THE CHARACTERISTICS, BEHAVIOUR AND HETEROGENEOUS CHEMICAL REACTIVITY OF ESTUARINE SUSPENDED PARTICLES

A. J. BALE

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"Tamaris"

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I dedicate this work to my wife Diana: without her encouragement and unerring support, the production of this thesis would not have been possible. Primarily, though, I would like this dedication to record my gratitude to her for bearing and raising our daughters, Nicole and Julia, who have given me so much enjoyment during their early years.

DECLARATIONS

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other CNAA or University degree. None of the material herein has been used in any other submission for an academic award. The practical work reported in this thesis formed part of the Estuarine Chemistry Programme of the Insitute for Marine Environmental Research, a component of the Natural Environment Research Council.

A programme of advanced study was undertaken in parallel with the research programme and included reading in estuarine and marine chemistry, attendance at a five day course on colloid science at the University of Bristol, a similar period undertaking tuition in the operation of scanning electron microscopes at Plymouth Polytechnic, and training in BASIC and FORTRAN programming at IMER. During the period of this registration the candidate has attended relevant seminars and conferences; the conferences are listed below:-

Conferences attended

Estuarine and Brackish Waters Sciences Association meeting: "Transfer Processes in Cohesive Sediments". Held at the Fresh Water Biological Association, Windermere, September 1981. Paper presented by Bale *et al.* entitled "Size distributions of suspended material in the surface waters of an estuary as measured by laser Fraunhofer diffraction".

Estuarine and Brackish Waters Sciences Association meeting: "The Tamar". Held at the Institute For Marine Environmental Research, April 1982. Presentation by Bale *et al.* entitled "Particle dynamics at the oxygen minimum".

International Association for the Physical Sciences of the Ocean (IAPSO), 18th General Assembly, Hamburg, August 1983. Poster/verbal presentation by Bale *et al.* entitled : "Estuarine Particulates: physico-chemical properties, transport processes and the implications for chemical reactivity."

Challenger Society meeting: "Physical Oceanography 84". Held at the UCNW Marine Sciences Laboratories, Menai Bridge, September 1984. Presentation by Bale _et al._ entitled:" A submersible laser diffraction particle sizing apparatus".

Natural Environment Research Council sponsored meeting of: "Geocolloids Group". Held at Lancaster University, April 1985.

Natural Environment Research Council sponsored meeting of: "Geocolloids Group". Held at Lancaster University, April 1986.

Estuarine and Brackish Waters Sciences Association meeting (EBSA 16) entitled "The Dynamics of Turbid Coastal Environments." Held at Plymouth Polytechnic, September 1986. Presentation by Bale of Paper by Morris _et al._ entitled: "Controls of the chemical composition of particle populations in a macrotidal estuary (Tamar Estuary, U.K.)."

External visits

One week was spent at Professor Liss's laboratory at the University of East Anglia learning the principles and operation of particle micro-electrophoresis under the guidance of Dr T.C. Loder.

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ESTUARINE SUSPENDED PARTICLES

by

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The South West Water Authority freely provided invaluable information on the composition and flow rates of the Tamar River and its tributaries and I am grateful for their assistance.

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THE CHARACTERISTICS, BEHAVIOUR AND HETEROGENEOUS CHEMICAL REACTIVITY OF SUSPENDED PARTICLES IN ESTUARIES.

by Anthony John Bale LRSC

Abstract

A systematic, seasonal study of the distribution, behaviour and characteristics of the suspended and sedimentary particulate material in the macro-tidal Tamar Estuary and its influence on solution chemistry has been undertaken. This work has attempted to characterise the variability in particle properties associated with the major cyclic influences of the semi-diurnal and spring-neap and the seasonal climatic signals and to relate these findings to the distribution and transport of trace metals in estuaries.

Characterisation of the particles involved measurements of surface charge using electrophoretic techniques, particle size, settling rates and densities, bulk compositional analysis and visual examination by scanning electron microscopy. At the same time, the internal cycling of particulate material between the sediment and suspended phases through oscillations in tidal energy and the transport of particles associated with the seasonal migration of the mobile estuarine sediment shoal and turbidity maximum material were estimated.

Distributions of the dissolved metals, Cu, Zn, Ni and Cd were measured in the estuary over a range of seasonal and tidal conditions. The close co-variance between the degree of soluble metal removal and the location and magnitude of the turbidity maximum indicated that sorption on to particles was a major factor influencing metal distributions in the low salinity region of the estuary. A series of laboratory experiments using radio-isotopes were carried out to examine the factors which influence the partitioning of metals between natural suspended particles and the soluble phase in estuaries. A comprehensive picture of the interactions of salinity, pH and temperature on the partition coefficients for Zn, Cd and Cs was derived.

With the aid of a recently developed mathematical model, realistic simulations of the distributions and fluxes of salt and particles (suspended and sedimentary) in the Tamar Estuary were produced. Corresponding distributions of dissolved zinc were generated by the model using the partition coefficients derived from the radio-tracer work. The simulated profiles of soluble zinc measured in this way accurately followed the major features of the measured metal distributions as well as closely replicating the absolute values. Manipulations of the model parameters indicated that tidally dominated, up-estuary pumping of metal poor particles was the primary factor controlling the degree of metal removal at the turbidity maximum.

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SECTION ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

Over the past half century and particularly in the last 20 years, it has been realised that estuaries play a key role in the transport and dispersion to the world oceans of both natural chemical species, derived from crustal weathering, and the pollutant materials which are the by-product of man's activities on earth. The importance of the estuarine link in the global picture of geochemical cycling and environmental pollution can be gauged from the explosion of research interest in estuaries and estuarine processes during this period (see, for example, Lauff, 1967; Nelson, 1972; Cronin, 1975; Goldberg, 1978; Burton and Liss, 1976; Wiley, 1976; Olausson and Cato, 1980; Kennedy, 1980; Neilson and Cronin, 1981). The specialised nature of estuarine environments has necessitated the development of many new approaches and techniques to study them and several excellent practical guides have been written (Dyer, 1979; Morris, 1983; Head, 1985).

Recurrent themes throughout these works and numerous individual published articles are firstly, that estuaries are typically energetic, turbid environments and secondly, that the presence of elevated levels of suspended solids that undergo periodic resuspension and sedimentation under the influence of tidal action can strongly influence their chemistry and biogeochemistry. The hydrodynamic processes that give rise to elevated and often localised concentrations of suspended sediments in estuaries and their influence on estuarine chemistry are reviewed fully in subsequent sections.

This study attempts to characterise the properties, behaviour and heterogeneous reactivity of estuarine particulate material with the aim of an improved understanding of the transport and dispersion of natural and pollutant chemicals through estuaries. For the purposes of this study, heterogeneous reactivity has been considered in terms of trace metal exchanges. Nevertheless, it is anticipated that the underlying physical controls of heterogeneous processes in estuaries will be sufficiently general for these findings to apply to the wide spectrum of chemical species which experience sorptive exchange at the surfaces of natural particles.

1.2 ESTUARIES

1.2.1 What is an estuary?

The Oxford English Dictionary defines an estuary as:

"the tidal mouth of a large river"

This is consistent with the popular concept of an estuary but to those charged with the study, description or management of these environments this definition has many disadvantages. Questions such as, where does the river end and the estuary start, emphasise the need for a precise definition on which to base studies and with which to relate the findings to adjacent environments or other estuaries. Ketchum (1951) presented this definition:

> "....an estuary may be defined as a body of water in which the river water mixes with and measureably dilutes seawater."

This limits an estuary to the region of brackish water but is geographically vague. Pritchard (1967) suggested:

> "....a semi-enclosed coastal body of water which has free connection with the open sea and within which seawater is measureably diluted with fresh water derived from land

drainage."

Here, the extent of the estuary is again defined by the mixing of fresh and saline waters but not necessarily within a river or a tidal environment. Fairbridge (1980), in a thorough review of estuarine systems, proposed an extended definition based on hydrodynamic rather than purely hydrochemical criteria:

> ".... an estuary is an inlet of the sea reaching into a river valley as far as the upper limit of tidal rise, normally being divisible into three sectors; (a) a marine or lower estuary, in free conection with the open sea; (b) a middle estuary, subject to strong salt and freshwater mixing and (c) an upper or fluvial estuary, characterised by freshwater but subject to daily tidal action."

This definition describes the geographical and physical limits of an estuary except for the marine boundary about which most workers are vague. In practical terms, no boundary exists as riverine components transported seaward are continuously diluted until they become indistinguishable from the marine composition. Nominal seaward boundaries to estuaries are therefore adopted, usually on the basis of coastline morphology except where clearly identifiable plumes of fresh or brackish water extend into the coastal sea. This latter definition is particularly relevant in the Tamar as it encompasses the tidally energetic zone in the fresh water immediately landward of the point of maximum saline intrusion. This area is strongly influenced by the turbidity maximum generated within the estuary and has been shown to be a region of marked chemical changes (Morris _et_ _al_., 1982b).

The infinite variability of the geomorphology and hydrodynamics of estuaries makes it convenient to recognise various subdivisions. Pritchard's (1955) widely adopted scheme, based on the physical processes that dominate the internal mixing of estuaries, is shown in Table 1.1. This approach has been developed quantitatively by Hansen and Rattray (1966) who proposed a classification based on two dimensionless factors, a circulation parameter (u_s/U_f), the ratio of net surface current to the mean fresh water velocity through the section, and a stratification parameter ($\delta S/S_o$), the ratio of the top-to-bottom salinity difference to the mean salinity over the section. It must be borne in mind that various regions of an estuary can exhibit different classifications (see Section 1.3 for Tamar classifications) and that the classification of a particular estuarine region can change with factors such as river run-off and tidal range.

1.2.2 Estuaries as pathways

In geochemical terms, estuaries are regions in which land run-off, containing the soluble and particulate products of crustal weathering, mixes and interacts with the world's oceans (Mason, 1952). The primary concern of the estuarine chemist is the fate of these weathered materials and pollutants following their introduction to the estuarine system. Very rarely, however, are the distributions of chemical species in estuaries simply the result of mixing of fluvial and marine waters. Marked gradients in ionic strength, pH and Eh as well as tidal and seasonal variations in, for example, suspended particulate load and primary productivity give rise to pronounced chemical reactivity within the mixing zone (Liss, 1976; Morris et al., 1978, 1981, 1982a, 1982b).

Chemical reactivity, in terms of loss or gain of a particular component within the estuarine mixing zone, can be deduced by comparing the distribution of the component relative to a conservative property such as salinity or chlorinity. The theoretical dilution line that is

Table 1.1 Pritchard's (1955) classification of estuarine types.

type	dominant process	vertical structure	Nomenclature
salt wedge	riverflow	very sharp halocline	A
fjord	riverflow with entrainment	sharp halocline	
partially mixed	riverflow and tidal mixing	no marked interface; salinity increases with depth	B
well mixed	tidal mixing	uniform vertical salinity profile	C (D with lateral salinity gradient)

obtained by simple mixing of the two end-member concentrations of the component would be a straight line on a plot of component concentration against salinity. In simple cases, a negative deviation indicates removal whereas a positive deviation indicates an input of the material within the mixing zone (Figure 1.1). Additionally, a plot of the parameter of interest against salinity indicates the extent and the approximate location of the process. In reality, these plots are often complex, especially where net removal occurs in one region whilst inputs are located in another area or where, for instance, the reaction rate changes with salinity. It must also be borne in mind that this approach requires the composition of the end-members to have remained constant throughout a pre-investigational period equivalent to the flushing time of the estuary. Whilst this is generally true for the marine end-member, it is often not the case for the riverine supply. Rapid changes in riverine composition induce curvature into the salinity/component relationship of an unreactive component (Loder and Reichard, 1981). Generalised conclusions concerning the behaviour of dissolved species in estuaries using mixing curves require the examination of a large number of profiles under different conditions (Morris et al., 1981).

1.2.3 Estuarine dynamics

Estuaries are subject to both tidal and seasonal influences which, along with marked compositional gradients (Morris, 1978; 1982b), contribute to the complexity and often cyclical nature of the chemical, biological and physical processes that occur within their boundaries (Allen et al., 1976, 1980; Morris et al., 1982a; Cloern et al., 1983; Bale et al., 1985).

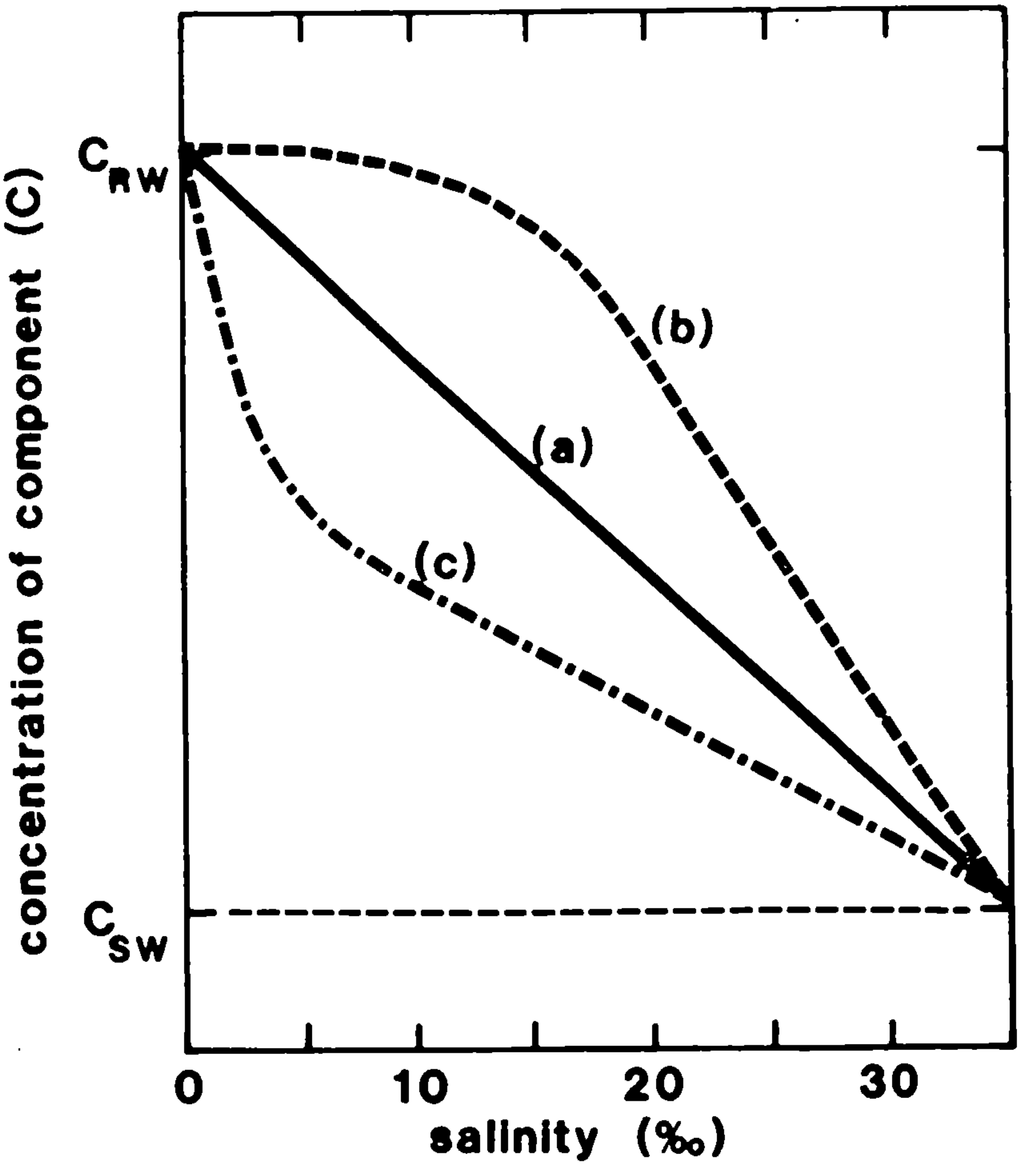


Figure 1.1 Relationships between the concentration (C) of a dissolved component and salinity under steady state conditions. Line (a) represents conservative mixing, (b) and (c) represent mobilisation and removal respectively.

The majority of tidal estuaries in mid-latitudes experience predominantly semi-diurnal tides with a period of roughly 12.5 hours. The spring/neap cycle with a period of 14-15 days has the effect of modulating the daily tides such that the tidal range, and hence current velocities, increase from neap to spring conditions and decrease again towards neaps. The principal effect of the tides is to increase the volume of water within the estuary at high water over the volume at low water. This introduces oscillations into the velocity and direction of the tidal streams with minimum velocities occurring at, or about, high and low water and maximum velocities at mid-ebb and flood.

The predominant seasonal signal in estuaries arises from changes in river flow with rainfall. Changes in river flow affect the flushing time of the estuary and the location of the fresh/brackish water interface. The mixing regime moves down-estuary under high (winter) river flow and, conversely, saline water intrudes further up-estuary under low (summer) river flow conditions. Additionally, seasonal changes in solar radiation (Kirk, 1983) affect primary production directly through light availability and chemical and biological reaction rates through temperature changes.

To accomodate this range of natural variability when making the field measurements described in subsequent sections, a sampling strategy was adopted whereby surveys were executed under specific environmental conditions chosen to cover the full range of seasonal and tidal extremes. Thus, sampling was undertaken to monitor selected particle properties over complete semi-diurnal tidal cycles under both spring and neap tide conditions. Additionally, estuarine profiles were monitored over complete spring to neap tidal cycles at two-day intervals under high (winter) and low (summer) river flow conditions.

1.2.4 Suspended solids in estuaries: physical aspects

As evidenced by large areas of intertidal mudflats and generally turbid waters, estuaries tend to be regions of net sediment accumulation (Guilcher, 1967; Postma 1967; Meade, 1969; Dyer, 1979). In addition, many estuaries exhibit localised areas of significantly enhanced suspended solids concentration commonly referred to as turbidity maxima (Postma, 1967; Schubel, 1969) situated at or close to the fresh/brackish interface. Tidally mediated resuspension and deposition of bed sediments mainly account for the turbid nature of estuarine waters although shore erosion is a contributory factor in some estuaries (Schubel and Carter, 1977). However, the trapping and localised accumulation of particles is more complicated and various mechanisms have been postulated. These include flocculation with increasing ionic strength (Krone, 1972; Aston and Chester, 1976; Kranck, 1979), gravitational circulation (Postma, 1967; Schubel, 1969; Officer and Nichols, 1980) and tidal pumping (Allen *et al*., 1980; Uncles *et al*.,1985) associated with asymmetric tidal flow. Each of these processes probably contributes to the accumulation of particulate material but to differing degrees in different estuaries (and at different times in one estuary), depending on the prevailing physical conditions.

Gravitational circulation occurs in stratified or partially mixed estuaries as a result of the density difference between the two water masses. Particles of marine and estuarine origin within a specific range of settling characteristics are carried up-estuary in the net landward intrusion of saline water at depth. Similarly, riverine particles that are neither too heavy to sediment rapidly nor so light that they behave as dissolved species can become entrained into the saline water by slow sedimentation and again become subject to up-estuarine transport. This results in the concentration of particles in a null tidal region at or near the limit of saline intrusion (Figure 1.2).

Net up-estuarine transport of particles through tidal pumping occurs in the upper reaches of macro-tidal estuaries through a combination of frictional effects and the influence of fresh water run-off (Uncles _et al._, 1985). In practical terms this means that the flood is often of shorter duration and therefore higher velocity than the ebb and leads to the situation where sediment erosion thresholds can be exceeded on the flood but not on the ebb resulting in net up-estuarine transport. Both these mechanisms are potentially particle selective, in terms of settling characteristics, and probably contribute to the unique combination of properties observed in the particle population that comprises the turbidity maximum (Schubel, 1969; Morris _et al._, 1982c; Loring _et al._, 1983; Bale _et al._, 1984).

1.2.5 Suspended particles in estuaries: chemical aspects

Stumm and Morgan (1981) have pointed out that the majority of natural chemical processes in aqueous media occur at phase discontinuities. It is not surprising, therefore, that suspended particles dominate the chemistry and hence distribution of many species in natural waters (Wangersky, 1986). In estuaries, the impact of heterogeneous chemical processes is greatly increased by the localised concentration of particles in the turbidity maximum (Section 1.2.4) and the tidally induced exchange of particles between the reducing

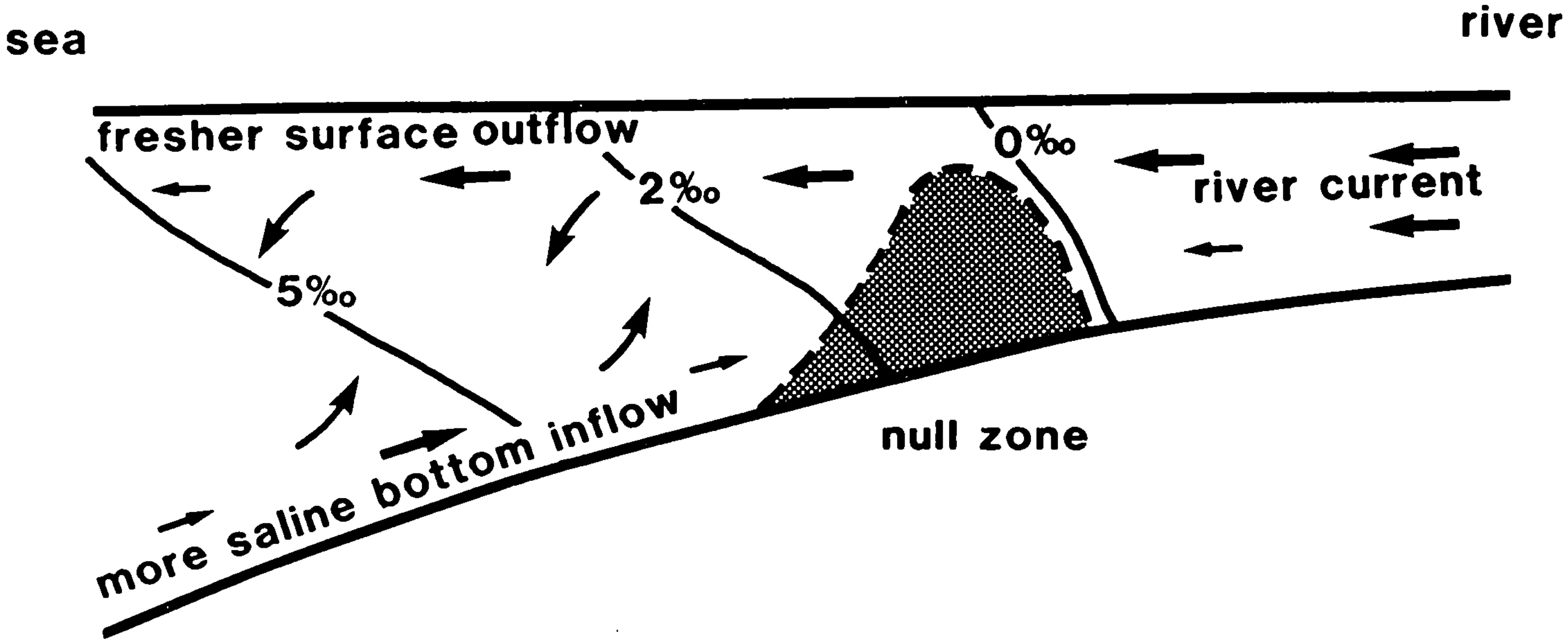


Figure 1.2 A schematic representation of non-tidal (residual) estuarine circulation and the location of the resulting turbidity maximum (stippled) at the null zone.

conditions within anoxic sediments and the generally oxic conditions in the suspended phase.

Estuarine particles can be assigned to one of three main categories, lithogenous, hydrogenous or biogenous depending on their origin (Mantoura and Morris, 1983). Lithogenous particles are the products of crustal weathering. Hydrogenous particles are formed within the estuary and result from precipitation processes. These can occur as discrete particles (Eisma *et al.*, 1980) or as coatings on existing particles. Examples of this type are hydrous metal oxides (Crossby *et al.*, 1983) and humic precipitates (Sholkovitz, 1976; Sholkovitz *et al.*, 1978). Biogenic particles are generated by biological activity and consist of living and dead organisms and their remains as well as faecal pellets and terrigenous plant debris.

Few studies of the bulk properties of estuarine particles exist to date. However, it is evident from available geochemical (Martin *et al.*, 1978; Duinker *et al.*, 1980; Eaton *et al.*, 1980) and mineralogical (Feuillet and Fleischer, 1980; Manickham *et al.*, 1985) data that physical processes, sedimentation and resuspension, are the primary factors controlling the distribution of particles from various sources within estuaries. However, localised variations in particle composition also result from selective particle retention at the turbidity maximum (Loring *et al.*, 1983; Wellershaus, 1981), from increased heterogeneous reactivity associated with the elevated turbidities at the turbidity maximum (Sundby and Loring, 1978; Gobeil *et al.*, 1981) and from hydrodynamically localised biological activity (Morris *et al.*, 1982c).

Particle sizes measured in estuaries range from the sub-micron, colloidal particles (Sigleo *et al.*, 1982), comprising mainly organic material, upwards. Schubel (1969) measured suspended particle sizes in the turbidity maximum of the Chesapeake Bay system using optical and sedimentation techniques and found particles that ranged from 0.1-60µm with typical mean sizes in the range of 1-2µm. Mean particle sizes in samples abstracted from the Tamar Estuary ranged from 20-80µm and minimised in the turbidity maximum (Bale *et al.*, 1984). However, these earlier results are possibly erroneous since it has been shown that sample handling and analysis can seriously disrupt fragile aggregates (Gibbs, 1981, 1982a, 1982b; Gibbs and Konwar, 1982, 1983). Recent observations in the Delaware Estuary (Gibbs *et al.*, 1983) indicate that the majority of particles exist as large (up to 300µm), fragile aggregates *in situ* and that primary particles are rare.

Surface area measurements of estuarine particles (Glegg *et al.*, 1986; Millward *et al.*, 1985) give values of 19-22$m^2 g^{-1}$ which are higher than for aluminosilicate minerals but much less than those of some metal oxyhydroxides which range from 100-240$m^2 g^{-1}$ (Crosby *et al.*, 1983). There is evidence that organic material associated with particle surfaces reduces or obscures some of the potential surface area (Millward *et al.*, 1985). Further evidence for the association of organic films with particle surfaces comes from electrophoretic mobility studies (Neihof and Loeb, 1972, 1974; Hunter and Liss, 1979) which suggest that adsorbed humic compounds dominate the surface charge characteristics of natural particles.

1.2.6 Heterogeneous trace metal reactivity in estuaries

Trace metal reactivity, in terms of the removal of soluble metal (Duinker and Nolting, 1976, 1977, 1978; Grieve and Fletcher, 1977), metal mobilisation (Thomas and Grill, 1977; Windom *et al.*, 1983) or both (Morris *et al.*, 1978; Ahlf, 1983; Ackroyd, 1983; Elbaz-Poulichet *et al.*, 1984), has been observed in numerous estuaries. However, the wide range of hydrodynamic, sedimentary, and environmental conditions involved have lead to conflicting interpretations of the relative importance of the processes affecting the distributions and transport of dissolved metals (Duinker, 1980). Nevertheless, in nearly all the studies where metal reactivity was observed it was concluded that sorption on to suspended and sedimentary particulate phases and co-precipitation with manganese and iron oxyhydroxides were the most likely causes of removal, while desorption from particles and diffusion or physical mixing of sediment pore water into overlying waters were the prime causes of metal mobilization (Hart, 1982). Indeed, numerous laboratory studies have demonstrated both reversible and irreversible uptake of metals by a range of natural and synthetic mineral substrates (Krauskopf, 1956; Kharkar *et al.*, 1968; Salomons, 1980; Millward and Moore, 1982; Davies-Colley *et al.*, 1984; Li *et al.*, 1984a). It has also been shown that humic materials associated with natural particles can strongly influence trace metal behaviour (Gardiner, 1973; Mantoura, 1976). However, it is only relatively recently that comprehensive sets of field data over wide ranging environmental conditions have provided conclusive, albeit circumstantial, evidence for localised heterogeneous reactivity in estuaries for Mn (Morris *et al.*, 1982a), Cu, Zn and Mn (Ackroyd, 1983; Ackroyd *et al.*, 1986) and Al (Morris *et al.*, 1986a).

As well as undergoing removal and remobilisation, it is clear that cycling of metals can occur in estuaries as a direct result of the hydrodynamic processes that give rise to the temporal and spatial variability in the concentration and composition of the suspended particle population (Morris et al., 1982b; Loring et al., 1983). Dissolved Mn (Morris et al, 1982a) and Pb (Elbaz-Poulichet et al., 1984), for example, have been shown to exhibit pronounced internal cycling in estuaries related to the physical cycling of particles. While it is appreciated that no two estuaries are identical, the physical-chemical processes that control heterogeneous chemical reactivity are universal. Clearly, a knowledge of the behaviour, transport and characteristics of the particle phases in an estuary is crucial to an overall understanding of trace metal distributions and transport.

1.3 THE TAMAR ESTUARY

1.3.1 The geography and physical hydrography

The Tamar Estuary is a drowned river valley or ria (Pritchard, 1967) in the south west peninsula of the United Kingdom (Plate 1.1). The Tamar River rises in North Cornwall and runs practically due south for a distance of 100km before flowing into Plymouth Sound on the south coast. For a large part of the distance the river forms the boundary between Devon and Cornwall. The Tamar is tidal for 32km up to Weir Head near Gunnislake at which point a weir has been constructed to maintain water depths in the river above. Two major tributaries, the Tavy and the Lynher, join the Tamar at 21.2 and 25.0km, respectively from the weir at Gunnislake (Figure 1.3). Uncles et al. (1983) have calculated that the Tavy contributes an input of about 30% of the Tamar flow and the Lynher about 20%. Typical monthly averaged river flow values for the Tamar at Gunnislake range from a maximum of $38m^3sec^{-1}$ in January to a minimum of $5m^3sec^{-1}$ during June although the

Plate 1.1 The topography of the Tamar Valley showing the locations of of the various landmarks mentioned in the text, reproduced with the permission of J. Bartholomew & Son Ltd.

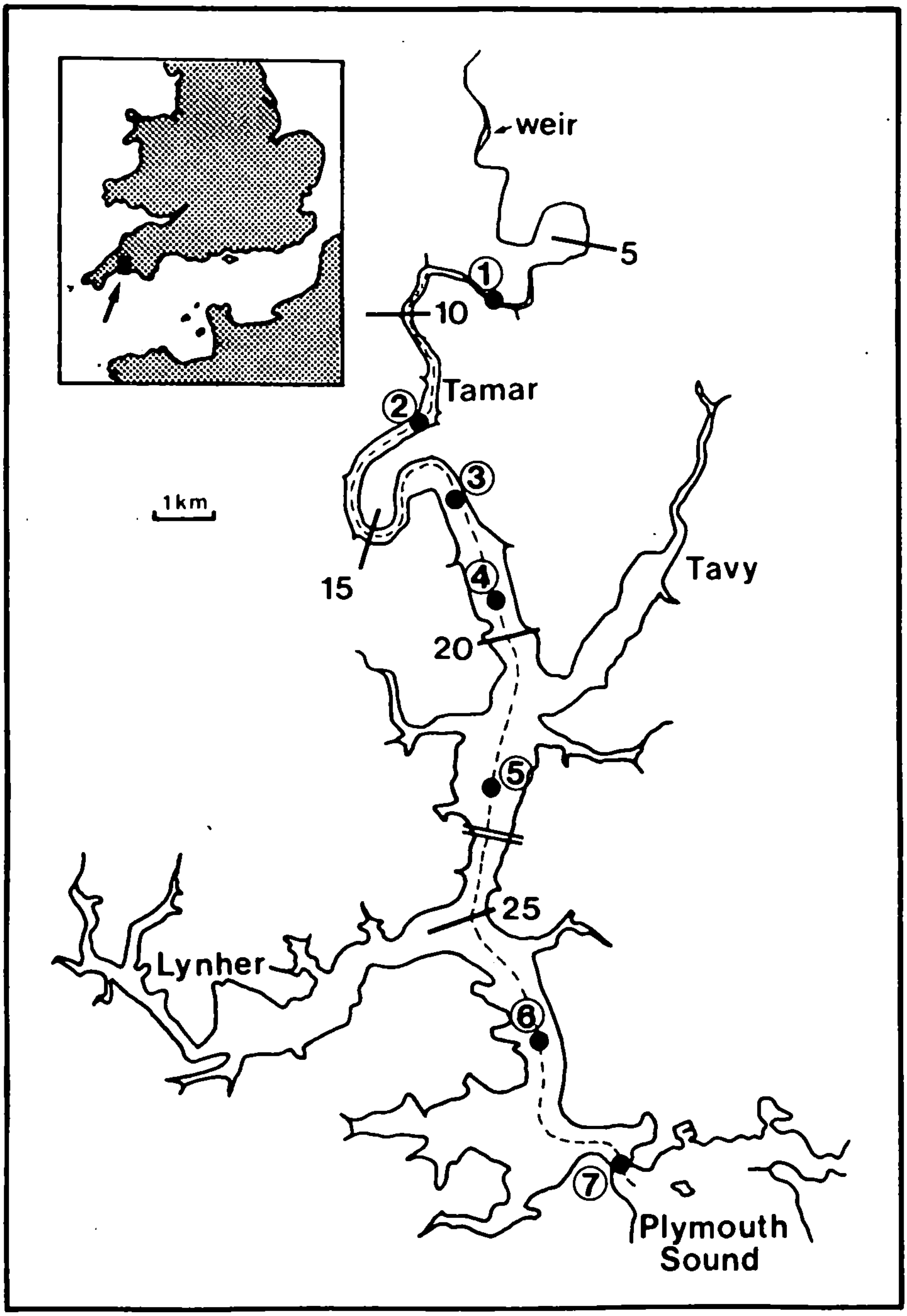


Figure 1.3 The Tamar Estuary system showing the major axis marked at 5 km intervals from Weir Head and the location of stations (1-7) occupied by Uncles et al (1985).

instananeous flows can exceed $100m^3sec^{-1}$ after periods of heavy local rainfall. The flushing time of the Tamar Estuary varies with riverflow (Figure 1.4) and is typically about one week for the whole estuary; for the low salinity region in summer (the upper 5km) it is less than one day.

Salinity distributions in the tidal estuary vary with the state of tide and with river run-off. Figure 1.5 shows examples of summer and winter salinity distributions under high and low water conditions. Devonport, at the mouth of the Tamar, is a 'Standard Port' for which accurate tidal information is available (Admiralty Tide Tables, Vol I). The mean tidal ranges at spring and neap tides are 4.7m and 2.2m, respectively. Although the tidal curve for Devonport is basically of a regular sinusoidal form, close examination shows that is not the case. In fact, frictional effects within the estuary lead to pronounced asymmetry in the tidal streams particularly in the upper estuary (George, 1975; Uncles _et_ _al_., 1985). This results in the flood tide being of shorter duration and consequently of greater velocity than the ebb (Figure 1.6). In the Hamoaze, off Devonport, where water depths are of the order 30m and frictional effects are minimal, the tidal streams run southerly (ebb) for seven hours and northerly (flood) for five hours (Admiralty Chart No. 1901).

Using Pritchard's (1955) classification, the Tamar generally falls between partly and well-mixed conditions and this is borne out by data of Uncles _et_ _al_. (1985) applied to Hansen and Rattray's (1966) stratification/circulation diagram (Figure 1.7) in which it can be seen that the majority of stations (identified in Figure 1.3) fall into the partly mixed category. Stations 1 and 3 in the upper estuary,

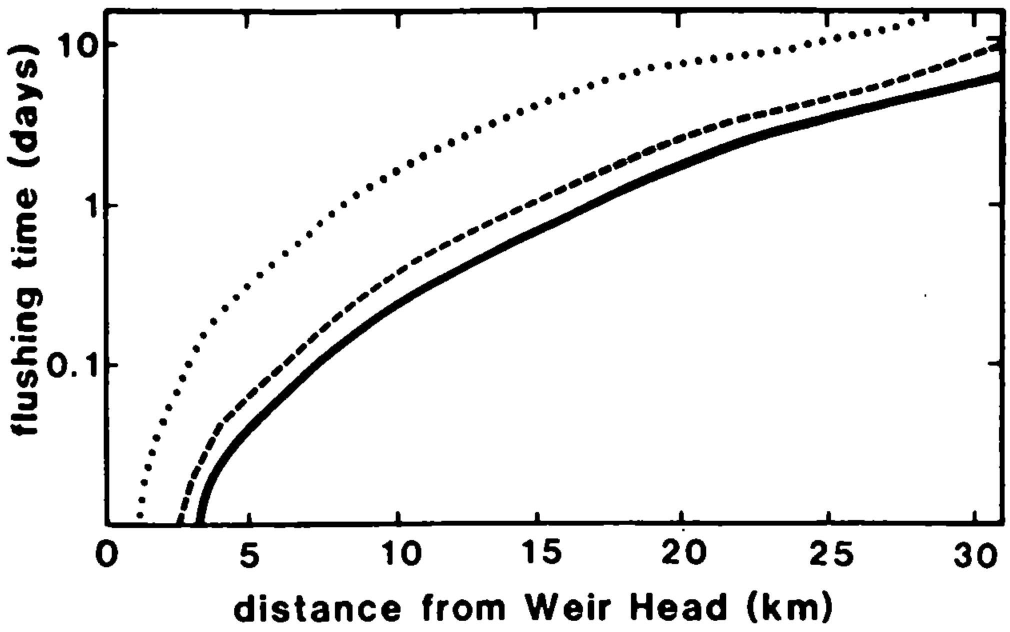


Figure 1.4 Flushing times for the Tamar Estuary under summer (•••••), mean (---) and winter (▬) river flow conditions (Uncles *et al*., 1983).

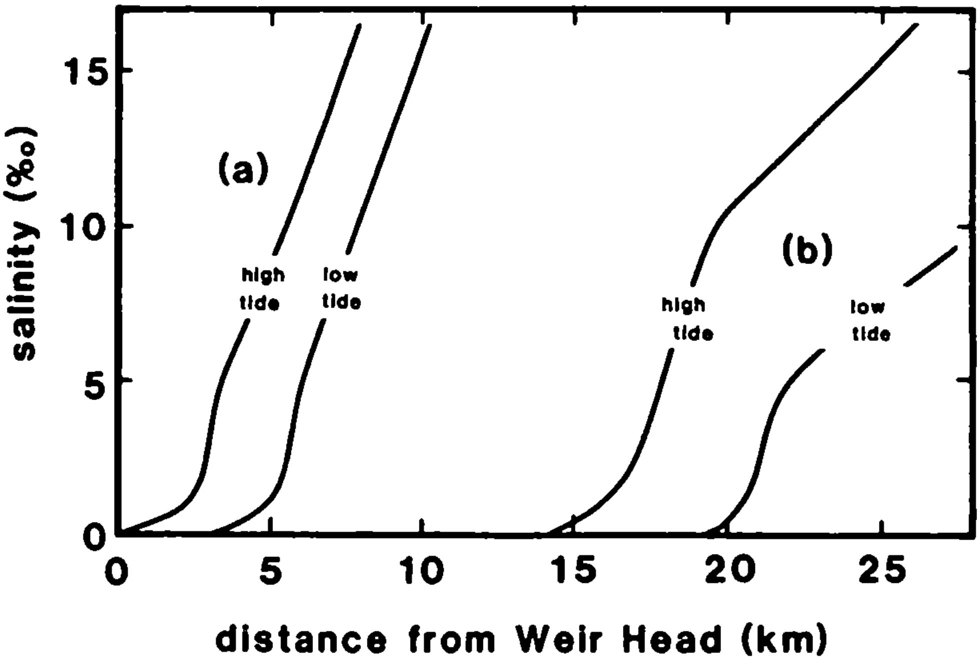


Figure 1.5 Salinity distributions measured in the Tamar Estuary at high and low tide under (a) low river flow, August 1976, and (b) high river flow, December 1976, conditions (redrawn from Morris *et al*., 1982b).

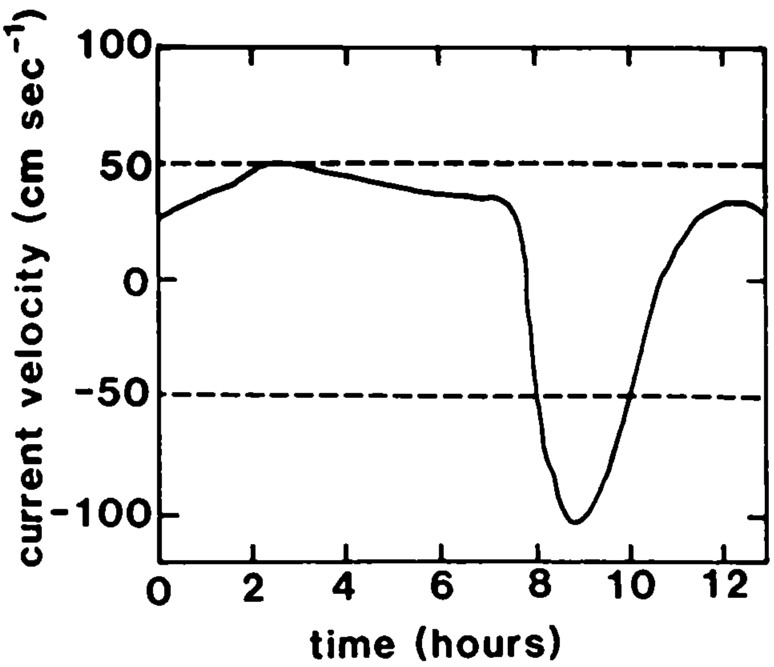


Figure 1.6 Current velocity measurements over a tidal cycle at station 1 in Figure 1.3, illustrating the marked asymmetry due to frictional effects. Critical erosion values (Odd and Owen, 1972) are shown as dashed lines.

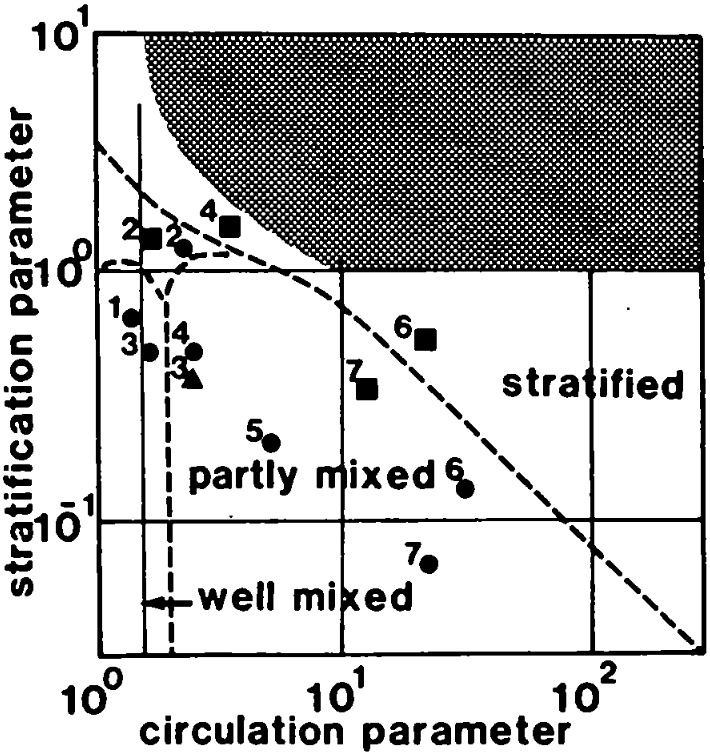


Figure 1.7 Uncles et al (1985) data applied to Hansen and Rattray's stratification/circulation diagram. Numbers refer to stations identified in Figure 1.3. Spring tides are shown (●), neap tides (■) and mid-tide as (▲).

especially under spring tide conditions, are classed as well-mixed and Station 2 is transitional between well mixed and partly mixed. Station 6, at neap tides, resembles fjord conditions due to the low current velocities and relatively great depth at that point.

1.3.2 Advantages of studying the Tamar Estuary

In general terms, the Tamar is typical of a large number of macro-tidal estuarine systems in temperate regions. Although small on a global scale, the tidal length of the Tamar is very close to the average length for estuaries of the United Kingdom (Gameson, 1973). In terms of water quality, the Tamar Estuary is relatively "clean", flowing mainly through agricultural land and suffering little industrial effluent. Anthropogenic pollutant inputs derived from nitrogenous fertilizer entering the river and the effect of sewage disposal, primarily at the mouth of the estuary, have been reported (Morris _et_ _al._, 1981). Dissolved metal pollution associated with the dockyard facilities at Devonport has been reported (Stebbing _et_ _al._, 1983) and some trace metal levels, especially copper, are higher than world average values in the riverine input (Ackroyd, 1983). This is attributed to the mineralised catchment (Dines, 1956) but is aggravated by run-off from large areas of mine spoil left over from the intensive metalliferous mining in the region during the mid to late 19th Century (Booker, 1967). This apart, the chemical and biological processes occurring in the Tamar are predominantly those of a natural rather than a polluted estuarine system.

The Tamar system is particularly suitable for the study of estuarine processes and has several strategic advantages. The estuary is easily navigable to the weir at Weir Head so that the entire salinity gradient can be traversed for sampling and measurements. Except under extremely high river flow, the low salinity region, which has been shown to be a particularly reactive zone (Morris _et_ _al_., 1978), is located within 20km of Weir Head and is therefore largely uninfluenced by the tributaries in the lower estuary. This, combined with a regular U-shaped channel (George, 1975), renders processes in the upper Tamar potentially easy to interpret and model. Lastly, the Tamar has been studied extensively over the past decade providing a substantial core of background information for new studies.

1.4 OBJECTIVES OF THIS STUDY

To carry out field and laboratory studies of estuarine particulate material, its composition, distribution, behaviour and reactivity, with a view to enhancing our understanding of the effects which the complex interactions between the physical behaviour and the heterogeneous chemistry of the particles have on the distribution of dissolved constituents in estuary waters.

In practical terms, the project divided easily into three primary areas of study: (1) a seasonal examination of suspended particle characteristics and their behaviour, (2) a study of the bed sediment distribution and properties and (3) an examination of the mechanisms and kinetics of trace metal uptake and release from particle surfaces. In this work, these three primary areas of study are reported separately. Only in the final sections, which cover the modelling of metal behaviour in estuaries and the major conclusions, are the interactions beween the three primary areas considered together. The individual components of this study are summarised below.

Particle characteristics and behaviour

1. A field study of the principal tidal and seasonal variations in the characteristics and distribution of suspended particles was undertaken. This has included particle size measurements using a novel laser optic system, surface charge measurements employing micro-electrophoresis and basic compositional and physical determinations including observations by scanning electron microscopy.

2. The development of a submersible version of the laser particle sizing apparatus has been undertaken to evaluate the effects of sampling on the integrity of particle aggregates.

Bed sediment characteristics

3. Surveys under high and low river flow conditions were carried out to determine the distributions and variations of silt, loss on ignition and water content in the bed sediment.

4. The seasonal migration of mobile bed sediment within the estuary was monitored over a period of 14 months using a series of wooden stakes driven into the intertidal mudbanks.

5. Estimates of the particle masses in the various reservoirs, their sources, sinks and the fluxes between them were derived from the physical extent of the measured distributions and the concentration and/or mass of particles within them.

Heterogeneous chemical reactivity

6. Analytical techniques that would allow the assay of trace metals at ambient concentrations in low volume estuarine water samples were evaluated for reaction studies.

7. Experiments using radio-tracers and natural water samples from the Tamar River mixed with suspended particles from the turbidity maximum region were undertaken to determine the equilibrium partition (K_d) values for a selection of trace metals under controlled conditions of salinity, temperature, pH and particle concentration.

The combination of particle behaviour and chemistry

8. Modelling techniques were employed to combine the information on the sorptive behaviour of trace metals with the current knowledge of particle dynamics and behaviour in order to develop the understanding of the transport and distribution of trace metals in estuaries.

SECTION TWO

SUSPENDED PARTICLE CHARACTERISTICS

2.1 INTRODUCTION

This section describes the field and laboratory studies that were undertaken to elucidate the temporal and spatial variability in the. concentration, behaviour and characteristics of suspended solids in the Tamar Estuary.

During this study, axial profiles of suspended solids concentrations were obtained over a seasonal cycle and under various tidal conditions and, at the same time, samples were taken for subsequent surface charge and particulate carbon analyses in the laboratory. Particle size measurements were initially undertaken on-board using a laser diffraction technique but were later carried out using a submersible version of the instrument, developed during this project. A number of samples were treated with glutaraldehyde for visual examination by scanning electron microscope (SEM) although a systematic optical study was not undertaken. Detailed descriptions of these determinations are given in the following sections.

2.2 FIELD MEASUREMENTS

2.2.1 Sampling procedures

Field measurements and sampling were undertaken from the IMER estuarine research craft "Tamaris", a 12m Rotork Seatruck fitted out as a floating laboratory. Measurements and samples were taken whilst underway at 3 to 4 knots. Water samples were obtained for analysis by a submersible pump arranged to draw from a fixed depth of 0.5m, and situated well forward of the various waste outlets. This supply fed a rapidly flushing flowcell in which various sensors were placed.

On each survey, the master variables (salinity, temperature, dissolved oxygen, pH, and chloride ion activity) were recorded continuously on a multi-channel chart recorder using the procedures developed by Morris *et al.*, (1981, 1982b). Position, relative to conspicuous landmarks along the estuary, and time were recorded simultaneously, thus fixing the survey data in a time-space framework. Descriptions of the methods used to determine each parameter are set out below.

Total suspended solids

Suspended solids were monitored using a Partech Instruments Ltd. suspended solids monitor. The meter response was checked regularly using formazin suspensions and calibrated by reference to discrete samples analysed gravimetrically.

Salinity and temperature

Salinity and temperature were measured using a portable thermosalinograph (Partech Instruments Ltd.). Calibration was effected by comparing discrete samples with IAPSO Standard Sea Water using an inductively coupled bench salinometer (Auto Lab Industries Ltd.). The temperature response was checked using a certified mercury thermometer.

Dissolved oxygen

Oxygen concentrations were determined using a Yellow Springs Instrument Co. Model 57 oxygen meter. This was calibrated against freshwater-saturated air according to the manufacturer's instructions. Field measurements were subsequently converted to saturation (%) relative to the equilibrium value at the appropriate temperature and salinity with the aid of tables published by UNESCO (1973).

pH

pH was measured using a conventional glass electrode with a double liquid junction reference electrode and a Corning model 113 mV/pH meter. Standard pH buffer solutions of pH 7.02 and 9.20 were prepared using NBS buffers.

Chloride ion

At low salinities ($<1^{0}/_{00}$), where conventional conductive or inductive instruments lose resolution, a Philips IS 550-Cl chloride electrode in conjunction with a double liquid junction reference electrode and a Corning model 109 mV/pH meter was used to measure chlorinity from which salinity measurements could be obtained. The electrode response was calibrated by comparison with salinity over the range $10^{0}/_{00}$ to $1^{0}/_{00}$ and an extrapolation of the plot of the logarithm of salinity against electrode response was used to determine salinity values below $1^{0}/_{00}$.

2.3 PARTICLE SIZE DETERMINATIONS

2.3.1 Introduction

Size is one of the prime physical characteristics determining the behaviour and reactivity of suspended particles in fluid media. In estuaries, particle size, density and concentration (Odd and Owen, 1972; McCave, 1979) determine the settling rate of suspended particles under quiescent conditions and, to an extent, size controls the threshold at which bed mobilisation occurs under increasingly energetic tidal conditions (Postma, 1967). Indirectly, particle size is also an important consideration in heterogeneous chemical reaction kinetics as the specific surface area of particles, and hence the number of reaction sites, increases with decreasing size.

2.3.2 Apparatus

Particle size distributions were measured using a Malvern Instruments Ltd. Model 2200 particle sizer. A review of the relative advantages and disadvantages of the methods and apparatus available for particle size analysis (Table 2.1) indicated that the laser diffraction technique would provide the most suitable method for this study considering the fragile nature of natural particles and the problems associated with the variable matrix in estuaries.

The main factors influencing our choice were the rapidity of measurement compared with, for instance, sedimentation techniques and the advantage of being able to deploy the laser instrument in the field thus minimising sample preservation and transportation problems. Another consideration was that, unlike the Coulter instrument, the Malvern system performs size analyses without the addition of an electrolyte. This is important in systems where ionic strength affects particle aggregation through changes in the inter-particle repulsion by the double layer (Shaw, 1966). The Malvern system also precludes calibrational variations with changes in the refractive index, density, temperature and ionic strength of the sample suspending medium. Laser diffraction itself is non destructive and therefore ideal for estuarine aggregates which Gibbs (1981, 1982a, 1982b) and Gibbs and Konwar (1982,1983) have shown to be highly susceptible to damage by pumping, Coulter analysis, light blocking analysis (Hiac), pipetting and sampling with Niskin water bottles. Although laser diffraction measurements are non destructive, sampling procedures obviously need careful evaluation. On the negative side, several

Table 2.1 A comparison of techniques available for particle size determination including their relative advantages and disadvantages for field measurements.

Method	Advantages	Disadvantages	Working range
Conventional sieve analysis	Relatively simple and inexpensive apparatus	very time consuming; not suitable for fragile materials	mm down to 62.5μm; (Frisch micro-sieves 50-5.0μm)
Sedimentation (pipette)	widely used in industry; standard method	not suitable for field application; very slow	0.1-100μm
Electronic counters (Coulter)	rapid; semi-automatic	requires addition of an electrolyte; may damage fragile aggregates	0.6-216μm over nine orifice sizes
Optical microscopy	nature of particles can be evaluated	requires large number of particle counts for valid statistics	down to 0.5μm, limited by optical resolution
Electron microscopy	good sample identification	time consuming; qualitative rather than quantitative	down to 10^{-1}nm
Light blocking sensors (Hiac)	rapid; automated; unaffected by suspending matrix	potential disruption to fragile particles by small bore flowcell	1.0-600μm (six sensor size ranges)
Laser diffraction (Malvern)	rapid; automated; potentially non destructive; unaffected by suspending matrix	minimum particle size limited by wavelength of laser light; accuracy near lower size limit reduced by presence of colloids	1.2-1800μm (six lens choices)

authors have expressed doubts over the absolute accuracy of the laser diffraction technique compared with sedimentation or Coulter analysis (Coulter Electronics Ltd, 1985; McCave, 1986). Essentially, they claim that the presence of relatively small (sub-micron) particles in the samples introduce errors in the mathematical transformation of the diffraction pattern into size spectra, particularly in the region of 4-5µm particle sizes. Nevertheless, we concluded that for the fragile, amorphous, non-spherical particles that typify estuarine suspended material, laser diffraction offered the only practical method of undertaking a large scale systematic study of the particle size characteristics.

The Malvern particle sizing apparatus, shown schematically in Figure 2.1, employs a low power He-Ne laser to provide a parallel beam of coherent, monochromatic light. Near-forward, Fraunhofer diffraction of the beam by particles randomly distributed in its path is detected on an array of 30, semi-annular concentric photodiodes mounted normal to and concentric about the beam. A microcomputer repeatedly scans the detector array and continuously updates the average light intensity falling on each ring through the chosen measurement period. The computer then uses an heuristic approach to determine the particle size distribution that corresponds to the measured diffraction pattern. That is, an initial estimate of the size distribution is made from the relative strengths of the primary diffraction modes and the diffraction pattern of this distribution is generated from Fraunhofer diffraction theory. By comparing the computed with the observed diffraction pattern, the estimated size distribution is refined until the least-squares correlation coefficient between the observed and estimated patterns is minimised.

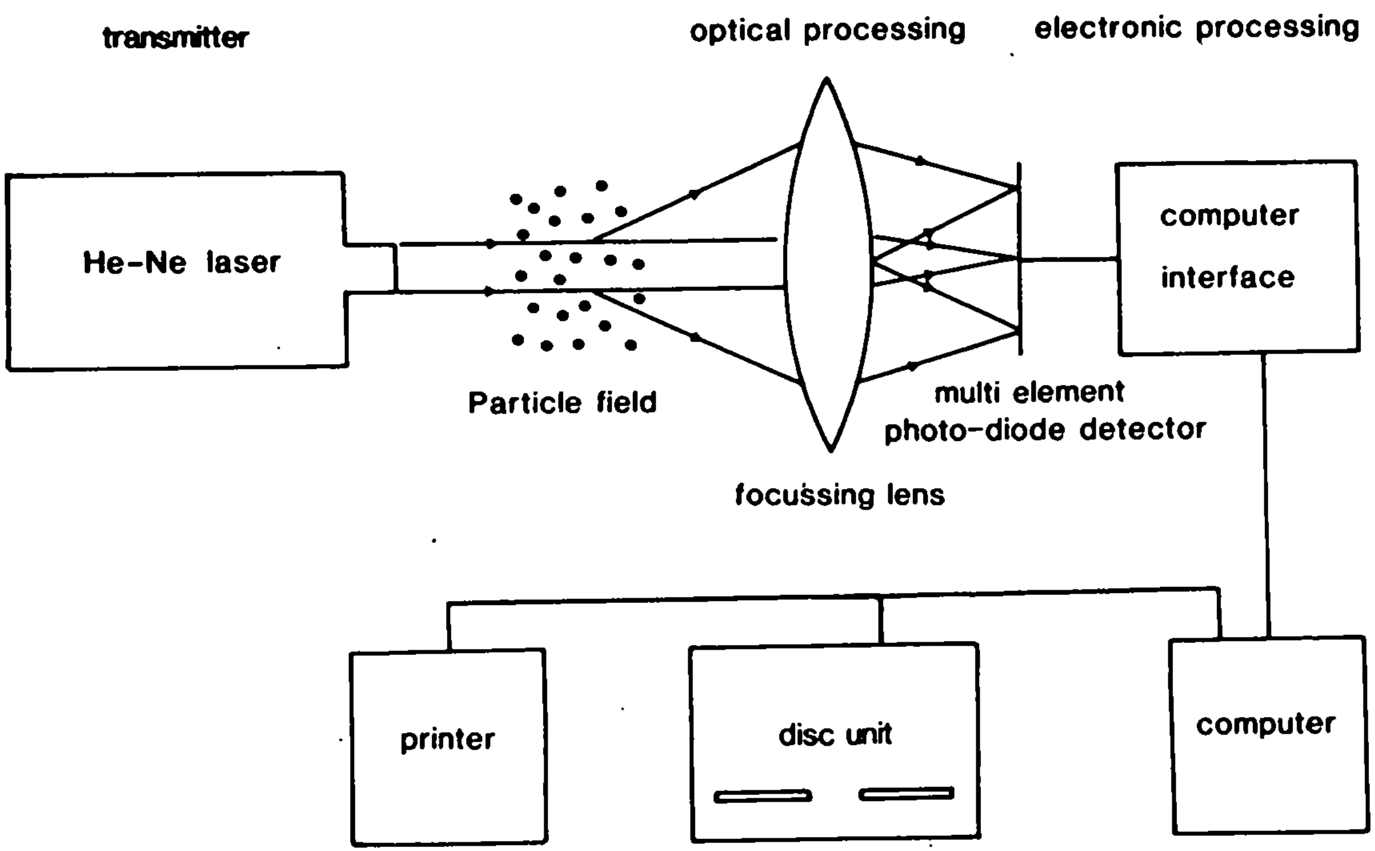


Figure 2.1 A schematic representation of the optical and computational components of Malvern Instruments' laser diffraction particle sizing apparatus.

2.3.3 Procedure for field measurements

Field measurements were undertaken using the technique described by Bale *et al.* (1984) in which the Malvern particle sizer was deployed with a 12mm path length flow cell connected by 6mm bore tubing to a separate intake mounted slightly ahead of the main sampling pump inlet (Section 2.1). In order to minimise the physical disruption of aggregates (Gibbs, 1981; Bale *et al.*, 1984), the samples were drawn through the flow cell under low vacuum (12.5mm Hg) and were collected in a large receiver. This gave a flow of 200mℓ min^{-1} which was equivalent to a flushing time for the supply line of less than 1.2 minutes. Tests had indicated that raising the flow rate by increasing the vacuum resulted, through degassing, in the formation of bubbles which were recorded as particles. The size distribution of test samples also indicated that disaggregation of particles increased significantly above this flow rate. On humid days and when sample temperatures were low, the flow cell windows required demisting to prevent them from becoming obscured; this was achieved with a domestic hair dryer.

At the start of each survey, the alignment of the detector and lenses were optimised and a background signal obtained for water from the estuary that had been filtered through a 0.45μm pore-sized membrane filter. The background signal, due mainly to optical defects, was recorded and automatically subtracted from subsequent measurements. Although laser diffraction provides an absolute size determination requiring no calibration, a suspension of commercially available latex or glass micro-spheres was measured during the course of each survey to check instrument efficiency. Diffraction measurements could be taken at the rate of one per minute, but the subsequent calculation stage took up to twelve or fifteen minutes per sample. During field work the 'raw' diffraction data was therefore stored on magnetic discs and the corresponding size distributions calculated at a more convenient time, usually overnight, thus allowing a much faster sampling rate. Underway, measurements were taken every 3-4 minutes and the corresponding station positions were logged together with the ancillary environmental data. Particles in the size range 1.9-188.0µm diameter were monitored.

2.3.4 Results: suspended solids and particle size

Axial distributions of mean particle size, derived through statisical fitting of the particle size spectra to unimodal, asymmetric log normal and/or Rosin Rammler models (Bale et al., 1985) showed consistent patterns throughout the twelve month survey period (Figure 2.2). Mean particle size at slack water generally decreased slowly from 40-60µm (equivalent spherical diameter) in the outer estuary to 20-40µm at 5-10°/$_{00}$ salinity. Within well defined turbidity maxima, the mean sizes often fell more sharply, reaching values of 6-12µm coincident with the core of the turbidity maximum. Mean sizes in the fresh water were generally much higher and variable but the errors were larger because of the typically low particle concentrations there.

Data from the April survey (Figure 2.3) indicate that the size minimum is a persistent feature of the turbidity maximum. Suspended solids concentrations in the turbidity maximum on that day increased from 50mg ℓ^{-1} one hour after low water to 200mg ℓ^{-1} at mid-flood tide, after which concentrations reduced with the decreasing tidal energy towards the high water slack tide. The corresponding mean particle

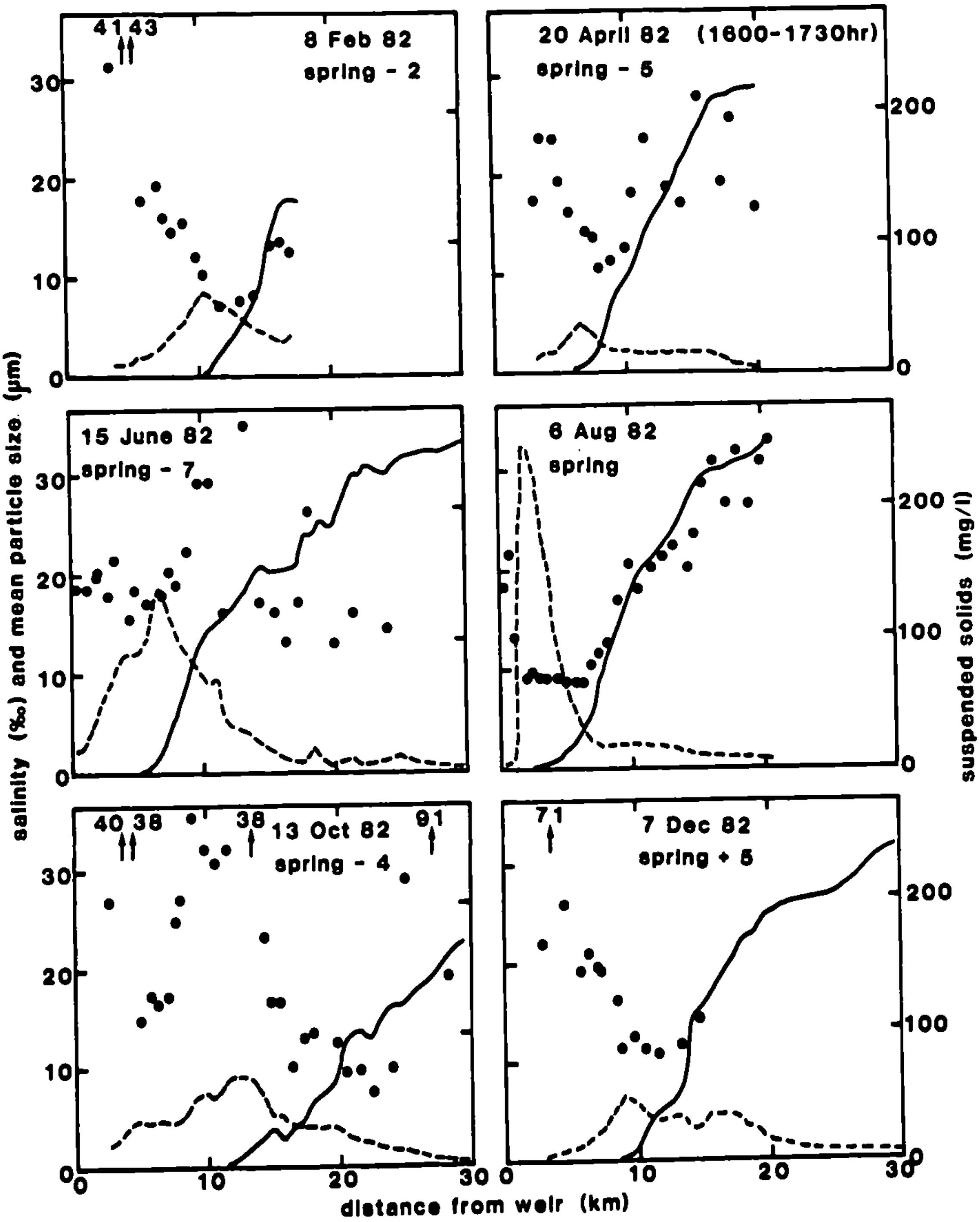


Figure 2.2 Axial profiles of mean particle size (●) in the Tamar Estuary. Salinity is shown as a solid line and suspended solids as a broken line. The timing of each survey in relation to the spring/neap cycle is shown as spring + or - the number of days.

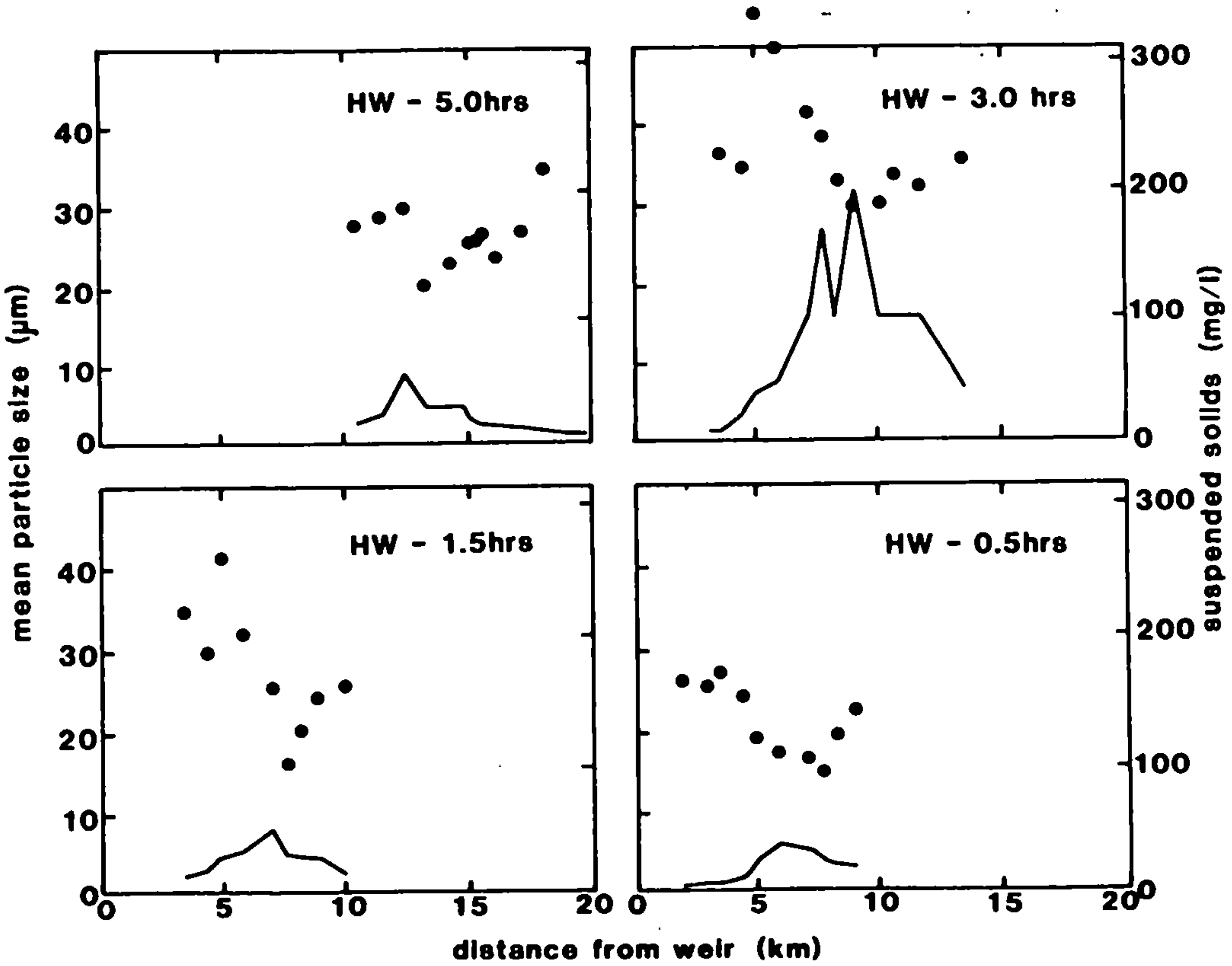


Figure 2.3 Successive profiles of mean particle size (●) and suspended solids (solid line) measured over a flood tide period in the Tamar Estuary on 20.4.82.

size increased from 20µm one hour after low water to 30µm at mid-flood tide. From mid-tide the mean size decreased, reaching a minimum of 15µm over high water slack tide. Throughout this period of substantial sediment mobilisation and a tidal excursion of some 6km, a minimum in particle size persisted within the turbidity maximum.

Over a spring-neap cycle (July 27-Aug 9) rainfall, and hence river flow, was uniformly low (Figure 2.4) and the turbidity maximum was located only 1-2km from the weir at Weir Head (Figure 2.5). The concentration of suspended solids in the turbidity maximum at slack water high tide varied 5-fold with tidal range from a minimum of 100mg ℓ^{-1} at neaps (2.2m range) on the 31st July to a maximum of 500mg ℓ^{-1} at spring tide (4.1m) on the 9th August. Throughout this period and irrespective of the concentration of suspended solids, the mean particle size within the turbidity maximum consistently fell within the range 6-8µm.

Throughout the year in which measurements were taken the axial distributions of mean size followed similar trends to those described above. However, the seasonal variation in the location and magnitude of the turbidity maximum exhibited a pronounced internal migration. This is illustrated by the profiles in Figure 2.6 which are for neap high water slack tides (for which the greatest number of profiles were recorded). During winter high run-off periods, the fresh/brackish water interface and turbidity maximum were located 12-15km from the weir and the turbidity maxima were small and diffuse. During the summer, under similar tidal conditions but much lower run-off, the peak of the turbidity maximum migrated upstream with salinity and became much more pronounced and well defined. Size minima coincident with the

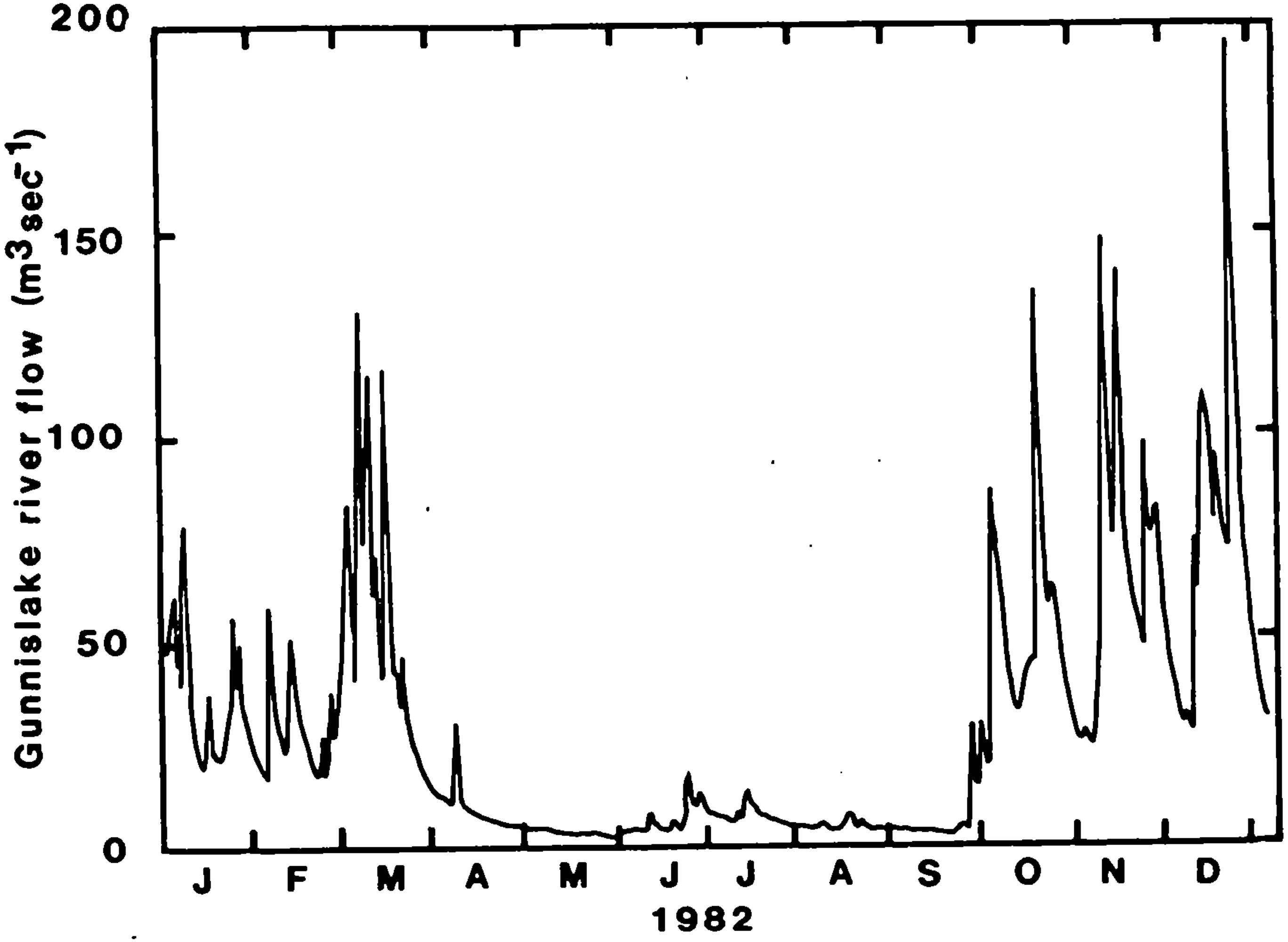


Figure 2.4 Daily river flow for the Tamar at Gunnislake. Values from May onwards were derived, through regressional analysis, from the flow at Pillaton Mill on the Lynher. Data courtesy of the South West Water Authority.

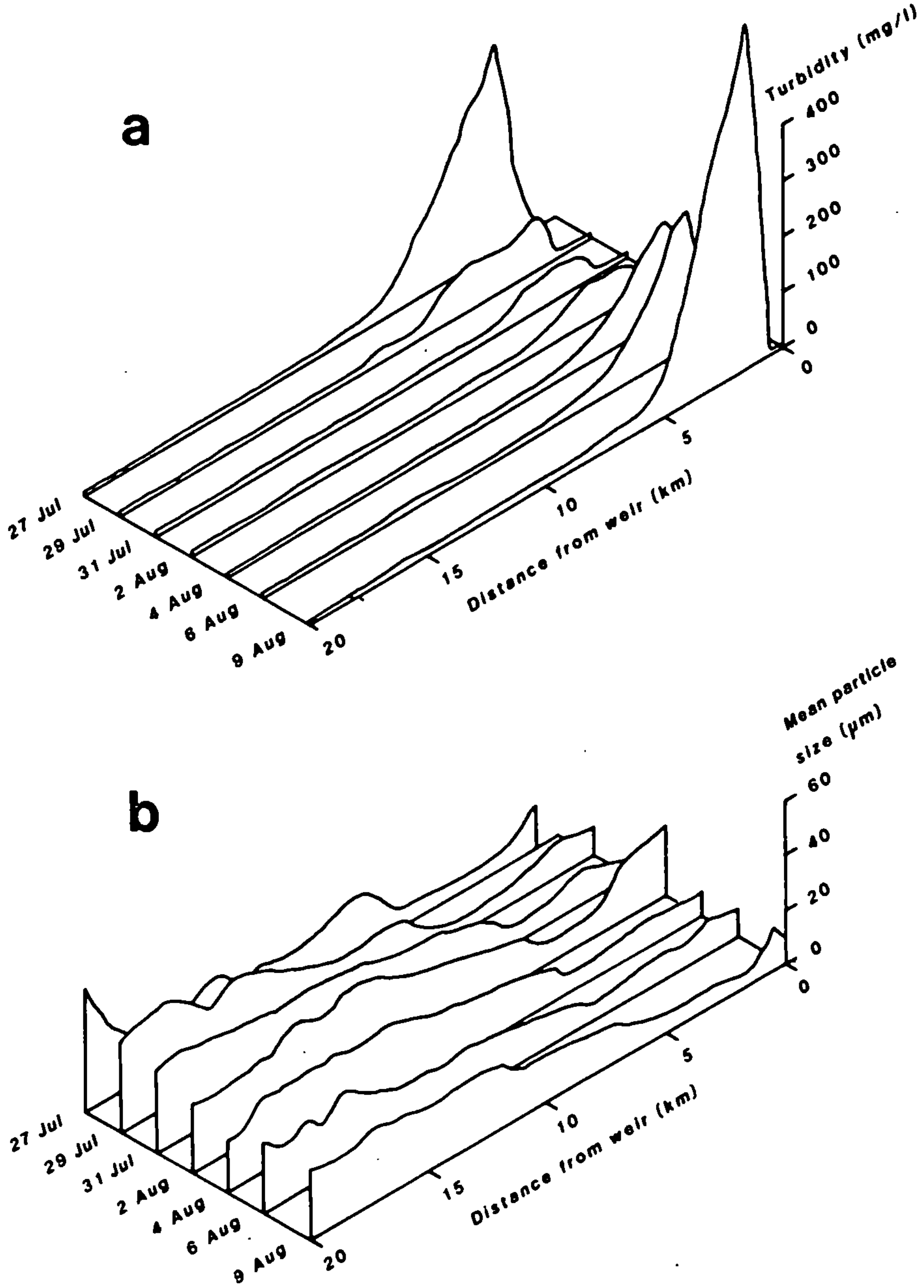


Figure 2.5 Profiles of (a) suspended solids and (b) mean particle size measured at two day intervals over a spring-neap tidal cycle.

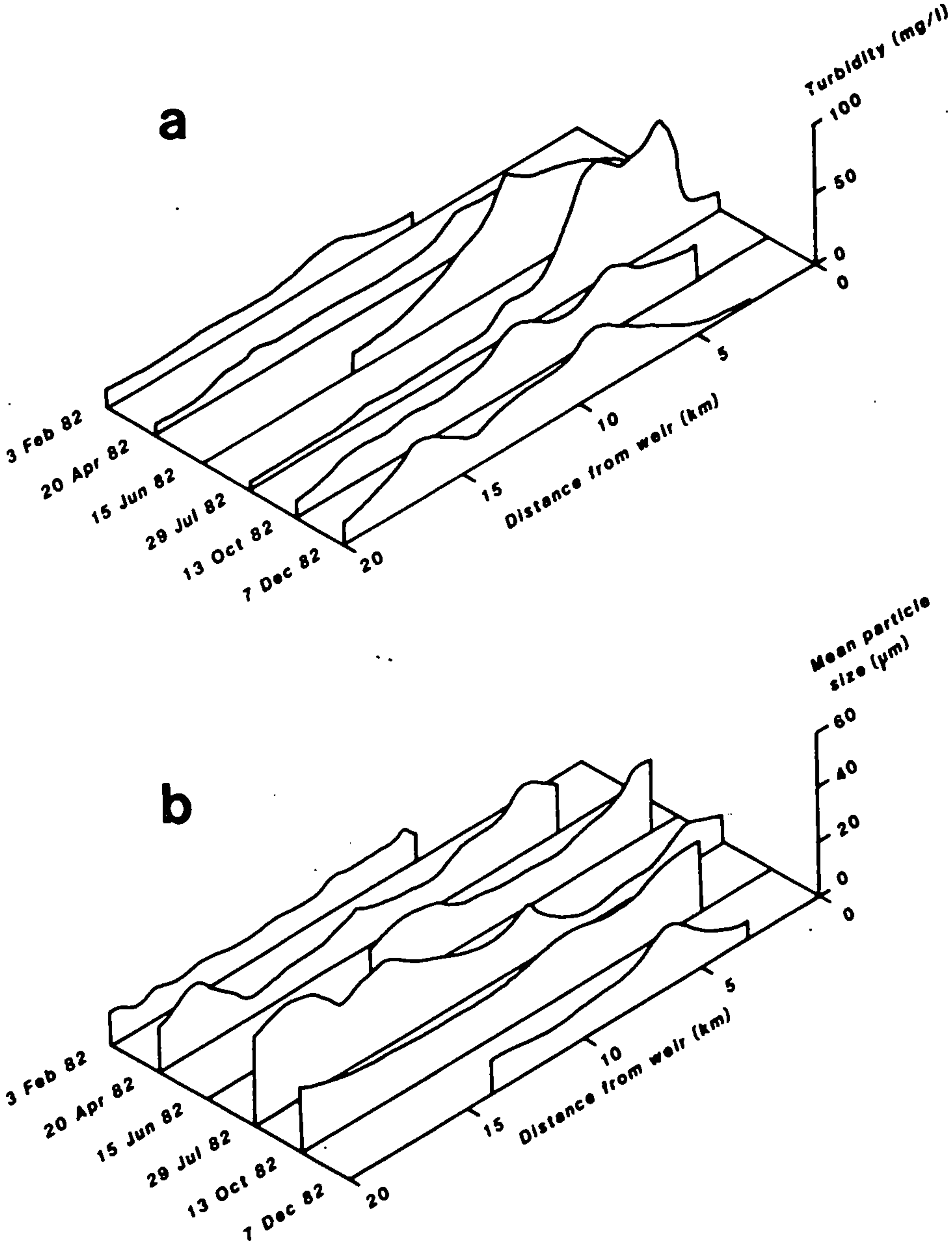


Figure 2.6 High water slack-tide profiles of (a) suspended solids and (b) mean particle size measured at intervals throughout a year.

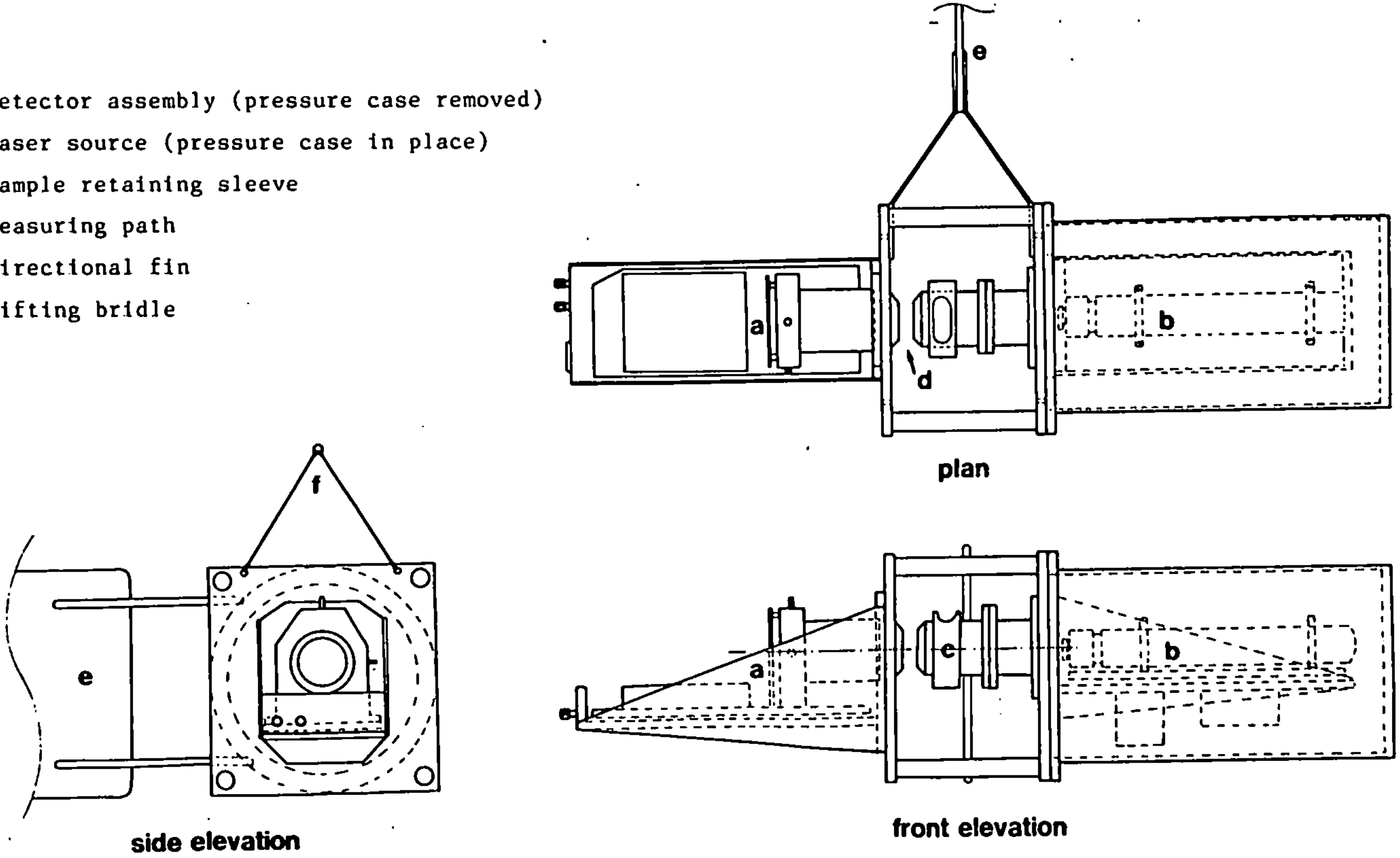
turbidity maximum were generally much less distinct during the winter (high run-off) months than in the summer (low run-off) months.

2.3.5 Development of an in situ particle sizing instrument

Practical experience with the Malvern Instruments particle sizer and observations by other workers (Trent *et al*., 1978; Gibbs, 1981; Gibbs and Konwar, 1982; Honjo *et al*., 1984) suggested that the collection of discrete samples, whether by pumping or by using sample bottles, almost certainly caused disruption of fragile aggregates and therefore size distribution measurements would be biased towards smaller particles. It was reasoned that a well designed submersible apparatus would avoid the disruption to fragile aggregates caused by sampling. The sedimentation of larger particles in discrete samples would also be avoided. A project was therefore initiated to develop a submersible version of the Malvern Instruments apparatus.

This was achieved by constructing two cylindrical pressure vessels which contained the laser source and detector assembly, respectively. The two containers were held apart with rigid steel bars as shown in Figure 2.7 and arranged such that the collimated laser beam emerged via an optical window in the cylinder end-plate to illuminate the particles in the space between the cylinders. The diffraction pattern generated by these particles was detected, via a second window, on the photo-diode array in the opposite cylinder. Care was taken to minimise the disturbance to suspended particles in the vicinity of the optical windows by streamlining all the components and ensuring, through the use of a directional fin, that the windows remained parallel to the direction of any current flow. Command signals and analytical information were transmitted via multi-core cable between the

a detector assembly (pressure case removed)
b laser source (pressure case in place)
c sample retaining sleeve
d measuring path
e directional fin
f lifting bridle



plan

side elevation

front elevation

Figure 2.7 Plan and elevation of the prototype submersible particle sizing apparatus showing the arrangement of the main components.

submersible unit and the microcomputer used for data processing and storage on the ship. A fuller technical specification and a description of the arrangement of this apparatus are contained in Appendix 3 (published work).

2.3.6 In-situ size measurements compared with discrete samples

A limited number of *in-situ* measurements obtained during trials of the submersible instrument are available to date. An example comparing size distributions measured using the submersible instrument with measurements undertaken on discrete samples drawn from the same depth is shown in Figure 2.8. At each station the bulk of the particles (expressed as percent by weight) measured *in-situ* were recorded in the three largest size bands covering the range 37.6-188µm. The truncation of the size distributions indicated the presence of even larger particles. In contrast, the size measurements undertaken on discrete samples showed consistently broader distributions with more of the sample weight located in the smaller size bands. Median sizes ranged from 60µm in the marine sample to 16µm at $14^{\circ}/_{00}$. These values are broadly consistent with the measurements of discrete samples obtained previously with this instrument (Section 2.3.4).

Clearly, the methods used to collect discrete samples for size analysis in this work and, presumably in other studies, physically reduced loosely aggregated particles to smaller components. This implied that the data reported earlier (Section 2.3.4) significantly underestimated the size of suspended particles throughout most of the estuary. The data obtained by discrete sampling in the turbidity maximum, however, may be acceptable since the *in situ* instrument also measured smaller particles in that region.

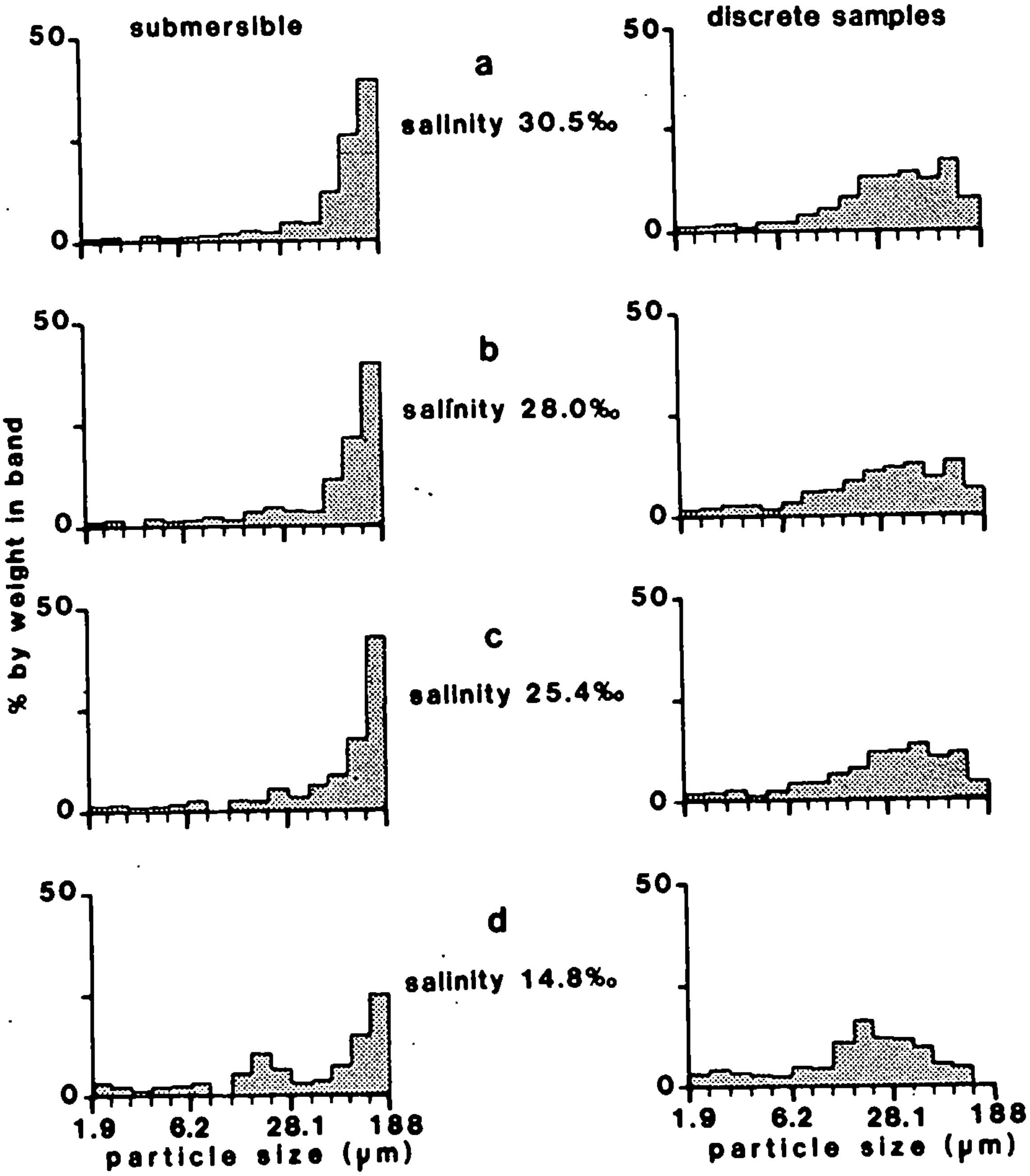


Figure 2.8 Comparisons of particle size distributions in the Tamar Estuary obtained using the submersible instrument with distributions obtained for discrete samples taken from the same depth by pumping.

2.3.7 Discussion: particle size minima in the turbidity maximum

What are the processes that can give rise to a predominance of small particles at the core of the turbidity maximum? This data would suggest that the process of tidal pumping which generates the turbidity maximum must be particle selective and effectively acummulates a narrow range of particles which are small/light enough to be mobilised by tidal currents but which are sufficiently heavy to experience some retention due to sedimentation at slack water and which, in addition, are less readily mobilised on the ebb than on the flood due to the ebb/flood current asymmetry. This would be consistent with the observations undertaken during periods of active sediment mobilisation (as on April 20th, Figure 2.3) where, although the mean size increased slightly over the slack water situation, the structure of the size minimum was retained. This would not be the case if considerably larger particles were being mobilised even considering the dilution effect of the existing suspended particles. Another factor can be added to these selective processes; Odd and Owen (1972) observed that sedimentation rates were directly proportional to the concentration of suspended particles due to the flocculation that results from a higher incidence of collision. Thus, in the turbidity maximum, small particles which were mobilised during the flood tide may be sedimented more rapidly than Stoke's settling would predict and therefore more effectively retained within the region. Since the presence of flocs was not detected at the turbidity maximum it must be assumed they were too fragile to be measured even with in-situ techniques. The relationship between settling rates and particle sizes required to account for the retention of particles within this particular hydrodynamic region are examined later in this Section.

2.4 SURFACE CHARGE

2.4.1 Introduction

Many aspects of suspended particle behaviour and chemistry are dominated by electrostatic attractive or repulsive forces occurring between individual particles of colloidal dimensions or between suspended particles and colloidal materials such as organic macromolecules (Van Olphen, 1963; Shaw, 1966). Colloidal flocculation, for example, has been invoked to explain iron removal in estuaries (Figueres et al., 1978; Murray and Gill, 1978; Moore et al., 1979) and the co-removal of humic compounds and trace metals (Sholkovitz, 1976; 1978; Sholkovitz and Copeland, 1980). Similarly, the association of organic molecules with particle surfaces in natural waters (Neihof and Loeb, 1972, 1974; Readman et al., 1982; Davis, 1982) is also a charge dominated processes. Determination of the surface charge of natural particles should, therefore, prove valuable in the prediction and interpretation of heterogeneous estuarine processes.

2.4.2 Apparatus and methods

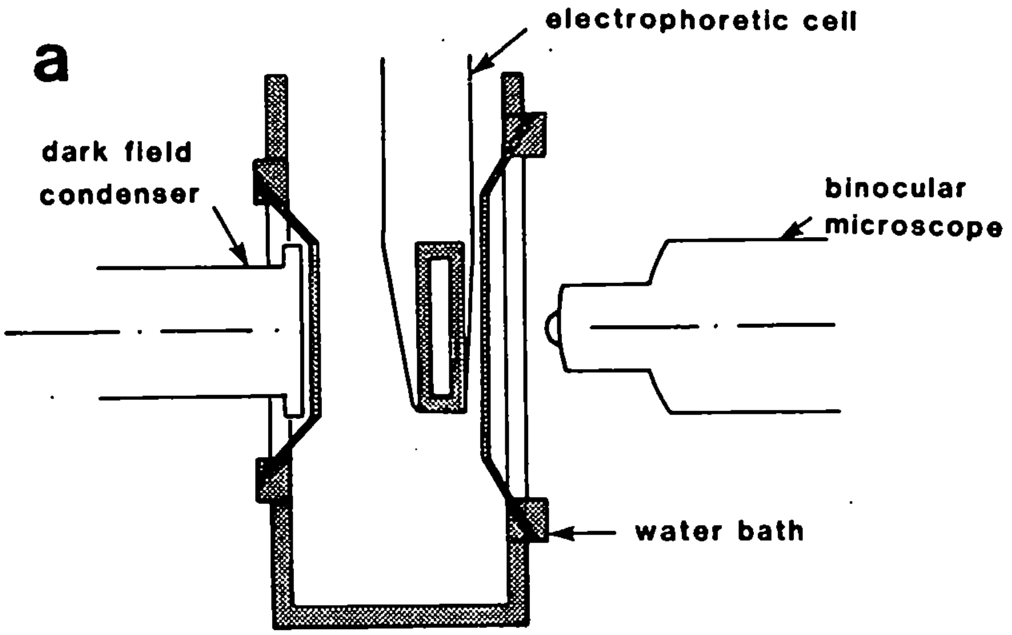
Determinations of surface charge were carried out on discrete samples collected during the routine surveys (Appendix 1) using a Rank Mk II micro-electrophoresis apparatus. The method and procedures described by Hunter and Liss (1982) were used. The electrophoretic apparatus consisted of a rectangular section (0.4mm by 4.0mm) quartz viewing cell rigidly supported in a thermostatted water bath set at 25°C. Particles within the cell were viewed using a binocular microscope (magnification 200x) which was focussed through an optical window in the side of the water bath (Figure 2.9a). Dark field illumination was employed. An accurately measured D.C. voltage applied between reversible Ag/AgCl electrodes located in chambers at each end of the cell resulted in the migration of individual particles which were measured using a calibrated eye-piece graticule and an electronic timer. The potential required to provide suitable migration rates depended on the conductivity of the suspending medium but fell in the range 20-100V for estuarine samples.

Electrophoretic measurements are complicated by electro-osmosis, in which electrolyte within the cell migrates relative to the cell faces in an applied field. In the rectangular cell, electrolyte transport adjacent to the front and rear walls of the cell is balanced by a counter-flow along the central axis of the cell (Figure 2.9b). To obtain reproducible electrophoretic mobilities, particles must be viewed at the, so-called, stationary levels that occur at the boundaries between the contra-flowing bands of electrolyte. The positions of the stationary levels can be determined experimentally or by calculation (Bangham *et al.*, 1958) using the formula:

$$s/d = 0.500 - [\ 0.0833 + 32d/\ h\pi^5\ ]$$

where s is the depth of the stationary level, d is the depth and h the height of the rectangular cell. Both methods were used in this study and gave equivalent results (Figure 2.10).

Samples were collected in one litre glass bottles which had been rigorously cleaned with chromic acid and rinsed with deionized water and were stored prior to analysis in the dark at 4°C to minimize biological activity. A sub-sample of particles concentrated by sedimentation within the sample bottle during storage was withdrawn



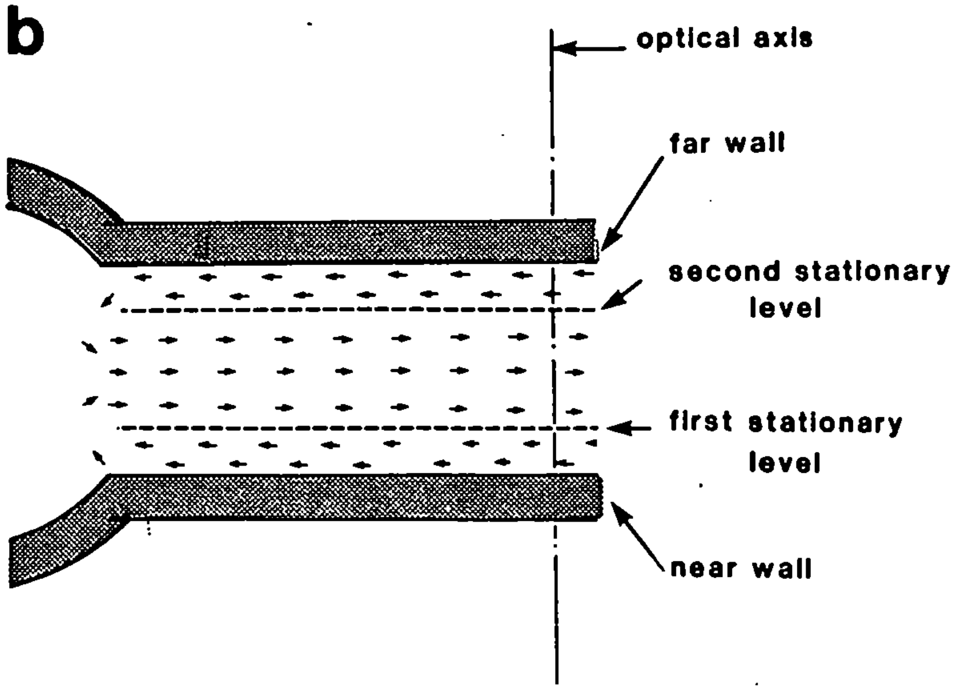


Figure 2.9a A cross-section through the Rank Mk II rectangular section electrophoresis cell.

Figure 2.9b A plan view of the rectangular cell showing the contra flowing bands of electrolyte that result from electro-osmosis and the positions of the 'stationary levels' that occur at the boundaries between them.

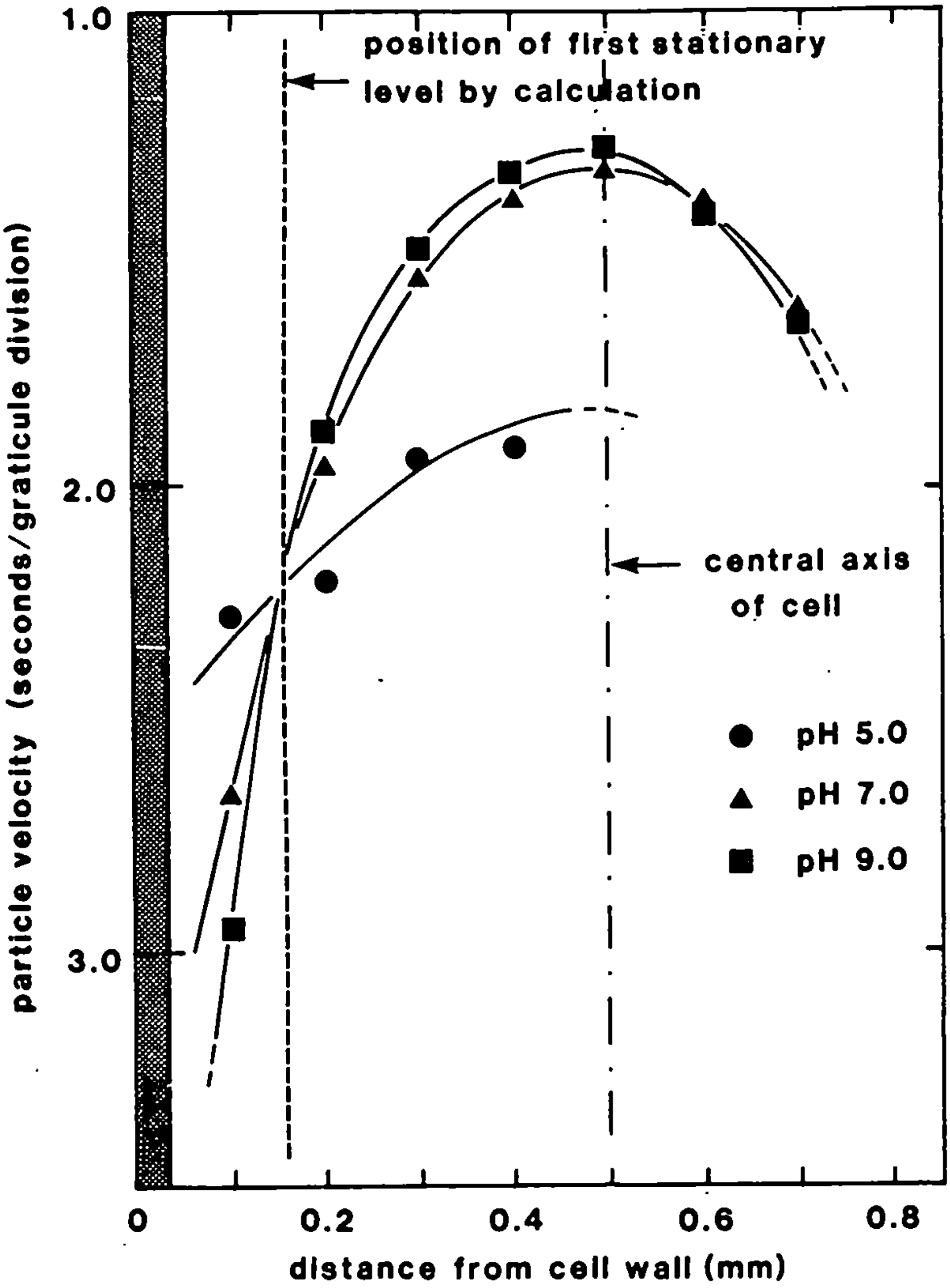


Figure 2.10 Experimental confirmation of the position of the forward stationary level in a cylindrical cell obtained by measuring the electrophoretic mobility of human blood cells at three pH values. The calculated position of the stationary level has been superimposed and the front wall of the cell is shown stippled.

using a glass pipette and redispersed in sufficient of the sample liquid to provide a suitable density for observation. The suspension was brought to thermal equilibrium with the viewing cell in a separate water bath and then briefly ultrasonicated (2-3 seconds) to dissociate flocs prior to rinsing and filling the viewing cell. For each sample, measurements were obtained for 10 particles at both stationary levels under both positive and negative fields and the results averaged. Electrophoretic mobility U_E, was calculated using:

$$U_E = \nu/\varepsilon$$

where ν is the migration rate in m sec^{-1} and ε is the field strength in V m^{-1}.

2.4.3 Results

Analysis of up to 10 replicate samples were carried out on several occasions and the standard errors, which included variation due to sampling and analytical precision, were calculated; these values were plotted as error bars where appropriate. Two sets of 10 replicate samples collected in December were analysed over a 10 day period. The results (Figure 2.11) showed that no significant change in electrophoretic mobility occurred with storage over periods of at least 1 week.

Thirteen axial profiles of the electrophoretic mobility of suspended particles in the Tamar estuary were obtained from six surveys during 1982 (Appendix 1). The salinity relationships for the six surveys are depicted in Figure 2.12. The major features in the distribution of electrophoretic mobility relative to salinity were very similar throughout the year. Fresh water values apparently

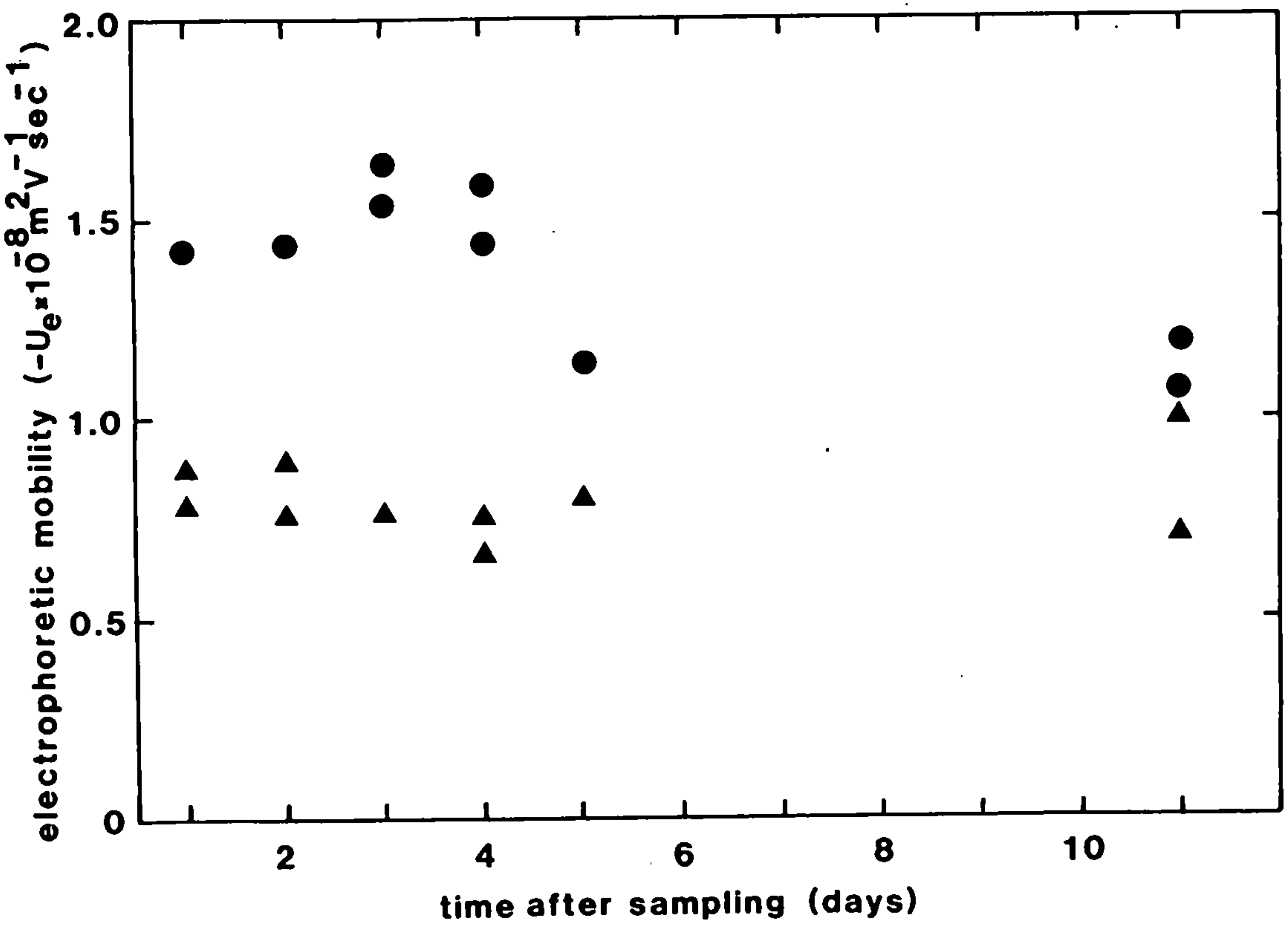


Figure 2.11 The variation in electrophoretic mobility with time for two sets of replicate samples analysed after increasing time intervals to examine the effect of sample storage.

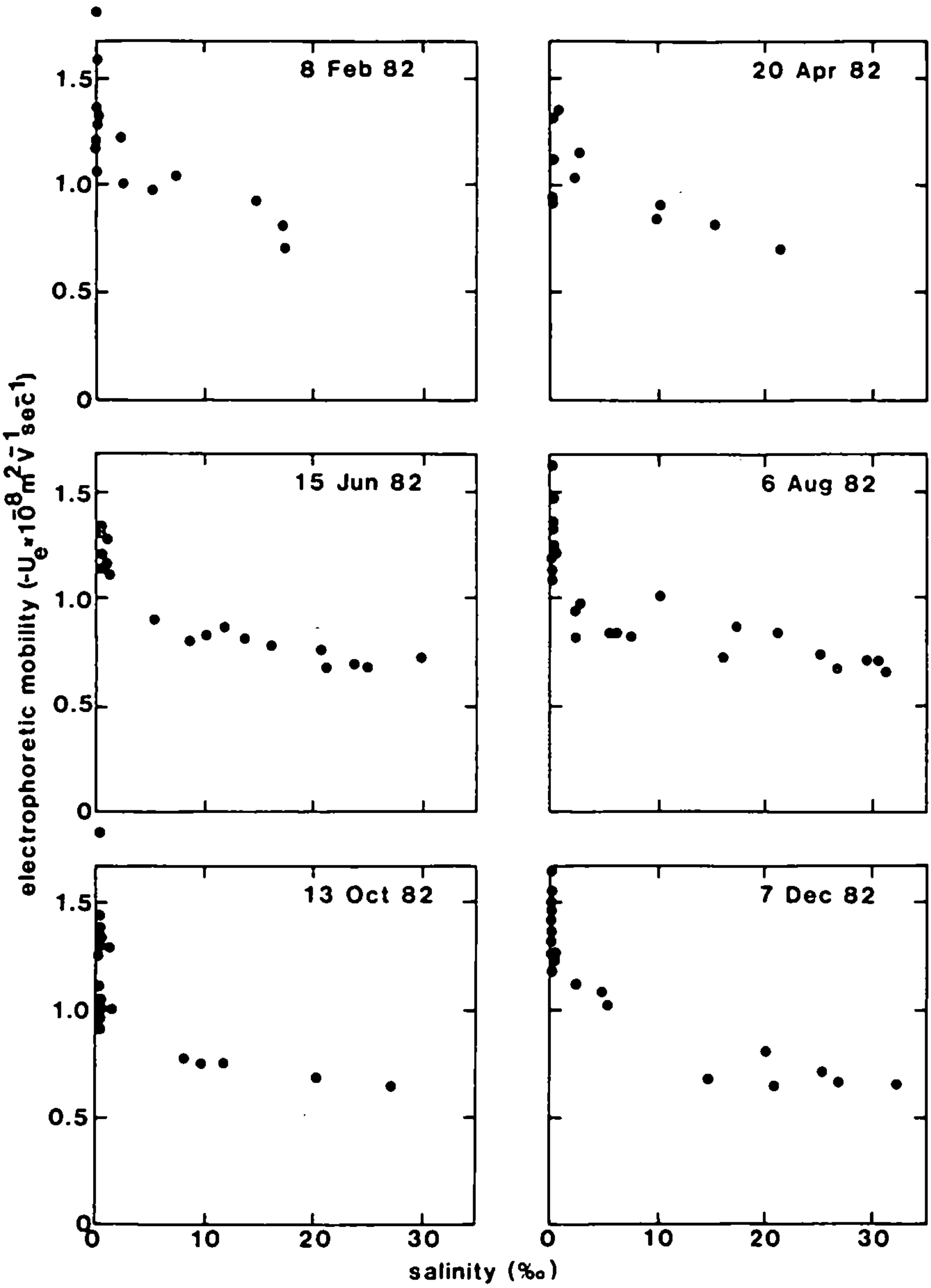


Figure 2.12 The electrophoretic mobility of suspended particles from the Tamar Estuary relative to salinity for six surveys at various times of the year.

ranged from -0.9 to -1.7x $10^{-8}m^2V^{-1}sec^{-1}$ and fell sharply to -0.8 to $-1.0x10^{-8}m^2V^{-1}sec^{-1}$ at 2-3°/₀₀ salinity and then more gradually to values of -0.6 to $-0.7x10^{-8}m^2V^{-1}sec^{-1}$ at 30°/₀₀ salinity.

Examination of the electrophoretic mobility data relative to distance along the estuary (Figure 2.13) provided additional information and also showed more variation between surveys than was apparent previously. This was principally due to the better resolution that was obtained in the low salinity region of the estuary with this technique. Values obtained in the fresh water fell in the range -1.0 to $-1.2x10^{-8}m^2V^{-1}sec^{-1}$ which is a lower and narrower range than the salinity/mobility relationships suggested. A maximum in negative electrophoretic mobility occurred in the region of the fresh/brackish water interphase at or about spring tides but this feature diminished towards neap tides.

2.4.4 Discussion and conclusions

The electrophoretic mobilities measured in this study were consistent with values recorded in a number of British estuaries by Hunter and Liss (1979, 1982). The narrow range of negative charges at salinities greater than 2-3°/₀₀ support the hypothesis that the electrophoretic mobilities of natural particles, irrespective of their basic composition, are dominated by the adsorption of dissolved humic substances (Neihof and Loeb, 1972, 1974; Hunter and Liss, 1979, 1982). The measurement of electrophoretic mobility clearly reflects the charge condition at the outer limit of this organic coating, not at the particle surface. Removal of the organic coating from natural particles by photo-oxidation resulted in mainly positive surface charges (Loder and Liss, 1985).

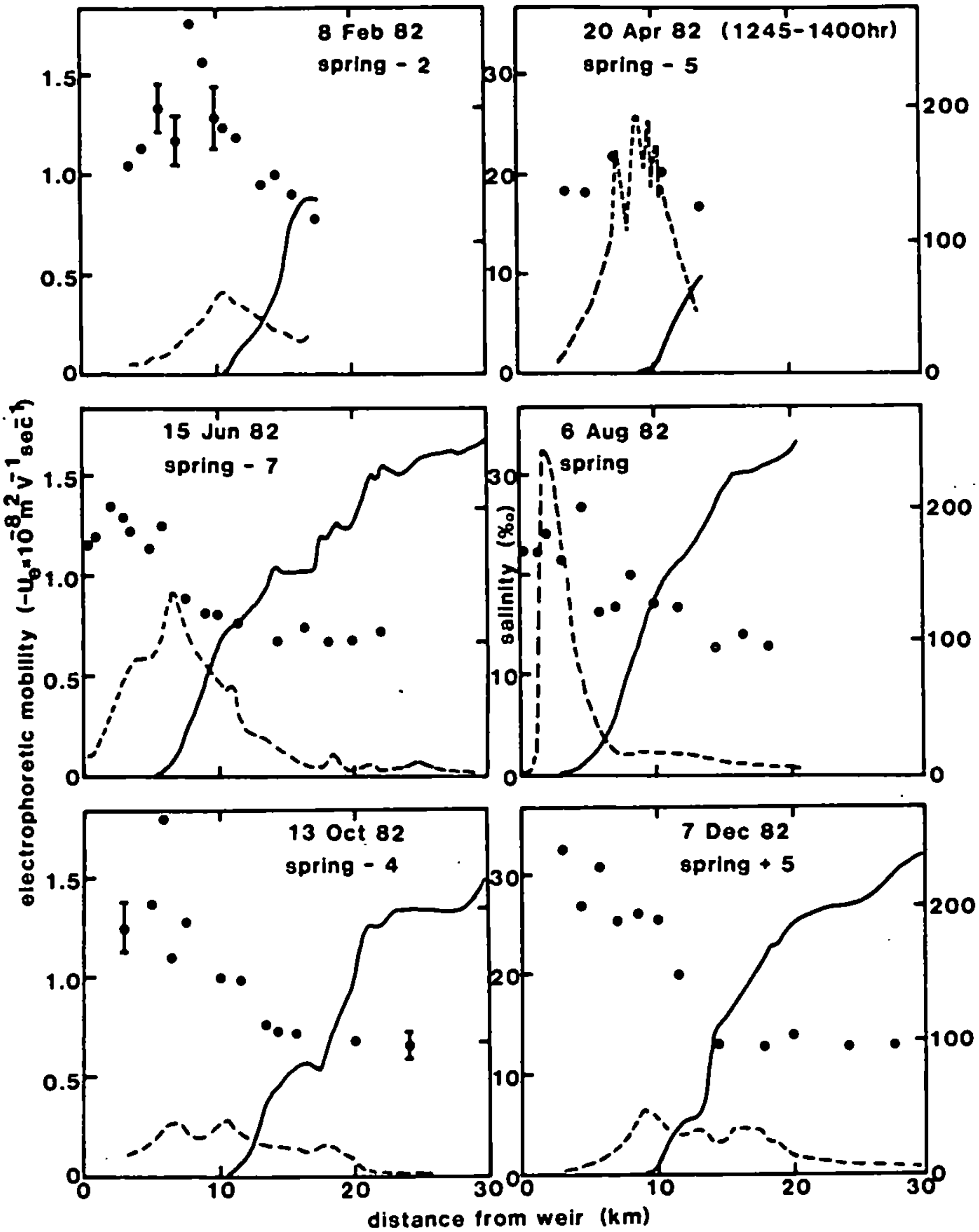


Figure 2.13 The distribution of particle electrophoretic mobility (●) relative to distance along the estuary. Salinity is shown as a solid line and suspended solids as a broken line.

The rapid reduction in negative electrophoretic mobility at low salinities was consistent with the data of Hunter and Liss (1979) for estuaries in which the river water was low in dissolved cations, especially Ca^{2+}, and they suggested that neutralisation of surface charge in this localised region of the estuary was due to the incorporation of polyvalent cations into the double layer. Particles in hard water rivers are already equilibrated with these cations and do not show this change with initial increases in salinity.

Despite these observations which demonstrate the ubiquitous presence of organic coatings on natural particles, it should not be inferred that the particle surfaces are saturated. Observations of inherently inorganic heterogeneous processes in estuaries such as the removal of aluminium at low salinities (Hydes and Liss, 1977; Morris et al., 1986a) and manganese (Morris and Bale, 1979; Morris et al., 1982a) in fact, suggest that the basic particle surface sites are neither totally saturated nor rendered inert by adsorbed organic molecules. Of course, humic substances themselves possess a significant capacity to adsorb metal ions, particularly copper (Reimer and Toth, 1970; Mantoura, 1976). The extent to which organic macromolecules contribute to the reactivity and behaviour of suspended particles remains an important question.

The indication of slightly more negative electrophoretic mobilities in the turbidity maximum region of the estuary, especially at spring tides, may reflect compositional differences in the particle population that result from selective sediment mobilisation. Heterogeneous chemical changes cannot be invoked since transient changes in the surface characteristics of the particle population by the adsorption of, for example, hydrous metal oxides (Hydes and Liss, 1977; Morris et al., 1982a) should be masked by the adsorption of dissolved organic material (Neihof and Loeb, 1972; 1974) from the sample during storage prior to the analyses. Relationships between particle size and electrophoretic mobility have not been investigated but a consideration of the optical part of the measuring system suggests there is both an upper and lower limit to the size of particles that can be observed within the electrophoretic cell. In the case where the size distribution of the particle populations within a series of samples varies for any reason the electrophoretic mobility values may be influenced.

Hunter and Liss (1979) concluded that the uniform electrokinetic charge on natural particles arising from the presence of organic surface coatings could explain the lack of evidence for differential mineral flocculation in estuaries. However, flocculation of iron microcolloids with increasing ionic strength (Figueres et al., 1978; Moore et al., 1979; and since the start of this work, Duffy, 1985) has been shown to bring about the removal of riverine iron in the low salinity region of estuaries so this hypothesis is not universally applicable. It would seem that the true suspended particles in estuaries (i.e. particles of greater than colloidal dimensions) observed in electrophoretic studies are of a size, or have reached a size through aggregation, where electrokinetic processes are not the major influence controlling their interactive behaviour. This is apparently not the case for estuarine particles of colloidal (submicron) dimensions.

2.5 CARBON CONTENT

2.5.1 Introduction

The organic content of estuarine, suspended, particulate material provides information on its provenance and physical properties and, if *in situ* production and respiration processes can be interpreted, an indication of its residence times within the estuary (Wellershaus, 1981; Morris *et al.*, 1982c). This section describes the carbon analyses that have been undertaken and their interpretation.

2.5.2 Apparatus and methods

The total carbon content of suspended solids samples collected during routine surveys of the Tamar estuary (Appendix 1) were determined combustimetrically using an automated CHN elemental analyser (Carlo Erba Model 1106). Sample combustion, within this instrument, takes place in a highly oxidising environment. The combustion products are subsequently reduced to nitrogen, hydrogen and carbon dioxide over hot copper metal, separated chromatographically and quantified using a "hot-wire" detector. The detector response was calibrated by analysing accurately weighed, micro-gram quantities of ultra pure acetanilide.

Samples were collected by vacuum filtering known volumes of estuarine water (200–1000mℓ) through pre-weighed, ashed (12 hours at 450°C), glass-fibre filter pads (Whatman GF/C). The filter pads were rinsed with deionized water on the filter unit to remove salt and stored, deep frozen (-20°C), in aluminium foil envelopes. When required for analysis, the filters were dried to constant weight (110°C) and their particulate load determined.

Using a leather punch, small discs were removed from the central portion of the filter pad; these were folded and placed in tin capsules for analysis. Blank determinations of the filter material were performed on discs cut from the borders of the filter pads. The fraction of the filtered sample analysed on a punched disc was determined by calculating the relative surface areas of the disc and filter from measurements made with a travelling microscope.

2.5.3 Results

All analyses were carried out in duplicate and the results averaged. Analyses of five discs from the same filter gave a mean and standard deviation of 31.95μg and 1.63μg, respectively. Total particulate carbon, expressed as a percentage of the particulate weight for the six surveys are shown plotted against the corresponding particle concentrations in Figure 2.14.

Apart from December, when the carbon contents of the material from regions of medium to high suspended particle concentration (10-100 and 100-1000mg ℓ^{-1} respectively) were low, each survey shows a broadly similar distribution of carbon relative to the concentration of particles. Total carbon values at the lowest particle concentrations (< 10mg ℓ^{-1}) in June and August were particularly high, reaching 25% by weight of the total suspended load. The majority of results though, fell in the range of 5-8% carbon corresponding to particle concentrations in the range 10-100mg ℓ^{-1}. Particulate material collected from regions of elevated suspended solids contained uniformly low levels (4-5%) of total carbon over the range 100-500mg ℓ^{-1}. Deviations from this generalised description mainly reflect contrasting seasonal changes between the composition of the fresh and marine

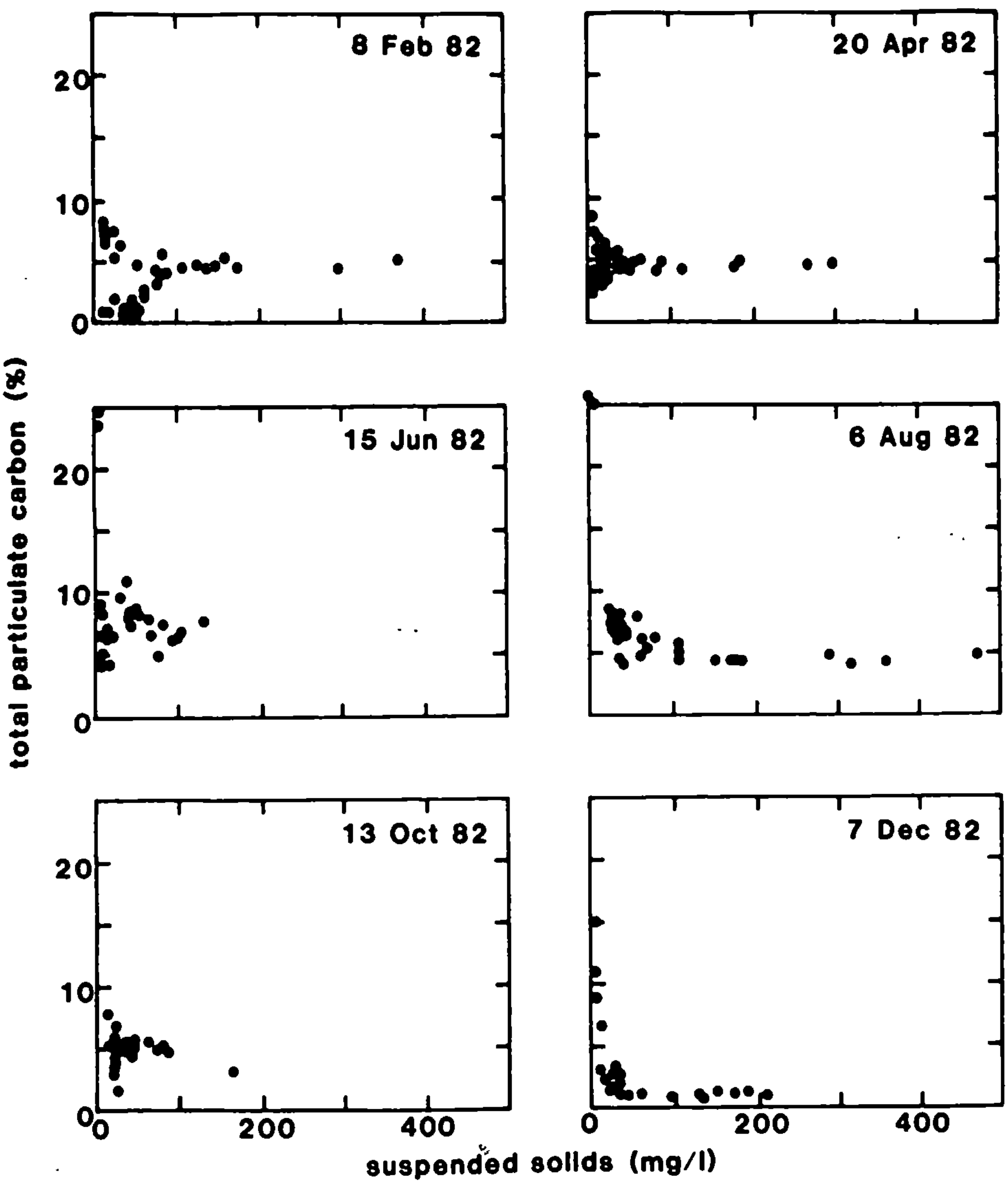


Figure 2.14 The distribution of total particulate carbon as a function of suspended solids for six surveys of the Tamar Estuary.

endmembers. From October through to April, and particularly in February, the carbon content of the riverine particles was lower than that of the marine material suggesting that either primary production in the river was reduced, possibly through lower temperatures, or that the wash-out of terrigenous inorganic particles had increased. Low carbon composition in the riverine particles may have been the reason for the carbon-poor composition of the turbidity maximum material in December but this might also reflect re-working of low-carbon bed sediments with increased fresh water run-off.

2.5.4 Discussion and conclusions

The analysis of particulate carbon on punched discs of filter material is a relatively quick and simple technique that requires no sample weighing. Nitrogen, though analysed, has not been reported here as doubt exists as to the efficiency of the instrument to detect refractory nitrogen compounds. Fractionation of the total carbon into nominally "organic" and "inorganic" carbon was not undertaken in this study. However, earlier work in this estuary (Morris et al., 1982c; Figure 2.15) has shown that, in a summer study, the organic fraction of the total carbon ranges from 50% in the turbidity maximum to 80-90% in the low turbidity, more productive, regions of the estuary. The limited light penetration in the turbidity maximum presumably minimises photosynthetic production and contributes to the lower organic contents. Nevertheless, living cells and biogenic debris derived from productive regions of the estuary must constitute a significant proportion of the particulate material advected into the turbidity maximum through tidal pumping (Uncles et al., 1985). In this case, the low carbon contents of particles comprising the turbidity maximum and

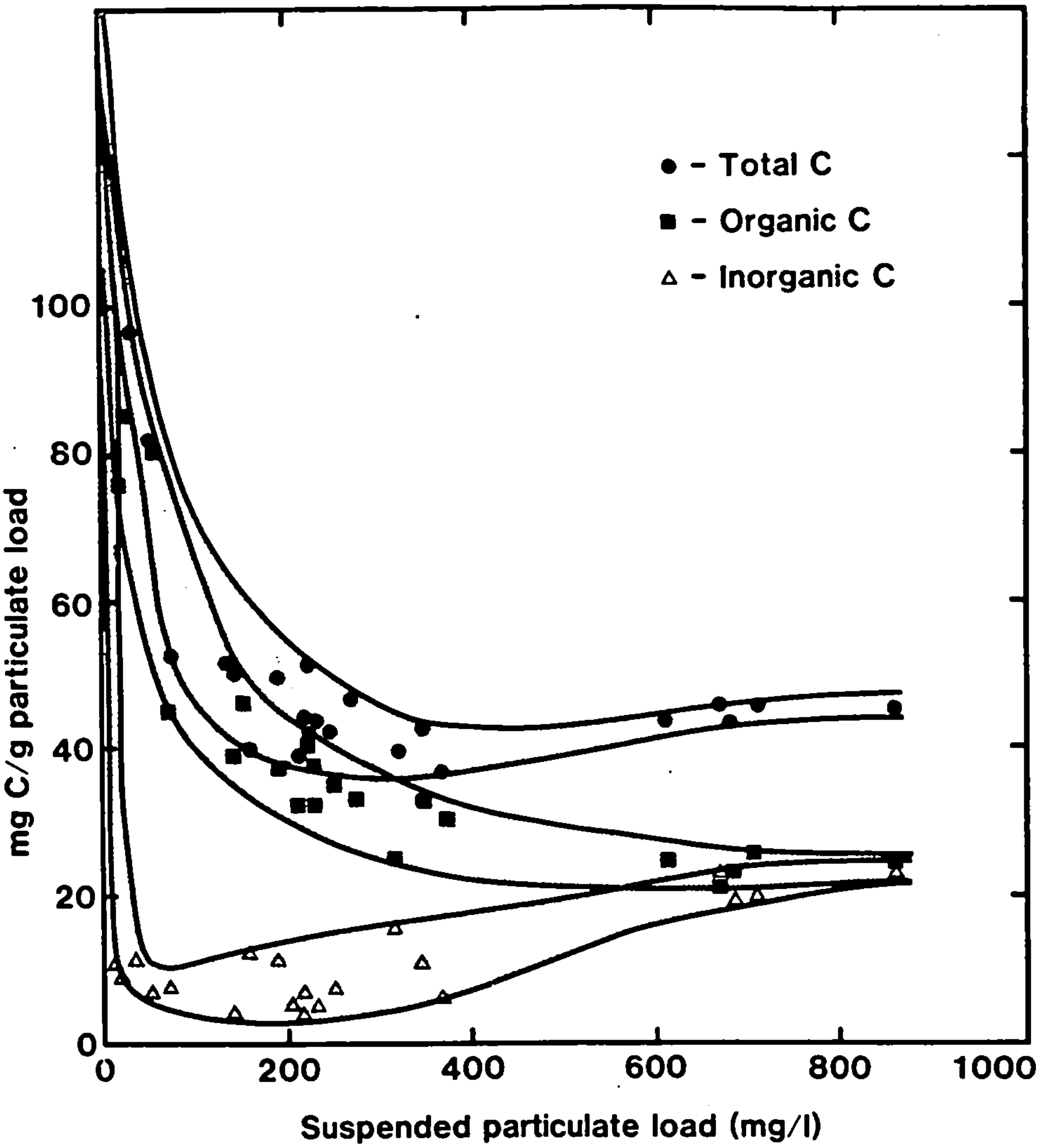


Figure 2.15 The relative proportions of organic and inorganic carbon that make up the total particulate carbon in the Tamar Estuary (taken from Morris *et al.*, 1982).

their relatively low organic fraction indicate that the turbidity maximum is a site of net respiration. This is consistent with distributions of dissolved oxygen which show marked under-saturation coincident with the turbidity maximum (Morris et al., 1982b) and with distributions of ammonia (Knox et al., 1981) which maximise in the same region. Owens (1986) has demonstrated that nitrification by ammonia oxidising bacteria maximises in the turbidity maximum. From these results he deduced that these bacteria have evolved a strategy of attachment to particles that enables them to maintain their numbers within the turbidity maximum against the residual seaward transport of water. This is contested by Clark and Joint (1986) who present visual evidence to the effect that free-living bacteria predominate. However, since doubling times for the bacteria are generally longer than one day and flushing times for the upper 5km of the Tamar range from 0.1-1.0 day (Section 1.3) there must be a mechanism acting to maintain bacterial numbers within the turbidity maximum.

Studies of macroflocs in the marine environment where organic material is abundant suggest that their organic contents can be greater than 50% and that organic content is a prime factor influencing the formation, relative stability and behaviour of flocs (Wilcox-Silver et al., 1978; Shanks and Trent, 1979; Kranck and Milligan, 1980). The carbon results presented here suggest that the reduced organic content of material comprising the turbidity maximum may directly influence the particle size distribution found there. Despite the greater probability of particle collisions at high suspended particle concentrations, as demonstrated by Odd and Owen (1972), the chances of long term particle adhesion and subsequent development of stable aggregates in the turbidity maximum may be limited by available organic material. Low organic contents and therefore reduced cohesion would also render bed material more easily mobilised during periods of increasing tidal energy.

2.6 EXAMINATION BY SCANNING ELECTRON MICROSCOPY

2.6.1 Introduction

Visual examination of estuarine suspended particles was undertaken using scanning electron microscopy (SEM). Limited access to the microscope and the laborious nature of microscopic examinations, which require many fields of view to be observed in order to obtain statisically reliable data, precluded a systematic study. Nevertheless, this technique provided a valuable insight into the morphology, size and composition of estuarine particles.

2.6.2 Methods

Estuarine water samples (25mℓ) were obtained from stations throughout the estuary during the axial profiles of the Tamar (Appendix 1) and were preserved by the addition of glutaraldehyde (BDH Chemicals, special for microscopy) at a final concentration of 1% by volume. In the laboratory, sufficient sample was filtered onto a 0.45μm pore-size Millipore membrane (0.4μm pore-sized Nuclepore membranes were also used) to produce a uniform covering of particles without significant overlaying. The papers were then rinsed with deionised water to remove salt and air-dried under a low power infra-red lamp, after which a small section of each filter (approximately 1cm^2) was removed with a scalpel and attached to a similar sized piece of double-sided adhesive tape. A 4mm diameter disc was punched through both layers, firmly anchoring the filter to the tape in the process, and the disc was stuck on to a standard microscope stub. Earthing between the sample and the stub was ensured with a drop of metallic paint placed on the edge of the sample. After this had dried, the stub and sample were plated with gold to a thickness of 15nm in a Polaron E1500 vacuum coating unit. The samples were examined using a Jeol JSM-35C microscope at various magnifications up to 3000 times.

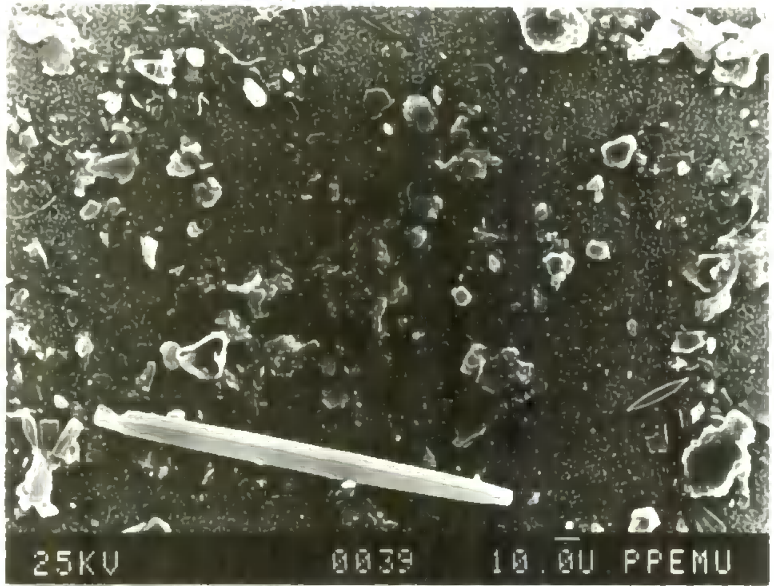
2.6.3 Observations and conclusions

Throughout the estuary, including the turbidity maximum, the material comprising the suspended particle population was highly varied and no spatial compositional trends could be detected. Likewise, compositional difference between winter (Plate 2.1) and summer samples (Plate 2.2) could not be discerned. Although there was no attempt to size or quantify the particles in these samples, it appeared qualitatively, that there were no major differences in the size distributions between particles comprising the turbidity maximum and those from elsewhere in the estuary. The largest particles observed throughout the estuary were faecal pellets. These occured in varying degrees of fragmentation and ranged in size from 20-80μm in diameter. This range was comparable with measurements by laser diffraction on discrete samples through the bulk of the estuary (Section 2.3). The rest of the material consisted mainly of discrete primary particles of around 5-10μm although a few particles of up to 20μm were seen. This range of sizes also seemed typical of component particles incorporated into pellets and was typical of the sizes measured in the turbidity maximum by laser diffraction.

Most of the discrete particles appeared to be mineral grains of

Plate 2.1 Electron micrographs of suspended particles from the Tamar Estuary collected during a winter (8.2.82) axial profile. Magnification x 200.

Photomicrograph 0039	Freshwater, suspended solids 10.4 mg ℓ^{-1}	Photomicrograph 0056	Salinity 0.1‰, suspended solids 63 mg ℓ^{-1} (turbidity maximum).
Photomicrograph 0058	Salinity 7.5‰, suspended solids 36.4 mg ℓ^{-1}	Photomicrograph 0057	Salinity 17.3‰, suspended solids 33.6 mg ℓ^{-1}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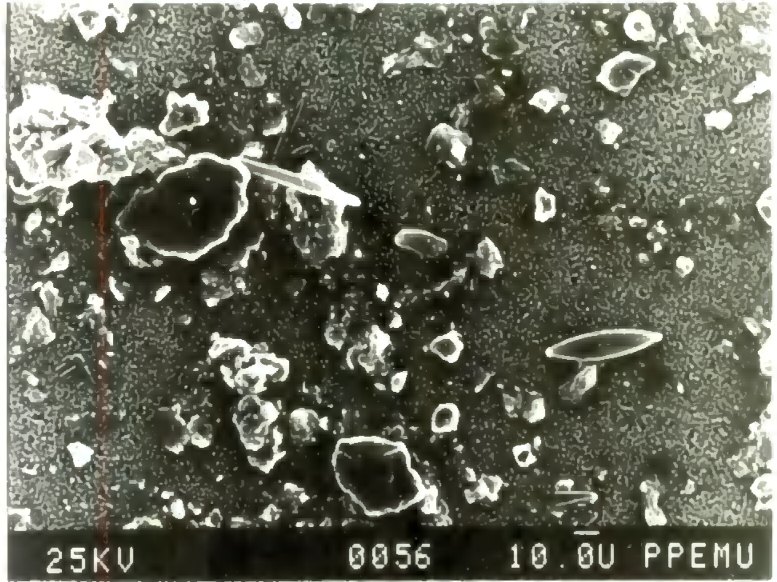
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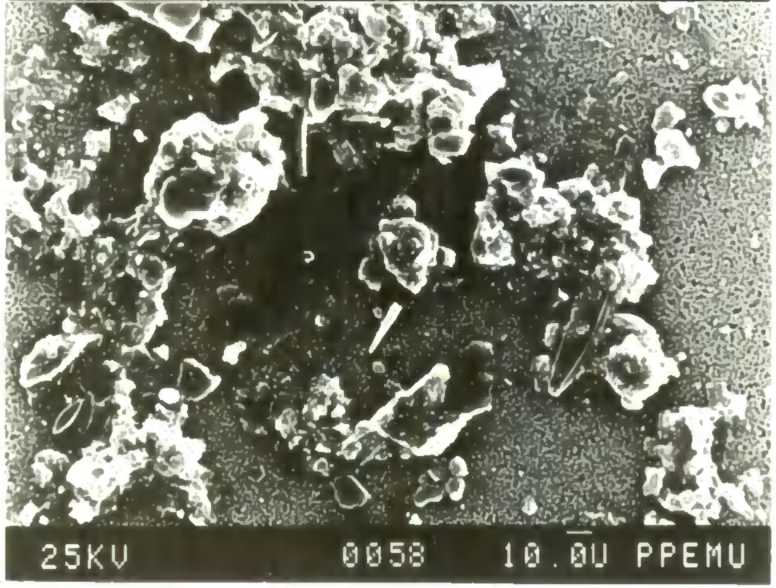
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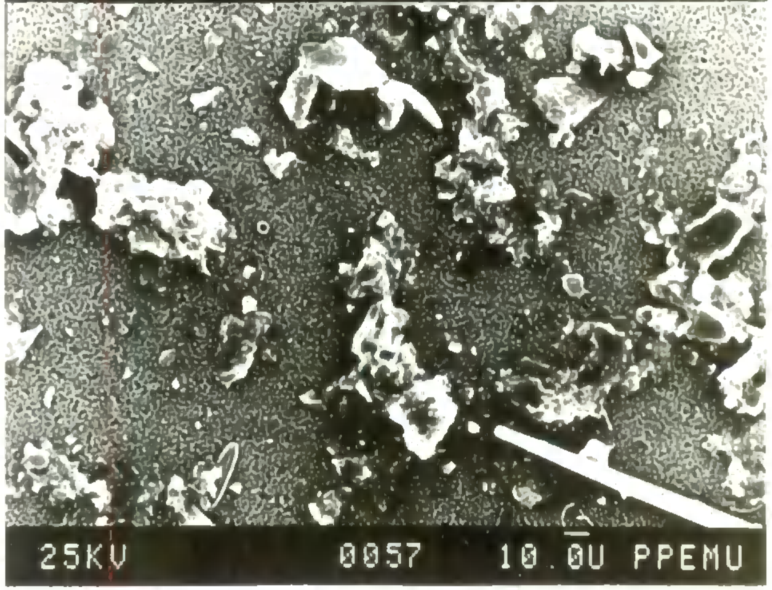
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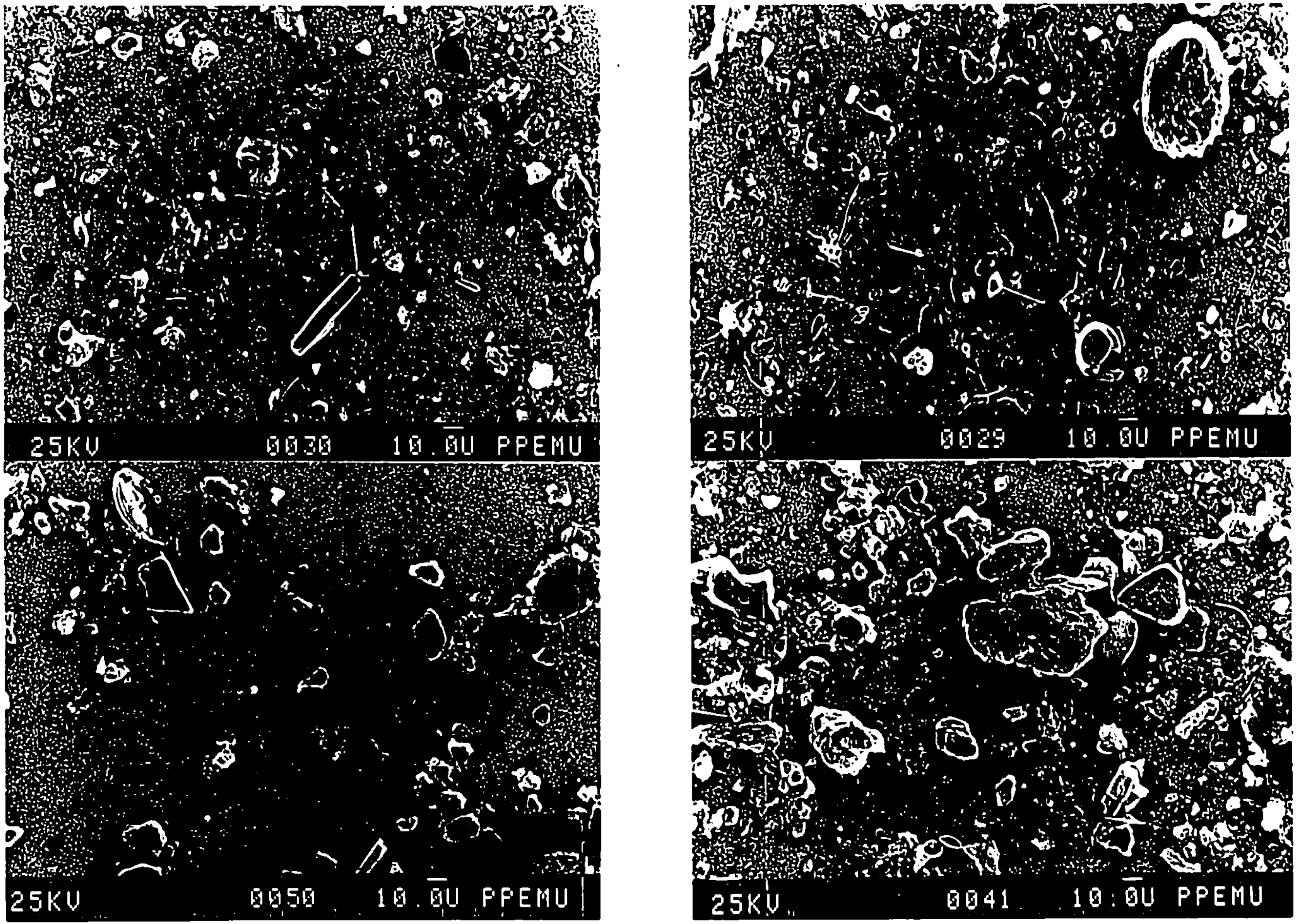
Plate 2.2 Electron micrographs of suspended particles from the Tamar Estuary collected during a summer (6.8.82) axial profile. Magnification x 200.

Photomicrograph 0030	Freshwater, suspended solids 5 mg ℓ^{-1}.	Photomicrograph 0029	Salinity 0.1‰, suspended solids 245 mg ℓ^{-1} (turbidity maximum).
Photomicrograph 0050	Salinity 10.3‰, suspended solids 14 mg ℓ^{-1}.	Photomicrograph 0041	Salinity 30.7‰, suspended solids 7.0 mg ℓ^{-1} (salt crystals apparent).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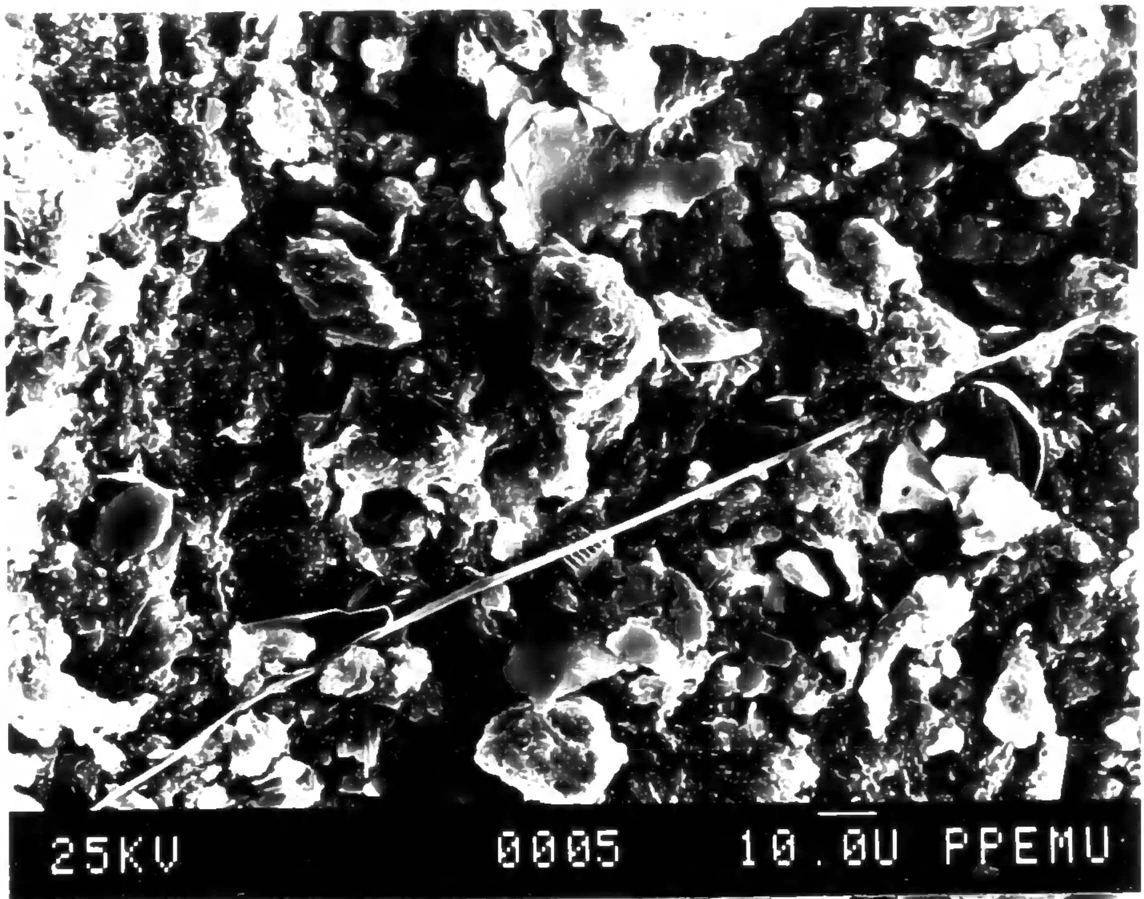
either quartz or clay platelet types. At higher magnification (Plates 2.3 and 2.4), it was evident that some of these particles were of very small size (<1.0μm) and were trapped within the matrix of the filter membrane. Clearly, many of the primary particles had resulted from natural fragmentation of diatom frustules and from fragmentation during collection as shown by the diatom in picture 0003. There was no evidence of the much larger fragile aggregates observed with the *in-situ* particle sizer but these samples had also been subject to the physical disruption associated with collection and filtration.

A striking feature of these pictures was the large number of particles of biogenic origin. In addition to faecal pellets a large number of the total particles were pennate benthic diatoms principally of the genus *Navicula* although, occasionally, centric diatoms were also observed. In addition, large numbers of discrete particles were obviously fragments of diatom frustules and many of these had been incorporated into faecal pellets. Other non-mineral particles were probably refractory organic debris and, in some pictures, fibrous material, probably of plant origin, was discernible.

Very few unshielded cells were observed, those that were visible had collapsed. Bacteria were also scarce which suggested that the dehydration technique used in the preparation of these samples was unsuited to the preservation of delicate biological material. This almost certainly explains why there was little evidence of seasonal or spatial variability in the composition of the particle population. Presumably this also accounts for the lack of visual evidence for organic films associated with the particle surfaces.

Plate 2.3 Electron micrographs of suspended particles from the turbidity maximum seen under increasing magnification.

Photomicrograph 0005	A heavily loaded filter paper illustrates the range of particle types and the wide spectrum of sizes. The impact of the biota is clearly evident. Magnification x 300.
Photomicrograph 0010	At higher magnification (x 3000), the component particles of faecal pellets are clearly visible. Clay platelets constitute the majority of the component particles.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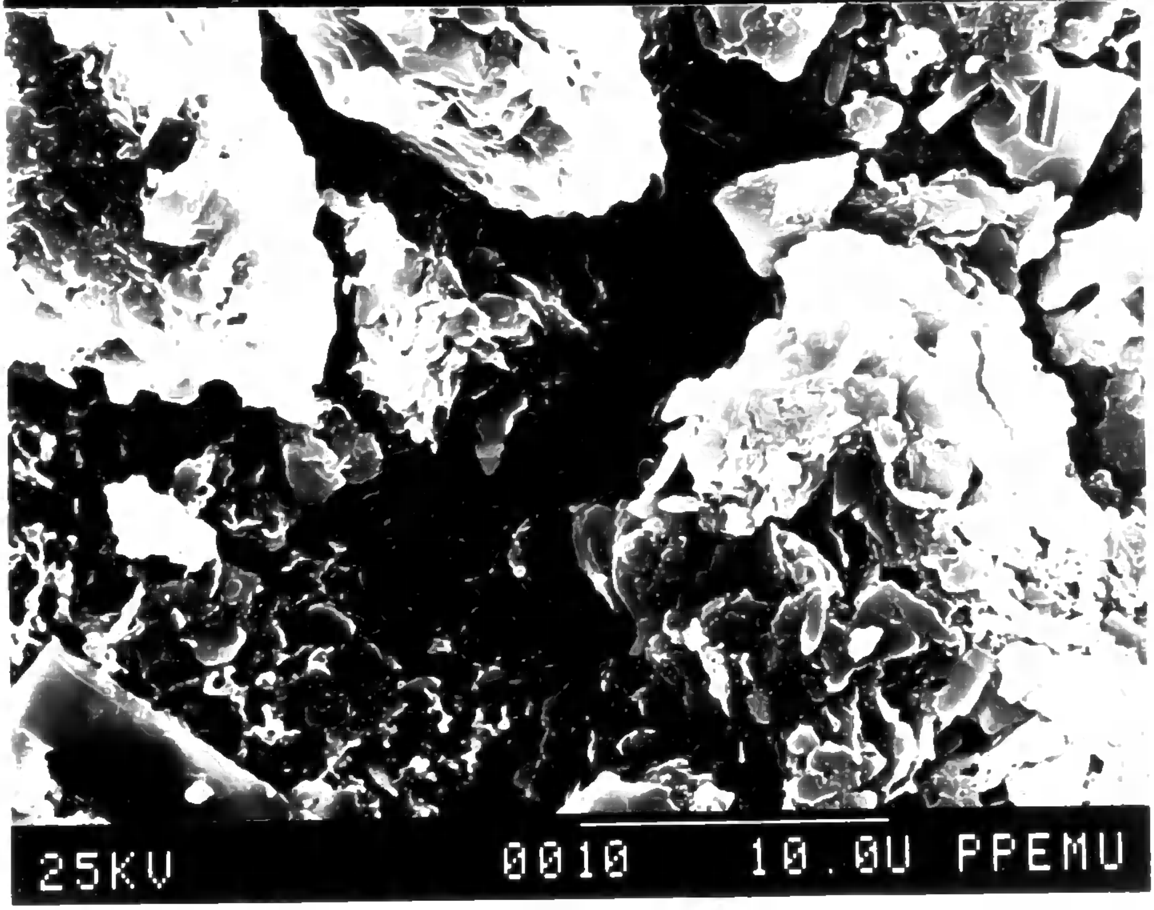
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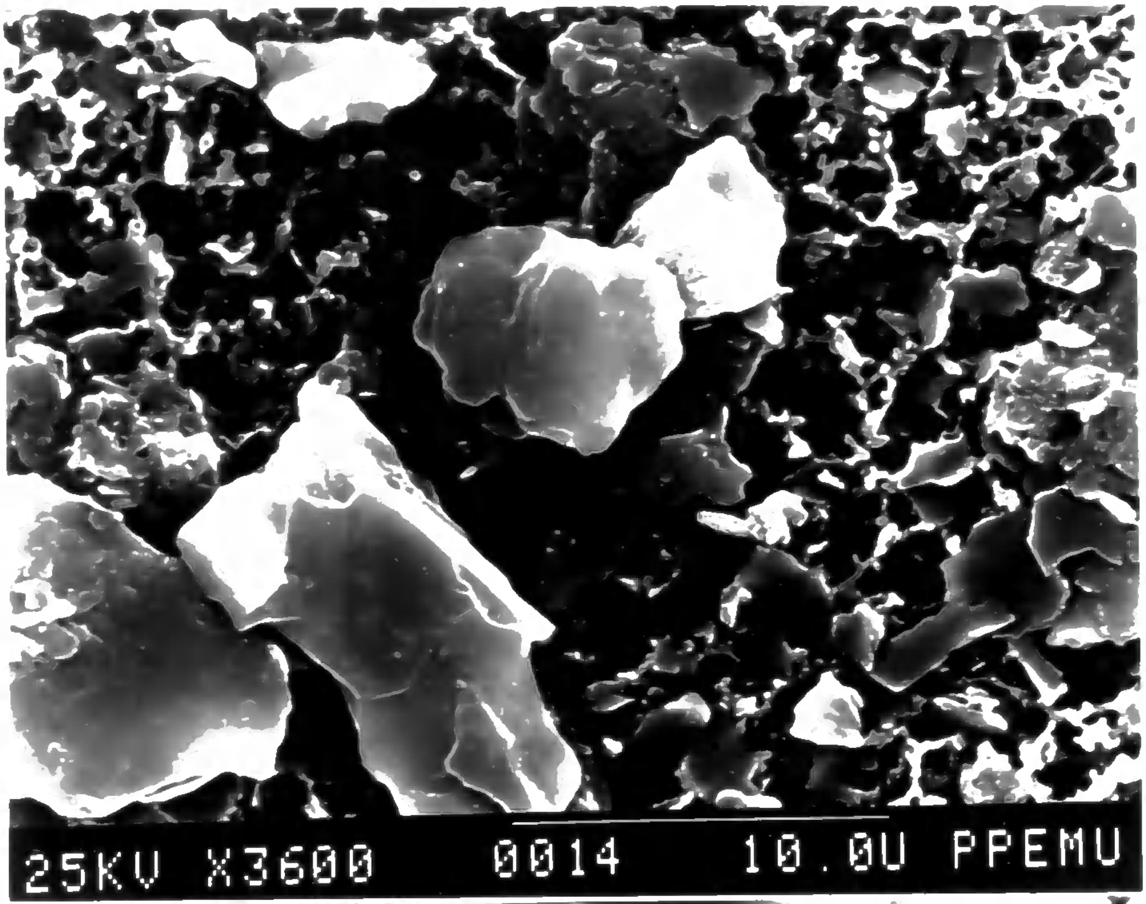
Plate 2.4 Electron micrographs of suspended particles from the turbidity maximum.

Photomicrograph 0014

At this magnification (x 3600), the number of particles which can be seen per field of view are sacrificed for high resolution. This plate shows discrete mineral grains as well as sub-micron particles trapped in the filter matrix.

Photomicrograph 0003

Shows the intricate and attractive structure of a diatom frustule but illustrates the potential for particle disruption even for relatively coherent structures during sampling.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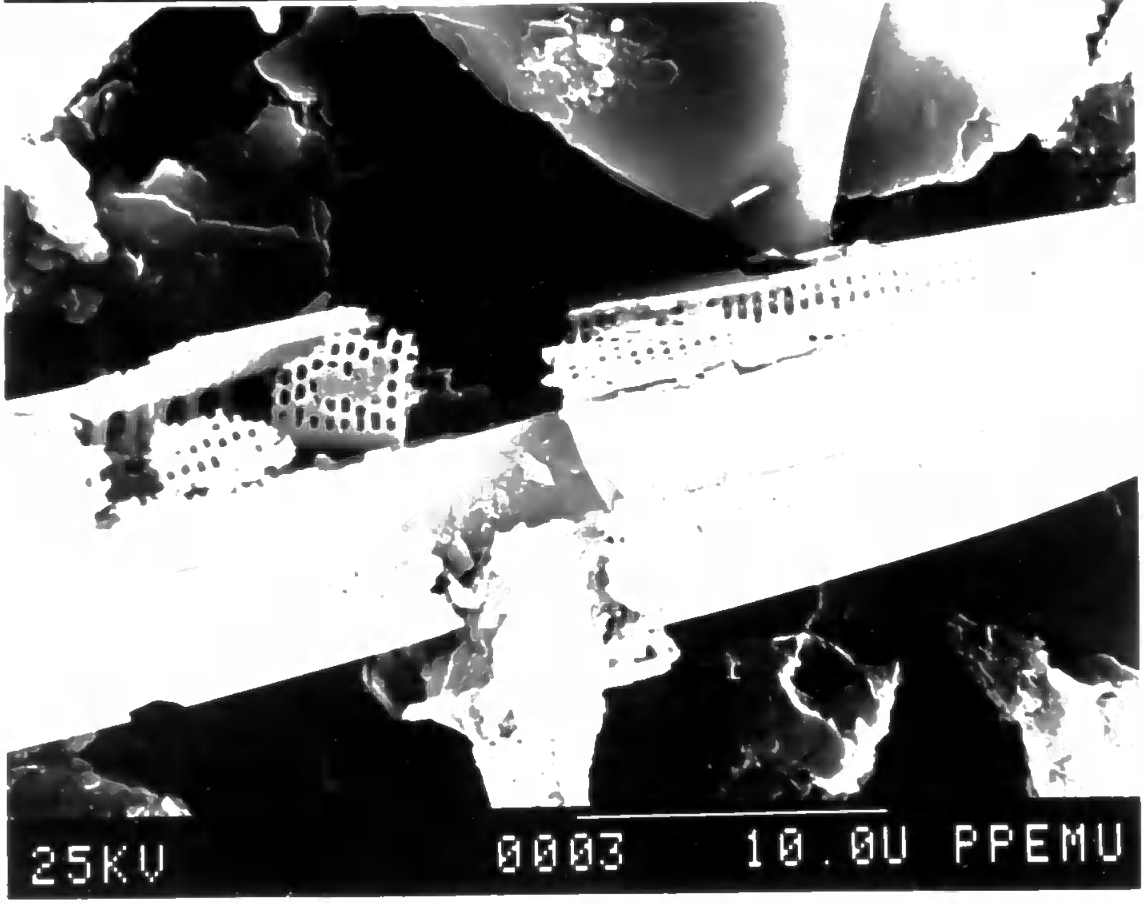
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2.7 EFFECTIVE DENSITY DETERMINATIONS AND AGGREGATE COMPOSITION

2.7.1 Density from Stoke's settling: Introduction

Settling can be employed, in conjunction with Stoke's Law, to provide particle size information. This method forms the basis of the Andreasen pipette analysis technique for determining particle size (Lauer, 1966). Having the ability to measure particle sizes independently of settling rates, settling information was used to infer effective density values for estuarine particles.

2.7.2 Methods

Estimates of density were obtained for a limited number of samples using two similar approaches. Firstly, the size distributions of natural suspensions were measured in a magnetically stirred sample cell using the laser diffraction apparatus. Afterwards, the stirring was switched off and the size distributions re-measured at suitable intervals whilst settling occurred within the cell. The height of fall from the top of the cell to the bottom of the laser beam was 2.5cm. The second approach used the estuary as the settling chamber. On occasions when particle sizes had been measured in the estuary before and during slack water, the reduction in mean particle size over slack water was interpreted as preferential settling of the larger particles through a depth of at least 0.5m (the depth at which the sampling pump inlet was set) in the time interval between the observations. No attempt to introduce factors for shapes other than spheres was made since the size measurements assumed spherical particles.

2.7.3 Results of settling measurements

The pooled results obtained using both approaches are shown in Figure 2.16 which relates particle size (Stoke's diameters) to settling rate for materials of various densities according to the Stoke's relationship in which the rate at which particles sink (V cm sec^{-1}) is given by:

$$V = \frac{(\rho_1-\rho_2)\ gd^2}{18\eta}$$

where ρ_1 = density of the solid in g cm^{-3}

ρ_2 = density of the liquid in g cm^{-3}

g = acceleration due to gravity in cm sec^2

d = Stoke's diameter of the particle in cm

η = the viscosity of the liquid in g cm^{-1} sec^{-1}

The particles studied were mainly from the turbidity maximum region and fell in the density range 1.1g cm^{-3} to 1.4g cm^{-3} over the limited size range 20-60µm. Density decreased slightly with increasing particles size whereas the settling velocity increased considerably. This is consistent with the Stokes equation in which the settling velocity (V) increases as the square of particle size but only linearly with density. These values are comparable with density values of up to 1.5g cm^{-3} derived by Sheldon (1968) for suspended material in the River Crouch. In a review of marine particle characteristics, McCave (1984) found that densities derived from settling rates, ranged from 2.0g cm^{-3} for particles of < 1.0µm to 1.003g cm^{-3} for particles over 2000µm and marine particles of 20µm, 50µm and 100µm diameter exhibited densities of 1.3, 1.2 and 1.1g cm^{-3} respectively. This implies that aggregation and inclusion of water filled voids are important factors determining

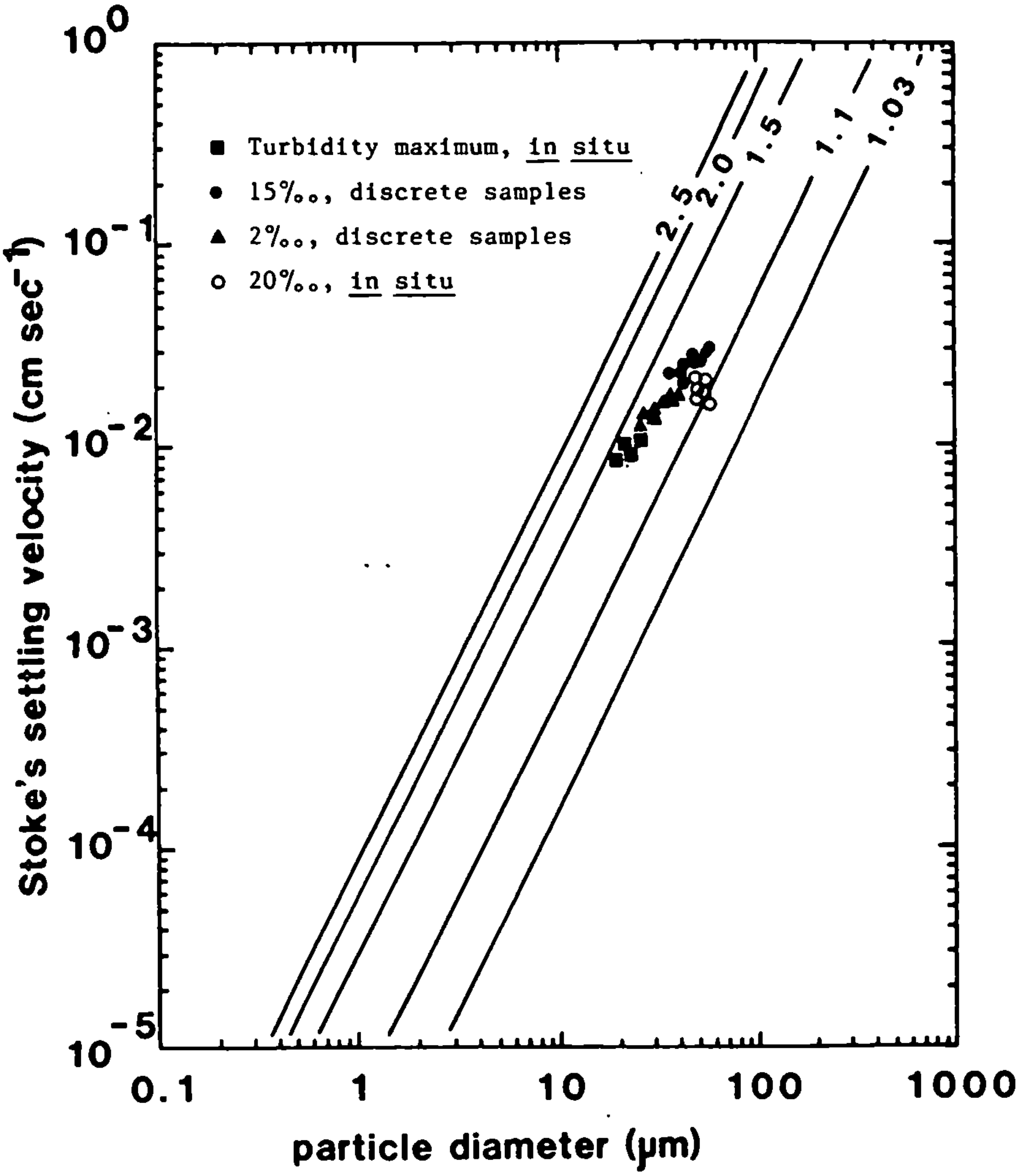


Figure 2.16 The relationship between settling rate and size for particles of various density from the Tamar Estuary.

suspended particle density. Odd and Owen (1972) measured settling rates, but not sizes, at various concentrations of suspended solids in the Thames Estuary. Assuming that particle sizes in the Thames are similar to the typical range of Tamar particles, <u>i.e.</u> 10-100μm, their data yield densities between 1.4 and 1.2g cm^{-3}.

2.7.4 The composition of estuarine aggregates

Having obtained data on the size, density and organic content of suspended particles, an exercise was undertaken to describe the range of compositions that would account for the observed characteristics. Assuming typical densities of 0.9g cm^{-3} for organic material and 2.5g cm^{-3} for the detrital phase, the effective densities of aggregates containing various proportions of organic and mineral phases over a range of compactions were calculated. It was assumed for this exercise that the voids contained water of the same composition as the suspending medium.

The calculations are summarised in Figure 2.17 which shows the densities of particles that range in composition from 0-100% organic content over a similar range of void spaces. For particles with an effective density of 1.4-1.1g cm^{-3} and with organic contents in the range 10-20% (using: organic content = total carbon x 2), the voids must account for approximately 50% of the volume of the most dense particles, and reach >90% for the lightest particles. Cubic packing of spheres, for comparison, produces a void space of 48%. This suggests that aggregates, especially the larger, lower density particles are very loosely associated, which accords with their observed fragile nature.

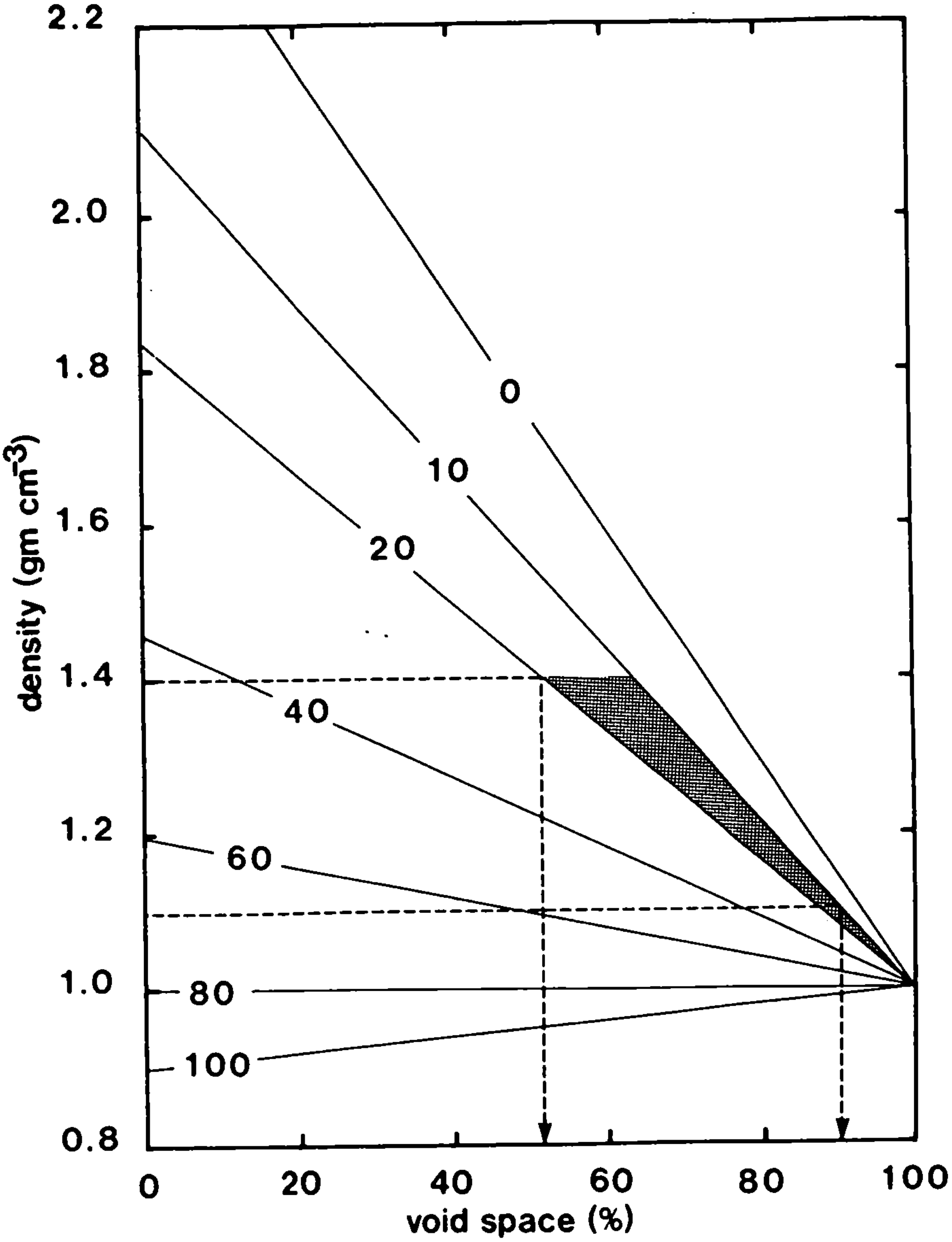


Figure 2.17 The relationship between density and void-space (degree of close packing) for particles of various organic/mineral composition.

Using a similar approach and taking typical values for density and particle size, the theoretical specific surface areas for a range of particle sizes were calculated by assuming the particles were spherical. For example, 1g of particles with a density of 1.3g cm^{-3} is equivalent to a volume of $7.7x10^{-1}cm^3$ and therefore to $1.5x10^9$ particles each of volume of $5.23x10^{-10}cm^3$ (10μm diameter). By multiplying the surface area of one 10μm particle by the number of particles in one gram, the specific surface is calculated as $0.5m^2$. Particles of 1.0μm and 0.1μm dia. give values of 5 and $50m^2$, respectively. This can be compared with values of $16\text{-}20m^2\ g^{-1}$ for particles from the Tamar turbidity maximum (Glegg _et al._, 1986) measured using the nitrogen adsorption (BET) technique. Particles in that region would be of the order 8-12μm dia. and therefore comparable with the 10μm particles which gave calculated values of only $0.5m^2\ g^{-1}$. It is clear, therefore, that porosity due to aggregation and internal structure is a major factor affecting the surface area of natural suspended particles.

A summary of particle characteristics and their distribution within the estuary is produced in Table 2.2. This illustrates the marked dependence of the settling rates of suspended material on size and, to a lesser extent, on density and shows that particles in the turbidity maximum, through their unique composition and properties, are typically slower settling than elsewhere in the estuary by at least an order of magnitude.

2.8 SUMMARY AND CONCLUSIONS

1. Mobilization of particulate material is accentuated in the

Table 2.2 The physical characteristics of 'typical' particles from various regions of an estuary. Settling times have been calculated with the assumption that particles in the turbidity maximum are completely dissociated; the retention of particles in this zone, however, suggests that this is not the case.

salinity, $^{\circ}/_{oo}$	typical turbidity mg ℓ^{-1}	effective density g cm^{-1}	typical size µm	time taken to settle 1m at slack water Hours
0	2	1.1	20-60	11.6-1.3
0.1	500	1.5	8-12	14.6-6.3
1.0	100	1.3	20-40	5.5-1.3
10	50	1.2	40-100	1.9-0.3
20-30	10-2	1.1	100-300	0.45-0.05

upper reaches of the Tamar Estuary by amplification of the tidal energy as the channel reduces in size (Uncles *et al.*, 1985). Tidal pumping concentrates the suspended particles in a localised region at the null tidal point associated with the fresh/brackish interface. The magnitude of the turbidity maximum depends on a balance between sedimentation and periodic augmentation by tidal resuspension of bed sediment on semi-diurnal and spring-neap freqencies. The location of the null tidal point and hence the turbidity maximum varies between high and low water and seasonally with changes in river run-off.

2. Axial profiles suggest that particle sizes are reduced in the turbidity maximum compared with other regions of the estuary either by selective processes or by transformations that occur within that zone. Microscopic examination failed to detect any systematic change in the composition of particles through the turbidity maximum but carbon measurements showed that the organic content was reduced, presumably by localised microbial activity.

3. Measurements of similar, slightly negative electrophoretic mobility values throughout the estuary indicate that particles acquire a sheath of refractory humic macromolecules which are ubiquitous in natural waters. Electrophoretic mobilities almost certainly reflect the charge conditions at the outer boundary of this adsorbed layer. However, consideration of the role that particles play in heterogeneous processes would suggest that the surface sites are not completely utilised.

4. Despite greater densities, particles in the turbidity maximum exhibited much slower settling rates than in other regions of the estuary because of their typically small mean particle size.

5. Low light penetration at the turbidity maximum minimises photosynthetic activity and helps to bias particles towards an inorganic composition as does degradation of organic detritus by bacterial respiration. Both these processes may reduce the facility for permanent aggregate formation despite the greater probability of collisions at high particle concentrations. Nevertheless, temporary (fragile) aggregation is required to explain the settling and hence retention of the small particles within the turbidity maximum.

It is clear that the overiding influences affecting the behaviour of suspended material in the Tamar Estuary are tidal range and riverflow and that these effects are similar to those discussed by Postma (1967) for macro-tidal systems in general. In this section, the natural variability in the distribution and concentration of suspended particles in the Tamar system have been evaluated and the masses and fluxes of material quantified. The bulk chemical nature of the suspended particles has been examined, as have the size characteristics, which, presumably governed by settling characteristics, appear to be similar to material in the Chesapeake Bay turbidity maximum (Schubel, 1969) and the Thames (Odd, 1970). However, in-situ particle sizing techniques developed for this research, have suggested that the sizes of fragile estuarine aggregates, away from the turbidity maximum, are much greater than have been previously recorded. The close coupling between sediment particle populations and the suspended particles through tidal action, indicates that the bed-sediment population, comprising a much greater reservoir of particulate material than the suspended particles, is an important factor controlling heterogeneous estuarine processes.

SECTION THREE

BED SEDIMENT CHARACTERISTICS AND DYNAMICS

3.1 INTRODUCTION

This work was introduced as a result of observations made in the previous section which highlighted the continuous cycling of particulate material between the suspended and sedimentary phases through oscillations in tidal energy and river run-off. These observations posed the questions: (a) how comparable are the bed sediment characteristics to those of the suspended particles (or *vice versa*), and (b) to what extent are the spatial distribution and dynamics of the bed sediments related to suspended sediment dynamics within the estuary?

In response, sediment surveys were undertaken under winter (high run-off) and summer (low run-off) conditions to examine the distribution and properties (silt content, organic content and water content) of the bed sediments in conjunction with a seasonal study of the bed sediment mobility.

3.2 SEDIMENT CHARACTERISTICS

3.2.1 Sampling details and methods

Using a small inflatable craft at low tide, 96 surface-scrape (0-2cm) sediment samples were taken from each bank along an axial transect of the Tamar estuary in February 1983. On this survey, 42 stations were occupied between Morwellham (3.0km) and Torpoint (29km). In August 1983, another 62 samples were taken from 32 stations between Morwell Rocks (1.2km) and Torpoint (29.4km). Replicate samples were taken at some sites to assess the variability due to sampling. On returning to the laboratory, samples were stored at 4^{o}C in the dark to minimise biological activity. A record of the station positions is given in Appendix 2.

3.2.2 Sample analysis

Each sample was first weighed so that its water content could be derived at a later stage and then wet-sieved using the method described by Buchanan and Kain (1971). To achieve this, the samples were made up to 500ml in a one litre beaker with deionized water, 25ml of "kalgol" deflocculating agent (sodium hexametaphosphate, 6.2g ℓ^{-1}) was added and the resulting slurry stirred for one hour. On the following day the slurry was restirred and then wet-sieved through a 63μm test sieve (Endecotts, Ltd.) using a mechanical sieve shaker. The fraction passing the sieve, termed silt (<63μm see Table 3.1), was retained and the total volume of the suspension (sediment plus washings) recorded. This suspension was then mechanically stirred to uniformly suspend the sediment and two accurately measured volumes (10 or 20ml) were filtered on to pre-weighed, ashed (12hr at 450°C) glass-fibre filter pads (Whatman GF/C) for gravimetric determination of the sediment concentration. Allowance for the weight of deflocculant incorporated in the sample was not required using this technique as the filter pads and sediment were rinsed with deionised water prior to drying. Following this operation, the filter pads were ashed (12hr at 450°C) to estimate their organic content (McCave, 1979). Finally, the size distribution of the silt fraction was measured using the Malvern Instruments' particle sizer (described in Section 2.2). A few drops of thoroughly homogenised suspension were added to particle-free, deionised water in the measuring cell until a suitable optical density for the measurement was obtained.

Table 3.1 Comparison of the Malvern size bands (2-200µm size range) with the conventional Wentworth particle size classification.

Malvern size band		Wentworth grade classification			
No	µm	φ	µm	Nomenclature	
1	1.9 - 2.4				
2	2.4 - 3.0				CLAY
3	3.0 - 3.8				
4	3.8 - 4.8	+8	3.9	———	
5	4.8 - 6.2			very fine	
6	6.2 - 7.9	+7	7.8	----	
7	7.9 - 10.1			fine	
8	10.1 - 13.0				
9	13.0 - 16.7	+6	15.6	----	SILT
10	16.7 - 21.5			medium	
11	21.5 - 28.1				
12	28.1 - 37.6	+5	31.3	----	
13	37.6 - 53.5			coarse	
14	53.5 - 87.2	+4	62.5	———	
15	87.2 - 188.0				SAND

The fraction retained by the sieve was quantitatively transfered either into a pre-weighed 250ml beaker or on to a watch glass (depending on the amount) and dried to constant weight. Accurately weighed sub-samples (10 to 20g) of this material were ignited (12hrs at 450^{o}C) to determine their organic content by their loss in weight.

3.2.3 Results

The sieve analysis of ten replicate samples from the station at 24.4km (Appendix 2) yielded a mean and standard deviation for silt content of 85% and 1.28%, respectively. A second exercise in which four samples were dried and weighed prior to the sieving operation gave a mean recovery of 97.4% (s.d. = 5.1%). In Figure 3.1 the analyses of silt, water content and loss on ignition for both surveys are plotted against distance along the estuary. Not surprisingly, disparate values were obtained from opposite banks in many cases and the data were therefore smoothed by averaging the values for each parameter over 1km sections of the estuary.

Sieve fractionation

Under high river flow conditions in February, sediment was not found above 3km from the weir, the majority of stations being either bed-rock or gravel, and the percentage fraction of silt was therefore zero. Between 3 and 14km, mobile sediment was more abundant and its size composition changed rapidly from about 50% silt at 3km to 90-95% silt between 7 and 13km. Between 13 and 16km the fraction of silt fell to 30-50%, with individual values as low as 5%. This corresponded to an area of prominent sand banks. Down-estuary of this region the silt content increased to 80-85% reaching a peak at 20km before falling steadily towards a value of 60% at the marine end of the estuary

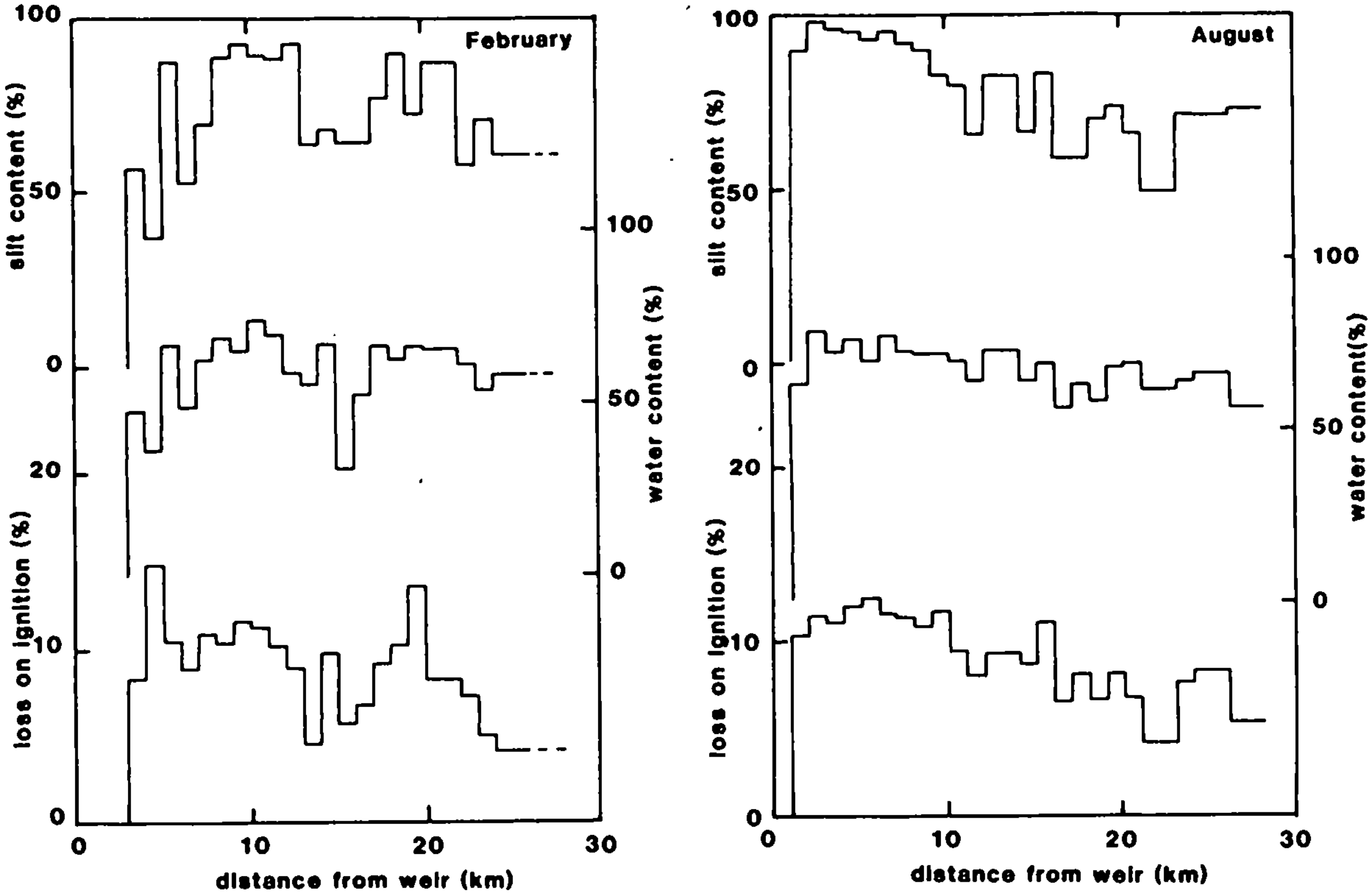


Figure 3.1 Axial distributions of the silt, water and organic content of bed sediments from the Tamar under winter (February) and summer (August) conditions.

(30km). In the August, low river flow survey, silt contents changed steadily from 60-70% at the marine end to 90-95% at the head of the estuary. The silt contents of the sediments in the lower-estuary (17-22km) were noticeably reduced compared with winter conditions and the mid-estuarine silt minimum was much less prominent. Most significantly however, sediment containing a high silt content was observed within 1.2km of the weir in summer. The compositions of the marine end-members in summer and winter were virtually identical.

Loss on ignition

The axial trends in weight lost on ignition were very similar to the silt distributions in both data sets. Weight lost on ignition was about 10% at the riverine end of the estuary in summer and winter and increased to approximately 12% in regions of high silt content. In the mid-estuarine sand bank region in winter and the sandy marine end-members in summer and winter, weight loss reduced to values of 4-5%. The relationship between silt content and weight lost on ignition are shown for all samples in Figure 3.2(a). Although the majority of points are concentrated in the high silt (85-95%), high organic content (11-12%) region of the plot and exhibit a high degree of scatter, no significant difference in composition was detectable between the summer and winter surveys.

The loss on ignition of the separate silt and sediment fractions obtained by the sieving operation are summarised in Figures 3.2(b) and (c), respectively. The variation of the loss on ignition with silt content in the silt fraction closely resembled that of the total sediment which was not surprising as silt comprised the major portion of most samples. However, the loss on ignition of the fraction

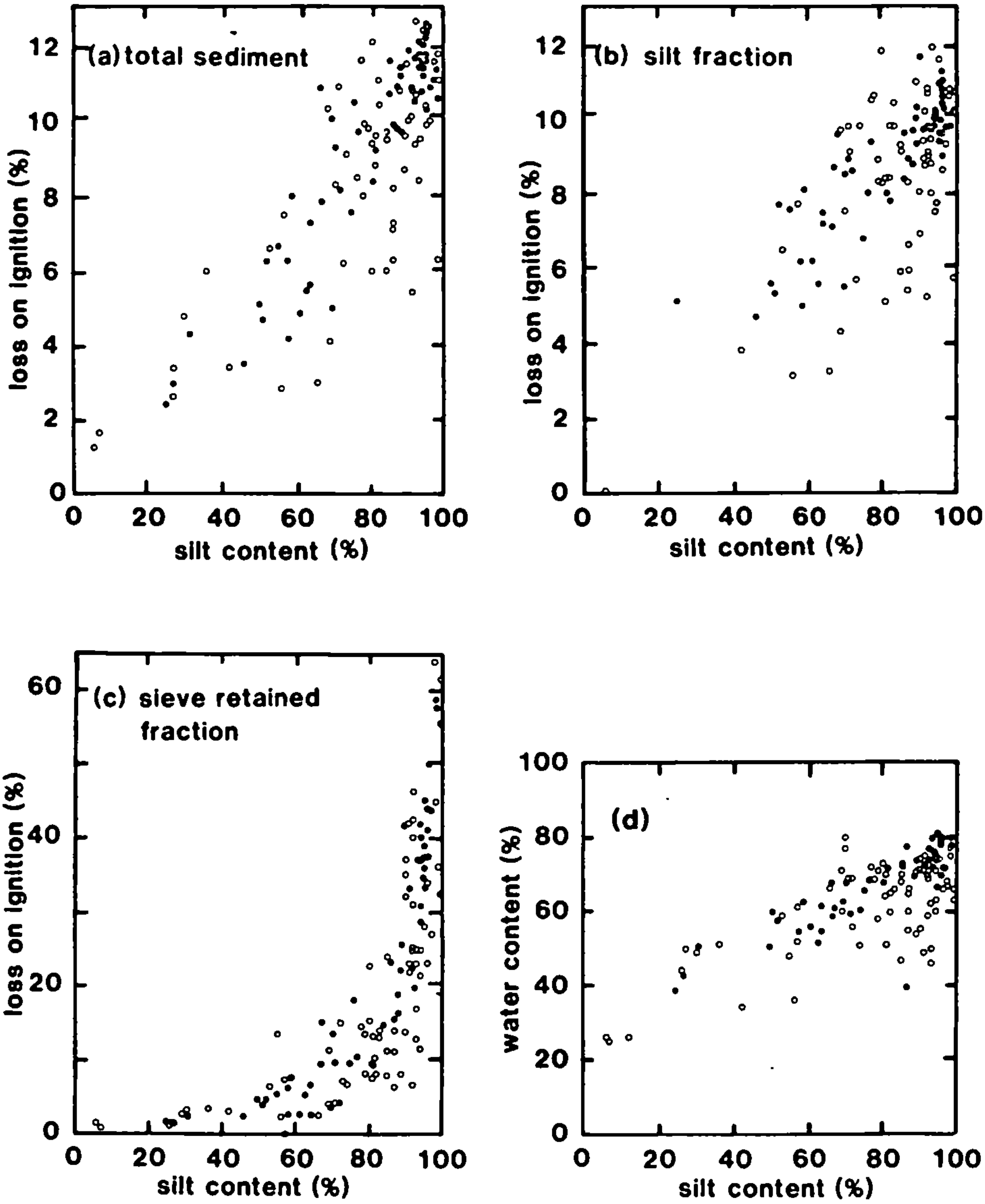


Figure 3.2 The organic content of Tamar sediments relative to silt content for (a) the total sediment, (b) the silt fraction and (c) the sieve-retained fraction. The relationships between water content and silt content of the sediments is shown in (d). February values are shown as solid circles, August values as solid circles.

retained by the sieve exhibited a much greater spread of values. These ranged from 1-3% in the regions of low silt content to 50-60% in samples with very high (95%) silt content.

Water content

Water content measurements also followed the axial trend in silt content and appeared closely correlated (Figure 3.2(d)). Sediment water content was highest at about 70% by weight in the areas of high silt content and reduced to 20-30% in both the riverine end member and the predominantly sandy marine and mid-estuarine regions.

Silt size analyses

The results of the size analyses of the silt fraction obtained using the Malvern Instruments apparatus are summarised in Figure 3.3. This depicts the mean values (±1 standard deviation) obtained by averaging the analyses within distinct estuarine regimes. In the winter data, set the results were averaged for the up-estuarine silt maximum (8-11km), the mid-estuarine silt minimum (12-15km) and the lower estuary silt maximum (18-22km). These distinct sedimentary regimes were not so apparent under summer conditions but samples were examined from corresponding regimes, now located at 2-7km, 14-17km and 23-26km, respectively.

Generally, the particle size distributions were similar throughout the estuary in summer and winter with modal values in the range 16.7-28μm. The summer modal values tended to be slightly lower (16.7-21.4μm) than in winter and in both data sets the distributions became less peaked, the standard deviations increased and the distributions tended more towards bi- or tri- modality with increasing distance down the estuary. In each analysis, from 3 to 7% by weight of the

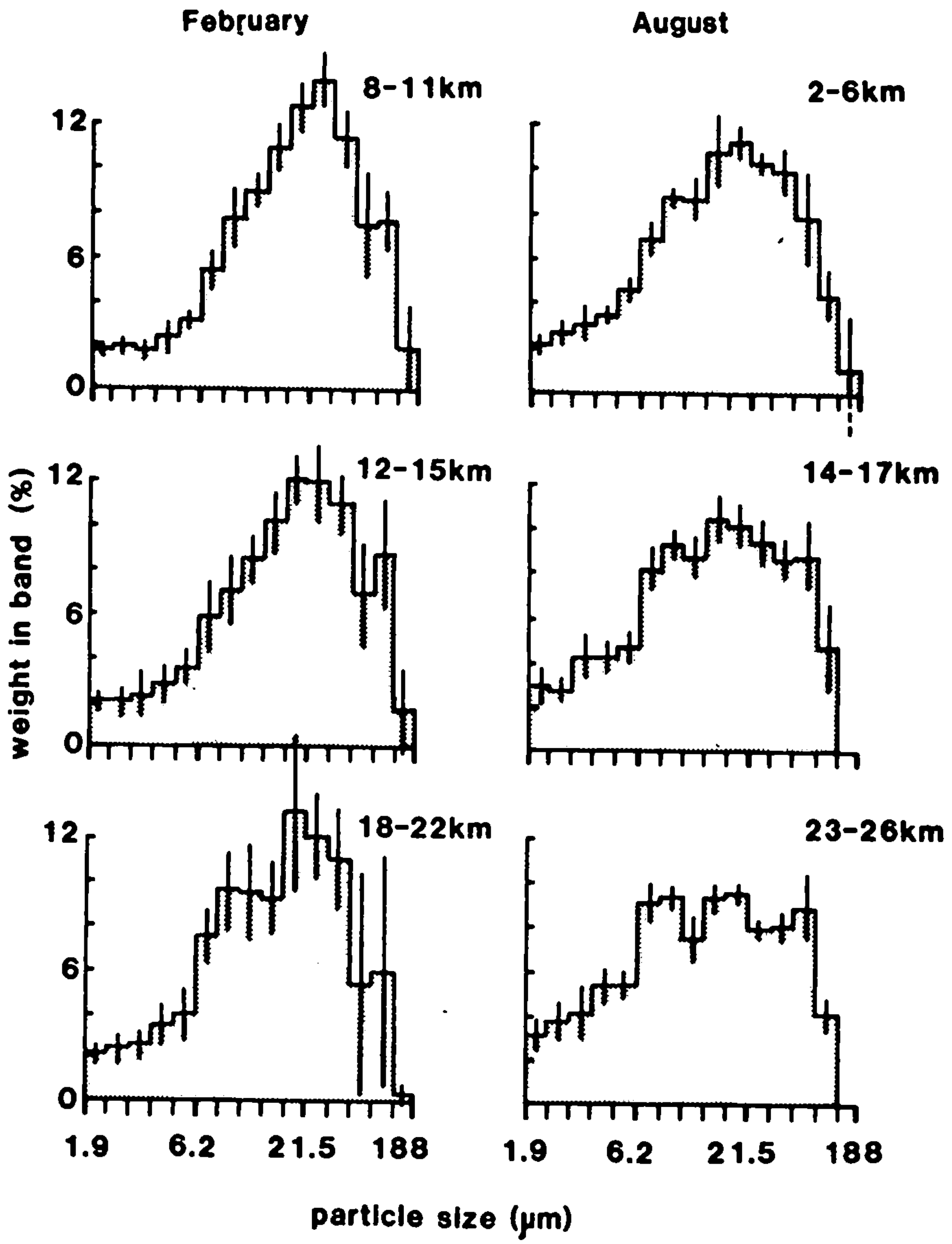


Figure 3.3 The mean particle size distribution of the silt fraction of sediments from various regions of the Tamar Estuary in winter (February) and summer (August) as measured by laser diffraction.

distribution fell below the smallest size interval (1.9-2.4μm).

3.2.4 Discussion and conclusions

Axial distributions of size and composition are, for the most part, consistent with observations of the suspended particle characteristics (Section 2). It must be remembered, however, that the sediment material has been subject to chemical and physical deflocculation prior to the size analysis. Despite sieving at 63μm, up to 8% by weight of the samples was measured in the size band 87.2-188μm illustrating the effect of particle shape on size determinations where the majority of techniques assume a spherical form. The tendency away from well sorted, monomodal size distributions with distance down-estuary is consistent with the suspended particle behaviour and reflects the topographical complexity of the lower estuary (Figure 1.2) which gives rise to various source materials and provides a wide range of errosional and depositionary environments. In contrast, the narrower, regular channel of the upper estuary, combined with hydrodynamic selectivity implicit in the generation of turbidity maxima by gravitational circulation and tidal pumping, leads to a much narrower particle size distribution and far less variability between the samples. The difference between the summer and winter size distributions almost certainly reflects the more quiescent summer conditions which allow a higher proportion of smaller particles to be incorporated into the sediments.

Estimation of the organic content of sediments by their loss on ignition is crude but simple and widely used (McCave, 1979). However, the results must be viewed with caution as some of the weight loss can be attributed to bound water from clay minerals (Mook and Hoskin, 1982). Nevertheless, it has been shown (Meade et al., 1975) that loss on ignition is approximately equal to 1.6 times the concentration of particulate organic carbon (POC) which is consistent with data from the Tamar for both sedimentary and suspended particles. At very high (>95%) silt contents the organic content of those particles retained by the sieve (i.e. >63μm) is extremely large although these particles represent only a small percentage of the total weight. This reflects the strong physical sorting and selection of material, based on settling rates, that occurs in this estuary. For the larger particles to possess comparable settling characteristics to the smaller, mainly mineral (organic content about 10-12%) silt particles, they must be much less dense e.g. plant debris.

Establishing the provenance of the various components of estuarine silt and the processes that control their distribution will ultimately require better information derived from specific "tracer" components and an improved understanding of estuarine hydrodynamics. However, coupled with the information on seasonal sediment fluxes (below), these data provide a substantial core of basic information on sedimentary properties that complements the studies of suspended particle behaviour and heterogeneous chemical processes.

3.3 BED SEDIMENT DYNAMICS

3.3.1 Introduction

Observations of sediment accretion in the upper reaches of the Tamar during summer months combined with measurements of seasonal changes in the silt distribution (Section 3.1) suggested that, besides experiencing periodic resuspension and deposition under the influence of diurnal tidal action, large quantities of sediment undergo significant axial migrations on a seasonal time scale. A study was therefore initiated to quantify the extent and rate of this process.

3.3.2 Choice of method

Sediment cores and various dating techniques have been employed to derive average sedimentation rates over periods of ten years or more (Robbins & Edgington, 1975; Clifton & Hamilton, 1982). However, the study of sediment movements over short (<1 year) time scales requires that the measurement technique takes account of erosional events as well as deposition. Conventional levelling techniques have been used to record vertical changes in sediment altitude, usually along a series of lateral transects (Anderson & Rust, 1979; Anderson et al., 1981). These techniques are particularly suited to observations in small bays and inlets where the tide allows complete access at low water but were considered impractical for a transect over 30km in length with regions where the only access was by small boat. The use of vertical stakes is much less precise although they have been used to good effect in sediment mobility studies (Pickrill, 1979; Frostick & McCave, 1979). This technique offerred the most practical approach for this study for which the indications were that the signal would be large relative to potential errors introduced by this particular measuring technique.

3.3.3 Fieldwork procedure

Thirty wooden stakes, each 2m long by 4cm square, were treated with a wood preservative and positioned on the mud-banks and intertidal flats along the estuary at roughly 1km intervals (see Table 3.2). The positions were chosen to provide optimum coverage of representative sites whilst avoiding areas where accessibility could result in tampering or where the presence of the stakes might be a nuisance, for example, in areas worked by salmon fishermen or local boatmen. Additionally, sites adjacent to streams or drainage ditches were avoided to minimise local perturbations. The stakes were installed, and later monitored, from small inflatable craft which proved to be the most practical means of access to the mud banks. The majority of the stakes were positioned such that they became uncovered at tidal elevations between the neap and spring low-water levels and were driven approximately 1.8m into the mud taking care to keep them as near vertical as possible. Measurements were carried out monthly during spring tides at low water. Generally, there was insufficient time in one semi-diurnal tidal "window" to measure all the stakes and measurements were taken over two consecutive days.

Net sediment loss or gain at each stake site was determined by measuring the exposed portion of the stake to the nearest 1mm with a plastic ruler and comparing the reading with that obtained on the previous month. The ruler was fitted with a 20cm plastic T-bar indexed at 0cm which was placed on the mud, parallel with the axis of the river, on the side nearest the river. This procedure ensured operational consistency especially on sloping mud banks. In cases where the stake caused localised scouring, the T-bar was placed across the hollow to rest on the mud on either side. These observations extended over a period of 14 months.

3.3.4 Data reduction

For each station, sediment altitudes relative to the stake were compared from month to month and a net loss or gain (cm month^{-1})

calculated. For plotting purposes, the data were normalised by the addition of an altitude factor, equivalent to the largest negative change in sediment altitude from time zero at each station. This effectively defined a plane throughout the estuary, indexed at 0m, below which no further erosion occurred during the year. The changes in altitude were converted to changes in volume (m^3 wet sediment) by multiplying the change in altitude per month, for the given station, by the surface area of the 1km section of estuary in which each stake was situated. Some segments contained two stakes and two segments were 2km in length.

3.3.5 Results and discussion

Monthly changes in sediment altitude at each pole are listed in Table 3.2 and depicted as a series of axial profiles (Figure 3.4). From January to April mobile sediment was absent in the upper 5km of the estuary but accumulated to depths of 10 to 20cm in localised depositional areas between 10 and 20km from the weir. From mid to late summer, however, the mobile sediment in the mid-estuarine region (10 to 20km from the weir) became depleted but marked accumulations, up to 40cm in depth, were recorded in the upper 8km of estuary. The greater depth of sediment observed in the upper estuary in summer compared with the mid-estuary in winter almost certainly reflected the reduced width of river in that area and hence smaller surface area available for sedimentation.

For a given river flow, the position of the turbidity maximum oscillates through 12km, or more, between high and low water (Morris, et al., 1982b). Semi-diurnal cycling of particulate material between the sediment and suspended phase through this region, coupled with the

Table 3.2 Positions of mud pole sites, monthly changes in sediment elevation at each site and area of each 1km segment of the estuary.

Pole No	Position of pole (km below weir)	Segment of estuary (km below weir)	Area of segment (m^2)	Monthly changes in sediment altitude (cm)											
				J-F	F-M	M-A	A-M	M-J	J-J	J-A	A-S	S-O	O-N	N-D	D-J
1	3.1	3-4	4.0×10^4	0	0.8	1.5	11.1	8.9	9.0	7.9	-2.9	-18.8	-15.0	-2.4	0
3	3.6	4-5	4.0×10^4	-3.4	-0.7	0.1	6.0	7.8	5.5	5.3	0.9	-0.5	-0.8	-3.2	-8.3
6	6.2	5-6	5.0×10^4	-1.2	-0.1	0.1	4.3	0.3	12.0	8.7	3.7	2.7	-15.4	-13.8	-0.9
7	7.2	6-7	5.5×10^4	10.5	8.1	8.6	9.0	-0.9	0.7	-3.8	-0.6	5.0	-4.6	-14.6	-6.9
8	7.6	7-8	6.0×10^4	-0.2	4.6	4.6	3.9	11.1	1.5	-1.6	0.5	4.4	-0.9	-4.6	-4.0
9	9.4	8-10	1.4×10^5	-1.9	1.6	1.7	-2.8	2.3	-2.2	-2.2	-2.3	4.8	-1.8	-2.2	-0.6
10 & 11	10.2, 10.5	10-11	9.0×10^4	-0.1	0.2	0.8	0.9	0.4	-3.1	0.1	1.3	-1.8	-0.1	1.0	-1.5
12	11.4	11-12	1.3×10^5	0.5	0.1	1.1	-2.5	-1.5	-2.0	-1.9	-1.7	-0.6	0.3	-0.8	1.9
13	12.0	12-13	1.7×10^5	1.0	2.6	-2.2	-1.2	-3.2	-2.6	-4.0	-2.9	-4.9	5.2	17.6	0.8
14	13.3	13-14	1.6×10^5	-0.2	1.0	2.9	-1.5	1.5	-2.0	-0.7	-2.4	-0.8	-0.1	0	0.3
16	14.7	14-15	2.8×10^5	-0.2	0.2	0.4	-0.2	-0.1	-0.1	0.1	-0.2	1.0	-1.2	-1.0	0.3
17	15.2	15-16	3.1×10^5	0.2	-0.1	1.0	-0.8	3.2	0.3	-0.8	3.6	-2.4	1.9	-0.9	-0.8
18	15.9	16-17	2.7×10^5	0.7	-0.7	-1.0	-1.8	-3.5	-3.3	-1.7	-0.1	0.9	3.6	7.7	0.7
20	17.7	17-18	4.0×10^5	-0.3	-1.5	-3.0	2.2	1.0	-0.8	1.1	-0.5	-2.1	-0.6	-0.3	0.7
21	18.1	18-19	4.8×10^5	7.6	0.5	-2.6	-1.9	-1.4	-7.9	-8.5	-1.1	4.3	7.4	6.0	6.0
22 & 23	19.0, 19.9	19-20	6.6×10^5	5.2	0.6	0.1	0.8	-1.5	-3.1	1.8	-0.8	-4.3	0.1	1.8	1.3
24	20.2	20-21	8.9×10^5	1.3	1.9	2.0	5.1	0.8	0.6	2.5	0.2	0.6	0.1	-0.8	1.6
25	21.0	21-22	8.9×10^5	0	-1.0	0.5	-0.3	-0.5	0.1	0.6	-0.2	-2.9	-0.9	-0.6	3.8
26	22.2	22-23	8.9×10^5	-1.3	-0.2	0.6	-1.8	-0.3	-1.1	-0.1	0.5	-1.3	-1.1	-0.2	-0.3
27	23.6	23-25	9.2×10^5	2.2	-1.1	-1.8	0.9	-4.4	-1.8	0.8	8.2	1.3	0.1	-0.4	-1.5
28	26.9	25-27	1.4×10^6	0.5	0.4	0	-0.2	-2.5	-0.8	1.9	0.3	1.1	0.4	-0.6	-0.2
29	28.9	27-29	1.6×10^6	-1.5	-0.9	0.4	0.3	0.3	0.1	-0.5	-0.3	-0.4	0.1	-0.4	-0.5
30	30.0	29-30	9.8×10^5	-0.1	-0.4	-1.0	-0.5	-1.2	2.5	1.4	-2.6	-1.3	4.0	-1.8	-0.3

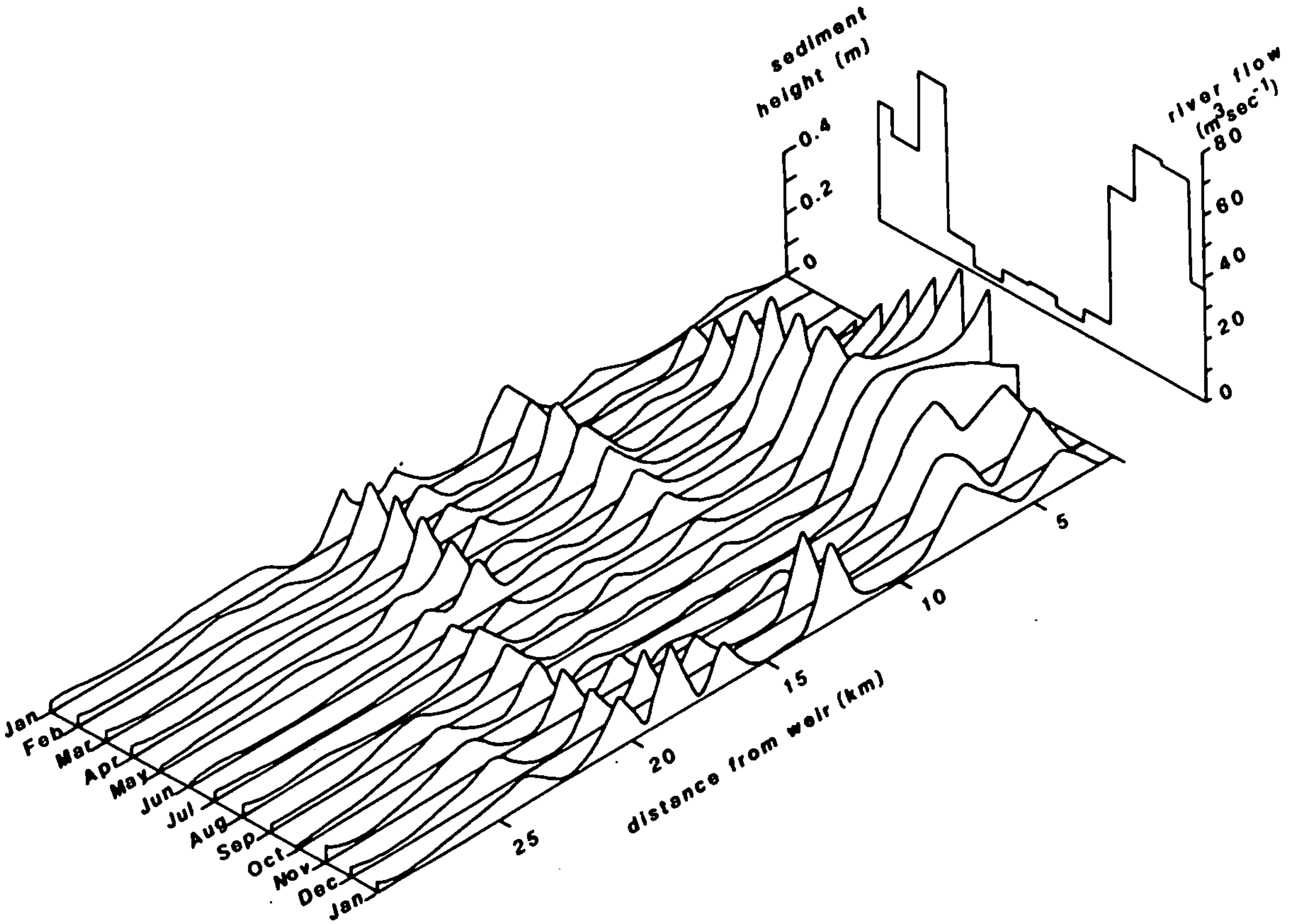


Figure 3.4 Axial profiles of bed-sediment depth over a seasonal cycle and monthly mean river flows at Gunnislake for the period of the measurements.

hydrodynamic trapping of particles in the turbidity maximum, can therefore account for the observed localisation and seasonal migration of a bed sediment shoal. For example, over a stable period of low river flow, sedimentary material mobilised into the water column up- or down-estuary from the turbidity maximum will tend to become entrained into the turbidity maximum region by the forces that generate and localise the turbidity maximum. Over a sufficiently stable period of river flow, therefore, the majority of mobile sediment in the estuary will be entrained either within the turbidity maximum or, through settling, within the sediment shoal that is delineated by the tidal excursion of the turbidity maximum. As river flow increases, the zone of the turbidity maximum migrates down-estuary and the mobile bed sediment tends to accompany it (Figure 3.5).

River flow exhibits a marked seasonality in response to annual rainfall (Figure 3.6) and is probably the controlling, though not necessarily sole, factor driving this cyclic process. For instance, the distribution of particulate material between the sediment and suspended phase is primarily a function of tidal energy although other factors are involved e.g. wind/wave action, scour on bends or at sites of reduced cross section and internal waves caused by discontinuities in the bed profile (New et al., 1986). Once in suspension, the asymmetry in the ebb/flood tidal currents combined with the location of the turbidity maximum will determine the distribution of the bed sediment. It may be significant therefore, that both major directional switches in bed sediment flux correspond with periods of increased tidal range at the spring and autumn equinoxes (Figure 3.6) as well as with seasonal changes in river flow.

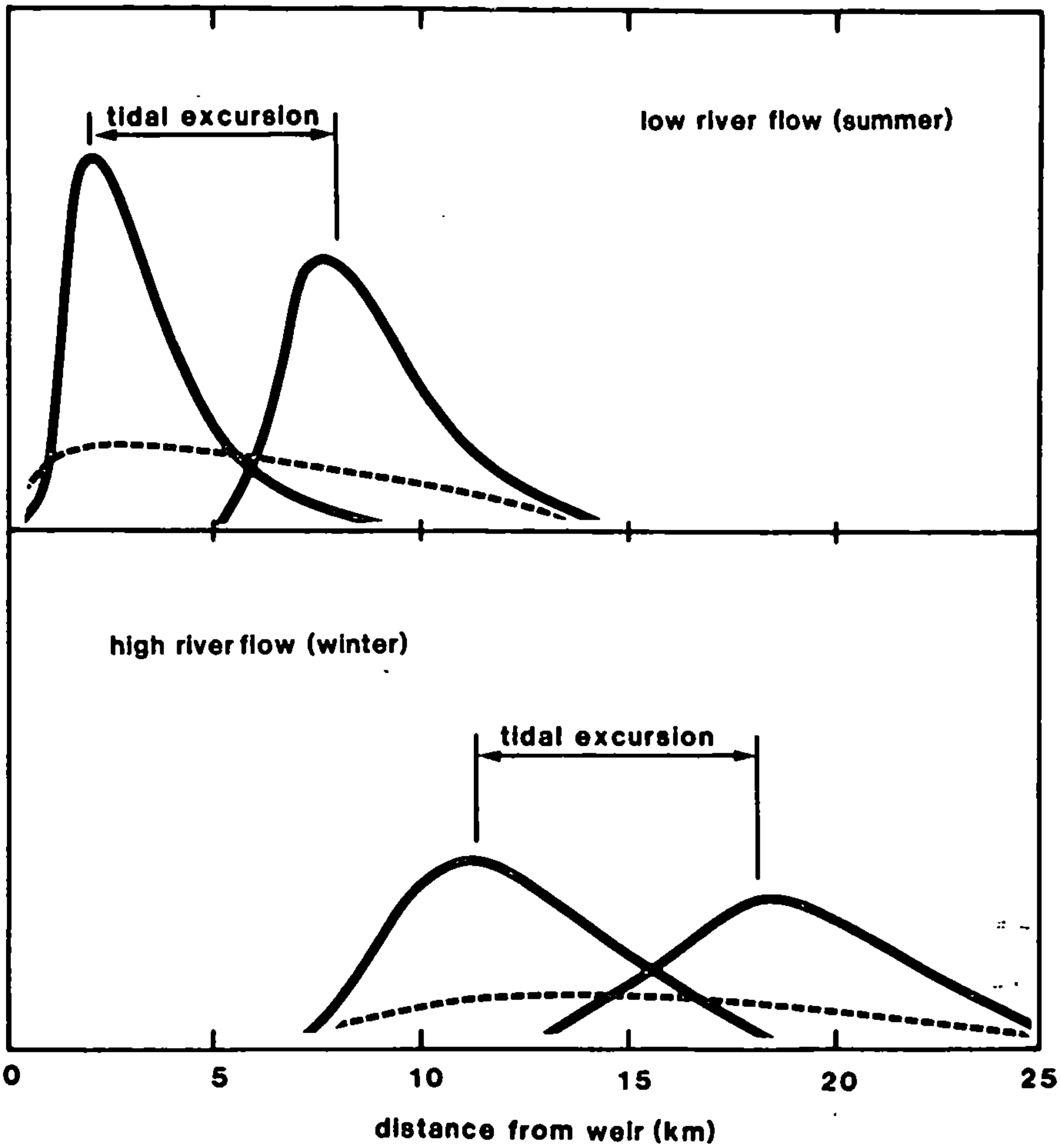


Figure 3.5 A schematic representation of the positional relationships between the turbidity maximum and the bed-sediment shoal under high and low river flow conditions. The solid lines represent suspended solids and the broken line bed-sediment.

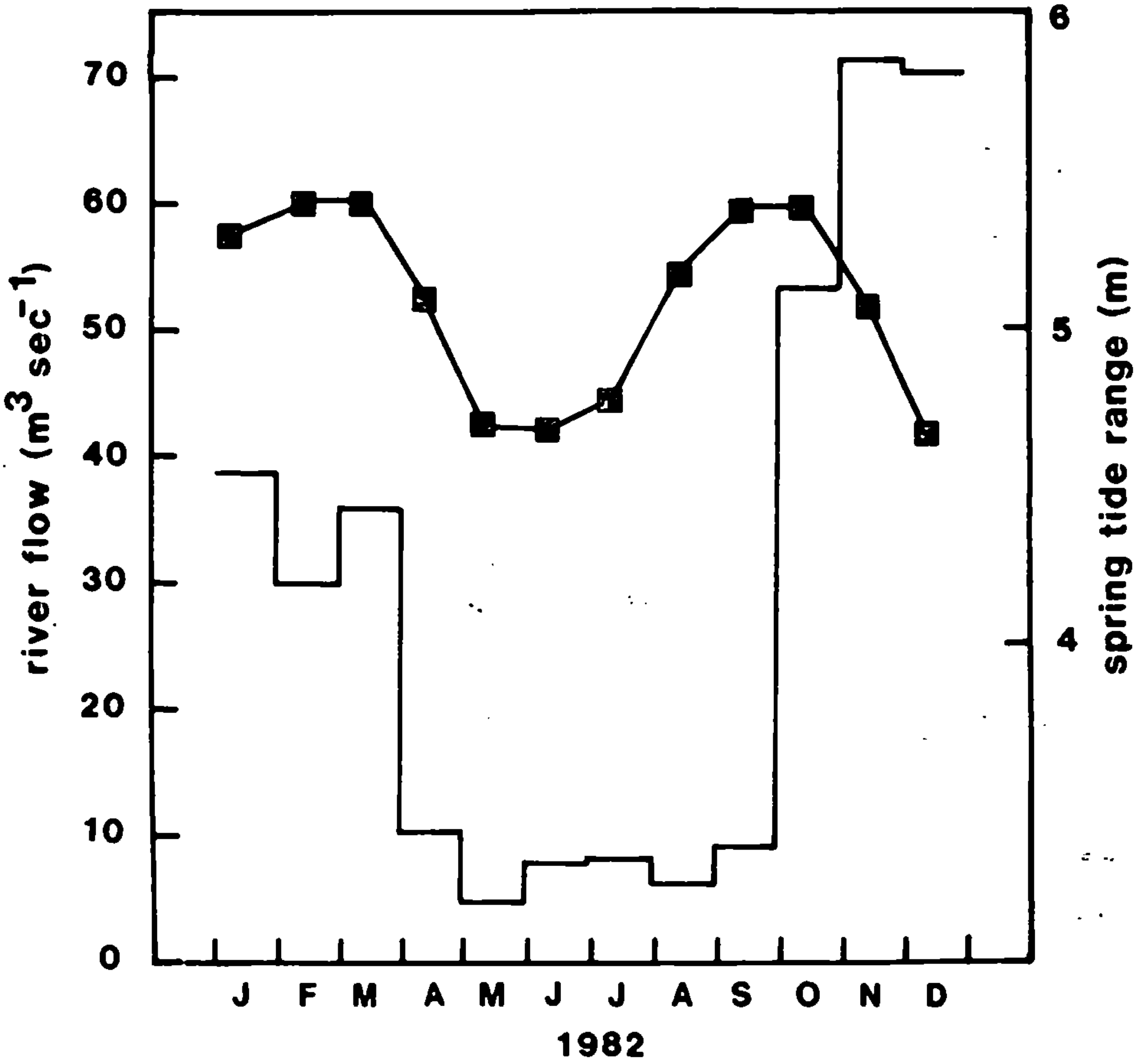


Figure 3.6 The seasonal variation in mean monthly river flow at Gunnislake (histogram) and in the range of spring tides at Devonport (■) for the period of the bed sediment mobility survey.

This pronounced cyclic migration of mobile sediment in which sedimentary material is accumulated in the upper estuary during summer months to be redistributed in depositional regions of the mid-estuary in the winter must significantly affect the accumulation and fluxes of chemical species which associate with particles or which, through reductive solubilisation, become concentrated in the sediment pore water.

3.4 AN ESTUARINE SEDIMENT BUDGET

3.4.1 Introduction

Using the information obtained in the previous sections, an attempt was made to quantify the principal particle reservoirs and determine the fluxes between these reservoirs. To do this, the physical dimensions of the estuary were required as well as the rate of particle influx from the river.

3.4.2 Determination of the bathymetry, surface area and volume of the Tamar.

The cross-sectional widths of the Tamar at 1km sections along the axis of the estuary and information on the bathymetry of the central channel were taken from British Admiralty chart No 871 and from George (1975) and are listed in Table 3.3. From this information the surface areas and mid-tide volumes of each 1km section of the estuary were calculated. This treatment was restricted to the region from Weirhead (0km) to the confluence of the Tamar with the Tavy (21km) below which the river widens markedly and the topography becomes much more complex. Within this area, the width increased gradually from 40m at the weir to

Table 3.3 The bathymetry and widths at mid-tide of the cross sections at 1km intervals along the Tamar Estuary from Weir Head (0km) to Weir Point (21km) and the calculated surface areas and volumes of the segments between adjacent 1km sections.

distance from Weir Head km	width at station m	surface area of segment m^2	mean depth at mid-channel m	volume of segment m^3
0	40	-	1.6	-
1	30	3.5×10^{4}	1.6	5.6×10^{4}
2	30	3.0×10^{4}	1.6	4.8×10^{4}
3	40	3.5×10^{4}	2.3	6.8×10^{4}
4	40	4.0×10^{4}	2.0	8.6×10^{4}
5	40	4.0×10^{4}	2.3	8.6×10^{4}
6	60	5.0×10^{4}	2.3	1.2×10^{5}
7	50	5.5×10^{4}	2.8	1.4×10^{5}
8	70	6.0×10^{4}	2.9	1.7×10^{5}
9	60	6.5×10^{4}	5.9	2.9×10^{5}
10	80	7.0×10^{4}	3.1	3.2×10^{5}
11	100	9.0×10^{4}	3.0	2.8×10^{5}
12	150	1.3×10^{5}	3.8	4.3×10^{5}
13	180	1.7×10^{5}	2.9	5.5×10^{5}
14	160	1.7×10^{5}	4.8	6.6×10^{5}
15	160	1.6×10^{5}	7.8	1.0×10^{6}
16	400	2.8×10^{5}	5.3	1.8×10^{6}
17	220	3.1×10^{5}	6.0	1.8×10^{6}
18	310	2.7×10^{5}	4.9	1.4×10^{6}
19	480	4.0×10^{5}	5.0	2.0×10^{6}
20	480	4.8×10^{5}	7.3	3.0×10^{6}
21	840	6.6×10^{5}	6.2	4.5×10^{6}

840m at 21km. Although localised "holes" caused by scour on bends were often much deeper, the mean depths at mid-tide were not large and increased gradually from 1.6m at the weir to 6.2m at 21km. Seaward of this point, the depths increased considerably.

3.4.3 Seasonal sediment fluxes derived from bed sediment mobility

Mobile sediment fluxes through each lateral 1km section (kg per month) were calculated by cumulatively summing the changes in volume of sediment per segment from the weir (0km) to Cargreen (19.9km) and applying a factor of 424kg per m^3 to convert volume of wet sediment to mass of particles. Riverine sediment inputs were estimated from South West Water Authority (SWWA) data. This was achieved by regressing suspended particle loads, measured at the water authority gauging station at Gunnislake, against instantaneous river flow to derive a mean particle concentration typical of a particular monthly mean river flow. The product of monthly mean river flow and the appropriate particle concentration are tabulated for the period of the sediment mobility survey in Table 3.4.

The sediment fluxes derived from changes in sediment volume per unit area combined with riverine sediment input do not show a regular seasonal pattern (Figure 3.7) but the trends shed some light on the relationship between seasonal changes in river flow and internal sediment migration. Fluxes between 3 and 15km were relatively low and variable from January to March. They were briefly negative, (i.e. directed down-estuary) during the March-April interval corresponding to a spring increase in river flow. After this, fluxes became predominantly positive and from April throughout the summer there was a dominant up-estuary flux of up to 10×10^6kg per month across each

Table 3.4 Monthly mean river flows for the Tamar at Gunnislake for 1983 and the corresponding sediment inputs calculated from measurements of suspended solids in the river water at the same point. Data courtesy of the South West Water Authority.

Month	Monthly mean river flow $m^3 sec^{-1}$	Riverine suspended sediment input kg
J	37.4	2.48×10^6
F	28.5	1.19×10^6
M	54.5	7.54×10^6
A	8.9	1.44×10^5
M	3.3	4.66×10^4
J	6.6	6.36×10^4
J	6.8	5.09×10^4
A	4.7	3.82×10^4
S	7.9	1.61×10^5
O	51.9	3.08×10^6
N	70.1	8.10×10^6
D	69.4	8.98×10^6

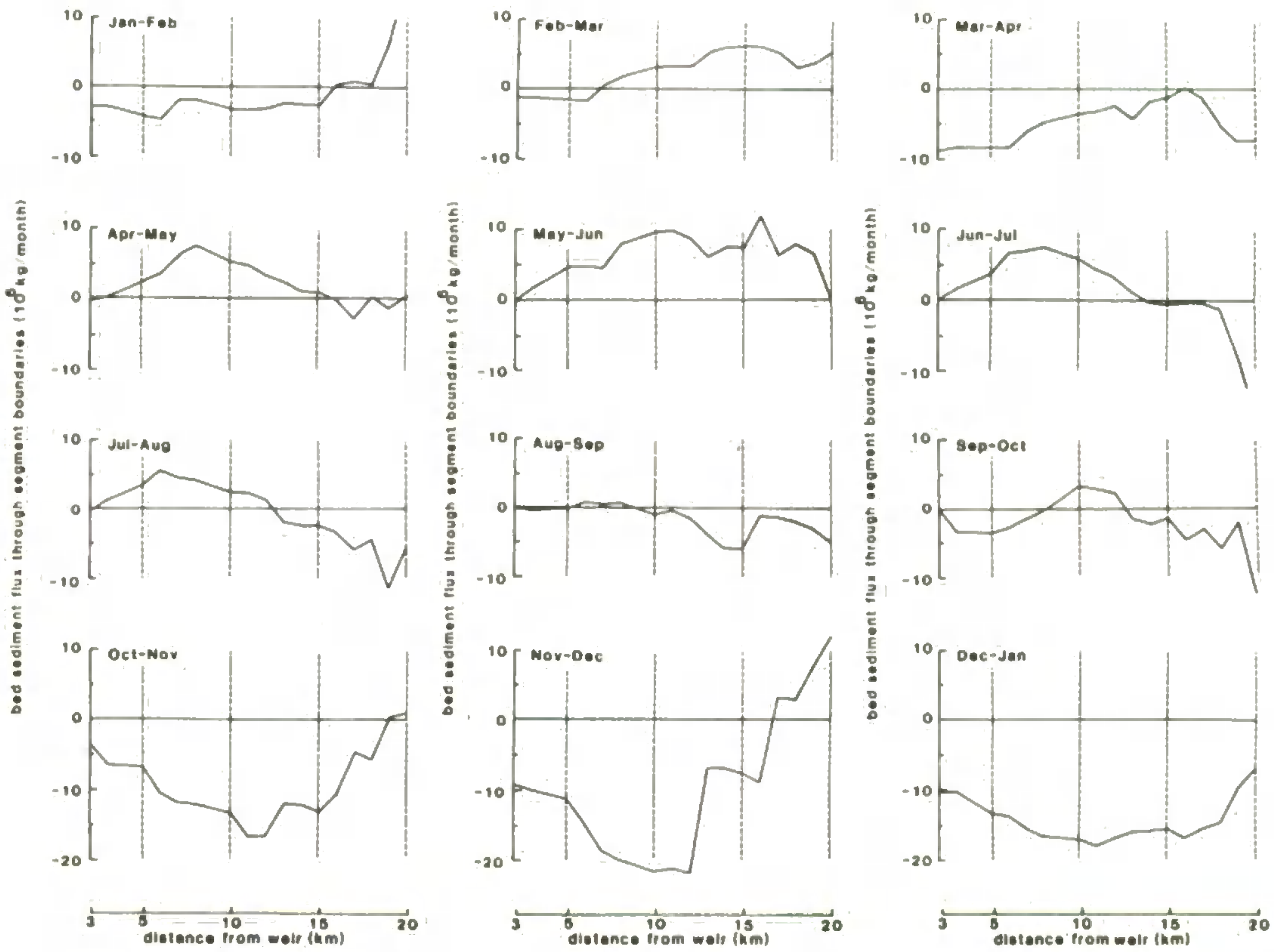


Figure 3.7 Sediment fluxes through the boundary of each 1 km section of the estuary, derived from monthly variations in sediment altitude and riverine sediment inputs.

lateral segment boundary of the estuary as far as 6km from the weir. From this point the fluxes decreased to zero at 3km since significant sediment accumulation was not recorded above this station. After July, the up-estuarine flux persisted in the upper 10km of the estuary whilst fluxes between 12 and 20km first fell to zero and then became negative. From August to September, the positive flux in the upper estuary fell to zero and thereafter the negative (down-estuary) flux became more prominent and extended to the head of the estuary, so that from October through to January negative fluxes of up to 20×10^6kg per month dominated.

The examination of sediment fluxes in this way has revealed a seasonal asymmetry in the internal migration of sediment in that the bulk of up-estuarine movement occurred slowly over five months whereas the down-estuary migration took place in only three months in late autumn. A second feature which became apparent from this treatment was the existence of divergent fluxes at approximately 10-12km for three or four months in late summer. This is consistent with the measurement of low silt concentrations (Section 3.2) in this region of the estuary.

3.4.4 Sediment fluxes and reservoirs

Profiles of suspended solids measured under various seasonal and tidal conditions in the estuary (Section 2) were examined to assess the mass of material suspended in the turbidity maximum. In each 1km section, the mass of suspended particles was estimated from the product of the suspended particle concentration and the volume of the section. The 1km sections were then summed to provide an estimate of the total mass of suspended particles. Similarly, the sediment shoal was quantified by estimating the mean depth of mobile sediment in each 1km section and multiplying it by the appropriate bed areas to produce a volume of wet sediment. During the sieving operation (Section 3.2) a mean value of 424±31kg per m^3 was determined for a range of sediments and this was used to convert the volume into mass of dry particles.

The mass of mobile suspended and sedimentary particles accumulated between April and September in the upper 3-10km of the estuary was approximately 4.0×10^7kg and even if the total riverine influx of suspended material through this period (Table 3.4) was deposited in this zone, its contribution would have amounted to little more than 5.0×10^5kg or 1% of the mass of particles. Following the down-estuary migration of the turbidity maximum zone in autumn, the summer shoal was eroded by river currents. The eroded material was redistributed to be incorporated directly within the relocated turbidity maximum/sediment shoal zone, deposited further seaward where it was subject to up-estuarine tidal pumping, or lost permanently from the system.

The mass of material in the winter sediment shoal was approximately $6.7\text{X}10^7$kg and the influx, between October and March, of fresh riverine suspended material to the estuary was equivalent to a sediment volume of $3.1\text{X}10^7$kg. Thus, material delivered to the estuarine mixing zone in winter from up-estuary of the limit of salt intrusion comprised fresh riverine material and recycled estuarine material, roughly in the proportion 1:1.3. If steady-state conditions are assumed, it is apparent that, without hydrodynamic selectivity, 48% of the material contributing to the turbidity maximum and its associated sediment shoals would be replaced annually by the fresh riverine influx. This is equivalent to a turnover time of two years.

However, only a proportion of the particles in the river influx will have settling characteristics appropriate for selective retention and most of the material is delivered episodically, during short periods of river spate when net export of sediment from the estuary is also strongly favoured. It is possible therefore that the trapped material comprising the turbidity maximum and its associated sediment shoals has a residence time which is considerably longer than 2 years. The extreme case would be where all the material entering the estuary became trapped. In this case, the annual influx of particles (at present day levels) would be equivalent to $7.5\times10^4m^3$ of wet (66% water) sediment which would fill the existing volume of the Tamar ($1.7\times10^8m^3$) in approximately 2.3×10^3 years. This could take, perhaps, 3-5 times longer if sediment compaction was taken into account. The present estuary would have come into existence around 6000 yrs BP (before present) when mean sea level reached its present elevation following the retreat of the glaciers at the end of the last ice age (Fairbridge, 1980). The Tamar is therefore relatively middle-aged and with a good life expectancy even in the extreme case where all the riverine particulate material is trapped within the estuary. In the short-term though, it is reasonable to assume that relatively steady-state conditions exist in which the influx of marine and riverine derived particles approximately balance the loss to the coastal regions.

3.4.5 Tidally dominated fluxes between particle reservoirs

Under low river flow conditions in summer, and mid-way between neap and sping tides, the mass of suspended particles in the turbidity maximum amounted to 6.1×10^4kg at slack water and 5.3×10^5kg during maximum tidal energy at mid-tide. This represented a 7.7 fold increase in the concentration of suspended particles and elevated the proportion of particles from 0.2% to 1.3% of the bed sediment shoal. This mobilisation of sediment equated to an erosion of roughly 4-8mm of sediment over the total surface area of the summer sediment shoal.

In winter, the turbidity maximum was generally located further down the estuary than in the summer. The greater surface area available for deposition and the increased volume of water per 1km segment in the lower estuary meant that the depth of the sediment shoal and average concentrations of suspended particles both decreased. Nevertheless, calculations indicated that the quantities of material in both particle reservoirs were actually greater than in the summer situation. Allowing for a proportion of the potential surface area, equivalent to the central channel at low water, to be exempt from deposition/resuspension processes the mass of particles in the turbidity maximum at slack-water amounted to about 1% of the sediment in the bed shoal and rose to roughly 5% at mid-tide. This was equivalent to an erosion of only 1-2mm over the sediment shoal.

3.4.6 A schematic representation of the sediment budget of the Tamar Estuary

The principal particle reservoirs and their relative location within the estuary under three conditions of river flow are illustrated schematically in Figure 3.8 along with the major pathways and fluxes between them. Under stable condition of low to high river flow, two major reservoirs, the turbidity maximum (A) and the underlying bed sediment shoal (B), are produced. Seasonal changes in river flow cause the locations of these reservoirs to migrate axially within the

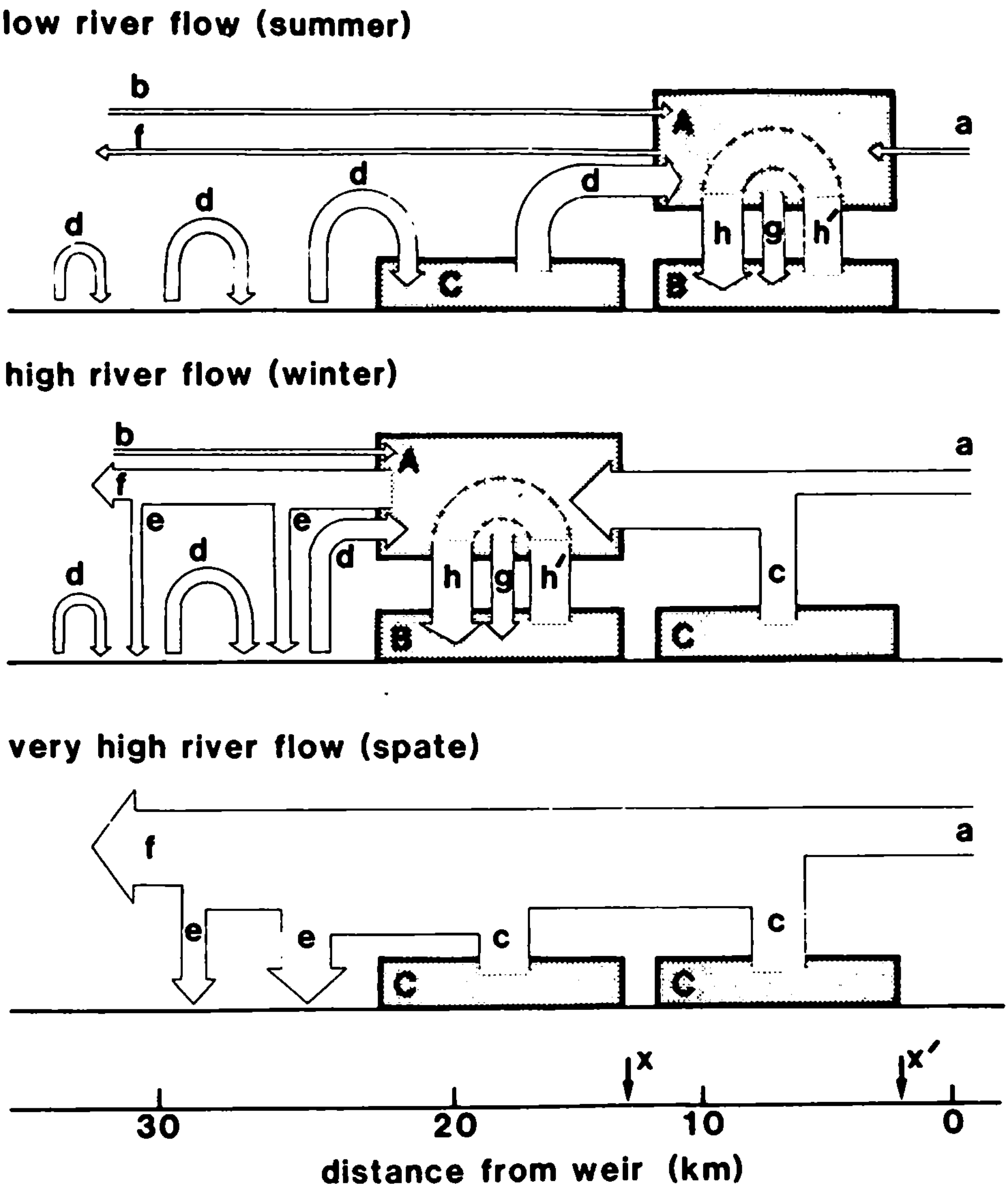


Figure 3.8 Schematic representation of the suspended particle reservoirs (stippled) and fluxes (arrows), enumerated in Table 3.5. The turbidity maximum is box A and the present and earlier sediment shoals are B and C, respectively. The riverine and marine sediment inputs are a and b, respectively. Loss to the coastal region is f, tidal pumping is d, resuspension and deposition are h and h' and deposition within the estuary and the sediment shoal are e and g, respectively. The winter and summer limits of salt intrusion are X and X' respectively on the distance scale.

Table 3.5 Estimation of the masses in the principal particle reservoirs and the fluxes of material between them under summer, winter and spate river flow conditions.

	Particle reservoir size (kg)			
	Reservoir	Summer	Winter	Spate
A	turbidity maximum	3.0×10^5	3.4×10^6	-----
B	sediment shoal	4.0×10^7	6.7×10^7	6.7×10^7
C	previous shoal	$^*6.7\times10^7$	$^*4.0\times10^7$	(decreasing rapidly)

* = decreasing from

	Fluxes between particle reservoirs, (kg month^{-1})			
	Pathway	Summer	Winter	Spate
a	riverine input	8.3×10^4	5.2×10^6	$>10\times10^6$?
b	marine input	small	small	-----
c	winter erosion	-----	6.7×10^6	$>6.7\times10^6$?
d	tidal pumping	$5-10\times10^6$	-----	-----
e	deposition in the lower estuary	-----	$<5.2\times10^6$	-----
f	loss to ocean	(similar to a)	(similar to a)	$>5.2\times10^6$?
g	deposition in the turbidity maximum	d+a-f	c+a-f	-----
h	tidal resuspension and deposition		no net flux	

estuary such that often a second bed-sediment shoal (C), situated at an earlier site of the turbidity maximum, can be identified for a period until it becomes incorporated into the new sediment shoal. Under spate conditions, a turbidity maximum is not generated but suspended solids are elevated because of the large riverine particle influx combined with significant erosion in the upper estuary. This greatly increases the potential for net transport of particulate material from the estuary to the coastal zone and may also lead to deposition in the lower estuary.

Estimates of the principal particle reservoirs and major fluxes are listed in Table 3.5. The turbidity maximum (A), is reinforced through resuspension and deposition (h and h') of shoal sediment (B), with oscillations in tidal stream caused by the semi-diurnal tides. This process is modulated by the spring/neap tidal variation. The other major fluxes are the marine and riverine inputs of suspended particles (a and b respectively), loss to the ocean (f), erosion of sediment at times of high river flow (c), tidal pumping (d) and deposition of sediment in the lower estuary (e).

3.5 SUMMARY AND CONCLUSIONS

1. Surficial sediment characteristics from the region of the turbidity maximum compare closely, in terms of size and organic content, with suspended particles from the same region.

2. Estimates of the quantity of material in the major reservoirs suggest that, except under spate conditions when net export of material from the estuary is favoured, the mass of mobile particulate material held in the estuary is relatively constant over a seasonal cycle and

therefore the outflux to the coastal waters must approximately balance the influxes from the river and marine sources.

3. It is clear from the composition, distribution and internal migration of the bed sediments that the existence and geographical position of the turbidity maximum effectively controls the location of a much greater mass of sedimentary particles contained in an underlying sediment shoal through a combination of cyclic resuspension and deposition and tidal pumping.

Similar mobile sediment shoals have been observed in the Gironde (Allen _et al._, 1980), and in the Thames, the so-called 'Sediment Reaches', (Odd and Owen, 1972; Kendrick and Derbyshire, 1976). By measuring the seasonal flux of bed-sediment material within the Tamar Estuary it is now possible to estimate the contribution which this major transport pathway makes to the distribution of heterogeneously reactive chemical species within the system.

SECTION FOUR

THE HETEROGENEOUS BEHAVIOUR OF TRACE METALS

4.1 INTRODUCTION

4.1.1 Why choose trace metals?

The behaviour of trace metals was chosen to illustrate the importance of heterogeneous processes in estuaries. As mentioned earlier (Section 1.3), the determination of trace metal distributions and behaviour in estuaries has been undertaken by the Chemistry Section at IMER for some years and these, and other studies, have demonstrated marked non-conservativeness for most metals, especially in regions of high turbidity. Trace metal distributions were likely, therefore, to be strongly influenced by particle behaviour. In addition, the behaviour and fate of many trace metals in natural waters are of great interest from environmental and toxicological viewpoints (Harris *et al.*, 1984).

In the Tamar Estuary, Morris *et al.* (1978), Ackroyd (1983), Ackroyd *et al.* (1986), and Morris (1986) have shown consistent, rapid removal of riverine Zn and Cu in the low salinity, high turbidity region of the estuary as well as evidence of inputs of these elements to the mid-estuary (salinity 10-15°/$_{oo}$). The localised nature of the removal at the turbidity maximum and its co-variance with the concentration of suspended solids has been interpreted as strong circumstantial evidence for sorption processes on to solid surfaces being a controlling factor (Morris, 1986). Elsewhere, recent experimental and theoretical work has shown that sorption/desorption interactions with solid phase surfaces can strongly influence the distribution of metals in estuaries (Salomons, 1980; Bourg, 1983; Li *et al.*, 1984a). This section attempts to improve the understanding of the factors that affect trace metal sorption by particle surfaces in estuaries.

The work in this section was undertaken on two main fronts. Firstly, profiles of soluble trace metals were measured in the Tamar Estuary over a range of tidal and seasonal conditions. This helped to consolidate the seasonal coverage obtained in earlier work (Morris _et al_., 1978; Ackroyd, 1983), but more importantly, extended the axial coverage further into the fresh water and improved the frequency of sampling in the turbid, 'reactive' region of the estuary at the interface between the fresh and brackish regions of the estuary. Secondly, laboratory studies were undertaken to examine the partitioning of trace metals between the particle and solution phases under estuarine conditions.

4.1.2 Metal speciation in natural waters

A knowledge of the speciation of a metal is important to the understanding of its transport and behaviour. It has been recognised for some time that the total pool of a particular metal in an aquatic environment is distributed between several physically and chemically separate compartments (see for examples, Chau and Lum-Shue-Chan, 1974; Florence, 1977; Batley and Florence, 1976a, 1976b; Duinker and Kramer, 1977; Florence and Batley, 1977; Batley and Gardner, 1978; Laxen and Harrison, 1981a, 1981b; Hart and Davies, 1981).

Studies of metal speciation invariably employ operational criteria based on analytical fractionation. Several procedural schemes have been presented (see for example, Batley and Florence, 1976a; 1976b and Laxen and Harrison 1981a) to evaluate the fraction of a metal incorporated in each species. The concept of determining speciation through operational criteria is illustrated in Figure 4.1 in which the total pool is divided firstly into soluble and particulate metal by filtration with a 0.45μm pore-sized filter. The soluble fraction is considered, additionally, to be comprised of colloidal, complexed and free ionic metal whilst the particulate fraction is subdivided into adsorbed (exchangeable or non-detrital) and structural (detrital) components.

The distribution of a metal between these various species depends upon the degree of interaction of the metal with the components of its environment. Under any given set of environmental conditions the resulting speciation is a balance between the affinity of the metal for the various reservoirs (organic complexes, particle surfaces, ion-pairs or free ions). In estuaries, the chemical environment changes continuously along their axes giving rise to marked temporal and spatial changes in speciation. This is clearly illustrated in the model speciation diagrams (Figure 4.2) for the metals Cu, Zn, Ni and Pb produced by Bourg (1983). In this model, a variant of the mathematical model developed by Mantoura et al., (1978), the relative proportions of all species undergo pronounced changes with salinity alone. Both the pH (8.0) and suspended solids (30mg ℓ^{-1} having the surface properties of silica) were maintained at constant values throughout the estuary.

The relative contribution of particular species to the total pool of a metal can be assessed by various analytical methods. For instance, direct electrochemical methods measure free (labile) metal which is considered to be the significant species in terms of biological effects whereas ion-exchange resins extract labile plus complexed fractions but exclude most colloidally bound metals. Solvent

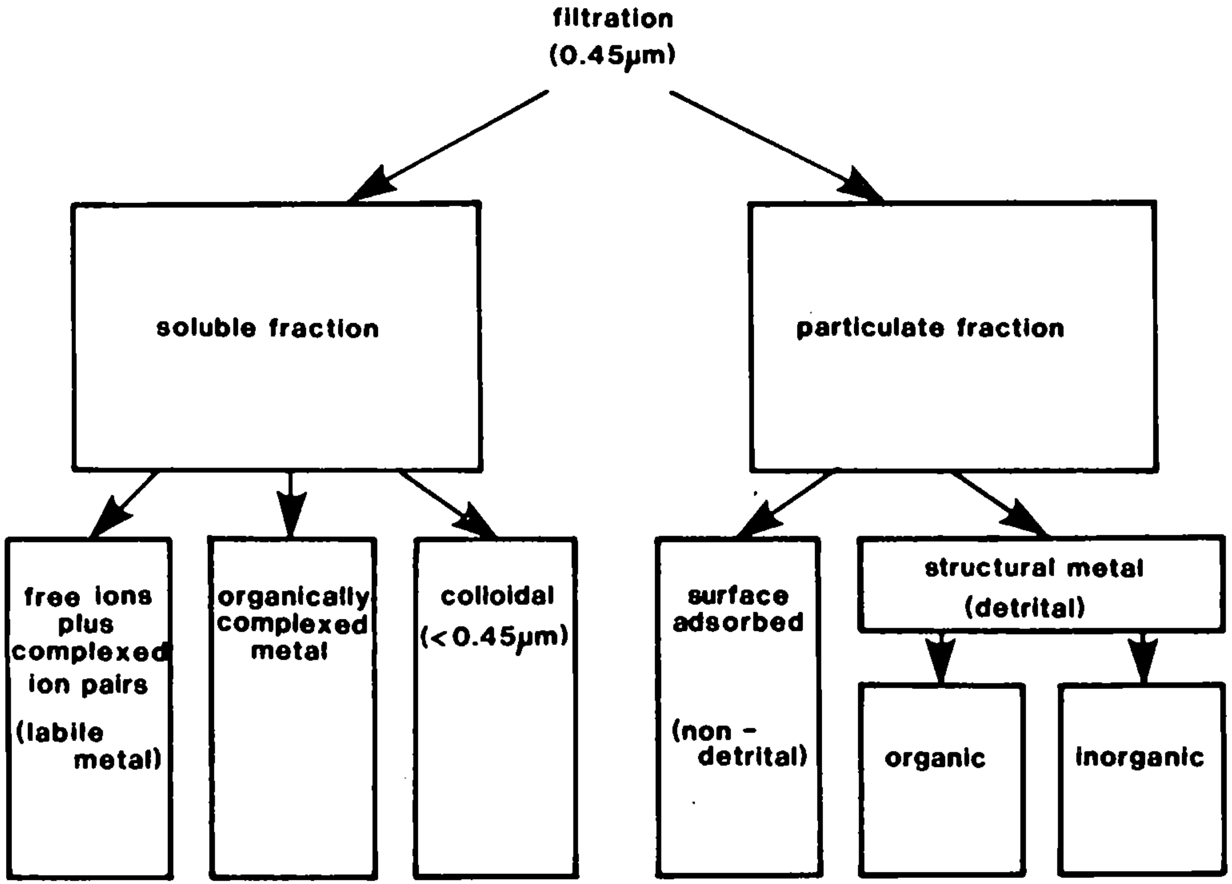


Figure 4.1 Metal speciation by operational criteria.

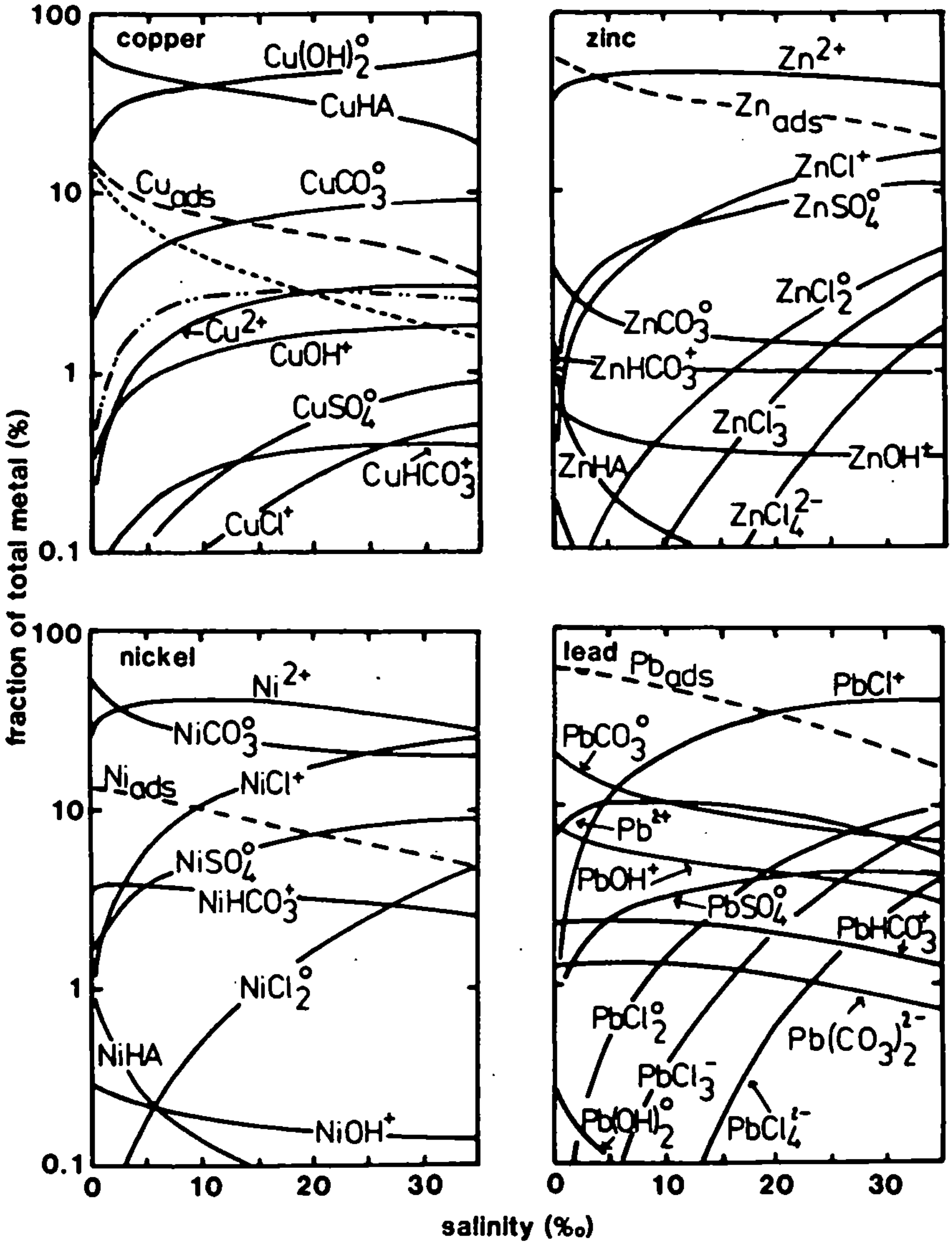


Figure 4.2 Equilibrium speciation of the metals, Cu, Zn, Ni and Pb in a model estuary at constant pH and suspended solids concentration. Reproduced from Bourg (1983) with the permission of Plenum Press, New York.

extraction with complexing agents such as APDC (ammonium pyrrolidine dithiocarbamate) and DDTC (diethylammonium diethyldithiocarbamate) in suitable solvents MIBK (methyl isobutyl ketone) or freon, will recover similar fractions to ion-exchange resin but will not measure 'kinetically robust' complexes or colloidally bound metals (Danielsson et al., 1978). Chemical manipulations such as acid digestion, solubilisation (or exposure to ultraviolet light in the case of organically bound metals) are required to convert these inaccessible species to a labile form that can be determined using the above methods.

Evaluation of the particulate metal species can be simply achieved by splitting the metal into detrital and non-detrital fractions through the use of a mild leaching agent, for example, dilute acetic acid or ammonium acetate. Graduations in the degree of availability of particle-associated metals can be measured using progressively stronger leaching agents to successively remove increasingly strongly bound fractions (Hirst, 1962; Luoma and Bryan, 1981).

For this study, the principal requirement was to evaluate the relative transport of the two major species, that is, the soluble metal and metal associated with particulate phases. This was accomplished by determining the total soluble fraction analytically and assuming that departures from conservative behaviour were attributable to exchange with the particle phases. The following procedure was adopted, samples were filtered using 0.45μm pore sized filters and the soluble metals determined by flame atomic absorption after extraction with Chelex 100 ion-exchange resin.

4.2 THE DISTRIBUTIONS OF TRACE METALS IN THE TAMAR ESTUARY

4.2.1 Sample collection, preconcentration and analysis

Samples for trace metal analysis were collected using a pre-cleaned, all-plastic bucket (reserved strictly for this work) and stored in 10ℓ polyethylene carboys. Filtration was accomplished as quickly as possible using a large volume pressure filtration system on board the vessel. When samples were not filtered immediately, the time delay was recorded but all samples were filtered within six hours. The filters were 142mm dia., 0.45μm pore-sized membranes (Sartorius Ltd.) and were rinsed prior to use with 500mℓ of sample which was then discarded. After collection the samples were returned to the laboratory in 10ℓ polyethylene carboys which were well rinsed with filtered sample prior to filling. The carboys were kept strictly for trace metal work and except for an initial acid soak (10% HNO_3 for 24 hours) when first purchased, the containers were simply rinsed with deionised water after use and with sample before filling.

In the laboratory the samples were passed through columns of Chelex 100, ion-exchange resin (Bio Rad Laboratories Ltd.) following the method of Kingston et al. (1978). Each column contained 15mℓ of settled resin slurry in the ammonia form (Figure 4.3). The preparation of the resin was undertaken in batches to minimise inconsistencies in the performance and efficiency of individual columns. The procedure involved two successive washings with 50mℓ volumes of 2N HNO_3 to remove any metals followed by copious rinsing with deionised water to bring the pH to above 6.0. At this stage the resin was converted into the ammonia form with two 50mℓ aliquots of 2N NH_4OH and again washed with deionised water until the pH was less than 8.0.

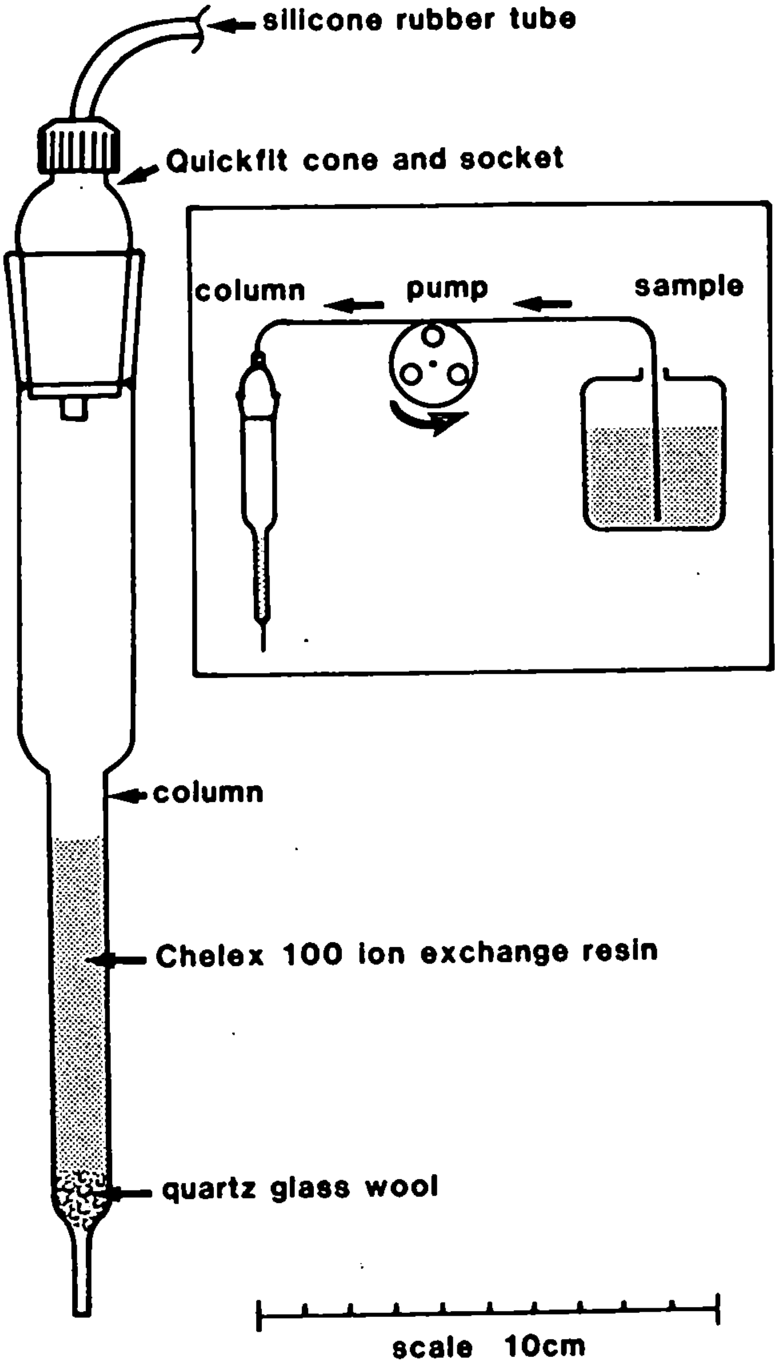


Figure 4.3 Details of the ion exchange columns used for the extraction of trace metals and, inset, a schematic diagram of the pumping arrangement used to transfer samples to the columns.

The samples were transferred to the columns directly from the carboys using 10 channel peristaltic pumps delivering 4-5mℓ min^{-1}. The volume of sample passed through each column was determined by marking the initial level of sample on the carboy and then measuring the volume required to regain that level once the sample transfer was complete. Operational blanks were obtained by taking the effluent from a column and passing it through a second column which was then eluted and analysed using the same conditions as for the samples.

To elute the metals from the columns, the ion-exchange resin was first washed with approximately 50mℓ of deionised water to remove residual seawater and then 25mℓ of 2N HNO_3 was passed dropwise through the resin and collected in a volumetric flask. This gave a concentration factor which, depending on the original volume of sample, was of the order of 200-350 times. The acid eluates were subsequently analysed by flame atomic absorption (Pye SP9) using the standard conditions and wavelengths listed in the manufacturer's handbook; details are given in Table 4.1. Working standards were prepared in 2N HNO_3 from suitable dilutions of commercially available standard solutions. Background correction with a deuterium-arc lamp was employed to correct for non-specific absorption associated with elements that absorb at low wavelengths e.g. Cd and Zn.

4.2.2 Results of the estuarine surveys

Approximately 20 surface samples were taken on each of ten surveys carried out between July 1984 and August 1985. The ten surveys covered neap-spring cycles in July/Aug 1984 and Jan/Feb 1985 and extreme neap and spring tide conditions in Aug 1985 when the river flow was unseasonably high (Table 4.2). Each survey consisted of an axial

Table 4.1 The principal absorption lines, sensitivities and limit of the linear working range for the analysis of the trace metals Cd, Cu, Zn and Ni by atomic absorption spectrometry.

element	principal line nm	sensitivity mg ℓ^{-1}	upper limit of linear range mg ℓ^{-1}
Cd	228.0	0.010	2.0
Cu	324.8	0.035	5.0
Ni	232.0	0.059	5.0
Zn	213.9	0.010	1.0

Table 4.2 Environmental conditions in the Tamar Estuary at the time the measurements of trace metal distributions were undertaken (survey dates identified as (a) to (j) in Figures 4.4 - 4.11).

Survey	date	days relative to neap (N) or spring (S) tides	river conditions		
			flow $m^3\ sec^{-1}$	temperature °C	suspended solids $mg\ \ell^{-1}$
a	23 July 84	N	1.1	21	4
b	27 July 84	S-4	1.0	24	108
c	31 July 84	S	1.0	19	23
d	3 Aug 84	S+4	2.2	19	9
e	31 Jan 85	N	52.4	9	17
f	4 Feb 85	S-4	30.0	9	10
g	8 Feb 85	S	52.9	8	61
h	12 Feb 85	S+4	24.5	3	4
i	12 Aug 85	N	28.8	14	41
j	19 Aug 85	S	16.9	14	6

confidence limits

transect of the estuary covering the salinity range from fully marine to fresh water and was conducted so that sampling at the fresh-brackish interface (FBI) coincided with slack tide at high water. The basic environmental parameters (salinity, temperature, turbidity, pH and dissolved oxygen) were measured simultaneously using continuous techniques (see Section 2.1).

In the summer low-river flow series, the FBI was located within 0-2km of the weir from which the axial distances along the estuary are taken. On the 31st July, which coincided with spring tides, traces of saline water reached the weir and there was no discernible region of fresh water as measured by chloride ion electrode (see Section 2.1). By contrast, during the winter survey (Jan/Feb 85) the FBI was located around 10-14km from the weir. Consistent with previous observations (see Section 2.2), the turbidity maximum was invariably located at the FBI, which moved up-estuary with decreasing river flow. The concentration of suspended particles in the turbidity maximum increased and their distribution became more peaked as the maximum moved up-estuary and with increasing tidal range.

The profiles of dissolved Zn, Cd, Cu and Ni measured in the Tamar estuary during this series of surveys are plotted against axial distance from the weir at Weir Head (see Figure 1.3 for distance scale) in Figures 4.4-4.7 and as metal/salinity relationships in Figures 4.8-4.11. Metal concentrations measured in this study are comparable with published values for estuarine and river systems and approach values for coastal waters at the seaward end of the profiles (Table 4.3). The dissolved metal profiles for the individual metals and their inter-relationships with the prevailing environmental conditions are

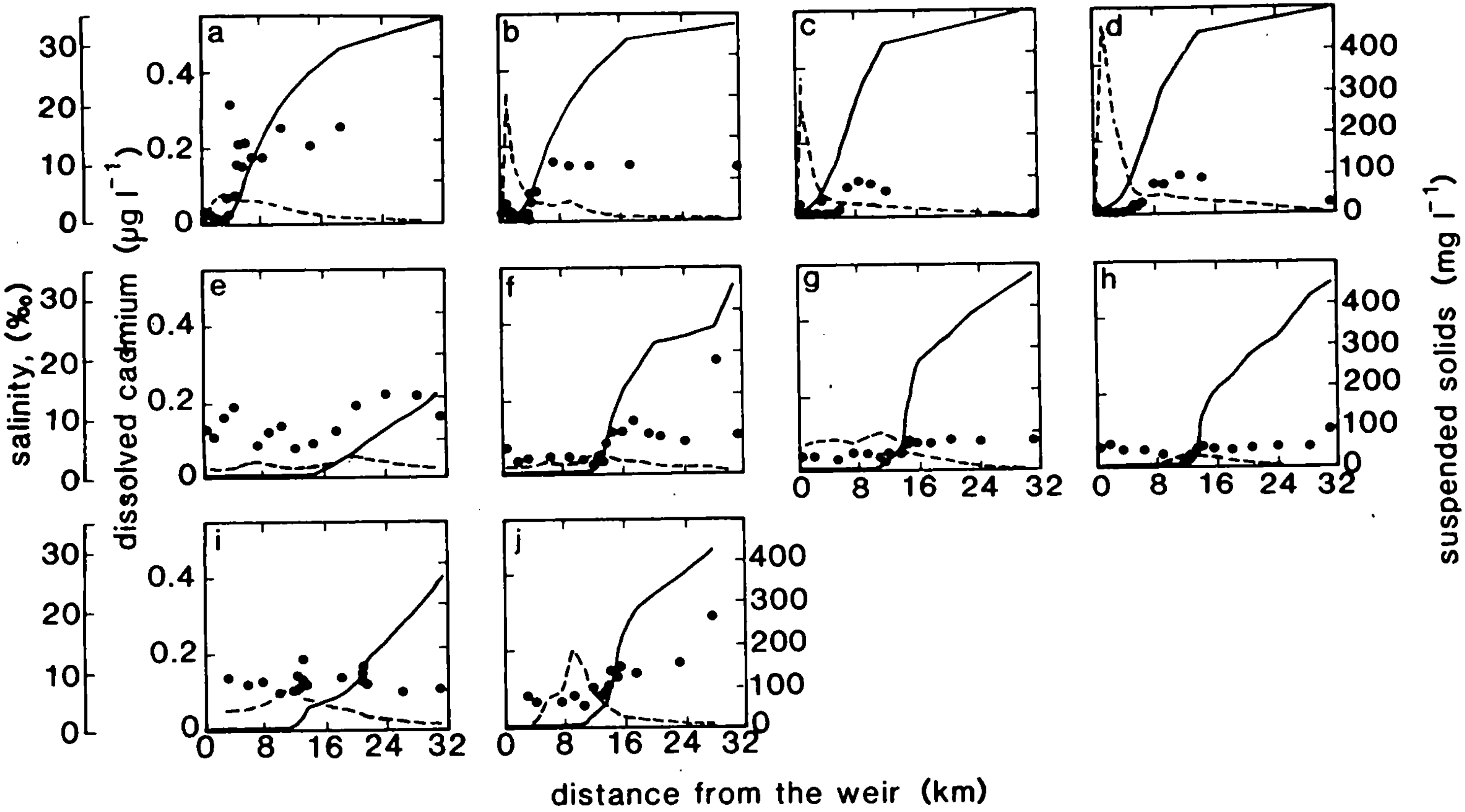


Figure 4.4 The distribution of dissolved cadmium (●), suspended solids (hashed line) and salinity (solid line) relative to distance along the Tamar Estuary on the ten surveys listed in Table 4.2.

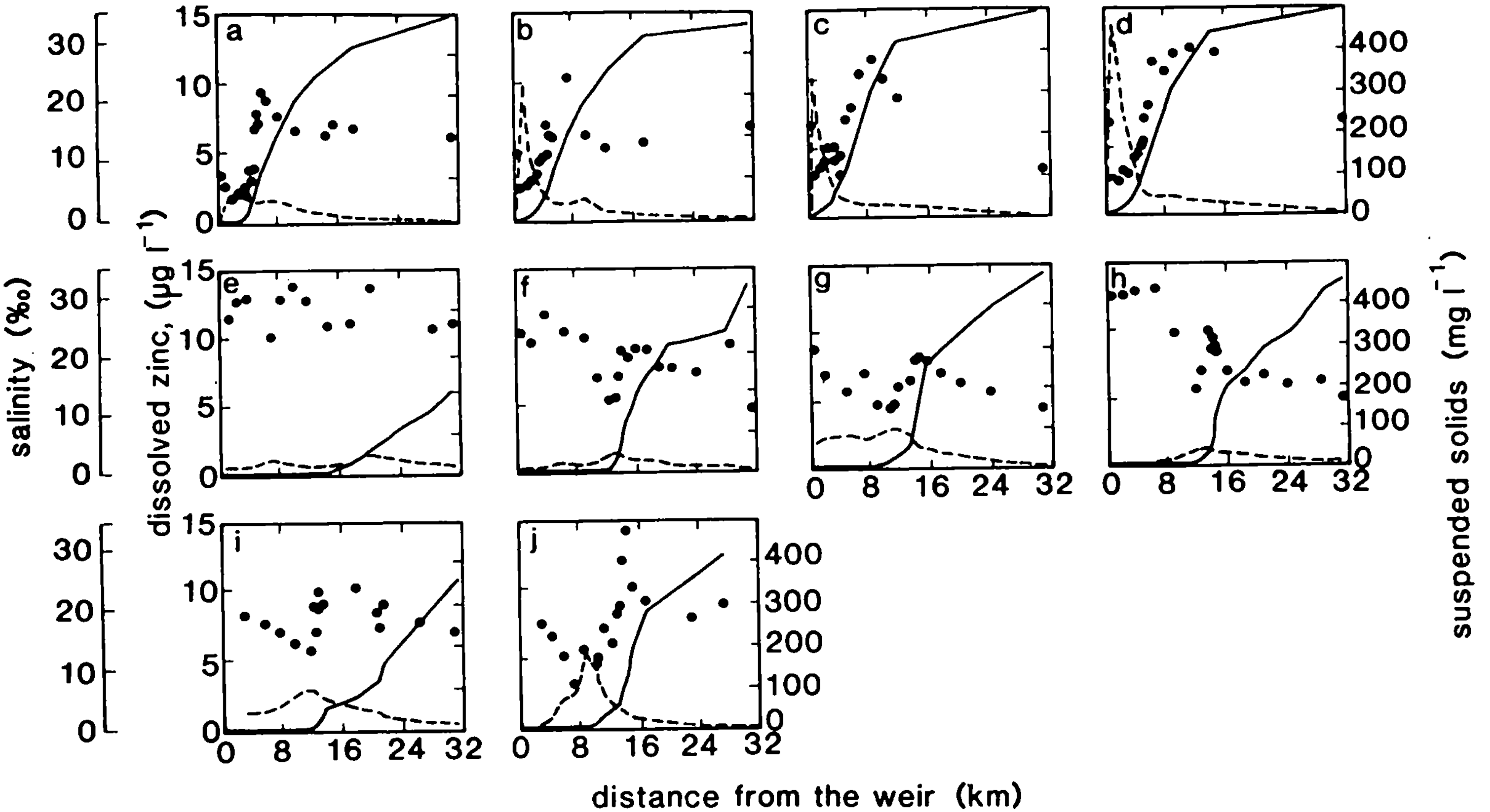
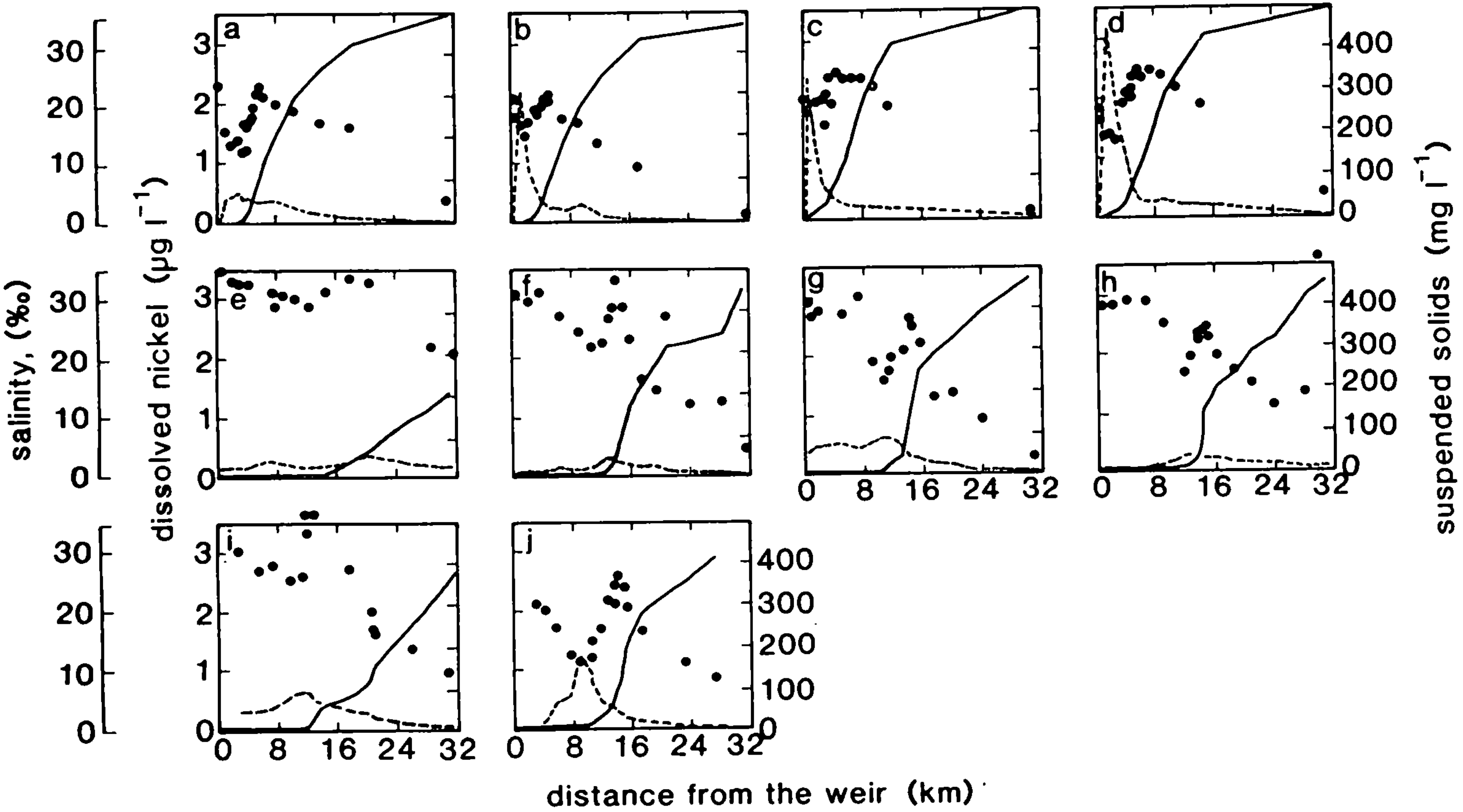


Figure 4.5 The distribution of dissolved zinc (●), suspended solids (hashed line) and salinity (solid line) relative to distance along the Tamar Estuary on the ten surveys listed in Table 4.2.



4.6 The distribution of dissolved nickel (●), suspended solids (hashed line) and salinity (solid line) relative to distance along the Tamar Estuary on the ten surveys listed in Table 4.2.

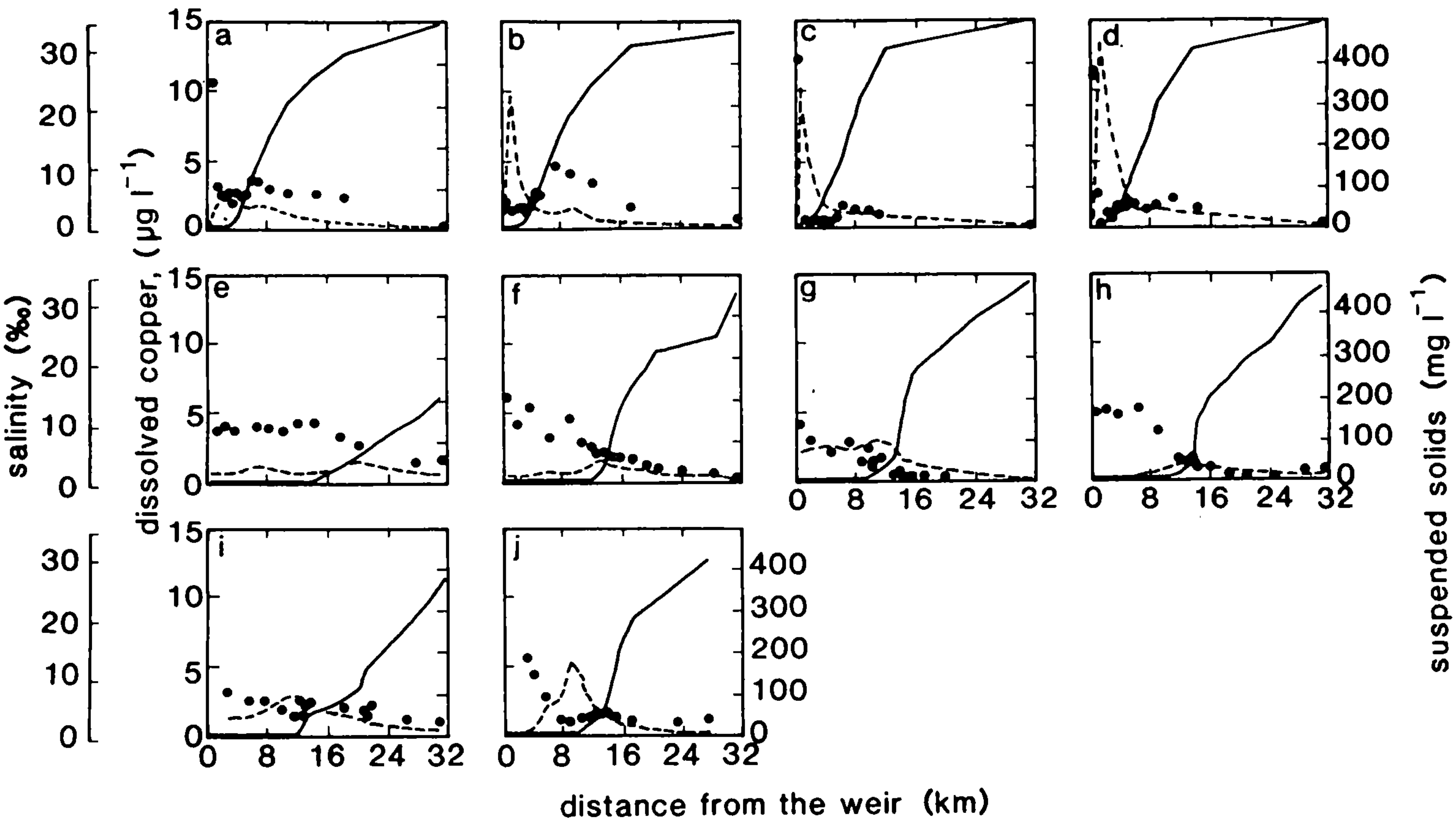


Figure 4.7 The distribution of dissolved copper (●), suspended solids (hashed line) and salinity (solid line) relative to distance along the Tamar Estuary on the ten surveys listed in Table 4.2.

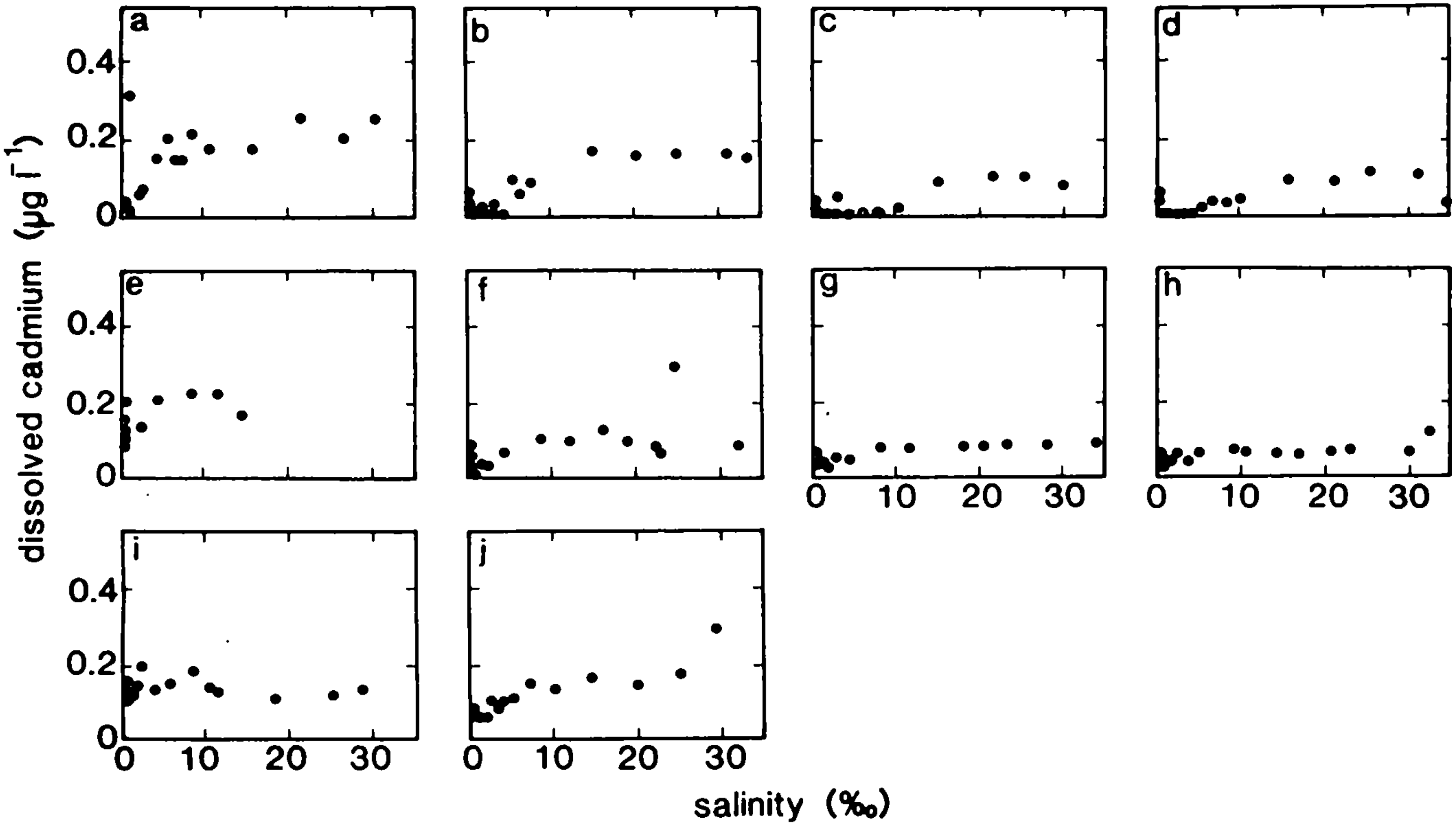


Figure 4.8 The distribution of dissolved cadmium relative to salinity in the Tamar Estuary on the ten surveys listed in Table 4.2.

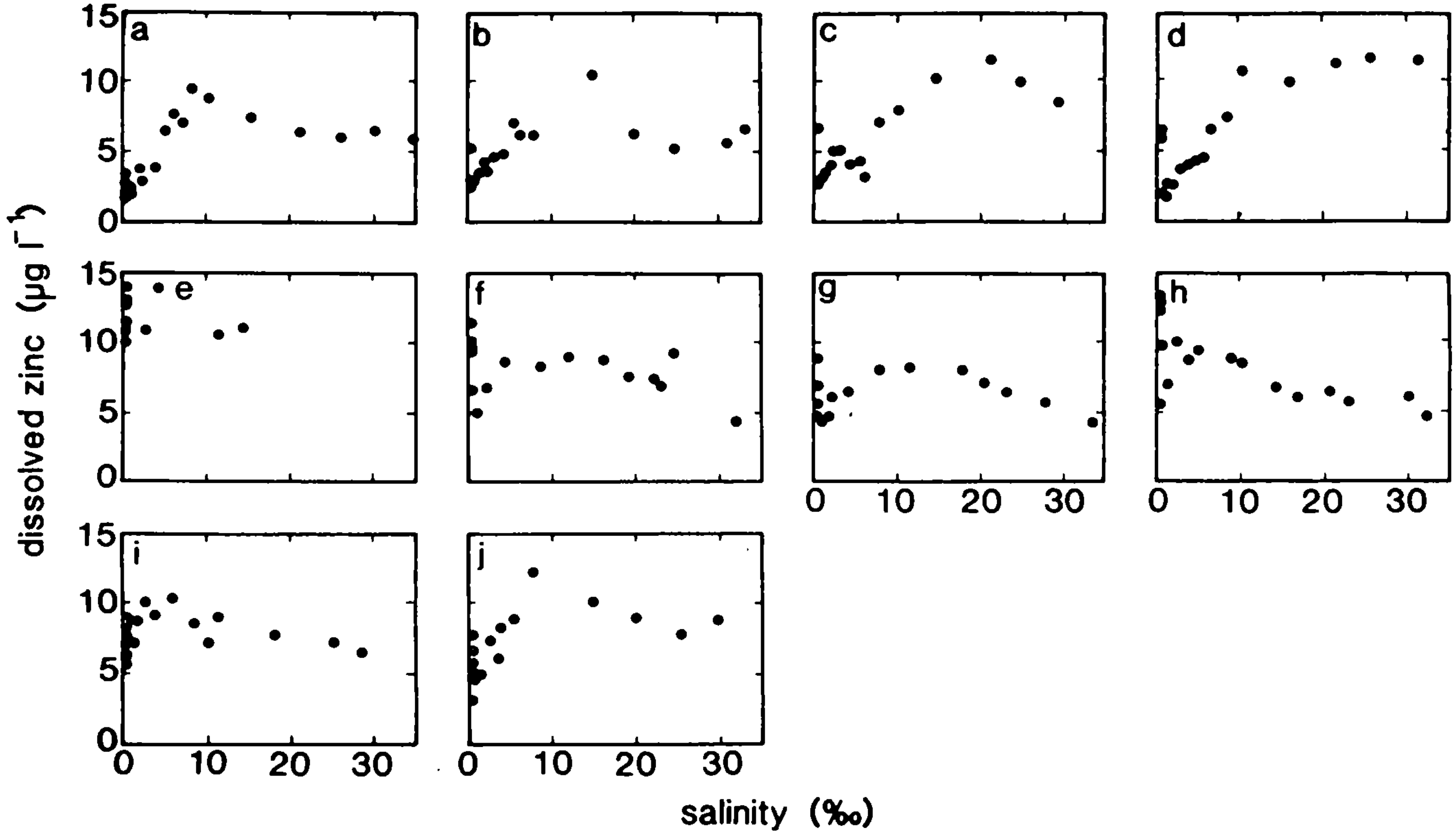


Figure 4.9 The distribution of dissolved zinc relative to salinity in the Tamar Estuary on the ten surveys listed in Table 4.2.

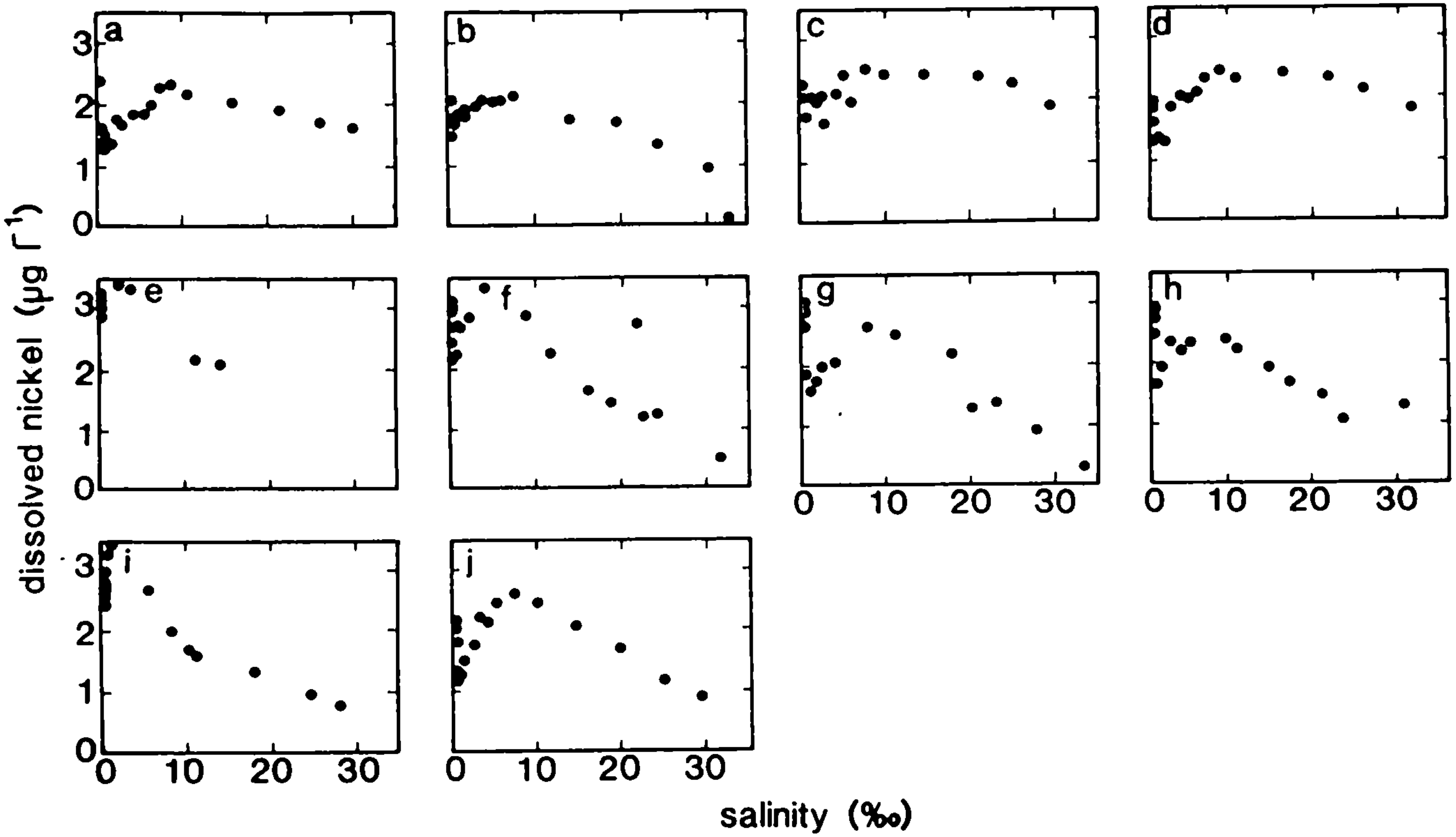


Figure 4.10 The distribution of dissolved nickel relative to salinity in the Tamar Estuary on the ten surveys listed in Table 4.2.

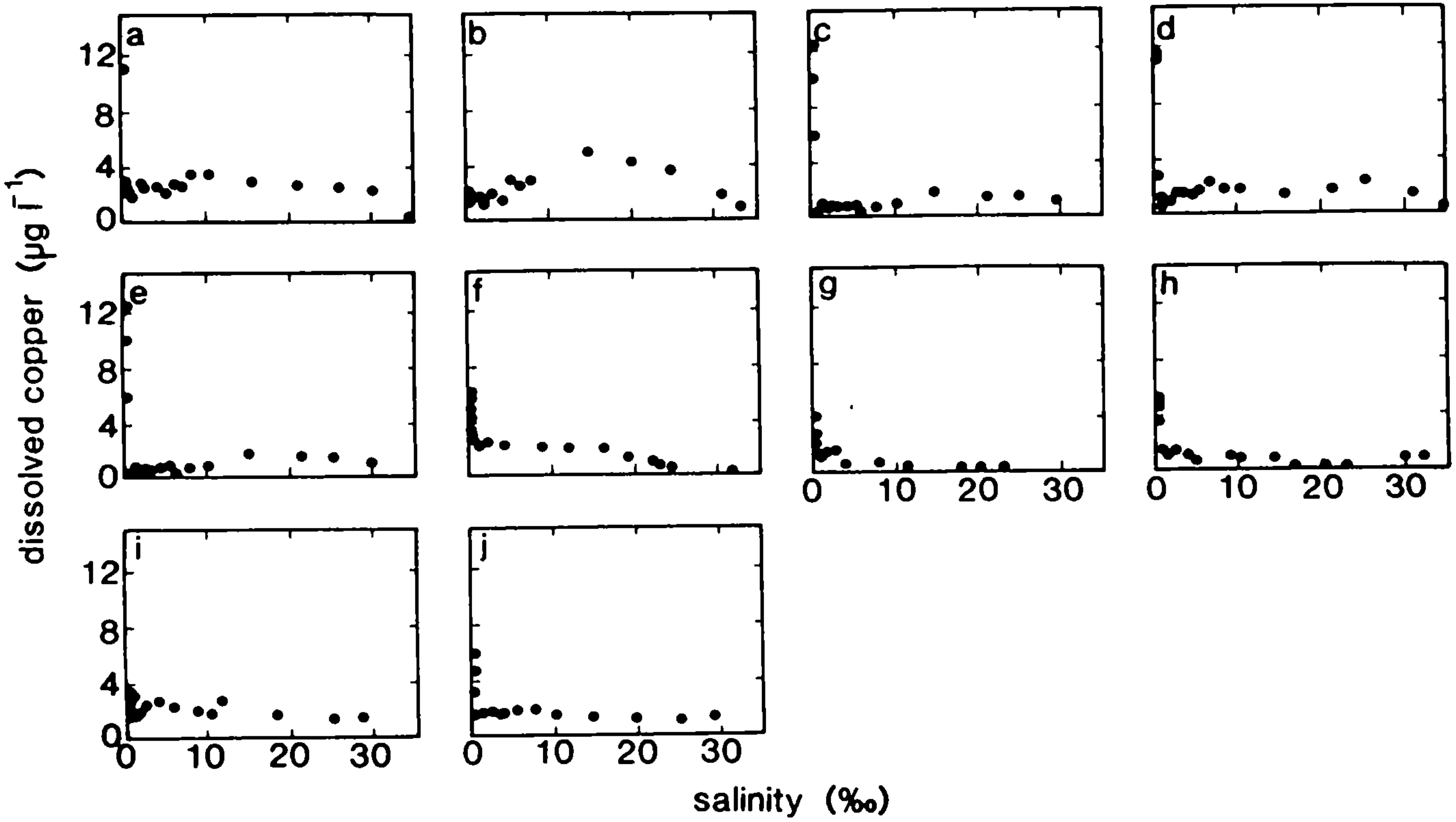


Figure 4.11 The distribution of dissolved copper relative to salinity in the Tamar Estuary on the ten surveys listed in Table 4.2.

Table 4.3 Dissolved metal levels in rivers, estuaries and oceans.

location	Zn	Cu	Cd	Ni	reference
	µg ℓ$^{-1}$				
Rivers					
Amazon	---	1.6	0.006	0.23	Boyle *et al.*, (1982)
Conwy	0-3000 (60)	2-6	0.5-3.0	1-10	Elderfield *et al.*, (1979)
Magela Creek	1.8-5.2	0.13-.78	0.02-0.08	---	Hart *et al.*, (1982)
World Average	30	10	---	2.2	Martin & Meybeck, (1979)
Tamar	5-15	4-12	0.1-0.2	3-4	This work
Estuaries					
Bristol Channel	2.8-25.4	0.6-5.5	0.4-9.4	0.2-3.0	Abdullah & Royle, (1974)
Amazon	---	0.12-1.6	---	0.11-0.23	Boyle *et al.*, (1982)
Rhine	5-20	1-7	0.05-0.5	---	Duinker & Nolting, (1978)
Yarra	12-24	1.6-5.9	0.22-0.43	---	Hart & Davies, (1981)
Restronguet/ Helford	7-300	2-26	0.1-0.5	1-18	Boyden *et al.*, (1979)
Baltic	2.2-5.5	0.7-1.1	0.03-0.05	0.6-0.9	Magnusson & Westerlund (1980)
Tamar	1-12	0-12	0.1-0.4	0.5-3.5	Ackroyd, (1983), Morris, (1986) This work
Oceans*					
N.E.Pacific	6-600	34-319	0.26-127	146-670	Bruland, (1980)
N.W.Atlantic	2.6-106	41-75	0.2-34	112-346	Bruland & Franks, (1983)
Indian	---	220-240	15-64	300-500	Danielsson,(1980)

(* - Oceanic values in ng ℓ$^{-1}$)

described separately below.

Zinc

In the surveys where the fresh water end-members were adequately characterised, riverine zinc concentrations varied from 4-12μg ℓ^{-1} and were highest at periods of high river flow. At the marine end, in Plymouth Sound, zinc concentrations ranged from 4-6μg ℓ^{-1} although, on three ocasions, values of up to 10μg ℓ^{-1} were measured. This was attributed to sporadic anthropogenic inputs from the city of Plymouth and, in particular, the Naval Dockyard (Stebbing et al., 1983).

Dissolved zinc removal was observed to varying degrees on each survey and was always coincident with the turbidity maximum. The degree of the removal varied with the concentration of suspended solids at the turbidity maximum but typically ranged from 20% of the riverine input value at low turbidities, under neap and high flow conditions, to 60% when turbidity values maximised. An equally persistent feature was a mid-estuarine input of zinc, between salinities of 5 and 20°/₀₀, where concentrations typically reached 10-12μg ℓ^{-1}, and were often double the concentration in the fresh water.

Copper

Copper exhibited similar axial trends to those of zinc with marked removal occurring at the turbidity maximum. However, the mid-estuarine inputs of copper were far less prominent. The fresh water concentrations ranged from 4-12μg ℓ^{-1} but, unlike zinc, were highest at times of low river flow. The removal of dissolved copper at the turbidity maximum was typically 50% of the riverine input at low turbidities but increased to 95% at the highest turbidities. The mid-estuarine input of dissolved copper was negligible at neap tides, but increased slightly as the turbidity maximum migrated up-estuary under low river flow and at spring tides. Under these conditions, the concentration of copper in the mid-estuarine input occasionally reached 4μg ℓ^{-1}. The marine end-member values were consistently low at 0.1-1.0μg ℓ^{-1}.

Nickel

Nickel concentrations in the fresh water varied from 2.0-3.5μg ℓ^{-1} and, like zinc, were highest under high river flow conditions. Nickel removal in the region of the turbidity maximum ranged from 12% at low turbidities, to 50% when turbidities were highest, such as at spring tides and under low river flow conditions. Nickel also exhibited a pronounced input, as evidenced by a prominent peak in the Ni/salinity relationship, between 5 and 10°/₀₀. Concentrations here reached 2.5-3.5μg ℓ^{-1}. Marine end-member values ranged from 0.5-1.5μg ℓ^{-1}.

Cadmium

Dissolved cadmium concentrations in the fresh water and turbidity maximum region were often at, or close to, the detection limit for the method but the axial trends were still apparent and its behaviour was consistent with the other metals described. Unlike the other metals, however, the riverine input of cadmium 0.05-0.1μg ℓ^{-1} was negligible compared with the mid-estuarine input, especially around spring tides when concentrations reached 0.2μg ℓ^{-1} and with concentrations of 0.3μg ℓ^{-1} centred around 28-30km. This latter source of metal, like zinc, was probably associated with anthropogenic inputs from the Naval Dockyard and City of Plymouth. Although the major sources of cadmium stemmed from the mid and lower estuary, marked removal still occurred at the site of the turbidity maximum and the intensity of the removal increased with turbidity. Under conditions of maximum turbidity, the dissolved cadmium was reduced to levels below detection.

4.2.3 Discussion

Individual metals, whilst exhibiting similar trends, showed a gradation of character in both the degree of removal and of the mid-estuarine input. Dissolved zinc, nickel and cadmium were highest in the riverine input at times of high river flow whereas copper was relatively depleted at high river flows when riverine particle loads were highest. This suggests that copper has a greater affinity for the particulate phase in river water and this is consistent with the relative degree of removal observed at the turbidity maximum:

$$Cu \gg Zn > Ni > Cd$$

This is also consistent with the work of Morris (1986), who demonstrated, using a simple sorption model and K_d values from Li *et al.* (1984a) that, with increasing turbidity, the fraction of metal associated with the particle phase, as a proportion of the riverine levels, followed the sequence:

$$Cu > Zn > Ni$$

Bourg's (1983) speciation model shown in Figure 4.1 indicates that the proportion of particle associated metal follows the order:

$$Zn > Ni > Cu.$$

However, bearing in mind the high affinity of copper for humics, also shown in these diagrams, then particles having associated organic films would attract a much greater proportion of the total copper and Bourg's (1983) model scheme would be more in keeping with measured values.

The degree of mid-estuarine input observed in the field data generally followed the reverse order:

Zn > Ni : Cd > Cu

Again, this reflects the strong affinity of copper for the particulate phase. These sequences do not bear any simple relationship to the individual physical and chemical properties of the metal ions (see Table 4.4). It is more likely that the affinity for particles, as for other individual species, results from a complex combination of properties.

Nevertheless, in good agreement with the work of Ackroyd (1983), Ackroyd _et_ _al_., (1986) and Morris (1986), these results demonstrate a close relationship between the position and magnitude of the turbidity maximum and the location and degree of dissolved metal removal, providing strong circumstantial evidence for metal sorption on to particles being the controlling mechanism for removal.

Similarly, the coupling between the degree of metal input and tidal state, and the absence of alternative sources, indicates that the mid-estuarine inputs of these four metals are derived from a common source. This might be associated with metal desorption from particles advected seaward from the turbidity maximum to conditions of reduced ambient soluble metal levels, _i.e._ re-equilibriation of the metal loaded particles with overlying waters of lower metal concentration, as shown for aluminium by Morris _et_ _al_. (1986a), and/or the infusion of metal-rich pore waters (see Table 4.5). This latter process has been invoked to explain the mid-estuarine maxima of ammonia and manganese (Knox _et_ _al_., 1981; Morris _et_ _al_., 1982a) whose distributions share several similarities, particularly with zinc and nickel, and which also vary cyclically through the spring-neap tidal cycle, showing increased

Table 4.4 The physical properties of the isotopes used in the radiotracer experiments.

element	ionic radius* 10^{-10}m	volume 10^{-10}m^3	charge per unit volume	atomic weight*	charge per unit mass
Zn^{2+}	0.74	1.7	1.18	65.4	0.052
Cd^{2+}	0.97	3.8	0.53	112.4	0.068
Cs^{1+}	1.67	19.5	0.05	132.9	0.147
Na^{1+}	0.97	3.8	0.26	23.0	0.164

* data from Mason (1952).

Table 4.5 Dissolved metal levels in sediment pore water from various estuarine and coastal environments.

location	Zn	Cu	Cd	Ni	reference
	$\mu g \ \ell^{-1}$				
Loch Fyne	40-340	15-256	---	30-78	Duchart *et al.* (1973)
Los Angeles Harbor	10-21	0.4-1.3	0.1-0.5	0.6-2.5	Gupta & Chen (1975)
Narragansett Bay	---	2-20	<0.05	2-12	Elderfield *et al.* (1981)
Coastal Sediment	---	2.6-10.3	0.2-3.2	---	Hoshika *et al.* (1977)
Conwy Estuary	40-60	---	---	---	Elderfield *et al.* (1979)
Puget Sound	---	1.3-11.6	0.5-2.2	1.2-5.2	Emerson *et al.* (1984)
Lake Sediment	7.2-37	3.2-42	0.2-0.9	38-200	Tessier *et al.* (1985)

input with tidal range and hence sediment disturbance.

If the turbidity maximum acts as a sink for soluble metal, as the previous data implies, then the effects of metal sorption should, theoretically, be reflected in the composition of the suspended particle population. However, measurements of the non-detrital fraction of the particulate metals of the Tamar Estuary have invariably shown that particles in the turbidity maximum are actually impoverished with respect to trace metals in comparison with particles in the fresh water and further seaward (Loring _et_ _al_., 1983; Morris _et_ _al_., 1987). On reflection, this is consistent with (and neccessary for) the removal of soluble metal, since the capacity for the uptake, and hence removal, of soluble metal would rapidly diminish as the particles reached equilibration with the soluble phase. One explanation for this apparent paradox is provided by the up-estuary flux of particles, brought about by tidal pumping. This supplies the material required to maintain the turbidity maximum and mobile bed sediment shoal and which has been estimated previously (see Section 3.4.5). Using the estimated values for the up-estuary particle flux and the removal rate of soluble Fe at the turbidity maximum, it was possible for Morris _et_ _al_. (1986b) to calculate that the enrichment of particles with Fe in the turbidity maximum would be less than 1% and therefore not detectable within the analytical uncertainties. Corresponding values of approximately 2%, 5% and 8% were calculated for Zn, Cu and Mn, respectively.

4.3 STUDIES OF HETEROGENEOUS METAL REACTIVITY

4.3.1 Introduction

To determine trace metals at environmental levels most analytical techniques require a pre-concentration stage which often serves to control matrix problems at the same time. For example, the ion-exchange technique described previously (Section 4.2.) typically requires 4-6 litres of estuarine water to provide 25mℓ of concentrated eluant suitable for analysis by flame atomic absorption. This method is therefore quite impractical for the study of reaction kinetics and mechanisms which typically involve analysing numerous succesive subsamples from a reaction vessel in order to follow the process with time. The processing of samples of 4-6 litres from a reaction chamber alone would severely limit the sampling frequency and would require an initial reactor volume which was unrealistically large for controlled laboratory experiments.

Two adaptions of the Chelex technique were examined to assess the possibility of reducing the sample volume required. Firstly, an electrochemical technique, anodic stripping voltammetry (ASV), was employed to analyse column eluents because its enhanced sensitivity compared with atomic absorption spectroscopy (AAS) required lower concentration factors and therefore smaller sample volumes. Secondly, flow injection analysis (FIA) was used to automate the extractions and allow direct injection of the eluant stream into the nebuliser of the AAS. However, because of insufficient time for development, neither approach proved entirely satisfactory for routine analyses of estuarine samples. Instead, gamma spectroscopy and radio isotopes were adopted for the series of experiments required to examine the variation in the sorption/desorption of trace metals in the presence of particles under estuarine conditions.

4.3.2 Radiochemical measurements

Modern gamma counters can easily resolve mixtures of gamma ray emmitting elements and with extremely high sensitivity (10^{-12}-10^{-14} mole of each active metal). This enables small additions of suitable carrier-free isotopes to be made to natural samples with negligible changes to the total concentration of a particular element. Providing the equilibration of the radioactive species with their stable counterparts can be assumed (Duursma, 1976) this technique provides a versatile tool for the study of natural heterogeneous processes (Li *et al.*, 1984a, 1984b).

In this work, the gamma emitters were detected as photons using a coaxial, Li drifted, Ge crystal semiconductor (EG & G Ortec) interfaced with a multichannel analyser (Canberra Industries Inc.). The multichannel analyser assigned charge pulses associated with individual photons into specific channels depending on their characteristic energies and recorded the number of disintegrations occuring at each energy in a given period (see Figure 4.12).

Experiments to examine the partitioning of various metals between particle and solution phases were undertaken using the suspension technique described by Duursma and Bosch (1970). Solutions of estuarine water of various salinities and pH were equilibrated with the radiotracer mixture for 16-18 hours in a stirred, 1ℓ reaction vessel. The reaction was initiated by the addition of a known quantity of suspended solids in the form of a concentrated suspension. Samples of 100mℓ were withdrawn from the reaction vessel at various time intervals following the injection, using a plastic syringe, and filtered, using 45mm dia., 0.45μm pore-sized membranes (Millipore Ltd.) and vacuum

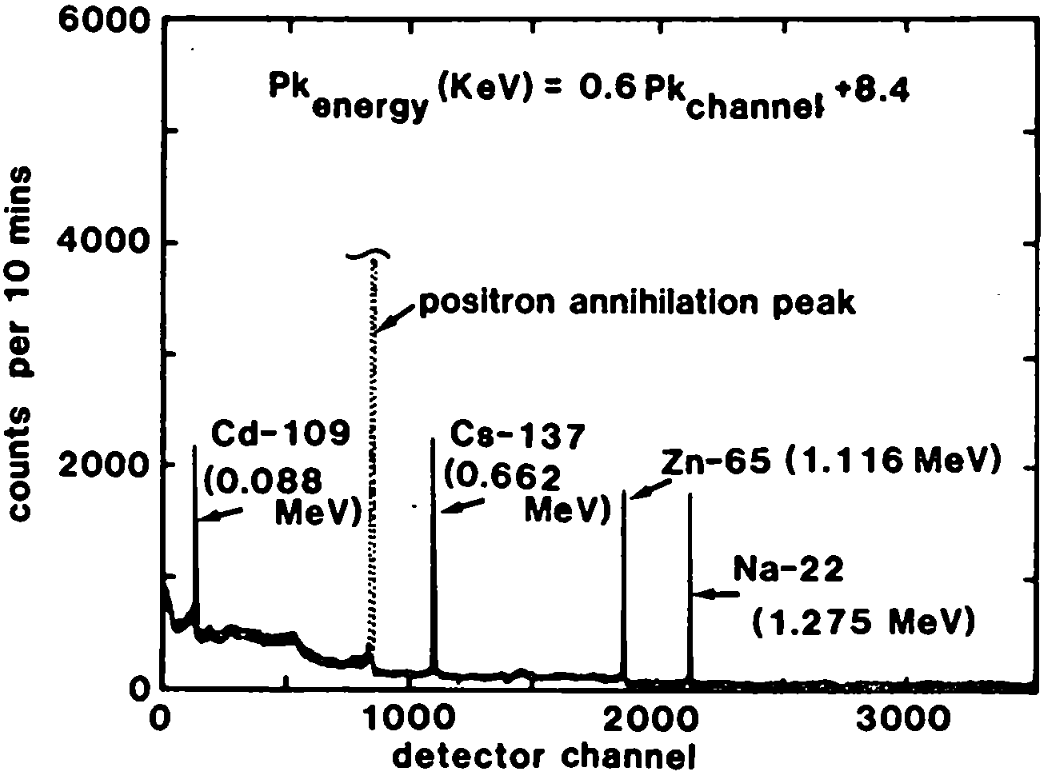


Figure 4.12 A typical gamma spectrum of a solution containing Cd, Cs Zn and Na radioisotopes.

filtration. The filtered particles were not washed but allowed to dry under vacuum on the filter support. This minimised the activity associated with residual solution on the filtered particles. Filtered subsamples were placed directly on the Ge(Li) detector in 100mℓ rigid polystyrene weighing bottles with snap-on caps and the number of disintegrations counted over a period of 50 minutes. The corresponding filter papers were placed in 50mm dia. disposable petri dishes and counted in the same way; corrections for blank papers placed under the first filter were generally negligible for the elements studied. A factor for each isotope was determined that corrected for the geometry of the two sample types. This was achieved by counting a known volume of the isotope cocktail which had been evenly distributed and dried on to a filter paper containing the appropriate quantity of suspended solids. The counts obtained for control solutions containing no particles were taken as representing the situation with 100% of the added activity in the solution phase. No evidence of the isotopes being adsorbed on the surface of the 100mℓ weighing bottles was observed when they were recounted after an active sample had been discarded. Similarly, adsorption by the blank filter papers was found to be negligible.

The adsorption experiments were undertaken using the isotopes: Zn-65, Cd-109, Cs-137 and Na-22, obtained from Amersham International. These were mixed in proportions that took account of the relative activity and counting efficiency (see Table 4.6) of each of the isotopes so that an aliquot of the mixed tracer gave similar a similar activity for each of the elements. The final activities used in experiments were such that counting periods of 50 minutes gave between 10,000 and 1000 counts, giving random errors of 1 to 3.2% respectively,

Table 4.6 Radiochemical properties of the isotopes used for the study of sorption exchange processes with natural suspended solids.

isotope	energy KeV	counting efficiency %	effective disintegrations %	specific activity Bq g^{-1}	half life year	total metal added* µg ℓ^{-1}
Zn 65	1110	0.4	49	3.0×10^{14}	0.67	5.8×10^{-3}
Cd 109	88	3.4	4	9.1×10^{13}	1.29	5.6×10^{-3}
Cs 137	661.2	0.8	86	3.3×10^{12}	26.6	1.3×10^{-2}
Na 22	1280	0.4	100	2.2×10^{14}	2.58	1.6×10^{-3}

* for tracer additions giving 10,000 counts per isotope and including stable carrier contamination where applicable

($\sigma = \sqrt{n}$) at the 68.3% confidence limit (Faires and Parkes, 1960).

4.4 SORPTION EXPERIMENTS AND RESULTS

4.4.1 Experimental materials

For the tracer experiments, bulk samples (140ℓ) of fresh and saline water were obtained from the River Tamar above the weir at Gunnislake and from outside the breakwater off Plymouth (salinity $34.0^{o}/_{oo}$) respectively. These samples, which were collected in August 1985 when turbidity was low (<1mg ℓ$^{-1}$), were membrane-filtered using 0.45μm pore-size filters (Sartorius Ltd.) and a large volume pressure filtration system. Following filtration, they were stored in polyethylene carboys in the dark at 4°C. To provide a stock of estuarine particles, 100ℓ of water was collected from the turbidity maximum of the Tamar Estuary around high water when the concentration of suspended solids was 560-600mg ℓ$^{-1}$. These samples were returned to the laboratory and the particles concentrated by sedimentation for approximately 48 hours in darkness at 4°C. After this period, the supernatant water, though still slightly turbid, was removed by syphoning and pressure filtered through 0.45μm membranes. The filters were then subjected to a combination of ultrasonic vibration and gentle brushing which effectively dislodged the colloidal particles allowing them to be re-combined with the sedimented particles thus preserving, as nearly as possible, the original composition. This operation produced a stock suspension containing 12.5mg mℓ$^{-1}$ of natural turbidity maximum particles. All the experiments performed in solutions of varying salinity and turbidity were produced from mixtures of these three stock components.

The basic properties of the end-member solutions determined at the start of the experiments are given in Table 4.7. The size distribution and surface area characteristics of the stock particle population were monitored at intervals during the experimental work and are shown in Figure 4.13. Despite, or perhaps because of, the vigorous shaking each time subsamples were abstracted from the stock suspension, it appears that particles in the 28-188μm range were generated at the expense of particles of less than 6μm, presumably through aggregation. The median size of the particle population increased from 9.8μm to 16.3μm over the eight month period that the stock suspension was kept in storage. Paradoxically, the specific surface area of the suspension, determined by B.E.T. plots of N_2 adsorption isotherms, increased slightly from $17.2 m^2 g^{-1}$ to $23.4 m^2 g^{-1}$. Glegg et al. (1986) have shown that oxidation of the organic material associated with particle surfaces has the effect of increasing the specific surface area of a sample. Hence, this increase in surface area could have been due to a reduction of adsorbed organic material through microbial respiration. Unfortunately, the organic content of the particles was not measured. Alternatively, it has been suggested (J. Titley, pers. comm.) that changes in the crystal state of oxide phases associated with the particles as the material aged may acount for this increase in surface area.

4.4.2 Preliminary metal sorption experiments

Preliminary experiments were undertaken to assess the degree of tracer uptake by estuarine particles and the time scale of the sorption process. Four experimental solutions with salinities in the range 0-5°/₀₀ were prepared from the stocks of fresh and saline water and were

Table 4.7 The composition of the fresh and saline end-members used in the sorption experiments.

	composition	
constituent	freshwater	seawater
salinity (°/₀₀)	0.03	34.0
dissolved organic carbon (mg DOC-C ℓ^{-1})	3.76	*
pH	7.2	8.2
dissolved metals$^{\nabla}$ (μg ℓ^{-1})		
Cu	12.3	*
Zn	14.1	*
Ni	2.95	*
Cd	0.16	*

∇ by Chelex extraction/atomic absorption

* not determined

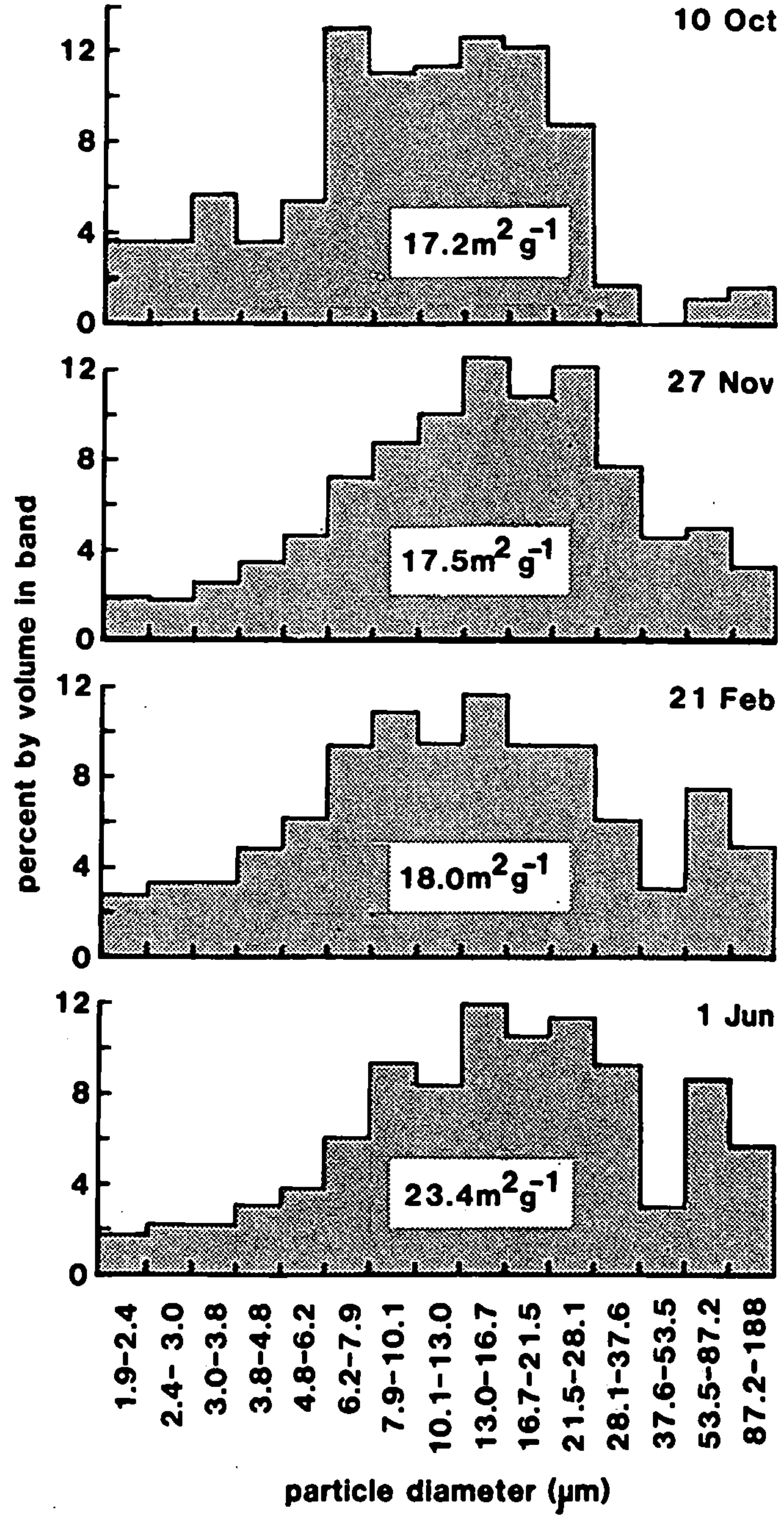


Figure 4.13 The size distribution and B.E.T. surface areas of the suspended particle stock material measured at intervals over the period of the metal sorption experiments.

equilibrated with the tracer mixture. After dosing the mixtures with 124mg ℓ^{-1} of stock estuarine particles, subsamples were withdrawn at various time intervals, initially hourly and then at greater intervals over an 18 hour period. The results of this experiment are shown in Figure 4.14. Both particle and solution activities were determined for each sample in these experiments but, as the total activity was invariably accounted for, only the activities remaining in solution are presented.

The results provide two general conclusions. Firstly, the data produce reasonably smooth curves indicating that the sampling and counting procedures were sufficient to monitor the sorption process with a reasonable degree of confidence. Cadmium was an exception but this was due to insufficient cadmium activity in this particular mixture of tracer and hence more 'noisy' values. Secondly, the initial uptake was extremely rapid with up to 90% of the final exchange occurring in the first hour.

There was a systematic decrease in the degree of uptake with increasing salinity for all elements. The relative degree of uptake of the elements was in the order:

$$\text{Zn} > \text{Cs} > \text{Cd} \gg \text{Na}.$$

This order agreed with the earlier field measurements, in that the affinity of Zn for particles was greater than that of Cd. Sodium, however, showed no affinity for particle surfaces, even at higher salinities where it might have been expected to exhibit some competition for sites.

Following these preliminary experiments, a second trial was undertaken to assess the kinetics of the partition equilibrium of

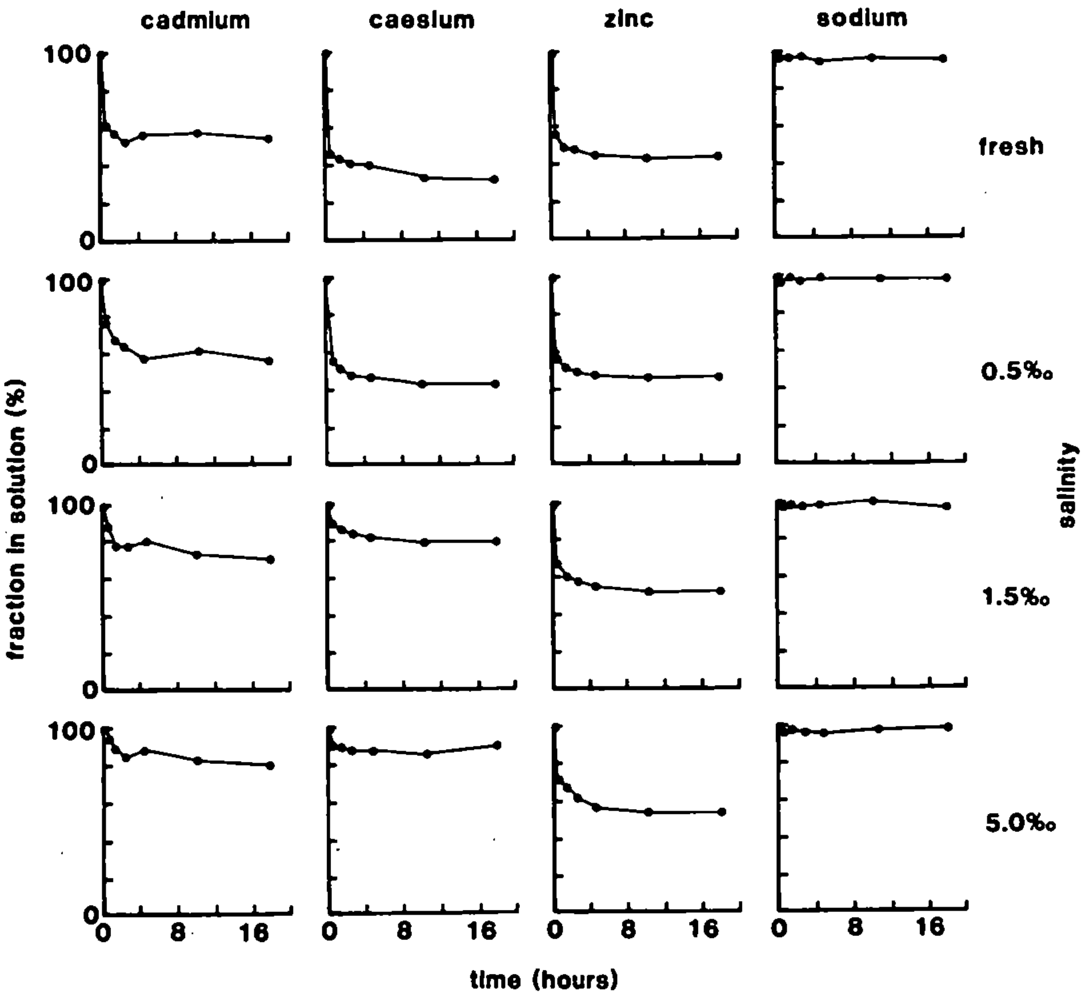


Figure 4.14 The uptake with time of the metals Cd, Cs, Zn and Na by suspended particles at a concentration of 124 mg l^{-1} at four salinities.

radio-tracer metal within the first minutes after the addition of particles. This experiment duplicated the previous experiment except that only the fresh water situation was studied. A control with no added particles was also monitored. Since, in the previous experiment, the filtration stage had restricted the practical sampling rate, provision was made to allow up to six samples to be filtered simultaneously.

The results of this experiment are shown in Figure 4.15 and demonstrate that for Cd, Zn and Cs, 80-90% of the uptake was complete well within 10 minutes of the addition of particles and that subsequent changes were comparatively negligible. In later experiments the equilibration values were calculated from a single measurement taken after four hours as this accounted for > 95% of the observed change and was compatible with the relatively short residence time for water in the 'reactive', low-salinity region of the Tamar Estuary (Section 1.3). In addition, this data set closely replicated the results for freshwater conditions obtained in the previous test (shown in Figure 4.15) and gave a measure of confidence in the experimental procedure.

4.4.3 The use of distribution coefficients in sorption studies

Models of heterogeneous chemical processes have generally sought to express the uptake, or release, of a particular material in terms of a single 'pseudo-equilibrium' factor. Concentration factors (CFs) are used in certain circumstances, mainly to describe biological accumulation of pollutants. Duursma and Gross (1971) first used the term 'distribution coefficient' (K_d) for the relationship between radionuclide concentrations in sediment and water. This concept has also been applied by geochemists in the interpretation of crustal

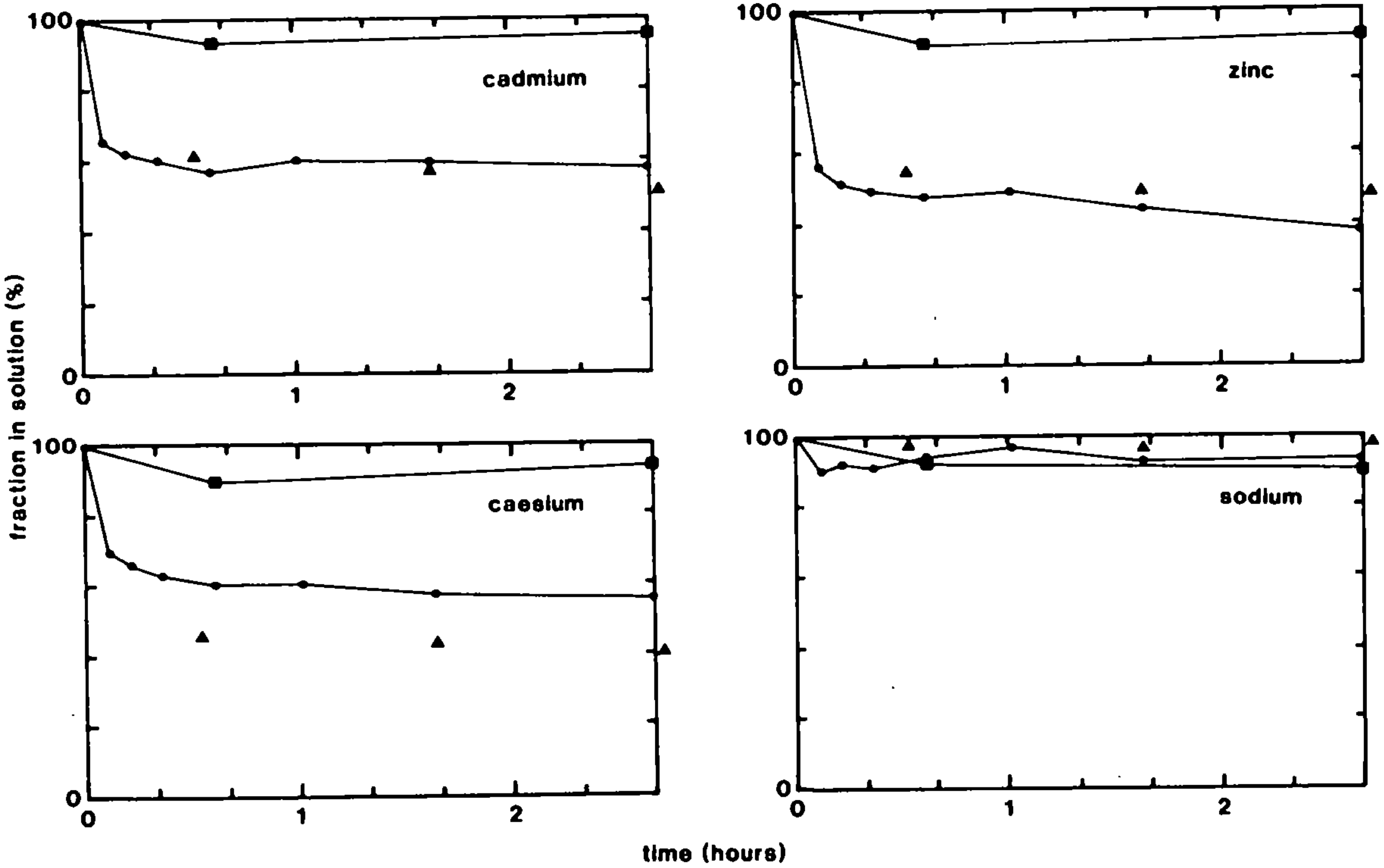


Figure 4.15 The uptake of trace metals (●) on estuarine particles illustrating the rapidity with which equilibrium is reached. The experiment was carried out at a particle concentration of 124 mg l^{-1} and in fresh water. The corresponding data from the previous experiment (▲) is superimposed and controls (■), with no added particles, are also shown.

weathering and the elemental mass-balance (Bowen, 1979). The ratio of the concentration of an element in pelagic clays to that in deep ocean water provides an estimate of the maximum K_d value. However, it should be remembered that K_d factors are not equilibrium constants but operational values that vary as pH, solution composition, and the physical properties of the solid phase change. In practical terms, particularly in estuaries, the empirical K_d value must reflect the short-term equilibration between the soluble phase and the non-detrital component of the suspended particulate phase and is strictly applicable only to the system in which it was determined. The operational distribution coefficient, K_d, is defined thus:

$$K_d \ (\text{kg kg}^{-1}) = \frac{[\text{ concentration of species on solid phase}]}{[\text{ concentration of species in solution }]}$$

Although a simple percentage factor should be adequate to describe the uptake of a sorbed species, in practice, as the percent adsorbed approaches 100% (or 0%), the resolution of the factor is lost. The K_d factor, on the other hand, is far more sensitive; for example, as the percent adsorbed goes from 99% to 99.9% (a factor of 1.01), the K_d increases by a factor of 10 (Li <u>et</u> <u>al</u>., 1984b). In this work, distribution coefficients were determined using radio-isotopes as described by Li <u>et</u> <u>al</u>. (1984b):

$$K_d \ (\text{kg kg}^{-1}) = \frac{\text{activity on particles}}{\text{activity in 100 m}\ell\text{ solution}} \quad \frac{10^5}{m\ f}$$

where: m = dry weight of solids on filter (mg)

f = factor to convert from solution to solid counting geometry.

4.4.4 Metal partitioning under estuarine conditions

Salinity and suspended solids

The effects of particle concentration and salinity on the sorption of radio-isotopes were investigated with a series of experiments. Using the reaction vessels and procedure described in Section 4.3.2, the partitioning of trace metals between solution and solids was studied over a range of salinities (six samples ranging from fresh to $34^{\circ}/_{oo}$) and turbidities (six samples ranging from 117 to 818mg ℓ^{-1}).

Salinity and pH

The variation of the distribution coefficients with pH and salinity was examined using a matrix similar to that produced for the previous experiment. In the Tamar Estuary, typical pH values range from around 7.0 in the fresh water to a fairly uniform 8.2 in the marine end-member. However, at intermediate salinities, pH values deviate from simple conservative mixing of these end-member values because the carbonic acid dissociation constants are salinity dependant (Mook & Koene, 1975). Also, perturbations to the pH/salinity relationship can be induced by localised respiration and photosynthesis (Morris *et al.*, 1982b). In the Tamar Estuary, pH values in the fresh water and low salinity region can range from 6.0 under high run-off conditions to 9.5 under conditions of vigorous photosynthetic activity (Morris, unpublished data).

In this experiment, the partitioning of radio-isotopes was measured at four pH values, 6.0, 7.0, 8.0 and 9.0 ±0.2 pH units respectively, and six salinities ranging from fresh to $34^{\circ}/_{oo}$. The pH values of samples were adjusted by dropwise addition of 0.1M NaOH and/or 0.1M HCl and the pH values monitored using a glass and calomel reference electrode combination calibrated against two NBS buffer solutions (7.0 and 9.25 at 20°C). Suspended particles from the stock suspension were added at a concentration of 364mg ℓ^{-1} to each pH/salinity combination after allowing the radio-tracer to equilibrate. The behaviour of the radio-tracer in control solutions (duplicate salinity/pH, but with no added particles) was monitored for each combination.

Temperature effects on metal partitioning

Examination of the local water authority data showed that river temperatures over a six year period from 1976 to 1982 ranged from 3.5°C in February to 18.5°C in August. However, values of 24°C have been recorded (unpublished data) in the low salinity/mid-estuary region in late afternoon when low tide occurred around midday. Under these conditions, the temperature of the flood tide water was significantly elevated through contact with inter-tidal mud banks which had been heated by solar radiation during the previous low water. It is possible that the reverse effect may induce a mid-estuarine minimum in winter but this has not been recorded. The temperature of the marine end-member varies much less, from 8.5°C in February to 16.0°C during August (Lee and Ramster, 1981).

The effect of temperature on metal partitioning was investigated by an experiment in which the uptake of radio-isotopes by estuarine particles was followed at four temperatures over a range of six salinities, including freshwater and full seawater. For this experiment, hydrogen ion activity was held constant at pH 7.5 and the concentration of particles at 364mg ℓ^{-1}. Using various temperature controlled environments, the experiments were performed at 20°C, 16°C, 12°C and 2°C giving a reasonable coverage of environmental values. Controls with no added particles were monitored at each salinity and temperature.

4.4.5 Trace metal desorption studies

Desorption was studied using a similar experimental approach to the sorption studies. A 400mℓ aliquot of the stock suspended sediment suspension was equilibrated with a radio-isotope mixture for a period of 24 hours. After this operation, the slurry was centrifuged in 35mℓ aliquots and the supernatant liquid decanted. The particles derived from 35mℓ of slurry were then resuspended into one litre samples covering a range of salinities prepared by mixing fresh and saline water from which the trace metals had been removed using Chelex 100 ion-exchange resin. The slight reduction in the pH values of the fresh and saline stock samples brought about by the action of the ion-exchange resin was adjusted by the dropwise addition of dilute NaOH.

Desorption from the labelled particles was followed by removing and filtering a 100mℓ sub-sample and measuring the activity of both the solution and particulate phases. Sampling was undertaken after 4 hour and 40 hour intervals.

4.4.6 Experimental results

Suspended solids and salinity

The results of these experiments, carried out at room temperature (23°C) and with no pH control, are given as K_d values in Table 4.8. At each salinity, the K_d values for a particular radio-isotope were reasonably constant (within experimental error) over the range of suspended solids studied. The mean and standard deviations of these K_d

Table 4.8 The solution/particle distribution coefficients for the metals Cd, Cs and Zn measured over a range of suspended solids concentrations, at ambient estuarine pH and at room temperature (about 22°C).

Salinity	Suspended Solids mg ℓ$^{-1}$					
‰	117	234	351	584	818	mean (K_d)
Cadmium						
0	$1.2x10^{4}$	$1.1x10^{4}$	$1.1x10^{4}$	$9.8x10^{3}$	$1.3x10^{4}$	$(1.1x10^{4})$
1.65	$6.4x10^{3}$	$4.9x10^{3}$	$5.9x10^{3}$	$6.1x10^{3}$	$5.5x10^{3}$	$(5.8x10^{3})$
4.95	$7.1x10^{2}$	$6.8x10^{2}$	$1.3x10^{3}$	$1.4x10^{3}$	$1.3x10^{3}$	$(1.1x10^{3})$
9.90	$9.6x10^{2}$	$9.1x10^{2}$	$6.0x10^{2}$	$5.0x10^{2}$	$5.8x10^{2}$	$(1.7x10^{2})$
20.0	$^{*}6.0x10^{1}$	---	$1.3x10^{2}$	---	$1.4x10^{2}$	$(1.4x10^{2})$
34.0	$1.1x10^{2}$	---	$1.1x10^{2}$	---	$^{*}2.6x10^{2}$	$(1.1x10^{2})$
Caesium						
0	$4.4x10^{3}$	$5.1x10^{3}$	$6.2x10^{3}$	$5.8x10^{3}$	$6.0x10^{3}$	$(5.5x10^{3})$
1.65	$4.2x10^{3}$	$3.0x10^{3}$	$3.2x10^{3}$	$3.4x10^{3}$	$3.5x10^{3}$	$(3.5x10^{3})$
4.95	$^{*}3.3x10^{2}$	$1.4x10^{3}$	$1.4x10^{3}$	$1.4x10^{3}$	$1.4x10^{3}$	$(1.4x10^{3})$
9.90	$7.6x10^{2}$	$1.1x10^{3}$	$1.0x10^{3}$	$6.7x10^{2}$	$6.6x10^{2}$	$(8.4x10^{2})$
20.0	$4.2x10^{2}$	---	$3.0x10^{2}$	---	$2.6x10^{2}$	$(3.3x10^{2})$
34.0	$2.4x10^{2}$	---	$2.9x10^{2}$	---	$2.4x10^{2}$	$(2.6x10^{2})$
Zinc						
0	$1.3x10^{4}$	$1.2x10^{4}$	$1.2x10^{4}$	$1.2x10^{4}$	$1.6x10^{4}$	$(1.3x10^{4})$
1.65	$9.4x10^{3}$	$6.8x10^{3}$	$1.0x10^{4}$	$9.2x10^{3}$	$1.0x10^{4}$	$(9.1x10^{3})$
4.95	$4.7x10^{3}$	$5.4x10^{3}$	$6.3x10^{3}$	$5.5x10^{3}$	$5.9x10^{3}$	$(5.6x10^{3})$
9.90	$4.2x10^{3}$	$4.7x10^{3}$	$4.8x10^{3}$	$4.3x10^{3}$	$4.1x10^{3}$	$(4.4x10^{3})$
20.0	$^{*}3.6x10^{2}$	---	$2.8x10^{3}$	---	$2.4x10^{3}$	$(2.6x10^{3})$
34.0	$^{*}4.6x10^{3}$	---	$2.5x10^{3}$	---	$2.6x10^{3}$	$(2.6x10^{3})$

*- data excluded in calculating the mean K_d value

values have also been plotted against salinity in Figures 4.16-4.18 which show the effect of temperature and pH on the K_d values of the three radio-isotopes. For all three elements, the K_d values were highest in the fresh water and fell quickly with increasing salinity up to 20‰ where they reached steady values. Zinc exhibited the highest K_d in the fresh water and was least affected by salinity. Cadmium and caesium displayed similar values in the fresh water but cadmium showed a much greater salinity effect.

Hydrogen ion concentration

The K_d values derived from this set of experiments are shown in Table 4.9. The effect of the interaction of pH and salinity on the partitioning of the radio-tracers can be seen in Figures 4.16-4.18 which compare the K_d values for the three metals measured at fixed pH values (6,7,8 and 9 ±0.2) with those obtained at the pH values that resulted from mixing the fresh and saline end-members with no pH control. Cadmium and zinc showed a marked pH dependence. The K_d values for both these elements decreased with decreasing pH and the values obtained at ambient pH values closely followed the neutral (pH 7) pH/salinity relationship although they might have been expected to approach the pH 8 values at seawater salinities. Caesium, on the other hand, showed no pH dependence in that all four, fixed pH data sets, as well as those measured at ambient pH values, were virtually identical over the full salinity range.

Temperature

The effect of temperature on the partitioning of trace metals is shown in Figures 4.16-4.18 and the corresponding K_d values are listed in Table 4.10. For cadmium and zinc, the K_d values for any salinity

Table 4.9 The variation of K_d with pH for the metals Cd, Cs and Zn measured at room temperature (about 22°C) and a constant suspended solids concentration of 364mg ℓ^{-1}.

Salinity °/oo	pH 6.0	pH 7.0	pH 8.0	pH 9.0
Cadmium				
0	2.6×10^3	5.7×10^3	6.8×10^3	1.0×10^4
1.36	1.1×10^3	2.1×10^3	3.8×10^3	8.2×10^3
5.78	2.8×10^2	6.6×10^2	1.4×10^3	6.8×10^3
17.0	9.9×10^1	1.7×10^2	6.1×10^2	3.6×10^3
27.2	6.5×10^1	9.9×10^1	2.8×10^2	2.0×10^3
34.0	3.2×10^1	6.5×10^1	2.8×10^2	1.3×10^3
Caesium				
0	7.9×10^3	9.1×10^3	7.9×10^3	7.5×10^3
1.36	2.8×10^3	2.6×10^3	3.3×10^3	2.4×10^3
5.78	8.5×10^2	8.5×10^2	8.5×10^2	8.5×10^3
17.0	3.2×10^2	3.2×10^2	3.2×10^2	3.2×10^2
27.2	2.1×10^2	2.1×10^2	2.1×10^2	2.1×10^2
34.0	1.7×10^2	1.7×10^2	1.7×10^2	1.3×10^2
Zinc				
0	3.0×10^3	9.1×10^3	1.1×10^4	9.1×10^3
1.36	2.2×10^3	5.7×10^3	8.2×10^3	8.2×10^3
5.78	1.4×10^3	3.9×10^3	9.1×10^3	8.2×10^3
17.0	8.5×10^2	2.7×10^3	1.1×10^4	1.0×10^4
27.2	1.1×10^3	2.6×10^3	1.1×10^4	9.1×10^3
34.0	6.1×10^2	2.4×10^3	1.3×10^4	1.2×10^4

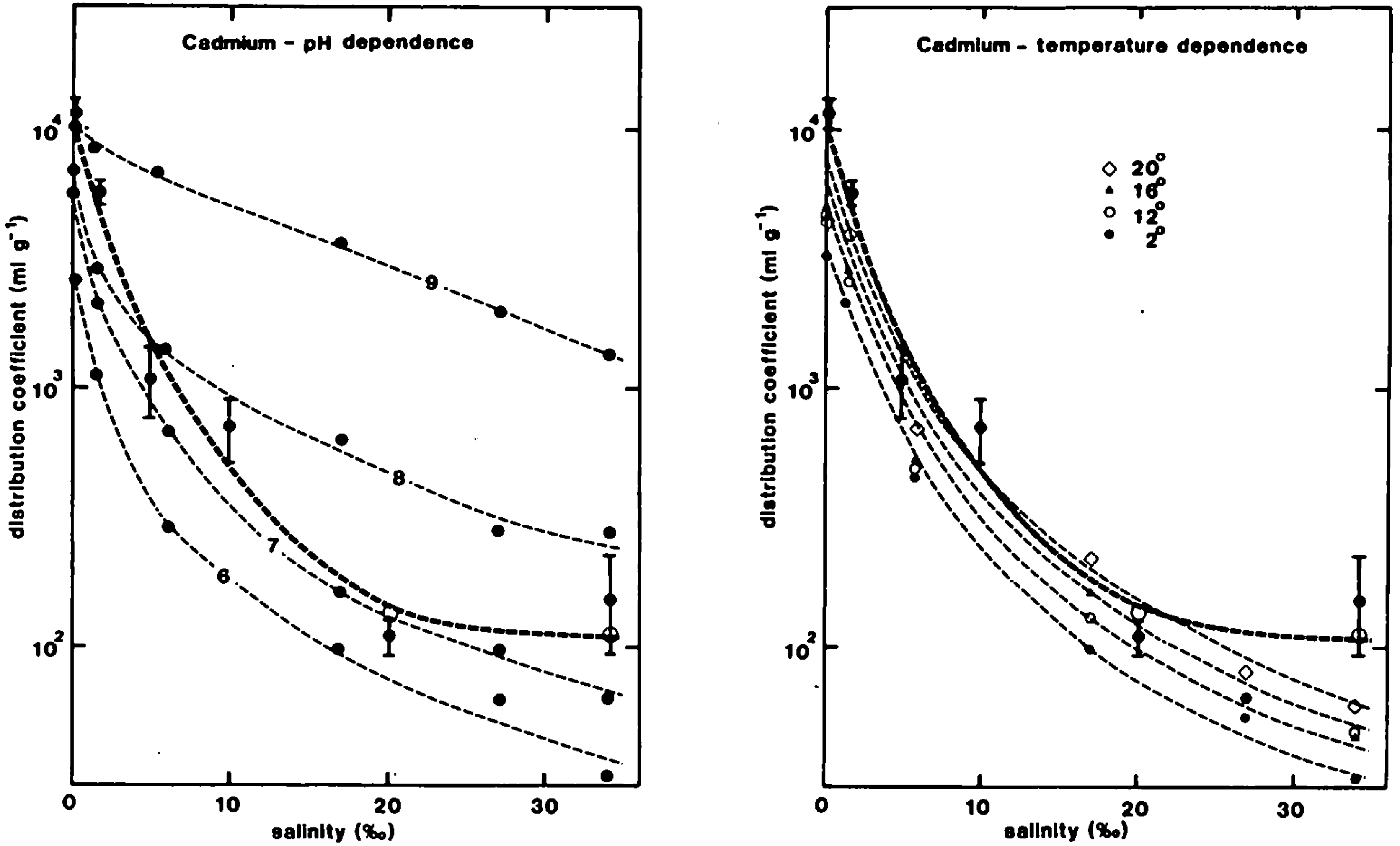


Figure 4.16 The effect of pH and temperature on the relationship between the distribution coefficient (K_d) and salinity for cadmium. The heavy broken line indicates the best fit through the data (solid circles with error bars) acquired under ambient conditions.

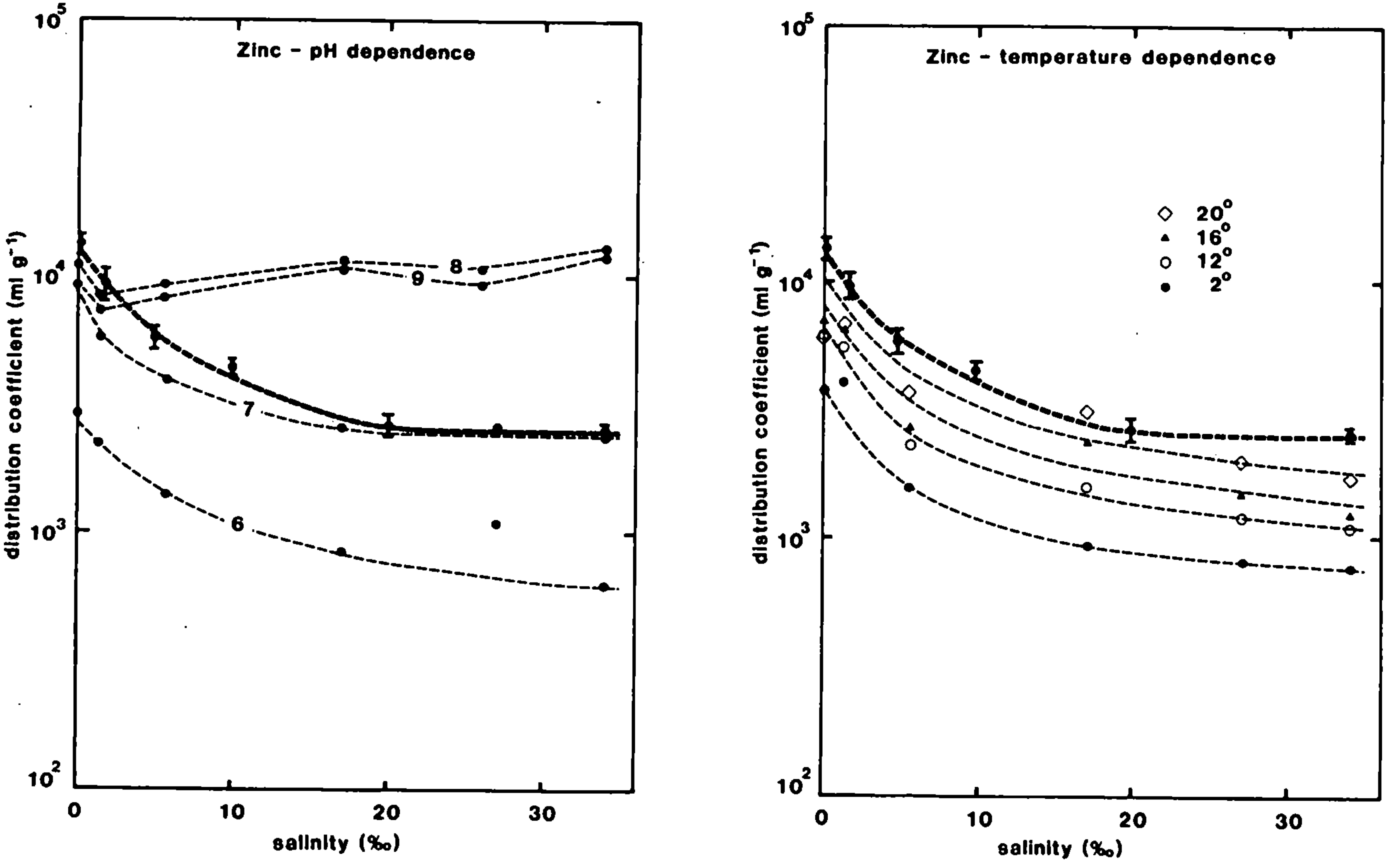


Figure 4.17 The effect of pH and temperature on the relationship between the distribution coefficient (K_d) and salinity for zinc. The heavy broken line indicates the best fit through the data (solid circles with error bars) acquired under ambient conditions.

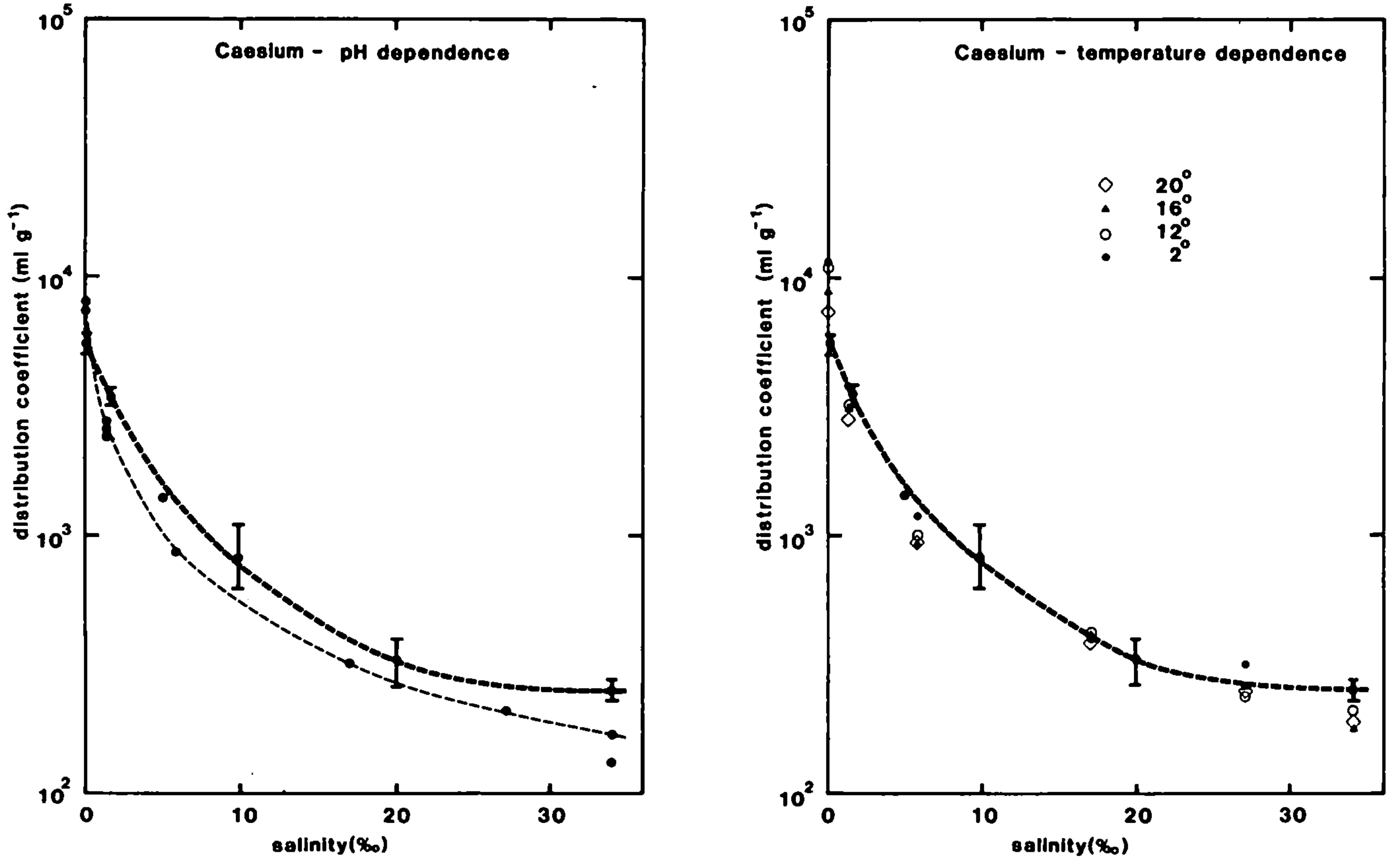


Figure 4.18 The effect of pH and temperature on the relationship between the distribution coefficient (K_d) and salinity for caesium. The heavy broken line indicates the best fit through the data (solid circles with error bars) acquired under ambient conditions.

Table 4.10 The variation of K_d with temperature for the metals Cd, Cs and Zn measured at pH 7.5 and a suspended solids concentration of 364mg ℓ$^{-1}$.

Salinity	Temperature °C			
°/₀₀	2	12	16	20
<u>Cadmium</u>				
0	3.2x10^{3}	4.6x10^{3}	4.7x10^{3}	4.4x10^{3}
1.36	2.1x10^{3}	2.5x10^{3}	2.7x10^{3}	3.8x10^{3}
5.78	4.4x10^{2}	4.8x10^{2}	5.2x10^{2}	6.9x10^{2}
17.0	9.9x10^{1}	1.3x10^{2}	1.7x10^{2}	2.2x10^{2}
27.2	5.5x10^{1}	6.5x10^{1}	6.5x10^{1}	8.2x10^{1}
34.0	3.2x10^{1}	4.9x10^{1}	4.6x10^{1}	6.2x10^{1}
<u>Caesium</u>				
0	1.2x10^{4}	1.1x10^{4}	8.9x10^{3}	7.4x10^{3}
1.36	3.8x10^{3}	3.2x10^{3} 3	3.1x10^{3}	2.8x10^{3}
5.78	1.2x10^{3}	1.0x10^{3}	9.4x10^{2}	9.3x10^{2}
17.0	4.0x10^{2}	4.1x10^{2}	4.2x10^{2}	3.8x10^{2}
27.2	3.2x10^{2}	2.4x10^{2}	2.6x10^{2}	2.5x10^{2}
34.0	2.6x10^{2}	2.1x10^{2}	1.8x10^{2}	1.9x10^{2}
<u>Zinc</u>				
0	3.7x10^{3}	6.0x10^{3}	6.5x10^{3}	5.9x10^{3}?
1.36	4.1x10^{3}	5.6x10^{3}	6.3x10^{3}	6.8x10^{3}
5.78	1.6x10^{3}	2.3x10^{3}	2.7x10^{3}	3.8x10^{3}
17.0	9.4x10^{2}	1.6x10^{3}	2.4x10^{3}	3.2x10^{3}
27.2	8.1x10^{2}	1.2x10^{3}	1.5x10^{3}	2.0x10^{3}
34.0	7.7x10^{2}	1.1x10^{3}	1.2x10^{3}	1.7x10^{3}

value decreased regularly with decreasing temperature and the form of the K_d/salinity relationships was consistent at each temperature. Caesium showed no clear temperature dependence. The data at all four experimental temperatures agreed closely with the values measured at room temperature.

Desorption results

The results of the desorption experiment are shown in Figure 4.19. The three metals exhibited similar responses in that they all showed minimal desorption in the fresh water and the degree of desorption increased with salinity. However, they varied significantly in the proportion of the total metal that was desorbed at higher salinities. Caesium desorption after 40 hours increased from 12% in the fresh water to reach values of 76% at salinities above $20^{\circ}/_{oo}$. Cadmium desorption was around 5% in fresh water over the same period, maximised around $20^{\circ}/_{oo}$ at values of approximately 90% and reduced slightly at higher salinities. The corresponding desorption of zinc increased rapidly from 8% in the fresh water to 25% at $1^{\circ}/_{oo}$ but then more slowly to reach values of 50% above salinities of $20^{\circ}/_{oo}$. Zinc, however, showed the least change in desorption between 4 and 40 hours and, furthermore, reached values which were predictable from the K_d measured in the adsorption experiments. Both the cadmium and caesium results indicated that the approach to partition equilibration reached through desorption was much slower than <u>via</u> adsorption in that the extent of desorption was significantly greater after 40 hours compared with 4 hours. In addition, after 40 hours, both metals had reached only 84% of the value that would be predicted from adsorption equilibration K_d values.

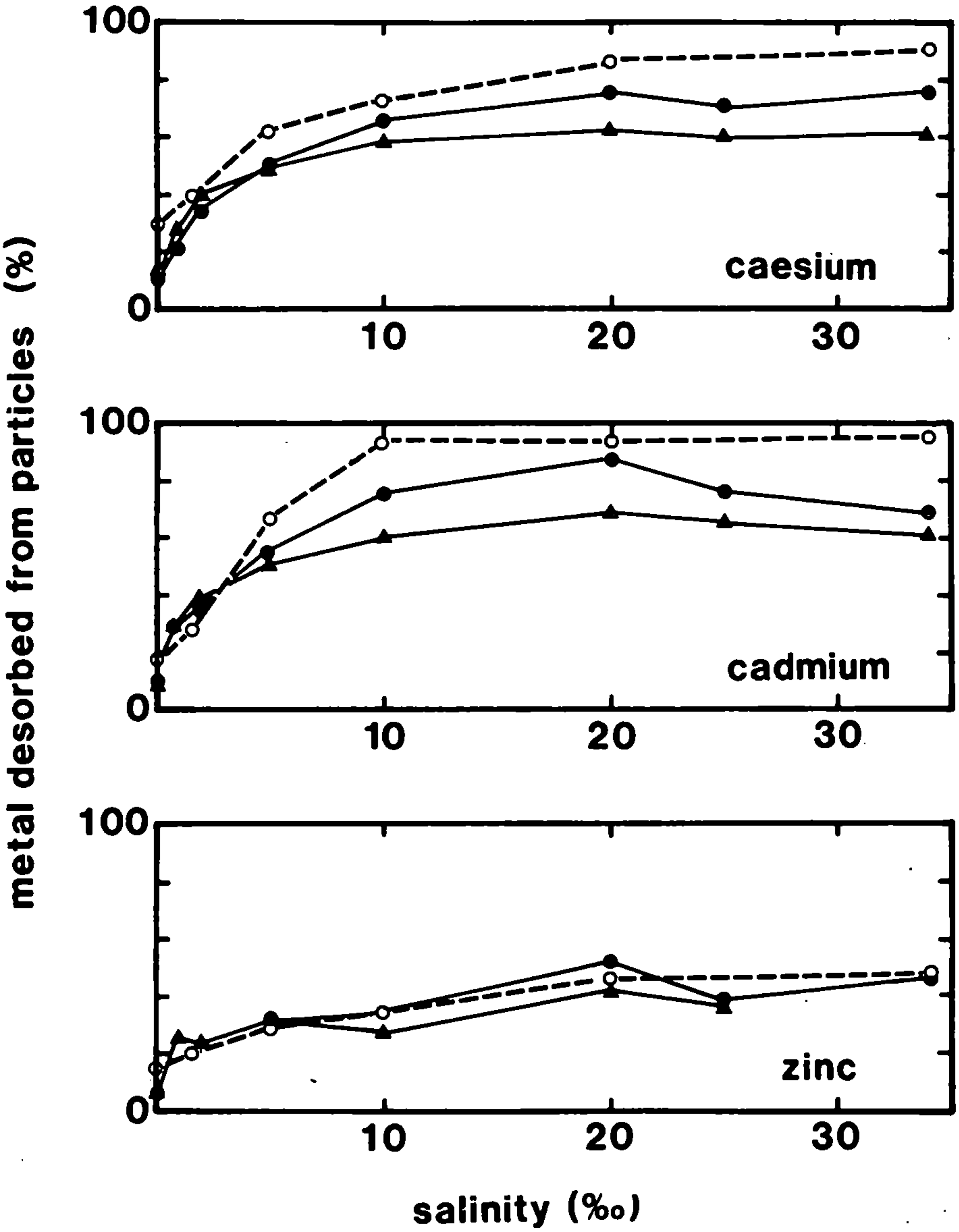


Figure 4.19 Desorption of the metals Cd, Cs and Zn from estuarine particles after 4 (▲) and 40 hour (●) intervals. Predicted values using adsorption Kd values are shown as (○).

4.4.7 Discussion

For given conditions of pH and temperature, and over the range of suspended solids studied (up to 818mg ℓ^{-1}), the adsorption of radioisotopes on to suspended particles increased linearly with concentration of particles giving reasonably constant K_d values. The influence of salinity acted to decrease K_d values, non-linearly as salinity increased, presumably through competition for sites by major ions (predominantly Ca and Mg).

The effect of pH on metal distribution coefficients was generally consistent with predicted behaviour. For cadmium and zinc the proportion of metal in solution increased as pH values decreased and, therefore, the K_d values decreased. Examination of the sorption characteristics of natural particles under controlled temperatures indicated that, for zinc and cadmium, increasing the temperature increased the proportion of metal associated with the particles.

Caesium distribution coefficients showed no temperature or pH dependence. Temperature independent reactions are often indicative of simple sorption processes and caesium is shown as predominantly ionic at all salinities by Turner _et_ _al_. (1981). From the behaviour of only three metals, it is not possible to draw generalised conclusions regarding the underlying properties affecting the different speciation behaviour, however, this subject is discussed in detail by Turner _et al_. (1981).

Comparison of the K_d values measured here with values obtained by other workers (Table 4.11) shows that, although the variations with salinity are similar, absolute K_d values vary by an order of magnitude.

This probably reflects differences in the nature of the particulate material, for example, its source, oxide content, organic content and age. In addition, the method used to determine K_d values must have an effect on the numerical value of the constants. Those workers who have employed radio-isotope uptake/release have generally derived similar data (Li et al., 1984a). However, methods that rely on direct chemical analyses to determine the relative fractions of soluble and particle associated metals are limited by their ability to characterise the exchangeable metal on the particles. This is illustrated by the data of Valenta et al. (1986) for which low temperature (oxygen plasma) ashing and dilute hydrochloric acid were employed to solubilise the particle associated fraction. This would significantly over-estimate the exchangable metal on the particles compared with desorption into metal-poor estuary water and account for the correspondingly high K_d values reported by these authors.

Desorption increased with salinity, as would be predicted from the adsorption study. However, the increase in desorption with time after 4 hours indicates that the process was slower than adsorption. Similar results were found for cadmium and zinc desorption from Rhine sediments (Salomons, 1980) where it was also noted that the proportion of desorbable metal decreased, as the time during which the metals were equilibrated with the particles was increased. This indicates that sorped metals tend to become irreversibly bound within the matrix of the particles and therefore less available for desorption.

Table 4.11 A comparison of K_d values measured in various estuarine environments.

Location	K_d values		reference
	freshwater	seawater	
cadmium			
Hudson/ Mississippi	$1.7x10^4$	$3.7x10^3$	Li et al. (1984a)
Rhine	$3.1x10^4$	$5.3x10^3$	Salomons (1980)
Tamar	$1.1x10^4$	$1.1x10^2$	This work
Mean Coastal Values	---	$2.0x10^3$	IAEA* (1985)
zinc			
Hudson/ Mississippi	$1.2x10^4$	$1.7x10^3$	Li et al. (1984a)
Rhine	$2.6x10^4$	$4.5x10^3$	Salomons (1980)
Tamar	$1.3x10^4$	$2.6x10^3$	This work
Mean Coastal Values	---	$2.0x10^4$	IAEA (1985)
Caesium			
Hudson/ Mississippi	$1.4x10^5$	$9.2x10^2$	Li et al. (1984a)
Tamar	$5.5x10^3$	$2.6x10^2$	This work
Mean Coastal Values	---	$3.0x10^3$	IAEA (1985)

* - International Atomic Energy Agency

4.6 SUMMARY AND CONCLUSIONS

1. The close relationship between the location and magnitude of the turbidity maximum and the position and extent of dissolved, riverine metal removal in the Tamar Estuary provide a strong indication that sorptive exchanges with suspended particles exert a controlling influence on the distributions of soluble metals.

2. The presence of a localised sink for soluble metal situated at the turbidity maximum requires either, an additional metal removal process to 'strip' the particles of metal or, a continual input of metal-deficient particles to counteract the tendency for the particle population to equilibrate with soluble metal. This latter option is consistent with the concept of tidal pumping of particles and the formation and maintenance of the turbidity maximum discussed in earlier sections.

3. The use of radio-isotopes to examine the effect of the estuarine master variables on the partitioning of the metals Cd, Cs and Zn between the solution and particulate phases has proved to be efficient and sensitive. Under laboratory conditions, the empirical distribution coefficients (K_ds) pertaining to suspended particles from the Tamar Estuary and their dependence on salinity, temperature and pH have been measured. Comparisons of these values with published data (Table 4.11) show similar trends with changes in salinity but also indicate that the absolute values are site specific and their predictive value, therefore, limited to the system in which they were measured.

To use distribution coefficients in a predictive mode is relatively straightforward in a steady-state, single reservoir system. However, in estuarine environments, with complex hydrodynamics, independent sediment dynamics and localised turbidity maxima, a sophisticated simulation model is required to predict metal concentrations. In the next section, the feasiblity of employing the K_d values derived in this work to simulate observed metal distributions is examined with the aid of an existing model of the Tamar Estuary.

SECTION FIVE

SIMULATION MODELLING
OF
METAL BEHAVIOUR IN ESTUARIES

5.1 SIMULATION MODELLING

5.1.1 Objectives

This section evaluates the use of distribution coefficients to reproduce the behaviour and transport of trace metals within an estuarine environment. The study was accomplished using an existing model of the Tamar Estuary (Harris *et al.*, 1984) which simulates the fluxes and distributions of salt, sediment and suspended particles.

5.1.2 Description of the model

The Tamar model is based on a one-dimensional simulation of net solute and particle fluxes between mid-tidal values. For this purpose, the estuary was divided into 31 one-kilometre sections and the mid-tide volumes of each segment were calculated from the bathymetry and cross-sectional dimensions. Distances were measured from the estuary mouth at Plymouth Sound and water velocities and other fluxes were notionally positive in the upstream direction. Concentrations were determined at the one-kilometre intervals and fluxes at the intervening half kilometres.

Solute dispersal was determined according to a finite-difference approximation to a one-dimensional, advection-diffusion model. The dispersion coefficents required for this were derived from salt budgets based on salinity observations between 1977 and 1980 (Uncles *et al.*, 1983) and were found to be linearly related to river run-off within any segment of the estuary. However, at salinities below $0.2^{\circ}/_{oo}$ the finite difference approximation provided poor agreement with observations and, for this part of the model, a steady state formulation was employed in which the dispersion parameters were derived empirically to provide optimal agreement between simulated and observed distributions.

In order to describe the distribution of suspended particles within the model estuary, the suspended particle population was taken to comprise marine, riverine and estuarine materials which were treated separately. Particles of either marine or fresh origin were considered to be distributed conservatively and not deposited within the estuary. The concentration of riverine particles was related to run-off at any time and this regression (Harris *et al.*, 1984) was used to generate the concentration of riverine particles in the model. Marine particle loads were set at $5 \mathrm{mg}\,\ell^{-1}$. The concentration of suspended particles comprising the turbidity maximum, i.e. the excess material to that predicted from a conservative distribution of the end-member concentrations, was found to be related to salinity, tidal range and river run-off at salinities between full seawater and $0.2^{\circ}/_{oo}$. At salinities less than $0.2^{\circ}/_{oo}$, the particles were taken to be conservatively distributed (Uncles *et al.*, 1985). The particle distributions generated in this way closely simulated observed distributions of turbidity maxima and varied realistically with the state of the spring-neap tide and river run-off.

An exchange of material between the suspended particle population in the water column and the bed sediment typically occurs around the mid-ebb and mid-flood period in the real estuary and varies with the tidal range. This was simulated using an empirical, but adjustable, exchange factor set at 2.0 that is, the total suspended sediment was exchanged with bed material twice over a 24 hour period. No structure was assigned to the bed-sediment which was, therefore, effectively completely mixed within the entire bed-sediment reservoir of each segment. The exchange of sediment between segments was achieved using sediment fluxes derived from the measurements of mobile sediment migration made over the period Jan 82 to Jan 83 which are reported in Section 3.3. The particles from all sources were considered to be identical in terms of their chemistry. The equations governing the processes included in the Tamar model are described in detail by Harris et al. (1984).

Simulation runs with the Tamar model were confined to a 12 month period covering 1982 for which daily information on the tidal range, the flow rates of the major fresh water sources to the estuary and the internal mobile sediment fluxes were available. River flow data for the Tamar, Tavy, and Lynher were obtained from the South West Water Authority and the tidal ranges from the Admiralty Tide Tables. The physical model was allowed to run for 21 days before undertaking any metal chemistry. This allowed salinity and particle concentrations to achieve values independent of their arbitrary starting states.

5.1.3 Incorporation of the metal K_d/salinity relationship

Examination of the K_d factors obtained under ambient estuarine conditions in Section 4 indicated that for the metals Cd, Zn and Cs the natural logarithm of the K_d was linearly related to the natural logarithm of salinity over the full salinity range:

$$\log_e K_d = a\left(\log_e (S+1)\right) + \log_e K_o$$

where a = the slope of the regression of $\log_e K_d$ against $\log_e (S+1)$

K_o = the intercept on the y axis

The comparison between the experimental data derived in Section 4 and the values generated by these relationships can be seen in Figure 5.1. The correlation coefficients for each of the regressions and the derived a and K_o values that define the 'ambient' conditions and the variations introduced by temperature and pH are given in Table 5.1. However, in the modelling studies reported here, salinity was the only variable affecting the value of the metal distribution coefficient.

Initial modelling trials were undertaken using the distribution coefficients measured for zinc, but, in practice, any of the three metals could have been employed. At the level of tuning the model and evaluating its ability to predict metal behaviour and distributions, these trials simply required a 'typical' metal. Dissolved zinc was introduced to the model with the river water at a concentration of $16 \mu g\ \ell^{-1}$. The concentration of the metal in the marine end-member was constrained by setting a value of $1 \mu g\ \ell^{-1}$ in segment 31 at the mouth of the estuary. The linear regression relating the K_d for zinc to salinity was incorporated in the model such that for each time step the appropriate distribution coefficient value would be determined in each estuary segment. These values were then used to partition the metal between the soluble and particulate phases in the water column within each segment. The exchange factor then redistributed particle-associated metal between the suspended and sedimentary particle reservoirs.

Earlier experiments had indicated that this model required approximately 20 simulated years to obtain equilibrium with a soluble component subject to uptake on the particles at natural rates. This was because the volume of bed-sediment required to balance the internal

Table 5.1 The correlation coefficients and factors describing the regression of the distribution coefficients for Cd, Cs and Zn against salinity. There were six pairs of data in each regression.

metal	slope a	intercept K_o	correlation coefficient
Ambient Conditions			
Cd	-1.414	1.51×10^4	-0.985
Cs	-0.922	6.75×10^3	-0.989
Zn	-0.511	1.37×10^4	-0.976
Controlled temperature			
Cd 2°C	-1.397	6.04×10^3	-0.972
12°c	-1.329	5.83×10^3	-0.996
16°C	-1.332	6.26×10^3	-0.992
20°C	-1.274	6.96×10^3	-0.983
Cs 2°C	-1.062	1.01×10^4	-0.997
12°C	-1.093	9.33×10^3	-0.997
16°C	-1.057	8.13×10^3	-0.998
20°C	-1.012	6.96×10^3	-0.999
Zn 2°C	-0.513	4.56×10^3	-0.970
12°C	-0.515	7.59×10^3	-0.984
16°C	-0.478	7.69×10^3	-0.967
20°C	-0.365	7.36×10^3	-0.937
Controlled pH			
Cd pH6	-1.188	2.80×10^3	-0.996
pH7	-1.248	6.15×10^3	-0.999
pH8	-0.933	7.67×10^3	-0.995
pH9	-0.538	1.28×10^4	-0.934
Cs pH6	-1.073	7.30×10^3	-0.999
pH7	-1.094	7.71×10^3	-0.997
pH8	-1.093	7.80×10^3	-0.999
pH9	-1.081	6.85×10^3	-0.998
Zn pH6	-0.391	2.96×10^3	-0.954
pH7	-0.368	8.37×10^3	-0.991
pH8	-0.062	9.13×10^3	+0.552
pH9	+0.077	7.77×10^3	+0.628

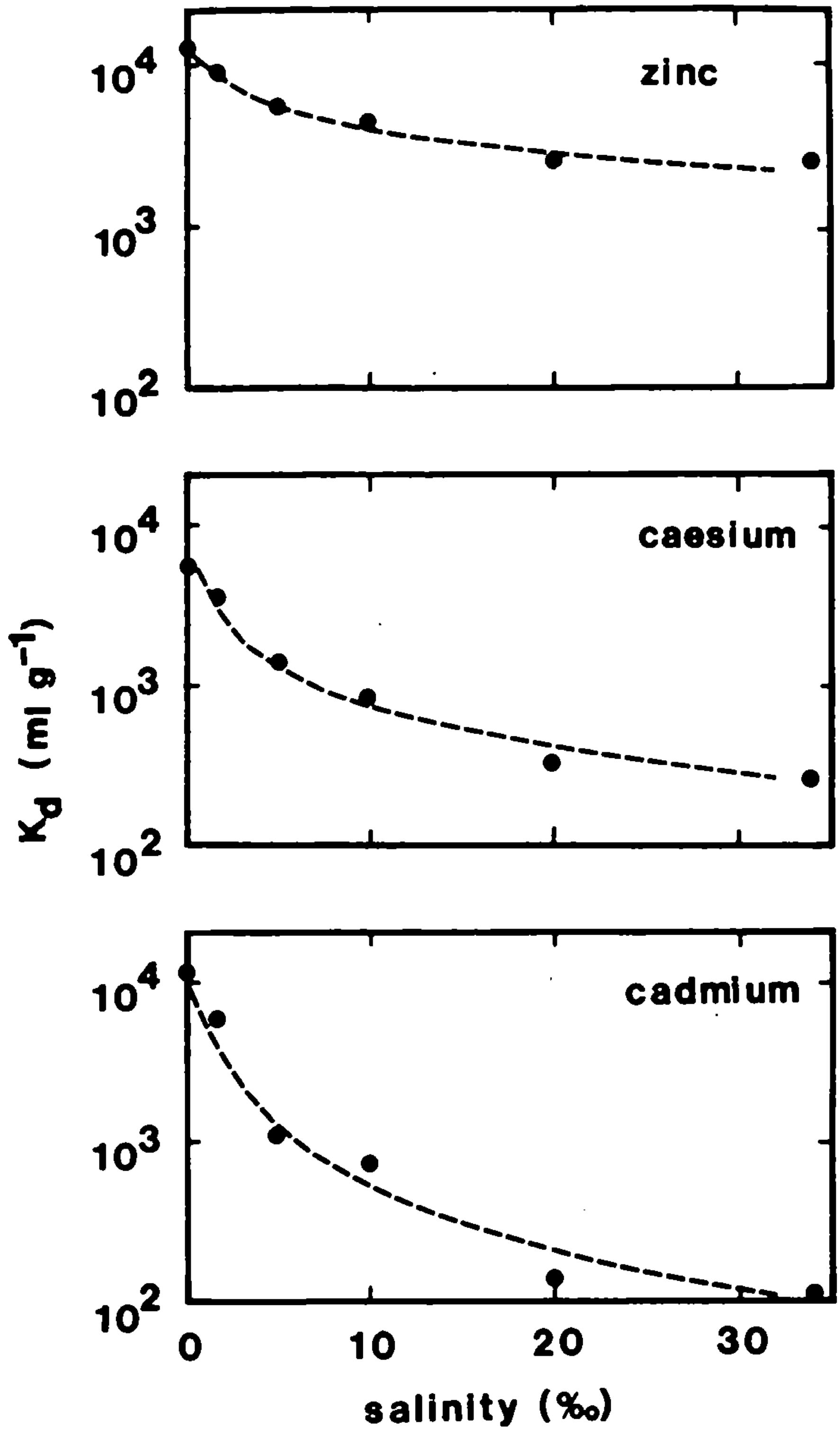


Figure 5.1 Comparisons of the regression: $\log_e K_o$ versus $\log_e(S+1)$ (hashed line) with distribution coefficient data (●) measured in Section 4.

sediment fluxes dictated by the observations in Section 3 was extremely large and represented a significant reservoir for metal within the estuary. To avoid the large amount of computing time* required to attain equilibration, the sediment-associated metal concentrations in each segment were pre-set to values predicted by the distribution coefficients for an average estuarine salinity distribution (river run-off, 15m^3 sec^{-1}).

5.1.4 Results of the preliminary experiments

Using the conditions described above, the model was run for the entire period of 1982. Examples of stable low (July) and high (November) river run-off conditions are presented for spring and neap tides in Figure 5.2. From these diagrams it is clear that adequate reproductions of measured distributions of the metal were generated in which removal of soluble metal occurred at the site of the turbidity maximum and the extent of metal removal was of realistic proportions. In addition, under low river flow conditions, a mid-estuarine input of metal was evident. These simulated distributions were very similar in form to distributions of dissolved metals, particularly zinc and nickel, measured in the Tamar (see Section 4.2). However, it is clear from a comparison of the spring and neap data for July in Figure 5.2 that the degree of metal removal and remobilisation is not sensitive to changes in the concentration of suspended solids at the turbidity maximum. It is likely that the removal of trace metal at the turbidity maximum, in this model, is simply dependent on the rate of positive (up-estuarine) flux of metal-poor sedimentary particles. This implies

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* One simulated year of the Tamar model required nearly two hours of central processor time on a GEC 4190 computer.

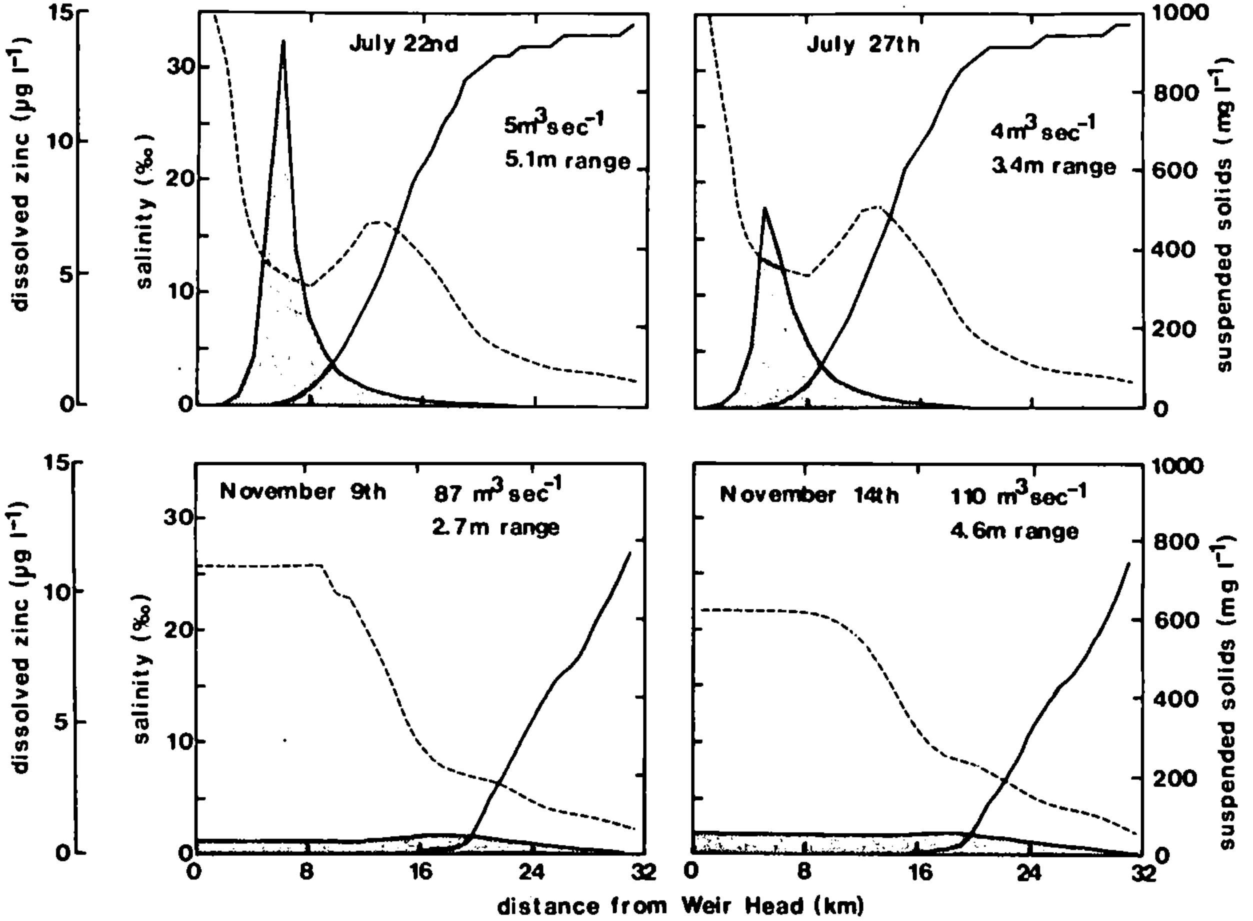

Figure 5.2 Computer simulations of dissolved zinc distributions (hashed line) obtained with the Tamar Model under low river run-off (July) and high run-off (November) conditions. Salinity is shown as a solid line and suspended solids are stippled.

that additional chemical processes, possibly within the bed-sediment population, are required to explain the more pronounced and resuspension-linked, removal of trace metal observed at the turbidity maximum in the Tamar Estuary.

5.1.5 Conclusions from the model results

The use of distribution coefficients with a validated hydrodynamic model, that incorporates suitable sediment and suspended particle behaviour, allows estuarine metal distributions to be computed. The distribution coefficients derived in this work were of sufficient accuracy to allow metal profiles to be generated in which the magnitude of the changes was essentially correct when compared with distributions of soluble metal measured in the Tamar.

The demonstration of both localised removal (roughly coincident with the turbidity maximum) and a mid-estuarine input of soluble metal (at approximately $10^{\circ}/_{\circ\circ}$ salinity under low run-off conditions) indicates that bed-sediment fluxes are essential to the simulation of estuarine metals. Bed-sediment fluxes are the only mechanism of transporting metal-rich particles down-estuary where subsequent remobilisation with the onset of net up-estuarine sediment pumping can introduce desorption into metal-poor water. Similarly, up-estuarine transport of metal-poor particles to the turbidity maximum is the only mechanism within the model that will prevent particulate material at the turbidity maximum from becoming equilibrated with the soluble metal and thereby limiting further metal removal.

5.1.6 Limitations of the present model

It is recognised that the present model has several weaknesses but its overriding strength is the facility to tune individually various parameters so that their contribution to the overall picture of estuarine metal behaviour can be investigated. Obvious candidates for examination in controlled experiments are the sediment/suspended particle exchange factor, the bed sediment fluxes and the validity of K_d values derived from a single particle population to metal behaviour throughout the estuary.

On the negative side, it is clear that the assumption of uniform mixing of deposited sediments within the entire mobile sediment population in a particular segment is a weakness in the present model. No consideration is given to diagenetic processes within the buried sediments. The only mechanisms that are considered are inputs to the sediment through sedimentation of particles plus adsorbed metal and removal through remobilisation of the sediment into metal-poor water. In reality, depositing sediments settle on the surface of the existing sediment and are mobilised first during the subsequent resuspension phase. Bioturbation would tend to effect slow mixing through the sediment, but it is not known whether this process is significant in the dynamic, turbid region of the turbidity maximum. Most work on estuarine bed-sediments points to markedly non-uniform vertical structure dominated by redox chemistry (Emerson et al., 1984; Watson et al., 1985). The large concentration gradients generated under these conditions give rise to diffusion of solubilised components which contributes to physical remobilisation. However, the incorporation of depth-related profiles for particular parameters within the bed-sediment effectively requires a two-dimensional model with a concomitant increase in complexity and computing power.

Similarly, generation of the turbidity maximum from an empirically derived relationship between salinity, tidal range and river run-off conditions is limited. In reality, this feature is generated by asymmetry in the flood and ebb tidal velocities (Allen *et al.*, 1980; Uncles *et al.*, 1985) which also generates the internal fluxes of bed sediment (Bale *et al.*, 1985). Next to salinity, suspended solids are probably the most important factor influencing the behaviour of chemical components in estuaries. It is unlikely, therefore, that realistic simulations of internally cycled elements such as Mn (Morris *et al.*, 1982a) and possibly trace metals, that respond to the different redox environments existing in the suspended and sedimentary phases and which are also subject to different transport regimes within each phase, can be generated using a tidally averaged model and exchange factors.

The adoption of a nominal marine value for the metal of 1μg ℓ$^{-1}$ set at segment 31 was also flawed. With hindsight, this value should have been related to a marine salinity value (e.g. 34-35°/$_{oo}$). Under high run-off (November, Figure 5.2) the salinity at 31km was less than 20°/$_{oo}$ such that, under conservative dilution, the metal concentration at that point should have been considerably higher (5-8μg ℓ$^{-1}$).

SECTION SIX

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

6.1 CONCLUSIONS FROM THIS STUDY

Particulate material in estuaries experiences a relatively long residence time compared with soluble components because of the hydrodynamic processes that act to trap particles within the estuary. In addition, the particles are subject both to cyclical remobilisation and sedimentation, under the influence of semi-diurnal and spring-neap tidal action, and to cyclical, axial redistribution on a seasonal time scale under the influence of river run-off.

Primarily because of the long residence time, the estuarine particle population, including readily mobilised bed-sediment, comprises material of a reasonably uniform composition and surface characteristics. However, measureable local modifications to the bulk composition occur due to changes in the organic content through biological activity. The particulate carbon content increases when suspended solids concentrations are low enough to allow photosynthetic activity within the water column and generally decreases in the turbidity maximum which is a zone of net respiration. Similarly, dilution of the organic content of spm by the resuspension of lower organic content bed-sediment can be observed. The distribution and properties of suspended particles indicate that the organic content of estuarine particles affects their tendency to aggregate and, indirectly, their settling behaviour. Selective retention of specific particle size ranges within the turbidity maximum also introduces measurable compositional differences to the particle population within this region.

Suspended particles are shown to exert a profound influence on the distribution of numerous soluble components in estuaries. This is due primarily to surface sorptive exchanges. These effects are particularly marked in the turbidity maximum because of the high particle concentration. Cycling of particles between the contrasting redox environments of the water column and bed-sediment by the semi-diurnal tides, as well as between high and low salinity regions on a seasonal time-scale, provide a mechanism for cycling of heterogeneously reactive species in estuaries.

The combination of relatively constant particle composition and regular cycling of material within the estuary implies that laboratory-derived distribution coefficients measured on bulk samples may be applicable to predictions of metal behaviour throughout an estuary. However, comparison of measured distribution coefficients for the Tamar with published values for other estuaries (Salomons, 1980; Li *et al.*, 1984a; Valenta *et al.*, 1985) suggests that the coefficients are relatively site-specific. It is not possible, from this work, to predict how seasonal changes in the composition of estuarine suspended particles would affect the overall picture of dissolved metal behaviour, nor to what extent semi-diurnal tidal resuspension of sediment affects the net surface quality, and hence distribution coefficient, of the suspended particles. However, measurable differences in particulate carbon, both seasonally and over tidal cycles, implies that the surface adsorption characteristics of estuarine particles may well change with time within a particular system.

With the use of a validated hydrodynamic model of the Tamar Estuary, adequately realistic profiles of soluble zinc were obtained using laboratory-derived distribution coefficients. The simulated dissolved metal profiles exhibited removal and, under low river flow conditions, remobilisation into the water column, which were essentially of the same magnitude as those measured in the estuary. In addition, the general form of the dissolved metal distributions, and the location of both the removal and input phenomena, closely duplicated observed distributions. This implied that, for the Tamar system, the measured distribution coefficients were of the right magnitude but, more importantly, that, in this estuary, the metal exchange processes were totally dependent on the exchange of particles between sediment and water column and the along-estuary fluxes of bed-sediment generated by the seasonal variation in river run-off.

The influence of physical sediment transport and particle cycling have been recognised as the controlling factors determining the distribution of particulate Zn, Pb, Cu and Ni in parallel studies of the macro-tidal Garonne-Gironde system. Jouanneau et al. (1983) concluded that the observed distributions, indicating metal impoverishment in the zone of the turbidity maximum, particularly of non-detrital Zn, were controlled by the physical processes that developed and transported the turbidity maximum although degradation and solubilisation of organically bound Zn within the turbidity maximum was also implicated. Similarly, the behaviour of soluble Pb in the same estuary (Elbaz-Poulichet et al., 1984) has been shown to be directly related to a combination of sorptive exchange with, and internal cycling of, particles driven by tidal asymmetry as described in this work.

This study has added to the general understanding of estuarine chemical processes by quantitatively relating the contributions made by particle cycling and sorptive exchanges to the overall distribution and transport of estuarine metals. This was only made possible by measuring the masses of the various particle reservoirs and the fluxes of particulate material between them. It has enabled successful simulation modelling of metal behaviour within the estuary and will allow the importance or effect of numerous factors to be assessed by experimentation.

Consideration of the form of the dissolved metal distributions measured in this estuary (and others), with removal at the turbidity maximum and remobilisation in mid-estuary, suggests that the net effect probably has little influence on the long term transport of soluble metals to the oceans. However, Duinker and Nolting (1976) deduced that the Rhine was a net sink for trace metals associated with particles. Perhaps, it can only safely be concluded that no two estuaries are alike and we must simply strive to reduce the component processes to a generalised level where they can be incorporated into the appropriate hydrodynamic models.

Nevertheless, the ability to model the behaviour of metals in turbid estuaries, albeit only within the chemical environment of a relatively oxygenated, unpolluted estuary at present, has great potential for predicting the short-term effect of events such as sporadic pollutant discharges or, conversely, the influence of engineering operations, e.g. drinking water abstraction or the construction of barrages, that affect the hydrodynamic regime.

6.2 RECOMMENDATIONS FOR FURTHER STUDY

In preparing this report, it became clear that various facets of the study would have benefitted from additional research (the power of hindsight) and that four, at least, of these areas would provide focal points for subsequent studies. For example, on examining the seasonal series of axial profiles of supended solids, particle size and particle composition, it was evident that we had not acquired data corresponding to episodic conditions such as extreme river run-off or severe weather, when sediment transport and disturbance could, predictably, be very significant. The reasons for this omission are simple: surveys are planned in advance and, therefore, have only a limited chance of corresponding to a period of extreme conditions. More importantly, conventional logistic reasons of comfort and safety tend to make boatmen, particularly in small craft, avoid these adverse conditions. This is one area where studies of sediment transport by remote sensing, moored instruments or, if feasible, rapidly mobilised surveys would provide valuable information.

The development of general estuarine models capable of simulating complex, cyclical chemical processes, particularly those involving redox changes within the sediment and heterogeneous reactivity in the water column, require a more sensitive interpretation of sediment behaviour than is currently available. To achieve this, modellers require much more information about the underlying physical characteristics of particles that affect sediment mobilisation and settling and their responses to changes in tidal state (current strength) in estuaries. Progress in these areas will allow the development of models which can simulate the extensive changes in suspended solids and, consequently, in water chemistry that occur with a semi-diurnal frequency.

Lastly, the use of a single bulk sample of suspended material from the turbidity maximum to undertake laboratory measurements of metal distribution coefficients provided valuable information. However, it is clear from this work (Section 2.7) that the organic composition of suspended material, and probably therefore, the surface characteristics also, change significantly along the length of the estuary. Although the turbidity maximum mediates most of the trace metal reactivity, it would be valuable to undertake a series of field-type incubations with radio-isotopes to assess metal distribution coefficients on fresh particulate material throughout the estuary. In particular, the role of adsorbed organic coatings and the increased organic composition of particles away from the turbidity maximum zone, as well as seasonal and tidally mediated variations in particle surface characteristics, would provide an interesting area for further study of metal exchange processes in natural waters.

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APPENDICES

Appendix 1.

Dates of the suspended particle characterisation surveys carried out during 1982.

Sampling dates	Work undertaken
February 1	axial profiles, spring-neap series (winter)
" 3	
" 5	
" 8 *	
" 10	
" 12	
April 20 *	repetitive profiling over diurnal tidal cycle
June 15 *	axial profile (low run-off)
July 27	axial profiles, spring-neap series (summer)
" 29	
" 31	
August 2	
" 4	
" 6 *	
" 8	
" 9	
October 13 *	axial profile
December 7 *	axial profile (high run-off)

* = sampling for POC and electrophoretic mobility

Appendix 2.

Station positions occupied during the bed-sediment surveys in 1983.

February		August	
km from weir	No of samples	km from weir	No of samples
3.0	2	1.2	2
3.5	2	1.5	1
4.4	1	1.9	2
4.5	1	2.5	2
4.6	2	3.0	2
4.9	1	3.6	2
5.6	2	4.1	2
5.9	2	4.9	2
6.2	1	5.2	2
6.6	2	5.7	2
6.8	2	6.3	2
7.0	2	6.8	2
7.4	1	7.6	2
7.7	2	8.9	2
8.2	2	9.9	2
8.8	2	10.5	2
9.3	2	11.6	2
9.8	2	13.3	2
10.3	2	14.2	2
10.8	1	15.6	2
11.2	2	16.2	2
11.6	3	17.2	2
12.0	2	18.1	2
12.6	7	19.9	2
13.3	2	20.6	2
13.8	3	22.0	2
14.2	2	23.8	2
14.6	2	24.4	2
15.5	2	26.3	1
16.0	2	26.6	2
16.4	1	28.9	2
17.1	2	29.4	2
17.4	3		
18.1	6	total 32	62
18.7	2		
19.6	2		
19.9	1		
22.0	2		
23.0	2		
23.6	2		
24.4	10		
29.0	2		
total 42	96		

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PAPERS IN PRESS

*Bale, A.J. and Morris, A.W. In situ measurement of particle size in estuarine waters. Estuarine, Coastal and Shelf Science.

*... Papers enclosed with this thesis.