

ESTUARINE TRANSMISSION OF HEAVY METALS

A literature review

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ABSTRACT

As understanding of the transmission of metals in estuaries has gradually increased it has become evident that many processes occur which overlap the accepted academic boundaries. This review, carried out by engineers at Hydraulics Research, Wallingford was prompted by the need to try and draw together the contributions from different disciplines. It presents the information and discussion in terms that most readers from a scientific background should be able to understand.

ABBREVIATIONS

- As Arsenic
- Bi Bismuth
- Cd Cadmium
- Co Cobalt
- Cr Chromium
- Cu Copper
- Fe Iron
- Hg Mercury
- La Lanthanum
- Mn Manganese
- Ni Nickel
- Pb Lead
- Sb Antimony
- Se Selenium
- Ti Titanium
- V Vanadium
- Zn Zinc

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1 INTRODUCTION

1.1 Legislation

Legislative control of marine pollution from freshwater sources, along with government interest and an increase in public environmental awareness has led to numerous recent scientific investigations into the subject both within the United Kingdom and overseas.

Metal pollutants, which may occur naturally or be anthropogenic, enter an estuary in both dissolved and particulate form mainly through the river input at the tidal limits, freshwater runoff and outfalls discharging from the banks. A more thorough understanding of the transmission of metal pollutants through a tidal estuary is required to determine to what extent the pollutants are accumulated within an estuary or passed out to sea.

The United Kingdom has obligations, under international agreements to control marine pollution resulting from land based sources and dumping at sea. There are also EEC directives dealing with the quality of bathing water and the discharge of dangerous substances into the aquatic environment.

1.2 HR Studies

The Department of the Environment has a specific interest in such pollution and commissioned Hydraulics Research (HR) to carry out a programme of strategic research investigating the estuarine transmission of heavy metal pollutants. Consequently HR has been engaged in a three year field study of the River Parrett, a tributary of the Severn Estuary in South-West England. Some of the conclusions reached from this pilot study were as follows:

 most of the metals in the estuary were attached to sediment

- the relative proportions of different metals on the sediment were in roughly the same proportions as in the inputs to the estuary
- metals were mainly attached to the finer, cohesive sediment (i.e. the silt/clay fraction)
- the longitudinal distribution of metals (normalised for particle size) revealed higher concentrations at the river mouth than elsewhere in the estuary
- the concentration of metals on the superficial sediment showed a systematic seasonal variation which correlated with fresh water flow data (and therefore salinity)
- there was no detectable increase in adsorbed metals over the 3 years of sampling

This study provided insight into the overall framework of the processes involved in the transmission of metal pollutants through a tidal estuary but was by no means an exhaustive investigation of the mechanisms involved.

1.3 Basis of the

review

In order to obtain a greater understanding of the processes involved in the transmission of metal pollutants it became necessary to consider the work done by, for example, chemists and marine biologists. As a first step it was decided to survey the literature reporting on recent associated studies and thus put the HR study in better perspective. As a next step, at a later stage, taking into account the knowledge acquired from the literature survey a multidisciplinary research team could be set up for further field and laboratory investigations. The



Fig 1 Pathways of metals in aquatic ecosystems, adapted from Salomons & van Driel (58)

interactions between the estuarine eco-system and heavy metals is illustrated in Fig 1.

1.4 Outline

This literature survey draws on the information obtained from about 70 references. Much contention was found to exist between authors over a number of issues particularly the factors governing the mechanisms of adsorption and desorption of metals from sediments. The effect of salinity emerged as the main controversial issue with authors such as Sholkovitz (62), Duinker at al (19), Grieve and Fletcher(27), Thorn and Burt (67) and Morris et al (48) supporting the view that salinity enhances the adsorption of metals onto sediments and the other group including Salomons et al (57), Thomas and Grill (66), and Eaton (20 and 21) supporting the view that salinity enhances desorption. Other issues included the effect of pH, the conservative/non-conservative behaviour of metals, the exchanges between interstitial and overlying water, the importance of particle size, the significance of organic content and the methods of sample collection and analysis, all of which are discussed in this report. Some of the main protagonists to emerge from the literature survey have already been mentioned. The works of Bewers and Yeats (4), Boyden et al (8), Chester and Stoner (14), Elderfield et al (23) and Jones (37) were also of particular value to the current HR study.

Although the intention was to review studies from throughout the World most of the material reviewed originated from the Western World, in particular North America and Europe. This is indicative of the availability of material published in the English language rather than of any specific selectivity. North American studies concentrated mainly on the East coast estuaries; the St Lawrence being investigated by the Bedford Institute of Oceanography in Nova Scotia and the Hudson and rivers flowing into Chesapeake Bay

the subject of research by various US universities and research institutions. European interest was predominantly in the Rhine and Scheldt Estuaries with the Delft Hydraulics Laboratory the main contributor. In the British Isles the Thames Estuary and the Severn Estuary system received the most attention with interest also in the Conwy in North Wales, the Tamar in South-West England, the Tyne, Tees and Humber in North-East England, the Tay in Scotland and the Liffey in Ireland. The most prominent research establishments included the Institute for Marine and Environmental Research, Plymouth, the Universities of Leeds, Lancaster, Liverpool, Edinburgh and Dublin, the Welsh National Water Development Authority and Hydraulics Research.

Whilst acknowledging the dangers of oversimplification the following report sets out to interpret and summarize, in an engineer's terms, the results of recent research into the estuarine transmission of heavy metal pollutants and in particular the chemical interactions involved in the adsorption and desorption of metals from estuarine sediments.

The report falls into 2 main areas of discussion. Firstly it traces the general course of metal pollutants from their sources outlining their mode of occurrence progressing through their means of transportation and possible accumulation, the mechanism of adsorption onto the estuarine sediments and factors affecting their concentration. Secondly it describes the various techniques adopted by current researchers and any bearing this may have on the comparison of results. The conclusions are summarized in Chapter 9.

2 SOURCES OF METALS

Heavy metals, those from the first row of transition elements as set out in the periodic table including

Cr, Mn, Fe, Co, Ni, Cu and Zn, are common constituents of sediments (12). In marine environmental chemistry the term heavy metal is usually applied to toxic elements and to those which are essential to living organisms below their respective critical levels but which become toxic above these thresholds. Thus in addition to the above-mentioned metals Hg, Cd, Pb, As, Sb, Bi, Ti, Se and V would be regarded as heavy metals (9).

These metals may occur naturally or be anthropogenic. They may enter an estuary from terrestrial, aqueous or atmospheric sources and may be transported in a dissolved or particulate form. Examples of potential metal sources are outlined below but the list is by no means exhaustive.

2.1 Terrestrial sources

Freshwater runoff and groundwater flow from the catchment area may carry:

- a) the various mineralogical constituents of the weathered local rock. Taylor (65) discusses the significance of this for heavy metal concentrations measured in deposited sediments along the North-East coast of England and Schneider and Angino (60) for suspended sediment in several eastern Kansas rivers, USA. Taylor concluded that the geology of an area may be a more important factor than the industrial input in deciding the metal content of marine sediments. Schneider and Angino identified (geologically) regional trends from studying the mineralogy of the suspended load;
- b) outwash material from mine tailings. This occurs in the Conwy valley, North Wales, and was studied by Elderfield et al (23). In

the Cornish rivers Restronguet Creek and Helford Estuary it was studied by Boyden et al (8). The concentrations of tin in Restronguet Creek were high enough for a commercial firm to consider reprocessing the sediment;

c) agricultural fertilizers and pest controllers, etc spread on the land percolating into the water system.

2.2 Aqueous Sources

 a) inland and coastal sewer outfalls discharging industrial and domestic waste into the aqueous environment. The identification of such estuarine outfalls as sources of metal pollutants has been investigated by Burt (10) in the HR study of the River Parrett. Some examples demonstrating the range of inputs to the Parrett are given in the table below:

		Estimated total annual input (kg)						
	Zn	Mn	Fe	Cu	РЪ	Cd	Cr	Ni
<u>Domestic sewer</u> (untreated) mean daily flow 1745 m ³	2655	282	47115	66	3618	2	12	20
<u>Industrial sewer</u> mean daily flow 10000 m ³	2866	1380	16420	150	786	18	852	70

Note that the flow from the industrial sewer is nearly 6 times greater than from the domestic sewer so it is evident that the concentrations of Zn, Pb and Fe in the domestic sewer are much higher than in the industrial sewer but the latter contributes relatively very large amounts of Cr;

 b) offshore and coastal dumping of industrial and domestic waste. An example is that carried out in Liverpool Bay, UK where

industrial spoil and sewage sludge is dumped. Norton and Rowlatt (51) have correlated the temporal trends in concentration of some metals in sediments in Liverpool Bay with the dumping of sewage sludge.

Laboratory and field studies of the chemical behaviour of metals in dredged spoils dumped at sea have been carried out by Murray and Norton (50) who concluded that most metals in dumped spoils remained within the particulate material and that significant adverse effects on water quality at the disposal site were unlikely either during or after dumping. In another laboratory study, however, Hoff et al (33) simulated the disposal of mine tailings in a coastal inlet, the results of which indicated that mine tailings are not chemically inert in marine sediments or seawater;

- c) shipping spillages and wreckages such as the oil slick caused by the Amoco Cadiz disaster (and the chemicals used to disperse the slick);
- d) dredging and storm turbulence agitating bed deposits and re-exposing new surfaces as potential sources. Observations made by Bohlen et al (5) have indicated that dredging and storm-induced resuspension show physical similarities but the effects of dredging on estuarine sediments are localized and thus appears negligable relative to those produced by storms.

2.3 Atmospheric

sources

Metals can enter an estuary directly as fallout or indirectly via precipitation (rainout) eg acid rain, from gases and solids released into the atmosphere by;

- a) volcanic eruptions
- b) detonation of explosive devices
- c) industrial and domestic chimneys
- d) internal combustion engine (high levels of atmospheric lead in urban areas has instigated the widespread use of lead-free petrol in the USA)
- e) crop spraying
- f) burning of industrial, domestic and agricultural waste

Some figures may help to illustrate the significance of these atmospheric sources. According to Brügmann (9) the sources of heavy metal inputs to the Baltic sea are river inflow, providing 53-83% of Cr, Ni and Zn and atmospheric fallout providing some 50-80% of Pb, Hg, Cd and Cu.

The practical and financial problems of monitoring the total environment are obvious and the vast majority of authors concentrate their studies on the aqueous environment. A notable exception is Hellström (32) who carried out a case study of a smelter industry in northern Sweden to assess and mathematically model heavy metal transport in the terrestrial, aqueous and atmospheric environment, albeit from a single source. The monthly atmospheric emissions from this source in 1975 were calculated to be 20 ton Pb, 19 ton Cu and 0.7 ton Cd. Atmospheric transport was modelled and deposition calculated for distances up to 70 km from the source. Within this distance about 60% of the emissions was deposited. Aqueous transportation of heavy metals in this area is highly seasonal, i.e. accumulation in snow followed by transportation as snow melts.

3 MODES OF OCCURRENCE

3.1 General

classification

Without becoming involved in the complex chemistry of speciation which, put simply, means that metals can occur in many different forms, isolated or compounded with other elements it is possible to classify their mode of occurrence broadly as follows.

a) in surface water:-

That is water above the bed which can contain metals in dissolved or particulate form. The distinction between these two forms is discussed in 3.2 below.

b) in interstitial water:-

The framework (or soil skeleton) of the bed material contains interstitial or pore water trapped between particles. This is important to the chemistry of adsorption and desorption and therefore the mobility of metals.

c) in the biota

Metals can be present in the various marine organisms which live in an estuary. They can exist in their tissue or shell or in the gut through consumption.

d) attached to sediment

The term 'attached' is used loosely as the mechanism of attachment and precisely what the metals are attached to remain ambiguous. Some authors hold the view that they are attached as a surface layer on clay particles, other authors maintain that the metals adhere to an organic layer which surrounds the particle. There is also a

secondary attachment phenomenon whereby Fe and Mn attach to the clay and other metals adhere to the Fe and Mn compounds.

3.2 Particulate and dissolved

Some authors study only the total metal content but the two phases are frequently separated by filteration at 0.45 μ m. Harrison and Laxen (30) suggest that a better convention would be to term the two fractions filterable and non-filterable since some of the metal passing through the filter may be associated with collodial particulate matter (particles which are larger than those present in a true solution but which pass through the 0.45 μ m filter). Their point is illustrated in Table 1 which identifies the relationship of the various metal species with size, using Pb as an example. For this report, however, use of the more commonly adopted terms of dissolved and particulate metal has been maintained.

Table 1 The range of forms of heavy metals in water classified according to size association, after Harrison and Laxen (30).

Size/nm			1	10	100	100)0
Soluble			Colloidal		Particulate		
Metal species	Free metal ions	Inorganic ion pairs organic chelates	Organic complexes	Metal species bound to high molecular weight organic material	Metal species adsorbed on colloids	Metals incorp- orated with organic particles and remains of living organisms	Mineral solids; metals adsorbed on solids; precipitates co- precipitates
Example	_{РЪ} 2+	РЪНСО ₃ + РЪ-EDTA	Pb - fulvic acid	Pb-humic acid	Pb-Fe (OH) ₃ Pb- MnO ₂	Pb- organic solids	Pb-clay PbCO ₃ (s)

a) Particulate metals

Both Salomons and Förstner (56) and de Groot et al in Burton and Liss (12) distinguish five major mechanisms for metal accumulation on sedimentary particles.

- 1) adsorptive bonding on fine-grained substances
- 2) precipitation of discrete metal compounds
- coprecipitation of metals with hydrous Fe and Mn oxides and carbonates
- 4) associations with organic compounds
- 5) incorporation in the crystal lattice of the minerals which make up the sediment (lithogenous fraction).
- b) Dissolved or Soluble metals

Hart and Davies (31) identify three forms within this fraction;

- ion-exchangeable; contains free metal ions and simple organic and inorganic complexes (also referred to as 'labile' by some authors)
- bound; mainly colloidally bound metal species (also termed non-labile)
- dialysable; ion-exchangeable species with low molecular weights.

A more detailed scheme for the classification of this fraction is presented by Harrison and Laxen (30) and reproduced in Fig 2.

Not released by uv irradiation Not moved by Chelex-100 non-labile metal adsorbed on inorganics MA4 Non-labile inorganic complexes Released by uv irradiation Total metal minus labile metal Class 4 Non-labile organic complexes non-labile metal adsorbed on organics ML4 + Not released by uv frradiation by Chelex-100 Bound metal Non-labile Inorganic complexes MA3 Not retained by 0.45 µm filter Released by uv irradiation m Class Removed Non-labile organic complexes ML3 Soluble metal Noc released by uv irradiation Not removed by Chelex-100 labile metal on inorganics Labile inorganic complexes Direct asv in acetate buffer pH 4.8 adsorbed + MA2 Heavy metals in natural waters Class 2 labile metal adsorbed Released by uv irradiation asv labile metal Labile organic complexes on organics + ML2 Labile inorganic complexes MA1 organic complexes Removed by Chelex-100 Labile Free metal fons Class Ę Σ Particulate metal Retained by 0.45 µm filter

Fig 2 Scheme for the classification of heavy metal species in water, after Harrison and Laxen (30)

There is thus a great natural variability in the forms in which heavy metals occur in the estuarine environment. A generalized model of the principal forms, as given by Jones (37), is illustrated in Fig 3.

As well as metals being present in a number of forms in the estuarine environment there are also exchange reactions between the various forms. Some metal species are 'fixed', for example those held in the crystal lattice of the sediment, while others are mobile and depending on certain physical, chemical and biological factors are able to transfer between the dissolved and the particulate state.

It is these mobile metals and the conditions under which they change from the dissolved to the particulate state (i.e. adsorption) or vise versa (i.e. desorption) that are of specific interest to the HR study. The factors affecting the adsorption/desorption process are discussed in Chapter 6.

4 MEANS OF TRANSPORT

4.1 The estuarine eco-system

Metals are distributed over a large range of chemical compounds and minerals both in suspension and in the deposited matter. A proportion of the metals take part in short-term geochemical processes and/or are bio-available; other metals, such as those incorporated in the mineral lattice for example, are not bio-or geochemo-available. Although some metal species may be more readily available than others they are all transportable by one means or another. The most chemically active zone in an estuary is where fresh and saline water mix and where cohesive sediments also tend to accumlate. Boyden et al (8)



Fig 3 Forms in which a heavy metal may be present in an estuary, after Jones (37)

maintain that the effects of the mixing on the occurrence and distribution of trace elements are of greater significance in estuaries than in the open sea.

The estuarine eco-system, depicted in Fig 1, provides many possible pathways for the transportation of both dissolved and particulate heavy metals. These are largely inter-dependent processes working to maintain a natural equilibrium. For identification purposes these processes may be categorized as biotic (biological) and abiotic (chemical and physical). The abiotic processes are the more important but the biotic processes are also of some significance.

4.2 Biotic

processes

These include the diurnal and seasonal migration of aquatic biota; animals ingesting both dissolved and particulate metals and plants generally ingesting only the dissolved fraction as discussed by Luoma et al (45). Loring (43 and 44) estimated that 8-39% of total Zn, 7-20% of total Cu, 15-26% of total Pb and some 2-24% of total Co, Ni, V and Cr in the St. Lawrence Estuary is bio-available; the proportion which is actually taken up by the biota is not, however, established. Bioturbation or benthic mixing (the turning over of the bed sediments by burrowing organisms), the significance of which is indicated by Santschi (59) is another although somewhat localized means of transport.

4.3 Abiotic

processes:

Chemical

These mainly affect mobilization rather than transport of metals. Chemical processes in isolation transfer heavy metals from one phase to another rather than directly transport them over any distance; their significance is to the relative mobility of different

phases which can affect rates of transport through biological and physical interactions. So although chemical processes are not directly responsible for, they are vital to the mechanism of heavy metal transportation in the estuarine environment.

Hart and Davies (31) suggest that the most important chemical change in an estuary is the progressive increase in ionic strength, or salinity, from the tidal limit to the ocean. As a result of this change combined with concurrent variations in redox potential (Eh) and acidity (pH), the trace metals carried to the estuary by the river may also be changed from one species to another.

Elderfield and Hepworth (22) maintain that the distribution of metals in estuaries can be modified as a result of chemical reactions (termed diagenesis) that occur within the sediment column. These reactions may drastically alter the partition of metals between solid phases and solution. This allows metals to diffuse through the interstitial water which may result in their enrichment at the sediment surface or in the overlying waters. In their report on zinc behaviour in the Conwy, Elderfield et al (23) conclude that diagenetic remobilization processes were responsible for Fe, Mn and Zn enrichment detected in the surface layers of the estuarine sediments. Oxidation-reduction reactions (i.e. reactions in which an oxidizing agent is reduced and a reducing agent is oxidized electrons transferring from one atom, ion or molecule to another) are the main means of metal mobilization and the subject of much research including that by Chapman (13), de Groot et al in Burton and Liss (12), Duinker et al (19), Jones (37), Morris et al (48) and Salomons and van Driel (58). These oxidation-reduction reactions are commonly measured in terms of redox potential, the potential required in a cell to produce oxidation at the anode and reduction at the cathode.

Khalid et al (38) present a useful outline of these reactions: the redox potential (Eh) and acidity (pH) of the sediment system affects the exchange of heavy metals between sediment and surface water; some of the physical, chemical and biological reactions involved are adsorption, desorption, precipitation with oxides and hydroxides of Fe and Mn, complexation with organic matter, sulphides and carbonate reactions, and mineralization and immobilization processes.

Some of the most rapid chemical reactions take place when a sewer enters an estuary. For example dissolved metals can be adsorbed onto suspended sediment. Burt (10) suggests that in the River Parrett this takes place within a few kilometres of the outfall. Since the tidal excursion distance was about 18-20 km this indicates a time of only approximately 2 hours for almost total adsorption of all the metals measured. The suspended solids concentrations in the River Parrett are, however, exceptionally high, in the region of 50 g/l, so although metals may enter the estuary as dissolved or particulate the relative proportions can change very rapidly.

4.4 Abiotic processes: Physical

> Physical processes are perhaps the most important means of transport in the estuarine environment; flowing water has the ability to transport both suspended and dissolved constituents over considerable distances. The importance of physical processes is upheld by Sholkovitz (61) who believes that there have been very few estuarine studies which have presented convincing evidence for significant chemical reactions involving river-borne suspended matter (as opposed to settled deposits). He demonstrates that sedimentological and hydrological processes rather than chemical ones are responsible for variations in

the chemical composition of suspended matter in the Tay Estuary and extends this hypothesis to all estuaries.

Flowing water may be non-tidal (unidirectional) or tidal (multi-directional).

4.5 Non-tidal flow

Non tidal flow is that in the rivers (upstream of the tidal limit), ditches, canals and sewers draining into the estuary and is usually freshwater (i.e. non-saline). This unidirectional flow can only supply metals from the catchment area to the estuarine system but the rate of supply may be subject to fluctuations. For example in their study of the suspended flood material from several eastern Kansas rivers Schneider and Angino (60) found that storm-induced increases in sediment load were not accompanied by equivalent increases in particulate trace metal concentrations. Higher trace metal concentrations were measured during average discharge than during flooding; this is attributed to dilution of the suspended materials by leached soils transported to the rivers by sheet wash. Boyden et al (8), however, found that an increase in suspended particulate load in two Cornish estuaries during winter was accompanied by higher concentrations of most sediment-attached trace elements, a result of increased weathering and transport in the catchment area.

The Water Quality Division (formerly the Water Data Unit) of the Department of the Environment keep computerised records of regular water sample analyses from the tidal limits of most major UK rivers.

Sewers draining into an estuary can also be a major contributor of metals. Their load is as variable as their origins, from light domestic to industrial.

Some examples of the load in the case of the River Parrett are given in Section 2.2.

4.6 Tidal flow Tidal flow is far more complicated than non-tidal flow because it undergoes continuous change due to semidiurnal and lunar cycles. It is most complicated where these two types of flow interact. The hydraulic regime of each estuary is unique. It is subject to fluctuations in freshwater flow, the effects of the geometry and stability of the flow channel on local currents, tidal range and local climate to name but a few. Estuaries may, however, be classified into three main types; stratified (or salt wedge), partially mixed and vertically homogenous (or well-mixed).

4.6.1 Stratified

Stratified estuaries such as the Fraser (27) occur when the river discharge is high compared to the tidal flow; the outflowing freshwater overides a wedge of saline water. Penetration of the salt wedge up the estuary varies according to the freshwater flow conditions but there is very little variation in salinity throughout the wedge. Sedimentation in such estuaries is usually dominated by river floods.

4.6.2 Partially

mixed

Partially mixed estuaries, for example the St. Lawrence (4), Hudson (42) and Tay (61) occur when the tidal motion of the water mass is as significant as the river discharge. Water movement causes increased turbulence exchanging salt water from the lower layer with freshwater from the overlying layer, the salinity in both layers increasing towards the mouth. A net landward flow near the bed transports sediment up the estuary. The sediment accumulates near the landward end of the saline layer. This net flow is controlled by variations in river discharge.

4.6.3 Vertically

homogenous

Vertically homogenous or well-mixed estuaries such as the Parrett (67) and, under certain conditions, the Tay (61) generally occur in shallow conditions where the tidal range is the predominant factor causing thorough mixing of the water column. Seaward or landward flow, depending on the tidal state, occur throughout the cross-section of the channel and transport is largely controlled by the estuarine topography (and the physical characteristics of the suspended material i.e. fine sediment will remain in suspension at a lower velocity than coarse sediment).

4.7 Mixing Zone
 (turbidity
 maxima)

In a partially mixed estuary the body of water in which the saline and freshwaters meet is known as the mixing zone. The mixing zone is recognised by Morris et al (49) to have important consequences on the mobility and transport of suspended particles so its geographical position is important: this is dependent on the river discharge and the tidal conditions in existence at any given time.

A partially enclosed sediment transport mechanism occurs at the turbidity maxima. Sediment suspended in the overlying fluvial flow settles into the underlying (net) landward flowing saline water and is returned upstream. Tidal action mixes the sediment back into the surface layer, completing a continuous exchange process. A certain amount of sediment sorting occurs, the coarser particles being deposited and the finer ones retained in suspension within the turbidity maxima.

4.8 Residence

time

Residence time (also referred to as flushing, turnover and replacement time) is the length of time it takes for a given parcel of water entering an estuarine system to work its way out, it depends on many different hydraulic, hydrological and climatological factors and varies greatly from one estuary to another. Some examples found in the literature are listed below.

Estuary	Residence Time	Author
Rhine (Rotterdam to Hook of Holland)	l-2 days	Duinker et al (19)
Tawar	'a few days'	Morris et al (48)
Conwy	~ 1 week	Elderfield et al (23)
Scheldt	~ 2 months	Duinker et al (19)
Severn (in summer)	~ 200 days	Uncles (68)
Bristol Channel (Inner Channel)	~ 200-400 days	Chester & Stoner (14)

Residence time for a given estuary alters with fluctuations in discharge such as those brought about by seasonal variations in freshwater flow. Morris et al (49) estimate that reduced freshwater inflow during summer decreased the 'turnover' time for water within the Tamar estuary some 2-3 fold. Eaton (20 and 21) on the other hand found that the net effect of decreased river flow resulted in an increase in water residence time for any given portion of the Potomac Estuary and that under such conditions insitu exchange processes have more time to occur. According to Salomons et al (57) the recirculation of mud in an estuary causes a longer residence time for the suspended matter compared with the water; a long residence time of the suspended matter favouring the fixation of trace metals. This view is supported by Bewers and Yeats (4) who measured low cobalt concentrations in the outflowing water of the St. Lawrence Estuary along with cobalt enrichment of the particles within the turbidity maxima. They attribute this to the trapping

and resuspension of material in the turbidity maxima, thus acquiring the equivalent of a long residence time. Klinkhammar and Bender (42) found that (anthropogenic) Zn, Ni and Mn escaped from the Hudson River Estuary in the dissolved form.

Thus the end result of the same tidal (abiotic physical) processes may be different for dissolved and particulate metals.

4.9 Sediment movement

In the case of sediment attached metals the type of sediment is significant; the finer the sediment the longer it is likely to remain in suspension. Since metals have an affinity for fine particles the movement of such particles is reviewed in some detail.

On the basis of extensive studies of fine sediments in the Severn Estuary Kirby and Parker (41) have distinguished three basic states of occurrence; settled mud, stationary suspensions and mobile suspensions.

<u>Settled mud</u> is deposited fine sediment in which individual particles are supported by the surrounding particle framework. Such muds are formed by the consolidation of those stationary suspensions which occasionally survive, developing over a period of days or weeks. Their residence time may be measured in months or years.

<u>Stationary suspensions</u> (or fluid muds) have been detected in the Thames, Humber, Mersey and Severn Estuaries (40) but are not present in all estuaries. They are fluid-supported or partly framework-supported assemblages of particles having no lateral component of movement. They evolve by settling from concentrated mobile suspensions and consolidate

slowly, their lifespan may be measured in hours or days.

<u>Mobile suspensions</u> are moving, fluid-supported assemblages of particles originating from several sources:

sea and river input,

gradual erosion of settled mud,

rapid entrainment of stationary suspension from the bed.

Much of this material returns to the stationary suspension state over hours or days.

These mobile suspensions therefore present the most readily available means of transport for sediment-attached metals. Metals within stationary suspensions and settled mud deposits may be less readily transportable but the occasional agitation of these sediments by, for example, storms or dredging activities also present an effective if somewhat erratic means of transport.

In some estuaries movement of sediment enables dissolved and sediment-attached (particulate) metals to be transported out of an estuary into the open sea although in others the sediment appears to accumulate and is only removed by dredging.

4.10 Dredging

Dredging operations are another means of both direct and indirect transport, for example by,

 direct removal of sediment (and therefore sediment-attached metals),
- ii) agitation of particulates by dredging machinery - Bohlen et al (5) studied the suspended material distributions in the wake of dredging operations in the Thames River Estuary, Connecticut, USA and concluded that dredge induced resuspension was a localized phenomenon. A plume of suspended material extended downstream approximately 700m and the highest concentrations (background x2) occurred within 300m of the dredge. Such resuspension would, however, be affected by the efficiency of the dredger bucket, local tidal flow conditions, physical properties of sediment etc,
- iii) exposure of new sediment surfaces for diagenesis,
 - iv) resiting of sediment elsewhere i.e. by dumping offshore or for reclamation,
 - v) movement of metals within dredged material that has been dumped on land i.e. by leaching and by transfer of metals from the consolidating sediment to the local groundwater. A case study of a recently reclamined Dutch polder has been reported on by Salomons and van Driel (58). The heavy metal concentration in the groundwater of the polder (dredged sediment being the infill material) are 2 to 10 times higher than those in the surface waters of the nearby Rhine Estuary.
- 4.11 Estuarine

cycling of metals

> Before going on to discuss the processes of accumulation and adsorption in more detail it is appropriate at this stage to review the overall transport cycles so that the significance of these factors may be recognised and seen in context.

Several authors have investigated the cycling of metals within the estuarine environment and have developed their own rational models accordingly, e.g.

- Morris et al (48) Manganese cycling in the Tamar Estuary
 - i) Dissolved Mn is mobilized internally from reduced sediments during advective resuspension of bed material - this input is regulated by temporal and spacial variations in tidal stress.
 - ii) Mn is returned to the sediments by continuous uptake onto suspended particles, the rate of which is responsive to changes in suspended particulate load, ionic strength and temperature.
 - iii) Changes in the relative effectiveness of both the input and removal mechanisms which lead to internal cycling of Mn are closely coupled with the internal behaviour of particles and to tidally-induced oscillations in bed stress.
- (b) Salomons et al (57) Manganese and Iron cycling in a salt wedge estuary. This model is illustrated in Fig 4a.
 - Freshwater discharge generates a residual seaward flow in the upper layer.
 - ii) River water and interstitial waters of the estuarine sediments supply the main sources of dissolved Fe, Mn and organics.
 - iii) The seawater which is entrained from the lower wedge of flow is compensated by a residual landward flow along the bottom transporting

sinking particles and newly formed particles (see iv below) upstream.

- iv) The concentration of dissolved Fe, Mn and organic matter is higher in interstitial waters than in overlying waters giving rise to a flux of dissolved components from the interstitial waters to the surface waters. Once the dissolved (reduced) Fe and Mn encounter the oxygen-rich surface water a reprecipitation takes place. The newly formed particulate matter or coatings on existing particulate matter adsorbs or co-precipitates trace metals.
- v) Flocculation of organic matter and precipitation of Fe and Mn as hydroxides generally take place at low chlorinities (metal ions having less competition from chloride ions for complexation with particulate matter). The newly formed particulate matter, or the formation of coatings on the suspended particles, create additional adsorption sites and therefore an increase in adsorption.
- (c) Duinker et al (19) Manganese cycling in the Rhine and Scheldt Estuaries. This model is illustrated in Fig 4b.
 - Dissolved Mn is removed from water in the lower estuary into particulate form giving rise to elevated Mn concentrations in coastal suspended matter.
 - ii) Particulate Mn is partially returned to the upper estuary by estuarine circulation processes.
 - iii) Dissolved Mn is produced in the upper estuary by dissolution of particulate Mn either in the water column owing to the low pH and Eh



Fig 4 Cycling of metals in estuaries

prevailing at low salinities or in the anoxic sediments from where it subsequently diffuses into the overlying water.

- iv) Budget calculations show that a significant part of the Mn carried down by the river is recycled between the lower and upper estuaries. An important part accumulates within the sediments; the fraction that escapes to the marine environment is mainly in particulate form.
- (d) Thorn and Burt (67) Rational model of transmission of heavy metal pollutants in the Parrett Estuary. This model is illustrated in a simplified schematic form in Fig 4c.
 - Dissolved and particulate metals enter the tidal River Parrett in the freshwater rivers and the domestic and industrial outfalls.
 - ii) Some desorption of metals from the estuarine sediments to the overlying water occurs in the zone of low salinity.
 - iii) As the metals enter the progressively more saline environment of the Parrett Estuary they become attached to the fine, cohesive sediment particles.
 - iv) The tidal exchange of fine sediments between the River Parrett and the Severn Estuary is such that adsorbed metal concentrations are not rising within the tidal River Parrett, the metals are dispersed into the incomparably larger sediment deposits of the Severn Estuary system as a whole.

5 ZONES OF

ACCUMULATION

According to Meyerson et al (47) there are 3 reservoirs in which metals may be accomodated in the estuarine environment, biota, water and sediment. However, since the waters of an estuary are continually exchanged (Section 4.8) they cannot be regarded as a zone of accumulation. Also, as a corollary, any metals which remain in dissolved form must pass out to sea except for a very small proportion which can be trapped as interstitial water in deposited sediments. This leaves the biota and the sediment as potential zones of accumulation.

5.1 Biota

Metals may be accumulated by many and various forms of estuarine biota, for example algae, crustaceons and fish from suspended (including dissolved) and deposited matter. The ability of seaweed to concentrate metals has been studied and used as an indicator of the degree of metal contamination (45). Biota, however, have a limited life span and metals taken in to biodegradable tissue must be capable of being remobilized. There are also toxic levels of metal contamination for each form of biota which would kill it. The eco-system effectively limits the numbers of each type of organism. Taken together these 3 factors indicate that the biota reservoir for metals has a limit. One possible exception is the metals taken into the shell or skeleton (i.e. the least bio-degradable material). In this case when the creature dies this material becomes part of the sediment in the estuary and can be treated as such for the purposes of this review although it is recognised that remobilization of the metals may require different chemical processes.

Meyerson et al (47) hold the view that the biota reservoir is very much smaller than the sediment reservoir.

5.2.1 Adsorption

Adsorption onto sediments is perhaps the most significant means of metal accumulation. One of the conclusions arrived at by Burt (10) from the HR studies of the Parrett Estuary was that metal concentrations on suspended sediment were higher than those on the bed sediment at the same locality. This view is supported by references in Burton and Liss (12) and by Kirby and Parker (40) who found that the metal content of the settled muds in the Severn Estuary was less than that of the overlying (surface film of) fluid mud. Adsorption (and desorption) processes are more likely to occur under dynamic conditions i.e. particles retained in suspension will have more opportunity than deposited matter to scavenge metals (either dissolved or particulate). Ιt has already been mentioned that the longer the residence time the more favourable the conditions are for the fixation of trace metals (57). Enhanced metal concentrations have been detected in areas of high turbidity, for example Bewers and Yeats (4) report enrichment of particulate cobalt within the turbidity maxima of the St. Lawrence Estuary.

5.2.2 Deposition

Deposition of particulate metals ultimately occurs, albeit for a limited period of time in some circumstances. Loring (43) reports that the sediments at the head of the St. Lawrence Estuary are a sink and an enrichment zone for Zn, Pb and Cu, conditions being well disposed to the adsorption of dissolved metals onto fine-grained suspended sediment and consequent deposition. Thy hypothesis arrived at by Burt (11) from the HR studies of the Parrett Estuary gives no reason to suppose that metals entering the Severn Estuary system ever leave it unless the fine sediment itself leaves the system. The Severn Estuary thus appears to be an enormous sink for heavy metal

accumulation but detection of this accumulation is virtually impossible due to the vast quantity of sediment involved.

Several attempts at detecting metal accumulation in sediment deposits have been made:

The HR study of metal concentration variation with depth in a recently silted up disused berth at Combwich on the Parrett Estuary (67) showed that although some variation with depth was indicated (possibly reflecting seasonal variations) there was no evidence of an overall increase in metal concentrations during the period of accumulation (10 years). Cranston (17) found no evidence of a mercury concentration gradient in sediment cores taken from Le Havre Estuary, Nova Scotia; this was apparently due to physical and biological mixing within the sedimentary environment.

Bothner et al (6) carried out a study to determine whether trace metals had accumulated in the surface sediments off the South-East coast of the USA. The results of core sample analysis indicated that metal concentrations were uniform with depth, i.e. there was no identifiable accumulation in the surface sediments.

6 MECHANISMS OF

ADSORPTION AND DESORPTION

Adsorption/desorption processes are the subject of much controversy between authors, reflected in the literature by, for example, the documented exchanges between Eaton (20 & 21) and Sholkovitz (62).

Salomons and van Driel (58) summarise: Trace metals are distributed over the various chemical compounds and minerals in the sediment. A proportion of the metals present in sediments take part in geochemical processes and/or are bio-available. Again these processes are interdependent but may be subdivided into biotic and abiotic mechanisms, the latter being of most interest to the current HR studies. A detailed description of these processes is given in Burton and Liss (12).

6.1 Biotic mechanisms

A close association between most heavy metals and organic particulate matter in Liverpool Bay sediment is reported by Kiff and Nunny (39). Other studies which support this link are summarised below.

- i) de Groot et al (18) state that organic matter which is in excellent scavenger for a number of metals is more abundant in river deposits than in marine sediments.
- ii) de Groot et al in Burton and Liss (12) conclude that in the sediments of the Rhine-Meuse and Ems Estuaries the decrease in concentrations of heavy metals in the seaward direction is paralleled by a decrease in organic matter content. Part of this decrease is caused by decomposition of unstable land-derived organic matter.
- iii) Jones and Jordan (36) found that freshwaters contained approximately 10 times as much dissolved organic matter as seaweed, mainly as humic material leached from the catchment soils. The authors attribute metal enrichment in the Liffey Estuary to an increase in the organic carbon, nitrogen and humic acid levels.
- iv) Griggs and Johnson (28) refer to the well-documented inverse relationship between organic carbon content and grain size (this may also tie in with the increase in grain size with distance downstream). The authors found elevated metal concentrations coincided with

increased organic carbon content in the bed sediment in the Bay of Naples.

- v) Elderfield and Hepworth (22) suggest that when metal concentrations in natural waters fail to conform to prediced solubility controls, the observed levels may be maintained as a result of complexing of the metals with natural organic materials such as humic acids which stabilize heavy metals in solution.
- vi) Hellström (32) found colloidally dispersed organic matter efficient in removing heavy metals from water. The adsorption process caused by Fe, Mn and organic matter are not reversible, except organic matter in the form of humic and fulvic acids.
- vii) Organic complexes in the Yarra River Estuary, however, appeared to be of little importance with Pb and Zn but affected Cu speciation according to Hart and Davies (31).
- viii) Pellenbarg (53) makes the point that organically associated metals are presumably more available to estuarine biota than those metals associated with the inorganic phases.

6.2 Abiotic

mechanisms

Research, including that by Mayer and Fink (46), Förstner and Salomons (24), Loring (43) and Voutsinou-Taliadouri and Satsmadjis (69), has shown the preferrential association of most trace metals with fine-grained particulate matter (depending on mineralogical make-up) as they provide relatively large surface areas for the adsorption of elements from solution. Sholkovitz (61) suggests that physical processes rather than chemical ones may be responsible for variations in the chemical composition of

suspended matter in estuaries but most reactions must be a combination of physical and chemical processes.

Physochemical reactions involving different metal species are highly complex and not yet fully understood. There are discrepancies between authors over the cause and effect of these mechanisms but it is widely accepted that coatings of insoluble hydrous oxides of Fe and Mn coagulate on particulate matter in the freshwater/saline water mixing zone and scavenge other metals, especially Zn. The findings of the studies reviewed is given in Table 2.

Table 2 References identifying scavenging processes

Oxide/	General Scavenging of Trace Metals	Scavenging of Specific Metals		
Hydroxide		Zn	Cu	
Fe	19	23	34	
	42	34		
	38	27		
	20			
Mn	19	34		
	38			
1				

The main factors controlling the adsorption/desorption processes are:

- 1. the particle size
- the mineralogical composition of the particulate matter
- 3. the ambient conditions.
- 6.3 Sediment

particle size

The effect of grain size is virtually undisputed in the literature, it is generally acknowledged that most trace metals have a strong affiliation to fine-grained sediments. Such fine-grained sediments are considered to be those less than 63 µm by several authors including Förstner and Salomons (24), Mayer and Fink (46), Smith et al (63) and Rae and Aston (54). An example of the grain size dependency of Cd concentration is shown in Fig 5.

Grain size is also likely to increase with distance downstream. Analysis of the HR study of the Parrett Estuary gave reason for Burt (10) to conclude that the highest concentrations occurred in bed sediments with the highest silt content and lowest in samples with lowest silt content. Similar conclusions have been arrived at by other authors:

- i) Loring (43) found particle size to be the main factor controlling the abundance and distribution of detrital and non-detrital contributions in the St. Lawrence Estuary. The author attributes this to the detrital host minerals being fine-grained and the adsorption of the elements to particles increases as their surface area increases.
- 11) Voutsinou-Taliadouri and Satsmadjis (69) state that the average concentrations of trace metals in the Pagassitikos Gulf sediment tends to increase with the fineness of the sediment, although the influence of the latter depends greatly on the element. Different metals, however, seem to have a preference for different size fractions. The authors adopt the use of 'sand equivalent', s', an index of grain size given by the formula s' = $\frac{s+t}{5+0.2s}$ where s = % sand t = % silt



Fig 5 Grain size dependencies of cadmium concentration in sediment samples from the Main and Rhine rivers, W. Germany



Fig 6 Chromium concentration vs (a) percentage smaller than 63μ m, (b) percentage smaller than 16μ m, (c) CPB-area

Metal concentrations are related to this 'sand equivalent' value which is considered to be a reliable guide to the general distribution of metals. The relation between metal concentration and 'sand equivalent' is given in Table 3.

Table 3 Relation between trace metal concentration (parts 10^{-6}) and 'sand equivalent', after Voutsinou-Taliadouri and Satsmadjis (69)

	Sand equivalent (%)				_
t <u>80</u>	50	20	10	8	Ratio C ₈ %/C ₈₀ %
0.61	0.66	0.76	0.85	0.89	1.46
81	105	176	258	292	3.60
547	689	1079	1515	1690	3.09
73	86	116	147	158	2.16
23	26.5	34	41	44	1.91
19.5	22	28	33	35	1.79
93	103	126	145	153	1.65
27500	29900	35300	40000	41700	1.52
26	27	29	305	31	1.19
	t <u>80</u> 0.61 81 547 73 23 19.5 93 27500 26	Sar 2 80 50 0.61 0.66 81 105 547 689 73 86 23 26.5 19.5 22 93 103 27500 29900 26 27	Sand equi ± 80 50 20 0.61 0.66 0.76 81 105 176 547 689 1079 73 86 116 23 26.5 34 19.5 22 28 93 103 126 27500 29900 35300 26 27 29	Sand equivalent ± 80 50 20 10 0.61 0.66 0.76 0.85 81 105 176 258 547 689 1079 1515 73 86 116 147 23 26.5 34 41 19.5 22 28 33 93 103 126 145 27500 29900 35300 40000 26 27 29 305	Sand equivalent (%) $\underline{80}$ 50 20 10 $\underline{8}$ 0.610.660.760.850.898110517625829254768910791515169073861161471582326.534414419.52228333593103126145153275002990035300400004170026272930531

- iii) Salomons and de Groot (55) found trace metal concentrations in the Rhine to correlate positively with the proportion of finely-grained particles. The mineralogical composition and major element composition also correlate with this parameter.
 - iv) Smith et al (63) observed a notable relationship between Hg and particle size composition in the Thames Estuary, the highest Hg concentrations usually occurring in sediments containing a high proportion of fine particles.

v) Mayer and Fink (46) emphasise that the specific surface area of a particle is dependent on grain size and is the real factor controlling the accumulation of metals onto sediment surfaces. They advocate that sediment specific surface area is superior to measurements of the proportion of fine-grained sediment in defining variations of Cr concentration with sediment texture. Their point is clearly illustrated in Fig 6 which compares the results of their technique with those more commonly adopted techniques based on grain size.

6.4 Mineralogical composition

The mineralogical composition often varies among grain sizes fractions. The considerable metal enrichment often found in clay-sized relative to sand-sized sediments is not due to grain size alone; clay minerals are more readily available for ion exchange processes (12).

6.5 Ambient

conditions

The ambient conditions controlling adsorption/ desorption processes can be further subdivided into four categories:

- a) ionic strength or salinity
- b) redox potential and acidity (Eh/pH)
- c) turbidity
- d) temperature

6.5.1 The salinity

effect

controversy

Salinity seems to play a key part in adsorption/ desorption processes but authors are clearly divided into two groups regarding its effect; those who postulate that the presence of salt aids adsorption and these who claim that it aids desorption

1) Aids adsorption

Based on the HR investigations in the Parrett Estuary, Burt (11) hypothesises that on entering the saline environment the dissolved metals attach themselves to the fine sediment within the estuary. This view is supported by several other authors

- i) In his review, Jones (37) notes that several authors have recorded that much dissolved Fe is precipitated when freshwater mixes with saline water in the estuarine environment.... the ability of hydrated Fe and Mn oxides to act as adsorbents for metals is well documented.
- ii) Duinker et al (19) found that dissolved Mn was removed in the lower estuary (10-15 ppt salinity) of both Rhine and Scheldt Estuaries into particulate form.
- iii) Cranston's studies (17) of Hg in La Havre Estuary indicated that dissolved Hg was adsorbed onto suspended matter and was precipitated at the river/salt water boundary.
- iv) Sholkovitz (62) concludes that the removal of soluble Fe in the Potomac River Estuary is a result of coagulation as the riverborne Fe colloids interact with seawater cations at low salinities (i.e. 0-1 ppt) in accordance with

removal methods observed in estuaries of all types.

- v) Under laboratory conditions Bale and Morris (1) reproduced the well documented general features of Fe removal involving rapid aggregation of river-borne colloids at low salinities (0-4 ppt).
- vi) Morris et al (48) refer to the persistently high turbidity and long freshwater residence times in the Severn Estuary which favour the removal of dissolved Mn. For example a typical mean concentration of 40 μ gl⁻¹ dissolved Mn at the limit of saltwater intrusion reduces with increased salinity to less than 2 μ gl⁻¹ by 18 ppt salinity and remains low thereafter.
- vii) Grieve and Fletcher (27) conclude that adsorbed Zn values increase with distance downstream of the Fraser River Estuary and appear to be associated with the finer fractions of the river-borne material remaining in suspension. It is not clear whether scavenging takes place in brackish waters throughout the estuary or only in a narrow zone at the transition from fresh to brackish waters.
- viii) Hart and Davies (31) observed that coagulation of bound forms of Fe occurred between the freshwater and estuarine sections of the Yarra River.
 - 2) Aids desorption

Conversely a number of other authors report that increases in salinity aid desorption or at least do not favour adsorption.

- i) Thomas and Grill (66) attribute the large increases of dissolved Cu and Zn detected off the mouth of the Fraser River, British Columbia, in spring and early summer (the period of maximum water and sediment discharge from the river) to the desorptive exchange reactions that occur when river-borne sediment mixes with seawater.
- ii) Eaton (20 and 21) claims that all of the apparent removal of soluble Fe in the Potomac River Estuary occurs in freshwater. This claim is disputed by Sholkovitz (62) as mentioned above.
- 111) Kirby and Parker (40) refer to de Groot who showed that in freshwater metals are adsorbed onto the sediments as organo-metallic complexes. As the sediments pass into more saline water downstream the metals are leached due to the progressive decomposition of the organic fraction of the sediments. Hg was reported to be the most liable to leaching followed by Zn and Pb whilst La, Se and Mn were reported to be unsusceptible.
- iv) Under artificial estuarine conditions Salomons et al (57) found that with an increase in chlorinity (salinity) the amount of Zn and Cd which adsorbed onto the suspended sediment decreased; the ratio of dissolved to particulate metal increased. For Cd particularly an increase in chlorinity caused a drastic decrease in adsorption.
- v) Khalid et al (38) suggest that the presence of organics and high concentrations of chlorides in estuarine sediments may modify existing relationships and enhance metal ion release.

6.5.2 Redox potential and acidity/ alkalinity

The redox potential (Eh) and acidity/alkalinity (pH) of the sediment system effect the exchange of heavy metals between sediment and surface water.

- i) Khalid et al (38) identify two schools of thought:
 - a) toxic metals are more soluble under reduced conditions due to the reduction of Fe and Mn hydrous oxides which tend to sorb or coprecipitate metals under oxidised conditions
 - b) the presence of sulphide under reduced conditions will precipitate toxic metals resulting in a very low solubility: oxidation of sulphide to sulphate under oxidising conditions will release these metals into the overlying water.

The results of experiments carried out by Khalid et al (38) showed that an increase in redox potential values was accompanied by a decrease in suspended pH. The authors suggest that the expected adsorption or coprecipitation of soluble trace metal ions by oxides and hydroxides of Fe and Mn as an estuarine sediment is oxidised may be offset by concurrent redox potential mediated decreases in pH.

ii) Duinker et al (19) found that dissolved Mn was produced in the upper Rhine and Scheldt Estuaries by dissolution of particulate Mn in the water column owing to low pH and Eh values prevailing at low salinities.

- iii) Elderfield and Hepworth (22) state that since estuarine sediments are generally reducing and contain high levels of hydrogen sulphide it might be expected that the mobility of metals in the sediment is governed by the metal-sulphide solubility. Metals such as Cu, Pb and Zn which form very insoluble sulphides should be immobile and remain fixed in reducing estuarine sediments whereas metals such as Mn which have more soluble sulphides should be relatively mobile.
- iv) Bourg (7) comments that sediment surfaces are positively charged at low pH and negatively charged at high pH but some natural solids, especially clay minerals, can possess a constant charge (pH dependent) due to isomorphous substitution.
- v) Elderfield et al (23) found that Zn and Mn in the Conwy Estuary were pH dependent, the more alkaline waters seem to have lost these elements through precipitation or sorption processes.
 Most removal occurs at riverine pH values but this does not preclude some removal in saline waters especially where acid streams may enter stretches of the river under tidal influence.
- vi) Salomons et al (57) postulate that a small decrease in pH at low chlorinities causes a decrease in adsorption although this effect may be cancelled out by high turbidity and formation of new particulate metals in the low chlorinity region. At higher chlorinities the effect of any increase in pH is cancelled out by the competition of chloride ions for complexation of cadmium but for zinc the competition by chloride ions is less and any increase in pH may enhance removal of dissolved zinc from solution. The authors conclude that if no changes take place

in the pH value and suspended matter concentrations and if there is no formation of new particulate matter the adsorption of metals in an estuary will always be small compared with the river due to the increase in chlorinity, the chloride ions competing against the metal ions for complexation with particulates. (This however, rarely happens in nature).

6.5.3 Turbidity

Adsorption processes also seem to be affected by the suspended solids concentration in the estuarine waters, the abundance of suspended matter presenting more potential sites for adsorption to occur.

- i) Salomons et al (57) found that (under laboratory conditions) adsorption was turbidity dependent; more sediment was required under saline water conditions to achieve a given level of adsorption achieved under freshwater conditions.
- ii) Grieve and Fletcher (27) observed that suspended Fe concentrations and suspended sediment concentrations followed the same trend, both reducing in value with distance downstream of the Fraser River Estuary. This was not, however, the trend with dissolved and particulate Zn which increased with distance downstream.

6.5.4 Temperature

It is generally recognised that reaction rates are temperature dependent, an increase in temperature acting as a catalyst.

 Morris et al (49) found that chemical reaction rates approximately doubled with a 10°C increase in temperature in the Tamar Estuary. Chemical interactions in summer may be 2-4 times that attained in winter in this estuary.

ii) In his study on the settling velocities of an estuarine mud, Owen (52) found a slight tendency for increased flocculation of particles with an increase in temperature but the effect of temperature change was less significant than the effects of changes in concentration, salinity and depth of settling.

6.6 Summary

It is evident that none of these processes function in isolation; adsorption is a highly complex mechanism dependent on a combination of processes and a certain balance of conditions.

The results of laboratory studies reported by Salomons et al (57) are of particular interest in this respect and are outlined below.

- Under constant suspended matter concentrations (controlled conditions) a small increase in salinity caused a decrease in adsorption.
- ii) An increase in pH increased adsorption.
- iii) If pH and suspended matter concentrations are constant the adsorption in an estuary will be smaller than that in the river purely as a result of the increase in salinity but an increase in the suspended matter concentration may cancel out the decrease in adsorption.
 - iv) Whether adsorption in estuaries causes removal of dissolved trace metals depends not only on the processes in the low-salinity region but also on the sedimentation pattern and the reversibility of the adsorption process.
 - v) Adsorbed Cd and Zn apparently become more strongly bound to the sediment with time.

Although many adsorption studies have been conducted it is not yet possible, according to Salomons and van Driel (58), to evaluate the importance of the individual sedimentary components for the adsorption of trace metals by fluvial sediments; are trace metals adsorbed by one component in particular or are they more or less evenly distributed over the various components?

The distributions and proportions of the sedimentattached metal pollutants in the Parrett Estuary were found to be similar throughout the HR study (67) suggesting that the effects of adsorption/desorption were similar for all metals. However, conditions which aid the adsorption of one metal may not necessary aid adsorption of another. This is indicated by the findings of Klinkhammar and Bender (42) who found that suspended material was removed in the mixing zone of the Hudson River Estuary (8-10 ppt salinity). Dissolved (anthropogenic) Cd, Fe and Cu became associated with the suspended material which was subsequently deposited at the estuary mouth; dissolved (anthropogenic) Zn, Ni and Mn inputs remained dissolved and left the estuary in this form.

7 MEASUREMENT OF TRANSPORT RATE

The discussion now returns to the original question which prompted this review; what proportion of metals entering an estuary are accumulated there or pass out to sea? Three different methods have been tried by various authors to answer this question, total budget calculations, conservation calculations and study of historic deposits.

With budget calculations the authors attempt to quantify total inputs, total accumulation and total transmission. Knowing any two parameters leads to an inferred value for the third. Conservation calculations are applied to dissolved metals. By

comparing measured dissolved metal concentrations with expected dilutions along the length of an estuary (based on dilution of saline water) it is possible to deduce whether metals are being removed from or added to the water. Estimating historic trends is usually attempted by some method of dating sediment horizons within a bed, then measuring the concentration of metal in each layer. These three methods are now discussed in turn.

7.1 Budget calculations

7.1.1 Problems

Few authors have carried out total budget calculations because of the amount and complexity of the monitoring required.

Input

The range of sources of metals entering an estuary has been discussed in Chapter 2. Each source may be continuous, spasmodic or seasonal in its emmission but rarely steady state. This means that each source has to be sampled as part of a carefully designed monitoring program and ideally for a period of at least a year.

Accumulation

The discussion in Chapter 5 illustrates the complexity of direct measurement of accumulation. The major site of potential metal accumulation is the fine estuarine sediment. Burt (10) attempted to measure the rate of such accumulation by sampling sediments from the intertidal mud banks along the tidal reach of the River Parrett at 6 monthly intervals for 3 years. The first 6 month comparison showed a significant change in metal concentrations but subsequent surveys proved

this to be a seasonal fluctuation. Burt concluded that any long term trends were completely masked by seasonal fluctuations.

Monitoring of accumulation must, therefore, be both frequent, to obtain a statistical mean of short term (up to 1 year) fluctuations, and prolonged (probably at least 10 years) to identify any significant trend.

Output

Monitoring the output involves measuring the flux of metals across the seaward boundary of an estuary. This can be done in theory but a large number of accurate measurements are required and many problems may be encountered. For example, the outflow is the net difference between flood and ebb tide transport so to obtain the flux for a single tide detailed sampling in the whole cross section for the full tidal cycle is required. There are also variations in transport due to variations in tidal range, freshwater flow and other physochemical parameters.

Despite these problems several authors have attempted budget calculations, or mass balances as they are sometimes called, three of which have been selected and briefly presented below.

7.1.2 Manganese in

the River Scheldt

> An attempt was made by Duinker et al (19) to establish a mass balance for Mn in the River Scheldt. Annual mass balances of suspended matter were estimated from intensive measurements of input, transport and accumulation by sedimentation during a three-year period. The Scheldt was divided into an upper zone (km 100 to km 55) and a lower zone (km 55 to the mouth). From a total load of 1.52 M Tons of suspended

matter discharged in the first zone in a year 1.2 M Tons are deposited in the upper zone, 0.32 M Tons are transported into the lower zone and 0.12 M Tons pass out to sea.

The mass balances for Mn (Fig 7) were constructed by considering the net flow due to river discharge, the longitudinal turbulent dispersion (estimated from the salinity profile), the sedimentation process and the lateral input due to tributaries and sewers.

The authors state that a value of 300 Tons/yr for the lateral input of dissolved Mn into the upper zone satisfies the mass balance and that this was close to the measured value (about 250 Tons/yr). Similarly, a value for the transfer of dissolved Mn from the pore water to the surface water in the lower zone was evaluated by difference in order to satisfy mass conservation.

7.1.3 Mud and metals in the Rivers Rhine and Meuse

Salomons et al (57) obtained data on the trace metals transported by the Rivers Rhine and Meuse for one year. The total weight of Cu, Ni, Zn, Pb, Cd and Cr was 14,457 Tons entering the Rhine and 2,060 Tons entering the Meuse. The total budget calculations involved estimating the accumulations in the freshwater basins and estimating the water and mud discharge. In addition concentrations of trace metals in dredged material from Rotterdam were obtained and the total movement of dredged spoil was estimated. Fig 8 is based on this data. It was not possible to measure the direct output to the North Sea but Salomons et al assumed that this was the major factor in the "not accounted for" metals balance. The diagram (Fig 8) illustrates that more than two thirds of the metals input is accumulated in the fresh water



Fig 7 Tentative mass balance of manganese in the Scheldt estuary. The unit of measurement is tons year⁻¹, after Duinker et al (18)



Fig 8 Metal balance for the Rhine and Meuse after Salomons et al (57)

basins and less than one third is transmitted to the North Sea of which about 17% is attributed to disposal of dredged spoil.

7.1.4 Zinc in the

River Parrett

Burt (10) attempted budget calculation of Zn transport in the tidal River Parrett which enters the estuary of the River Severn. He estimated that about 200,000 t of sediment were available to adsorb Zn within the estuary. By comparing this figure with the estimated total annual Zn input of about 25 t Burt deduced that if all the Zn were adorbed a detectable increase in concentration should occur in a year. Observations over 3 years did not show a significant change in concentrations within the intertidal sediment so it was concluded that a high proportion of Zn entering of the Parrett passed out in the Severn Estuary.

7.2 Conservative and non-conservative behaviour

This method of measuring transport rate uses the variation in salinity along an estuary to indicate whether metals are being added or subtracted from the water. The assumption is that the salt is entirely conserved i.e. no salt is lost from or added to the water, it is simply diluted according to the amount of fresh water present. Thus if a dissolved metal exhibits an inverse linear relationship with salinity it is inferred that the metal is also being conserved. The method is well described in Burton and Liss (12).

It is a relatively straightforward method of interpreting data and does not require a vast number of samples: consequently it is popular. A number of examples have been found and a selection summarised below.

- i) Holliday and Liss (34) studied the Beaulieu Estuary in southern England and found substantial non-linearity in the iron-salinity relationship, interpreted as indicating large scale removal of iron from solution during the early mixing of river and sea water in the estuary. In marked contrast Mn and Zn appeared to behave conservatively.
- ii) In contradiction Morris et al (48) state that observations of the distribution of dissolved Mn in estuaries have usually indicated appreciable non-conversative behaviour.
- iii) Eaton (20) studied removal of iron in the Potomac River and states that it has been shown numerous times that iron behaviour in estuaries is strongly non-conversative and that extensive removal occurs rapidly in saline waters with the consequence that early estimates of the flux of iron to the oceans, based on fresh water measurements were over estimates.
 - iv) In studying the behaviour of Zn in the Fraser River, British Columbia, Grieve and Fletcher (27) concluded that non-conservative behaviour of dissolved iron and suspended sediments in estuaries is significant with respect to the natural flux of trace elements to the oceans and also to the fate of heavy metals discharge into rivers or estuaries.

The mention of suspended solids in (iv) is important because it points to the fundamental problem of this method of estimating transport processes. It is summed up well by Morris et al (48)..... "These varied observations indicate that the extent to which each of these processes is operating in an estuary is determined by a dynamic interaction between transport mechanisms and chemical transfer processes".

In other words if the water is moving and the sediment is settling and re-eroding during a tidal cycle a conservation calculation of the type described would be inadequate and misleading.

7.3 Historial

measurements

One approach to estimating the rate of accumulation of metals is to study core samples taken from the bed. The principle is that if horizons of sediment can be separately identified and dated, then metal concentrations on the sediment can also be dated.

7.3.1 Examples

For example, Bothner et al (6) tried to determine the magnitude of changes in trace metal concentrations with depth in sediment cores collected from the continental shelf off the South-Eastern United States. This study was to determine whether anthropogenic sources or natural processes had contributed trace metals to the surface sediments in sufficient quantities to raise their concentrations above those measured in sediments at greater depth. They found that the variations correlated with variations in texture of the material rather than depth and they concluded that there was no evidence of accumulation of anthropogenic metals.

Clifton and Hamilton (16 and 29) studied ²¹⁰ Pb chronology at a number of sites in the Severn Estuary with limited success. The problem in the Severn Estuary is that a considerable amount of deposition and resuspension takes place due to the high energy of the tidal processes. They were, however, able to demonstrate a link between mining activity and increased concentrations of specific metals on the sediment in St. John's Lake and in the Tamar Estuary.

The method is probably most applicable where deposition takes place without the complication of re-erosion. Thorn and Burt (67) found the opportunity

to sample historic deposits at a small berth at Combwich on the River Parrett. The berth was in regular use until 1972 since when it has been allowed to silt up. Calculation of siltation rates indicated that the berth silted up to near its present level during the first two years. At its highest point the bank is now 5m above the original level. Cores were taken and contoured profiles of the distribution of metal pollutants within the bank were plotted. An example of the result for Cu is shown in Fig 9. The profiles showed broad bands of high and low concentrations, consistent with seasonal deposition but no historical trend over the 9 years of siltation.

Goldberg et al (25) attempted to reconstruct the metal pollution history of Narragansett Bay from three box cores. Time marks in the sedimentary column were identified through ²¹⁰ Pb and plutonium chronologies and through the appearance of a shell layer associated with a 1954 hurricane. They deduced high anthropogenic metal fluxes from the fact that recent strata contained higher concentrations of Pb, Cd, Zn, Cu and Cr than those deposited several decades previously. The conclusion was, however, challenged by Santschi (59) who claimed that neglecting bioturbation led to a gross overestimation of trace metal fluxes.

7.3.2 Problems

The examples quoted and other examined show that there are severe problems with estimating rates of accumulation from historic deposits. These are summarised below.

- They can only be applied in siltuations where there is no re-erosion of deposited sediments.
- ii) The bed itself is not physically stable due to bioturbation.



Copper concentration profiles of Combwich mud bank, after Thorn and Burt (67)

iii) The bed is not chemically stable. Elderfield and Hepworth (22) describe how metals can be enriched at the sediment/water interface through movement of pore water.

8 SAMPLING AND ANALYSIS

There is great variability in the sampling and analytical techniques adopted by researchers investigating the aqueous transmission of heavy metals. This is largely a consequence of the diverse interests in and approaches to the subject. For example detailed chemical studies of metal speciation obviously require different techniques than those investigating more general trends. According to their interest some researchers confine their work to the aqueous environment, some to the settled deposits and others study both.

There is also a great deal of variability in the amount of associated information recorded and reported, for example co-incidental monitoring of water temperature, depth, salinity, pH, dissolved organic content etc. and sediment grain size distribution, redox potential and organic matter content. The degree of detail regarding the reporting of techniques differs between authors; some give specific details whilst others barely mention them.

Sampling procedures, storage and subsequent analysis depend on sample type i.e. essentially water or sediment. (It is recognised that water samples will contain some suspended sediment and sediment samples will contain some water but for the purposes of this review these classifications will suffice).

8.1 Sampling

Any sampling program will depend on the nature of the estuary and the purpose of the survey. There is, therefore, some diversity in the sampling methods and

procedures adopted although they fall into three categories, water sampling, sediment sampling and biota sampling. The last category is beyond the scope of this review and is not discussed.

8.1.1 Water sampling

In general, concentrations of metals in water are very low and thus the risks of contamination are high. Consequently careful selection and preparation of sampling equipment and storage containers is important. Acid washing of new equipment reduces the risk of contamination from plastics and other component materials which may contain high levels of heavy metals. This procedure is maintained by the majority of researchers. Sampling of surface waters may be carried out by pumping, submergence of a specifically designed water sampler or submergence of a hand held container. (Interstitial water is an integral part of deposited sediment and as such is included in the discussion of sediment sampling). Examples of each collection method are given below.

i) pumped samples are particularly suitable for continuous monitoring and the collection of large numbers of samples. Morris et al (48) pumped a stream of water from a depth of lm in the Tamar Estuary aboard their research vessel for continuous monitoring of salinity, temperature, pH, dissolved oxygen concentration and suspended solids concentration. Discrete samples were abstracted from the pumped supply and later analysed for dissolved manganese. A similar boat-mounted continuous flow system was used by Eaton (20) in the Potomac River Estuary. As a check for possible contamination Eaton also took occasional bottle samples from the same location as the pumped samples. To obtain vertical profiles of the chemical composition of suspended material in the Tay Estuary, Sholkovitz (61) pumped samples from 4-5 depths

between surface and bottom directly into pre-cleaned plastic bottles aboard a plastic-hulled boat. Concurrent measurements of temperature, salinity, current speed and direction were carried out insitu.

ii) specifically designed water samplers include those with proprietory names such as NIO (National Institute of Oceanography), IOS (Institute of Oceanographic Sciences), Niskins and van Dorn which are all varieties of oceanographic water samplers and Cassella which is a sampler more suited to fluvial field work. All these samplers are designed to allow samples to be collected from a pre determined depth. NIO bottles were used by Boyden el al (8) to collect samples of surface and bottom waters at hourly intervals for the duration of 4 different spring tides in order to establish the tidal and seasonal variation of trace elements in two Cornish estuaries. Concurrent salinity and temperature observations were made. NIO bottles were also used by Thomas and Grill (66) to take an array of samples from the Strait of Georgia to assess the effect of exchange reactions between river sediment and seawater on dissolved metal concentrations. Niskins bottles were used by Klinkhammar and Bender (42) to collect deep water samples from the Hudson River Estuary during two cruises over a two-year period to identify the distributions of dissolved and particulate metals in the estuary. Bewers and Yeats (4) used a modified version of the Niskins sampler in their study to determine the spatial distribution of trace metals in the upper St. Lawrence. Samples from the Yarra River Estuary were collected in Van Dorn samplers by Hart and Davies (31) for their study of trace metal speciation in the estuary. Van Dorn samplers

were also used by Bohlen et al (5) in their investigation into the distribution of suspended material in the wake of dredging operations in the Lower Thames River Estuary,

iii) hand held samplers are frequently used for the collection of surface and near-surface water samples. For example Thomas and Grill (66) immersed 500ml polypropylene bottles to collect surface water samples from the Strait of Georgia; Klinkhammer and Bender (42) used plastic buckets to collect surface samples of the Hudson River Estuary and Batley and Gardner (2) immersed 14 litre polythene jerricans to collect surface water samples of the Port Hacking Estuary for their study of metal speciation in the estuarine water.

8.1.2 Sediment sampling

Jones (37) points out the advantages of monitoring heavy metal concentrations in sediments rather than in the overlying waters; firstly the concentrations associated with the sediment are higher (by approximately 3 orders of magnitude) thus reducing the problems of contamination and analysis, and secondly the sediments may act as integrators of fluctuations in heavy metal conditions over a period of time.

Sediments have been widely sampled and studied in the identification of heavy metal pollution processes. Sampling of the sediment may be achieved by using grab samplers or core samplers, collecting surface smears or by dredging.

 i) Grab samplers for underwater surface sediment are the most common type obtained and studied by the researchers reviewed for this report. Such studies include those by Taylor (65) off the
North-East coast of the England, Chester and Voutsinou (15) in the Gulf of Pagassitikos, Chester and Stoner (14) in the Severn Estuary, Loring (43 and 44) in the St. Lawrence Estuary and Wright et al (71) in the Loughor Estuary. Although popular this method off sampling may lead to contaminated samples if the metal grab is not lined with plastic or PTFE and loss of the finer sediment fraction may occur if the grab jaws are not completely closed following sample extraction, resulting in an unrepresentative sample.

ii) Core samples providing sediment profiles for assessing metal accumulation, sediment dating etc. are also widely collected. Clifton and Hamilton (16) applied lead 210 chronology methods to sediment cores taken from various locations in South West England and South Wales and identified a correlation between sedimentation patterns and local industrial history. Goldberg et al (25) studied sediment cores taken from Narragansett Bay, USA and correlated their heavy metal content with the local pollution history. Using cores taken from the Ravenglass Estuary, North West England, Stanners and Aston (64) took radionuclide activity profiles to determine the local sedimentation rates. Core samples may also be collected for studies of sediment diagenesis and interstitial water (23).

8.2 Analysis

8.2.1 Water analysis

Analysis of water samples depends on whether dissolved, particulate or total metal concentrations are being determined. For total metal concentration acidification is carried out to release all non-lattice metals prior to filteration. For

determination of dissolved and particulate metals filteration, commonly through a $0.4\,\mu\text{m}$ or $0.45\,\mu\text{m}$ filter, takes place prior to any further analysis. The metals then need to be separated from their host medium and presented in a form enabling identification and quantification.

There is a great variety of techniques available for the determination of heavy metals, including those based on colorimetry, atomic absorption, electroanalysis and neutron activation. Some examples of the methods reviewed are given below.

- i) Bewers and Yeats (4) acidified their water samples to pH <2 by the addition of hydrochloric acid and analysed them by solvent extraction and flameless atomic absorption methods. They analysed for both total and dissolved metals using this technique.
- ii) Wright et al (71) passed the dissolved fraction of their water samples through a glass column containing Chelex 100 ion-exchange resin in its ammonium form. Each column was subsequently rinsed with metal-free water and the trace metals determined by atomic absorption spectrophotometry. Particulates were dried and weighed, then digested in (50ml of 2N) nitric acid. The resulting solution was centrifuged to remove any undigested material and the liquid an then dried. The samples were subsequently redissolved in concentrated nitric acid and trace metals determined by atomic absorption spectrophotometry.
- iii) Holliday and Liss (34) analysed for dissolved metals using a chelation-solvent-extraction atomic absorption technique.

- iv) Boyden et al (8) give specific details of their analytical procedures. Their water samplers were subjected to preconcentration by extraction of a 500ml aliquot in a 2 litre separating flask with sodium-diethyl-dithiocarbamate. Ammonia was added to this solution to adjust it to pH 6.0-6.2. A chloroform extraction method was applied to extract the metal complexes. Concentrated nitric acid was added to the extract and the mixture evaporated to dryness. Hydrochloric acid was then added to the residue and the resultant solution analysed for trace metals by atomic absorption spectrophotometry.
 - v) Burt (10) analysed only for total suspended metal concentration. The dried residue of each sample was digested in a nitric/perchloric acid mixture. Digestion was started at a low temperature (to destroy organics) followed by strong heat to evaporate all the perchloric acid. The mixture was then leached with hydrochloric acid and the solution diluted with metal free water. Metal concentrations were determined using atomic absorption spectrophometric techniques.

8.2.2 Sediment

analysis

Jones (37) discusses this in some detail making the point that the method should relate to the objective. For example <u>total</u> concentration of a heavy metal within a sediment may not be the most relevant to determine since only the mobile fraction is involved in the estuarine transmission process.

Total concentrations may be determined by X-ray flourescence, d.c. arc spectrometry or by initial solution of the sample by any of a large variety of techniques, many of which are the same as those applied to dried water samples (8.2.1).

Subdivisions of the total concentrations can be carried out on the basis of particle size, adsorbed and detrital fractions and organic/inorganic fractions. Each have their own relevant applications.

8.3 Standardization

The lack of standardization has, throughout this review, made it difficult to compare the results of different authors. Table 4 presents typical metal concentrations in the bed sediment deposits of several estuaries but also indicates the lack of standardization particularly in particle size analysis.

It is evident that the result obtained from metal analysis depends heavily on the technique used. There is, as yet, no absolute standard. Jones (37) points out that one of the reasons for a lack of standard methods is the very rapid advances being made in instrumentation. It should be emphasised however, that until standards are agreed authors should state the techniques they have used. In one area in particular a lack of this information causes severe problems. It has been demonstrated that particle size is a major factor determining the concentration of metals associated with sediment yet a number of authors do not state the particle size of their samples or even whether their samples were of sand, silt or clay.

It is beyond the scope of this review to suggest standards, as the authors are engineers attempting to draw together the contributions from different disciplines and thus do not have the expert knowledge required to set standards. A strong lead is given in this matter by de Groot et al (18) and this is commended to interested readers.

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Loughor (SW Wales)	Humber (NE England)	Teesmouth (NE England)	Tynemouth (NE England)	Newark Bay (New Jersey, USA)	St. Lawrence (Canada)	Liffey (E Ireland)	Tolka (E Ireland)	Conwy (N Wales)	Severn Estuary (SW England)	Parrett Estuary (SW England)	Helford Estuary (SW England)	Restronguet Creek (SW England)	Mystic River (New York, USA)	Location
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TABLE 4 Typical metal concentrations on bed sediment deposits of several estuaries

SUMMARY OF

CONCLUSIONS

- Heavy metals enter estuaries from terrestrial, aqueous and atmospheric sources.
- 2 Terrestrial sources include natural minerals, mine tailings and agricultural fertilizers.
- 3 Aqueous sources, mainly anthropogenic, include sewers, coastal and offshore dumping, shipping spillages and disturbance of settled sediments.
- 4 Atmospheric sources include volcanic eruptions, industrial and domestic chimneys, vehicle exhausts, crop spraying and general burning of waste.
- 5 Metals occur in surface water (i.e. above the estuary bed), in interstitial water, in biota and attached to sediment.
- 6 Metals can be particulate or dissolved, the usual distinguishing characteristic being a particle size limit of 0.45 µm.
- 7 A proportion of particulate metals may become dissolved while the rest is fixed, usually that held in the crystal lattice structure of the sediment.
- 8 Dissolution usually means desorption from sediment.
- 9 Dissolved metals can become particulate through chemical reaction and precipitation.
- 10 Precipitation usually means adsorption onto sediment.

- 11 Processes of metal transport in estuaries can be divided into biotic (biological) and abiotic (chemical and physical).
- 12 Biotic processes include ingestion by biota and subsequent migration and bioturbation, the physical churning up of sediments by organisms.
- 13 Abiotic chemical processes mainly affect mobilization rather than the transport of metals. The most significant reaction in this respect is when an oxidizing agent is reduced and a reducing agent is oxidized, commonly measured in terms of redox potential (Eh).
- 14 Metals entering an estuary in dissolved form through sewers can be quickly adsorbed onto suspended sediment if it is available.
- 15 Abiotic physical processes are the most important means of transport.
- 16 Non-tidal river flow transports metals into an estuary. Higher inputs of metals occur during times of flood, but not necessarily the highest because the effect of dilution begins to overtake the transporting capacity of the flow.
- 17 Sewer discharges transport metals into estuaries. The load varies according to source and time of day (i.e. industrial processes are often discharged in batches).
- 18 Tidal flow is the most obvious abiotic physical process affecting transport of metals in estuaries, either dissolved or sedimentattached. It is classified according to how the freshwater mixes with saline water from the sea, as stratified, partially mixed or well mixed.

- 19 Stratified flow occurs when river discharge is high compared to tidal flow. Sedimentation in this case is usually dominated by floods.
- 20 Partially mixed flow occurs when the two balance. There is usually a net landward movement of sediment near the bed. The sediment accumulates where the water becomes fresh.
- 21 Well mixed flow occurs when the tidal discharge dominates the river discharge, usually in shallow estuaries. Sediment transport is governed by the topography of the estuary.
- 22 In partially mixed estuaries the sediment accumulation zone is known as the mixing zone or turbidity maxima because suspended solids concentrations are usually highest there. Chemical mobilisation and physical transport processes function here making it the most influential area for metal transport in the estuary.
- 23 In all estuaries there is a net evacuation of water equal to the river discharge. Water leaves the estuary by an oscillatory or ratchet motion.
- 24 The length of time taken for water to pass from the tidal limit to the estuary mouth is called the residence time. It can vary between a few hours and a year depending on the estuary geometry and river flow.
- 25 The suspended sediment residence time can be longer than the water residence time.
- 26 A long sediment residence time favours the fixation of trace metals onto the sediment.

- 27 The transport behaviour of sediment in estuaries varies according to (among other things) its particle size. Fine sediments are the most able to adsorb and therefore transport metals.
- 28 Fine (cohesive) sediments, silt and clays, exist as settled mud, stationary suspensions and mobile suspensions. The latter provide the most readily available means of transport for sediment-attached metals.
- 29 In some cases metals can pass out to sea attached to sediments either by net tidal transport of sediment or by dredging activity.
- 30 Dredging can also agitate settled sediments and expose new surfaces for diagenesis.
- 31 Four rational models for the estuarine cycling of metals are presented in Section 4.11, three of which are illustrated in Fig 4.
- 32 Metals may accumulate in an estuary either in the biota, the interstitial water or as part of the sediment.
- 33 The biota, while important, do not provide a large sink for metals.
- 34 Interstitial water is also a relatively small sink.
- 35 The sediment provides the largest sink for metals in an estuary.
- 36 Metals are adsorbed onto the sediment while it is in suspension thus in some cases concentrations are reported to be enhanced in the mixing zone.

- 37 The sediment settles to the bed carrying the adsorbed metals with it. Whether the metals stay there is a matter of debate. Historic deposits do not provide evidence because the deposited material is neither chemically nor physically inert.
- 38 Adsorption and desorption of metals are governed by biotic and abiotic mechanisms of which the latter is the more important.
- 39 Biotic mechanisms refer mainly to the affinity between organic compounds and metals. Strong correlations have been found between organic content and metal concentration in estuarine sediments.
- 40 The importance of abiotic adsorption and desorption mechanisms is mainly due to the large surface area provided by fine (cohesive) sediments. The quantity and distribution of metals in many estuaries is governed by the quantity and distribution of the sediment.
- 41 In addition to particle size abiotic mechanisms are governed by the mineralogical composition of the sediment and the ambient conditions.
- 42 Clay minerals are more readily available for ion exchange processes and therefore adsorption/ desorption of metals.
- 43 The three main relevant environmental factors are ionic strength (salinity), redox potential and turbidity.
- 44 Salinity appears to play an important part in adsorption/desorption but there are opposing views on what the effect is. One school of thought is that sediments are more able to

scavenge dissolved metals in a saline environment and the other is that metals are desorbed in the saline environment for example by progressive decomposition of the organic fraction.

- 45 Regarding the effect of redox potential it is suggested that metals are more soluble under reduced conditions such as might prevail in a deposited bed. It appears that this can lead to enhanced concentrations of dissolved metals in interstitial waters. It could, therefore, be a major factor in the re-entrainment of metals into the estuarine waters.
- 46 High turbidity (suspended fine sediment concentrations) implies a large surface area is available for potential adsorbtion of metals.
- 47 Notwithstanding the foregoing statements it must be said that all metals do not behave in the same way; what aids adsorption of one metal may not enhance that of another.
- 48 There are three approaches to the measurement of rate of transport of metals through estuary systems, budget calculations, conservation calculations and study of historic deposits.
- 49 Budget calculations are of questionable accuracy because of the difficulties of adequate monitoring of the inputs, the near impossibility of measuring accumulation and the practical difficulties of obtaining sufficiently detailed measurements to determine net outflow.
- 50 Conservation calculations based on comparisons of dilution of dissolved metal concentrations with salinity are popular and can give some

useful indications of zones of accumulation but can be misleading because they do not adequately take into account hydrodynamic processes.

- 51 Studying cores of sediment can give some indication of historic rates of accumulation of trace metals providing a reasonable dating method can be applied but there are three major problems:
 - the method only works where there is deposition without erosion,
 - ii) the bed is not physically stable due to bioturbation,
 - iii) the bed is not chemically stable (i.e. there is a flux of some metals within the bed towards the surface).
- 52 Variability of sampling and analysis techniques between authors makes it difficult to compare their results. There is a need for standardization. Until this is achieved it is suggested that authors fully document the techniques adopted by them when presenting their results.

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