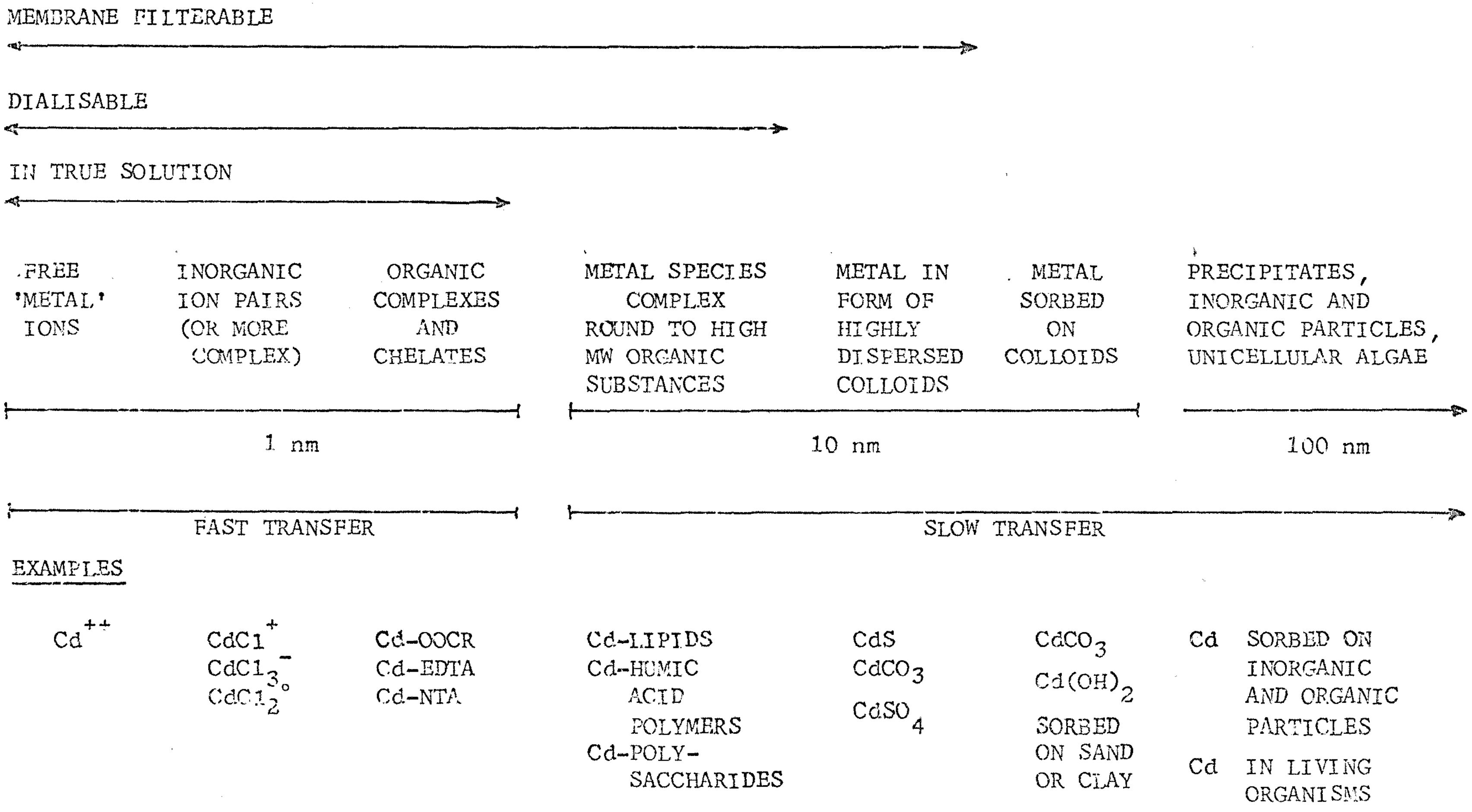
2.1 DISSOLVED SPECIATION

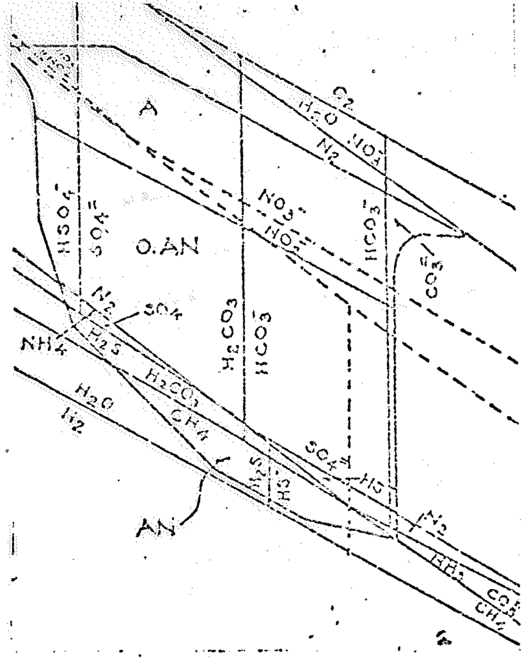
The problems regarding the speciation of metals in water have stimulated much research but as yet the experimental work is in its infancy. The use of models has therefore been extensively employed by chemists in order to gain insights into the inorganic and, to a lesser extent, organic speciation at varying pH, Eh, chloride concentration, anion/cation concentrations and with various organic ligands or groups of compounds. Bench studies with simple organic chelators e.g. nitritotriacetic acid (NTA) and ethylenediaminetetracetic acid (EDTA), have been carried out in an attempt to simulate naturally occurring chelating agents and examinations of humic and fulvic materials have also been instigated.

2.1.1 Inorganic speciation (theoretical models)

The stability diagrams devised from computer models are only as good as the data on which they are based and discrepancies in the findings of different workers do occur. A discussion of the theory of Eh-pH relationships will not be entered into here, since Khalid et al. (5) have covered the subject well. Figure 2 shows the computed C-N-S-O-H diagram for a freshwater system (6) whilst Figure 3 illustrates the Eh-pH limits encountered in natural aquatic systems (7). By comparing these two diagrams with Figure 4, it may be deduced that in freshwaters the predominant form of inorganic cadmium

FIGURE 1. Examples of cadmium speciation and size distribution in natural waters




O2
H2O
NO3
N2
A
HSO4
SO4
O.AN
NO3
NO2
HCO3
CO3
N2
SO4
NH4
H2S
H2CO3
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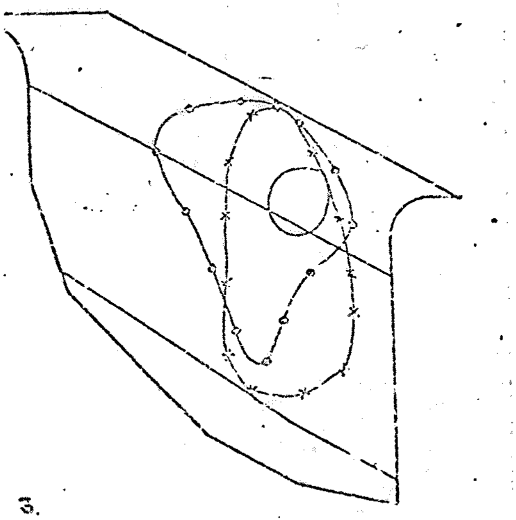
AN

2



3.

FIGURE 4. Eh-pH diagram for cadmium
--- = seawater, ~ = freshwater.
$P_{CO_2} = 10^{-3.5}$ atm.; total $Cd^{-} = 10^{-8.35}$ M;
total $S = 10^{-4}$ M. total $Cl^{-} = 10^{-0.26}$ M (seawater)
and $10^{-3.54}$ (freshwater)
(from Gong *et al.* (8)).

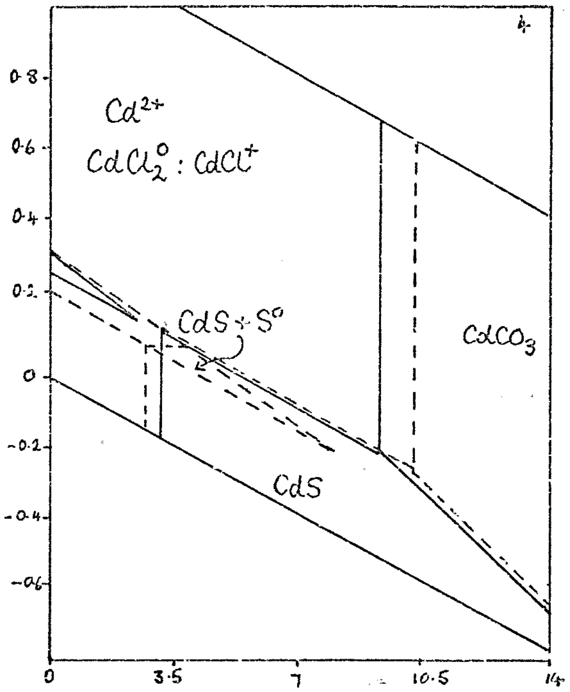


FIGURE 3. Eh-pH limits of the aqueous environment (after Baas Becking *et. al.* (7)).

o = freshwater
x = seawater (full range)
ı = 'normal' seawater.

FIGURE 2. Eh-pH diagram of the system C-N-S-O-H for a representative freshwater showing limits of the natural environment and major fields of metabolic activity (from Wollast *et. al.* (6) after Baas Becking *et al.* (7)).

A. = area of aerobic metabolism
O.AN. = area of oxidative-anaerobic metabolism
AN. = area of anaerobic metabolism

up to pH 8 will be the Cd^{2+} ion, and thereafter cadmium will be precipitated as the carbonate (8). CdS would only be formed under highly anaerobic conditions, as found in some sediments. In the study by Hahne and Kroontje (9), carbonate was not considered (Figure 5) whereas under oxidative-anaerobic conditions (Figure 2), Morel et al. (10) calculated that $CdCO_3$ precipitation would occur below pH 6.2 (Figure 6) in a multianion solution.

In moving from freshwater to seawater, the molar concentration of chloride ion increases from 0.0002 to 0.554 but the HCO_3^- concentration remains constant at 2 - 3 × 10^{-2}M. The major species of cadmium at pH 8.5 and in 25% seawater were found to be $CdCl^+ >> CdCl_2^o$; in 50% seawater $CdCl^+ > CdCl_2^o$; in 75% seawater $CdCl^+ \simeq CdCl_2^o$ and in 100% seawater $CdCl_2^o > CdCl^+$ (Figure 7) (11). The 100% seawater diagram compares favourably with that derived by Zirino and Yamamoto (12). Figure 8 presents speciation with respect to salinity (13) rather than pH and illustrates the rapid decrease of Cd^{2+} as the major species with increasing salinity and the replacement of $CdCl^+$ by $CdCl_2^o$ as the most abundant form at 25% salinity. In brines, $CdCl_3^-$ displaces $CdCl^+$ as the second most stable species (Figure 7f).

There are difficulties in comparing theoretical and experimental results, as demonstrated by Bubić and Branica (14). Using anode stripping voltametry (A.S.V.), they reported Cd^{2+} and $CdCl^+$ to be the stable species of cadmium in seawater but concluded that "The existence of the $CdCl_2^o$ form is possible but it cannot be proved in the solution of ionic strength I = 0.7 which corresponds to seawater".

2.1.2 Organic speciation (theoretical models and bench studies)

The interaction of cadmium with organic chelating agents might be expected to occur in the environment. However, calculations have predicted that humates (13) (Figure 8) and amino and carboxylic acids (15) (Figure 9) play only a minor role in the binding of cadmium in both fresh and seawater.

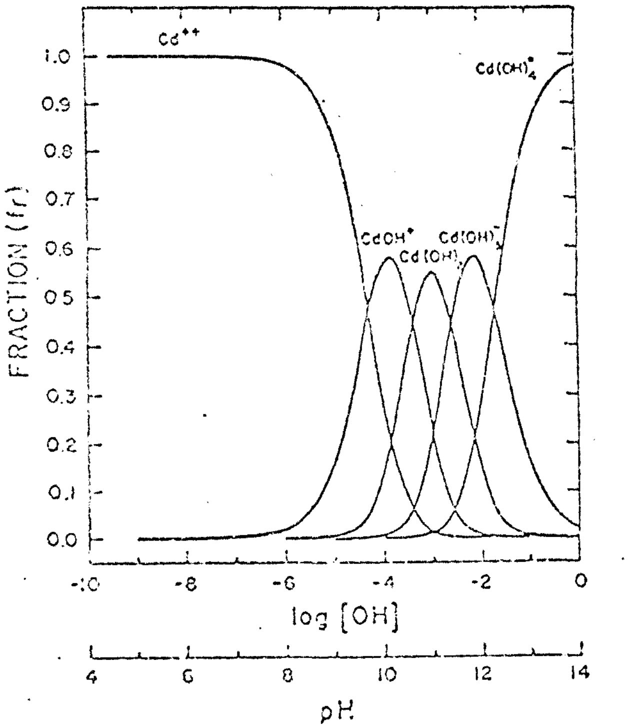


FIGURE 5. Distribution of molecular and ionic species of Cd^{2+} at different pH values (from Hahne and Knoontje (9)).

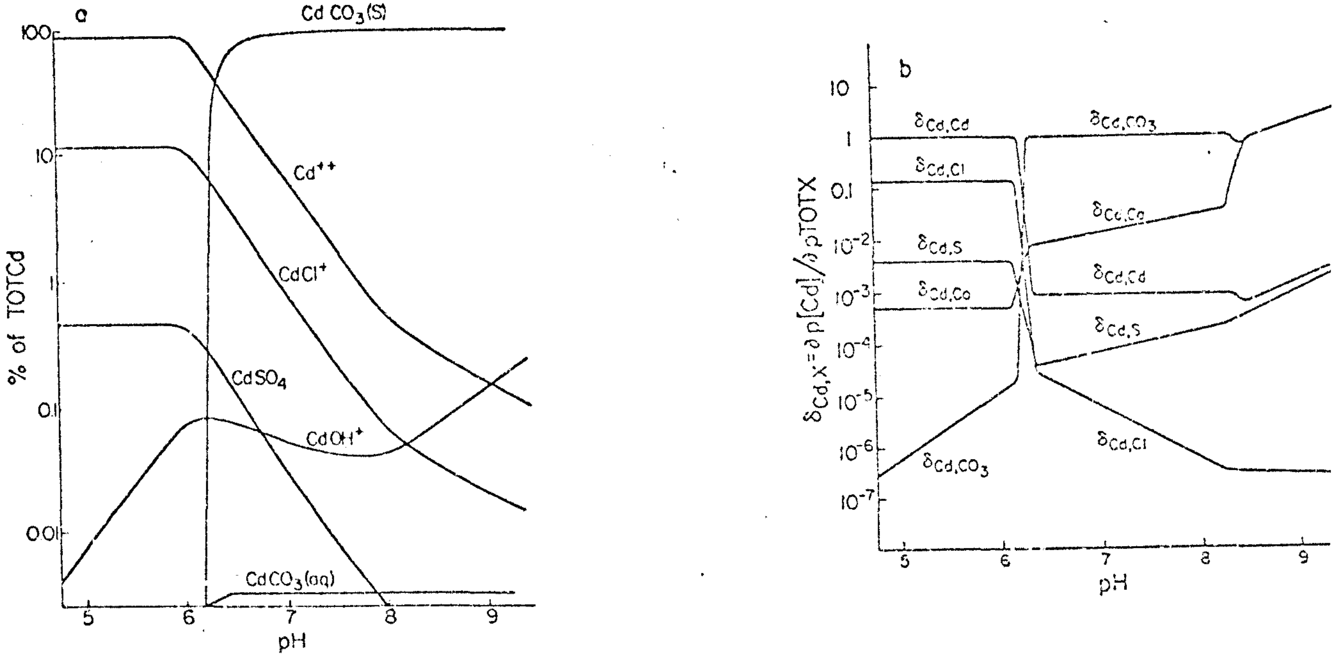


Figure 6 a) Case study for cadmium on the variations of speciation and interaction intensities as a function of pH. The equilibrium system was based on a 16-metal, 8-ligand system of pE = 12.

b) Below pH 6.2 there is a direct correlation between the interaction intensities and Cd speciation. pH 6.2-8.4 interaction intensities are correlated with higher order effects via Ca and CO_3. Above pH 8.4 $CaCO_{3(s)}$ precipitates and the titration of Ca^{2+} by CO_3 shows in interaction intensities in absolute value for δ Cd, Ca and δ Cd, CO_3 (after Morel _et al._ (10)).

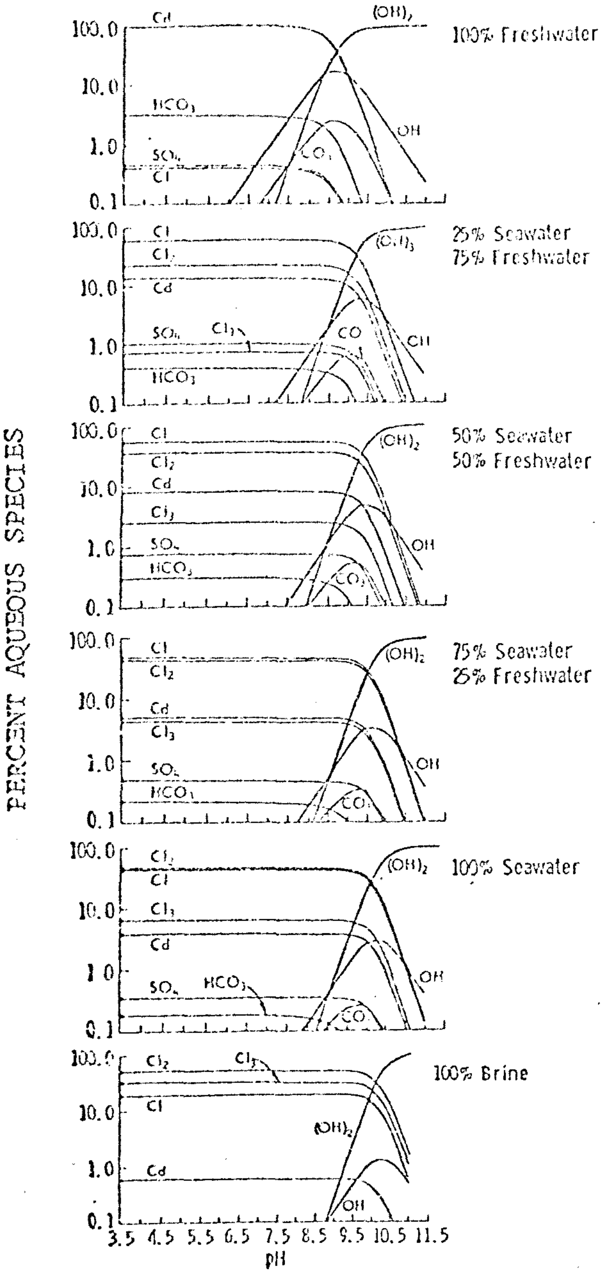
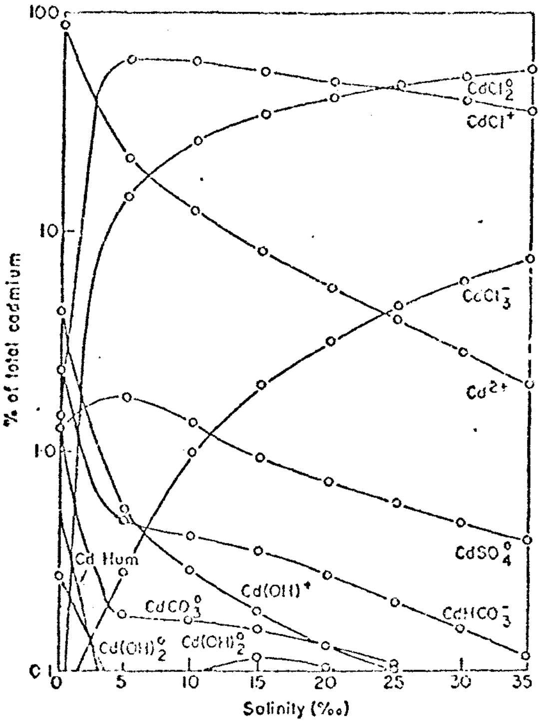


FIGURE 7. Cadmium speciation in freshwater-seawater mixtures and brine. (from Long and Angino (11)).

FIGURE 8. The equilibrium speciation of cadmium (II) as a function of salinity along a model estuary. (after Mantoura et. al. (13)).



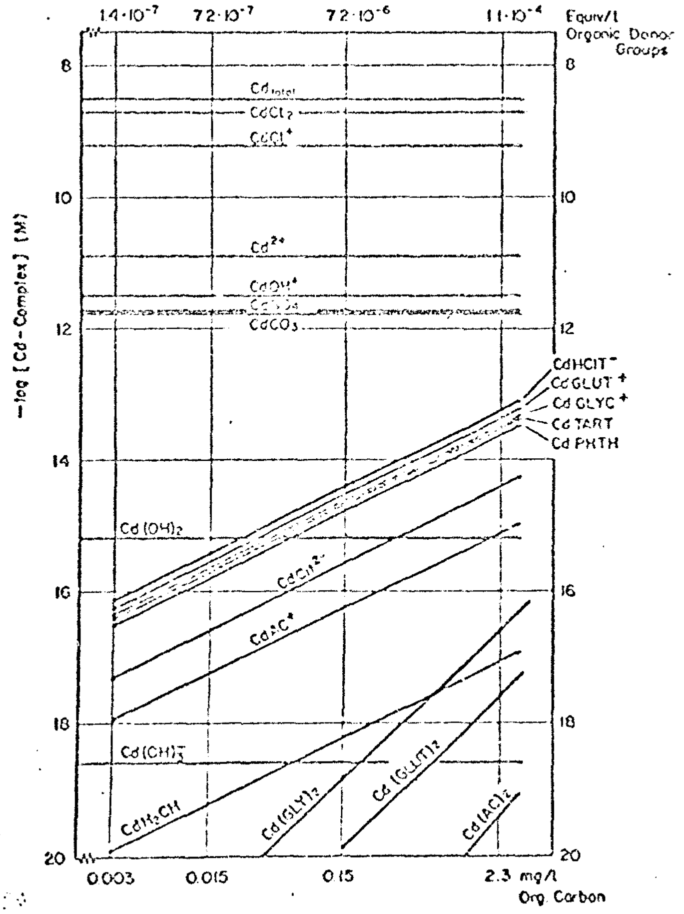


FIGURE 9. The distribution of Cd (II) species in seawater as a function of the amount of complex forming organic carbon added. There is little effect on the distribution of Cd species. (from Stumm and Werner (15)).

It was proposed that various organic compounds were important for the mobilization of cadmium and phosphate in soils (16,17). Cadmium formed a soluble three ligand system with phosphate and NTA up to pH 7 and a quaternary complex above pH 7. For freshwaters, Morel <u>et al.</u> (10), in their 16 cation and 10 anion model system at pE 12 and pH 7, demonstrated that NTA at 10^{-5}M could prevent the formation of $CdCO_3$ precipitate; in other words it would eliminate the buffering effect of carbonate. Such effects may be damaging in that NTA can be used as both a nitrogen and carbon source by organisms and therefore its metal complexes have particular significance in metal bioaccumulation (18). The stability of the Cd NTA^-(1:1) complex has been utilised for the polarographic determination of NTA in lake water at pH 9 in the presence of tripolyphosphates and alkylbenzsulphonates which normally interfere with the analysis (19). However, in solutions containing chloride, the formation of Cd NTA^- complexes was diminished because of competition between chloride for cadmium (20) and Mg^{2+} and Ca^{2+} for NTA. Similar effects were reported with ethylenediaminetetracetic acid (EDTA) complexes (21) where a greater than tenfold excess of EDTA was required to complex all the cadmium and to overcome the competition with Ca^{2+} (25×10^{-6}M : 2×10^{-6}M). With equimolar concentrations (2×10^{-2}M i.e. 10^3 × the 'normal' seawater concentration) in both seawater and 0.59M NaCl + 10^{-2}M Ca^{2+}, 50% of the cadmium was bound, reaching equilibrium in 30 minutes. As mentioned above, other simple organic chelators like acetic, citric and phthalic acids and amino acids, including cysteine, have little influence on the speciation of cadmium in aquatic systems even though they are thought to be typical residues that make up humic and fulvic acids, the carboxylic groups of phthalic acids and the HO  COOH of salicylic acid acting as the metal chelators, e.g. see (22). One possible reason for this is that (citrate) Cd (phosphate) and (cysteine) Cd(citrate) complexes are known to precipitate at pH 4.2 (17) (which may be true for some other XCdY complexes).

2.1.3 Organic speciation (Humic and Fulvic acids)

Humic matter is derived from the refractory organic matter in terrestrial soils or produced in the water, and consists mainly of random arrangements of breakdown products of lignin, amino acids, phenols and phenolic metabolites of micro-organisms (equivalent to 60-80% of the dissolved organic matter (DOM)); polysaccharides contribute a further 10% (23). Fulvic acids are distinguished from humic acids by their solubility in mineral acids and are often considered to have lower molecular weights (m.w.<10,000), although this is not always the case (24). Their chemical composition can differ from environment to environment; for example, fulvic acids from one river possessed high aromatic character whilst from another river had high aliphatic character (25). Marine humic materials, compared to river material, have lower metal binding constants, acidity, cation exchange capacity and phenolic OH but higher molecular weights (26). In freshwaters, soil derived fulvic acids reach levels of 3-33 ppm in rivers, up to 29 ppm in lakes and as high as 100 ppm in swamps. In seawater, levels of 0.5-5 ppm DOM are common (23), i.e. in the concentration range of 3×10^{-6} to 10^{-3}M. This non-uniformity in structure and therefore inability to classify dissolved organic species must be borne in mind when comparing the experimental work of different researchers.

In both simulated freshwater experiments with added humic acids (22, 27,28) and lake and river waters (29,30) there is evidence of organic chelation of cadmium. At low pH (<3.5) the complexation is negligible but as pH increases the degree of complexation increases (up to 80% at pH 7.5) (22). However, the extent of chelation is also controlled by the concentration of the organic component and is rarely found to be above 40%, even in sewage/river water mixtures (27), and is generally <10% (27) c.f. Figure 8).

Stability constants of cadmium-naturally occurring organic complexes for differing pH and ionic strengths are presented in Table 2. This

Table 2 Stability Constants for Cd - Natural Organic Complexes

Organic Form	log K	pH	Ionic Strength/Solution	Ref.
Soil humate	6.9 5.2	4	0 0.1	22
Soil fulvate	3.04	4.9	0.1	31
	3.64	5.95	0.1	31
Lake humate	4.57-4.70	8	0.02	13
Loch humate	4.87-4.95	8	0.02	13
Sea humate	4.69	8	0.02	13
'River water'	3.67	?	?	30
Fulvate	3.26	?	?	30

demonstrates a marked variability in the behaviour of the metal with organic matter of different type and origin. The stability constants for cadmium-organic complexes are lower than most other heavy metals, namely Co, Zn, Ni, Pb, Cu and Hg, but greater than Ca and Mg (13). The latter two metals, by virtue of their relatively high concentration in seawater, compete favourably with cadmium for humic/fulvic chelators. This competition, coupled with the large excess of Cl^- ion (forming $CdCl_2^o$ and $CdCl^+$), reduces organic chelation to a negligible level, as noted in North Sea water (32).

In sulphide-bearing marine waters (Eh-150 mV, pH 7, pS 10.5), Gardner (33) calculated that cadmium would be present as the soluble bisulphide with insignificant complexation with simple organic compounds.

The question remains of how reactive are the various species of cadmium in natural waters? In freshwaters, the precipitation of cadmium as the carbonate was suppressed by the presence of organics (10,27,30). O'Shea and Mancy (18) found that, in the presence of carbonate, the humic complexes formed were labile (fast dissociation rates with respect to the plating rate by A.S.V.) whereas the inorganic complexes were non-labile (slow dissociation rates). Similar effects with lake waters (34) and seawater (35) have been reported. In the latter instance 75% of the cadmium was present in a labile form adsorbed onto colloidal organics and 11% was present as Cd^{2+} and organic and inorganic complexes (total Cd = 0.28µg l^{-1}).

2.1.4 Conclusions

Gardiner (27) concluded from his experiments that "the ratio of complexed to uncomplexed cadmium depends only on the stability constant and concentration of ligand and not on the total cadmium concentration, provided the ligand remains in excess". However the use of cadmium concentrations generally in the mg l^{-1} range in these experiments cannot realistically be extrapolated to the environment, where concentrations are generally >1 µg l^{-1} (see below).

From this section some broad conclusions can be drawn:

(i) In freshwaters, Cd^{2+} will always be the major species; organic chelation will increase as the concentration of the chelating agents increase.

(ii) The binding capacity of the organic chelator depends on its origin and the ionic strength of the solution.

(iii) The stability constants of cadmium - fulvate/humate complexes are lower than those of other heavy metals.

(iv) Chloride species (e.g. $CdCl_2^o$ and $CdCl^+$) rapidly become the major species at increasing salinity in seawater.

(v) Organic speciation is of little consequence in seawater, except in the colloidal/particulate form (see below).

2.2 THE ROLE OF ADSORPTION

2.2.1 Theory

In reviewing the literature on the interaction between Cd and particulate and colloid material in aqueous systems, comparison of experimental data was difficult because of

(a) the wide range of cadmium concentrations employed;

(b) the variation in the methods of reporting results;

(c) differences in methodology;

(d) the omission of pertinent experimental data;

(e) the inconsistency in terminology (see Table 3).

Therefore, as a guide to the reader and the researcher, the elementary theory is discussed in Appendix 1.

From Appendix 1, the main points are

(i) the binding of metals by particulates is enhanced by a high surface area to weight ratio,

(ii) adsorption is of two types, coulombic and specific,

(iii) the cation exchange capacity (C.E.C.) of clay minerals is based on the external change and is larger if surfaces exist between layers,

Table 3 Variation in Experimental Parameters for Adsorption Studies onto Cadmium

Cd Conc'n ($\mu g\ l^{-1}$)	Clay Type^a	Clay Conc'n (w/v%)	Particle Size (μm)	pH	Support Media	Temp. (^oC)	Contact Time (hr)	Means of Reporting Results	Units Used	Experimental Objective	Ref.
52.6 to 1124	K, I M D.S.C.	0.2	<2	7-8	0.001M $CaCl_2$ and seawater	25	240	C_S v C_L	moles g^{-1} v moles l^{-1}	Cd^{2+} affinity for clays	36
2.25×10^6 to 22.5×10^6	K V M	10	63-74	5-6	0.01 to 0.1N (M^{2+})	?	164	$\overline{X}_A$ v X_A	(mole fractions)	Selectivity coefficients	37
0.1 to 100	C I	?	?	7.5	River water	25	?	Log C_S v Log C_L	$\mu g\ g^{-1}$ $\mu g\ ml^{-1}$	Cd^{2+} affinity for clays	38
9400 to 205,000	K M	4 1	<2	1.9 to 6.95	Deionized water and leachate	25	24	C_S v C_L	mg g^{-1} mg l^{-1}	Leaching from waste tips	39
19100	K I M	0.05 0.025 9.92	<2	3.5 to 12	Deionized water	25		i) C_S v pH ii) Cd removed v pH	mM kg^{-1} mM kg^{-1}	Adsorption/desorption	40
										Effect of organic chelators	41
22	V I M M	0.067 to 0.2	<0.2	5 to 7.7	0.03M $CaCl_2$	26	?	$C_S / \left(\frac{(Cd)}{(Ca)}\right)_L$ v pH	meq g^{-1}	C.E.C. of various clays	42
11240 to 112400	K I M	1% M^{2+} Conc'n	<2 <50 <2	4.8 to 6.5	Deionized water	?	4	K_{Ca}^{Cd}, K_{Cd}^{Pb}	-	Selectivity coefficients	43
0.05	M (various forms)	1	<2	7	0.01M $Ca(NO_3)_2$	?	48	C_S/C_L ("Kd"=Conc'n factor)	-	Adsorption onto cationic forms, with and without humic acids	44

(a) K = kaolinite, I = illite, M = montmorillonite, C = chlorite, V = vermiculite, D.S.C. = deep sea clay

(b) for rotation see text

(iv) adsorption may be described in three ways, the first according to the Berthelot-Nernst distribution law, second by Freundlich isothermal adsorption and third by Langmuir isothermal adsorption.

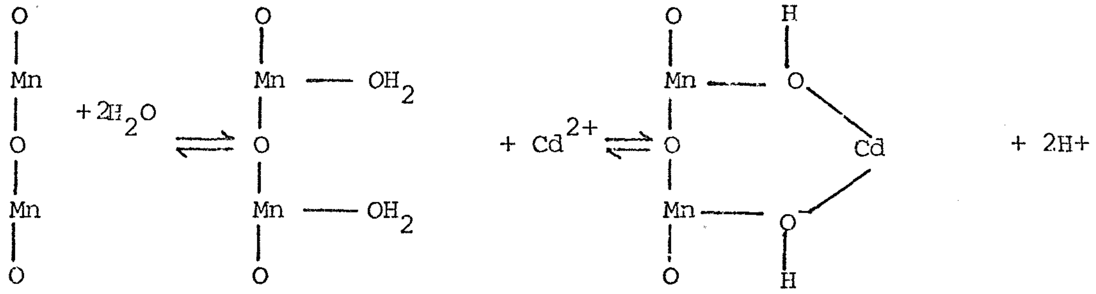
2.2.2 Experimental results

In the natural environment, adsorption onto organic and inorganic particles and metal hydrous oxides takes place. Studies in this area are complicated by the intimate admixture of particulate material, as illustrated, for example, by the coating of silicate mineral particles with hydrous iron oxides and by the flocculation of clays with organic material.

2.2.2.1 Adsorption onto inorganic particles

To understand something of the processes involved, several experiments have been conducted on 'simple' systems (Table 3). Guy et al. (45) found that the sorption of Cd onto freshly precipitated MnO_2 at pH 5 followed Langmuir adsorption with a limiting value of 0.124 gCd $g^{-1}MnO_2$.

Specific adsorption of the type:



was thought to be involved and was therefore dependent on pH in that at low pH the reaction equilibrium will lie to the right. The amount of metal adsorbed was proportional to the surface area and hence MnO_2, prepared in situ, adsorbed more cadmium than added ground MnO_2.

It is the high metal binding capacities of MnO_2 and FeOOH that makes the possibility of recovery of ferromanganese nodules an attractive commercial proposition. One of the mineral forms encountered in nodules is birnessite (0.7 nm manganite, MnO : MnO_2 = 5:13) and in terrestrial deposits a common mineral is nsutite (MnO : MnO_2 = 1:46). Both were examined for cadmium adsorption at pH3.5 to 4 by Van der Weijden (46). Nsutite has the more open and poorly crystalline structure and possibly this allows for the replacement of manganese by cadmium since they have similar divalent ionic radii (0.08 nm and 0.097 nm respectively).

Na^+ competes with Cd^{2+} for surface sites, the preference dependent on pH and ionic strength of the medium (for example, partial desorption of cadmium occurs in seawater). It was suggested that this accounted for the enrichment of zinc over cadmium in nodules (46); the basis of this proposal was an estimate for the Zn/Cd ratio in nodules of 133 compared to 20 in seawater. On the other hand, Ahrens et al. (47) gave the mean Zn/Cd ratio of nodules as 77 which is approximately the mean of the ratio for seawater.(App. 4, Table A7).

The concentration factors for cadmium of 10^5 found in oceanic nodules (47) are comparable to those reported with δ-MnO_2 by Van der Weijden (36) (Table 4a) and δ-MnO_2 is a common poorly crystalline form of manganese encountered in nodules. By reworking Van der Weijden's results (Figure 10) as Freundlich isotherms (Figure 11), log k values can be determined (Table 4b) (see Appendix 1). For C_L = 1 ng ml^{-1} in seawater the C_S value of the oxide is 2.1×10^5 ng g^{-1}.

Manganese may also form coatings on other particles. At pH5 to 6, adsorption of manganese onto montmorillonite, vermiculite and kaolinite was preferred to cadmium, although the opposite was true for albite and labradorite (C.E.C. = 0.6 and 2.5 meq 100 g^{-1} respectively) (37). However, cadmium may then bind to the manganese film as recorded with sediments (e.g. (48) and (49)). In a polluted stream, 2 µg g^{-1} Cd were associated with the hydroxylammonium chloride-leachable fraction, i.e. that held in the MnO_2/Fe_2O_3 phase, and only 1 µg g^{-1} in the refractive silicate fraction. Fast flowing stream waters have high Eh (and pH) which allows for the deposition of iron (III) oxides on silicate or carbonate particles, the iron then acting as a substrate for

Table 4 Cadmium Adsorption onto Clays, δ-MnO_2 and FeOOH

(a) Concentration Factors at varying Ionic Strength (I) and pH for experimental max. and min. Cd^{2+} concentrations.

(b) K Value derived for Freundlich Isotherms at 25°C and $\log (Cd^{2+})_{SOLUTION} = 0 \equiv 1 \mu g\ ml^{-1}$ (see Figure 11) and in brackets $0 \equiv 1 ng\ ml^{-1}$ (× 10^3 (see Figure 11)).

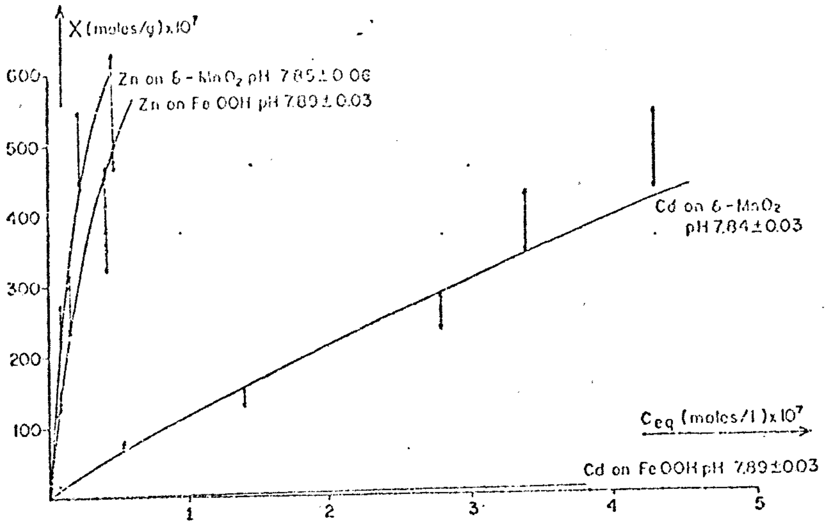
(c) Zn/Cd Ratios under similar physical conditions (taken and adapted from Van der Weijden (36)).

Clay/Oxide	Original Conc'n ($\mu g\ l^{-1}$)	pH7 $CaCl_2$ (I = 0.003)	 Seawater (I ≈ 0.7)	pH8 $CaCl_2$ (I = 0.003)	 Seawater (I ≈ 0.7)
(a) Montmorillonite	56.2	314	13	2000	175
	1124	151	0	465	20
Kaolinite	56.2	189	13	3086	205
	1124	69	0	490	24
Illite	56.2	1600	11	7800	177
	1124	400	0	810	15
Deep Sea Clay	56.2	1100	32	8800	176
	1124	270	16	3200	62
δ-MnO_2	56.2			290,000	
	1124			117,000	
FeOOH	56.2			32,900	
	1124			3,000	

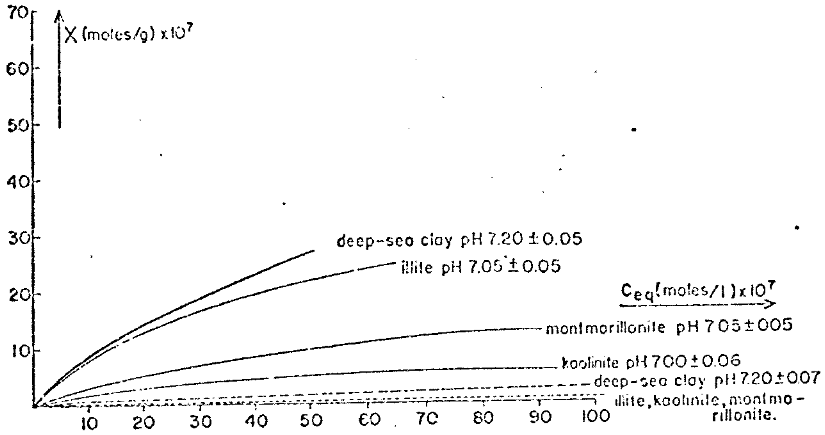
	($ng\ g^{-1}$)	($\mu g\ g^{-1}$)				($ng\ g^{-1}$)
(b) Montmorillonite	(2510)	125	12	320	20	(1260)
Kaolinite	(670)	72	13	320	32	(25)
Illite	(4000)	320	6	560	33	(1680)
Deep Sea Clay	(2113)	450	25	1600	60	(840)
δ-MnO_2					3800	(211000)
FeOOH					560	(7500)
(c) Montmorillonite		3	10	7	25	
Kaolinite		4-5	11	8	30	
Illite		5	11	10	25	
Average		4	11	9	30	

* Isotherms not shown in Figure 11.

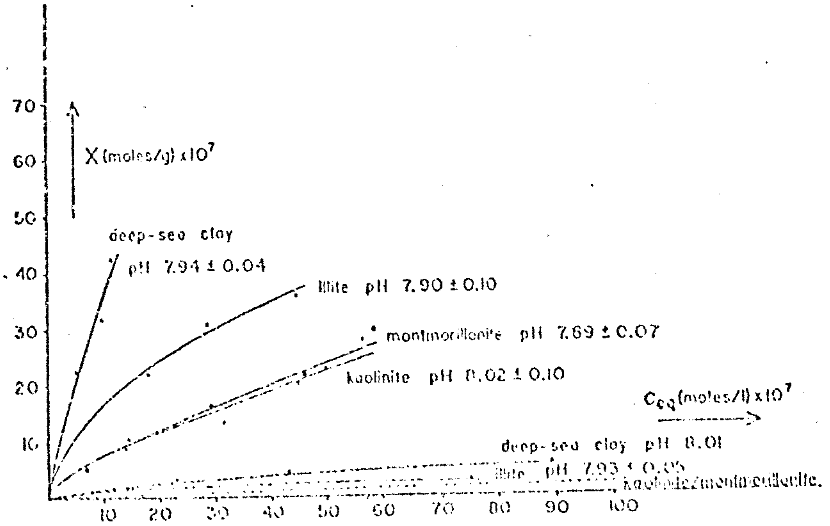
FIGURE 10. Adsorption of zinc and cadmium onto particulates in seawater and 10^{-3}m $CaCl_2$ solutions (After Van der Weijden (36)).



a) Sorption of Zn and Cd on δ-MnO_2 and Fe OOH at "pH8" in seawater.

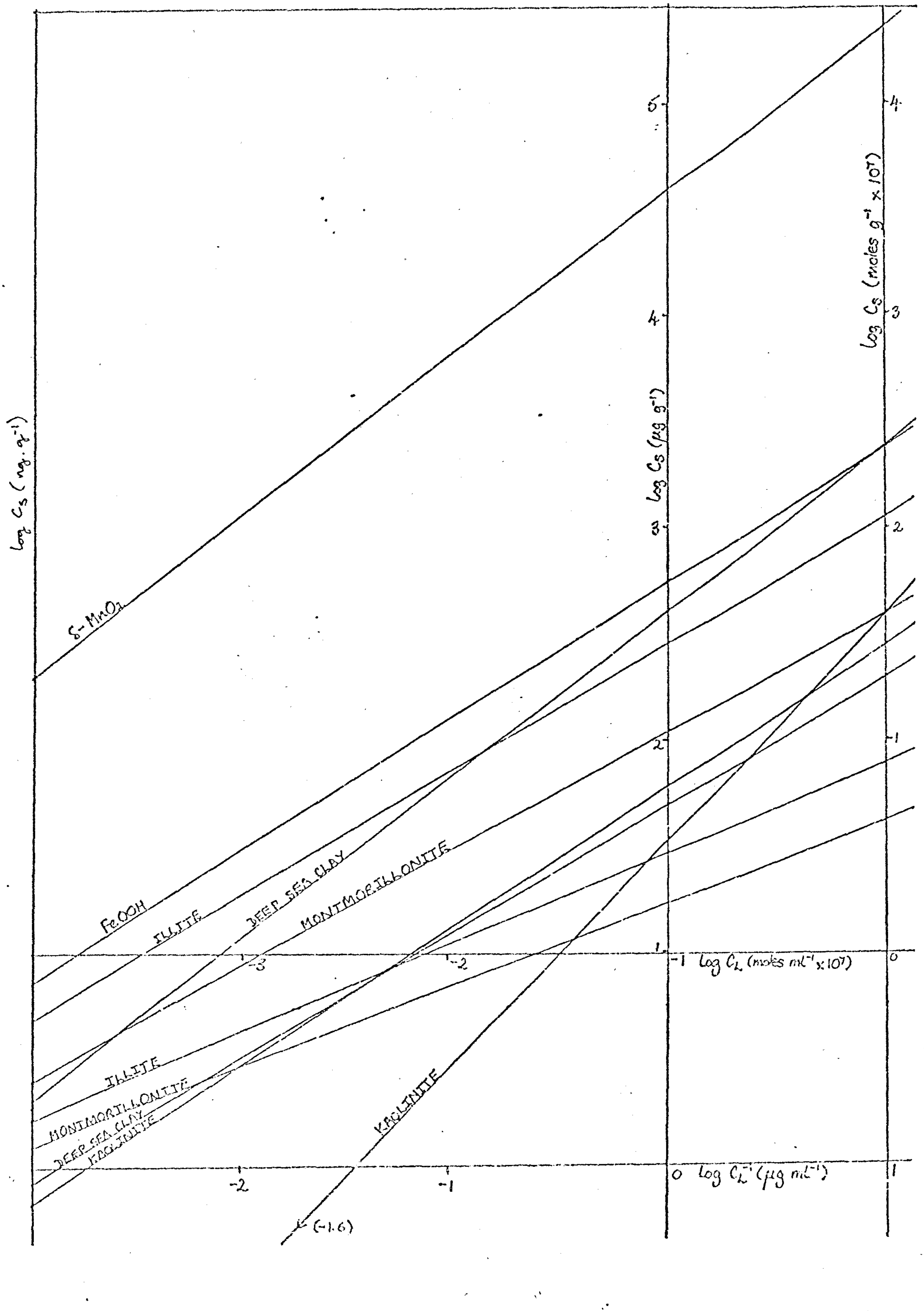


b) Sorption of Cd on clays at "pH7" in 10^{-3}m $CaCl_2$ (—) and seawater (-----)



c) Sorption of Cd on clays at "pH8" in 10^{-3}m $CaCl_2$ (—) and seawater (-----)

FIGURE 11. Freundlich isotherms of the data presented by Van der Weijden (36) (as log moles $g^{-1} \times 10^{-1}$ v log moles $ml^{-1} \times 10^{-7}$ and log $\mu g\ g^{-1}$ v log $\mu g\ ml^{-1}$)



manganese. In sediments of this nature, cadmium was found to be concentrated in the <2 μm fraction and the manganese/iron coated coarse sands and gravels (48).

The adsorption-desorption properties of clays have received much attention but, from the previous discussion, it was apparent that direct comparison of results was difficult (see Table 3 for experimental conditions). The order of affinities for cadmium of the substances studied was (a) for simulated fresh water at pH 7, deep sea clay > illite > montmorillonite > kaolinite, taking k values at solution equilibrium concentrations of both 1 μg ml^{-1} and 1 ng ml^{-1} and (b) for simulated seawater at pH 8, δ-MnO_2 >> Fe OOH >> deep sea clay > illite ≃ kaolinite > montmorillonite, taking k values at 1 μg ml^{-1}. But at lower concentration in the equilibrium solution (k at 1 ng g^{-1}) the order in seawater changes: δ-MnO_2 >> Fe OOH >> illite > montmorillonite > deep sea clay >> kaolinite (see Table 4b and Figure 11).

The general trend was that concentration factors (and k values) increase with pH but were greatly reduced by high ionic strength. From these results it may be proposed that adsorption onto particulates in freshwater is appreciable whilst in seawater δ-MnO_2 is the major scavenger for cadmium. One possible reason for the increase in Zn/Cd ratio (Table 4c) in moving from fresh to seawater is probably the difference in divalent ion concentration. In seawater 50% of the total dissolved zinc exists as Zn^{2+} but only 3% of the dissolved cadmium is present as Cd^{2+}.

From the graphical data for river water (presented by McDuffie et al., 38), at 1 ng ml^{-1}, the k values for chlorite and illite were 1.8×10^5 and 1×10^4 ng g^{-1} respectively at pH 7.5 with the value for suspended riverine solids falling between the two at 3.2×10^4 ng g^{-1}. Total desorption was noted below pH 3 and in seawater, i.e. at high H^+ or total cation concentration. Frost and Griffin (39) used isotherms as an aid in reporting their results on experiments with leachate from a landfill tip. Precipitation was observed at pH 7 (C_L = 5 μg ml^{-1}) and also at pH 6.5 (C_L ≃ 4.0 μg ml^{-1}) probably due to Cd CO_3 formation which is consistent with solubility product considerations.

An increase in adsorption onto montmorillonite was noted with an increase in pH from 4 to 6. With pure nitrate salt solutions at pH 5, adsorption followed the Langmuir isotherm for both montmorillonite and kaolinite with limiting values of $X_L = 32$ mg g^{-1} at $C_L \simeq 50$ µg ml^{-1} and $X_L = 5.5$ mg g^{-1} at 400 µg ml^{-1}. In comparison, leachate solutions with montmorillonite and illite at pH 5 followed Nernst-Berthelot adsorption and even at high C_L values of 770 µg ml^{-1} and 325 µg ml^{-1}, the corresponding C_S values were 7.5 mg g^{-1} and 0.7 µg g^{-1}. The difference between pure and leachate solution could be accounted for by the high dissolved organic content (1362 mg l^{-1}), and the concentration of competing cations (in the order of grams per litre). Cd-organic complexes were shown to comprise <2.5% of the total dissolved cadmium and therefore the competing ion effect was thought to be the most important factor, implicating cadmium as a highly mobile metal at pH<6.5. Farrah and Pickering (40) examined the sorption of metals onto kaolinite, illite and montmorillonite. Again, C_S was seen to increase with pH. The order of binding was montmorillonite > illite > kaolinite with C_S a maximum value of 250 at pH 6.5 (montmorillonite) down to 7 mmole kg^{-1} at pH 3.5 (kaolinite). Pb, Ca, Cu, Zn and Mg were all shown to be more readily adsorbed than cadmium (with the exception of Mg on illite), but sulphate and phosphate had little effect on cadmium adsorption or desorption. In 0.5M solutions as either NaCl or $NaNO_3$, complete inhibition of uptake was observed, i.e. dependent on Na^+ rather than chloro-complex formation.

Van Hook et al. (42) obtained similar results to other workers in that adsorption increased with pH but with low Cd^{2+} concentration in solutions (22 ng ml^{-1} at pH 5 in 0.03M $CaCl_2$). The ranking of binding was vermiculite > illite > montmorillonite > kaolinite with C.E.C. values ranging from a maximum of 100 meq g^{-1} at pH 7.5 for vermiculite to 0.1 meq g^{-1} at pH 5 for kaolinite. Stuanes (37) determined the C.E.C. for vermiculite, montmorillonite and illite to be 2.4, 44 (mean of two clay types) and 50 meq $100g^{-1}$ respectively in 0.01 N Cd^{2+} solutions.

Selectivity coefficients in binary solutions of the same clays were also measured by Stuanes (37). With a cadmium mole fraction of 0.25 and a total metal concentration of 0.01N, the order of selectivity was Zn>Mn>Cd>>Hg and the range of $K_{Cd}^{Zn\ (or\ Mn)}$ was 1.25 - 4.39 (pH 5-6). Other researchers (43) found that in the pH range of 4.8-6.5, lead was preferentially adsorbed (K_{Pb}^{Cd} = 0.31 to 0.58) whereas calcium K_S values were nearer unity (K_{Cd}^{Ca} = 0.89, 1.01, 1.04). Kaolinite gave the lower figures and illite approximated to montmorillonite. At pH 5 on montmorillonite the selectivity order was put at Ca>Pb>Cu>Mg>Cd>Zn although no figures were quoted (40).

In a similar vein, different cationic forms of clays bound cadmium to varying extents. Montmorillonite, coated with $Al(OH)_3$, $Fe(OH)_3$ or in the Ca^{2+}, Na^+, Fe^{3+} and Al^{3+} forms gave concentration factors of 614, 222, 104, 59, 43 and 33 respectively at 0.05 ng ml^{-1} Cd^{2+} and pH 7 (44). $Al(OH)_3$ and $Fe(OH)_3$ retained 40% to 20% respectively after five washes with 0.01m $CaCl_2$. Humic acid adsorption onto these coatings followed the order $Al^{3+} \simeq Fe^{3+} > Ca^{2+} > Al(OH)_3 \simeq Fe(OH)_3 > Na^+$. Decreased Cd^{2+} uptake was noted with the hydroxides (25 to 50% down) with a corresponding enhancement on the Al^{3+} and Fe^{3+} forms but little change with Na^+ and Ca^{2+}.

The effect of specific organic chelators, namely tartrate, ethylene diamine, bipyridyl, glycine, NTA and cyanide, on adsorption to montmorillonite, kaolinite and illite was investigated by Farrah and Pickering (41) (for conditions see Table 3). In the absence of organic ligands, precipitation (as $Cd(OH)_2$) was observed at about pH 7, but with glycine and bipyridyl, adsorption was taking place up to pH 9 because of the formation of cationic chelates. Tartrate had little effect on the system but masking of precipitation and prevention of adsorption was apparent with ligands forming stable species, i.e. NTA and CN^-.

In the case of naturally-occurring particulates and effluents, Gardiner (50) found that adsorption onto river muds and naturally-occurring solids was rapid, producing concentration factors in the range 5×10^3 to 5×10^4 depending on the state of subdivision, contact time, complexing ions, solids present and cadmium concentration. The proportions of Cd^{2+} adsorbed with time were 29.3 and 79.4% for two river muds after 2 min exposure to 2.1 μg l^{-1} Cd^{2+} and 49.6 and 94.7% after 24 hrs. In the latter case, C.F.'s ranging from 6×10^{3} to 2.6×10^{4} were recorded. As with the clay experiments, a decrease in C.F. was observed with increasing Cd^{2+} concentration for suspended solids (S.S.) = 34 μg l^{-1}, Cd^{2+} = 2.1 and 177 μg l^{-1} with C.F. = 2.5×10^{4} and 1.2×10^{3} respectively. At fixed (Cd^{2+}) (5.9 μg l^{-1}) and varying suspended solid loadings (7 to 210 mg l^{-1}) the C.F.'s were reasonably constant (7200 to 3800 respectively).

The effect of organic complexation or adsorption was simulated by the addition of EDTA to solutions containing 88 mg l^{-1} S.S. and 2.1 μg l^{-1} Cd^{2+}. At zero EDTA, the C.F. was 4.2×10^{4} and at 300 μg l^{-1} C.F. = 6.9×10^{3}. It was suggested that the high C.F. values for sediments cannot be explained by adsorption onto inorganic particulates alone since the 24 hr C.F. for silica was 10^{3} and for kaolin was 3.8×10^{2} at 7.3 μg l^{-1} Cd^{2+}. On the other hand, 2.1 - 4.3 μg l^{-1} Cd^{2+} solutions with humic acids gave a C.F. of 1.8×10^{4}. Although humus solids from sewage effluent initially followed the adsorption patterns of the humic acids, after 24 hours 50% desorption of the cadmium initially bound occurred and this was shown not to be due to microbial action or change in Eh.

Gardiner (50) concluded that humic material appeared to be mainly responsible for cadmium adsorption even though there was some evidence for direct competition between the two and no allowance was made for the manganese content of the mud samples.

Murray and Meinke (51) investigated the effect of soluble sewage materials on sediment adsorption-desorption of cadmium. The river sediment used was composed of 45% calcite, 35% quartz and 20% mica (>2000 μm) and equilibration was for 96 hrs under oxic conditions. The findings may be summarised as follows:

(a) on mixing river water with sewage effluent (0–100%) at pH 8.1 and 1 g l^{-1} sediment, >90% adsorption occurred in river water alone and only 35% in sewage effluent alone,

(b) 25% desorption was noted in river water alone and 62% in 50% sewage solutions,

(c) 'adsorption' was zero at pH 6.5 but 100% at pH 7.9 in unpolluted river waters,

(d) desorption of Cd in seawater from unpolluted freshwater sediment was only 25% in the absence of sewage, but nearer 60% at 25% sewage and greater,

(e) at pH 8.1 in freshwater-sewage mixtures, adsorption was greatly affected by the presence of phosphate (80% to 30% at 0 and 3.5 mg l^{-1} phosphate), as was desorption in seawater (80% at 2 mg l^{-1} phosphate in the absence of sewage).

From the above, it is obvious that the soluble sewage fraction, particularly with a high phosphate concentration, alters the distribution of cadmium both in freshwater and at the freshwater-seawater interface. However, this effect is not necessarily due to the organic complexation of cadmium but may be explained by direct competition of organic compounds and other metals for surface binding sites. Similarly, 'adsorption' reported at pH 7.9 may well have been precipitation as $CdCO_3$ or $Cd(OH)_2$ and the low desorption (only 25%) in seawater may have been caused by the presence of manganese or iron in the sediments provided the Eh was great enough.

2.2.2.2 Cadmium transport within organic particulates

Organic particles also prove to have a low affinity for cadmium adsorption. For instance, the adsorption of Cd^{2+} onto faecal material produced by fish gave comparatively low C.F. values (10^2 – 10^3) but concentrations within faecal material were higher and may be of prime importance in cadmium transport. The difference is one of passive versus active uptake (52).

In a small lake used by migrating geese, cadmium concentrations in goose faeces were 0.53 µg g^{-1} net weight (C.F. = 5.9×10^2 compared to the water), a figure only exceeded by the sediment (1.85 µg g^{-1}) and this probably as a result of faecal sedimentation (53). The concentration in euphausiids from the Mediterranean was 0.74 µg g^{-1} dry weight (54). However, the faecal pellets from the same euphausiids contained 9.6 µg g^{-1} Cd dry weight which helps to substantiate the proposal put forward by Boyle *et al.* (55) that faecal pellets are responsible for the vertical flux of cadmium in the oceans. To maintain a concentration of 9.6 µg g^{-1} Cd, the food (brine shrimps, *Artemia*) with a concentration of 2.1 µg g^{-1} needed to be consumed at a rate of 0.113 to 0.32 g per day per animal (*Meganyctiphanes norvegica*) (56). If 10% Cd was retained by the animal, 84% could be attributed to the total flux of the faecal material, i.e. food:faeces = 1 : 5, water: faeces = 1 : 10^6. A more detailed discussion on faecal pellet transport and fluxes is to be found in Section 3.1.3 and Chapter 4.

Zooplankton moult their exoskeletons many times during growth and, since the moults contain cadmium at 2.1 µg g^{-1} dry weight, their sedimentation may play a small but significant role in cadmium deposition (54,56, 57). However, Martin (59) showed that the cadmium concentration in mixed oceanic zooplankton (>0.366 mm) did not increase with depth, unlike other metals. This suggests that either desorption and/or no adsorption of cadmium occurs.

Not all animals display the ability to concentrate the cadmium taken in with food. For example, the crab *Pugettia producta*, fed on brown algae containing 3.4 µg g^{-1} Cd ashed weight, produced faeces containing 3.2 µg g^{-1} Cd (58).

2.2.3 Conclusions

The following is a summary of the general principles involved in cadmium adsorption onto particulates and a resumé of experimental findings.

(i) The adsorption of cadmium onto particulates increases with increasing pH;

(ii) The adsorption of cadmium decreases with increasing ionic strength, i.e. increasing cation concentration;

(iii) Cadmium may be adsorbed onto clays and larger particles that are coated with manganese oxides in freshwaters;

(iv) Manganese dioxide in oxic waters is the major scavenger for cadmium, particularly in seawater. C.F. values are in excess of 10^5;

(v) Total desorption from clays may occur in seawater;

(vi) The presence of dissolved organics decreases adsorption of cadmium onto inorganic particulates, probably by direct competition rather than chelation;

(vii) The K_S values for cadmium show that cadmium is lowest in the order of preference for binding to clays relative to other heavy metals and the alkaline earth metals;

(viii) In freshwater, the ability of inorganic particulates to bind cadmium, decreases in the order MnO_2 >> FeOOH >> deepsea clay > illite > montmorillonite > kaolinite;

(ix) In seawater, at a concentration of 1 $\mu g\ l^{-1}$ the order of binding was MnO_2 >> FeOOH >> illite > montmorillonite > deepsea clay >> kaolinite;

(x) The biological concentration of cadmium in faecal pellets appears to be the major transport route of cadmium to sediments in the oceans, and hence, besides cadmium being concentrated in manganese nodules, high sediment levels would be expected in areas of high productivity (see below).

Illustrations of these points in an environmental context are to be found in the second part of this chapter.

2.3 CADMIUM DESORPTION FROM SEDIMENTS

2.3.1 Desorption in estuaries

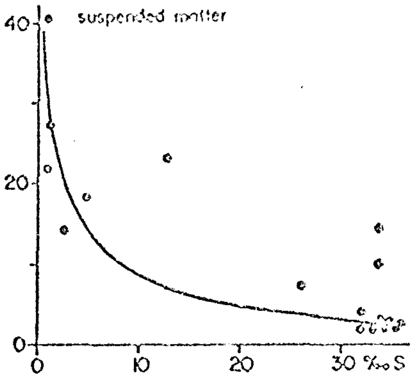
In order to explain cadmium-sediment interactions it is necessary to examine environmental data. The work carried out on metal transport in the Rhine and North Sea serves as a useful vehicle for such a discussion. Duinker and Notling (59) suggested that the Rhine estuary acts as a sink for 20-60% of the river-borne particulates and up to 50% of the suspended matter in the coastal area is accumulated in the Wadden Sea. The dependence on salinity of the amounts of suspended matter and dissolved Cd and Zn are shown in Figures 12(a) and (b). As the salinity increases, the relative amount of dissolved cadmium increases with respect to the suspended matter concentration, i.e. possible desorption effect, although removal does take place (roughly 40%). A further indication of cadmium desorption was taken to be the decrease in the Cd/Zn ratio in surface sediments (Figure 12c - experiment on the Back River (60)).

In a small slow moving tributary of the Rhine (Altrhein River), there was no evidence to suggest that there was any marked preference for binding according to grain size (<2 to 63 μm) nor was there a large positive correlation to organic content (r = +0.57 in both <2μm and 2-63 μm fractions (61).

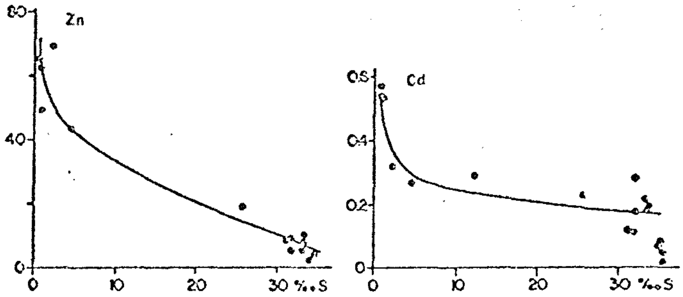
The research by de Groot and Allersma (25) on metal transport in the Rhine showed that the cadmium content of the sediments had doubled between 1960 and 1970 to 45 $\mu g\ g^{-1}$ in <16 μm fraction but the estimates of cadmium in water to cadmium in sediments ratio was 1 : 0.8. Again the decrease of cadmium concentration with increasing salinity in the sediments was taken as evidence for desorption (greater than the other eleven heavy metals monitored) although no allowance was made for precipitation or mixing.

Solomons and Mook (62) attempted to resolve the processes involved, that is, whether mobilization, mixing or precipitation was responsible for the lower concentrations in the estuarine and sea sediments, and concluded

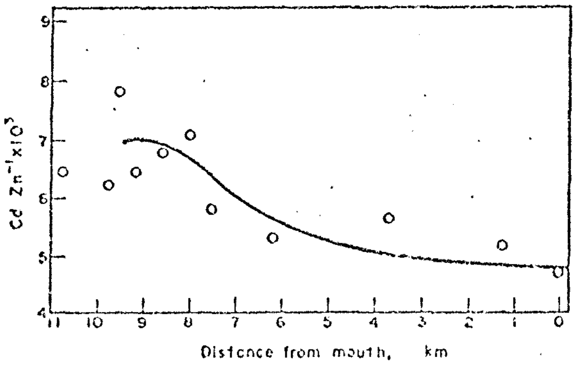
FIGURE 12. Illustration of cadmium-particulate interactions with increasing salinity.



a) Concentration of suspended matter in mg l^{-1} as a function of salinity. (after Duinker and Notling (59))



b) Concentration of dissolved metals as a function of salinity. (after Duinker and Notling (59))



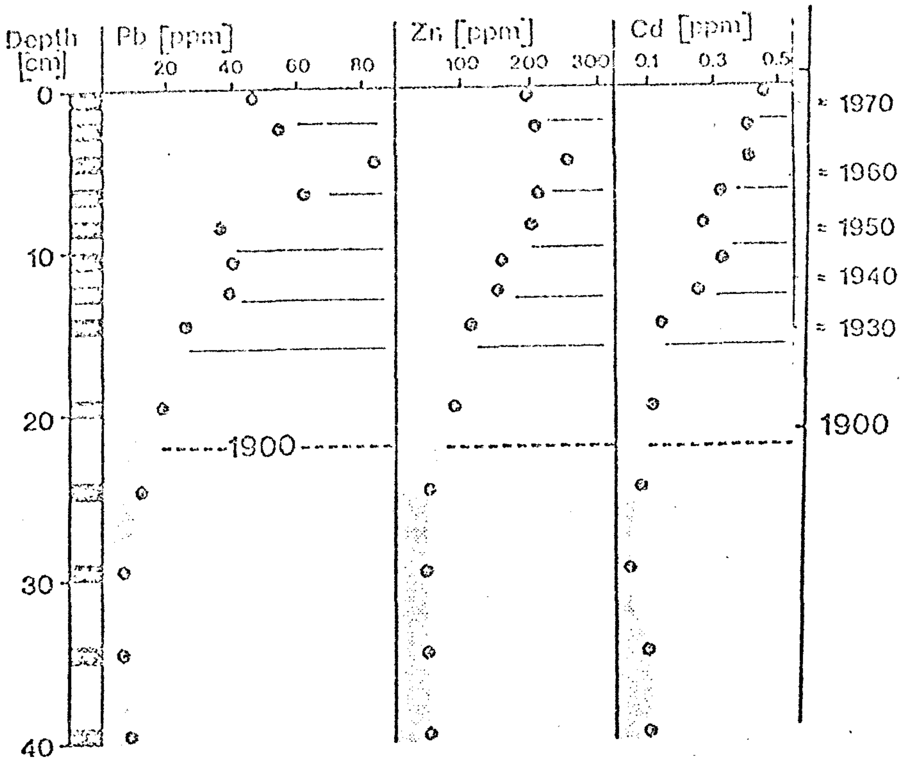
c) Cadmium to zinc ratio in the surface sediments of Back River showing the relative depletion of Cd toward the river mouth. (after Helz et. al. (60)).

the mixing of contaminated fluvial material with 'clean' marine solids was responsible for a dilution effect (supported by Müller and Förstner (63) from their work on the Elbe). However the drop in cadmium from 17 to 0.06 $\mu g\ g^{-1}$ in freshwater to marine sediments far exceeds that of the other metals measured, therefore desorption may still play a prominent role. This viewpoint is partly endorsed by desorption studies on suspended material from the Rhine (64) where the order of desorption found was Cd > Zn > Mn > Ni > Co > Cu > Cr > Fe = Pb. In the sediments of the lower Rhine about half of the cadmium present was associated with the reducible fraction, including that coprecipitated with $CaCO_3$, and the remaining half with the oxidizable organic anthropogenic fraction (65). About 98% of the cadmium present derives from anthropogenic inputs (65).

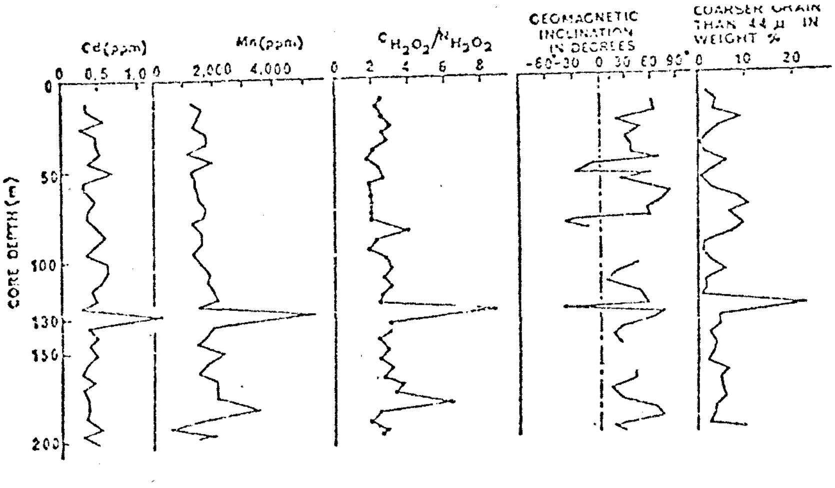
2.3.2 Remobilization from sediments

Since the highest levels of cadmium often appear in the top few centimetres, profiles of cadmium in marine and lacustrine sediments help to elucidate the pollution history of a body of water. Such interpretations have been applied particularly to lakes (e.g. 66 and 67) and marine bays (68,69) (see Figure 13a). However, such interpretations are complicated by metal migration in pore waters. For instance, the diagenesis of manganese is controlled by redox potential; soluble manganese is produced in the reduced part of the sediment and, because of the concentration gradient so produced and possibly by sediment compaction, manganese migrates upwards in the pore water. On reaching the oxidizing surface precipitation takes place. Cadmium migration under such reducing conditions, e.g. $\Sigma S = 10^{-3}$ M, may be caused by the formation of the soluble bisulphide. From K_{SP} considerations alone, the concentration of CdS in solution is expected to be 5×10^{-12} ng ml^{-1} but in practice in anoxic seawater concentrations of 0.2 - 8 ng ml^{-1} were found (69). The association of cadmium with manganese, organic matter and particle size in a 200 m lake sediment core shows a strong positive relationship (70) (Figure 13b) and similar observations have been made in

FIGURE 13. Examples of cadmium profiles in sediments.



a) Depth relationship of heavy metals in the sediment cores. (after Müller et. al. (67))



b) Relationship of the vertical distribution of cadmium and manganese to the $C_{H_2O_2}/N_{H_2O_2}$ ratio, to the oscillating geomagnetic field and to grain size distribution in a 2000 m core from the bottom of Lake Biwa. (after Kobayashi et. al. (70))

the Tennessee River sediments (63% Cd in the iron-manganese hydroxide fraction (71)).

Further evidence that the mobilization is dependent on the redox potential comes from Khalid et al. (72) and Lu and Chen (73). A sediment sampled from Barataria Bay had a clay composition of 15% montmorillonite, 15% illite, 10% kaolinite in 0.2 to 2 μm fraction and 40% montmorillonite, 5% illite and 5% kaolinite in the <0.2 μm fraction (total C.E.C. = 19.2 meq 100 g^{-1}). The original Eh was -60mV, pH 7.3, Cl^- 9100 mg l^{-1}, organic matter 5.15% and cadmium concentration of 4.1 μg g^{-1} (72). The sediment was first reduced to -150mV (pH 7.5) and aliquots purged with O_2/Ar at 21%, 2.1% and 0.11% O_2 at a flow rate of 20 ml min^{-1}, resulting in Eh and pH changes to +600 and 5.7 in 1 day, +600 and 6.5 in 7 days and no change in 60 days for each experimental batch respectively. In each case there was an increase in dissolved cadmium; 2μg l^{-1} to 6.9 (21% O_2), ≃ 6.0 (2.1% O_2) and 4.0 μg l^{-1} (0.11% O_2). The release mechanisms were thought to vary in such a way that, at low O_2, organic complexation or bisulphide formation was responsible, whilst at higher O_2 levels, $CdCl^+$ and Cd^{2+} may have been formed after the oxidation of sulphide to sulphate or by the release from Fe or Mn hydrated oxides (correlation with Cd, r = 0.67 and 0.57 respectively). In the latter case a "mechanism which is not very clear", possibly hydrogen ion displacement, was thought to be responsible.

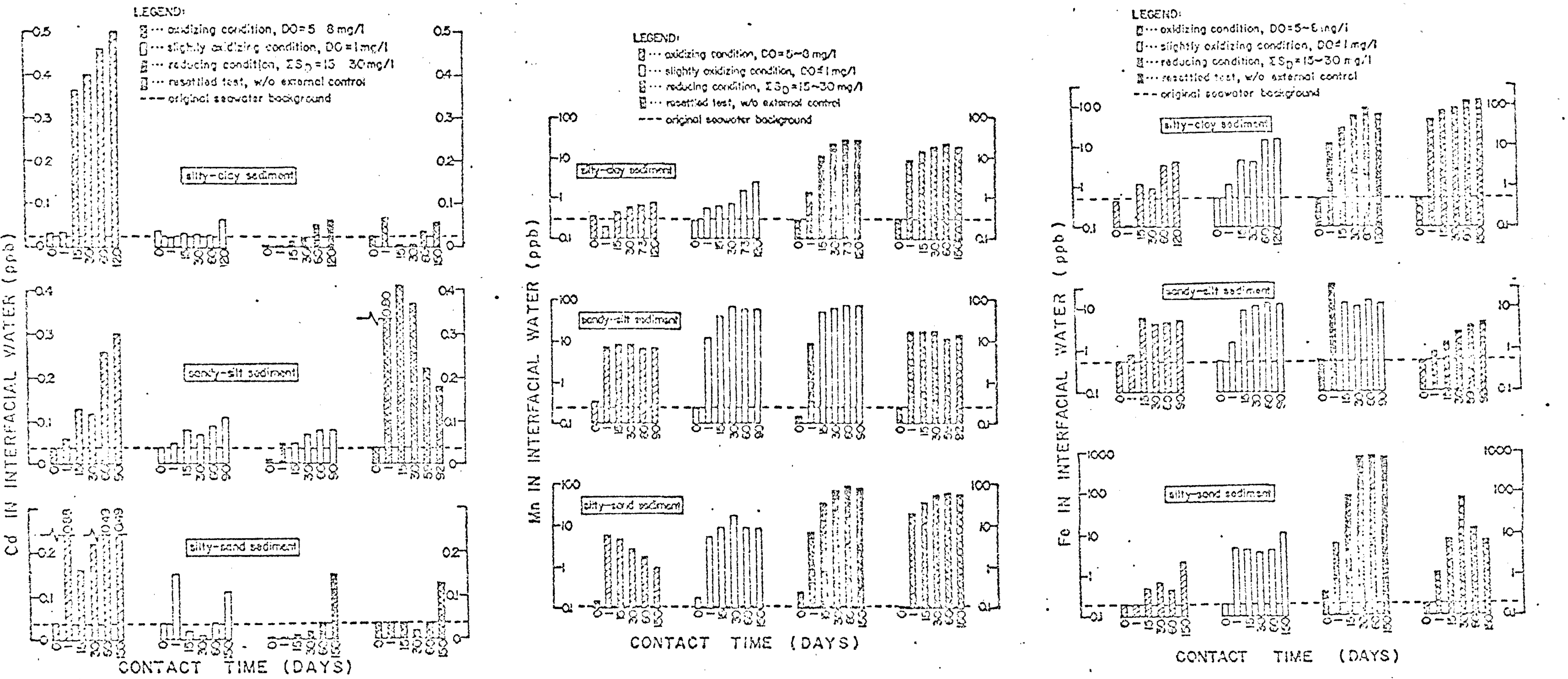
In Lu and Chen's experiments (73), the dissolution and resettling of iron, manganese and cadmium were studied (Figure 14). The histograms show an increase in cadmium concentration from 0.03 to 0.5 μg l^{-1} after 4 to 5 months at dissolved oxygen (D.O.) levels of 5-8 mg l^{-1} ($\Sigma S = 0$), with both silty-clay and silty-sand samples. Under low O_2 conditions (D.O. = 0-1 mg l^{-1}, $\Sigma S < 0.05$ mg l^{-1}) there was a slight increase above background but in an anoxic environment (D.O. = 0, ΣS = 15-30 mg l^{-1}) the cadmium concentration decreased (minimum at 60 days). In resettling experiments with the sandy-silt suspensions,

FIGURE 14. (after Lu and Chen (73))

a) Transport of Cd between the sediment-seawater interfaces

b) Transport of Mn between the sediment-seawater interfaces

c) Transport of Fe between the sediment-seawater interfaces



the cadmium pattern reflects manganese rather than iron distribution whereas the other two systems show immediate adsorption.

2.3.3 Conclusions

(i) The decrease in cadmium sediment concentration in moving down an estuary is due to two processes:-

(a) the mixing of fluvial particulates with incoming 'clean' marine particulates resulting in a dilution effect and

(b) the desorption of cadmium from suspended material on reaching highly saline water.

(ii) Remobilization of cadmium from sediments may be brought about by the following mechanisms (73):-

(a) Oxidizing conditions:

1. Diffusion from interstitial waters.
2. Desorption from clays, etc.
3. Chemical reactions, i.e. oxidation of organics and sulphides.
4. Ion exchange.
5. Dissolution.
6. Complexation.
7. Biological action.

(b) Reducing conditions - deposition → dissolution:

1. Sulphide complex formation.
2. Organometallic complexation.
3. Diffusion processes.
4. Release of metals from the dissolution of Fe and Mn hydroxy oxides by the formation of dissolved FeII and MnII ions.

CHAPTER 3

THE GLOBAL DISTRIBUTION OF CADMIUM IN SALINE WATERS AND THE DISPOSAL OF CADMIUM CONTAINING WASTES AT SEA

The collected data of cadmium levels in the sediments and waters of the world's estuaries, seas and oceans is presented in Table 5. In many cases dissolved and sediment samples were taken at the same stations, therefore the two phases are considered together so that direct comparisons can be made. A summary of the data is given in Table 6 and this general overview proves useful in the identification of abnormally high cadmium concentrations, particularly in association with dump sites.

3.1 THE GLOBAL DISTRIBUTION OF CADMIUM IN SALINE WATERS

There are severe limitations when comparing the work of different research groups because of variations in experimental methods. For example 'filtered' water in Table 5 refers to samples passed through membranes of between 0.2 and 0.8 μm. Similarly, sediment values quoted range from 'soft' leachable cadmium (acetic acid) to total cadmium (strong oxidation) on either specific size fractions or total sediment. There is also a heavy bias in the work towards the industrialised northern hemisphere (between 20° and 60°N) and also to areas thought or known to be contaminated with cadmium. The former difficulties can only be overcome by standardisation of sampling and analytical procedures and the latter by more exhaustive baseline studies.

The terms in Table 6 are defined as follows:-

Background - the minimum recorded value.

'Normal' range - based on values in uncontaminated systems, including areas where no mineralization is evident. The choice is subjective and open to debate.

Suspected contamination - refers to values in excess of the upper figure of the 'normal' range.

Top of range - maximum recorded value.

3.1.1 Estuaries and enclosed bays

Cadmium levels in sediments and water tend to be highest above the tidal limit and decrease towards the seaward end of an estuary, e.g. the

Table 5 Cadmium Distribution in Estuaries, Coastal Waters, Seas and Oceans of the World

Water values in µg l^{-1}, all values for sediments µg g^{-1}, E = Estuary, C = Coastal water, B = Bay, CB = Closed Bay/harbour, + = water disposal site, F = Fjord, OS = Open Sea, OO = Open Ocean.

Sea or Ocean	Place of Sampling	Sample Description	No. of Samples	Mean	Range	Type of Area	Ref.
Mediterranean	Gulf of Fos	Water - unfiltered	83		0.05-11.5	B	74
	North-west Med.	Water - filtered	14	<0.15	<0.03-0.8	C/OS	75
	" " "	Water - filtered	17	0.19	<0.1-0.7	OS	76
	South-west Med.	Water - filtered	10	0.15	<0.05-0.51	OS	"
	Tyrrenian Sea	Water - filtered	4	0.15	0.08-0.33	OS	"
	Ionian Sea	Water - filtered	3	0.08	0.06-0.12	OS	"
	Aegean/Cretan Seas	Water - filtered	3	0.08	<0.05-0.12	OS	"
			37	0.15			
Baltic	Gulf of Bothnia	Water - unfiltered	10	2.39	0.3-10.2	C	77,78
		Sediment	6	0.86	0.17-1.37	C	" "
	Gulf of Finland	Water - unfiltered	11	0.72	0.1-2.2	C	" "
		Sediment	3	1.17	0.47-1.88	C	" "
	Gotland Basin	Sediment - 1 core subsampled	21		0.6-2.2	OS	79
	Bornholm Basin	Sediment - 1 core subsampled	20		0.25-2.0	OS	79
		Water - filtered - 1 station, depth	126	0.12	0.05-0.2	OS	80
	Western Baltic	Water - unfiltered - 13 stations (surface -0-23 m)			0.02-0.2 0.02-0.3	OS	81
North Sea	Sörfjord, W. Norway	Sediments	14		16-850	F	82
	Rhine Delta:						
	Hoek van Holland	Water - filtered	3	0.53	0.3-0.7	E	64
	Rhine - Meuse	Water - filtered	6		0.45-0.7	E	59,67
		Sediment	10		0.6-28	E	62

	Ems Estuary	Sediment	6		0.5-3.0	E	62
	River Blyth	Sediment			0.17-3.4	E	83
	+East Coast U.K.	Water - filtered		0.5	0.1-6.2	C	84
		Water - filtered	4	0.41	0.29-0.6	C	85
	Southern North Sea	Water - filtered	15	0.3	0.1-0.6	OS	32
		Water - filtered - surface	41		<0.1-1.6	OS	84
		Water - filtered - bottom	14		0.1-0.5	OS	84
	Rhine and Southern Bight	Water - filtered	19		0.2-0.58	OS/C	32
	Western North Sea	Water - filtered	43	0.2	<0.1-1.4	OS/C	86
English Channel	Poole Harbour	Water - filtered - highwater	15	0.35	0.1-0.7	CB/E	87
		Water - filtered - low water	7	1.68	0.4-7.4	CB/E	"
		Water - filtered - (oyster hatchery)	30	5.7	0.7-20.5		"
		Sediment (<200μm)	10	4.2	<1- 10		"
	Coastal (England)	Water - filtered	4	0.06	<0.01-0.38	C	86
	West English Channel	Water - filtered (1954) July	6	0.096	0.024-0.163	C	88
		Oct.	6	0.081	0.057-0.146		
		(1955) Feb.	6	0.180	0.094-0.256		
Bristol Channel	Tawe Estuary	Water - filtered	11		0.25-7.4	E	89
		Sediment - strong oxidation	7		3-70		"
		acetic acid	7		10-37		
	Swansea Bay Rivers	Water - filtered	16		0.5-3.5	E	89
		Sediment - strong oxidation	6		2-6		"
		acetic acid	6		1-4		
	+Severn Estuary/Channel	Water - filtered	8		0.3-5.8	E	90
		Sediment	7		1.6-4.7	E/C	"
	+Bristol Channel/Estuary	Water - filtered	44	1.13	0.28-4.2	C	91

Irish Sea	Cardigan Bay	Water - filtered		20	1.11	0.48-2.41	B/C	91
		Sediment	river	10	1.7	0.8-3.5	E	92
			beach	15	1.0	0.4-1.9	C	
			seabed	86	1.1	0.2-3.4	OS	
	Irish Shoreline	Water - filtered		9	0.41	0.03-1.43	C	85
	Irish Sea and Cardigan Bay	Water - filtered		10	0.11	<0.01-0.52	B/C	86
	North-east Irish Sea	Water - filtered	(1956) Apr.	5	0.057	0.034-0.081	C	88
			Nov.	6	0.101	0.08-0.159		"
			(1955) May	6	0.166	0.083-0.252		
	+Liverpool Bay	Water - filtered	shoreline	11	0.46	0.15-1.14	C	85
		Water - filtered		27	0.27	0.14-0.74	B	91
	Irish Sea	Sediment - organic mud		2	0.39	0.363-0.417		88
Inner Seas - W. Coast of Scotland		Water - filtered		8	<0.01	<0.01-0.18	C	86
Atlantic	North	Sediment -	Green mud	1		0.268	OO	88
			Calcareous ooze	1		0.574	OO	"
			Foram ooze (5 stations and subsamples)	12	0.18	0.13-0.21	OO	93
			Deep sea	35	0.225	0.04-0.58	OO	94
		Water - filtered (6 stations)		83	0.06	0.02-0.15	OO	93
	North-east - U.K. Coastal	Water - filtered		5	0.04	0.01-0.41	C	85,86
	- Near shore	Water - filtered		16	0.08	0.04-0.16	C	95
	- Tropical shelf	Water - filtered (17 stations)		100	0.11	0.07-0.71	OO/C	96
	North-west - U.S. Coastal							
	Gulf of Maine	Water - filtered		10	0.23	0.078-0.52	B	93

+New Bedford Harbour/ Buzzards' Bay	Sediment - <2 µm clay	3 cores		1.4-52	CB/B	97
Narragansett Bay	Sediment	1 core		0.6-0.8	B	98
+Long Island Sound	Water - filtered				B	99
	Before dumping	26	2.79	<0.1-10.3		"
	After dumping	32	1.66	<0.1-5.96		
	Sediment - before dumping	8	6.9	3.8-14.5		100
	after dumping	11	10	4.3-17.5		
	residual		0			
	reduceable+	5	0.6			101
	organic & sulphide	5	14.8			"
	Sediments from all over the Sound	115		<1.0-4.2		102
Foundry Cove	Water - filtered					
	- before dredging	12		<0.1-1.1	CB	103
	- after dredging			0.7-45.7		
	Sediments - before dredging (two areas)			2500-18,400 30-50		103
Raritan Bay	Sediment	162		<1-15	B	104
+New York Bight	Water - unfiltered (Apr.)	74	0.42	0.16-1.6	B	105
	filtered (June)	81		(0.2-7.0		
	(July)	78	0.82	(0.2-7.0		
	(Sept. -Oct.)	77		(0.2-6.1		
Back River Estuary	Water - unfiltered	6		0.5-3.5	E	60
	Sediment (<62 µm)	11		1.8-5		60
Southern U.S.A. Rivers	Water - filtered			0.3-1.0	E	106
Salt marsh	Sediments	25	1.4	0.2-5.0	E	
Shelf waters 'North'	Water - filtered	39	0.11	0.02-0.23	OO/C	107
'South'		18	0.06	0.02-0.12		

	Card Sound, Florida	Sediments	82	0.07		C	108
	Turkey Point	Sediments	33	0.2		C	"
	Mangrove Lake, Bermuda	Sediments	32	0.7		E	"
	Sargasso Sea	Water - unfiltered					
		surface (<1 m)	19	0.005		OO	109
		deep (1800-4000 m)	25	0.025 (corrected)	0.016-0.055		
	Cuba - Puerto Rico	Water - unfiltered? 5 stations	15	0.57	0.13-1.2	OS/C	110
Caribbean	Western	Water - unfiltered?					
		(1-1000 m - 8 stations)	35	0.19	0.05-0.78	OS	111
	Eastern	(1-1000 m - 9 stations)	40	0.25	0.09-0.69		
		Sediments	18	3.1	1.9-4.8		111
Gulf of Mexico	Florida: Barron River Canal	Water - filtered		2.8		E	112
	Chokoloskee Bay	Water - filtered		4.2		B	
	Lostman's Bay	Water - filtered		1.4		B	
	Mobile Bay	Sediment (residual)	3	2.8		B	101
	Mississippi (Lower)	Water - filtered	90	<5			113
		Sediment (residual phase)	3	2.8			
	Mississippi Delta and Shelf	Sediment	72	0.3	0.02-0.7	E,C	68
	Galveston Bay	Sediment	44	<0.6	<0.02-4.9	B	68
	Houston Ship Canal	Sediment	24	<2.9	<0.01-10.7	E	"
	San Antonio Bay	Sediment	51	0.2	0.02-0.44	B	"
	Corpus Christi Bay	Sediment Harbour	287		0.1-1.9 2-130	B	113
		Water - unfiltered?	156		3-78	CB	114

	South: African Coast	Water - filtered	10	0.09	0.04-0.3	C	95
	Walvis Bay	Sediments (diatomaceous) <2 µm	47	16.7	<3.0-60		115
	Open waters	Water - filtered	15	0.07	0.04-0.17	OO	
		Sediments - radiolarian ooze	2	0.55	0.129-0.977	OO	88
		diatomaceous ooze	5	0.39	0.174-0.857		
Pacific	West - San Francisco Bay	Shoreline sediment	68			CB	116
		Top		1.22	0.06-4.69		
		Bottom		0.93	0.14-3.91		
	Monterey Bay	Water - filtered	26	0.15	0.02-0.51	B	117
		Intense upwelling	7	0.3	0.11-0.51	B/OO	"
		Low upwelling	8	0.11	0.06-0.16	B/OO	"
		Oceanic	4	0.03	0.02-0.05	OO	"
		Mixed	7	0.09	0.04-0.2	B	"
	Monterey - Hawaii Transect	Water - filtered	14	0.02	0.02-0.06	OO	"
	Santa Barbara Basin	Sediment	1	1.5	1-2	C	118
	+Los Angeles Harbour	Sediment (partitioned)	4		0.66-2.2		119
		Interstitial water	4		0.1-0.5		
		Water - unfiltered	1		6-11	CB	120
		Sediment	1		2-16	CB	
	Marina del Rey	Water - unfiltered	1		2.5-2.7	CB	120
		Sediment	3		1-8	CB	
	Long Beach Marina	Water - unfiltered	1		6.5-7.2	CB	120
		Sediment	1		2.5-5	CB	
	Santa Monica Bay	Water - unfiltered	1		10-11	CB	120
		Sediment	1		3-7.5	CB	

	North West Pacific	Water - filtered surface	46	0.06	<0.01-1.61	OO	121
		Water - filtered ≈ 1000 m	20	0.11	0.06-0.2	OO	"
			28	0.05	<0.01-0.65	OO	"
	Japan (coastal)	Water - filtered	38	0.07	<0.01-1.61	C	"
	North West Pacific	Water - filtered		0.064	0.01-0.37	OO	122
	Ariake Bay, Japan	Dry mud	47		0-15	B	123
	Tokyo Bay	Sediment	12	0.61	0.15-2.07	B	124
Inland Sea, Japan		Water - filtered	3	0.11	0.07-0.14	C	95
	South Japan	Water - filtered	1		0.13	C	"
	Sea of Japan	Water - filtered	2	0.11	0.09-0.12	C	"
			14	0.08	0.06-0.12	C	"
	Hong Kong waters	Water - unfiltered?	74	50	10-100	C	125
Java Sea		Water - filtered	3	0.06	0.05-0.07	C	95
Malacca Straits		Water - filtered	2	0.1	0.08-0.11	C	"
Australian Waters	Corio Bay	Water - 3 stations	19		0.06-0.4	CB	126
		Sediments - 4 stations	8		1.8-7.4		"
	Yarra River Estuary	Water - unfiltered	12		0.9-12.0	E	127
	Port Phillip Bay	Sediment - 20 cores	120		0.4-12	CB	128
		top	20		0.15-9.9		"
		bottom	20		0.04-1.7		
	Derwent Estuary, Tasmania	Water - filtered	19		<0.5-15	E	129
Indian Ocean	West Australian Estuaries	Water - filtered?	56		0.01-0.44	E	130
	Open Water	Water - filtered	23	0.07	0.02-0.14	OO	95

Red Sea	Atlantis II, Discovery and Chain Deeps	Interstitial waters (8 cores)	119	<0.03-3.9 (μg ml^{-1})	OS	131
	Atlantis II, Discovery and Chain Deeps	Sediment	122	2-600	OS	132

Table 6 A Summary of Cadmium Distribution in Saline Waters

	DISSOLVED $\mu g\ l^{-1}$				SEDIMENT $\mu g\ g^{-1}$			
	Background	'Normal' Range	Suspected Contamination	Top of Range	Background	'Normal' Range	Suspected Contamination	Top of Range
Estuaries and Closed Bays	0.01	0.05-0.2	>0.2	45.7	<1.0	0.1-2	>2.0	50,000
Bays and Coastal	<0.01	0.01-0.15	>0.15	10.3 (100)	<1.0	0.1-1.5	>1.5	60
Open Sea	<0.01	0.01-0.1	>0.1	1.6	<1.0	0.1-1.0	>1.0	(600)
Open Ocean	<0.005	0.01-0.1	>0.1	0.65 (1.61)	<1.0	0.1-1.0	>1.0	0.977

Rhine, discussed in 2.3, the River Tawe Estuary (mean dissolved Cd above the tidal limit of 125 $\mu g\ l^{-1}$ decreasing to 0.25 $\mu g\ l^{-1}$ at the estuary mouth (89)) and the Severn Estuary (90). The maximum cadmium levels measured in such an environment were in Foundry Cove, U.S.A., where sediment concentrations reached 50,000 $\mu g\ g^{-1}$ and dissolved concentrations 45.7 $\mu g\ l^{-1}$ (103). Each of these estuaries illustrate the various major sources of pollution, i.e. the Rhine - industrialization and urbanization; the Tawe - cadmium plating at a steelworks; the Severn - effluent from zinc smelting operations; and Foundry Cove - spillage from a battery manufacturing plant. The effects of such contamination may be seen over the length of estuaries and may extend into coastal waters (see below).

High cadmium concentrations in harbours and closed bays are exemplified by the work of Chen et al. (120), although the water samples in this case were not filtered. Obviously concentration will vary with season (high v. low runoff) and tide (87).

Levels above 0.2 $\mu g\ l^{-1}$ dissolved cadmium and 2.0 $\mu g\ g^{-1}$ dry weight in sediment suggest sources of contamination that require investigation.

3.1.2 Coastal waters

Elevated cadmium levels are again directly related to man's activities. Unfiltered samples taken from Hong Kong waters had cadmium concentrations in the range 10-100 $\mu g\ l^{-1}$ (125), samples being taken from the vicinity of drainage, domestic and industrial sewer outlets. Other high levels were associated with dredged waste disposal sites (Long Island Sound (100)) or industrial and estuarine influence, e.g. Gulf of Mexico. The extent of such contamination was noted on the eastern seaboard of the U.S.A. where the mean value in the north was 0.11 $\mu g\ l^{-1}$ in comparison to 0.06 $\mu g\ l^{-1}$ in the south (107). Dissolved concentration in excess of 0.15 $\mu g\ l^{-1}$ and sediment concentration greater than 1.5 $\mu g\ g^{-1}$ dry weight are considered to be abnormally high.

3.1.3 Seas and Oceans

The proposed 'normal' range of concentrations in seas and oceans are the same, i.e. 0.01-0.1 µg l^{-1} dissolved Cd and 0.1-1.0 µg g^{-1} Cd dry weight in sediment. Generally, increased surface concentrations are encountered in land-locked and shallow seas, as are found in the Mediterranean, Baltic and North Sea where circulation and turnover of the water masses are limited and/or estuarine/atmospheric inputs are large. The mean surface water values in the seas cited above are 2 to 4 times greater than those of the open oceans (= 0.06-0.07 µg l^{-1}) (93,95).

However, no significant variation in the dissolved vertical water column distribution is evident in shallow seas and shelf waters, e.g. New York Bight (99), the Baltic (80,81) and Caribbean <1000 m (111), as there is in the open oceans (see Table 7).

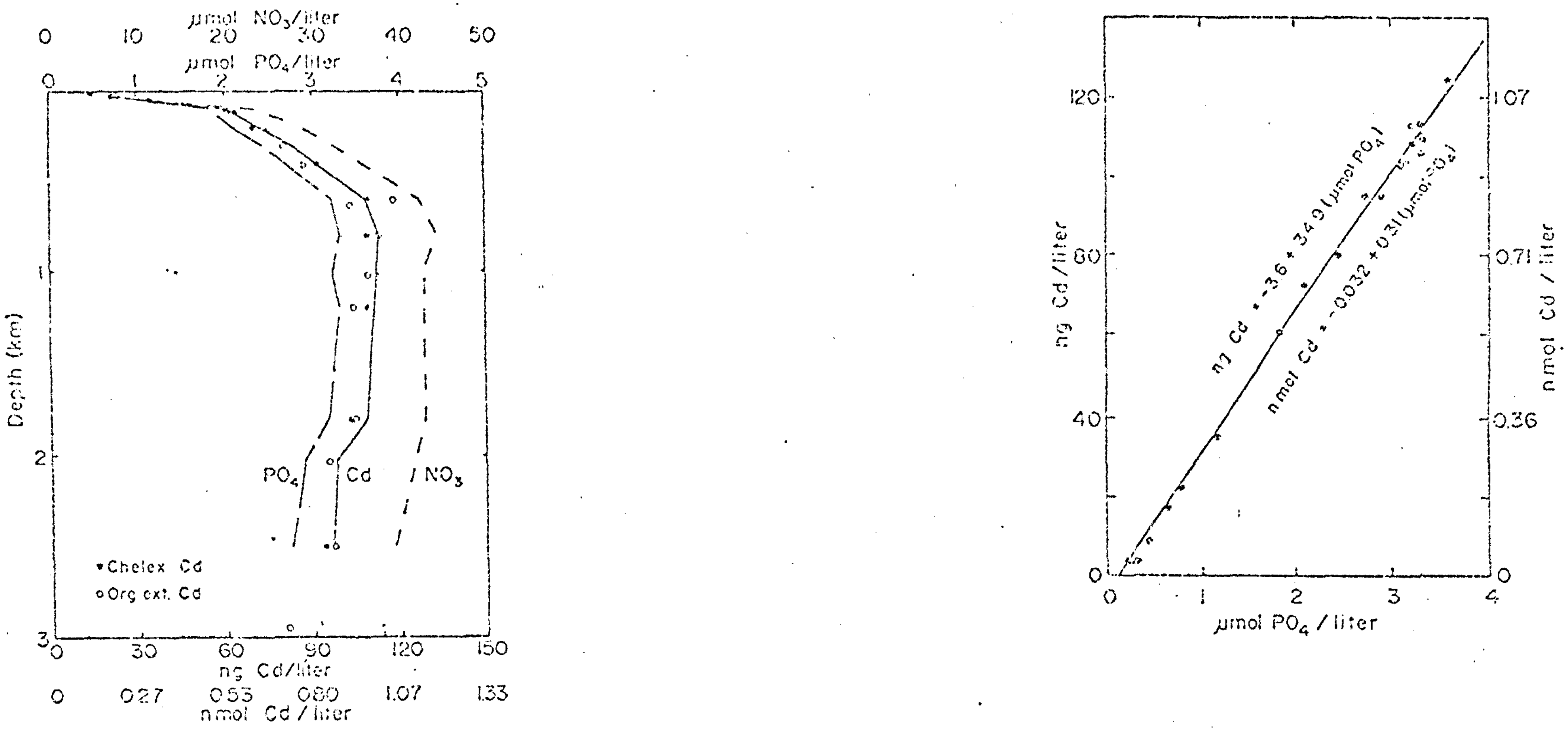
The cadmium concentration in the open ocean depth profiles was found to be positively correlated with the dissolved phosphate ($r = 0.957$ (134), $r = 0.878$ (55), $r = 0.998$ (133)). The plot of the latter result is shown in Figure 15a and the increase in concentration with depth for both ions is illustrated by Figure 15b. Since upwelling produces nutrient rich waters, plankton bloom and in so doing strip metals and nutrients from the surface waters, with subsequent transport to deep water in skeletons and zooplankton faecal pellets. Work carried out by Honjo and Roman (135) on copepod faecal pellet sedimentation showed that faecal pellet surface membranes were degraded in 3 hr at 20°C, but were intact for up to 20 days at 5°C. If the surface membrane, shown to be rapidly colonized by bacteria, is rapidly degraded in the warm upper layers of the ocean then biodegradation and leaching of pellets can take place on vertical transport through the water column. Such an effect may give rise to profiles such as those shown in Figure 15b, on the proviso that Cd is concentrated in faecal material.

Since the deep water returns to the surface on upwelling then enrichment of cadmium would be expected in such areas and this effect has been

Table 7 Variation of Cadmium Concentration with Depth (units $\mu g\ l^{-1}$)

	Surface	1000-2000 m	
Sargasso Sea	0.005	0.025	(109)
N.W. Pacific	0.06	0.11	(121)
N. Pacific & Bering Sea	0.01-0.05	≃0.11	(55)
Pacific (Hawaii)	0.02	0.06	(117)
N.E. Pacific	0.02	0.115	(133)

FIGURE 15. Cadmium/phosphate relationship with depth in open ocean water (after Bruland *et al.* (133))



a) Depth profiles for Cd, PO_4 and NO_3. Cd profile line represents average of PO_4 - predicted Cd and NO_3 - predicted Cd. Observed Cd values (by two methods) also are shown.

b) Cd v. PO_4 observed at central California stations (r ; 0.998; n = 21) reported (117). However, the dissolved cadmium in surface waters will vary with season depending upon upwelling intensity and plankton density (114,117).

Some cadmium will not be regenerated and will accumulate in the sediment and therefore elevated levels of cadmium may be expected in sediments underlying areas of high productivity. There is support for this hypothesis from Bremner's work on shelf sediments (Walvis Bay) (115) where cadmium concentrations of up to 60 $\mu g\ g^{-1}$ in sediments were correlated to the distribution of the diatomaceous mud belt. Furthermore the degree of correlation with opal rather than organic carbon suggests uptake by the diatom frustules.

The maximum sediment cadmium concentration was recorded in a Red Sea deposit rich in sulphide (600 $\mu g\ g^{-1}$ Cd (132)) and is far in excess of the normal sediment range of 0.1-1 $\mu g\ g^{-1}$ (88).

There is little data available on sea and oceanic sediment levels; comparisons in sediment concentrations between shelf, upwelling and low productivity areas are essential to the understanding of the geochemistry of this element. Similarly, there is little data of any value on the concentration of cadmium in suspended material in the oceans, data necessary for the calculation of fluxes.

Increased cadmium concentrations in sea and oceans may also be the result of the disposal of cadmium containing wastes at sea (see section 3.2 below).

3.1.4 Conclusions

(i) Although some workers have not found any significant variations between coastal and offshore cadmium concentrations e.g. (75), such variations are indicated on examination of the collected data. The gradient follows the order rivers > estuaries and enclosed bays > open bays and coastal waters > seas > open oceans. The gradient becomes exaggerated when polluted waters and sediments are considered (Table 6).

(ii) The ratio of dissolved to sediment cadmium in the 'normal' range in all four categories is 1 : 10^4 by weight.

(iii) The cleanest (oceanic background) and the most polluted waters are separated by four orders of magnitude.

(iv) The cleanest and most polluted sediments differ by about five orders of magnitude.

(v) Where cadmium levels exceed the upper value of the 'normal' range (Table 6) the cause for the increased concentration should be investigated.

(vi) The most common causes for grossly elevated cadmium levels near land masses are industrial activities, e.g. zinc and lead smelters, mine workings, steelworks and battery plants.

(vii) Offshore 'high spots' of cadmium concentrations may be related to (a) areas of upwelling and hence productivity which may in turn correlate with increased cadmium concentration at depth and in sediments or (b) be a result of dumping cadmium-containing wastes at sea.

3.2 THE DISPOSAL OF CADMIUM-CONTAINING WASTES AT SEA

There is barely enough data available to conclusively determine cadmium retention or mobilization from the dumping of wastes at sea. Much of the following discussion is based on inference from coincidental maximum cadmium concentrations with disposal sites. U.K. coastal waters and the New York Bight (including Deep Water Dump Site 106) have been chosen to illustrate possible effects.

3.2.1 U.K. coastal waters and the North Sea

Table 8a shows that the U.K. contributes more than half of the total cadmium budget to the waters within the Oslo Commission area (Figure 16) and U.K. dumping activities are equivalent to 8% of the total input from land based sources (136). In the areas of the dump sites (Table 8b and Figures 16 and 17), the cadmium content of the dumped waste is equal to that derived from land sources and nearly three times that of the river input (136).

If Figure 17, showing dumpsite location, is compared with the cadmium distributions around the U.K. monitored in 1971 (Figures 18a and b) it is

Table 8a Inputs of Cadmium into the Oslo Commission Area, U.K. Contribution to total inputs (tonnes yr^{-1}) (136)

	Total	Rivers	Domestic	Industrial	(Marine Dumping)
U.K.	225.2	160	36.6	26.7	(40)
Total	503.1	420.9	42.6	37.7	(80+)

+Incomplete data

Table 8b Marine Dumping compared to the Total River Inputs of Cadmium in the Oslo Commission Area (136)

		Cd Input (tonnes yr^{-1})		
Area	Description	Total	River	Marine Dumping
E8	River Wear to River Tyne	3.6	2.8	3
E8	Humber to Wash	1.3	0.2	1
E11	Colne Point to Haven Point	3.2	0.6	5
E20/25	St David's Head to Foreland Point	1.5	1.1	1
E22	Beachly Point	1.5	1.1	9
E26	Cardigan Bay	1.4	0.7	-
E27	Off Anglesey	5.6	4.9	2
E28	Mersey Estuary	22.4	3.4	18
		40.5	14.8	40
SC2	Ballantree to Sound of Mull	7.3	3.6	1
Netherlands	Rhine Delta	109	109	39
DK3	Limfjord	4.0	4.0	1.4

N.B. E9 to 18 (excluding E16) have domestic sewage input >1 tonne yr^{-1} with max. at E12 (River Thames = 6.6 tonnes yr^{-1}).

FIGURE 16. Area divisions for Sweden, Denmark, Federal Republic of Germany, Netherlands, Belgium, England/Wales, Scotland, Northern Ireland, Ireland and Iceland. (after Preston (136))

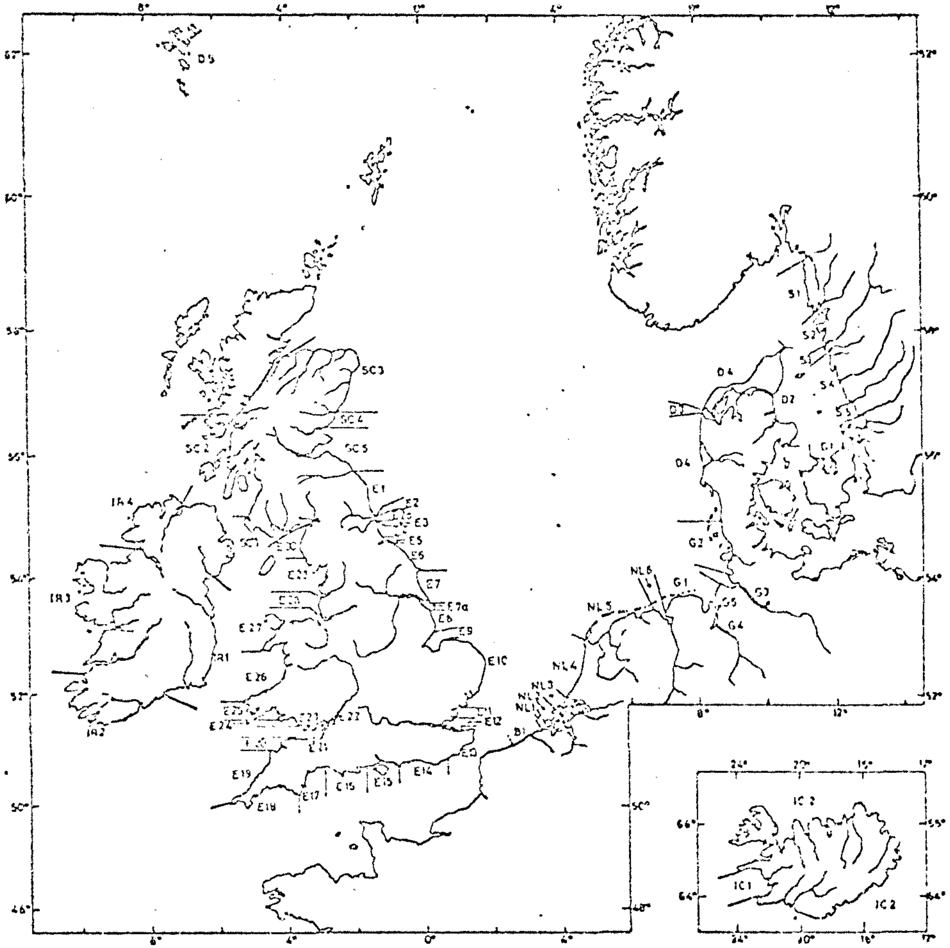


FIGURE 17. Position of dumping grounds which have been monitored by MAFF surveys 1970-1977. (after Norton and Rolfe (137))

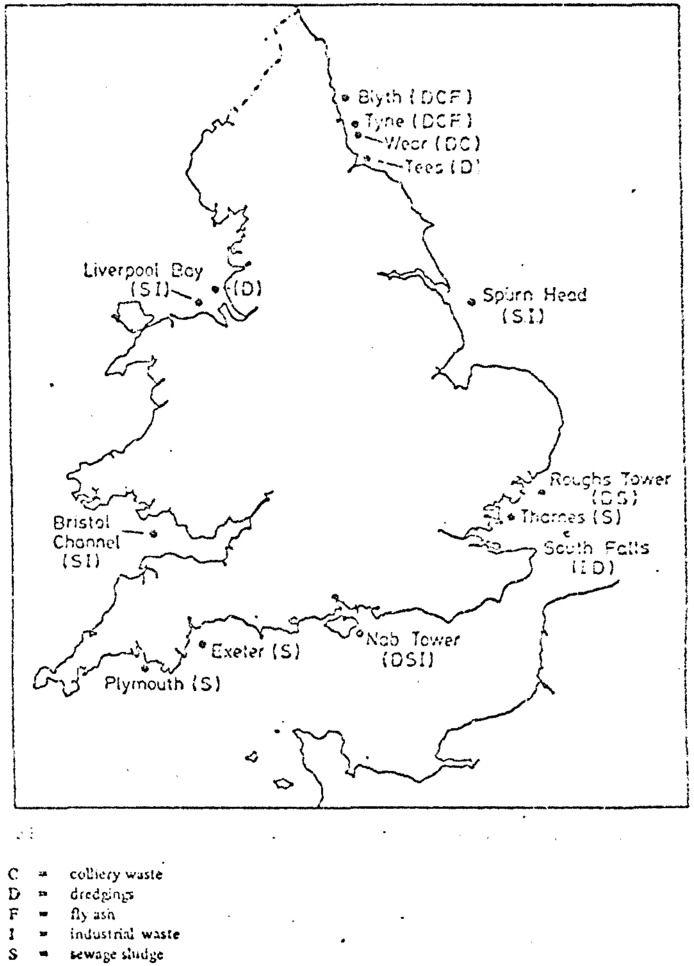
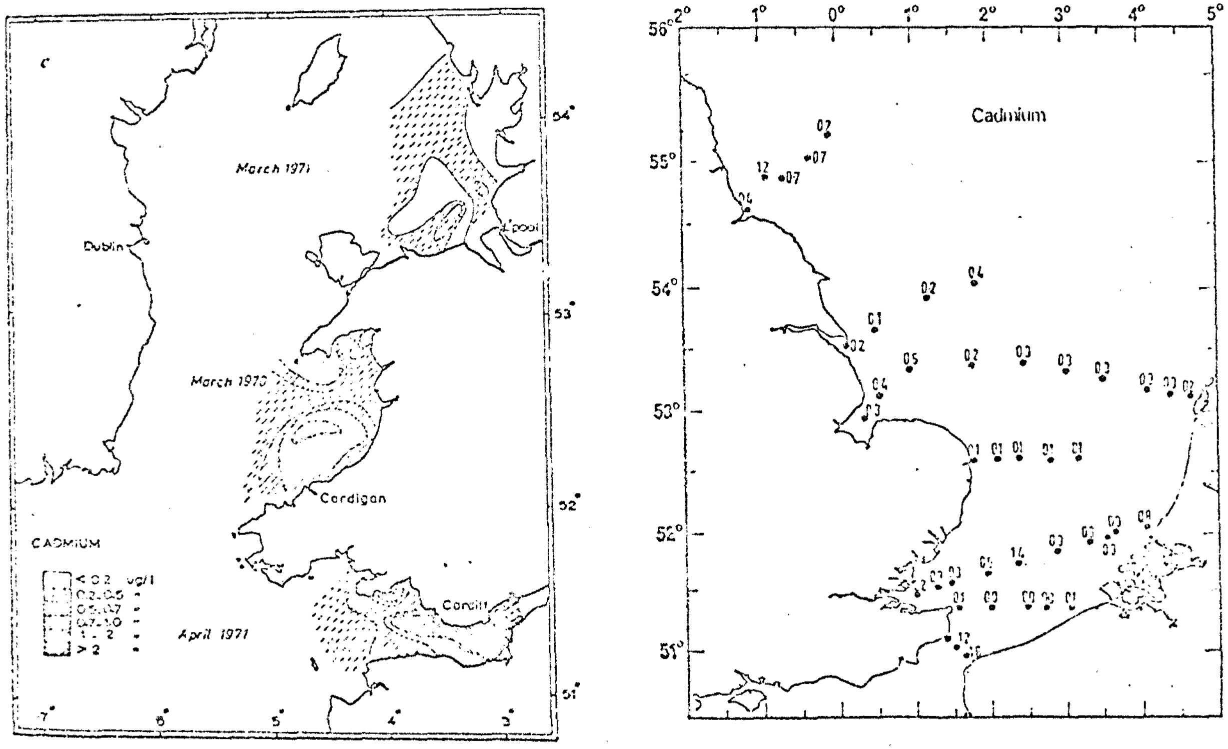


FIGURE 18. Cadmium concentrations in England and Welsh coastal waters and the North Sea.



a) West coast (after Abdullah et al. (91))

b) East Coast and North Sea (after Dutton et al. (84))

FIGURE 19. Current flow in the North Sea and British Coastal waters (after Edwards (139))

possible to separate the influences of rivers and industrial activity from effects of marine disposal.

The quantities of cadmium in sewage sludge dumped at sea were estimated as 8 tonnes yr^{-1} for the Thames and 2.6 tonnes yr^{-1} in Liverpool Bay out of a total 13.4 tonnes yr^{-1} for all the U.K. sludge sites (138). The cadmium concentrations in sludge range from 2 to 150 µg g^{-1} dry weight (138).

By geographical location, the following influences operate:-

North Sea

E2 Marine dumping < Total inputs

High levels of dissolved cadmium were noted (0.4-1.2 µg l^{-1}). The dumping of wastes is not solely responsible, other influences include engineering, shipbuilding and chemical industries in the area.

E8 Marine dumping < Total inputs

Cadmium at 0.4-0.5 µg l^{-1} was coincidental with sewage sludge and industrial waste disposal sites and direction of surface current flow (Figure 19).

E11 Marine dumping > Total inputs

Highest cadmium concentrations coincided with the Thames sludge disposal site and are consistent with current flow. The South Falls site, which receives industrial waste, had the highest dissolved cadmium level (1.4 µg l^{-1}).

Bristol Channel

E22 Marine dumping >> Total inputs

An estimated 9 tonnes yr^{-1} of cadmium was dumped in this area and was concurrent with >2 µg l^{-1} dissolved Cd. However, the exceptionally high levels were more probably associated with zinc smelting operations at Avonmouth. Similarly, the effects of dumping at the site in Swansea Bay are probably masked by rivers entering the bay, notably the Tawe.

West Wales

E20,25,26, and 27	Marine Dumping << Total input Although little dumping was carried out in this area, there are many old mines on the rivers and estuaries entering the coastal waters and these are possibly responsible for the observed high levels (140,141). A reassessment of the river inputs (E26, Table 8b) is required.

Liverpool Bay and the Mersey Estuary

E27,28	Marine dumping >> Total input The highspots in cadmium concentration coincided with disposal sites of dredged, industrial and sludge waste. The influence of mining and industrialization cannot be discounted.

From the above it would appear that dissolved Cd in, and leaching of surface adsorbed cadmium from, wastes is evident in seawater. The latter is in accordance with the chemistry of cadmium discussed in Chapter 2. Sediment data for these sites would greatly increase our knowledge of time effects and the extent of desorption.

3.2.2 New York Bight

The New York Bight receives between 80 (142) and 93% (143) of the total waste dumped at sea by the U.S.A. Table 9 gives rough estimates of the total cadmium input based on a variety of sources. The major contributor appears to be dredged wastes if the figure of 130 $\mu g\ g^{-1}$ Cd is correct (146). The dump locations are shown in Figure 20, with deep water dumpsite no. 106 (DWD 106) situated on the continental slope due S.E. of the grid. The designated acid waste site is a minimum distance of 20 km off the New Jersey coast but the Earth's Resources Technology Satellite produced pictures of dumping in operation at only 15 km off the coast (147).

Segar and Cantillo (105) examined the total trace metal levels in April 1974 and dissolved metals from May to November 1974 in the Bight. In

Table 9 Rough Estimates of Inputs of Waste Materials into New York Bight for 1974

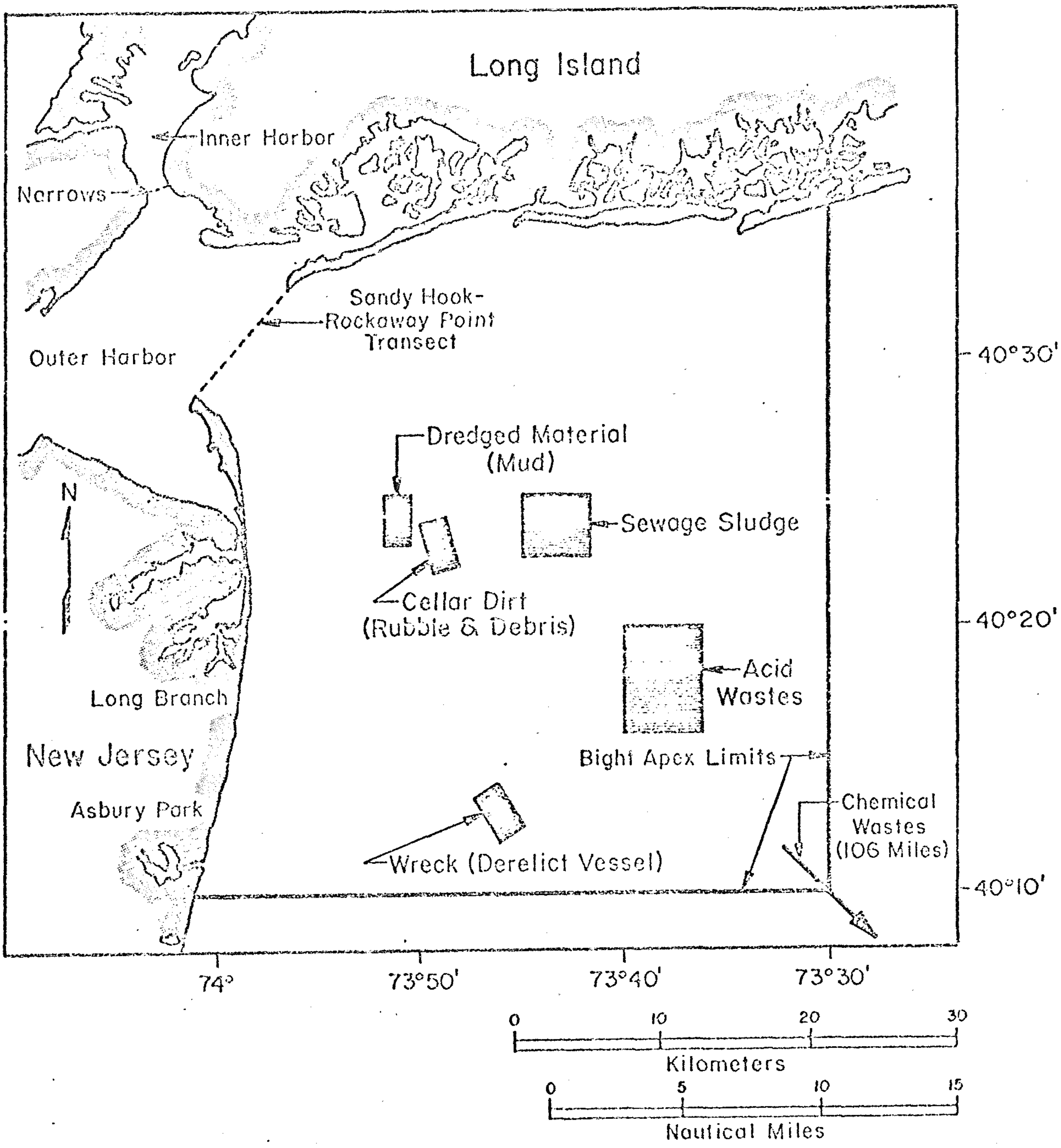
Type of Waste	% U.S.A. Total (142)	Volume(142) Discharged (1×10^9)	[a] Solid(145) Discharged	Estimated Cd Conc'n ($\mu g\ g^{-1}$)	Total Cd Dumped (tonnes yr^{-1})
Sludges	85	3.7	0.21	[b] 50	10
Industrial	65	2.7	-	-	50?
Acid-iron	90	2.7	0.27	[c] 10/30(145)	27/8
Dredged	-	5.0(144)	2.0	130(146)	260
					355

a. Conversion factors from volume to weights taken from (145).

b. Estimate from figures in (138).

c. Middle of range.

FIGURE 20. New York Bight Apex and existing dump sites. (after Dewling and Anderson (142))



the first instance, high levels of total cadmium were associated with the acid waste site (0.4-1.6 µg l^{-1}). High dissolved cadmium levels were found in the proximity of the sludge mud and cellar dirt site during June (max. 1.5 µg l^{-1}) and in the water column at the sludge site during July (max. 2.9 µg l^{-1}). Also in July elevated levels were noted in the acid waste site (max. 3.9 µg l^{-1}). Cadmium concentrations were not strongly influenced by estuarine discharge, although in September and October high levels were recorded during a period of high runoff. It was concluded (105) that in bottom waters elevated cadmium concentrations were associated with manganese that originated from the dredged waste dump. From May to November the overall mean was 0.82 µg l^{-1} dissolved cadmium. Dump site effects were at their most evident in July and August in waters > 10 m (mean 2.2 µg l^{-1}, compared to offshore control figures of 1.5 µg l^{-1} and shelf waters of <0.1 µg l^{-1}).

Sediment cadmium data is not available for the area, but the dredge spoil at the site has shoaled to a depth of 15 m in recent years and there is evidence that fine sediments are spreading over the rubble strewn bottom (148). Where sludge is dumped, the sea floor is sandy but the Christiaensen Basin to the north may also be contaminated with this material (148) (see Figure 21). Other heavy metals are associated with this material as, for example, zinc (149) (Figure 22). Zinc concentrations in the sediment were vastly increased over the background levels of 5-10 µg g^{-1}, particularly in the dredge spoil site (mean, 264 µg g^{-1}; max. 1500 µg g^{-1}) and in the sludge area (mean, 254 µg g^{-1}; max, 415 µg g^{-1}).

D.W.D. 106 was estimated to have received 0.77 tonnes of cadmium in 1975 and only 0.03 tonnes in 1974 (150). Elevated concentrations at both <100 m and >200 m during 1974 were noted (max. 0.6 µg l^{-1}, versus near-site values of 0.1 µg l^{-1}) (151). Samples taken at >2000 m had a mean concentration

FIGURE 21. Superficial sediment distribution in the New York Bight Apex, based on macroscopic, ship-borne observation of samples. (From unpublished data by A. Cok and G. Freeland in Stubblefield _et. al._ (148)) Depth in fathoms.

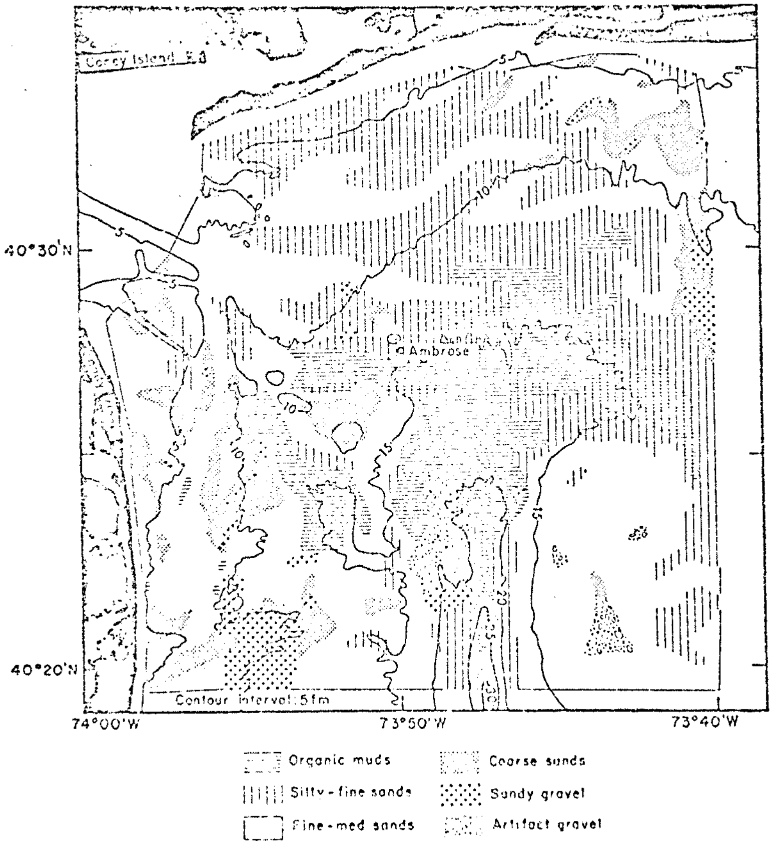
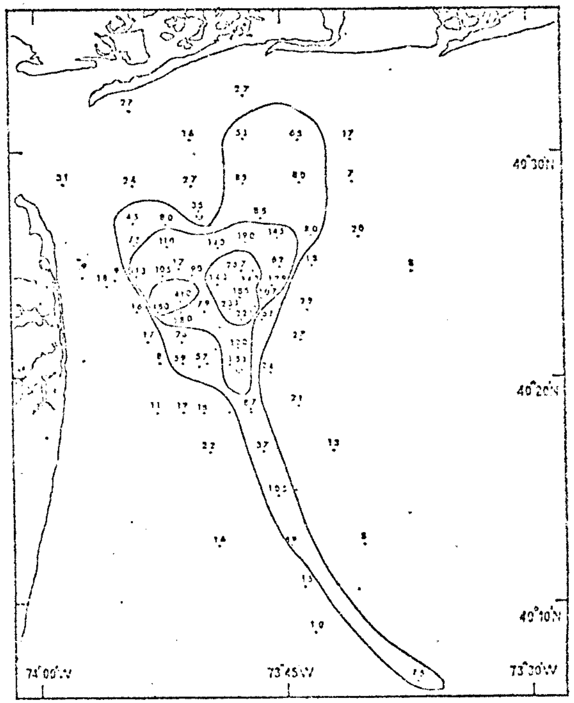


FIGURE 22. Concentration of Zn in $\mu g\ g^{-1}$ dry weight in sediment. Isopleths at 50,100 and 200 $\mu g\ g^{-1}$) (after Carmody _et. al._ (149))



of 0.39 µg l^{-1} (151). Repeated experiments in 1976 showed elevated concentrations both outside and due southwest of the dump site (151) (Figure 23). One possible explanation for this may be the passing of warm isolated eddies of water (warm rings) that break off from the Gulf Stream and move due south west (counter to the stream) through the dumping area (152) (Figure 24). Maximum levels in the warm ring (1.4 µg l^{-1}) are 20 times that of average open ocean surface waters.

3.2.3 Conclusions

(i) There is circumstantial evidence for elevated dissolved cadmium levels in the water column around dump sites in the sea.

(ii) Dissolved cadmium may already be in solution when dumped, e.g. in acid wastes, or desorbed from solids on contact with sea water.

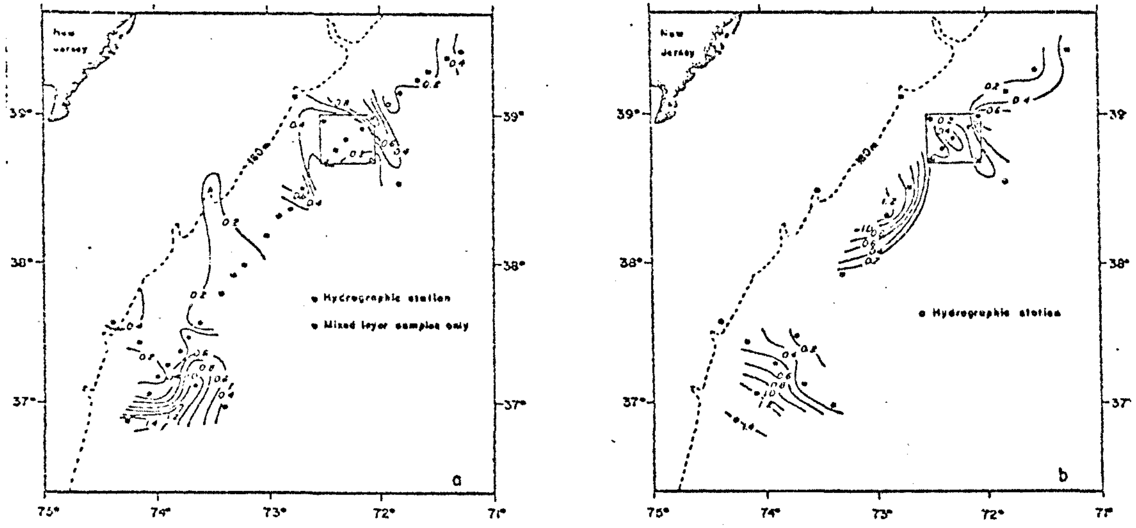
(iii) There may be a slow release of cadmium from dredged spoils (associated with dissolution of manganese).

(iv) Elevated levels were reported even at depths >2000 m (sediment release?).

(v) When monitoring dump sites, allowance should be made for the movement of dissolved cadmium in the area by water currents and eddies.

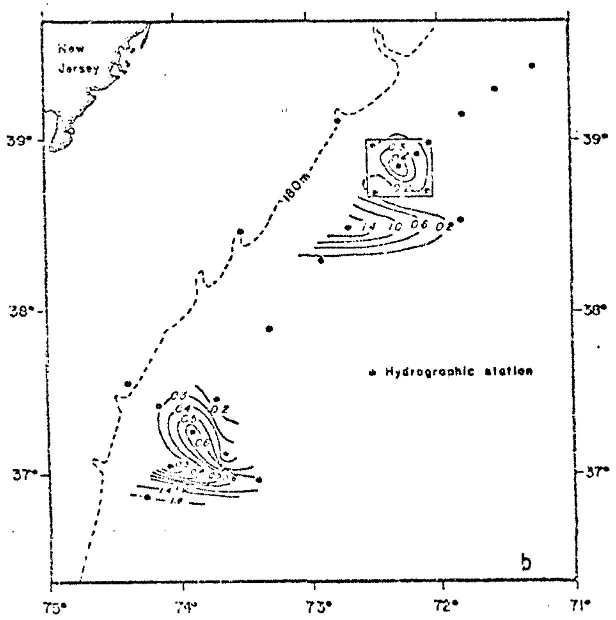
(vi) There is insufficient data available to comment on the proportion of cadmium released from sediments into the water or its rate of mobilization within the sediments.

FIGURE 23. Cadmium and manganese concentrations off the east U.S.A. shelf (after Hausknecht (151))



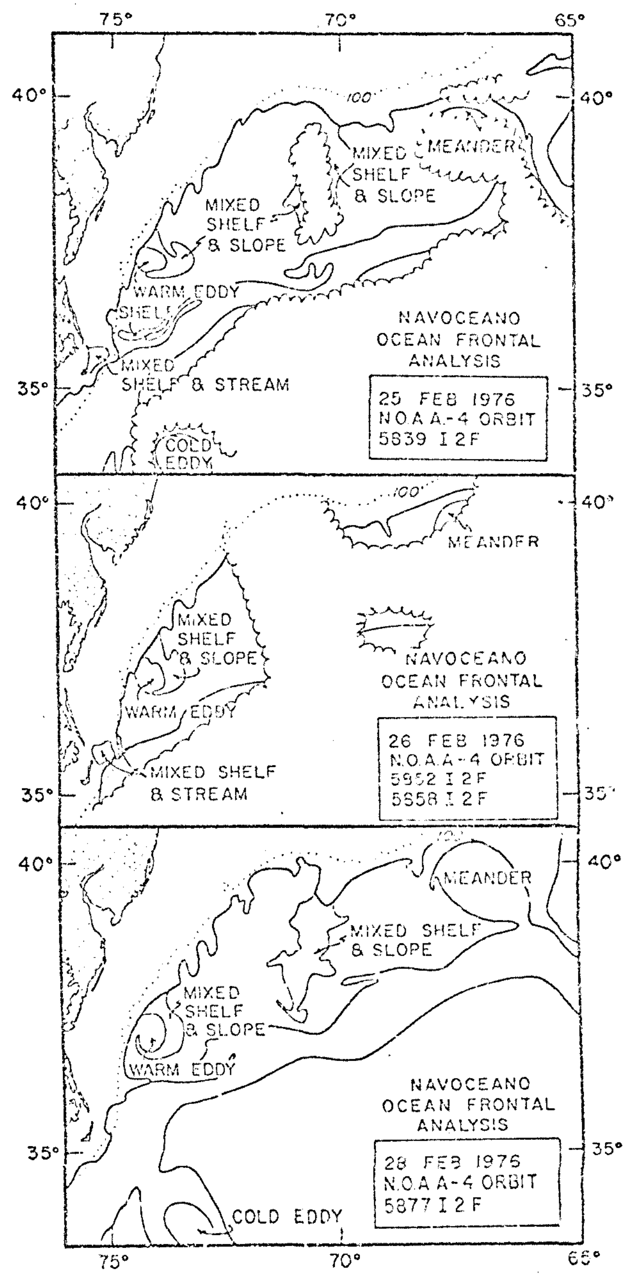
a) Average Cd concentration in the mixed layer (< 250m) in February 1975

b) Average Cd concentration in samples (> 250m) in Feburary 1976



c) Manganese concentration in deep water samples (> 250m) in February 1976

FIGURE 24. Ocean frontal analysis for east U.S.A. shelf (after Bisagni (153))



CHAPTER 4

ESTIMATES OF OCEANIC CADMIUM FLUXES AND RESIDENCE TIMES

4.1 THEORY

Estimates of oceanic residence times (T) based on fluxes are somewhat crude because of the sparcity of relevant data. In order to minimize the errors involved and obtain a range of values of T, various methods have been employed. These include estimates from dissolved inputs, sedimentation and a method which entails both input and output. The first two mathematically describe a rate of increase in a given reservoir according to:

$$T = \frac{M}{p_x} \text{ yr} \qquad (1)$$

where M = the mass of an element present in the oceans,

p_x = dM/dt = the mass of an element supplied to or removed from a reservoir each year.

At steady state the rate of increase of the mass flux under consideration (dM/dt) is zero, an anomaly which does not occur if input and output are taken together (154) (section 4.1.3).

To avoid confusion, it has been necessary in some instances to alter the notation and units given in the original papers.

4.1.1 Dissolved inputs

Barth (155) described the residence time of an element as:-

$$T = \frac{A}{dA/dt} \text{ yr at steady state.} \qquad (2)$$

where A = M in (1)

and dA/dt = dM/dt = p_x = the total mass of the element supplied to, or removed from, the oceans each year.

Goldberg and Arrhenius (156) used river input to calculate T. This method does not allow for atmospheric inputs which may be considerable as, for example, in the North Sea where cadmium atmospheric inputs have been estimated as half or even equal to <u>all</u> other inputs (136,157). To make allowances for this T may be rewritten as

$$T = \frac{M}{F_R C_R + F_A C_{AS} A_O} \text{ yr} \qquad (3)$$

$$= \frac{M}{P_R + P_{AS}} \qquad (4)$$

where F_R = the mass/volume of water supplied to the oceans by rivers per year

C_R = the mean element concentration in river water

F_A = the rain/particulate input to the oceans per unit area per year

C_{AS} = the dissolved/soluble concentration of the element in the atmospheric input

A_O = the area of the oceans.

Reasonable estimates of F_R and C_R can be made but estimates of F_A and C_{AS} are few in number and highly variable. An estimate given by Hodge et al. (158) for cadmium of 10 $\mu g\ m^{-2} yr^{-1}$ was selected.

From Chapter 2 it was noted that cadmium in seawater exists primarily as dissolved species (e.g. the particulate phase in deep Atlantic waters bound <5% of the total cadmium present (93)) and therefore this model should produce a useful first estimate.

4.1.2 Fluxes to sediments

Equations for residence times based on sedimentation processes may be described by the general form:-

$$T = \frac{C_{SW} V_O}{C_x F_x A_O} \qquad (5)$$

where V_O = the volume of the oceans

C_{SW} = the concentration of an element in seawater

F_x = the input to sediments of a particular phase per unit area per year

C_x = the element concentration in that phase

($C_{SW} V_O$ = the mass of an element in the oceans,

V_O/A_O = the mean depth of the oceans, 400,000 cm).

4.1.2.1 Total sediment deposition

Cherry et al. (159) described T by

$$T = \frac{C_{SW}}{C_{SED_{TOTAL}}} \frac{M_{SW}}{\rho_{SW} A_O F_{SED}} \text{ yr} \qquad (6)$$

where M_{SW} = the mass of seawater

ρ_{SW} = the specific gravity of seawater

(hence $M_{SW}/\rho_{SW} = V_O$)

$C_{SED_{TOTAL}}$ = the concentration of an element in a non-fractionated sediment

F_{SED} = the annual flux of particules to sediments per unit area.

Equation 6 reduces to

$$T = \frac{C_{SW}}{C_{SED_{TOTAL}}} (3.8 \times 10^5) \text{ yr} \qquad (7)$$

when values of $M_{SW} = 1.4 \times 10^{21}$ kg, $\rho_{SW} = 1.028$ kg l^{-1} and $F_{SED} = 1.1 \times 10^{-3}$ g cm^{-2} are substituted (159).

4.1.2.2 Deposition to manganese nodules

In the previous chapter it was shown that hydrous manganese oxides were the only inorganic phase to show any appreciable binding of cadmium in seawater. Hence the model described by Elderfield (160), using flux calculations by Krishnaswamy and Lal (161), is a useful means of calculating T.

The rate of deposition of a metal to nodules is given by:

$$P_N = \frac{K}{E} \rho_N G_N C_N \qquad (8)$$

where ρ_N = the specific gravity of nodules

G_N = the time averaged growth rate of nodules

C_N = the concentration of the element in nodules

K = geometric factor for nodules (increase of exposed hemispherical surface area of nodules compared to level sediment) = 2

E = the fraction of time the nodule grows on average = 0.1.

If $\rho_N = 2.5$ g cm^{-3} and $G_N = 3 \times 10^{-7}$ cm yr^{-1} then the flux of matter to nodules is

$$F_N = \frac{K}{E}\rho_N G_N = 1.5 \times 10^{-5} \text{g cm}^{-2}\text{yr}^{-1}$$

which on substitution into equation 5 gives

$$T = \frac{C_{SW}}{C_N} \frac{4 \times 10^5}{1.5 \times 10^{-5}} = \frac{C_{SW}}{C_N}(2.67 \times 10^{10}) \text{ yr} \qquad (9)$$

The assumption in using this method is that metal accumulation in manganese nodules and deep sea sediments are related processes and that the "nodules represent a pure separated sample of the manganese oxide component" (160).

4.1.2.3 Shale correction method

By this method only the authigenic component, that produced within the oceans, of the sediment is considered (160). To obtain $C_{SED_{AUTH}}$ the residual metal concentration derived from terrestrial and crustal material is subtracted from the total sediment concentration:-

$$C_{SED_{AUTH}} = C_{SED_{TOTAL}} - C_{SHALE}$$

According to Krishnaswamy and Lal (161) the authigenic deposition rate of a metal is given by

$$P_{SED_{AUTH}} = \rho_{SED} G_{SED} C_{SED_{AUTH}} \qquad (10)$$

where ρ_{SED} = the specific gravity of surface sediments

G_{SED} = the time averaged growth rate of sediment strata

$C_{SED_{AUTH}}$ = the concentration of the element in the authigenic fraction.

The flux of particles to sediments is given by

$$F_{SED} = \rho_{SED} G_{SED}$$

which on substitution of $\rho_{SED} = 0.5$ g cm^{-3} and $G_{SED} = 3 \times 10^{-4}$ cm yr^{-1} gives $F_{SED} = 1.5 \times 10^{-4}$g cm^{-2}yr^{-1} (161).

Therefore on substitution into equation 5

$$T = \frac{C_{SW}}{C_{SED_{AUTH}}} \frac{4 \times 10^5}{1.5 \times 10^{-4}} = \frac{C_{SW}}{C_{SED_{AUTH}}}(2.67 \times 10^9) \text{ yr} \qquad (11)$$

4.1.2.4 Zooplankton faecal pellet deposition

Cherry et al. (159) have suggested that faecal pellets could be the major supply route of several metals to sediments (see previous chapter). Further support for this argument comes from data collected by Bishop et al. (162) where it was demonstrated that faecal pellets, though only equivalent to <5% of particulate matter in surface waters, were responsible for 99% of the vertical particulate flux, having a residence time in the water column of only 10-15 days. Faeçal pellets also contain lithogenic inorganic material and may therefore constitute an important role in inorganic particulate transport (163). If it is assumed that they are the only means of transport of material to sediments then

$$\frac{dM}{dt} = P_F = C_F M_F A_O = C_F F_F A_O \qquad (12)$$

where C_F = the element concentration in faecal pellets

and M_F (the notation used in the original paper) = F_F = the mass (wet weight) of faecal pellets transported to sediment per annum.

If a flux of $6.6 \times 10^{-4} g\ cm^{-2} yr^{-1}$ (159) is assumed, then substitution into equation 5 gives

$$T = \frac{C_{SW}}{C_F} \frac{4 \times 10^5}{6.6 \times 10^{-4}} = \frac{C_{SW}}{C_F} (6.06 \times 10^{-8}) \qquad (13)$$

All pertinent physical parameters necessary for the above calculations are given in Table 10.

4.1.3 T based on input and output rate

Li (154), to eliminate the inaccuracy of the 'rate-of-increase methods', introduced an expression which includes both the input and output of an element where

$$\frac{dM}{dt} = Q - R \qquad (14)$$

where Q = the input rate

and R = the output rate.

If the output rate is proportional to the total mass, M, then

$$\frac{dM}{dt} = Q - kM \qquad (15)$$

Table 10 Physical parameters and flux estimates employed to calculate T. (+ indicates number computed from data therein)

Description	Symbol	Magnitude	Units	Ref.
Mean depth of oceans	D_O	4×10^5	cm	-
Volume of oceans	V_O	1.36×10^{21}	1	
Area of oceans	A_O	3.3×10^{18}	cm^2	-
Mass of seawater	M_{SW}	1.4×10^{24}	g	159
Density of seawater	ρ_{SW}	1.028	$g\ cm^{-3}$	159
Density of surface sediments (bulk)	ρ_{SED}	0.5	$g\ cm^{-3}$	161
Density of Mn nodules	ρ_N	2.5	$g\ cm^{-3}$	161
Growth rate of sediments	G_{SED}	$3\quad 10^{-4}$	$cm\ yr^{-1}$	161
Growth rate of nodules	G_N	$3\quad 10^{-7}$	$cm\ yr^{-1}$	161
Mass flux to sediments	F_{SED}	1.1×10^{-3} 4.5×10^{-4} 1.5×10^{-4}	$g\ cm^{-2}\,yr^{-1}$ $g\ cm^{-2}\,yr^{-1}$ $g\ cm^{-2}\,yr^{-1}$	159 164 161
Mass flux to nodules	F_N	1.5×10^{-5}	$g\ cm^{-2}\,yr^{-1}$	161
Mass flux of faecal pellets	F_F	6.6×10^{-4}	$g\ cm^{-2}\,yr^{-1}$	159
Mass flux of river water	F_R	3.25×10^{19}	$cm^{-3}\,yr^{-1}$	165
Mass flux of river particulates	F_P	1.8×10^{16}	$g\ yr^{-1}$	165

where k = the removal rate constant.

At steady state

$$0 = Q - kM$$

$$\text{or } \frac{1}{k} = \frac{M}{Q} = T \qquad (16)$$

If Q is altered then so is M, therefore at $t < t_o$, $Q_o = k_M$ and at $t_o < t < t$, Q increases exponentially:

$$Q = Q_o \, e^{m(t - t_o)} \qquad (17)$$

and it can be shown that solving for equation 15

$$M_1 = M_o \left(\frac{m}{m + k} e^{-k(t - t_o)} + \frac{k}{m + k} e^{m(t - t_o)} \right) \qquad (18)$$

M_1/M_o gives the ratio of the increase in mass of an element in the oceans at t, compared to the original mass of the element in the oceans at t_o.

Therefore, rearranging equation 18 and dividing through by m + k:-

$$\frac{M_1}{M_o} (m + k) = m \, e^{-k(t - t_o)} + k \, e^{m(t - t_o)}$$

then multiplying out the first term and dividing by m we get:-

$$\frac{M_1}{M_o} + \frac{k \, M_1}{m \, M_o} = e^{-k(t - t_o)} + \frac{k}{m} e^{m(t - t_o)} \qquad (19)$$

Since k is expected to be small ($10^{-5} - 10^{-7}$), $e^{-k(t - t_o)}$ approximates to $1 - k(t - t_o)$

$$\therefore \frac{M_1}{M_o} + \frac{k \, M_1}{m \, M_o} = 1 - k(t - t_o) + \frac{k}{m} e^{m(t - t_o)}$$

$$\frac{M_1}{M_o} - 1 = k \left(\frac{e^{m(t - t_o)}}{m} - \frac{M_1}{M_o m} - (t - t_o) \right)$$

$$k = \frac{1}{T} = \frac{(M_1/M_o) - 1}{\left(\frac{e^{m(t - t_o)}}{m} - \frac{M_1}{M_o m} - (t - t_o) \right)} \qquad (20)$$

Since m can be estimated graphically, if estimates of M_1/M_o can be derived, and if $(t - t_o)$ is known, then this equation can be solved. The result can be checked by back substitution of the k value obtained into equation 18, solving for M_1/M_o.

4.2 RESULTS

4.2.1 By $T = M/p_x$

The cadmium concentration required for the calculation of T described in the theory section parts (i) and (ii) are presented in Table 11.

Most of the data has been taken from the summaries in Tables 6 and 7; the depletion of dissolved cadmium in surface waters was included to allow for comparisons with the phosphate cycle (below). The residual (lithogenic) cadmium concentration of 0.06 $\mu g\ g^{-1}$ was taken from reference 166 and the mean nodule concentration from Ahrens et al. (47). The concentration of cadmium in faecal pellets was estimated by the extrapolation of results obtained in the laboratory (56) to measured concentrations in the oceans (see Table 12). From the experiments of Benayoun (56) the wet weight : dry weight ratio in zooplankton was 4.7. In their single culture experiments the whole zooplankton concentration was one third of the microplankton food concentration (0.7 and 2.1 $\mu g\ g^{-1}$ dry weight respectively) but in oceanic samples zooplankton-microplankton concentrations appear to be similar or indistinguishable (Table 12). If, using the Benayoun et al. data, the faecal concentration is divided by the microplankton concentration (9.6/2.1), a concentration factor of 4.57 results. Multiplying this C.F. by the computed plankton wet weight concentration of 0.69 $\mu g\ g^{-1}$, the faecal pellet wet weight concentration produced is 3.15 $\mu g\ g^{-1}$. If 3 $\mu g\ g^{-1}$ is taken as the working figure then the faecal pellet flux of cadmium equals $6.53 \times 10^9\ g\ yr^{-1}$ for $F_F = 6.6 \times 10^{-4} g\ cm^{-2} yr^{-1}$ (159).

The resulting values for T are given in Table 13. Differences in the first decimal place between M/P_x and 'constant' methods are due to rounding errors.

Table 11 Cadmium concentrations, masses and mass fluxes for the calculation of residence times.

Reservoir/Input/Output		Cadmium$^{(a)}$ Concentration	Mass (M) or Mass Flux (P_x)
Ocean (Dissolved)	4000 m	0.1 µg l^{-1}	1.36×10^{14} g
	Surface 300 m	0.05 µg l^{-1}	5×10^{12} g
	Depth 3700 m	0.1 µg l^{-1}	1.31×10^{14} g
River (Dissolved)		0.1 µg l^{-1}	3.25×10^{9} g yr^{-1}
	Particulate (residual)	0.06 µg g^{-1}	1.08×10^{9} g yr^{-1}
Atmosphere	Leachable	(flux = 10µgm^{-2} yr^{-1}, 80% soluble)	2.64×10^{9} g yr^{-1}
	Residual		6.6×10^{8} g yr^{-1}
Sedimentation Processes	Total	0.5 µg g^{-1}	1.81×10^{9} g yr^{-1} (b) 2.48×10^{8} g yr^{-1} (c) 7.43×10^{8} g yr^{-1} (d)
	Mn nodules	10 µg g^{-1}	4.95×10^{8} g yr^{-1}
	Authigenic	0.44 µg g^{-1}	2.178×10^{8} g yr^{-1}
	Faecal pellet	3.0 µg g^{-1}	6.53×10^{9} g yr^{-1}

(a) References within text
(b) Sediment flux = 1.1×10^{-3} g cm^{-2} yr^{-1} (153)
(c) Sediment flux = 1.5×10^{-4} g cm^{-2} yr^{-1} (161)
(d) Sediment flux = 4.5×10^{-4} g cm^{-2} yr^{-1} (164)
(e) Faecal pellet flux = 6.6×10^{-4} g cm^{-2} yr^{-1} (153)

Table 12 Cadmium levels in plankton (µg g^{-1} dry weight) (Dry/wet weight ratio = 4.7 (56))

	Mean	Range	Sample No.	Net Size (µm)	Reference
Phytoplankton					
Monterey Bay and Hawaii (organic fraction)	2.3	0.4-6.5	28	64	167,168
+Off Baja California	13.2	8.9-19.5	10	64	168
	13.6	4.2-20.9	32		167,168
Microplankton					
Monterey - Hawaii	1.63	1.0-2.2	4		
Microplankton/Zooplankton					
Mediterranean					
Monaco and Hyeres	2.61	1.6-5.1	11	132	169
Mediterranean East to West	2.0	0.7-3.8	22	60	169
Zooplankton	2.9	2.0-4.6	6	132	169
Euphausia spp.	0.6	0.4-1.4	6		
Megonyetiphanes norvegica	1.3	0.8-2.0	3		169
North East Atlantic					
Euphausids	0.35		8		170
North East Pacific					
Euphausids	1.4	0.9-2.2	5		171
North Sea	4.5	1.6-7.8	23		172
Monterey Bay					
Euphausids	2.98	0.8-5.5	9	366	167,168
Copepods	4.27	1.6-6.0	10		
Radiolarians	6.17	3.0-9.6	6		
Mixed		6.0 & 6.4	2		
Monterey Hawaii Transect	2.44	1.9-3.5	14		
Microzooplankton					
Clyde		0.92-1.0		250	173
Copepods Clyde		0.75-0.81			
Large zooplankton Clyde		0.37-0.67			
Plankton					
Caribbean	5.9		29	6-20 mesh	111
Gulf of Mexico	2.6				
New York Bight	3.2	0.9-7.8	34		174
North West Africa	5.2	1.4-8.8	11		
U.S.A. East	3.1	0.4-24	25		
U.S.A. Southeast	3.9	0.6-11	20		
Northwest Atlantic	1.8	0.6-3.7	22		
All in Ref. [illegible] 174	3.2	0.4-24	112		

+Overall mean (dry weight) = 3.24 Overall sample = 298

Computed wet weight = 0.69

+not including the atypical values for Baja

Table 13 Cadmium Oceanic Residence Times by
$T = M/P_x$ yr ($M = 1.36 \times 10^{14}$ g)

INPUT	RESIDENCE TIME M/P_x	(Equation)	C_{SW} (constant)/C_x	(Equation)
Dissolved river	4.2×10^4	(2)	-	
Dissolved river and atmospheric	2.3×10^4	(4)	-	
OUTPUT				
Total sediment[(a)]	7.5×10^4		7.6×10^4	(7)
	5.5×10^5			
	1.8×10^5			
Mn nodules	2.8×10^5		2.7×10^5	(9)
Authigenic	6.2×10^5		6.1×10^5	(11)
Faecal pellet	2.1×10^4		2.0×10^4	(13)

(a) See Table 19 for P_{SED} data

4.2.2 The estimation of T by the Li method

Cadmium has only been mobilized by man in any large quantities since the turn of the century and, compared to the total mass of cadmium in the oceans, the amount added to the oceans will be relatively small. Hence M_o, the mass of cadmium in the oceans at t_o (1900) may be taken to equal M in the previous estimates of T. The estimate of M_1, taken in this instance to be the total mass of cadmium in the oceans by the year 2000, relies on knowledge of cadmium mobilization, production, emission and dissipation over the 100 year interval and some means of estimating the quantity of cadmium entering the oceans.

4.2.2.1 The mobilization of cadmium by industrial activity

The more informative publications in this area are the 'Fulkerson' report (2), the Cadmium '77 report (175) and a technical and economic analysis published by the U.S. EPA (176).

Since interest in cadmium as a pollutant is recent, there are few available records of the cadmium content of zinc ores, ore tailings, atmospheric emissions or effluent discharges of the zinc producing industry, probably the major contributor to cadmium pollution. The total amount of cadmium mobilised can be estimated by assuming a Cd/Zn ratio in zinc ores to be 0.45% (166) (put at 0.5% by some authors (2,4)). Besides the smelting process, other major man-made sources are the weathering of zinc products (content = 10% of cadmium mobilised) (2), the disposal of products containing cadmium (= 20% of the annual production figure) (177), the burning of fossil fuels, the application of phosphate fertilizers in agriculture and the use of detergents. Table 14 presents data for cadmium production and mobilisation.

The smelted Cd/Zn ratio of 0.3% suggests that industry is operating at 66% efficiency, but allowing for 10% of the mobilised cadmium remaining in the smelted zinc i.e. 0.04% of the final product, the accounted for cadmium is about 77% of that mobilised, in agreement with figures presented in the

Table 14 The Major Sources of Cadmium Mobilisation

(Thousand tonnes)

	1. Zinc Smelted	2. Cadmium Produced	3. Cd/Zn (%)	4. Cadmium Mobilised	5. Cadmium in Zn	6. Production Losses	(%)	7. Accumulative Dissipation	8. Losses in Manufacture	Incidental Emissions		
1901-1910[a]	7322	0.174	0.002	32.9	3.3	29.5	(89)	0.7				
1910-1920	9636	1.056	0.011	43.4	4.3	38.0	(88)	1.6				
1920-1930	12156	7.922	0.065	54.7	5.5	41.3	(76)	4.0				
1930-1940	14662	29.453	0.16	66.0	6.6	29.9	(45)	10.4		(See Appendix 1)		
1940-1950	18284	52.062	0.28	82.3	8.2	22.0	(27)	20.4		Coal	Oil	Phosphate
1950-1960	29724	87.001	0.29	133.8	13.4	33.4	(25)	36.4	Up to 1970		Up to 1970	
1960-1970[b]	41061	136.900	0.33	184.8	18.5	29.4	(16)	60.2	9.4	33.0	0.4	0.5
1970-1980[b]	57221	169.152	0.30	253.7	25.4	59.2	(23)	87.0	5.1	8.3	0.3	0.4
TOTAL	190059	483.720		851.6	85.2	282.7		220.7	14.5	41.3	0.7	0.9
1980-1990[c]	71333	214	0.30	321.0	32.1	74.9	(23)	118.9	6.4			
1990-2000[c]	85667	257	0.30	385.5	38.6	90.0	(23)	154.2	7.7			
TOTAL	157000	471	0.30	706.5	70.7	164.9		273.1	14.1	19.1	1.0	1.4
By 2000	347000	955		1560	156	448		494	29	60	1.7	2.3
ESTIMATED												
1968-2000[a]	217000	660	0.30 (low)									
	270000	1040	0.39 (high)									
[d]	224700	674	0.30									

SUMMARY:-	by 1980	by 2000
Cd mobilized	909	1650
Cd in circulation	349	617
Cd lost	561	1033

The table was constructed as follows:-

Columns 1 and 2, by notation

(a) Figures for 1901-1960 and projections for 1968-2000 were taken from Fulkerson and Goeller (2).
(b) Data for 1960-1977 was taken from the "World Metal Statistics" (178) and the range 1978-80 was based on these figures.
(c) The period 1980-2000 was estimated by extrapolation (Figure 25).
(d) was calculated from (c) and the true figures 1968-1977. Less than 3% of Cd is recycled.

Column 3 was derived from Column 2/Column 1 × 100. Estimates for 1970-2000 were based on the 1970-1977 data.

Column 4 was calculated on an original Cd/Zn ratio of 0.45% and calculated from the zinc figures (Column 1).

Column 5 = 10% of Column 4.

Column 6 = Column 4 - (Column 2 + Column 5).

Column 7 was estimated on a dissipation rate of 20% of the cadmium in circulation (178) and hence was accumulative from decade to decade.

Column 8: Losses in manufacturing processes were put at 3% of production (based on 1974-5 figure (176)).

Column 9 was estimated by taking into account the other major sources of environmental cadmium contamination, namely the burning of fossil fuels (coal and oil, see Appendix 2) and the use of phosphate fertilizers.

Fulkerson report of 75-77% (2). The extrapolation of demand to 2000 gave 1968-2000 production estimates in excellent agreement with those given by other authors (2) (Table 14).

Thus, from man's activities alone, 9×10^5 tonnes of cadmium may have been mobilised by 1980 of which only 3.5×10^5 tonnes remain in circulation in products. By 2000 the respective figures may be 16.5×10^5 and 6.2×10^5 tonnes respectively.

4.2.2.2 Environmental distribution of industrially emitted cadmium

The questions addressed here are the distribution of the metal losses between the atmosphere, land and water and the amount of cadmium of anthropogenic origin entering the oceans.

Table 15 presents estimates of emission figures for 1968 (2) and 1974-5 (176) for the U.S.A. Even though there are limitations in the 1968 numbers in terms of missing data and the combination of direct emissions to water and land, the effect of pollution control is obvious, particularly in the use of electrostatic precipitators and building of new plants to reduce atmospheric losses. Precipitator efficiency can be as high as 95% but poor operation can lower this figure to 80% (2).

Table 16(a) shows the change in percentage losses with respect to the total in a given area and (b) relates these percentage figures to the quantities for a period given in Table 14. For ease of calculation and comparison, two broad assumptions have been made:

(i) the recent figures apply after 1980. This can only be justified on the supposition that the U.S.A. has implemented stricter and enforceable controls before other industrialised countries;

(ii) the U.S.A. figures can be applied to other nations.

From Table 16 it can be seen that the atmospheric emissions may decline if strict anti-pollution controls are used, although the amount of cadmium destined for land waste disposal by 2000 will be nearly half as much again as that produced prior to 1980. Whereas by present day standards the atmospheric

Table 15 Estimated Emission of Cadmium in the U.S.A. 1968 v 1974-75 (tonnes) (after Fulkerson & Goeller (2) and U.S. E.P.A. (176))

			To Air	To Water	To Land	Totals
Production	Extraction, Refining and Production	1968	953.2		475	1428.2
		1974-5	102.2	7	250	359.2
Manufacture	Industrial Conversion	1968	15.2		(0.2)	15.4
		1974-5	15	8	102	125
Consumption Disposal	Iron and Steel Industry	1968	<100		(<900?)	1000
		1974-5	10.5	0	330	340.5
	Incineration	1968	86		-	86
		1975-5	16	0	70	86
	Tyres, Galvanising Non-Ferrous Metals	1968	(5.2)		-	(5.2)
		1974-5	7.4	0	60	67.4
Minerals	Phosphates	1968	-		23-230	23-230
		1974-5	0	10.2*	100	110.2
	Coal	1968	113-907		?	113-907
		1974-5	80	0	370	450
	Oils/Petrol	1968	19.8-91.8		0	19.8-91.8
		1974-5	51	0	0	51
	Sewage Sludge	1968	-		22-57	22-57
		1974-5	20	0	250	270
Rounded Totals		1968	(1210-2160) 1725		(1420-1660) 1540	3265
		1974-5	300	25	1530	1855
Totals less 'Production'		1968	772		1055	1840
		1974-5	198	18	1280	1600

*From phosphate detergents

Table 16 Estimates of Direct Emissions of Cadmium to the Environment

		(a) By Percentage			(b) By Weight (Thousand Tonnes)		
		Air	Land	Water	Air	Land	Water
Production/Smelting Losses	pre 1980	66	30	4	186.56	84.80	11.31
	1980-2000	28	70	2	46.14	115.40	3.30
Disposal/Dissipation	pre 1980	30	70	0	66.21	154.48	-
	1980-2000	3	97	0	8.19	264.86	-
Coal	pre 1980	67	33	0	27.62	13.60	-
	1980-2000	18	82	0	3.42	15.66	-
Oil	pre 1980	100	0	0	0.66	-	-
	1980-2000	100	0	0	1.0	-	-
Phosphates	pre 1980	0	91	9	-	0.76	0.08
	1980-2000	0	91	9	-	1.26	0.12
Manufacture	pre 1980	(20	70	10)	2.90	10.16	1.45
(≡ 2-4% loss)	1980-2000	12	81	7	1.70	11.45	0.99
				Total 1980	283.95	263.7	12.84 = 561
				1980-2000	60.47	408.63	4.41 = 473
				2000	344.42	672.43	17.25 = 1034

(cf. Table 14)

losses are approximately equal to waste disposal on land (270,000 tonnes) the ratio will be about 1 : 2 by the end of this century. Direct emissions to water are small in comparison, although the contribution from domestic sewage and dissipation may considerably increase this figure.

The reason that the dissipation figure is so high may be seen from Table 17, which shows the annual consumption figures by industry for the U.K. between 1967-76. Much of the cadmium goes into 'throw-away' products, like plastics (colourings and stabilizers) and is non-recyclable. Losses in other industries, e.g. electroplating, will be unavoidable because of the nature of the processes.

The chemical forms of cadmium emitted are obviously important to the transport of the element. In an electrostatic precipitation of a roasting plant it was found that 69% was soluble in water ($CdSO_4$), 8-6% dissolved in 3% H_2SO_4 (free oxides), 14.5% was soluble in 10% H_2SO_4 ($CdO.Fe_2O_3$) and the remaining 6.7% was present in the residue as sulphide (4). The amount of water soluble cadmium was put at 0-70% with a mean of 15% (4). That 80% of the particulate atmospheric cadmium collected over the oceans was sea-water leachable (158) is probably indicative of the small particle size fraction ($<5\mu m$ - not efficiently retained by precipitators). The greater surface area of small particles allows for increased leaching and also there is the possibility of a predominance of simpler chemical forms, e.g. condensates. The enrichment of cadmium with respect to aluminium in the air above the oceans compared to air above land was noted by Duce et al. (179,180). The enrichment factor was 400-730 exceeded only by Pb, Se and Sb for the elements measured. The cadmium was thought to be of anthropogenic origin. There is evidence from Greenland glaciers to suggest that the atmospheric transport of cadmium has increased dramatically since 1900 (181). Even so, much of the cadmium emitted to the atmosphere has been shown to be precipitated within 10 km of the source (182,183). Cadmium deposited on soils

Table 17 U.K. Consumption of Cadmium (metric tons)
(compiled from World Metal Statistics 1970-1978)

Year	Plating Anodes	Plating Salts	Cd/Cu	Alloys	Solders	Colours	Others (+ Batteries)	Total
1967	489.89	120.35	28.04	28.35	65.03	430.45	205.85	1367.96
1968	444.78	134.57	27.59	24.38	90.07	526.01	191.98	1439.38
1969	402.81	141.69	27.89	15.34	95.56	581.18	208.60	1473.07
1970	370.99	119.47	33.68	15.25	84.08	502.50	186.93	1312.90
1971	314.03	107.83	35.38	14.08	46.35	461.60	197.57	1176.84
1972	306.79	171.83	32.57	14.91	37.94	566.09	223.71	1353.84
1973	292.28	176.55	26.99	17.49	61.42	659.95	328.79	1563.47
1974	276.59	180.42	47.36	13.31	34.83	623.05	264.94	1440.50
1975	263.62	105.43	35.31	12.14	27.99	368.97	218.44	1031.90
1976	281.35	182.31	28.45	14.32	30.39	640.04	236.74	1413.60
Totals	3443.13	1440.45	323.26	169.66	573.66	5359.84	2263.55	13573.46

from the atmosphere, contained in mine tips (183) and landfill sites (184) or applied to soil in phosphate fertilizers (185) and sewage sludges (186) is potentially transportable to the oceans via leaching and runoff.

4.2.2.3 Estimation of man-made oceanic inputs

Bertine and Goldberg (187) estimated that weathering mobilized 500 $t.yr^{-1}$ of cadmium in sedimentary material, i.e. < half the mass flux given in Table 11. If a similar ratio is assumed for dissolved species then approximately $1.6 \times 10^3 t.yr$ dissolved cadmium entering the oceans derives from man's activities.

The estimates of 230 $t.yr^{-1}$ (157) and 530 $t.yr^{-1}$ (136) for atmospheric input into the North Sea are equivalent to 1/8 and 1/4 of the total cadmium consumption by industry in Northern Europe annually. A similar figure can be obtained for the global cadmium input by an alternative method. If it is assumed that all of the seawater-leachable fraction in atmospheric particles derives from man-made sources (as is possible on the basis of Cd/Al enrichment factors (179,180) above)), the annual flux is $2.6 \times 10^3 t.yr^{-1}$. This figure corresponds to approximately 1/6 of the current global cadmium production and is the mean of the North Sea estimate.

Summing the dissolved river and atmospheric inputs and dividing by the current annual global production figure, i.e. $(2.6 + 1.6) \times 10^3/16.9 \times 10^3 t$, the oceanic influx equals 25% of the cadmium produced annually.

However, the cadmium that enters the oceans is not strictly related to production but to production losses and, more important, accumulative dissipation figures. This data is summarised in Table 18 and it can be seen that, through time, the totals are approximately equal.

4.2.2.4 Calculation of T

Plots of the data are presented in Figure 25 and regression analysis was applied to the two extremes.

Since Q, the oceanic input at time t, is given by

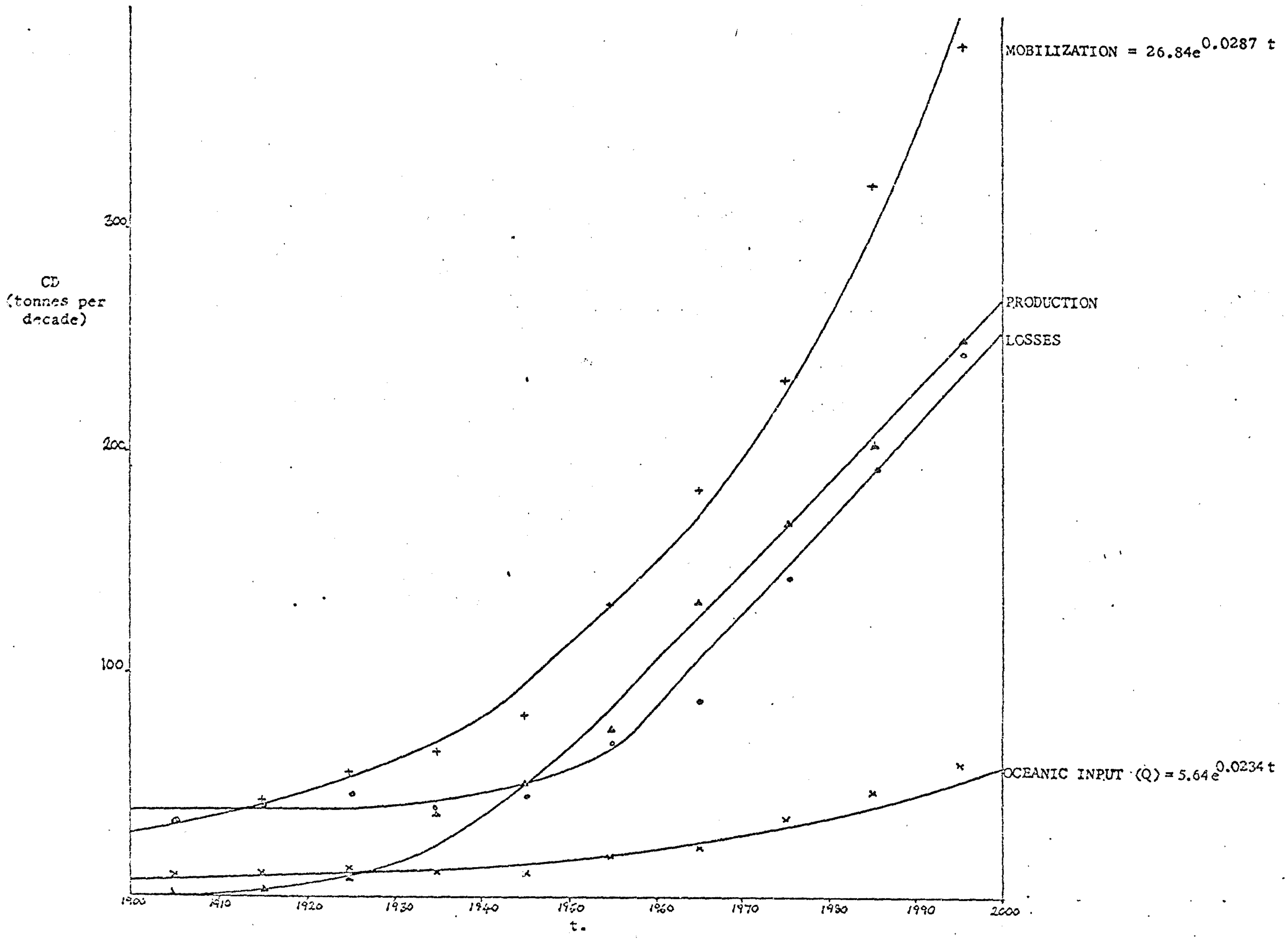
$$Q = Q_o e^{m(t - t_o)} \qquad (17)$$

Table 18 Production and Accumulative Dissipation (including Production Loss) Data giving Estimates of Man-made Oceanic Inputs (tonnes × 10^3)

	CADMIUM PRODUCTION	PRODUCTION LOSS+ ACCUMULATIVE DISSIPATION	OCEANIC INPUT
1900-1910	0.174	30.2	7.6
1910-1920	1.056	39.6	9.9
1920-1930	7.922	45.3	11.3
1930-1940	29.453	40.3	10.1
1940-1950	52.062	42.4	10.6
1950-1960	87.001	69.8	17.5
1960-1970	136.900	89.6	22.4
1970-1980	169.152	146.2	36.6
1980-1990	214	193.8	48.5
1990-2000	257	244.2	61.1
Totals	955	941.4	235.6

Oceanic input based on 25% of the total losses. The data was taken from Table 14; differences in totals are due to rounding errors.

FIGURE 25. Cadmium mobilization, production, loss and oceanic input, 1900-2000.



then a value for m can be substituted in equation 20 as can values for M_1/M_o

$$\left(= \frac{1.362356 \times 10^9}{1.36 \times 10^9} = 1.00173\right)$$

and $(t - t_o)$, (100 yr for the period 1900 to 2000)

$$\therefore \text{ from equation 20, } k = \frac{1}{T} = \frac{(M_1/M_o) - 1}{\left\{\frac{e^{m(t - t_o)}}{m} - \frac{M_1}{M_o m} - (t - t_o)\right\}}$$

$$= \frac{0.00173}{\frac{10.38}{0.0234} - \frac{1.00173}{0.234} - 100}$$

$$= \frac{0.00173}{300.83} = 5.75 \times 10^{-6}$$

$$\therefore T = 1.74 \times 10^5 \text{ yr.}$$

4.3 DISCUSSION AND CONCLUSIONS

As mentioned at the beginning of this chapter, the estimates of inputs and outputs to the oceans are crude but, bearing in mind the limitations of their accuracy, some useful data on transport (Figure 26a) and association with reactive phosphate (Figure 26b and c) have transpired:-

1. Fluxes

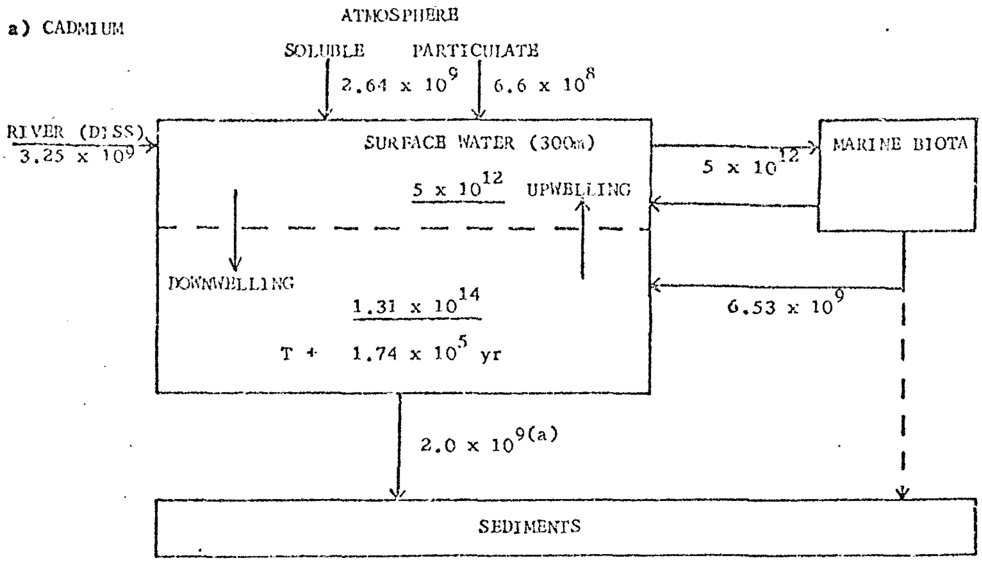
(i) The input of cadmium to the oceans is estimated to be 25% of annual total losses, i.e. both dissipative and direct industrial losses. (At present the total losses approximately equal the total annual production).

(ii) The authigenic cadmium input corresponds to 50% of the total current input to the oceans (3.66×10^9g to 7.63×10^9g respectively).

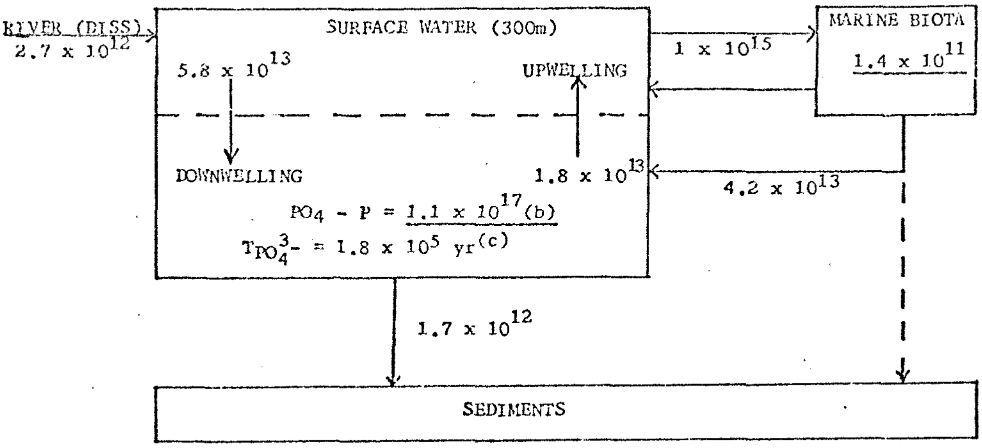
(iii) Since this estimate is higher than expected on the basis of industrial losses alone the slow accumulative dissipation of cadmium from 'throw-away' products and waste material should be considered as the most important contribution to the cadmium influx. Because of the delay between manufacture and destruction of a product and also the time dependence of the leaching of cadmium from waste materials, the peak of dissipative input may not arise until two or three centuries hence unless strict controls are imposed particularly on incineration and smelting processes (see iv).

FIGURE 26 CADMIUM AND REACTIVE PHOSPHATE FLUXES TO AND FROM THE OCEANS (FLUXES, g yr^{-1}; MASSES g)

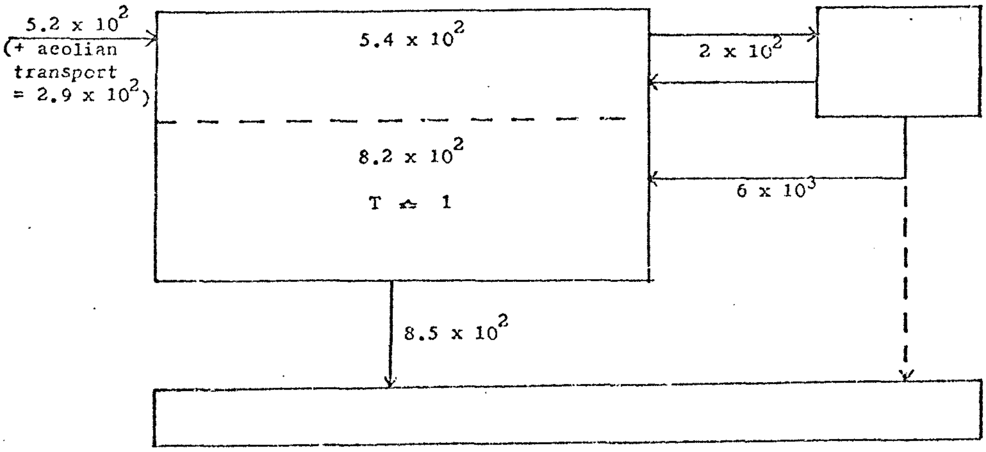
a) CADMIUM



b) PHOSPHATE (Lerman, Mackenzie and Garrels (188))



c) REACTIVE PO_4/Cd RATIOS OF MASSES AND FLUXES



a) Mean of sediment output values N.B. Mn nodule + authogenic as one value

b) Recalculated to give phosphate for 3700 m (rather than 3000 m).

c) $T_{PO_4^{-3}}$ from Wedepohl (189).

Ratio Phosphate : Cd = 6×10^2 (Brewer (190)

In productive areas = 3×10^3 (Bruland, Knauer and Martin (133))
" " " = 3×10^3 (Boyle, Sclater and Edmond (55))

(iv) The atmospheric input of cadmium to the oceans may be a more important source of dissolved cadmium than river runoff. Most of the seawater leachable cadmium (80% of the total) of the atmospheric input is thought to result from man's activities.

(v) The only major inorganic association of cadmium in the oceans is in manganese nodules (cf. section 2.2.2.1).

(vi) The output of cadmium to sediments may be controlled by the faecal pellet flux, emphasising the importance of biological activity in the global transport of the metal.

2. Residence time

(i) The range of values for T_{Cd} calculated by the input or output methods was 2×10^4 to 6.2×10^5 yr. Other estimates based on sedimentation flux were given as 1.4×10^5 yr (46), 9.2×10^4 yr (164) and 7.7×10^3 (164) by stream flow.

(ii) T_{Cd}, calculated by the input and output method was 1.74×10^5 yr, a value equivalent to that of phosphate (1.8×10^5 yr).

3. Phosphate/Productivity associations

(i) The PO_4/Cd ratios for stream input, oceanic mass, both surface and deep water, and averaged sediment output show good agreement with the literature PO_4/Cd ratio of 6×10^2.

(ii) The faecal pellet PO_4/Cd ratio of 6×10^3 shows good agreement with the dissolved PO_4/Cd ratio in productive areas of 3×10^3.

(iii) The difference of an order of magnitude between (i) and (ii) may reflect the retention of cadmium within marine biota.

CHAPTER 5

THE PHYSIOLOGICAL AND BIOCHEMICAL EFFECTS OF CADMIUM ON MARINE BIOTA

It is not intended to present an exhaustive coverage of all the literature on cadmium concentrations monitored in marine organisms since a recent review by Bernhard and Zattera (191) summarised much of the data (see Appendix 3). A useful source for updating the literature is an annotated bibliography collected by Corrill and Huff (192). Therefore this chapter will concentrate on the biochemical and physiological effects of cadmium on marine biota and, where necessary, will draw on data not specifically related to marine organisms.

5.1 PROTECTION MECHANISMS

There are four ways in which organisms protect themselves from toxins:

(i) detoxification by the secretion of enzymes or metabolites,
(ii) inhibition of transfer across the cell wall,
(iii) inactivation of the toxicant intracellularly,
(iv) the removal of toxic substances from inside to outside the cell.

5.2 BACTERIA

5.2.1 Secretion of metabolites

A mixed population of bacteria isolated from the sediments of Corpus Christi Harbour, U.S.A., precipitated 90% of added ^{109}Cd (0.5μCi ml^{-1}) as the sulphide (193). Field experiments at the same location indicated H_2S production in the water column was at its highest in the summer months, coinciding with the maximum rate of cadmium deposition to sediments (114). Under aerobic conditions it is possible for cadmium present as the sulphide to be remobilized by Thiobacillus thiooxidans which secretes sulphuric acid (194). Thiobacillus sp. are tolerant to large concentrations of Cd^{2+} e.g. T. ferroxidans was unaffected at 10^{-2}M Cd (195).

The secretion of metabolites by one organism may increase the susceptibility of a second organism to cadmium. This effect was demonstrated by the secretion of an antibiotic by Altermonas sp. which, in the presence of Cd and Hg in seawater, reduced the resistance of Staphylococcus epidermidis by 10^4 to the metals (<4 μg l^{-1}Cd and <0.1 μg l^{-1}Hg) and 8 fold to the antiobotic (to 1.8μg ml^{-1})(196).

5.2.2 Plasmid mediated resistance

The mechanism here may involve inhibition of transport across the cell wall or inactivation within the cell.

Plasmids are extra-chromosomal elements transferred by transduction and replicated autonomously, i.e. independent of bacterial chromosomes. Plasmids may confer resistance upon an organism to many potentially harmful agents, e.g. antibiotics like penicillin or streptomycin, X-ray and U.V. radiation, heavy metals including Bi^{3+}, Sb^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, AsO_3^{2-} and Cd^{2+} (see 197 and 198 for detailed discussion). In several cases, resistance is inducible, although it is phage-type and strain dependent, and the same plasmid may carry tolerance to a number of agents. Therefore, by exposure of an organism to a metal or a drug, it is possible to induce multimetal-multidrug resistant populations. Such bacterial populations are common in clinical isolates (e.g. 197-200) but the possibility of high metal levels in the environment producing multi-drug resistance in human and animal pathogens could have far reaching consequences (200-203). As yet, no such connection is proved; therefore, the following discussion on how plasmid-produced enzymes protect bacteria against cadmium centres on stock cultured human pathogens and clinical isolates.

The cadmium resistance of Staphylococcus aureus has been extensively studied (reviewed by Silver *et al.* (198)). There are two alternative hypotheses for the protection mechanism:-

(i) an active transport system which brings cadmium into the cell where it is inactivated,

(ii) an alteration in the cell membrane which reduces adsorption and absorption by the cell.

At present the second explanation is favoured for the following reasons:-

(a) Cadmium was shown to inhibit manganese transport across the cell membrane in cadmium-sensitive cells but not in resistant cells (198).

(b) After homogenization and low speed centrifugation, resistant organisms contained relatively more cadmium associated with cell debris compared to the supernatant than sensitive strains (198). The overall uptake was a factor of three less in the resistant organisms and resistance was mediated by the cell membrane acting as a permeability barrier (204, 205).

(c) Permeability was observed at 10^{-6}M Cd^{2+} in sensitive strains but not in resistant strains, even at 10^{-4}M Cd^{2+} (206).

(d) It was suggested that Cd^{2+} was locked out of the cell by some protective enzyme (207) and that phospholipids rather than sulphydryl groups bind cadmium (208).

(e) With other multidrug-multimetal resistant organisms, namely Aerobacter aerogenes and Bacillus megaterium, transport by the Mg^{2+} uptake pathway was implicated in the intracellular accumulation of Ni^{2+}, Co^{2+} and Zn^{2+}, but no such effect was observed with Cd^{2+} (209).

(f) There is no evidence of cytoplasmic Cd-binding proteins in S. aureus (198).

5.2.3 The removal of cadmium from inside the cell to the cell wall

Escherichia coli strain B were found to enter a long lag phase when cultured with 3 × 10^{-6}M Cd^{2+} (210). Initially large intracellular vacuoles and an inability to form colonies were noted. With time the cells regained normal morphology and viability, the process being one of accommodation rather than the selection of mutants. Accommodated cells had a Cd distribution of 56% on the cell wall, 13% in the cell membrane and 31% in the cytoplasm, compared to 2%, 75% and 23%, respectively, in unaccommodated cells.

The process of accommodation is possibly controlled by high molecular weight proteins which transport cadmium to the cell wall.

5.2.4 Conclusions

1. Due to the paucity of information on the effects of cadmium on marine bacteria, extrapolation of laboratory observations with clinical isolates have to serve as pointers for effects that may occur in the environment.

2. Sulphide-producing bacteria may precipitate cadmium to sediments.

3. Sulphur-utilizing (sulphuric acid producing) bacteria may remobilize sulphide-precipitated cadmium.

4. The secretion of metabolites by some organisms may increase the sensitivity of other species to heavy metals.

5. Elevated cadmium levels in water and sediment may bring about the selection to multidrug-multimetal resistant populations of pathogenic bacteria.

6. Plasmid-mediated resistance operates by reducing the permeability of the cell membrane to cadmium and/or cell wall which results in the concentration of cadmium at the cell exterior. This in turn may lead to elevated concentrations in their predators, e.g. in filter-feeders, such as mussels.

7. Accommodation to elevated cadmium concentrations has also been observed.

5.3 MARINE PHYTOPLANKTON

5.3.1 Cadmium uptake and effect on photosynthesis

A summary of the research on marine algae is presented in Table 19. From previous discussion the importance of phytoplankton in the cycling of the element in the marine environment was stressed and it may be important to the amplification of the element in the food chain.

In an attempt to examine Cd effects in a realistic manner, i.e. not in the confines of a laboratory flask, Kremling et al. (220) carried out controlled ecosystem enclosure experiments in the Saanich Inlet, British Columbia. The bags used were 68 m^3 in volume and cadmium concentrations

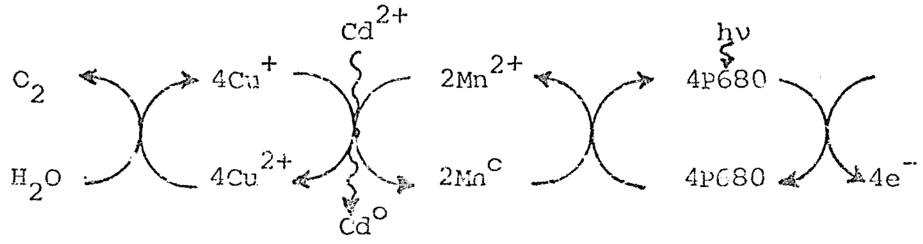
Table 19 Laboratory Experiments on Cadmium Uptake by and Distribution in Marine Phytoplankton

Organism	Cd Conc'n	Observed Response	Reference
Prasinocladus subsala *Chaetoceros* sp. + *Phaeodactylum tricornutum*	10-100 µg l^{-1}	Cd was accumulated to amounts proportional to the concentration of Cd in seawater (max. 400 µg g^{-1} dry wt. in *P. tricornutum* + *Chaetoceros* sp. and 670 µg g^{-1} dry wt. in *P. subsala*). Equilibrium with the solution was reached after 24 hrs in the diatom mixture with saturation at about 0.09 mg l^{-1}, but the green algae showed only a slight decrease in uptake at the maximum concentration.	211
"	10 µg l^{-1}	Major uptake by adsorption and gradual desorption by external metabolites.	212
" *Dunaliella tertiolecta*	10^{-4}-10^{-3}M	No effect on O_2 evolution was noted at the lower concentration although 25% suppression occurred at the higher concentration with both organisms, i.e. Cd was transported to the sites of light reactions of photosynthesis. No effect on K^+ loss or uptake was recorded; therefore no membrane damage was evident.	213
" *Carteria* sp. *Nitzschia closterium*	20-80 ng l^{-1}	Rate of uptake increased with increasing Cd^{2+} concentration, uptake being rapid in the first hour. 24 hr average for *D. tertiolecta* and *Carteria* sp. at 80 ng l^{-1} was 2.5 × 10^{-3} ng (mg dry wt.)$^{-1}$hr^{-1} but *N. closterium* rate of uptake was higher at 3.5 × 10^{-3} ng (mg dry wt.)$^{-1}$hr^{-1}, probably due to its greater surface area.	214
" *Coscinodiscus granii* *Rhizosolenia alata*	1-1000 µg l^{-1}	*N. closterium* was the dominant species after 5 days incubation of a mixed population. 1000 µg l^{-1} Cd initially reduced carbon assimilation by 30% with respect to the control, although this increased with time.	215
Dunaliella bioculata		^{109}Cd uptake gave a concentration factor of 300 after 15 days.	216
Attheya decora *Brachimonas submarina* *Monochrysis lutheri* *Skeletonema costatum*	10^{-3}M	Cd was non-toxic to these organisms in that no inhibition of photosynthesis was observed.	217
"	25-100 µg l^{-1}	Cd initially increased cell division rate, followed by a marked decrease versus the control. Cells were reduced in volume but possessed the same C:N ratio.	218
"	50-140 µg l^{-1}	The uptake of Cd increased as the PO_4-P available for growth decreased, reaching a maximum at zero PO_4-P in the media (after 7 days) ≈ 50% desorption of Cd occurred over the following 5 days.	219

of 1.3 µg l^{-1}, 10 to 20 times the 'normal' surface seawater concentration, were added as spikes. Experiments were run for 2 to 4 weeks versus controls of Cd concentration of 0.075 µg l^{-1}. No marked differences in phytoplankton composition (predominantly *Chaetoceros* spp.) or biomass were observed. Most of the particulate metal was loosely bound to outer cell membranes and <1% of the added Cd was associated with settling material. It was concluded that "under the conditions established in these studies, no significant biological effects can be attributed to cadmium concentrations raised an order of magnitude above the natural level."

Lower cadmium-plankton concentrations were noted during periods of high productivity (high phytoplankton biomass) in the oceans (117), an effect also observed in enclosure experiments (220). Similar results were obtained in laboratory experiments with *P. tricornutum*, when at the onset of the stationary phase the cadmium-plankton concentrations dropped from 1.98 to 1.02 µg g^{-1} dry weight (212), and also with *S. costatum* (219). A fast, followed by a slow, release of cadmium on leaching cells was taken as evidence for surface versus protein bound cadmium (212,220), supported by the correlation of particulate Cd with particulate (protein) organic nitrogen (r = 0.5 and 0.69 for duplicate experiments)(220).

Besides a reduction in cell volume measured in *S. costatum* (218), the only sublethal effect of cadmium identified to date in marine algae is the suppression of photosynthesis and only then at concentrations at least two orders of magnitude above 'normal' concentrations (213,215). This may arise by interference in the electron transport in the photosystem II of chloroplasts (221) acting upon the manganoprotein (222) in the Mn-Cu-protein pigment complex (221):-



The uncoupling of the reaction in such a way may explain the formation of Cd granules proved to exist in the mitochondria of the freshwater algae *Ankistrodesmus falcatus*, *Chlorella pyrenoidosa* and *Scendesmus quadricauda* when exposed to cadmium (223).

The cadmium-phosphate relationship noted by Motohashi and Tsuchida (219) is an interesting one which may have some bearing on oceanic Cd-PO_4-P depth profiles discussed previously. Unfortunately, the subsequent release/retention of phosphate was not monitored as was the cadmium release. It is possible from the above that cadmium is taken into the cell by an anion transport mechanism as $CdCl_3^-$.

5.3.2 Conclusions

1. Marine algae are highly tolerant to cadmium.

2. Uptake is predominantly by surface adsorption, and is therefore dependent primarily on surface area.

3. Phosphate in the water limits cadmium uptake; cadmium may be taken into the cell as $CdCl_3^-$ when inorganic phosphate is removed from the water.

4. Suppression of photosynthesis by the uncoupling of the photosystem II electron transport system is the only biochemical interference proved to date.

5. The initial fast desorption rate of cadmium is due to the loss of surface bound metal and the second phase slow release is due to loss of intracellular cadmium.

6. To quote Kremling *et al.* (220) "the taxonomy of the organisms only plays a minor role in the uptake mechanism for cadmium".

5.4 CADMIUM IN HIGHER MARINE ORGANISMS

A summary of data of cadmium in marine organisms is presented in Table 20. The 'normal' concentrations given are rough estimates.

It can be seen that molluscs have a remarkable ability to concentrate cadmium from polluted water, food and sediments. Other organisms tend to have lower overall cadmium levels but elevated levels in specific organs. These organs include the gills, kidney and liver or digestive glands. Gill

Table 20 Cadmium Concentrations in Marine Organisms

($\mu g\ g^{-1}$ dry weight)

(based on data in Appendix 3 (191))

Organisms	Range of Means	'Normal' Conc'n	Maximum Values
Plankton	0.35-13.6	<2.0	20.9
Molluscs:			
Gastropods	0.8 -(100?)	<1.5	1,120
Bivalves	1.5 -249	<1.0	299
Invertebrates (various)	0.24-14.8	<1.0	14.8
Crustaceans	0.15-2.4	<1.0	2.8
Fishes	0.1 -2.2	<0.5	4.1
Sharks	0.1 -0.4		

uptake may reflect water concentrations and the uptake in internal organs may reflect concentrations in food, although it is difficult to discriminate between the two sources.

The following discussion will examine

(a) the uptake of cadmium by molluscs; the differences between filter feeders and grazers and their use as pollution indicators;

(b) the presence of cadmium-binding proteins in internal organs;

(c) the uptake of cadmium by gills and the effect of cadmium on oxygen consumption.

5.4.1 The accumulation of cadmium in molluscs

In highly contaminated areas, grazers, e.g. Patella sp. and Littorina sp., and carnivores, e.g. Nucella sp., were found to have dry weight Cd concentrations in excess of 500 µg g^{-1} (up to 1,120 µg g^{-1}) (224, 225). In the case of the grazers, this may in part be due to the high cadmium concentrations in marcophytes (see Appendix 3).

On the other hand, filter-feeding bivalves, such as mussels and oysters, rarely have concentrations in excess of 10 µg g^{-1} dry weight. However, mussels and oysters have been put forward as useful pollution indicators (226-230) because of their

(i) wide geographical distribution

(ii) high accumulation factors which are linear to cadmium water concentrations. Other considerations are given by Majori and Petronio (226), and limitations imposed due to environmental variables such as salinity and temperature are discussed by Jackim et al. (231) and Phillips (227). The two most promising organisms for such work are the mussels Mytilus galloprovincialis and M. edulis.

Studies on the acute effects of cadmium showed that these organisms are highly tolerant to cadmium with respect to other bivalves and marine organisms (Table 21) (the median tolerance of M. galloprovincialis was 0.36 µg ml^{-1} Cd (234)).

Table 21 (a) Summary of Acute Toxicities of Cadmium to Marine Bivalves ($mg\ l^{-1}$) (from Eisler (232))

<u>Mercenaria mercenaria</u> :	LC-3 (20 weeks)	0.1
	LC-38 (20 weeks)	0.2
<u>Mya arenaria</u> :	LC-50 (168 hrs)	0.15
	LC-50 (96 hrs)	2.2
<u>Crassostrea virginica</u> :	LC-32 (20 weeks)	0.1
	LC-45 (20 weeks)	0.2
(embryos)	LC-50 (48 hrs)	3.8
<u>Mytilus edulis</u> :	LC-50 (96 hrs)	25.0

(b) LC-50 (96 hrs) for a Cross-Section of Marine Animal ($mg\ l^{-1}$) (from Eisler (233))

Hermit crab, <u>Pagurus longicarpus</u>	0.32
Sand shrimp, <u>Crangon septemspinosa</u>	0.32
Common starfish, <u>Asterias forbesi</u>	0.82
Common soft-shell clam, <u>Mya arenaria</u>	2.20
Green crab, <u>Carcinus maenus</u>	4.10
Atlantic oyster drill, <u>Urosalpinx cinerea</u>	6.60
Eastern mud snail, <u>Nassarius obsoletus</u>	10.5
Sandworm, <u>Nereis virens</u>	11.0
Striped killifish, <u>Fundulus majalis</u>	21.0
Blue mussel, <u>Mytilus edulis</u>	25.0
Sheepshead minnow, <u>Cyprinodon variegatus</u>	50.0
Mummichog, <u>Fundulus heteroclitus</u>	55.0

However, there are differences in the distribution of cadmium concentrations within the organisms:- M. galloprovincialis (235) shell >> muscle > viscera (+ kidney?) > mantle > gills; M. edulis (236) kidney >> viscera > gills >> mantle > muscle; which may arise from differences in experimental conditions, organism or food source. The latter is particularly important. For example the chelation of cadmium with EDTA, pectin, and humic or alginic acids doubled Cd uptake, i.e. assisted transport across the cell membrane (236). High concentrations of zinc (500 $\mu g\ l^{-1}$) decrease cadmium uptake (231) and variation in food supply was put forward to explain differences in the cadmium half life in M. galloprovincialis calculated from laboratory experiments (1254 days) and *in situ* studies (307 days) (235).

Apparently, the shell and the kidney are the sites of Cd-accumulation in Mytilus sp. Examination of the M. edulis shell revealed that the metal is laid down with nacreous (aragonitic) layer but chelated with organics (237). Some mechanism related to Ca^{2+} is implied. The kidney controls the excretion of the metal in M. edulis (236) and the high metal concentration in this organ is related to the presence of the cadmium binding protein, metallothionein (238).

5.4.2 Metallothionein in marine organisms

The metallthionein family of proteins were discovered in 1957 by Margoshes and Vallee (239). The proteins are characterised by:-

(1) the presence of cadmium, zinc, copper and mercury (3-14 metal atoms per molecule),

(ii) the binding of 30-60% of the tissue cadmium,

(iii) an adsorption maxima in the U.V. at ≈250 nm due to metal-sulphur chromophores,

(iv) the lack of aromatic amino acids (low adsorption at 280 nm),

(v) a high cysteinyl residue content (≃30% of all amino acids present),

(vi) low molecular weights (6000-12000).

Equine renal metallothionein - 1B (240) and mouse liver metallothionein (241) were recently sequenced and it was confirmed that three cysteinyl residues and possibly one serinyl residue bind each metal.

Metallothioneins have been isolated from many organisms ranging from the most primitive blue-green algae (242) to man (243) and are found in many marine organisms, but not all (Table 22). The concentration effects have been shown in the liver (or digestive glands) of squid (up to 1,106 $\mu g\ g^{-1}$ dry weight (251)), lobster (252), scallop (253), tuna (254), sharks and swordfish (255) and the kidney of mussels (236), scallops (253) and sea lions (250).

In molluscs, there are obvious variations in the intracellular binding of cadmium. Indeed, the oyster Crassostrea gigas was shown to have 50% of the cadmium present as Cd^{2+} (256).

Fish from deep water dumpsite 106 were analysed for liver and muscle cadmium concentration (255, 257) and midwater fish were found to have lower levels of the metal in these tissues compared to coastal fish from the U.K. (257). However sharks and swordfish from the same area possessed liver concentrations of 0.28 to 7.2 and 16.1 to 26.9 $\mu g\ g^{-1}$ respectively, indicative of their position in the food chain.

5.4.3 Cadmium in gill tissues of marine organisms

Cadmium will accumulate in gill tissues either directly from the water or via transport in the blood stream.

Oxygen consumption may be elevated or depressed which is a demonstration of stress in various tissues not just the gills (Table 23). The elevation of oxygen consumption is indicative of an increase in energy demand produced by an increase in enzyme activity. Where a depression in oxygen consumption is observed presumably there is an inhibition of O_2 transport across the gill membrane and/or inhibition of enzyme activity.

Cadmium is known to be concentrated in gill tissues, e.g. the lobster Homarus americanus (259,260), the mussels Mytilus galloprovincialis and M. edulis (235,236), the fishes Pleuronectes platessa and Raja clavata (261) and the crabs Uca pugilator (262) and Carcinus maenas (263).

Table 22 Complexation of Cadmium in Marine Organisms

	Organism	Tissue	Molecular Weight	References
Oysters:	*Ostrea edulis*	Whole animal	Homarine and/or taurine? <3000	244,245
	Crassostrea gigas			
Scallop:	*Chlamys opercularis*			
Cockle:	*Cardium edule*			246
Periwinkle:	*Littorina littorea*			
Mussel:	*Mytilus edulis*		Metallothioneins:-	238
Limpets:	*Patella vulgata*		10,800 & 22,000 (dimer?)	247
	Patella intermedia			
Plaice:	*Pleuronectes platessa*	Liver	Not given	248
Copper Rock Fish:	*Sebastodes caurinus*		11,000	249
Grey Seal:	*Halichoerus grypus*		9,000	
Pacific Fur Seal:	*Callorhinus ursinus*		10,000	
Californian Sea Lion:	*Zalophus californianus californianus*	Kidney	7100	250

Table 23 Cadmium Effects on Marine Animals
(after Calabrese, Thurberg and Gould (258))
(see original paper for references)

Organism	Exposure period	Concen-tration (ppb)	Oxygen consumption	Osmoregu-lation	Enzyme activity	Other
Crassostrea virginica American oyster (eggs)	48 hr					LC_{50} = 3,800 ppb (2)[1]
Argopecten irradians Bay scallop (juveniles)	96 hr	940	Elevated (16)			LC_{50} = 1,480 ppb; significant Cd uptake (16)
Nassarius obsoletus Mud snail	72 hr	500	Elevated (13)			Distressed behavior (13)
Carcinus maenas Green crab	48 hr	500	Depressed (25)	Disruption (25)		
Cancer irroratus Rock crab	48 hr	120	Depressed (25)	No effect (25)		
	96 hr	1,000			Chloride salt increased transaminase, nitrate salt no effect (heart) (9)	Serum Mg unchanged (9)
	30 days	250	Depressed (u)		Chloride salt increased transaminase, nitrate salt no effect (heart) (u)	Serum Mg unchanged (u)[2]
Eurypanopeus depressus Mud crab	72 hr	4,000	Depressed (5)			LC_{50} = 4,900 ppb; LC_{100} = 11,000 ppb (5)
Homarus americanus American lobster	30 days	3-6	Elevated (22)	No effect (22)	Enzyme induction, lowered ligand sensitivity (heart, antennal gland) (22, u)	
	60 days	3-6	Elevated (22)	No effect (22)		Significant Cd uptake in gills (22)
Tautogolabrus adspersus Cunner	96 hr	3,000-48,000	Depressed (24)	Disruption (24)	Depressed transaminase, lowered ligand sensitivity (liver) (10)	Some histopathological effects (17); liver uptake 8.5 times greater than gills (12)
	30 days	50-100	Depressed (14)	No effect (14)	Depressed transaminase, higher shunt activity (liver) (14)	
	60 days	50	Depressed (14)	No effect (14)		
Morone saxatilis Striped bass	30 days	0.5-5.0	Depressed (7)		No effect (liver, skeletal muscle) (7)	
	90 days	5	No significant effect (7)		No effect (liver, skeletal muscle) (7)	90-day exposure and 30-day clearance; depressed transaminase and shunt activity (liver) (7)
Pseudopleuronectes americanus Winter flounder	60 days	5-10	Depressed (4)		Enzyme induction, lowered ligand sensitivity (heart, kidney, gonad, skeletal muscle) (8, u)	No detectable Cd uptake in blood or gills. No hematological or histopathological changes (4)
	150 days	10			Increased glycolysis and shunt activity, lowered ligand sensitivity (kidney, liver) (u)	

[1] Numbers in parentheses refer to citations in Literature Cited

[2] u means unpublished.

Changes in the gill ultra-structure of the shrimp Penaeus duorum were examined by Couch (264). After 15 days exposure to 763 μg l^{-1} Cd, cell death had occurred in the distal gill filament tissue, followed by autolysis, necrosis and the deposition of electron-dense granules. The initial appearance of the granules was in the mitochondria of the cells, the site of many oxidative enzyme systems and ATP production.

5.4.4 Conclusions

1. Molluscs are able to concentrate cadmium to a high degree and maybe useful as pollution indicator species.

2. In all higher marine organisms, cadmium concentrates in the liver or digestive glands, kidneys and gills.

3. Sublethal cadmium effects include

   (i) increased O_2 consumption due to an increase in energy demand produced by an increase in enzyme activity,

   (ii) decreased O_2 consumption possibly due to inhibition of O_2 uptake or enzyme inhibition,

   (iii) increased liver (or digestive glands) and kidney concentrations because of binding to metallothionein or to low molecular weight complexes like homarine or taurine.

4. There is no evidence of food chain amplification of cadmium on the basis of total body concentrations, but individual organs (e.g. kidney and liver) provide evidence of some bioaccumulation due to dietary habits.

CHAPTER 6

RESEARCH REQUIREMENTS

The report has highlighted many areas that require detailed investigation if the flux of cadmium in the oceans is to be understood. The work may be split into two parts.

(a) Cadmium influx to the oceans, both atmospheric and fluvial.

(b) Cadmium fluxes and cycles within the oceans. This will require a knowledge of the speciation, the distribution, the efflux of the metal to sediments and its recycling within sediments.

6.1 MARINE INPUTS

The work in this field lies essentially within the province of atmospheric and freshwater-brackish water scientists.

(i) Basic to the problem of cadmium cycling is the budget of cadmium throughput in the industries refining the metal and manufacturing goods from the metal. Some form of accounting by the industries concerned is urgently required.

(ii) Of prime importance is an assessment of the aerial transport of cadmium and the measurement of particulate/dissolved deposition. This is an area fraught with difficulties, such as the long time-span required to collect reasonable samples at stationary sampling sites, the positioning of sites to give truly representative samples, contamination during sample collection on land and on board ship and the logistic and financial problems of collecting samples from aircraft.

(iii) Data are required for the major freshwater inputs from South America and Asia.

(iv) More work is required on the estuarine deposition/mobilization of the metal. However, an estimate of the total lithogenic contribution in particulate phases may be possible from samples taken within the oceans (see below).

6.2 FLUXES WITHIN THE OCEANS

6.2.1 Some biological studies

In the estimation of fluxes, organisms are treated as 'black boxes' with an input and output. However, certain areas are of importance both ecologically and in the definition of the magnitude and form of cadmium in the biological reservoir. Studies should include:-

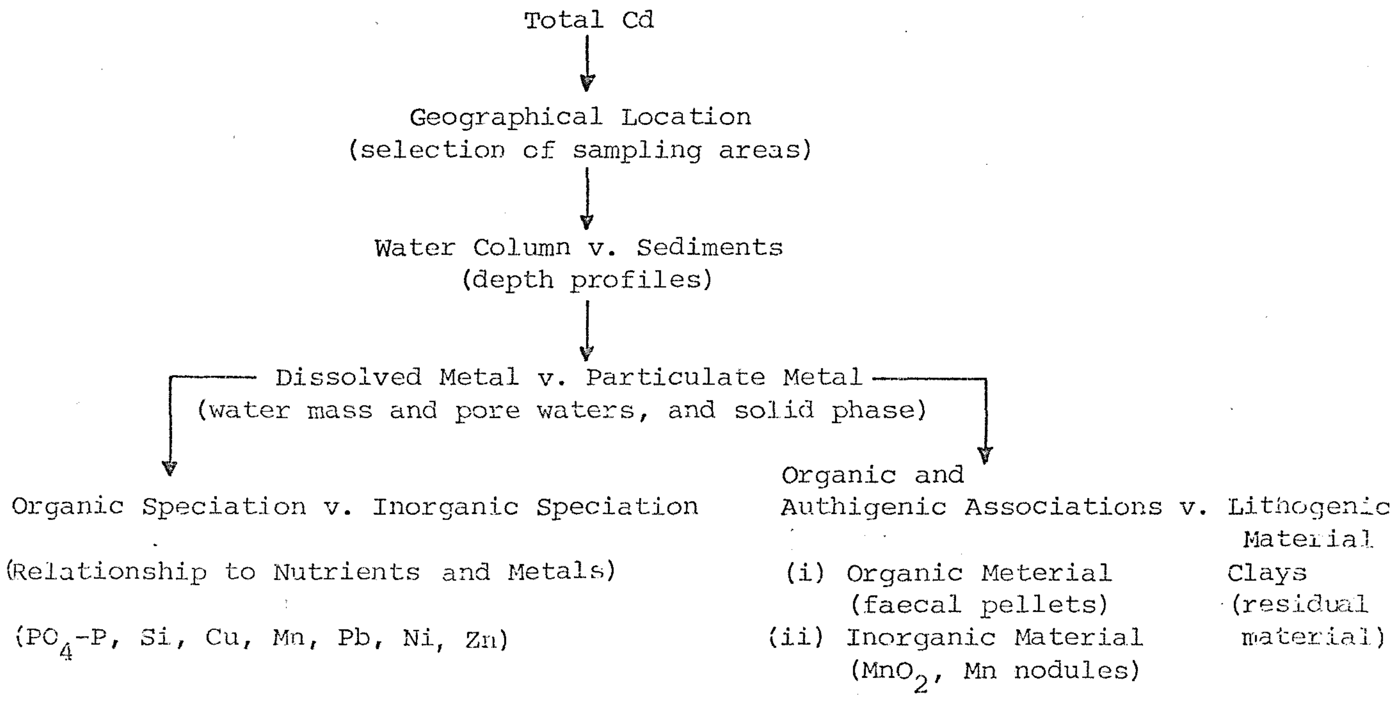
(i) An investigation into the selection of multi-drug, multi-metal resistant bacteria due to plasmid-mediated resistance in coastal waters contaminated with Cd and other heavy metals.

(ii) The assessment of amplification of cadmium in selected food chains by comparison of bulk analysis with metal levels in particular organs. As a first step in the identification of tissues which concentrate metals, morphological examination by transmission electron microscopy in conjunction with electron-microprobe analysis may prove to be a powerful technique (265, 266).

(iii) The isolation of organic complexation agents from tissue which lead to high metal concentration in particular organs, e.g. metallothionein.

6.2.2 Analytical scheme to determine fluxes

The analysis of the problem should take the following form:



6.2.3 Information to be gained from the analytical scheme

(i) Cadmium levels in the waters and sediments of contrasting areas are essential to gain knowledge of:

- background levels in waters and sediments
- differences between shelf waters and open ocean waters
- comparison of high productivity areas with low productivity areas
- differences between the industrialised, northern hemisphere and underdeveloped, southern hemisphere.

(ii) The relationship of dissolved cadmium in the water column to depth, other metals and nutrients should be investigated. This will provide an insight into

- the mechanism of transport and controlling factors
- association with productivity
- the bioavailability of the metal
- possible remobilization from sediments.

(iii) Work on suspended particulates will allow estimates to be made of

- the phytoplankton uptake of metals in the surface layers
- the flux of metals in association with faecal material
- the flux in association with hydrous manganese oxides (authigenic)
- the flux in association with lithogenic material.

From such data the influence of productivity on metal distribution should become apparent; the major factors controlling sedimentation of metals and better estimates of residence times may be calculated.

(iv) Sediment depth profiles and pore water studies may give information on input rates with time, diagenesis, correlations with other chemical species and hence an insight into the remobilization-retention of metals.

6.2.4 A brief outline of methods

(i) Dissolved metals - Total metals may be determined by solvent extraction followed by atomic adsorption spectroscopy (A.A.S. (267)).

Metal speciation may be examined by anodic stripping volatametry for which methods need to be developed.

Pore water samples may be obtained either by squeezing sediments or high-speed centrigugation with dense inert solvents (268).

(ii) Suspended particulates and sediments - Vertical fluxes can be determined by the sediment trap collection of material at various depths. Long residence time particulates and colloids i.e. those subject to horizontal current transport, can be collected by high volume filtration methods (269). Sediment samples can be taken by conventional coring methods.

Analysis of samples can be carried out by a number of methods:-

- Microdistribution of the metal in individual sediment components by scanning electron microscopy.

- Bulk analysis may be carried out by X-ray fluorescence spectrometry for the major and minor elements and wet oxidation followed by A.A.S. for trace elements.

- Organic content can be determined by gasometric methods (i.e. measuring CO_2 after combustion).

- Residual metals can be analysed after selective leaching procedures.

APPENDICES

1. The theory of metal adsorption onto particulates and colloids and ion exchange with clays.

2. Coal, oil and phosphate production.

3. Cadmium in marine organisms.

4. A summary of the effects of cadmium on man.

APPENDIX 1

THE THEORY OF METAL ADSORPTION ONTO PARTICULATES AND COLLOIDS AND ION EXCHANGE WITH CLAYS

1. METAL ADSORPTION

There are two mechanisms involved:

(a) the interaction of positively or negatively charged species with sites of the opposite charge, i.e. coloumbic attraction;

(b) specific adsorption of ions from solution, i.e. chemical reaction at the surface. Ions displace matrix ions from the adsorbent; strictly speaking this is an adsorption effect and it occurs, for example, in nsutite where cadmium can displace manganese.

2. ION EXCHANGE

With clay minerals, charge results

(a) at the surface from the isomorphous substitution of one atom by another within the lattice, e.g. Si by Al, and

(b) at the edge of the clay via interaction which broken bonds may produce both positive and negative charge.

The cation exchange capacity (C.E.C.) of a clay is the number of singly charged negative sites available for adsorption and it is usually expressed in milliequivalents per 100 grams (meq 100 g^{-1}). The C.E.C. is often determined by the displacement of Na^+ by NH_4^+. The C.E.C. for vermiculite, montmorillonite, illite and kaolinite are in the range 25-200, 70-100, 10-40, 3-15 meq 100 g^{-1} respectively, depending on the origin of the clay and the number of lattice defects and replacements.

3. METHODS OF REPORTING RESULTS

(i) A selectivity coefficient (K_s or K_B^A) provides a measure of the relative ability of an ion exchanger to hold one ion in preference to another (or others):-

$$K_B^A = \frac{\bar{X}_A \; X_B}{\bar{X}_B \; X_A}$$

where $\bar{X}_i$ and X_i are the mole fractions of the ions in the solid and liquid phase, respectively.

K_B^A (K_S) is not a constant but is dependent on the magnitude of the effective charge of the adsorbants given by:-

$$\text{Effective charge} = \frac{\text{Ionization potential}}{\text{hydrated ionic radius}}$$

and the total concentration, as well as the concentration ratio of existing ions.

(ii) The partition coefficient (K_p) is synonymous with the distribution constant, the concentration factor (C.F.), and accumulation factor (A.F.); its reciprocal is the instability partition coefficient (K_{INST}). All are described by the Berthelot-Nernst distribution law:-

$$K_p = \frac{C_S}{C_L} \quad \text{where } C_S = \text{conc'n in solid at equilibrium}$$

$$C_L = \text{conc'n in liquid at equilibrium.}$$

The value of K_p may alter by many orders of magnitude under various physical conditions such as temperature, pressure, concentrations of adsorbent and adsorbant, ionic strength, pH, Eh and contact time. Thus the conditions under which the experiments are conducted must be stated.

A useful distinction between a single observation and the gradient of the plot of a series of points for C_S v. C_L would be to call the former the C.F. or A.F. and the latter K_P.

(iii) The distribution coefficient (K_D or D) is given by the equation

$$K_D = \frac{f_S V}{(1 - f_S) M} \quad \text{where } V = \text{volume of solution}$$

$$M = \text{mass of adsorbent}$$

$$f_S = \text{fraction of ions adsorbed}$$

$$\text{or } \frac{\text{Meq \% } M^{2+}_S}{\text{Meq \% } M^{2+}_L}$$

This expression is analogous to K_p in that

$$\frac{f_S}{M} / \frac{(1 - f_S)}{V} \equiv C_S/C_L$$

and, similarly, holds only under ideal conditions.

(iv) Freundlich isothermal adsorption describes adsorption below the saturation of the clay or colloid surface and is given by

$$C_S = k\, C_L^{1/n}$$

The examples in Figure 11 show that the initial adsorption at low concentration is rapid but, as the surface becomes covered, adsorption decreases. Taking the logarithms of both sides, the equation becomes:

$$\log C_S = \frac{1}{n} \log C_L + \log k.$$

which is a straight line with intercept log k. This may be used to gain some ranking in the order of binding capability of various clays. Figure 11 describes the Freundlich isotherms derived from the data that gave the adsorption curves in Figure 10. The k values are presented in Table 4. However, caution must be exercised in quoting and comparing such values because log k depends on the units of $\log C_L$ and $\log C_S$, and $\log C_L = 0$ is arbitrary. For the isotherms in Figure 11, the log k values obviously vary with units (moles $g^{-1} \times 10^7$, $\mu g\ g^{-1}$, ng g^{-1}) but more importantly, the relative ranking of the affinity for clays varies with intercept (e.g. Table 4). As saturation is reached, the plot deviates from a straight line and then

(v) the Langmuir adsorption isotherm should be used.

Here the rates of adsorption and desorption are considered at equilibrium and the following expression can be derived:

$$X_S = \frac{X_L C_L}{1 + K_A C_L}$$

where X_S = the amount of metal adsorbed per unit volume of solute (original solution conc'n, C_L)

X_L = the limiting value of X_S

K_A = adsorption coefficient.

Dividing through by C_L:

$$\frac{X_S}{C_L} = \frac{X_L}{1 + K_A C_L}$$

and taking the reciprocal:

$$\frac{C_L}{X_S} = \frac{1}{X_L} + \frac{K_A C_L}{X_L}$$

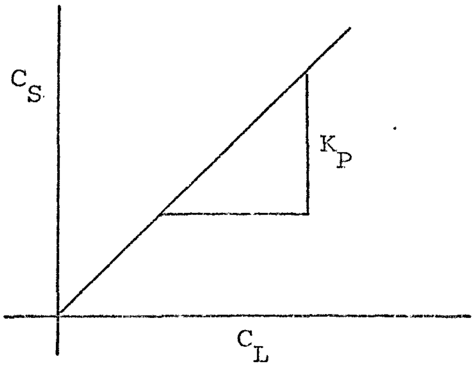
Thus a plot of C_L/X_S v. C_L gives a straight line with intercept $1/X_L$ and therefore the adsorption coefficient, K_A, may be calculated from the gradient.

The adsorption coefficient is the ratio of adsorption to desorption rate constants.

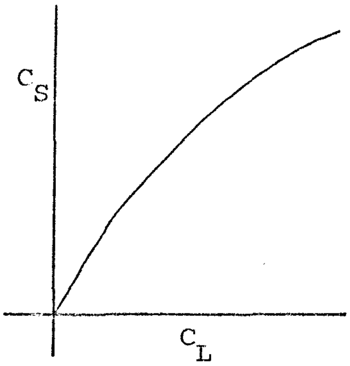
4. SUMMARY

To summarise adsorption phenomena, the three simplest and most commonly encountered in heavy metal work are:-

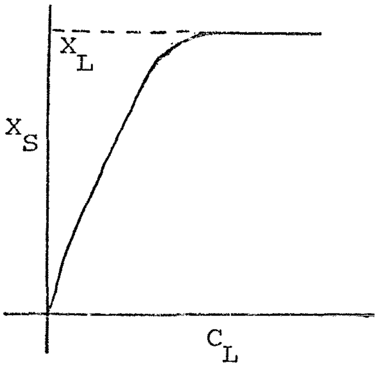
(i) Berthelot-Nernst



(ii) Freundlich



(iii) Langmuir

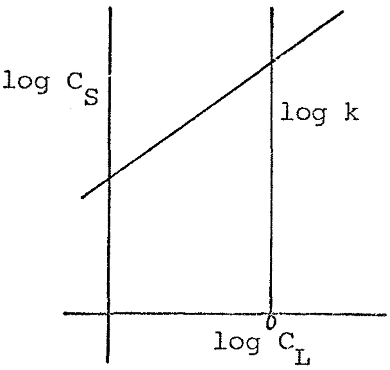


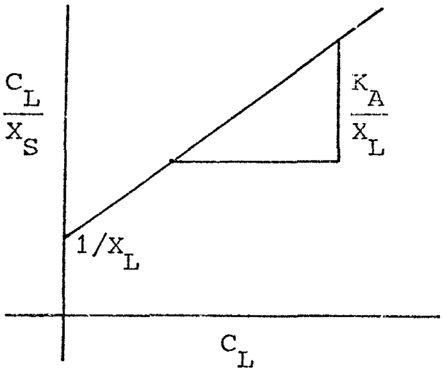
(i) $K_P = \frac{C_S}{C_L}$

(ii) $C_S = k\ C_L^{1/n}$

(iii) $X_S = \frac{X_L C_L}{1 + K_A C_L}$

rearranging (ii) and (iii) to produce linear plots given by (iv) and (v) respectively:-





(iv) $\log C_S = 1/n \log C_L + \log k$

(v) $\frac{C_L}{X_S} = \frac{1}{X_L} + \frac{K_A C_L}{X_L}$

K_P approximates to single points on small ranges of C_S v. C_L in the Freundlich or Langmuir curves; the early part of the Langmuir isotherm approximates to the Freundlich isotherm, and the Langmuir isotherm gives the adsorption coefficient for a full range of concentrations up to and exceeding saturation.

The selection of the method of presenting experimental results will be dependent on the conditions chosen for the experiment and, in particular, the metal to adsorbent ratio.

APPENDIX 2

COAL, OIL AND PHOSPHATE PRODUCTION (1865-2000)

The statistics for coal production were kindly supplied by J. McDonnell of the N.C.B. and those for oil by Brenda Tong of British Petroleum (Table A1).

Coal and oil totals were calculated by estimating areas under the curves given in Figure A1. The projections to 2000 were made by linear extrapolation.

The mean cadmium concentration in coal was taken to be 0.25 $\mu g\ g^{-1}$ and oil 0.01 $\mu g\ g^{-1}$.

A rough estimate of phosphate production was derived from the graphical/ numerical data presented by Stumm (270):-

pre 1970 ≃ 15×10^6 tonnes
1970-1980 ≃ 13×10^6 tonnes
1980-2000 ≃ 46×10^6 tonnes

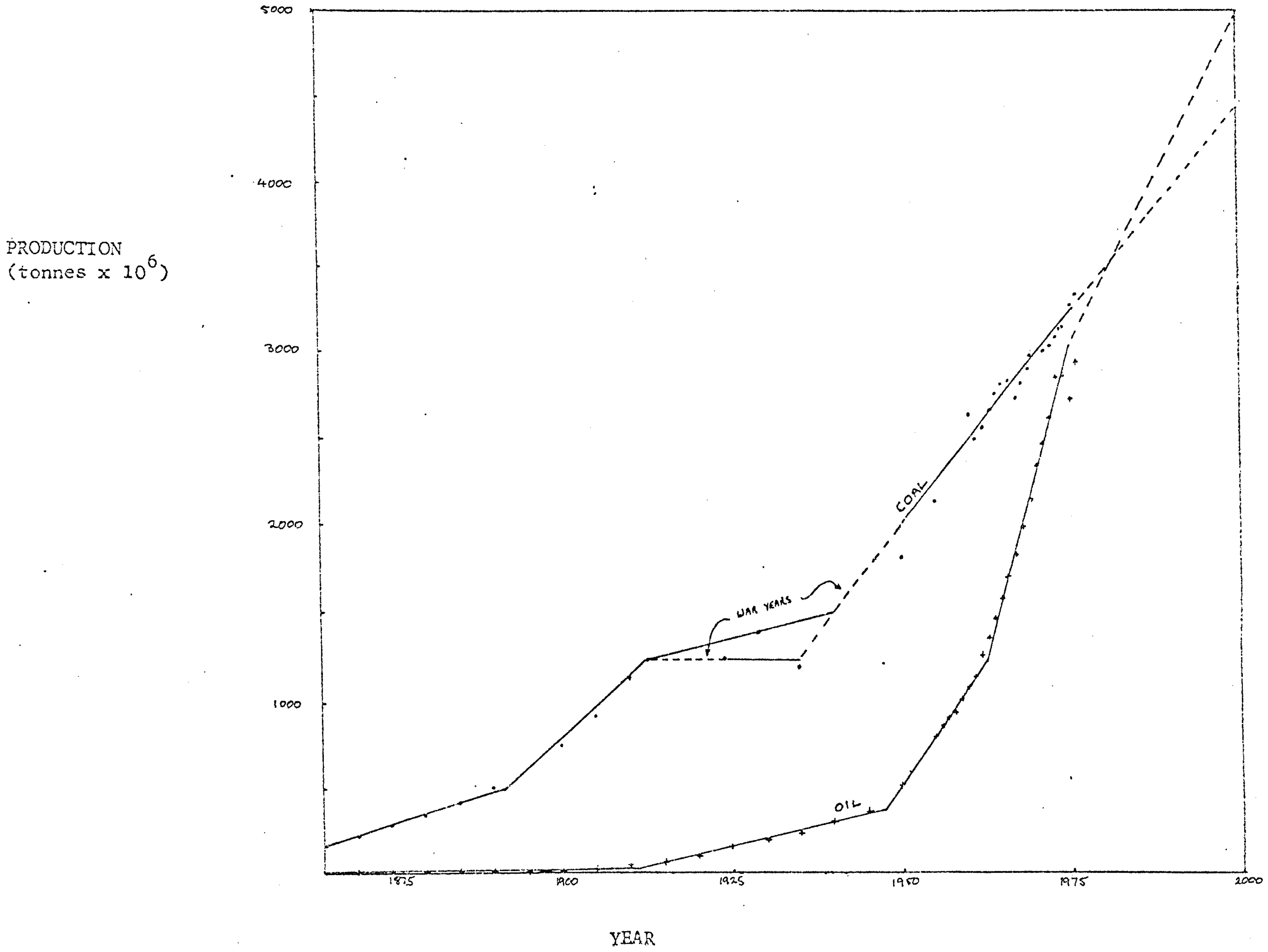
The concentration of cadmium in phosphate fertilizers was estimated to be $30 \mu g\ g^{-1}$.

Table A1 World Coal and Oil Production 1856-2000

Units = tonnes × 10^6

	Coal	Oil
1865	182	0.371
1870	218	0.796
1875	285	1.368
1880	340	4.127
1885	413	5.072
1890	513	10.56
1895	582	14.46
1900	766	20.54
1905	928	29.47
1910	1148	44.92
1915	1254 (1913)	59.39
1920	-	95.88
1925	1238 (1924)	148.6
1930	1391 (1929)	197.2
1935	1194	230.7
1940	-	293.2
1945	-	365.8
1950	1813	525.1
1955	2135	805
1960	2630	1096
1961	2482	1168
1962	2549	1267
1963	2652	1362
1964	2750	1470
1965	2793	1574
1966	2825	1697
1967	2719	1823
1968	2800	1990
1969	2892	2144
1970	3009	2351
1971	2995	2476
1972	3029	2612
1973	3084	2844
1974	3137	2861
1975	3278	2714
1976	3355	2936
(a) 1865-1970	131,900	35,630
1970-1980	33,000	30,000
TOTAL	164,900	65,630
(b) 1980-2000	76,400	100,000
TOTAL	241,300	165,600

FIGURE A1. COAL AND OIL PRODUCTION : 1865-2000



APPENDIX 3

CADMIUM IN MARINE ORGANISMS

(after Bernhard, M. & Zattera, A. (191))

(For references, see original paper)

	No. of samples in parens	FW, µg/kg		DW, µg/kg		Collecting place	Reference
		Mean	Range	Mean	Range		
Macrophytes							
Ascophyllum nodosum				290		Pacific Ocean	Malyuga, 1941
				350		Irish Sea, off Ports Erin and St. Mary	Mullin and Riley, 1956
Codium sp.				860			
Corallina officinalis				860		off Ports Erin and St Mary	Mullin and Riley 1956
Cymodocea	(8)	230	150–490	2300	2000–3100	Negro Reef, P. Rico	Lowman *et al.*, 1966
Fucus spp., 1961	(36)				50–21,000	British coasts	Preston *et al.*, 1972
1970	(40)				400–20,800		
F. serratus				340		Pacific Ocean	Malyuga, 1941
				790		Irish Sea, off Ports Erin and St. Mary	Mullin and Riley, 1956
F. vesiculosus				2050			
					15,000–220,000	Bristol Channel, Severn Estuary	Butterworth *et al.*, 1972
			2000–75,000				Nickless *et al.*, 1972
Halimeda gracilis				310		Indian Ocean	Mullin and Riley, 1956
Laminaria digitata				130		Irish Sea, off Ports Erin and St. Mary	
Lithophyllum sp.				360		(Origin unknown)	
Lithothamnion sp.				840		Irish Sea, off Port Erin	
Macrocystis pyrifera	(5)	(40)	(34–45)	(2250)	(1930–2530)	Pacific Grove, Calif.	Boothe and Knauer, 1972
Pelvetia canaliculata				500		Irish Sea, off Port Erin, St Mary	Mullin and Riley, 1956
Porphyra sp.	(21)				50–970	British coasts	Preston *et al.*, 1972
Sargassum sp.				3100	1300–5200	Carribean Sea	Forster *et al.*, 1972
Spartina alterniflora leaves	(8)	(150)		500		NW Atlantic	Windom and Smith, 1972
Thalassia testudinum	(8)	340	290–450	2200	1900–2600	Negro Reef P. Rico	Lowman *et al.*, 1966
Udotea flabellum	(31)	450	180–790	690	750–1700	Joyuda, P. Rico	
INVERTEBRATES							
Alcyonium digitatum				1150		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Asterias rubens				1100		Pacific	Malyuga, 1941
				1660		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley. 1956
Brittle cup sponge	(5)	300	170–360	2100	1200–2500	South coast Mona Island	Lowman *et al.*, 1966
Echinus esculentus				325		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Eusmilia fastigiata	(2)	4000	3500–4400	4000	3500–4400	150 ft off Anasco River	Lowman *et al.*, 1966
Halichonchia panicea				1850		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Henricia sanguinolenta				1120			
Luidia ciliaris				14,800			
Manicina areolata	(3)	3400	3200–3700	3400	3200–3700	150 ft off Anasco River	Lowman *et al.*, 1966
Marthasterias glacialis				1460		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Meandrina meandrite	(9)	3900	720–4600	4200	2900–4600	Off Anasco River, P. Rico	Lowman *et al.*, 1966
Mellita lata	(5)	2400	2300–2700	4300	4000–4700	Mani, Puerto Rico	
Ophiocomina nigra				950		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Pliable cup sponge	(6)	610	250–1000	3300	2000–4500	150 ft off Anasco River, P. Rico	Lowman *et al.*, 1966
Psammechinus miliaris				440		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Spatangus purpureus Whole org. less gut				240			
Stichastrella rosea				6300			
Crustaceans							
Balanus balanoides				150		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Callinectus sapidus	(17)	(80)	(40–120)	400	200–600	NW Atlantic	Windom, 1972
Cancer pagurus							
brown meat	(5)		30–3420				
				153		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Cancer pagurus		5000					
Carcinus maenas			14,300–33,100			Bristol–Severn, UK	Peden *et al.*, 1973
						English Channel	Bryan, 1973
Copepods, mixed species	(5)	(360)	(190–650)	1700	900–3100	NW Atlantic	Windom, 1972
Corystes cassivelaunus				149		Irish Sea, off Ports Erin, St. Mary	Mullin and Riley, 1956
Eupagurus sp.				1310			
Euphausia Pacifica (whole)	(2)		45–360		330–2600	Oregon-W coast	Robertson *et al.*, 1972
Homarus americanus	(5)	510		5300 (AW)		Rhode Island estuaries	Eisler *et al.*, 1972
muscle		200		10,000 (AW)			
exoskeleton		590		4100 (AW)			
gills		490		17,200 (AW)			
viscera		1210		33,800 (AW)			
	(4)	(40)	(<20–145)	<200	<100–500	NW Atlantic	Windom, 1972
H. vulgaris, tail	(6)	80	20–120			Scottish waters	Topping, 1973b
liver	(6)	4880	3600–8750				
	(30)	<30	<30–220				
Lysmata seticaudata		410		1700		Mediterranean Sea	Fowler and Benayoun, 1974
exoskeleton		760		3150			
viscera		910		2760			
muscle		90		390			
eyes		420		1260			
moults		1260		5460			
Pandalus jordanii							
whole animal	(5)	(160)	(60–300)	490	180–960	Off Oregon	Cutshall and Holton, 1972
edible part	(3)	(150)	(55–260)	620	230–1050		
	(5)	(160)	(110–200)	810	540–1000	Oregon coast	Robertson *et al.*, 1972
Panulirus argus	(1)	648		2400		NW Atlantic	Windom and Smith, 1972b
Penaeus setiferus	(6)	(<70)	(<35–175)	<200	<100–500		

	No. of samples in parens	FW, μg/kg		DW, μg/kg		Collecting place	Reference
		Mean	Range	Mean	Range		
Molluscs							
Aquipecten irradians	(5)	1150		43,000 (AW)		Rhode Island estuaries	Eisler *et al.*, 1972
adductor muscle		1410		49,200 (AW)			
remainder		1050		29,500 (AW)			
Calliostoma zizyphinum						Irish Sea, off Ports Erin and St. Mary	Mullin and Riley, 1956
soft parts				3050			
Chlamys opercularis							
soft parts incl. fluid		650		5300		Southampton	Bryan, 1973
kidneys		9300		41,000			
digestive glands		7100		27,000			
Crassostrea gigas			200–2100			US Pacific coast	Pringle *et al.*, 1968
C. virginica	(5)	330		9300 (AW)		Rhode Island estuaries	Eisler *et al.*, 1972
	(14)	(360)	(150–1200)	2400	1000–7700	NW Atlantic	Windom and Smith, 1972b
	(>100)	3100	100–7800			US Atlantic coast	Pringle *et al.*, 1968
Gibbula umbilicalis				830		Irish Sea, off Ports Erin and St. Mary	Mullin and Riley, 1956
soft parts							
Littorina littoralis							
L. littorea soft parts				1840			
		200	30–500			Scottish waters	Topping, 1973b
L. littorina					15,000–210,000	Bristol–Severn	Butterworth, 1972
			8000–7500			Irish Sea	Nickless *et al.*, 1972
Loliguncula brevis	(4)	(160)	(135–190)	600	500–700	NW Atlantic	Windom, 1972
Mercenaria mercenaria			100–730			US coasts	Pringle *et al.*, 1968
	(8)	(125)	(35–215)	700	200–1200	NW Atlantic	Windom, 1972
Mya arenaria	(>100)		100–900			US coasts	Pringle *et al.*, 1968
Mytilus californianus	(12)				200–4900	Off Monterey and Los Angeles, Calif.	Graham, 1972
Mytilus edulis			800–1200		400–60,000	Irish Sea	Nickless *et al.*, 1972
soft parts		330	100–930			Scottish waters	Topping, 1973b
		2000					
		570		5100		Irish Sea	Segar *et al.*, 1971
	(24)			5000	3100–6800	Off Monterey and Los Angeles, Calif.	Graham, 1972
				3210		Irish Sea, off Ports Erin and St. Mary	Mullin and Riley, 1956
M. galloprovincialis		66		1500	540–3370	Ligurian Sea	Macchi and Chamard, 1966
		1300		3940		Mediterranean	Fowler and Benayoum, 1973
shell		1780		5410			
mantle		420		1260			
gills		400		1210			
viscera		480		1440			
muscle		950		2080			
Octopus vulgaris	(1)	120		500		NW Atlantic	Windom, 1972
Ostrea sinuata	(6)			35,000	10,000–43,000	Tasman Bay New Zealand	Brooks and Rumsby, 1965
muscle				207,000			
gills				<20,000			
muscle				<20,000			
striated muscle				97,000			
visceral mass				61,000			
kidney				118,000			
heart				154,000			
shell				<20,000			
Patella vulgata							
soft parts				16,400		Irish Sea off Ports Erin, St. Mary	Mullin and Riley, 1956
					30,000–550,000	Bristol–Severn	Butterworth *et al.*, 1972
			10,300–118,500				Peden *et al.*, 1973
					9000–500,000		Nickless *et al.*, 1972
	(17)				2800–35,000	Irish Sea	Preston *et al.*, 1972
		5550		31,000		Irish Sea, Port Erin	Segar *et al.*, 1971
					62,000–425,000	Bristol–Severn	Butterworth *et al.*, 1972
Pecten maximus,							
muscle	(6)	770	550–1030			Scottish waters	Topping 1973b
P. novae-zelandiae				249,000	210,000–299,000	Tasman Bay, New Zealand	Brooks and Rumsby, 1965
mantle				<20,000			
gills				<20,000			
muscle				<20,000			
visceral mass				2,000,000			
intestine				<20,000			
kidney				<20,000			
foot				<20,000			
gonads				<20,000			
shell				<20,000			
Pecten maximus						English Channel, Southampton	Bryan, 1973
soft parts incl. fluid		4100		32,500			
kidneys		15,500		79,000			
digestive glands		91,700		321,000			
soft part		370		13,000		Irish Sea	Segar *et al.*,
Pecten maximus, muscle	(6)	770	550–1030			Scottish waters	Topping, 1973b
Polinices duplicata	(3)	(50)	(25–75)	200	100–300	NW Atlantic	Windom and Smith, 1972b
Strombus pugilis						150 ft off Anasco River, P. Rico	Lowman, 1966
shell	(2)		4200–4660				
muscle	(1)		160–180		660–810		
soft body	(2)		110–220		730–1400		
internal organs	(2)		180–320		1100–1400		
Tapes semidecussata	(5)			9600		Monterey Bay California	Graham, 1972
Thais emarginata	(10)			13,500			
Thais lapillus			31,000–72,500			Bristol–Severn	Nickless *et al.*, 1972
(= Nucella)				73,000		Irish Sea, Port Erin	Segar *et al.*, 1971
				37,900		Irish Sea, Ports Erin	Mullin and Riley, 195

	No. of samples in parens	FW, μg/kg		DW, μg/kg		Collecting place	Reference
		Mean	Range	Mean	Range		
VERTEBRATES							
Sharks							
Raja batis		470				Clevedon, Bristol Channel	Peden *et al.*, 1973
Squalus acanthias	(2)					NW Atlantic	Windom *et al.*, 1973b
muscle		(115)		400			
liver		(30)		100			
S. suckleyi	(4)	(40)	(20–70)	130	60–210	Off Oregon	Cutshall and Holton, 1972
Fishes							
Anchoa mitchilli	(6)	(150)		600		NW Atlantic	Windom *et al.*, 1973b
Calamus bajonada							
muscle		90		380		Mona Island, Puerto Rico	Lowman *et al.*, 1966
gills		90		790		Pta Cápitan	
GI tract		590		2600			
vertical col.		760		1300			
scales		1900		2700			
Carcharhinus longimanus	(4)	130	20–560	710	30–1300	Off Cangrejos at 100 fathoms	
Catengraulis edentulus	(51)	360	150–750	1300	590–2600	S of Boquilla	
Chloroscombrus	(23)	170	60–420	780	480–1000		
Clupea harengus	(62)	<30				Scottish waters	Topping, 1973b
fillet	(2)	30					
	(7)	80					
	(3)	120					
Crenimugil labrosus		80				Clevedon Bristol Channel	Peden *et al.*, 1973
Conger sp.	(1)	(75)		300		NW Atlantic	Windom *et al.*, 1973b
Esox lucius, muscle	(4)						
clean			2–3		11–16	Gulf of Finland	Jaakkola *et al.*, 1972
polluted			4–13		18–62		
Fundulus heteroclitus	(6)	330		5600 (AW)		Rhode Island estuaries	Eisler *et al.*, 1972
Gadus morhua			120–260			Clevedon Bristel Channel	Peden *et al.*, 1973
muscle and liver	(58)	120				Coasts of England and Wales	Portmann, 1972a
	(3)	180				North Sea	
	(13)	<50				Distant waters	
fillet	(77)	<30				Scottish waters	Topping, 1973a
Glyptocephalus zachirus	(2)		69–97		360–530	Oregon–Wash. coast	Robertson *et al.*, 1972
Harengula sp.	(6)	310	230–440	1080	780–1700	Puerto Rico. S of Boquilla	Lowman *et al.*, 1965
Holocentrus rufus	(3)	840	360–1600	2200	980–4100	Mona Island Sardinera P. Rico	Lowman *et al.*, 1966
Makaira nigricans	(10)	240	140–400	1000	390–1900	Off Puerto Rico	Lowman *et al.*, 1967
	(11)	230	100–400	970	420–1900	N of St. Thomas P. Rico	Lowman *et al.*, 1966
Melanogramma aeglefins	(60)						
fillet		<30				Scottish waters	Topping, 1973b
Meriangis merlangis		90				Clevedon, Bristol Channel	Peden *et al.*, 1973
Microstomus pacificus		30		140		Off Oregon	Cutshall and Holton, 1972
Mugil sp.				100		NW Atlantic	Windom, 1972
Opisthonema oglinum	(30)	200	110–320	770	420–1400	200 yds off Matei Island, P. Rico	Lowman *et al.*, 1966
	(10)	150	120–170	620	390–760	Puerto Rico, S of Boquille	Lowman *et al.*, 1965
Paralichthys lethostigma	(3)	(325)		1300		NW Atlantic	Windom *et al.*, 1973b
Parophrys vetulus	(2)		16–17		81–90		
	(1)	75		420		Oregon, Wash. coast	Robertson *et al.*, 1972
Platichthys flesus			620–1670			Clevedon, Bristol Channel	Peden *et al.*, 1973
Pleuronectes platessa	(95)	70				Coasts of Engl. and Wales	Portmann, 1972a
	(12)	120				North Sea	
	(9)	50				Distant waters	
fillet	(59)	<30				Scottish waters	Topping, 1973a
	(3)	30					
Pollachinus pollachinus		460				Clevedon, Bristol Ch.	Peden *et al.*, 1973
Psettichthys melanostictes	(2)		18–30		95–150	Oregon, Wash. coast	Robertson *et al.*, 1972
Scomberomorus cavalla	(5)	260	50–960	490	190–1400	Off Puerto Rico, NW coast	Lowman *et al.*, 1967
muscle	(6)	(100)		300		NW Atlantic	Windom *et al.*, 1973b
	(4)	300	50–960	600	190–1400	Tourmaline Reef, P. Rico	Lowman *et al.*, 1966
S. maculatus, liver	(6)			300		NW Atlantic	Windom *et al.*, 1973b
Trichiurus lepturus	(4)	44	29–57	190	150–250	Anasco Bay, P. Rico	Lowman *et al.*, 1966
	(31)	50	<5–110	200	<5–300	Puerto Rico, Anasco Bay and River	Lowman *et al.*, 1967
Tuna							
Euthynnus alletteratus						NW Atlantic	Windom *et al.*, 1973b
muscle	(5)			200			
liver	(5)			2600			
E. pelamis							
muscle	(1)			1000		Off Peru	Lowman *et al.*, 1967
head	(1)	1000		2000			
Thunnus albacares							
muscle	(1)			~1000			Lowman *et al.*, 1967
Birds							
Buffle head							
muscle	(2)		(110–110)		300–400	NW Atlantic	Windom, 1972
Hooded merganser							
muscle	(2)		(<25–90)		<100–300		
Red-breasted merganser							
muscle	(2)		(<20–50)		<100–260		

AW: ash weight, concentrations in parens are estimations from general data supplied by the authors.

APPENDIX 4

A SUMMARY OF THE EFFECTS OF CADMIUM ON MAN

The topic has been reviewed extensively elsewhere (1-4, 271-276); the report for the Commission of European Communities (271) is particularly notable for an informative treatment of the subject (560 references). A brief paper by Nordberg (272) was found to provide a good general background to the effects of cadmium on man. The reviews cited should be consulted for the original source material.

ROUTES OF CADMIUM EXPOSURE

The major sources of cadmium in day to day living are food, water, air and cigarette smoke. Table A2 presents typical values from these sources.

Rice (in Japan), wheat (in the U.S.A.) and seafoods in general account for most of the cadmium dietary intake (271). The metal in drinking water is leached from galvanised pipes and silver soldered joints (271). Air concentrations are generally low in rural areas but liver and kidney cadmium concentrations have been reported as 2.5 to 3 times greater in smokers than non-smokers. Estimates of the daily absorption of cadmium for smokers and non-smokers living in different localities is given in Table A3.

TOXIC EFFECTS

The organs most affected by exposure to cadmium are the lungs, e.g. from cadmium oxide or cadmium fumes in the atmosphere during industrial processing, and the kidneys via inhalation or ingestion.

Prolonged exposure to 0.1 mg m^{-3} Cd in air has been shown to produce pronounced effects on the lung (chronic bronchitis, emphysema) and also proteinuria (the excretion of low molecular weight serum proteins in urine). Proteinuria is the first symptom of tissue damage from cadmium exposure, and is caused by the malfunction of kidney tubules. Other effects from cadmium absorption are anaemia, resulting from decreased iron absorption in the gut, and the formation of $Ca_2(PO_4)_3$ stones.

Table A2 Cadmium Concentration in Food, Water, Air and Absorbed from Cigarettes (after Lauwerys (271))

'Normal' dietary intake	50-150 $\mu g\ day^{-1}$
'Abnormal' dietary intake	600 $\mu g\ day^{-1}$ (Jintsu)
Concentrations in food:-	
Shellfish	<0.05-50 $\mu g\ g^{-1}$
Fish: Total	0.001-4.82 $\mu g\ g^{-1}$
Muscle	0.08 -1.67 $\mu g\ g^{-1}$
Meat	<0.02-8.0 $\mu g\ g^{-1}$
Cereal, Eggs, Milk	<0.01-0.3 $\mu g\ g^{-1}$
(Rice in Jintsu Valley	0.35-3.36 ($\bar{x}$ = 1.0) $\mu g\ g^{-1}$)
Water: rarely exceeds	5.0 $\mu g\ l^{-1}$
Air: rural	0.001-0.01 $\mu g\ m^{-3}$
urban	0.002-0.7 $\mu g\ m^{-3}$

Table A3 Estimates of Daily Cadmium Intake and Uptake (from Lauwerys (271)) (µg day^{-1})

		RURAL AREA		URBAN AREA		INDUSTRIAL AREA	
		Non-Smoker	Smoker[b]	Non-Smoker	Smoker[b]	Non-Smoker	Smoker[b]
INTAKE	From Air[a]	0.005 -0.215	3.0005 -3.215	0.01 -3.5	3.01 -6.5	0.05 -25	3.05 -28
	From Food	Range 4 - 84 (median 43)					
	From Water	Range 2 - 10 (median 3)					
	TOTAL	6.005 -94.215	6.0005 -97.215	6.01 -97.5	9.01 -100.5	6.05 -119	9.05 -122
UPTAKE	From Air[a]	0.00032-0.1376	1.92032-2.0576	0.0064-2.24	1.9264-4.16	0.032-16	1.952-17.92
	From Food[c]	Range 0.24 - 5.04 (median 2.58)					
	From Water	Range <0.12 - <0.6 (median 0.18)					
	TOTAL	0.36 -5.78	2.28 -7.70	0.37 -7.88	2.29 -9.8	0.39 -21.64	2.31 -23.56

(a) daily inhalation of 20 m^3, 25% deposition, 64% absorption

(b) deposition of 3 µg from cigarettes, 64% absorption

(c) 6% absorption

There is, as yet, little evidence that cadmium causes hypertension (the arguments for and against are discussed in (2)).

Osteomalacia, normally associated with Vitamin D deficiency (272), was the most outstanding feature of Itai-Itai disease but this was observed predominantly in post-menstrual women on low calcium and protein diets who had borne many children.

The total 'normal' body burden of Cd has been estimated as 30 mg, although other estimates vary between 10 to 55 mg (273), depending on the country concerned. The liver and, predominantly, the kidneys, contain 50-75% of all the cadmium present in the body.

In the kidneys, the cortex/medulla ratio was put at 1.5-2 with 75-80% of all the cadmium present bound to a protein, metallothionein, of 6000-7000 molecular weight which contained 6% cadmium by weight and one third of its amino acid residues as cysteine (243). The purpose of this protein has been described as a detoxicant for cadmium or as an agent for the regulation and transport of copper and zinc, supported by the fact that it is also found in many other organs (271). The protein is constantly broken down and reformed and it is this that may allow for the release of small amounts of cadmium in urine (<2 µg l^{-1}). It is the non-protein bound cadmium that is thought to cause renal damage and when the excretion rate exceeds 6 µg l^{-1} Cd in urine, the critical level of cadmium in the kidney cortex of 200 µg g^{-1} is thought to have been reached, a value at which proteinuria may occur. 'Normal' concentrations of cadmium in the kidney are 24-50 µg g^{-1} at age 50, after which the concentration declines.

SINGLE DOSE AND LONG TERM EXPOSURE EFFECTS

Single dose effects are summarised in Table A4.

The daily intake of cadmium required to produce kidney damage by the age of 50 in man has been calculated (272). Table A5 presents estimates based on dietary intake and inhalation of contaminated factory air. Such calculations require detailed knowledge of adsorption rates, biological half

Table A4 Single Exposure Effects (for a 70 kg man)
(after Fulkerson *et al*. (2) and Lauwerys (271))

INGESTION		INHALATION	
CADMIUM (mg)	RESPONSE	Cd Oxide/Fume (mg m^{-3} for 8 hr)	RESPONSE
3	No effect level	0.01-0.1	No effect level (safety standard in U.S.A., U.S.S.R., U.K., Finland, Sweden, Germany)
3-90	Emetic threshold (gastro-intestinal cramps) (13-15 mg l^{-1} in drinks; reported effect)	0.25	Reported mild intoxication
		1	Produces pulmonary disease
10-326	Severe toxic symptoms, but not fatal	5	Estimated lethal dose
350-3500	Estimated lethal dose		
1530-8900	Reported lethal dose		

Table A5 Estimated Long Term Exposure to Cadmium to produce Proteinuria at age 50 in Man (after Nordberg (272))

Excretion of Cd (≡Biological Cadmium in Food)			Cd Concentration in Factory Air (µg m^{-3}) (8 hr day^{-1}, 244 days yr^{-1}, at 10 m^3 ventilation)						
				25%		Pulmonary Absorption		50%	
(% Total Body Cd day^{-1})	½ Time (yrs)	(µg day^{-1})	10	25	50	Exposure time (yrs)	10	25	50
0	(0)	164	21.3	8.5	4.3		10.7	4.3	2.2
0.002	(95)	196	22.1	9.3	5.1		11.1	4.7	2.6
0.005	(38)	248	23.3	10.6	6.5		11.7	5.3	3.3
0.01	(19)	352	25.4	13.0	9.3		12.7	6.5	4.7
0.02	(9.5)	616	30.0	18.6	16.0		15.0	9.3	8.0

time and excretion rates which vary appreciably:-

(i) retention on inhalation - 13-19% (271)
10-40% (273)
15-30% (274)

More precisely, it is estimated that, of the inhaled particles, 50% of the <0.1 μm particles compared to 10% of the 5 μm are retained in the lung (2, 271).

(ii) absorption by ingestion - 4.7-7.0% ($\bar{x} = 6.0\%$) (271)
3.0-80% (273, 274)

(iii) excretion - 0.004-0.015% of the total body burden is excreted daily (271, 273)

(iv) half-time: kidney - 10-40 yr (272)
17-33 yr (274)
body - 13-37 yr (271,273)
15-20 yr (275)

BIOCHEMISTRY

A detailed discussion is presented by Vallee and Ulmer (277). The toxic effects of cadmium are obviously a manifestation of interference in normal biochemical processes. Cadmium has a stronger affinity for sulphydryl groups than for nitrogen or oxygen containing ligands. However, it also shows a high affinity for phosphates, histidyl side chains of proteins, purines, pteridines and porphyrins, as well as cysteinyl residues. It may therefore inhibit enzyme activity, bind to functional groups to effect the conformation of nucleic acids and disrupt oxidative phosphorylation. The interaction of the metal with phospholipid monolayers could be the biochemical basis for the effect of cadmium on mitochondria, kidney tubules and nerve membranes. Information on the replacement of zinc by cadmium and a summary of the enhancement or inhibition of enzyme activity may be found in Tables A6 (a) and (b).

Table A6 Enzymatic Activities (a) Enhanced and (b) Inhibited by Cadmium (after Vallee and Ulmer (277))

(a)

Enzyme	Source
Acid phosphatase	rat liver
Adenosine triphosphatase	fowl red blood cells
Alanyl leucine dipeptidase	bacterial
Alkaline phosphatase	rabbit and rat liver; rat lung
δ-Aminolevulinic acid dehydratase	fowl liver
Amylase	malt
Arginase	yeast
Carboxypeptidase A (esterase)	bovine pancreas
Carboxypeptidase B (esterase)	swine pancreas
Carnosinase	swine kidney
Cholinesterase	rat brain, spleen, heart, kidney
Cytochrome oxidase	pigeon brain (B_{12} deficient)
Glucose oxidase	bacterial
Glucose 6-phosphate dehydrogenase	mouse liver and heart
Glutamate formimino transferase	bacterial
Histidine ammonia lyase	bacterial; rat and guinea pig liver
Malic dehydrogenase	mouse liver and heart
Oxaloacetate decarboxylase	bacterial
Phosphopyruvate carboxylase	plant
Phosphopyruvate hydratase	yeast
Phosphorylase	rat liver
Pyruvate dehydrogenase	bacterial
Pyruvate decarboxylase	wheat germ; yeast
Prolidase	swine kidney
Succinic dehydrogenase	pigeon liver; heart and skeletal (B_{12} deficient)

(b)

Enzyme	Source
Acid phosphatase	canine liver
Adenosine triphosphatase	rat liver; rabbit muscle
Aldolase	rabbit muscle; rat liver
Alcohol dehydrogenase	equine liver
Alkaline phosphatase	calf duodenum; *E. coli*; rat liver, kidney, and testis
δ-ALA synthetase	chicken liver
Amylase	bacterial
Aryl sulfatase	ox liver
Carbonic anhydrase	human erythrocytes; plants; rat testes
Carboxypeptidase A (peptidase)	bovine pancreas
Carboxypeptidase B (peptidase)	swine pancreas
Catalase	chicken liver
Cholinesterase	rat liver
Cytochrome oxidase	rat liver mitochondria
β-Fructofuranosidase	yeast
Gluconate dehydrogenase	swine kidney
Glucose-6-P-dehydrogenase	rat liver
Glutamic oxaloacetic transaminase	rat liver
Glycerol phosphate dehydrogenase	rabbit muscle
Glycyl-glycine dipeptidase	fish gut
Glycyl-serine interconversion	rabbit liver
Isocitrate lyase	yeast
Leucine aminopeptidase	swine kidney; rat kidney
Lipase	swine pancreas
Lipoamide dehydrogenase	swine heart; chicken liver
Peptidase	bovine thyroid
Phosphoribonuclease	spinach leaves
Plasmin	human serum
Prolidase	swine kidney
Proteinase	bacterial
Succinic dehydrogenase	rat liver, kidney, gonads
Tripeptidase	calf thymus
Tryptophan oxygenase	chicken liver
Urease	soybean
Xanthine dehydrogenase	chicken liver

SUMMARY

One obvious point arising out of the data presented is that absorption from the lungs is small compared to the dietary intake unless the individual smokes. The dietary estimates above may be on the conservative side since the mean and the range of means for daily intake in µg were quoted as 48 (Germany), 38-64 (Rumania), 60 (Japan), 100 (U.S.A.), 92 (U.S.A. - Institutions), 27-64 (U.S.A.), 80 (Canada)(2, 271). The U.K., France, Germany and Sweden were in the range 10-30 µg day^{-1} (271). 'Normal' intakes exceeding 200 µg have been recorded (2). The 'normal' range of intake has been put as high as 32 (rural, non-smoker) to 180 µg (urban, smoker)(2).

There are many discrepancies in estimates of half-time, pulmonary and gut absorption and excretion rates. Arising from such discrepancies, various critical long-term exposure levels will result, e.g. 132 µg Cd (87 µg for a smoker) in a daily diet over 50 years may produce kidney lesions at 0 elimination rate (2), whereas 200 µg per day is the 'safe' level quoted by others (271).

The only sure conclusion to be deduced from such data therefore is that more research is needed in this very complex area. However, the figures do serve to show that the FAO/WHO recommended safe daily intake of cadmium of 60-70 µg of cadmium seems justified whereas the Japanese accepted level of 300 µg Cd day^{-1} is definitely not.

The efficiency with which cadmium is amplified in the environment with respect to zinc, the element most closely related to cadmium chemically, is demonstrated by the decrease in Zn:Cd ratio on passing from the geological source, through the food chain (diet) finally to the lowest ratio in the human kidney (Table A7).

That the diet, and in particular, seafood, contributes most to cadmium intake is of particular relevance to this report. More detailed knowledge of how cadmium is acquired by marine organisms, and the amount of cadmium yet to find its way into the environment, is of prime importance in assessing the future exposures of man to the metal.

Table A7 Example of Zinc-Cadmium Ratios (adapted from Yamagata (1))

		Range	Mean
LITHOSPHERE		350 - 450	400
SOIL (normal)		180 - 12,000	833
SOIL (Jintsu)		142 - 363	279
FRESHWATER		100 - 330	200
SEAWATER		50 - 100	75
MARINE ORGANISMS		54 - 3500	140
HUMAN DIET		(80 - 123)	60(100)
HUMAN BODY:	TOTAL	-	80
	BLOOD	40 - 860	300
	LIVER	15 - 80	35
	KIDNEY	1.4 - 3.8	2.2

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