THE REMOVAL AND REMOBILISATION

OF HEAVY METALS

DURING ESTUARINE MIXING

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ABSTRACT

Elemental analyses have been made of dissolved, suspended particulate and sedimentary Cu, Mn, Zn following axial surveys of the Tamar Estuary. Continuous monitoring of the estuarine master variables was made during each survey. Selective digestion methods were applied to the particulate and sediment samples to determine the detrital and non-detrital fractions. These experiments showed that in general about 80-100% Mn, 60% Zn and 20% Cu were in the non-detrital form. Rank order correlation tests of the sediment results showed that the summer profiles were consistently different to 20 randomly generated profiles of the same data. In contrast the winter distribution showed a greater tendency to randomness which was related to the high energy resuspension processes dominant during that period. This temporal variation in sediment metal content has been interpreted in terms of a seasonal sediment accretion-erosion cycle observed in the estuary.

The axial profiles of dissolved Zn and Mn often showed similar trends with a minimum concentration in the freshwater above the salt-wedge and a mid-estuarine maximum. A statistical analysis of the data using F-ratio tables, which also took into account variations in both salinity and turbidity, showed that the relationship between Zn and Mn was in agreement with the hypothesis that the two elements are responsive to similar sorption processes in estuaries. Copper was rarely correlated with either Mn or Zn under the same reaction conditions, which suggested a different estuarine geochemistry.

The dissolved, suspended particulate and sediment data for the three metals were then used to develop a two-box model of the Tamar Estuary. The seasonal transfer of Cu, Mn and Zn was then determined using the model. In general the overall mass transport followed the sequence Mn > Zn > Cu, with large transfers of material from the upper to lower estuary occurring in winter. The model was of use in predicting the fate of metals input from the mineralised catchment area feeding the Tamar Estuary.

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1 PRELIMINARY REMARKS

The growing awareness of man's impact on the environment is currently
becoming an essential ingredient of the design and operation of
major industrial, urban and coastal development projects. This is
particularly important for those developments situated on and around
the World's estuaries (Turekian, 1971; Cato, et al., 1980). The
only reliable way to assess the likely consequences of these major
projects is by obtaining an insight into the physical, chemical and
biological processes prevalent in estuaries and, using the field
measurements, construct predictive models which simulate the estuarine
behaviour. The models can then be manipulated to assess the impact
of man's activities on the estuarine environment (Gerlach, 1975).

Pollution in estuaries (Förstner, 1980) creates social, economic and
ecological problems which directly, in decontamination measures, or
indirectly, in social and human health aspects, lead to a need for high
expenditure to remedy the situation. During the late sixties and early
seventies, environmental concern and subsequent political lobbying
added a new dimension to the cost analysis of major construction schemes,
namely 'the cost to the environment'. All modern schemes incorporate
an assessment of environmental impact, for example the GEMBASE study
(Radford, 1979) for the proposed Severn Barrage Scheme, be it directly
as in water quality, or indirectly, such as aesthetic quality of
building design. The main consideration is usually financial cost,
in which the price of unproductive antipollution measures is often of
low priority compared to efficiency of the industrial process.

The recent spectacular rise in the number of investigations into heavy metal concentrations in the environment followed few but much publicised catastrophes relating to mercury (Minimata Bay, Japan) and cadmium (also Japan, the Itai-itai disease) (Bryan, 1976). In many regions industrial effluents, local mining, sewage and dredge spoils contribute significantly to the supply of heavy, potentially toxic metals in estuaries and coastal waters (Abdullah, et al., 1972; Mackay, et al., 1972; Halcrow, et al., 1973; Ali, et al., 1975; Vivian and Massie, 1977; Taylor, 1979; Loring, 1981). The importance and long term effects of these metals, particularly with respect to marine life, have led to many biogeochemical studies (Elderfield, et al., 1971; Müller and Förstner, 1975; Burton, 1976; Olausson and Cato, 1980). Although some heavy metals, albeit at relatively low concentrations, are essential for enzymic activity (Bryan, 1976), they also form an important group of enzyme inhibitors when natural concentrations are exceeded; metals including Ag, Cd, Cu, Hg and Pb are particularly toxic and usually inhibit enzyme activity. Consequently most heavy metals are potentially harmful to living organisms (Wood, 1974; Thornton, et al., 1975; Bland, et al., 1982). The classification of Wood, (1974) segregated the metals into:

(i) non critical

(ii) toxic (insoluble or very rare)

(iii) very toxic (and relatively accessible)

The toxicity of the metal is dependent upon its chemical form and thus the species of metallic compound or ion (often metals associated with humic substances are required by organisms), its availability, solubility, binding affinity and biological activity (Burton, 1976; Mantoura, et al., 1978). Whilst the studies mentioned above have

evaluated the heavy metal impact on marine organisms, it is only recently that workers have concentrated on the internal biogeochemical cycling mechanisms within the estuary itself (Duinker, et al., 1974; Elderfield and Hepworth, 1975; Thomson, et al., 1975; Duinker and Nolting, 1978; Loring, 1978; Morris, et al., 1978; Duinker, et al., 1979; Eaton, 1979b; Elderfield, et al., 1979; Morris, et al.,1981; 1982a; 1982b; 1982c). The actual occurrance of heavy metals in the estuarine environment is complicated by the fact that they can be partitioned between the dissolved and particulate forms (Gibbs, 1973; DeGroot, et al., 1976). The internal chemical cycling mechanisms are controlled to a large extent by the availability of highly surface active particulates and,at the freshwater-brackishwater interface (F.B.I.), a continuously varying solution composition. The physical complexities of the estuarine system therefore exert a large influence on the chemical reactions in the water column and it is important that the timescales of the physical processes be separated from the chemical ones. In this study three metals of differing reactivity were selected for investigation, namely Cu, Mn and Zn. The major objective was to evaluate the pathways by which these elements were cycled within the Tamar Estuary. The quantitative information derived from such a study is of value to the refinement and further development of precise geochemical models of estuarine systems.

1.2   PHYSICAL PROCESSES IN ESTUARIES

1.2.1   Flushing Characteristics

The classification of estuarine types varies according to the specific
interest of the person concerned (Pritchard, 1967). The definition
by Fairbridge, (1980) incorporates the necessary hydrodynamic, as
well as hydrochemical factors, in a suitable definition of an estuary.
He states that: "An estuary is an inlet of the sea reaching into a
river valley as far as the upper limit of tidal rise, usually being
divisible into three sectors;

(i)   a marine or lower estuary, in free connection
with the open sea

(ii) a middle estuary, subject to strong salt and
freshwater mixing

(iii) an upper or fluvial estuary, characterised by
freshwater, but subject to daily tidal action."
The delineation between these three sectors will vary from estuary to
estuary and from day to day within a particular estuary.

Stratification parameters have also been used to define estuaries
(Ketchum, 1951; Hansen and Rattray, 1966; Dyer, 1973), the most widely
used is the stratification hydrochemical system first developed by
Cameron and Pritchard, (1963);

(i) salt-wedge estuaries, in which the freshwater, being
less dense than saltwater, flows outward over the seawater surface
which forms a saltwater wedge on the estuary bed.

(ii) fjords, a special case of salt-wedge estuary with deep
lower layer. Tidal oscillation will only affect the near surface

layer because of the overall depth of the fjord and entrainment is the main mixing process.

(iii) partially-mixed estuaries occur where tidal movement causes harmonic oscillation in the estuary and the turbulence created mixes the salt and freshwater more efficiently than entrainment. The surface salinity is observed to increase more slowly downestuary than in salt-wedge types.

(iv) well-mixed estuaries occur where the tidal range is large and the resultant turbulence is sufficient to break down the vertical salinity stratification so that the water becomes vertically homogeneous.

In the case of the Tamar Estuary (Moorehead, 1982) the variability of mixing throughout the length of the estuary produces a range of conditions; from well mixed at the mouth to partially stratified in mid estuary and well stratified in the low salinity region.

An important aspect of estuarine studies and consequent effects of pollutants is the residence or flushing time of the freshwater in the estuary. This is dependent upon several variables including; river discharge, estuary volume and tidal volume. The flushing characteristics are important to the chemical processes in that they determine the timescales for chemical reactions to take place under given water column conditions. The first characteristic is the flushing number (Arons and Stommel, 1951) which essentially describes the mixing within an estuary. The work of Arons and Stommel, (1951) defines a one-dimensional model in which the flushing number, F, is defined by observed salinities and distances from the head of the estuary. The

values of F were shown to be related to the hydraulic parameters of the estuary which basically represent the river flow : tidal flow ratio. In general, if F > 1, then the estuary is a salt-wedge type; if F = 0.25, then it is partially mixed and if F < 0.1, it is fully mixed. In addition to F, the flushing time, T, can be determined from the estuarine parameters;

$$T = \frac{Q}{R}$$

where Q = volume of freshwater in the estuary or segment, R = river flow rate. The value of Q is obtained from the equation

$$Q = Vf$$

where V = average volume of water in the estuary or segment, f = freshwater fraction obtained from measured salinities.

The determination of flushing time is important as it is a major component of the estuarine physical timescales. Figure 1.1 shows the approximate timescales of physical processes relevant to mixing in the estuarine system and upon which the chemical processes are super-imposed. The chemical reactivity of heavy metals (and any other dissolved species) will be dependent upon many of the physical processes such as mixing in the water column, the resuspension of bed sediment and the dwell time at a particular location. For example, transport of water and particles in the riverine region would tend to be rapid up to and including the mixing within the turbidity maximum. Thus, only relatively fast chemical reactions would have time to go to completion at relatively low pH and ionic strength. However, mixing through the freshwater-brackishwater interface would take hours and
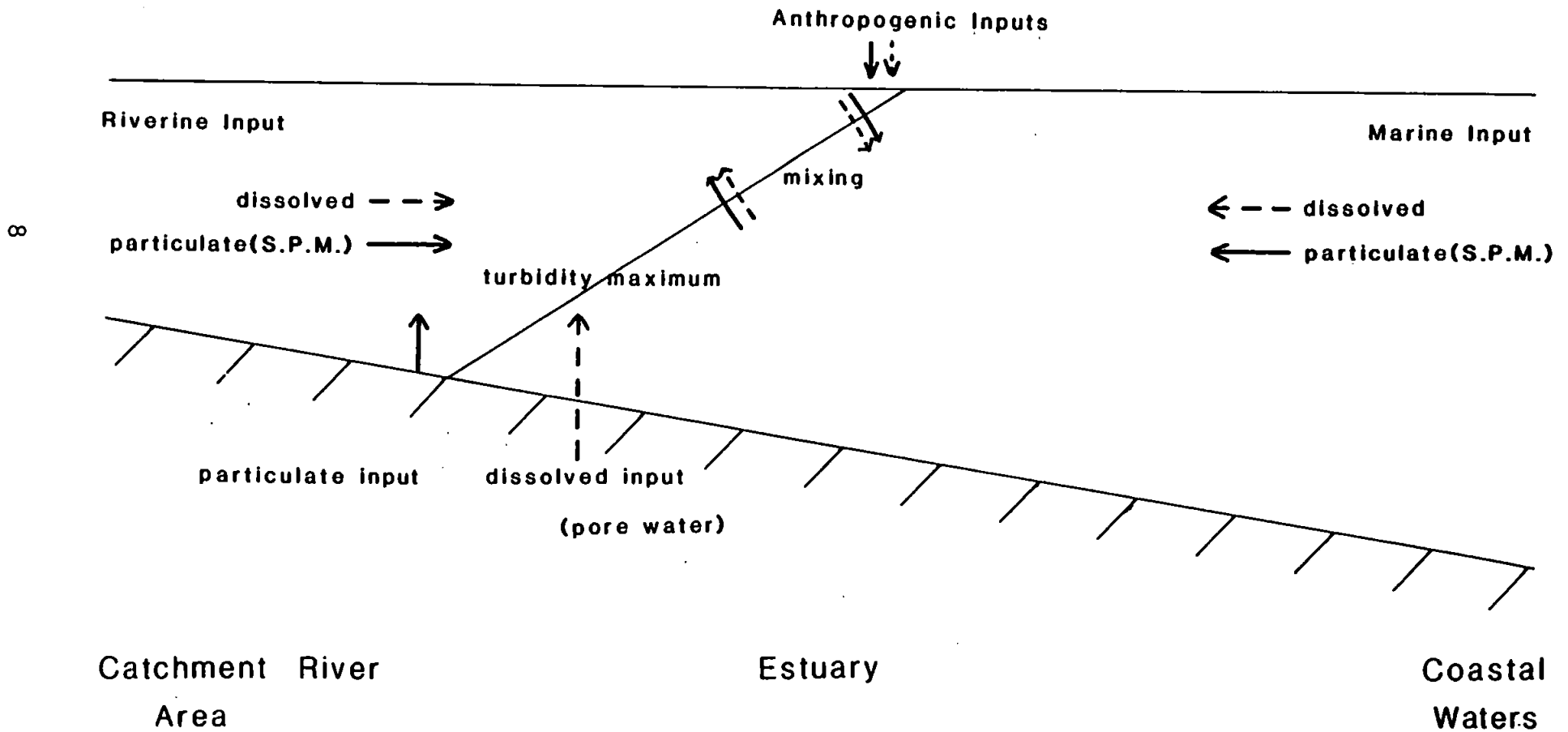
Figure 1.1 Physical processes and approximate timescales of relevance to estuarine chemical behaviour.
– – – dissolved phase transport; ———— particulate phase transport

even longer in the lower estuary and coastal waters. Here many adsorption/desorption reactions can reach a new equilibrium and it is only relatively slow reactions, like the oxidation of Mn (II). which may be incomplete.

1.2.2   Sediment Transport and Deposition

The tidal currents present in estuaries during ebb and flood conditions mobilise a considerable mass of suspended particulate material. A major characteristic of estuarine regions is their large and variable suspended load (Schubel, 1968; Sholkovitz, 1979; Loring, et al., 1982). Although much of this material is deposited at slack water, the finest material (< 2 μm) is in almost permanent suspension, consisting primarily of organic, clay and oxyhydroxide-metal particles together with a wide spectrum of living cells. These processes have recently been reviewed by Allen, et al., (1980) and they concluded that the processes are a complex function of the estuarine master variables, for example; particle size, sediment consolidation, current velocity, magnitude of tidal asymmetry, spring-neap cycle, stratification of the water column and the degree of estuarine circulation. Duinker, et al., (1974) suggested that a portion of this material can undergo a continuous exchange between the particulate and true dissolved phases. The high residence time for particles in the water column increases the likelihood of estuarine processes such as sorption reactions together with precipitation, coagulation and bioassimilation processes. Particle size fractionation can occur due to the erosion-deposition cycle and asymmetry of the tidal currents, together with

a range of settling velocities present in the estuary. Size fractionation occurs in the turbidity maximum of the Tamar Estuary Bale, (1983). Mean particle size in the outer estuary was generally from 40 - 60 μm and decreased upestuary so that at 5 - $10^o/oo$ salinity the particles were in the range 20 - 40 μm. This then decreased rapidly to a uniform value of 8 - 12 μm within the turbidity maximum region. Mean sizes in the fluvial input were generally higher but quite variable. The persistence of a mean size minimum at the turbidity maximum suggests that increased sedimentation rates due to flocculation play an important role in controlling the observed size distribution of the maxima. Physical selection of such a narrow range of particle sizes by the hydrodynamic regime alone would seem unlikely, likewise a localised minima in the mobile bed material as the maximum migrates up and downestuary with the spring-neap tidal cycle.

In summer conditions (low flow), the turbidity maximum is pushed upestuary as saline water penetrates further into the system. The reduced volume and depth of the estuary in this region, in combination with a regular trench-like section, give rise to a localised and prominent turbidity peak. In winter conditions (high flow) the null zone region is forced downestuary where the greater depth and volume combine to produce a less prominent peak over a wider area.

1.3   CHEMICAL PROCESSES IN ESTUARIES

1.3.1   Physico-chemical Processes

The estuarine regime can be thought of as a chemical system where

seawater and riverwater, which are of greatly differing composition,

interact. The composition of riverwater varies widely, depending on

the major source of dissolved salts. There are two major sources;

      (i)   sea salts recycled to the river via precipitation

      (ii) weathering of rocks by rain and water

the second being the predominant source (Burton, 1976). By contrast,

the concentrations of the major ions of seawater are relatively constant.

The major ionic constituents of seawater and riverwater are given in

Table 1.1 (after Dyrssen and Wedborg, 1980).

In general the riverwater concentrations of trace metals are higher than

those in seawater (see Table 1.2). However, it is only recently that

reliable open ocean values for dissolved Cu, Mn and Zn have become

available through the studies carried out by Bruland and coworkers (1980;

1983) and others (Moore, 1978; Klinkhammer and Bender, 1980). These

studies have shown that Zn has a nutrient-type, vertical profile which

is determined by biochemical processes, whereas the surface enrichment

of Mn could be due to atmospheric inputs or remobilisation from coastal

sediments. Copper appears not to be related to the nutrient profiles

(Moore, 1978), but it has increasing concentrations at depth, indicating

an input from sediment pore waters.

The concentrations of dissolved metals in estuaries are a function of

the hydrodynamical nature of the system. The variability is dependent

Constituent	SSW	HARW	LARW
CO_3^{2-} alkalinity (A_c)	2.4×10^{-3}	1.4×10^{-3}	0.1×10^{-3}
log K_{P12} ($25\,^\circ$C)	-1.51	-1.47	-1.47
log K_{12} ($25\,^\circ$C)	5.86	6.34	6.35
log K_1 ($25\,^\circ$C)	8.95	10.30	10.33
log K_{12}/K_1	-3.09	-3.96	-3.98
$[HCO_3^-]_t$	1.86×10^{-3}	1.36×10^{-3}	0.1×10^{-3}
$[CO_3^{2-}]_t$	2.75×10^{-4}	0.18×10^{-4}	9.4×10^{-8}
pH_t	8.12	8.43	7.30
Na^+	47.932×10^{-2}	3.0×10^{-4}	3.0×10^{-4}
K^+	10.45×10^{-3}	0.65×10^{-4}	0.65×10^{-4}
Mg^{2+}	54.39×10^{-3}	0.20×10^{-3}	0.30×10^{-4}
Ca^{2+}	10.53×10^{-3}	0.57×10^{-3}	0.87×10^{-4}
Cl^-	55.862×10^{-2}	0.20×10^{-3}	0.20×10^{-3}
SO_4^{2-}	2.889×10^{-2}	0.15×10^{-3}	0.15×10^{-3}
Ionic strength	0.7	0.4×10^{-2}	0.1×10^{-2}
Chlorinity ^{o}/oo	19.374	0.71×10^{-2}	0.71×10^{-2}
Salinity ^{o}/oo	35	0.144	0.041

Table 1.1   Ionic Concentrations in moles l^{-1} for The
Main Constituents of Standard Sea Water (SSW), High and Low
Alkalinity (HARW-LARW) Riverwater.   (After Dyrssen and
Wedborg, 1980)

Location	Dissolved Metal Concentrations, $\mu g \, l^{-1}$			Reference
	Cu	Mn	Zn	
Rivers				
Amazon	1.4	-	-	Boyle, et al., (1982)
Beaulieu	-	65-140	45	Holliday & Liss, (1976)
Conwy	1-7	-	0-3000	Elderfield, et al., (1979)
Fraser	-	-	< 1-1.4	Grieve & Fletcher, (1977)
Tamar	1.6	< 5-200	2	Morris, et al., (1978)
Zaire	0.3	-	-	Moore & Burton, (1978)
World Average	10	8.2	30	Martin & Meybeck, (1979)
Estuaries				
Amazon	0.1-1.7	-	-	Boyle, et al., (1982)
Beaulieu	-	20-120	7-45	Holliday & Liss, (1976)
				Moore, et al., (1979)
Bristol Channel	0.7-5.5	0.5-4.1	3-25	Abdullah & Royle, (1974)
Conwy	1.2-6.4	0.8-172	5-55	Elderfield, et al., (1971; 1979)
Fraser	-	-	2.6-5.3	Grieve & Fletcher, (1977)
Restronguet/ Helford	16-26	36-112	150-300	Boyden, et al., (1979)
Tamar	0.7-1.3	< 5-450	2.6-13	Morris, et al., (1978)
Zaire	0.2-1.4	-	-	Moore & Burton, (1978)
Oceans [a]				
N. Pacific	32-320	-	4.6-590	Bruland, (1980)
N. Pacific	-	11-330	-	Landing & Bruland, (1980)
Pacific	-	17-165	-	Klinkhammer & Bender, (1980)
E. Atlantic	70-700	-	-	Moore, (1978)
N.W. Atlantic	77-109	33-132	3.3-96	Bruland & Franks, (1983)

[a] Oceanic concentrations in $ng \, l^{-1}$

Table 1.2 Dissolved Metal Concentrations in Rivers, Estuaries and Oceans

on the relative magnitude of the marine, fluvial and terrestial influences and has recently been reviewed for the Tamar, (Morris, 1978; Morris, et al., 1978; Morris, et al., 1982b). These conditions include;

    (i)   marked gradients in ionic strength and pH caused by the mixing of poorly buffered, low ionic strength riverwater with highly buffered, high ionic strength seawater

    (ii)   large and extremely variable suspended particulate loads caused by the variable riverwater contribution and the complex inter-actions of tidal and residual current systems on the reservoir of recently sedimented material found in most estuaries

    (iii)   high levels of biological activity

    (iv)   considerable and variable ranges of redox potential in the underlying sediment and, occasionally, the water column.

The sediments play an important role in the overall chemistry of an estuary since the sedimentary particles often have labile cations attached to their surfaces. The exchangeable cations on the surfaces can participate in sorption reactions which can have significant implications for the dissolved phase concentrations, as Sayles and Mangelsdorf, (1979) have shown for the major ions. The available fraction of trace metals in sediments, as determined by various leaching methods (Luoma and Bryan, 1981), may only be a proportion of the totals (see Table 1.3). For example, Loring (1978) found that in St. Lawrence Estuary sediments 8-39% of Zn was in the non-detrital form, 7-20% of Cu was non-detrital and Sundby, et al., (1981) found 20-60% available Mn. Elderfield, et al., (1979) found a range of 10-50% leachable Zn in Conwy sediments, depending on the type of leach used. In addition, Loring, et al., (1983) have shown that in excess of 60% of Cu, Mn and Zn in Tamar suspended particulates is in the non-detrital form.

Estuary Location	Sediment Metal Concentrations, µg g^{-1}			Reference
	Cu	Mn	Zn	
Conwy	34	1500	900	Elderfield, et al., (1971)
Lynher	274	289	317	Bland, et al., (1982)
Restronguet	1690	1030	1540	Aston, et al., (1975)
Tees Bay	8.0	242	74	Taylor, (1979)
St. Lawrence	3-76	1256-7750	8-215	Loring, (1978)
				Sundby, et al., (1981)
Urr Water	6.9	333	41	Taylor, (1976)
Oceanic Deep-Clays	250	6700	165	Chester & Aston, (1976)

Table 1.3 Trace Metal Concentrations in Estuarine Sediments and Deep-Sea Clays

Despite the high chemical variability in estuaries, many global geo-chemical mass balance calculations assume a chemical continuity between riverwater and seawater. As estuaries are regions of fundamental importance to geochemical processes occurring on the global scale, they represent the major route whereby weathered lithospheric material is transported, modified and subsequently buried in the oceanic sedimentary basins. Thus, interactions between the fluvatile material, the diluting seawater and the truly estuarine material, together with the physico-chemical processes outlined above, have important consequences concerning the ultimate fate of the species involved.

1.3.2   Chemical Speciation

The forms in which metal species can occur in natural waters have been summarised by Stumm and Brauner, (1975). The use of equilibrium models in determining the species composition of natural waters has been developed by a number of workers (Perrin and Sayce, 1967; Zirino and Yamamoto, 1972; Sylva, 1976; Turner, et al., 1981).

The equilibrium speciation of the inorganic forms of the metals Cu, Mn and Zn were calculated using the method of Turner, et al., 1981. Copper is predominantly complexed as the hydroxy species in freshwaters, but in seawater, $S = 35^o/oo$, its major form is the copper carbonate complex (80%). Both Mn and Zn are only weakly complexing with sulphate (< 5% of the total metal at $S = 15^o/oo$) and their major form is the free metal, approximately 60% for Mn and 50% for Zn. These two metals do have a tendency to form monochloro-complexes which increase in importance with increases in salinity as shown in Table 1.4.

Table 1.4 % Monochloro-complexes of Mn and Zn at pH = 7 as a function of salinity

S^o/oo	Zn	Mn
5	7.8	13.9
10	11.3	20.2
15	14.7	24.6
35	35.0	37.0

These elements also show considerable differences in their complexation with organic material (Mantoura, et al., 1978). Copper is almost completely complexed with humic material in freshwater, but the relative proportion of the humate species decreases with increasing salinity, such that at S = $35^o/oo$ only 10% of the total Cu is associated with humic material. In contrast, both Mn and Zn have only 1-2% of the total metal as humate species in freshwaters with little or no complexation above S = $5^o/oo$. The data quoted here should be regarded with some caution since it is recognised that there is a wide variation in the chemical composition of natural organic compounds. Thus the values given above may only be applicable to the organic material isolated for the complexation experiments (Mantoura, 1978). However, it is possible to conclude that the geochemistry of Cu could be strongly coupled to that of the humic material.

1.3.3   Conservative and Non-Conservative Behaviour in Estuaries

As previously discussed (see Section 1.3.1) the levels of various elements will differ greatly between the riverwater and seawater. It

17

is therefore clear that the levels of particular elements will vary along the mixing gradients. It is also important to establish whether the behaviour of a particular element in such a system is reconcilable with simple conservative mixing or whether the element is exhibiting non-conservative behaviour, indicating some degree of physico-chemical or biologically mediated interaction (Liss, 1976). The concept of conservative and non-conservative behaviour related to salinity or chlorinity (Liss, 1976) is important when evaluating dissolved metal-salinity relationships, for as well as mere physical dilution, the metal species would be simultaneously undergoing addition or removal processes.

Duinker and Nolting (1976; 1977; 1978) found that Pb and Zn behaved both conservatively and non-conservatively in the Rhine Estuary. Similar conservative behaviour of dissolved Zn has also been reported for the Beaulieu Estuary (Holliday and Liss, 1976) and for the Conwy Estuary (Elderfield, et al., 1979). In contrast to this, non-conservative mixing profiles have been obtained for the Tamar Estuary (Morris, et al., 1978) and the Fraser River Estuary (Grieve and Fletcher, 1977). The behaviour of dissolved Cu was found to be non-conservative in the very low salinities of the Tamar (Morris, et al., 1978) and the Rhine Estuaries (Duinker, 1980). Moore and Burton (1978) found some evidence for non-conservative Cu behaviour in the Zaire Estuary. However, Cu exhibited conservative behaviour in the Amazon plume (Boyle, et al., 1982) which extends 200 km off the coast over deep waters. Dissolved Mn also appears to exhibit both types of behaviour, with conservative profiles being obtained in the Beaulieu (Holliday and Liss, 1976; Moore, et al., 1979). However, the majority of work on Mn shows a tendency toward non-conservative behaviour (Bryan and Hummerstone, 1973; Graham,

et al., 1976; Evans, et al., 1977; Morris, et al., 1978; 1982a). The conflicting evidence in the literature for these metals is often due to the fact that hypotheses for their behaviour are based on a limited number of surveys. Thus, they represent a metal distribution under a particular (and potentially unique) set of environmental conditions. The only element for which there appears to be almost universal belief in its non-conservative behaviour is Fe (Coonly, et al., 1971; Boyle, et al., 1974; Evans, et al., 1977; Eaton, 1979a).

The study presented here has emphasised the importance of recognising that while conservative behaviour may be exhibited over a wide salinity range, it is crucial to examine the potential for removal at specific salinities or over a narrow salinity range. In their investigations of estuarine chemical behaviour Morris, et al., (1978) have shown that the very low salinity range (0.1 to $10.0^o/oo$) is a site of great importance for biological and chemical reactions. This understanding has been complemented by the ability to carry out repeated surveys under different conditions, thus obtaining a more generalised picture of the chemical reactivity of a particular element.

1.3.4   Dissolved-Solid Interactions

1.3.4.a Surface Charge

All particles in natural waters possess a surface charge and these charges are predominantly negative (Neihof and Loeb, 1972; Hunter and Liss, 1979). The charges arise by three principal mechanisms (Stumm and Morgan, 1981);

(i)   chemical reactions at the solid surface such as the

19

amphoteric behaviour of oxides and hydroxides, ionization and specific adsorptions.

  (ii) lattice imperfections or isomorphous replacement of ions within the lattice structure of minerals.

  (iii) ion adsorption by Van der Waals forces and hydrogen bonding.

These negatively charged particles on the surface are counter-balanced by cations which form a layer of ions on the solid surface (Stern plane) and by a diffuse layer of ions in the aqueous phase near the surface (Gouy layer). The whole charge structure is designated the 'electrical double layer'. The thickness of the electrical double layer, and hence the stability of the dispersion of particles, is dependent on (Stumm and Morgan, 1981);

  (i) the valency of the sorbed ions

  (ii) the total ion concentration in the surrounding water

  (iii) temperature

  (iv) pH.

The presence of an organic sheath on the particles can also aid stabilization, possibly by the formation of 'an atmosphere' of negatively charged carboxyl groups (Boyle, et al., 1977).

The majority of these charged particles will be colloidal in riverwater and electrostatic repulsion between the particles will stabilize the dispersion by preventing collisions which are a prerequisite of coagulation. The gradient of ionic strength encountered in estuaries however can result in the destabilization of these dispersions. This may occur due to charge neutralization on compression of the electrical double layer or a specific adsorption of positive species (particularly

20

Ca^{2+} and Mg^{2+}) in seawater. The increased frequency of the collisions
between these destabilized particles can result in coagulation. These
conditions are primarily due to the influence of velocity gradients
and effects of differential sedimentation rates of the various
particle sizes. The high suspended sediment loads, turbulent mixing
and stratification prevalent in most estuarine regimes are also
conducive to promoting these collisions and thus the probability of
coagulation in estuaries is very high. This phenomenon has important
implications for the distribution of trace metals in estuaries.

1.3.4.b The Role of Organic Compounds

Although most of organic material in estuaries is authigenic, the
majority of the humic material originates from the fluvial input (Head,
1976), and is predominantly soil fulvic acid. The association of metals
with these humates is well documented (Mantoura, 1978; Mantoura, et al.,
1978) and the subsequent fate of these metals in the estuarine environ-
ment may be largely controlled by the behaviour of the humates (Mantoura,
1978; Sholkovitz and Copeland, 1981). Removal of 'dissolved' humic
material has been observed in laboratory simulations (Sholkovitz, 1976;
Eckert and Sholkovitz, 1976; Sholkovitz, et al., 1978). Eckert and
Sholkovitz (1976) concluded that the destabilization and subsequent
flocculation of humate colloids in estuaries was due to specific chemical
and electrostatic interactions with the major seawater ions and was not
merely a consequence of increased ionic strength. They also indicated
that, whilst the concept of colloidal destabilization is only applicable
to hydrophobic complexes, hydrophilic humic complexes can be converted
to hydrophobic complexes in the presence of electrolytes. Sholkovitz
(1976) and Eckert and Sholkovitz (1976) reported a substantial removal

21

of several heavy metals in conjunction with the flocculation of humate material during laboratory simulations of estuarine mixing.

1.3.4.c The Formation of Oxyhydroxides

Ferric iron is thought to constitute the large majority of dissolved iron, in the Eh-pH conditions found in most well oxygenated natural waters. The formation of hydrous ferric oxyhydroxide (am-FeOOH) is the dominant feature of Fe (III) solubility equilibria and hence a substantial fraction of this iron is present as a colloidal form in suspension with some dissolved Fe (III) as an organically bound fraction (Stumm and Morgan, 1981). Whilst most attention has been paid to Fe (III) under natural conditions, there are several important sources of Fe (II). The ferrous compounds are present at the oxic-anoxic boundaries in sediments, in stabilised lakes and fjords and in acid mine streams. Murray and Gill (1978) showed that Fe (II) had a half-life of 5 minutes in seawater, pH = 8, T = 15°C. The oxidation and hydrolysis of Fe (II) (Sung and Morgan, 1980) may produce an iron oxyhydroxide with different surface characteristics than that produced from the hydrolysis of Fe (II) (Crosby, 1982). Indeed, Crosby, et al., (1981) have shown that Fe (II)-derived oxyhydroxides have different adsorption capacities than Fe (III)-derived oxyhydroxides. Furthermore, using nephelometry Crosby (1982) has shown that Fe (III) hydrolysis occurs in less than thirty seconds, whereas Fe (II) oxidation and hydrolysis can take several minutes and is dependent on pH and ionic strength. It is probable that Fe (II) may be more important in the environment and that more attention should be focused on the latter.

The half-life for Mn (II) oxidation is usually of the order of a few days in seawater (Morris, et al., 1982a). In many estuaries the flushing time is less than the half-life of the oxidation process and Mn exits the estuary in the dissolved form. This compares with studies in the Rhine by Eisma, et al., (1980) where the flushing times (up to one hundred days) are much longer and the formation of Mn-rich particles has been observed.

1.3.4.d Clays

There are three types of exchange sites associated with clay sorption;

    (i)   basal surface sites,

    (ii)   edge-interlayer sites,

    (iii) interlayer sites.

Basal surface and interlayer sites result mainly from isomorphous substitutions within the lattice structure whereas edge-interlayer sites (Sawhney, 1972) are caused by broken bonds arising from weathering processes. The electrical charges on these types of site are neutralised by sorbed opposite-ions of the mobile layer, thus forming an electric double layer. The high selectivity of edge-interlayer sites at low solute concentrations is particularly relevant with regard to the adsorption of trace metals from freshwater by mineral particulates (Farrah and Pickering, 1979; Forbes, et al., 1976). The cation exchange capacity of clay minerals is considerable (Sayles and Mangelsdorf, 1979), but represents only a small fraction of the total sorption capacity for heavy metals of the particulate matter in rivers and estuaries. It is therefore unlikely that direct adsorption is important with regard to heavy metals, particularly as they would have to compete with the major bulk species (Ca^{2+}, Mg^{2+}, Na^+ etc.) for exchange sites (Duinker, 1980).

Clay minerals can be important, however, in their role as nucleation centres for Fe-Mn oxides both in freshwater and during estuarine mixing (Aston and Chester, 1973). They also serve as centres for the flocculation and precipitation of dissolved and colloidal organic matter during the estuarine mixing processes (Sholkovitz, 1976).

1:3.5   Adsorption-Desorption Processes

Interactions between the dissolved phase and various colloidal and particulate phases such as lithogenous material (e.g. clays), authigenic material (e.g. hydrous iron and manganese oxides), organic material and living biota are often explained by ion-exchange reactions within the electrical double layer, generally involving major seawater cations. Such reactions would be extremely rapid in estuarine conditions and slower reactions could be explained in terms of either complexation or a specific adsorption at the solid surface. If cations were substituted into the clay lattice structure, with subsequent eleimination of silicon and iron, the excess charge would be neutralised by the adsorption of other trace metals. Considerable scavenging capacity of the hydrous iron and manganese oxides present in estuaries is well documented (Gadde and Laitenen, 1974; Kinniburgh, et al., 1976); Davis and Leckie, 1978a; 1978b; Swallow, et al., 1980) and is usually explained in terms of either surface complex formation or ion-exchange (Stumm and Morgan, 1981). Hem, (1977) suggested viewing large sorption capacities in terms of co-precipitation and an incorporation of metal ions into the growing crystal lattice. Numerous factors influence the extent of metals participation in adsorption-desorption reactions in estuaries. Millward and Moore, (1982) found the adsorption of Cu, Mn and Zn to be a function of pH, activity of competing species and ionic strength of the media. Salomons,

24

(1980) observed that many competing processes accompany the initial increase in pH, suspended particulate material and ionic strength during estuarine mixing; the rise in pH favours a specific adsorption of trace metal cations by ion exchange, whilst the increase in ionic strength decreases the activity of the dissolved metal ions by inorganic complexation and increases the competitive adsorption of major seawater cations. The increased suspended particulate material provides an increase surface area for adsorption to take place.

The influence of organic material on adsorption-desorption reactions is complex. De Groot, et al., (1976) found that the presence of dissolved organics alters the stability of the metal complexes. The presence of organic material in the particulate phase can also affect adsorption-desorption reactions (Tipping, 1981). A reduction in sorption capacity can be attributable to either a masking of clay mineral adsorption sites or a binding together of the minute mineral particles to reduce the adsorptive surface area per unit weight of sediment. Hydrous ferric oxide coatings observed on many clay particles in estuaries can both prevent trace metal desorption from the mineral surface and facilitate adsorption of additional metal ions (Gibbs, 1973). This process has important consequences concerning the apparent sorption capacity of mineral particles, as Fe-Mn oxyhydroxides are much more efficient metal adsorbing agents than clay minerals (Murray and Gill, 1978). It is important to recognise that whilst many of these reactions may occur in estuarine regimes, some may be too slow to have any readily discernible effect on the overall distribution of the species involved in estuaries with low residence times (see Figure 1.1).

With the exception of a small surface oxidized layer, much of the

estuarine sediment column is often anoxic and hence conducive to substantial diagenetic alterations in the distribution of many chemical species (Elderfield and Hepworth, 1975; Bryan, 1976; Elderfield, et al., 1979). A major consequence of these reactions is the formation of concentrated solutions of metals and nutrients (e.g. Cu, Pb, Ni, Zn, Fe, Mn and ortho-phosphate) in near-surface sediment pore waters. These levels can often exceed those in the overlying water column by up to a factor of ten (Presley and Trefry, 1980). For example, Fe and Mn are deposited as oxyhydroxide particles or particle coatings. These are reduced in the deeper sediments to Mn (II) and Fe (II) forms, which are more soluble and may be stabilised at high concentrations by complexation with inorganic or organic bases (Elderfield, 1981). When the reduced oxyhydroxides are released into solution, adsorbed or coprecipitated metals are also remobilised and these form reservoirs of metal-rich (Elderfield, et al., 1979) and nutrient-rich (Knox, et al., 1981) pore waters which can be released to the overlying water column by upward diffusion (Elderfield and Hepworth, 1975) or by the effects of bio-turbation and sediment resuspension (Aller and Benninger, 1981; Elderfield and Hepworth, 1975; Elderfield, et al., 1981; Emerson, et al., 1983; Presley and Trefry, 1980). Also the microbial breakdown of organic matter within the sediment can release adsorbed or complexed metals into the interstitial waters which migrate to the oxic sediment-water interface where they can be re-adsorbed and thus cause enrichment of the surface sediment. Under initial reducing conditions, the metals are mobilised into the interstitial water, but in some cases further diffusion can be inhibited as the metals precipitate as sulphides. The complexity of the chemical and biological processes that influence pore water composition has led to some controversy concerning the mechanisms that control the trace metal behaviour. This is illustrated by the

fact that the values of the diffusive fluxes for trace metals shown in Table 1.5 can range from being negative (i.e. a metal flux into the sediment) to large positive fluxes out of the sediment. The models used in calculating some of the fluxes have inherent problems (Presley and Trefry, 1980) since a major concern exists about the selection of appropriate diffusion coefficients. Normally, these are only appropriate to Fickian diffusion rather than eddy diffusion which is more likely in the high energy estuarine regime. Furthermore, the estuarine situation is additionally complicated by the fact that the spring-neap tidal cycle leads to temporal variability in the trace metal concentrations of estuarine sediments, as implied from the studies of Mn in the Tamar by Morris, et al., (1982a). Nevertheless, given the sparsity of data in the literature the values given in Table 1.5 serve as a useful approximation in first-order estimates of the potential release of pore water metals into the overlying water column.

1.3.6   Biological Modification of Estuarine Processes

Estuaries are frequently areas of high fertility (Joint and Pomroy, 1981; Cloern, et al., 1983) and consequently biological processes can exert a considerable influence on the distribution of many chemical species. The magnitude of the biological influences is obviously affected by many factors characteristic of estuarine regimes. High turbidities found in many estuarine systems reduce the depth of the photic zone and can limit primary production (Joint and Pomroy, 1981; Morris, et al., 1982b). The water residence time is often too short to allow large scale biological removal of many chemical species within the estuaries unless productivity is enhanced by nitrogen and phosphate-rich effluents

Location	Benthic Flux[a], $\mu g\ cm^{-2}\ yr^{-1}$			Reference
	Cu	Mn	Zn	
Conwy	+2.6	+59	+2.6	Elderfield & Hepworth, (1975)
Tees	+4.1	-	+0.8	Elderfield & Hepworth, (1975)
Scheldt	-	+400	-	Duinker, et al., (1979)
Narragansett Bay	+1.1	+80 to +1300	-	Elderfield, et al., (1981)
Mississippi	-	+1000	-	Presley & Trefry, (1980)
Long Island Sound	- -	-1200 to +800	-	Aller & Benninger, (1981)
Puget Sound	+1	+100	-	Emerson, et al., (1983) Unpublished

[a] Positive values fluxes out of the sediment

Table 1.5 Benthic Fluxes of Trace Metals from Various Locations

(Boyle, et al., 1974). The estuarine mixing regime can act as a
particle trap, where particles at the surface are carried seaward,
eventually sink and encounter a residual landward bottom flow which
carries the particles back upestuary to a null zone where the net
seaward and landward currents cancel out. In the Tamar, this area has
often been associated with a pronounced oxygen minimum (see Figure 3.27)
which may be due to microbial degradation of organic-rich particles
trapped in this zone (Morris, et al., 1982c).

The biota can influence the transport pathways and cycling within the
estuary via assimilation by organisms in the water column. Both nutrient
and heavy metal species can be transported to the sediment surface in
a variety of forms, such as organic detritus, faecal solids or excreted
as soluble organic complexes which could affect their subsequent
behaviour as discussed previously. Organic detritus can be metabolised
by benthic organisms at the sediment surface, possibly with subsequent
release to the water column or incorporation into the sediment.

1.4   THE TAMAR ESTUARY

1.4.1   Physical Setting

The River Tamar is situated in the south west of England (see Figure 1.2) and is a prime example of a drowned river valley or ria (Pritchard, 1967) brought about by the extensive flooding of lowland areas during the general rise in sea level that occurred at the end of the Pleistocene epoch.   Its axis lies in a N-S direction between Plymouth Sound at the mouth and Gunnislake at the limit of tidal incursion, a distance of approximately 30 km.   The Tamar is joined by two major tributaries, the Lynher and the Tavy, but the Tamar constitutes the dominant fresh water input.   Extensive mudflats are present in the lower estuary, at St. John's Lake and upestuary of Saltash (see Figure 1.2).   It is in this region that large variations in physico-chemical parameters (the so-called master variables) occur and give rise to inhomogeneities in water structure as shallow water masses become isolated on the expanse of mudflats (Morris, et al., 1982b).   From 10 to 20 km from the weir, the estuary meanders across a flat, aluvial plain.   Upestuary of 10 km to the weir itself, the river is largely canalised and takes on more of the character of a river.

The river flow-rate was observed to exhibit pronounced seasonal extremes.   During the period of this study, the maximum range was from 1.5 $m^3 s^{-1}$ during a dry summer period to 252.0 $m^3 s^{-1}$ during an autumnal spate, annual averages are approximately 30 $m^3 s^{-1}$ (South West Water Authority data, 1980-82).   Tidal ranges at Devonport are 5.5 m at springs and 1.5 m at neaps, in the upper estuary ranges
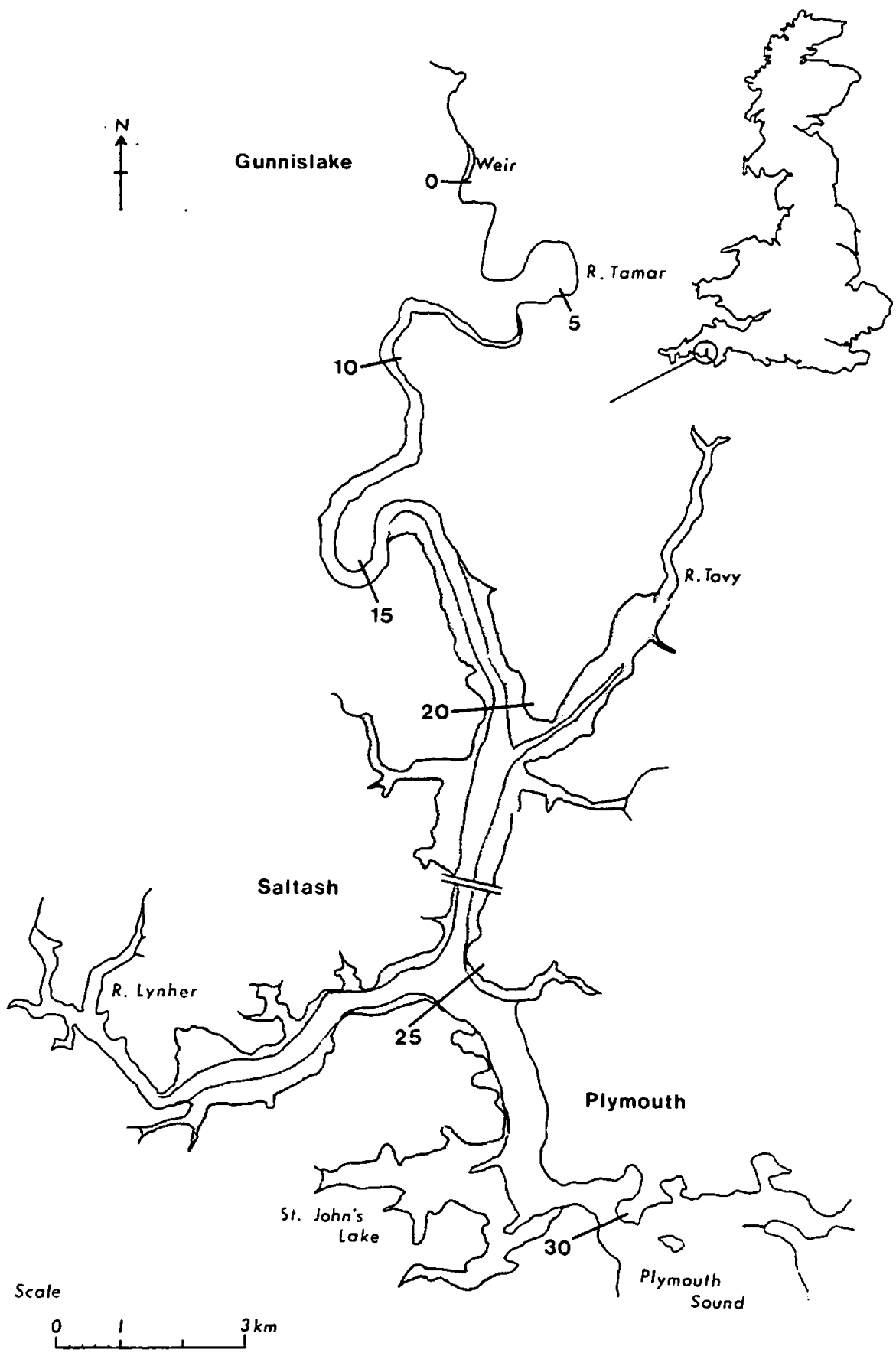
Figure 1.2   The geographical location of the Tamar Estuary.   Distances are marked from the weir at Gunnislake

31

of 1-2 m are observed. Tidal currents are generally rectilinear in
the estuary but exhibit pronounced asymmetry as one moves upestuary.
The asymmetry manifests itself in a short, high energy flood and a
longer, low intensity ebb flow (George, 1975). The flushing time of
the whole estuary can vary from 7 to 12 days (Uncles, personal
communication) dependent upon the prevailing conditions of river
flow and tidal state.

1.4.2   Sources of Heavy Metal Pollution

The Tamar, together with the Tavy and Lynher, drains the unpolluted
moorlands of the Dartmoor National Park. During the 19th century
there was extensive mining in this catchment area (there is evidence
of mining activity in pre-Roman times), particularly at the head of
the estuary (see Figure 2.1). The mining was associated with metal
lodes in the Dartmoor granite metamorphic aureole (Dines, 1956), which
is rich in copper, lead, arsenic, tin and manganese. These minerals
were the principal economic ores, though in the latter stages,
Wolfram became of importance (Barton, 1964; Booker, 1967; Hamilton-
Jenkin, 1974), however, most mines were exhausted by the mid-1890's.
The mining activity has left a legacy of spoil tips and mine drainage
adits which, due to their toxicity, still remain uncolonised by the
local flora and are thus open to aeolean and hydrological erosion.
This leads to subsequent input into the river and estuary via
subsidiary streams. Present day sources of heavy metal input in the
lower estuary include H.M. Dockyards at Devonport, Plymouth together
with domestic and industrial wastewater outfalls from urban Plymouth.
Storm water overflows, which often by-pass treatment works, have

inputs from road run-off and ultimately discharge into the estuary. It is within this environmental background that the study was undertaken. The unique setting of the Tamar Estuary has meant that it has been the subject of intense investigations, primarily by the Institute for Marine Environmental Research and the Marine Biological Association. The wealth of background information on this system has made an important contribution to this study (E.B.S.A., 1982).

1.5   AIMS OF THE PRESENT WORK

The overall objective of the project is to investigate the estuarine behaviour of selected heavy metals in the estuarine environment. The study also aims to model the observed chemical behaviour in the laboratory by manipulating natural waters in an attempt to identify the interrelationships between estuarine master variables, physical processes and the various phases of the metals. In summarising the data, the aim was to construct a two-box model of the estuary which would enable predictions of seasonal metal fluxes to be estimated. The approach to these objectives is enumerated below;

1. environmental studies of dissolved, suspended particulate material and sediment samples from the River Tamar were carried out in order to investigate the removal/remobilisation processes occurring in the estuary.

2. sediment surveys and subsequent chemical analyses were to be carried out at regular intervals over the seasonal cycle in the estuary. The chemical analyses were selected to distinguish between total metal and available (non-detrital) metal. Statistical analyses of the sediment data were designed to identify seasonal variation in the total metal-metal and metal-variable correlations, together with evidence from the non-detrital data of effects caused by variation in the particulate geochemistry in the estuary.

3. the dissolved metal surveys and chemical analyses were to be carried out, where possible, coincident with the sediment surveys.

Statistical analysis of the dissolved metal data using a modified programme by Knox, et al., (1981) was designed to identify similarities in estuarine addition/removal behaviour and also possible sources of dissolved copper, manganese and zinc in the estuary.

4. modelling of the estuarine system was to be undertaken in which the manipulation of natural samples would be used to assess the uptake of dissolved copper and zinc, under varying conditions of suspended particulate matter, and in solutions of varying pH and ionic strength. The aim of this part of the study was to model the conditions occurring at the F.B.I. and elucidate the behaviour of each metal under the given conditions.

5. the construction of a two-box model of the Tamar Estuary to integrate all the field data, together with pore water diffusion rates abstracted from the literature (Elderfield and Hepworth, 1975) was the culmination of this study. Basic hypotheses on the estuarine behaviour of copper, manganese and zinc were to be examined and the study given a predictive capacity (albeit a limited one) to estimate gross metal fluxes under given river and tidal states.

CHAPTER TWO

EXPERIMENTAL

2.1 ESTUARINE SEDIMENTS

2.1.1 Sample Collection

Previous heavy metal determinations had been made on sediments of the Tamar Estuary, analysed by an X-ray fluorescence technique (Morris, et al., 1980, unpublished data). The present sampling strategy was designed not only to complement the previous study, but also to concentrate in the more dynamic regions of the estuary. These were the mine spoil areas at the head of the estuary, the mid-estuarine region where large changes in the physico-chemical parameters could be expected and a marine end-member which was free from subsidiary inputs such as major tributaries.

The actual sampling surveys involved the use of two shallow draught vessels from the Department of Marine Science. Because of the distance involved, in excess of 30 km and the need to collect samples at low water for maximum exposure of the mudbanks, the vessels commenced sampling at the two extremes of the estuary, the weir at Gunnislake and Plymouth Sound, (see Figure 2.1).

In any study of a dynamic environment such as an estuary, there must be a measure of time dependence incorporated into the sampling programme to examine possible seasonal trends and to gain an insight into the variability within the sediment system. Consequently, sample collection was undertaken at approximately two-monthly intervals.

Each sample at the fourteen sites (Figure 2.1) comprised a surface scrape of the oxic sediment layer (0-2 cm in depth) using an acid-washed 'Teflon' spatula. The oxic sediment layer was assumed to be that layer which readily interacted with the water column and was
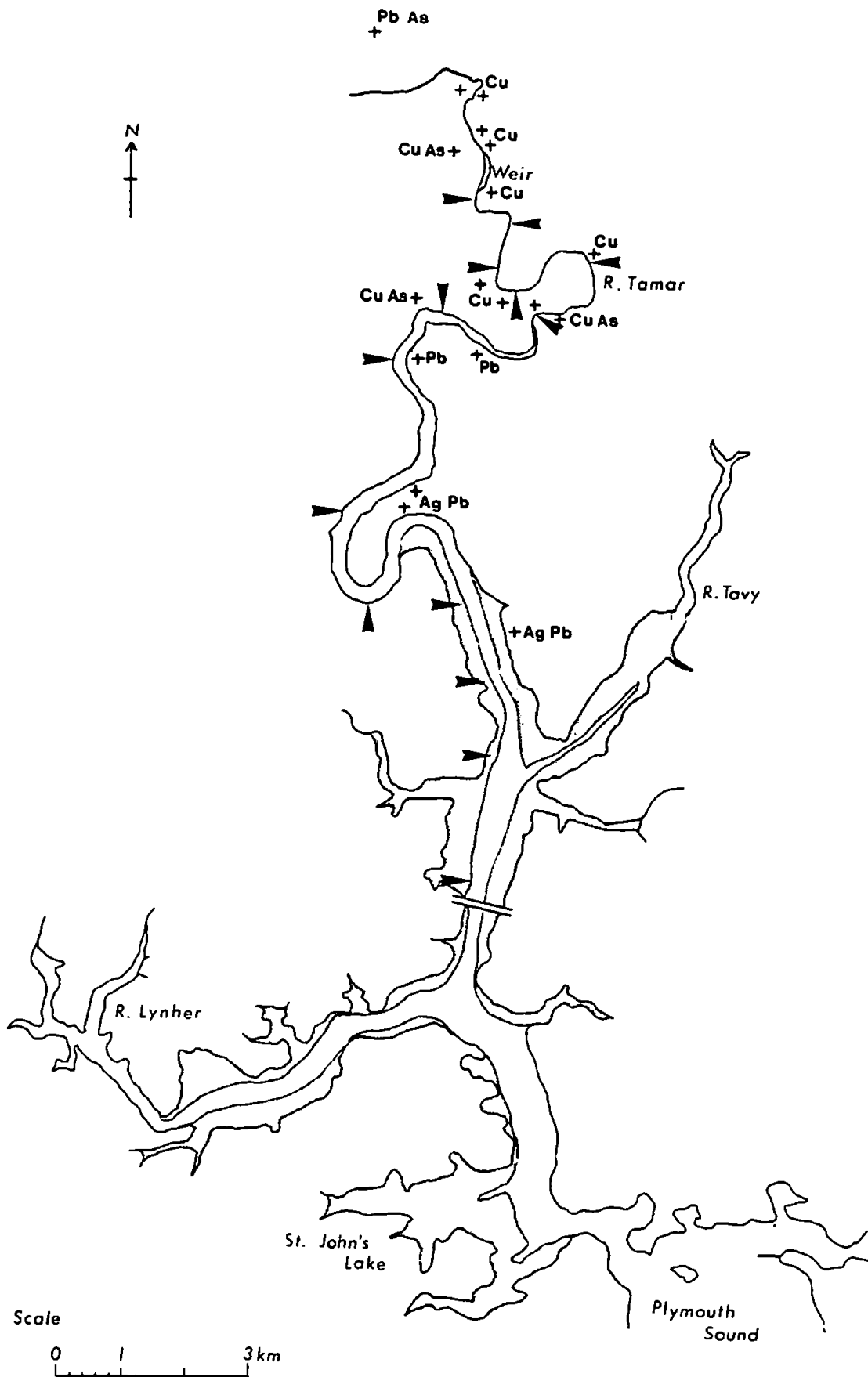
Figure 2.1   The Tamar Estuary; sediment sampling sites

►-- sample site; + - disused mine and principal ore body

38

thus susceptible to possible modification, in view of the highly variable
nature of the estuarine environment. The chemical composition of the
sediment would therefore reflect the short-term daily changes due to the
semi-diurnal tidal cycle and also changes associated with the variation in
riverine input, particularly during spate conditions (Morris, et al., 1982c).

Interactions at the sediment/water interface play a large part in influen-
cing the chemistry of heavy metals, particularly in estuaries (Duinker,
et al., 1974; Elderfield and Hepworth, 1975; Loring, 1976; Lu and Chen,
1977; Eaton, 1979a). The extraction of sediments using an established
geochemical technique would provide information as to the partitioning of
metals, which may in turn lend itself to a determination of the bio-
availability of the heavy metals. Most recent studies (Luoma and Bryan,
1981) have attempted to directly define metal partitioning into a readily
extractable phase (non-detrital form) and a residual phase (detrital
form). Measurement of the total metal concentration in sediments is a
poor means of assessing the potential or actual availability of a given
element to the biota as a whole. Total metal concentrations are
inadequate for such purposes because the largest part of the total metal
concentration is usually 'locked up' physically and/or chemically in
detrital particles and does not readily react with the biota.

The extraction methods and analyses (see Figure 2.2 for flow diagram of
analytical approach) employed in this study were based on the various
reviews of selective extraction techniques (Agemian and Chau, 1976;
Malo, 1977; Luoma and Bryan, 1981; De Groot and Zschuppe, 1981) and to
provide a continuity with the analysis of suspended particulate material
carried out at Bedford Institute of Oceanography, Nova Scotia, Canada
as part of the collaborative aspects of this study.

EXPERIMENTAL

Sediment collected

-1cm oxic layer at tidal edge

sediment washed and dried: homogenised.

T°C/S‰
measured
in situ

"Total" component
Aqua-regia/Hydrofluoric
acid -100°C / 1hr

"Non-detrital" component
25% v/v Acetic acid
room Temp/12 hr

Total
Organic Carbon
(T.O.C.)
670°C/6 hr

Cu, Fe, Pb, Mn,
Zn, Flame AAS

Hg
Atomic
fluorescence

Cd
Delves
cup

As
Hydride
AAS

Grain size
< 63 μm
wet-seived,
as % of total
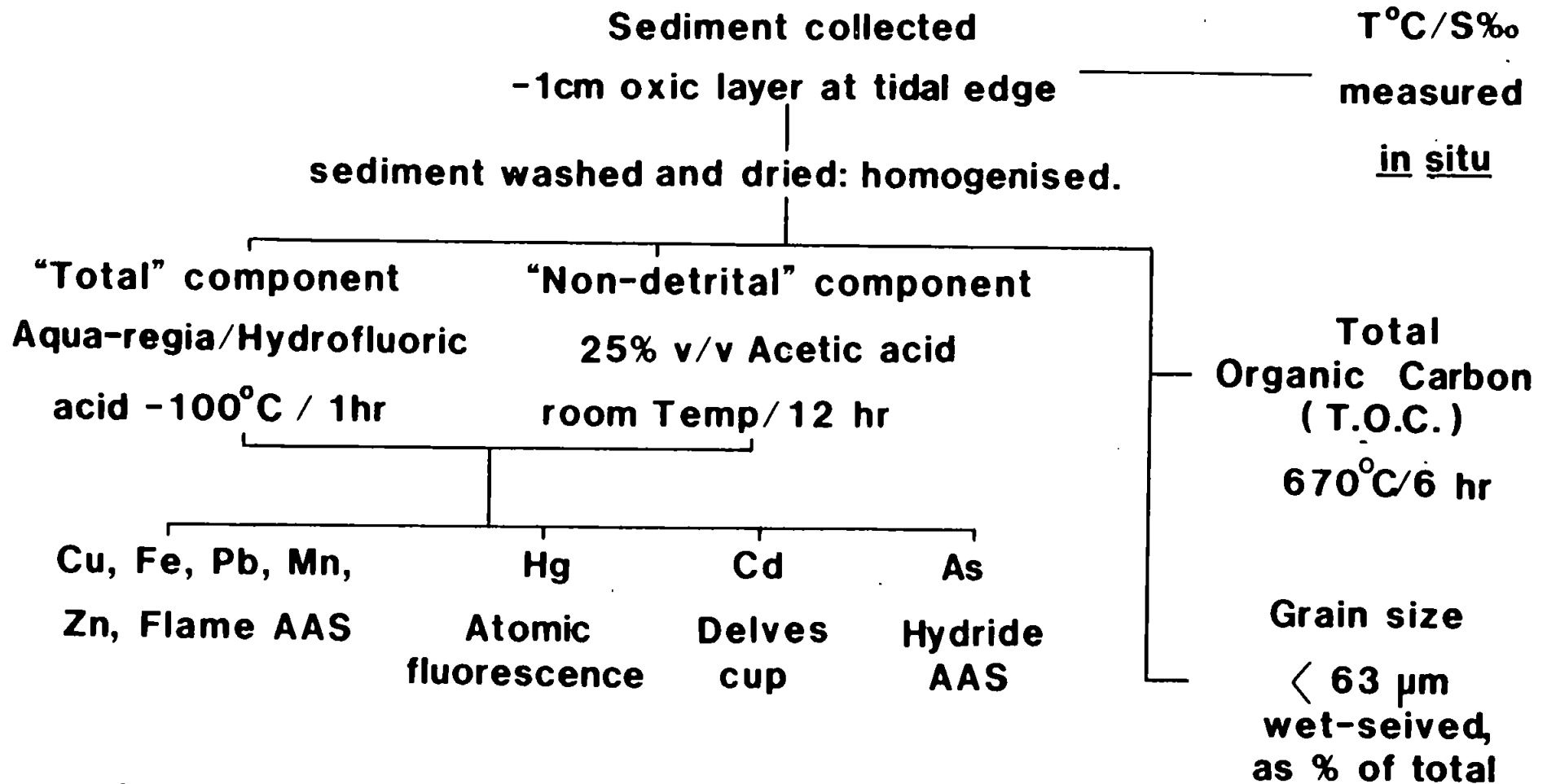
Figure 2.2 A flow diagram of the experimental procedure for
estuarine sediment analysis

40

2.1.2   Sample Preparation and Digestions

The samples were usually processed on returning to the laboratory,
but were occasionally stored overnight at 0°C to reduce bacterial
modification of the sediment. The sediment samples were washed with
deionised, distilled water to remove occluded, dissolved sea salt.
As distilled water has a pH value of approximately pH = 6, compared
with environmental pH ranges of 7 to 8, some metal leaching from the
non-detrital fraction of the particles may have occurred. The sediment
was oven-dried at 60°C to constant weight (with possible loss of volatile
metals such as cadmium and mercury) and lightly ground using a pestle
and mortar.

Two marine sediment reference materials, Miramichi Estuary Standard
Sediment (M.E.S.S.-1) and Baie des Chaleurs Standard Sediment
(B.C.S.S.-1), were obtained (National Research Council of Canada,
1981) and analysed in the same manner as the estuarine sediment
samples (see Sections 2.1.2.b and 2.1.2.c).

2.1.2.a Nitric Acid Digestions

Approximately 5 g of dried sediment were refluxed in 100 ml of
'Aristar' nitric acid (HNO_3) for 12 hours in acid-washed glassware.
The digests were filtered (Whatman N°' 1) and the filtrate sub-
sequently collected in acid-washed 250 ml volumetric flasks. Solutions
were made up to volume using deionised, distilled water. Sub-samples
of the sediment were re-analysed using the following methods (see
Sections 2.1.2.b and c) and the results compared (Loring and Rantala,
1980, personal communication).

2.1.2.b Hydrofluoric Acid Digestions

Approximately 1 g of dried sediment was digested in a stainless
steel 'Teflon' bomb (Rantala and Loring, 1973) using 6 ml 'Aristar'
hydrofluoric acid (HF) and 1 ml of aqua regia (HNO_3: HCl, ratio =
1:3 v/v) as a wetting agent. The vessel was heated in an oven at
100°C for 1 hour. The contents were washed into a 250 ml
polypropylene volumetric flask containing 5.6 g 'Aristar' boric
acid (H_3BO_3) which had previously been shaken with approximately
20 ml of deionised, distilled water (Rantala and Loring, 1975;
Loring and Rantala, 1977). When the samples were stored, it was
found that in concentrated trace metal solutions, a gelatinous
precipitate of borosilicates formed, due to high concentrations of
silicon in the sample. This had no effect on heavy metal determin-
ation (Rantala, 1982, personal communication). Reagent and analytical
blanks were determined by running the analytical procedure without
the sediment.

2.1.2.c Acetic Acid Digestions

Approximately 10 g of dried sediment was digested at pH = 4 and room
temperature for 12 hours using 50 ml of 25% v/v 'Aristar' glacial
acetic acid (CH_3COOH). The digest was filtered through 0.45 μm
'Millipore' filters and the filter paper washed with 5 ml of deionised,
distilled water. The filtrate was made up to volume in a 100 ml
volumetric flask with deionised, distilled water. Reagent and
analytical blanks were determined by running the analytical procedure
without the sediment.

2.1.3   Analytical Procedures

The analyses for copper, iron and manganese in all digests were undertaken by conventional air/acetylene flame Atomic Absorption Spectrophotometry (A.A.S.) using an Instrumentation Laboratory 151 atomic absorption spectrophotometer. Zinc and lead were analysed using standard conditions for the same instrument but a deuterium background correction lamp was used to reduce interferences at these shorter wavelengths. Mercury determinations were carried out using a flameless atomic fluorescence method (Thompson and Reynolds, 1971; Thompson and Godden, 1975). The stannous chloride reducing agent was purged with argon prior to use and the argon was also used as a shield gas in the fluorescence head. Cadmium levels were below the detection limit of flame A.A.S. A flameless method was attempted, but problems with tube deterioration and reproducibility produced results which were not of the desired precision. Determinations were finally made using the Delves cup method (Delves, 1970; 1977) in which 50 µl of sample were injected into a nickel micro-sampling cup. The sample was dried by placing the cup in close proximity to the air/acetylene flame, after which the cup was inserted into the flame and the dried sample atomised into an atom cell. The cadmium was then determined by absorption of the 229 nm line.

All metal determinations were calibrated using known, acidified standards in the linear range (I.L. Atomic Absorption Methods Manual, 1975).

2.1.4   Additional Parameters

2.1.4.a   Organic Carbon

The organic carbon content was defined as the percentage loss of weight of dried sediment after ignition at 670°C for 6 hours (Holme and McIntyre, 1971). The method produced an overestimate due to loss of the carbonate fraction and also loss of bound, interstitial water of the clay fraction (Mook and Hoskin, 1982). An attempt was made to quantify this loss. Much of the organic content of the Tamar sediments appeared to consist of lignified tissue (Bale, unpublished data). Sediment samples were subjected to a lignin stain test (Pocklington and Hardstaff, 1974) and the sediment was found to contain a large percentage of lignified tissue. Possible sources would include the extensive reed beds on the Tamar banks and leaf debris from the deciduous wooded valley. Ranges of 7 to 14% organic carbon content were observed, in agreement with results in the Tamar using the same technique (Gee, 1983, personal communication), but these were higher than levels obtained using carbon-hydrogen-nitrogen (C-H-N) analytical procedures, (see Chapter 3).

2.1.4.b   Grain Size Analysis

Heavy metals tend to be concentrated in the finer grain-size fractions of sediments (Loring, 1976; Grieve and Fletcher, 1976; Vivian and Massie, 1977; Thorne and Nickless, 1981), thus any study should include a measure of variation of grain size. The sediment samples were size-fractionated into two categories; greater or less than 63 μm by first re-suspending 10 g of the dried sediment in distilled water for 24 hours, stirring occasionally. It was assumed that aggregates

44

which formed when the sediment was originally dried would disassociate on re-suspension. The sediment was sieved and the two fractions collected, dried and re-weighed. The percentage less than 63 μm was calculated, loss due to sieving was below 10%.

2.1.4.c Temperature and Salinity Measurements

Salinity and temperature were routinely measured during the axial sediment surveys using a calibrated E.I.L. salinity/temperature bridge, type M.C.5. The geographical position of the freshwater-brackish water interface (F.B.I.) was observed to be a function of the river run-off and spring/neap tidal cycle.

2.1.4.d Scanning Electron Microscopy

Sub-samples of the dried sediment were examined using a Jeol 35 Scanning Electron Microscope (S.E.M.). A qualitative description of the chemical composition was obtained using X-ray dispersive analysis (Link Model 860 X-ray Spectrum Analyser). Samples for S.E.M. analysis were mounted on aluminium stubs and coated with a thin layer of gold. An accelerating voltage of 25 kV was used.

2.2 ESTUARINE DISSOLVED METALS

2.2.1 Sample Collection and Physico-Chemical Variables

There was a need to characterise the spatial and temporal variability,
within the Tamar Estuary, of a number of properties which could exert a
significant control over the in situ chemical reactivity. In particular,
the emphasis on physico-chemical changes occurring at the F.B.I. was
important. The relationship between, for example, the salinity
distribution and the turbidity maximum through common hydrodynamic forces
was important to monitor. The variation in geographical position of
the F.B.I. due to changes in river run-off and variation in the tidal
height, meant that the surficial sediment (most easily re-suspended) which
may have been in contact with saline conditions could at other times be
covered by waters of a completely different composition. Previous
studies have shown that the low salinity region is the site for the most
extreme changes in estuarine properties (Morris, et al., 1978, 1982b;
Eaton, 1979a). In this work the low salinity region was specifically
investigated and dissolved metal measurements were carried out at the
same time as suspended particulate and sediment measurements.

Field sampling was carried out during axial traverses of the estuary,
coincident with local high water. Water was pumped from a depth of 0.5 m
using a submersible centrifugal pump through a constant level reservoir
(flow cell) which contained the detecting sensors for the various
physico-chemical parameters. A subsidiary flow was used for dissolved
and particulate sampling. The design of the pumping system involved
all-plastic fittings and the motor was sealed from the water by plastic
glands. During the work-ups to previous surveys (Morris, et al., 1978)
a comparison of bucket and pumped samples showed that contamination was
not a significant factor.

46

Salinity and temperature were recorded discreetly using an E.I.L. salinity/temperature bridge, type M.C.5. Chloride ion measurements were used to provide a precise and sensitive indication of salinity at very low salt concentrations. The pH was determined with a Pye combination glass electrode standardised with N.B.S. pH standards. Dissolved oxygen concentrations were obtained using a Y.S.I. oxygen meter. Percentage saturation values were calculated with the aid of tables published by U.N.E.S.C.O. (1973). Turbidity measurements were carried out using a Partech Electronics Ltd. suspended solids monitor, which was calibrated against the gravimetric analysis of discrete samples collected at regular intervals during the axial survey. The outputs from the continuously recording devices were displayed together on a multi-channel pen recorder. Position was fixed at various times and landmarks were noted on the chart trace, thus the data was fixed within a framework of time and geographical location.

2.2.2 Sample Preparation and Experimental Techniques

Although all efforts to minimise contamination were taken, the work was not carried out in 'clean room' facilities and thus the results must be qualified in the light of the conditions under which the sampling and treatment were carried out.

2.2.2.a Copper and Zinc

Samples of ten litre volume were abstracted from the pumped supply (see Section 2.2.1) and collected in acid-washed polyethylene containers. Filtration through 0.45 μm 'Millipore' filters was undertaken on board the vessel or within 2-3 hours of collection. In the region of the estuarine turbidity maximum, GF/C filters were used as pre-filters, thus extending the capacity of the small-pore membrane filters. The

filters were not acid-washed, but sample-rinsed to remove any appreciable levels of trace metal contamination. The samples were filtered using 'Millipore' vacuum pumps and ten litre acid-washed Buchner flasks.

Because of low levels of dissolved copper and zinc, a preconcentration method was used rather than direct flameless A.A.S. Previous dissolved analyses in the Tamar had been made using the ion-exchange resin 'Chelex-100' as a preconcentration step (Morris, et al., 1978). The resin was regenerated to the ammonium form using a two-step process. It was first eluted with 2M 'Aristar' HNO_3 and rinsed with deionised, distilled water to pH = 7. Elution with 2M ammonium hydroxide (NH_4OH) solution and further rinsing to pH = 7 finally produced the regenerated resin.

The resin exchange columns were charged with 10 ml of regenerated resin which was constrained by a 'plug' of acid-washed glass-fibre wool. Using a peristaltic pump, adjustments were made to achieve flow rates of between 250-300 ml/hr. All tubing was washed with deionised, distilled water followed by a small volume of the sample. The samples were processed through the ion-exchange columns and blanks were prepared by passing the waste water from one column to a successive column. The resin was finally eluted with 2M 'Aristar' HNO_3 into a 25 ml volumetric flask to remove the available metals (Riley and Taylor, 1968).

In order to assess the efficiency of the 'Chelex-100' resin and also ascertain any changes of efficiency with salinity, six samples which had previously been passed through the ion-exchange columns were

'spiked' with various concentrations of dissolved copper, manganese and zinc and left to equilibrate for 12 hours. The analytical procedure was identical to that used for the samples.

Table 2.1   'Chelex-100' Efficiency

Salinity, ^{o}/oo	Metal Recovery, %		
	Cu	Mn	Zn
30.7	83	108	112
29.4	83	86	89
26.9	72	113	116
0.05	69	90	122
0.04	79	71	103
0.04	68	91	105

The efficiencies for the three dissolved metals showed some interesting variation, taking into account an analytical precision of 5-10% for each result (Morris, 1980, personal communication). Copper recovery was more efficient in saline waters than in riverwater.   This may be due to the increased competition for organic ligands by the greater concentration of magnesium and calcium ions, thus leaving a greater fraction of reactive copper to exchange onto the resin. For copper the recoveries were the lowest of the three metals, indicating that it may be more susceptible to complexation by humic material, and thus prevented from reacting with the resin. The recovery of manganese was greater than copper with slightly higher values in saline water than in riverwater.   Zinc recoveries appeared to be independent of salinity.

49

The results showed that dissolved metal recovery was affected by salinity in the order Cu > Mn > Zn. Although changes of up to 20% were recorded, no attempt was made to re-quantify the dissolved copper data obtained from the axial profiles.

Metal determinations for copper and zinc were undertaken using standard conditions for flame A.A.S. on a Perkin-Elmer X03 series, 306 Atomic Absorption Spectrophotometer using an air/acetylene flame. Calibrations were carried out in the linear range using acidified standards.

2.2.2.b Manganese

In the early survey work, manganese determinations were undertaken using a method similar to the chelating resin used for copper and zinc (Morris, et al., 1978). With early recognition of a rapid removal of dissolved manganese during storage of untreated samples a specialised sampling procedure was adopted (Morris, et al., 1982a).

Discrete samples (20 ml) were abstracted from the pumped water supply. The sample was filtered through a pre-rinsed membrane filter (0.45 μm 'Nuclepore') and stored in polyethylene vials at reduced pH with the addition of 20 μl of 1M 'Aristar' hydrochloric acid (HCl). Manganese in the samples was analysed by direct, flameless A.A.S. using a Perkin-Elmer X03 series, 306 Atomic Absorption Spectrophotometer with a Heated Graphite Atomiser (H.G.A.-72). 'Aristar' ammonium nitrate (NH_4NO_3) was used as a matrix modifier for the effects of sea salts which would otherwise provide interferences (McArthur, 1977). Calibration was carried out in the linear range using acidified standards.

2.3 SUSPENDED PARTICULATE MATERIAL

Substantial temporal and spatial variability in the chemical
composition of estuarine suspended particulate material is generally
acknowledged (Sundby and Loring, 1978; Sholkovitz, 1979; Sholkovitz
and Price, 1980; Loring et al., 1982). A measure of this variability
must be taken into account, since it is thought that the majority of
chemical transformations in estuaries are mediated at the surfaces
of particles.

2.3.1 Sample Collection

Surface suspended particulate samples were collected with a poly-
ethylene bucket during axial traverses of the River Tamar. The sample
stations were approximately co-incident with those of the dissolved
samples (see Section 2.2.1). Triplicate samples were isolated by
filtration onto pre-weighed 0.45 µm 'Nuclepore' membranes and washed
with deionised water to remove occluded, dissolved sea salts.
Samples were stored in dry plastic envelopes.

2.3.2 Sample Preparation

All analytical procedures were carried out by Loring and Rantala at
the Bedford Institute of Oceanography, Bedford, Nova Scotia, Canada.
The samples were analysed using the methods specified in Section 2.1.2
using validated A.A.S. techniques (Rantala and Loring, 1975; Loring,
et al., 1982).

51

2.4   MODELLING STUDIES OF THE ESTUARINE BEHAVIOUR OF

COPPER AND ZINC

The results from the estuarine axial profiles (see Section 3.2.2)
had shown that, under certain conditions, pronounced adsorption and
desorption reactions could have occurred in the low salinity region.
The use of large volume water samples however was a cumbersome
technique. Associated with this problem was the relatively long period
of time taken to filter ten litres of sample, particularly at high
turbidities. As the turbidity maximum was usually co-incident with
the F.B.I., the most important samples had taken the greatest length
of time to filter and any adsorption/desorption reactions occurring
in the natural samples would have been modified during this period.
Several techniques were examined with a view to improving the collection
procedure and developing a method suitable for small-scale laboratory
modelling. These met with varying degrees of success.

2.4.1   Comparison of Analytical Methods

2.4.1.a   Direct Flameless Atomic Absorption Spectroscopy

Discrete samples were collected on an axial traverse of the Tamar
Estuary with emphasis being placed on the low salinity region. The
20 ml samples were filtered (0.45 µm 'Nuclepore') using a syringe
and 'Swinnex' attachment, the filtrate was then acidified with 20 µl
of 1M 'Aristar' HCl and stored in a polyethylene vial. Determination
of dissolved copper and zinc levels was attempted employing a method
similar to that used for manganese (McArthur, 1977), but using standard
conditions for copper and zinc. A Perkin-Elmer X03 series, 306 Atomic
Absorption Spectrophotometer fitted with an H.G.A.-72 was used.

52

Ammonium nitrate proved to be unreliable as a matrix modifier due to the lower ashing temperatures necessary for copper and particularly zinc. Variations in ashing temperatures and programme rates, together with different concentrations of NH_4NO_3 were initiated to try to achieve an optimum instrumental performance. In saline waters, even at salinities of less than $10^o/oo$, double peaks associated with the salt matrix proved difficult to separate from the metal peak and subsequent replicate analyses gave poor reproducibility.

2.4.1.b Solvent Extraction Technique

To evaluate this method, which had a sound basis in the literature (Kinrade and Van Loon, 1974; Tessier, et al., 1979; Smith and Windom, 1980; Farley and Nelson, 1982), laboratory based experiments were devised for the determination of copper and zinc in estuarine samples. They were designed to determine optimum extraction pHs, sample stability and the analytical reproducibility of small (100 ml) sample volumes.

Small volumes (100 ml) of deionised, distilled water were 'spiked' with dissolved copper and zinc to levels consistent with those found in the natural environment and extracted using a chelation method (Farley and Nelson, 1982) involving ammonium pyrrolidine dithio-carbamate (APDC) and methylisobutylketone (MIBK). The optimum extraction pH was found to be pH = 2 for both metals, in good agreement with Kinrade and Van Loon, (1974). Extracts showed variation with salinity, as MIBK was less soluble in seawater than distilled or river-water, this created problems due to variation in concentration ratios. Sample stability in the organic phase was poor and pronounced sample

53

deterioration was observed over a short period (2 hours). This was in contrast to results reported by Kinrade and Van Loon, (1974). A back-extraction step was incorporated and the metals were re-extracted into 5 ml of 10% 'Aristar' HNO_3. Although there was a loss of sensitivity on metal determination, the improved sample stability compensated for that loss.

Five, ten litre samples were collected during an axial traverse of the Tamar Estuary. One litre of each sample was filtered immediately on collection and at selected time intervals thereafter. Each filtered sample was reduced to pH = 2 by the addition of 20 μl of 'Aristar' HCl and the acidified sample was extracted using the technique developed previously. Conspicuous differences were observed in overall concentration with time. With encouraging results for this technique forthcoming, a second more intensive survey was undertaken.

Eighteen samples were taken from an axial traverse of the estuary with a concentrated sampling regime in the low salinity region. Samples of ten litre volume were taken (see Section 2.2.1) and 1 litre sub-samples removed, filtered (0.45 μm 'Millipore') and acidified to pH = 2 on collection and at selected time intervals thereafter.

Following solvent extraction, copper and zinc analyses were carried out using flame A.A.S. on a Perkin-Elmer XO3 series, 306 Atomic Absorption Spectrophotometer with an air/acetylene flame. Calibrations were carried out in the linear range using acidified standards.

The results in Figures 2.3 and 2.4 show that the general trends of copper and zinc with salinity appear to exhibit the same profile for each time series. However, a problem exists whereby the concentrations
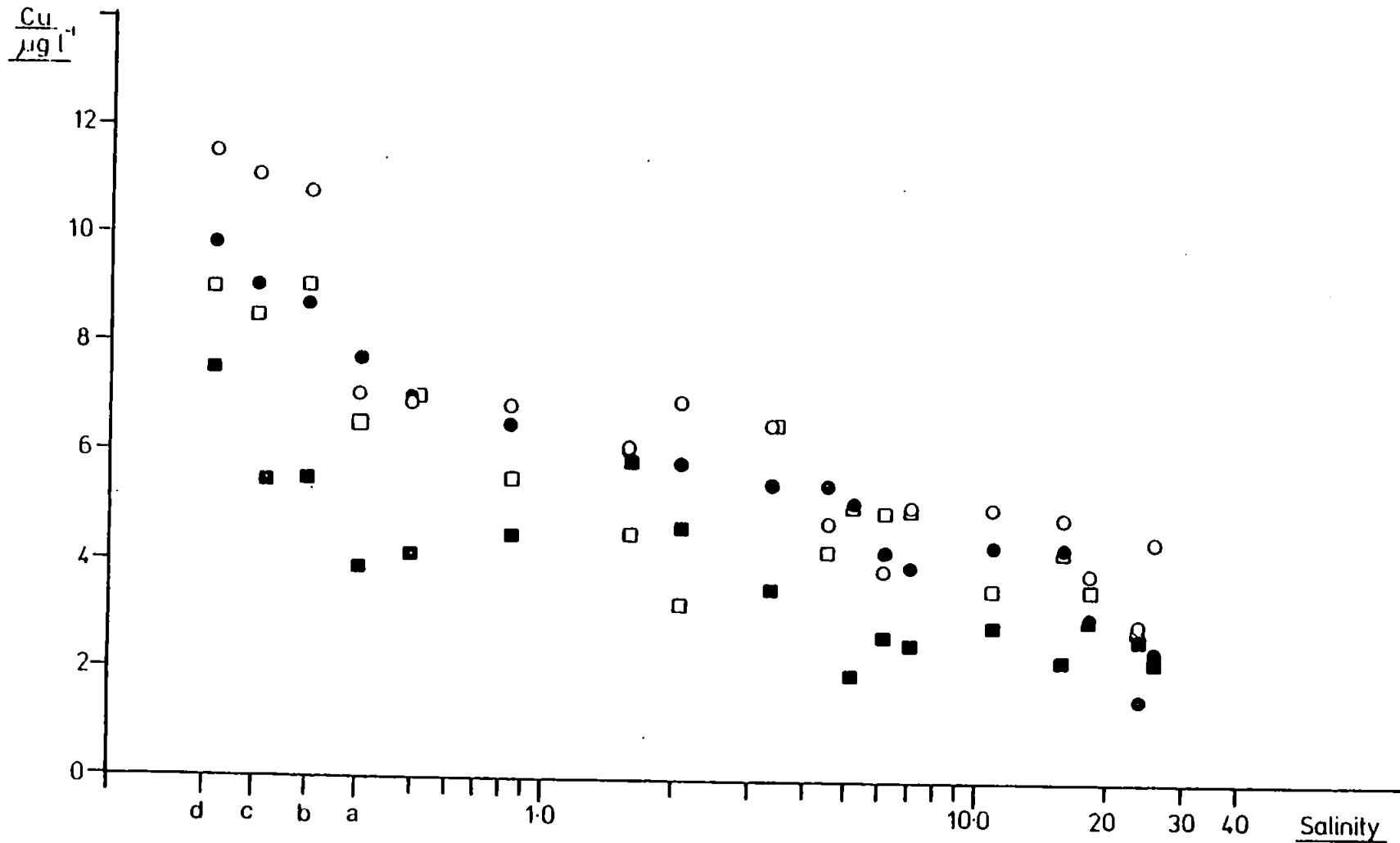
Figure 2.3 The variation in dissolved copper content of eighteen estuarine samples with time, determined by solvent extraction technique. Positions a, b, c and d were sampled upestuary of 0.5°/oo

●- initial dissolved copper content; O- after 24 hours; ■- after 48 hours; □- after 72 hours
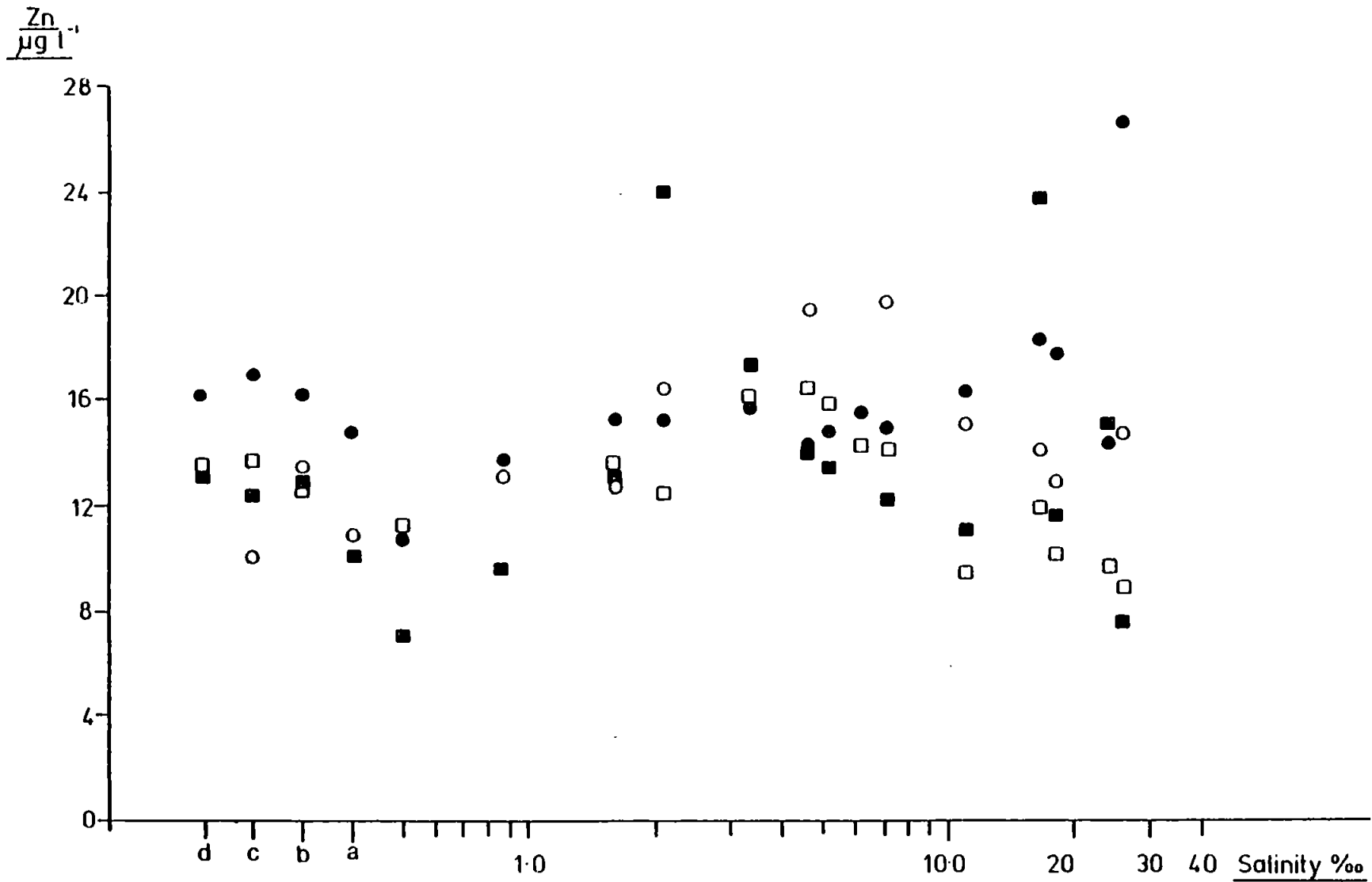
Figure 2.4   The variation in dissolved zinc content of eighteen estuarine samples with
time, determined by a solvent extraction technique.   Positions a, b, c and d were
sampled upestuary of $0.5^o/oo$

●- initial dissolved zinc content;   O- after 24 hours;   ■- after 48 hours;   □- after 72 hours

for each time series varied, often in an inconsistent manner. It was difficult to interpret such results, which may be due to either an analytical problem, such as reagent stability, or instrumental variability. Whilst the method may be viable for 'one-off' surveys, the problem of the lack of consistency meant that results suitable for detailed kinetic analyses could not be obtained.

2.4.2 Laboratory Modelling of Artificial Levels of Dissolved Copper and Zinc in Natural Waters

Because of the inherent problems of low levels of dissolved copper and zinc in the natural environment, a method was developed in which artificially high levels of dissolved metals were examined, thus circumventing the problem of concentration techniques or flameless analytical methods and thus allowing for flame A.A.S. of small samples.

A programme to assess the adsorption characteristics under varying natural suspended particulate loads, salinity and pH conditions was undertaken. Bulk samples (50 litres) of water were collected at low water, in the mid estuary (Halton Quay) where the turbidity was in excess of 500 mg l^{-1} and the salinity was zero. Seawater samples of greater than 30°/oo were also collected. A ten litre sample of seawater and 20 litres of riverwater were filtered (0.2 μm 'Sartorius') and stored, together with the high turbidity riverwater at 10°C. The filtered riverwater was mixed with the high turbidity riverwater to produce 1 litre samples with turbidities of 0, 10, 100 and 500 mg l^{-1} and in some cases seawater was added to give salinities of 0, 1 and 10°/oo. The solutions were equilibrated for 10 minutes and mixed using magnetic stirring platforms, and then 'spiked' with dissolved

57

copper and zinc to give concentration of 100 $\mu g\ l^{-1}$ for each metal. At regular intervals, 10 ml aliquots were removed using a syringe and filtered (0.45 μm 'Millipore') using 'Swinnex' filter attachments. The filtrates were acidified to pH = 1 using 'Aristar' HCl. Metal determinations were made using standard conditions for air/acetylene flame A.A.S. on a Perkin-Elmer X03 series, 306 Atomic Absorption Spectrophotometer. These were calibrated using known, acidified standards in the linear range.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1   ESTUARINE SEDIMENTS

3.1.1   Analytical Precision and Significance

In order to examine the efficiency of the selected digestion methods, two international sediment standards were analysed, using the HF digestion procedure. The results shown in Table 3.1 were in good agreement with the standard figures given for M.E.S.S.-1 and B.C.S.S.-1. The coefficient of variation (C.V.) for each metal was excellent in the majority of cases. The metal concentrations in the reference materials are regarded as totals. Therefore, it is possible to conclude that the HF digestion procedure adopted in this work gives total metals in the Tamar sediments.

Acetic acid digestions were also undertaken on the standard sediments and the results are given in Table 3.2.a. No data is available yet for the standard sediments, so a comparison is made with existing information on Tamar and Saguenay Fjord sediments (see Table 3.2.b). The intercomparison of acetic acid digestion results for Tamar sediments (Table 3.2.b) was reasonable, particularly when considering the range of sample sites used. Some discrepancies were present with the lead and copper results. Copper extraction can be particularly problematical using this digestion method (Luoma and Bryan, 1981). The digestion pH was approximately pH = 4, which is crucial to the extraction efficiency for copper, any variation in pH would decrease this efficiency markedly. The lead results were more difficult to interpret but it may be the case that lead was found predominantly in the detrital form, i.e. bound in the particle matrix, as would be expected if inputs were in the form of mine tailings. Thus, only a small proportion of the lead would be available to acetic acid leaching.

Element	Replicate Analyses			$\bar{x}$ and s	C.V. %	Standard Value
Cd M.E.S.S.-1	0.51 ppm	-	-	0.51 ppm	-	0.59 ± 0.10 ppm
B.C.S.S.-1	0.34 ppm	0.25 ppm	-	0.3 ± 0.06 ppm	20 *	0.29 ± 0.04 ppm
Cu M.E.S.S.-1	28.6 ppm	28.2 ppm	31.2 ppm	29.3 ± 1.6 ppm	6	25.1 ± 3.8 ppm
B.C.S.S.-1	24.9 ppm	24.2 ppm	20.5 ppm	23.4 ± 2.4 ppm	10	18.5 ± 2.7 ppm
Fe M.E.S.S.-1	2.96 %	2.40 %	2.89 %	2.75 ± 0.31 %	10	3.0 %
B.C.S.S.-1	2.68 %	3.21 %	2.09 %	2.66 ± 0.56 %	21	3.8 %
Hg M.E.S.S.-1	-	0.177 ppm	0.177 ppm	0.177 ppm	0 *	0.171 ± 0.014 ppm
B.C.S.S.-1	-	0.115 ppm	0.132 ppm	0.123 ± 0.01 ppm	10 *	0.129 ± 0.012 ppm
Mn M.E.S.S.-1	498 ppm	418 ppm	493 ppm	469 ± 44 ppm	10	513 ± 25 ppm
B.C.S.S.-1	252 ppm	238 ppm	226 ppm	238 ± 13 ppm	5	229 ± 15 ppm
Pb M.E.S.S.-1	-	44.2 ppm	41.6 ppm	42.9 ± 1.8 ppm	4 *	34.0 ± 6.1 ppm
B.C.S.S.-1	-	24.8 ppm	14.7 ppm	19.7 ± 7.1 ppm	36 *	22.7 ± 3.4 ppm
Zn M.E.S.S.-1	184 ppm	147 ppm	103 ppm	144 ± 40 ppm	28	191 ± 17 ppm
B.C.S.S.-1	116 ppm	104 ppm	103 ppm	107 ± 7 ppm	7	119 ± 12 ppm

* C.V. of two results only

Table 3.1 Analysis of Sediment Standards M.E.S.S.-1 and B.C.S.S.-1 by Hydrofluoric Acid Digestion

Table 3.2.a Analysis of Sediment Standards M.E.S.S.-1 and
B.C.S.S.-1 by Acetic Acid Digestion

Element	Analysis	% of HF Digest
Cd M.E.S.S.-1	-	-
B.C.S.S.-1	-	-
Cu M.E.S.S.-1	2.80 ppm	10
B.C.S.S.-1	1.68 ppm	6
Fe M.E.S.S.-1	0.146 %	5
B.C.S.S.-1	0.135 %	5
Hg M.E.S.S.-1	-	-
B.C.S.S.-1	-	-
Mn M.E.S.S.-1	27.0 ppm	5
B.C.S.S.-1	16.8 ppm	6
Pb M.E.S.S.-1	-	-
B.C.S.S.-1	-	-
Zn M.E.S.S.-1	72.9 ppm	40
B.C.S.S.-1	28.6 ppm	24

Table 3.2.b A Comparison of the Acetic Acid Digestion as a
Percentage of the Total Metal Level in Various Sediments

Element	This Work Tamar	Loring(1980)[b] Tamar	Luoma and Bryan(1981) Tamar	This Work[a] Tamar	Loring(1976) Saguenay Fjord
Cd	-	70-80	-	100	-
Cu	20	50-60	30-40	100	15-20
Fe	5-15	10-15	10	90-100	-
Mn	70-100	40-60	-	60-80	-
Pb	10-15	30-40	50-60	-	10-25
Zn	50-70	50-60	60-70	80-90	15-30

[a] Nitric acid digestion   [b] Personal communication

62

The percentage leach, however, was low relative to data obtained by Loring, (1980, personal communication) and by Luoma and Bryan, (1981). The results for iron, manganese and zinc were very consistent, thus verifying the accuracy and reproducibility of this method for sediment digestion.

It should be noted that the acetic acid digestions of the reference materials produced low metal extraction yields relative to the Tamar results (see Tables 3.2.a/b). The discrepancy is probably due to the different sediment mineralogy in the Tamar Estuary compared to the Miramichi Estuary and Baie des Chaleurs. The importance of the mineralogy to overall sediment composition has been discussed by Loring, (1976).

To summarise, the use of the HF digestion procedure has been vindicated by comparison with two standard sediments as an efficient total digestion method. The acetic acid procedure was, with some reservations, also endorsed as providing a good representation of the labile metal fraction.

Criticism could also be made of the ignition method used for the determination of total organic carbon (T.O.C.). Although this technique has been widely employed (Holme and McIntyre, 1971), a comparison with determinations made using other techniques for Tamar sediments indicated that the general levels given by this method were high. Mook and Hoskin, (1982) investigated weight loss on ignition of sediments which had had the organic fraction oxidised using 10% sodium hypochlorite (NaOCl). They found weight losses on ignition of up to 20%. This loss was assumed to be from structural water held within the clay mineral lattice.

Hydrogen peroxide digestions were carried out on both Tamar sediment samples and sediment standards M.E.S.S.-1 and B.C.S.S.-1. Weighed sediment samples were treated with 10 ml of 'Analar' hydrogen peroxide (H_2O_2), the samples were then filtered, dried (50°C) and re-weighed. Weight loss was calculated to be between 5-15%, depending upon the region of the estuary from which the sample originated. Weight loss due to the experimental procedure was estimated to be, at maximum, 2%. Weighed portions of organic-free sediment were then ashed at 670°C for 6 hours and re-weighed. The percentage weight loss recorded was 4-6%. This was presumed to be due to the loss of the carbonate fraction together with the structural water within the clay mineral lattice.

Weight losses from the untreated sediment standards were; B.C.S.S.-1 =9% and M.E.S.S.-1 = 8%. After treatment with hydrogen peroxide, the weight losses for both standards were 4%. When this figure was subtracted, the organic carbon contents are B.C.S.S.-1 = 5% and M.E.S.S.-1 = 4% which was in good agreement with the accepted values for the standard sediments. When the same procedure was carried out for the Tamar sediments, the following results were obtained (Table 3.3).

Table 3.3 Comparison of Organic Carbon Content by C-H-N Analysis (Watson, et al., 1982) and the Ashing Procedure Corrected for Structural Water Loss

Position (km from weir)	Organic Content (%)	
	This Work (corrected values)	Watson, et al., (1982)
0	4	2
1.9	5	4
8.1	6	6
13.3	5	4
21.5	4	4

The corrections made for water loss from the sediments brought the
Tamar data into good agreement with other work using more precise
analytical techniques (Watson, et al., 1982). Although it is recognised that
the T.O.C. values obtained using the ignition method were overestimates,
no corrections were made to the data.

Due to heavy metal concentration in the finer grain-size fractions,
estimates of the percentage < 63 μm fraction were carried out by
wet-sieving a weighed portion of sediment and re-weighing the
resultant two fractions. The main source of experimental error was
due to incomplete dis-aggregation of the dried sediment when re-
suspended in distilled water. This may have produced an under-
estimate of the total percentage of fine material. It would appear
from a recent study of Tamar sediments (Bale, 1983, personal communi-
cation) using a dispersant (sodium hexametaphosphate, 6.2 g l^{-1}) that
the underestimate due to incomplete dis-aggregation of the sediment may
be in the order of 10%.

3.1.2   Estuarine Sediment Data : Results

3.1.2.a   Scanning Electron Microscopy of Estuarine Sediments

Scanning electron micrographs of the oxic sediment layer were taken of
samples from the fourteen sites in the Tamar Estuary. The sediments
appeared to consist mainly of clay particles and quartz grains,
together with a proportion of biogenic material. (Plate 3.1).
Similar sample compositions from several sites throughout the Tamar
Estuary were observed. There were, however, some extremes in the
proportions of the constituents, particularly in the upper estuarine
sites where the samples were largely composed of quartz.

Plate 3.1

S.E.M. Photographs of Estuarine Sediments

Photograph 0001.   Clay platelets

Photograph 0003.   Clay platelets and biogenic material

Photograph 0008.   Large inorganic particle with
                          coating of iron oxyhydroxide, as
                          determined by X-ray dispersive
                          analysis

Photograph 2224.   Collapsed plankton cells (at centre
                          of photograph) and other biological
                          material
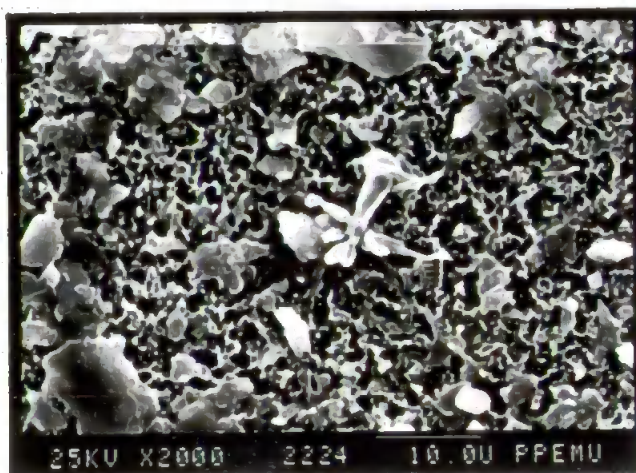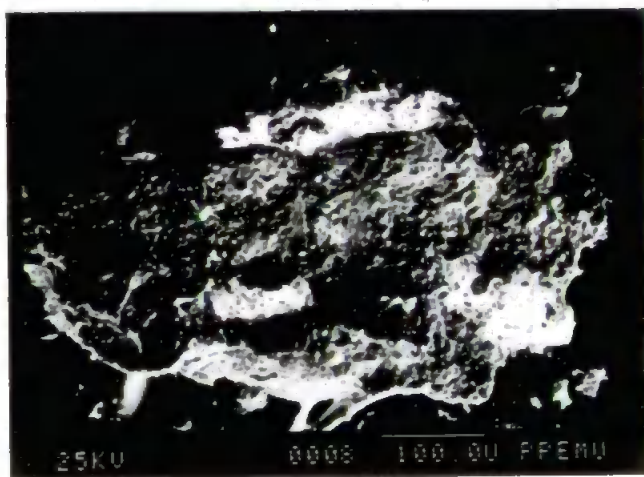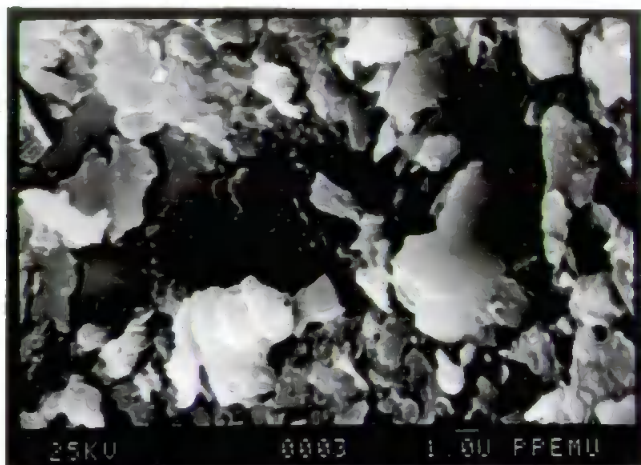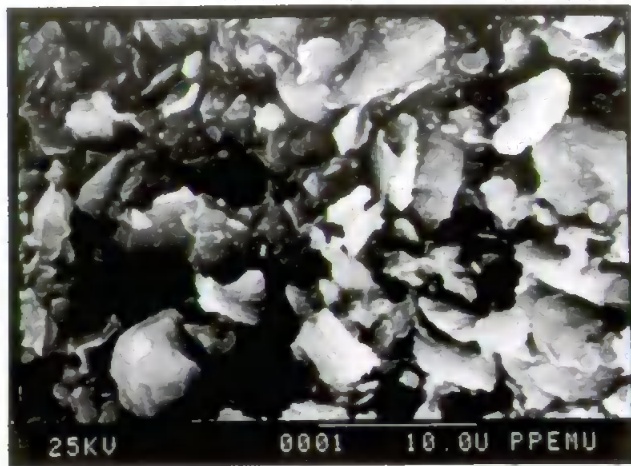
3.1.2.b Hydrofluoric Acid Digestions

The total metal data from nine sediment surveys taken over a period of eighteen months, for each sample site, were summarised by plotting the mean and one standard deviation against distance downestuary from the weir at Gunnislake. The axial profile indicated by the mean values showed the variation in the general metal levels within the estuarine system. In many cases large standard deviations were observed. However, it is important in the intersite comarisons of the variability in metal levels that the coefficient of variation be used. This is particularly so for those metals which exhibit pronounced changes in their mean and standard deviation values between the upper and lower estuary.

For cadmium (Figure 3.1) the mean axial profile was relatively constant at approximately 1.5 ppm, but peaked in the region of the mine spoils (6 km). There may have been a secondary input at 17 km accounting for the higher mean value and also increased standard deviation. Potential sources of input downestuary could emanate from the Naval Dockyard where cadmium is used in electroplating.

Copper (Figure 3.2) showed elevated levels, large standard deviations and a C.V. of approximately 50% in the vicinity of the mine spoils. A gradual decrease in mean levels and C.V.s (18%) was evident from 10 km which could be indicative of; desorption from the sediment in this region, or an input of marine sediment of low copper content 'diluting' the general levels, or both.

The profile for mean iron concentration (Figure 3.3) showed a

Figure 3.1   Total cadmium concentrations in Tamar sediments

69

Figure 3.2   Total copper concentrations
in Tamar sediments
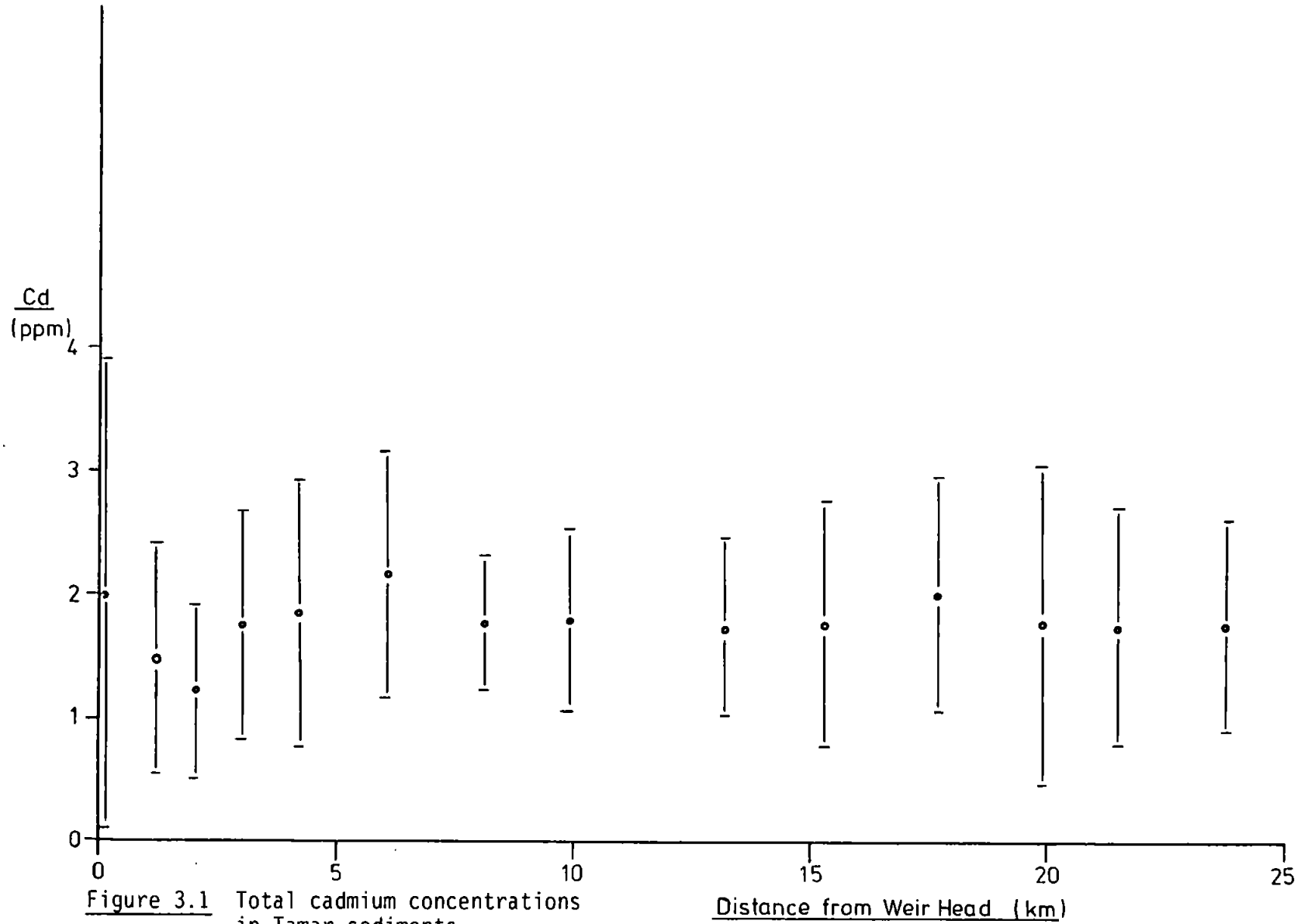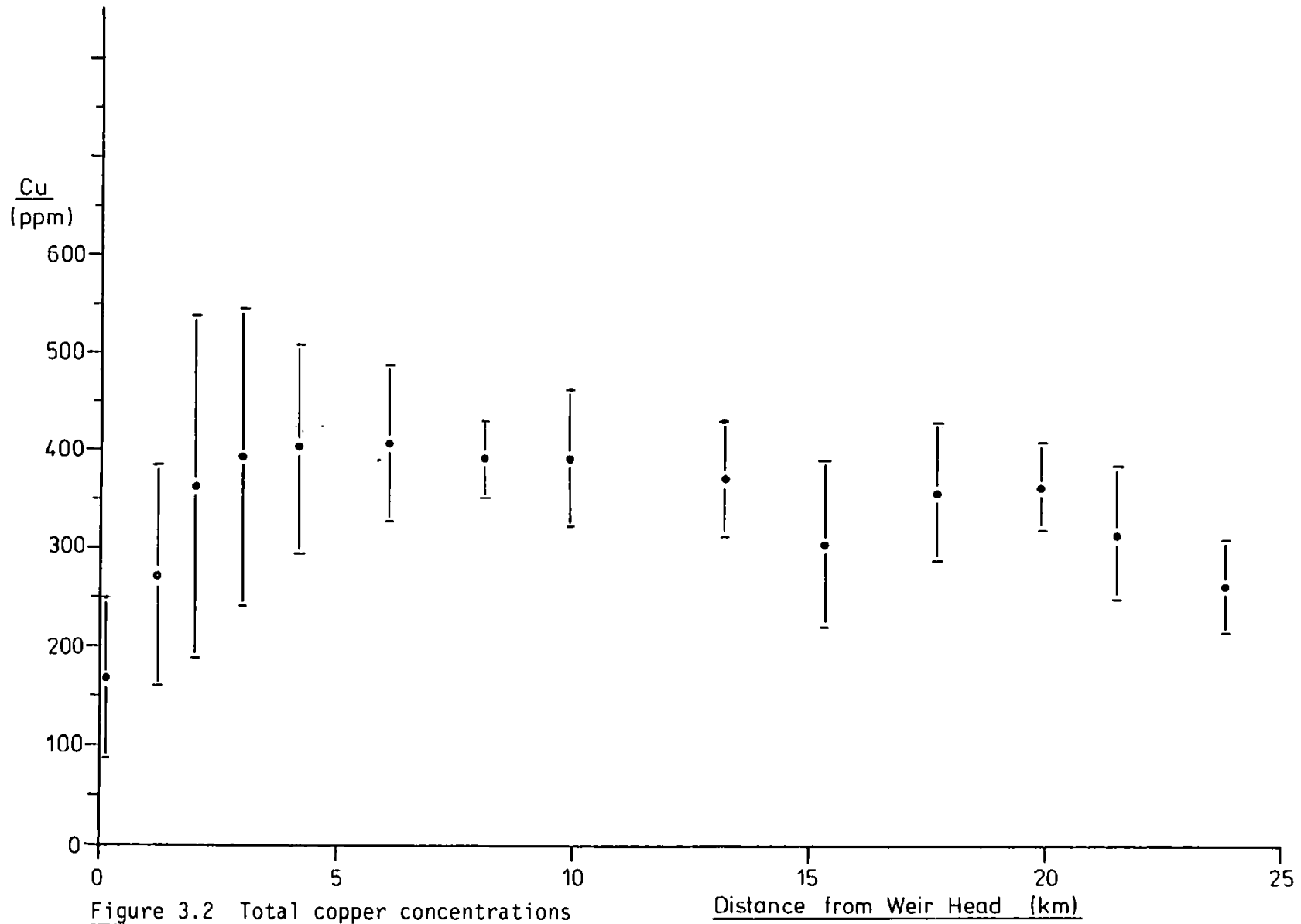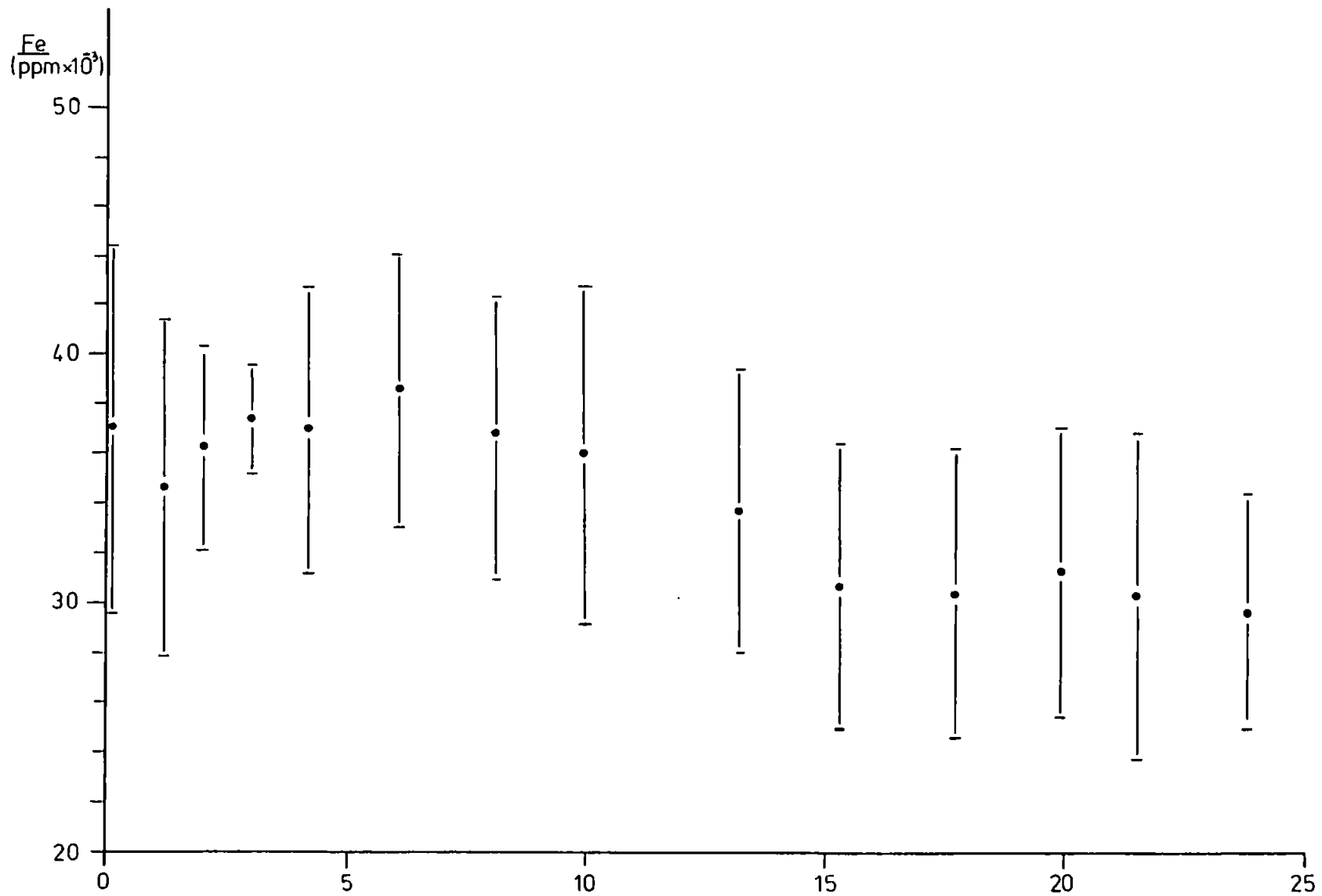
Figure 3.3   Total iron concentrations
             in Tamar sediments

Distance from Weir Head (km)

significant depletion in the lower estuary, the highest concentrations were present in the mine spoils region, with a slight decrease occurring upestuary of this point. The C.V. of iron levels decreased over the first 3 km, thereafter the variation was constant throughout the estuary at approximately 16%. This behaviour was consistent with the assumptions that riverine particulate iron would be mobilised from the sediments into the dissolved phase at the average position of the F.B.I., approximately 10 km from the weir.

The mercury profile (Figure 3.4) showed a departure from the previous three examples. In this case the lower estuary contained the higher concentrations of the metal with correspondingly larger standard deviations. The C.V.s for this profile, although highly variable (13-55%), were on average 30%. This would indicate that the inputs of mercury were in the lower estuary; as there has been no historical evidence of mining in this region, it may be concluded that the input was anthropogenic in nature. Possible sources include sewage effluent; two major outfalls are sited in the proximity of the 22 km sample sites, together with possible input from the Naval Dockyard. This may account for the high standard deviation in the lower estuary.

The manganese concentrations (Figure 3.5) showed a significant and rapid depletion downestuary of the weir and the C.V.s were relatively constant at 35%. One notable feature was the large standard deviation at the head of the estuary due to variation in the riverine input of particulate manganese. The profile obtained was compatible with the established estuarine chemistry of manganese (Knox, et al., 1981; Morris and Bale, 1979; Morris, et al., 1982a). Dissolved manganese in the freshwater is removed to the particulate phase at the turbidity maximum. During neap tides manganese will accumulate in the sediment
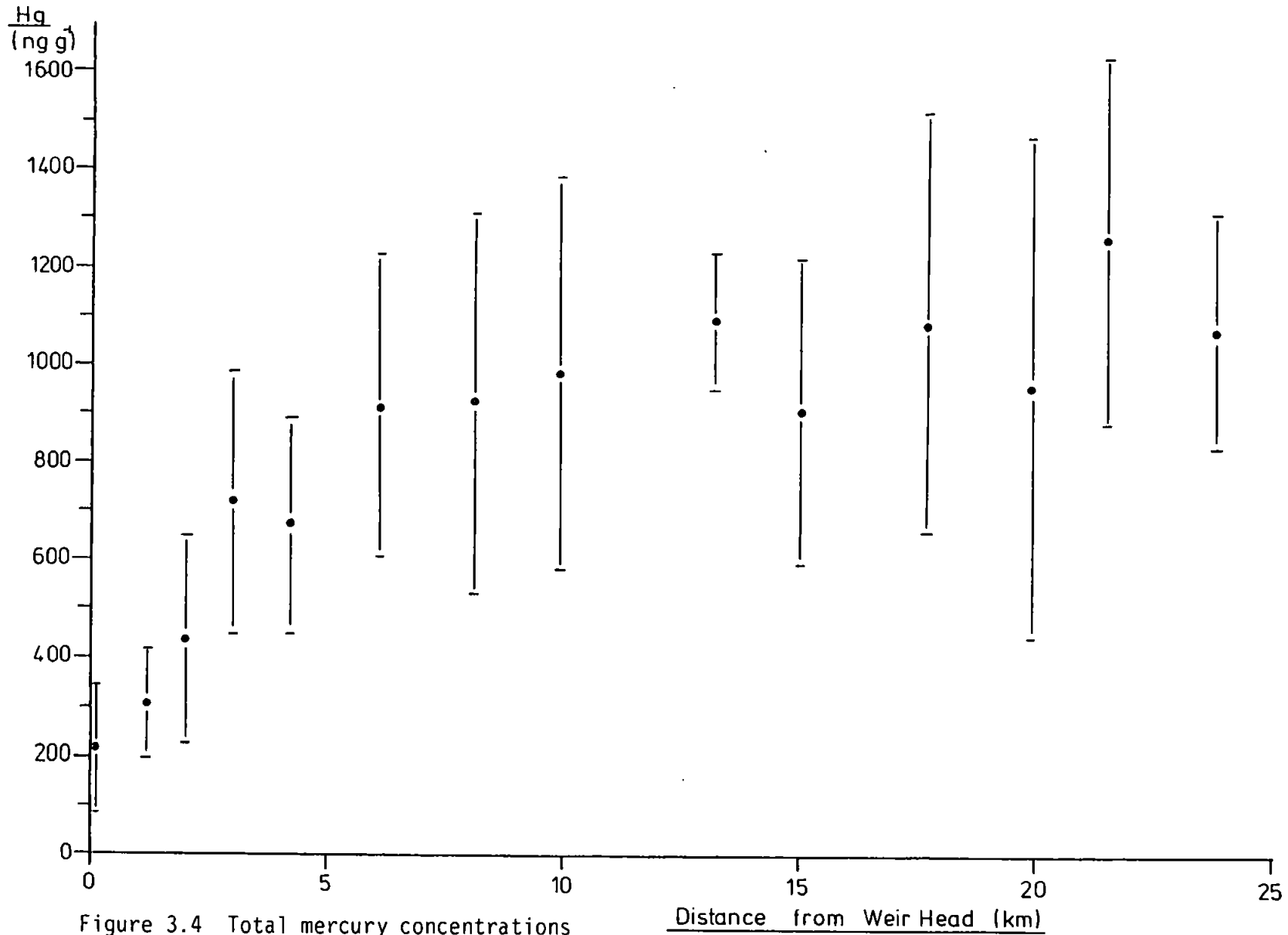
Figure 3.4   Total mercury concentrations
             in Tamar sediments
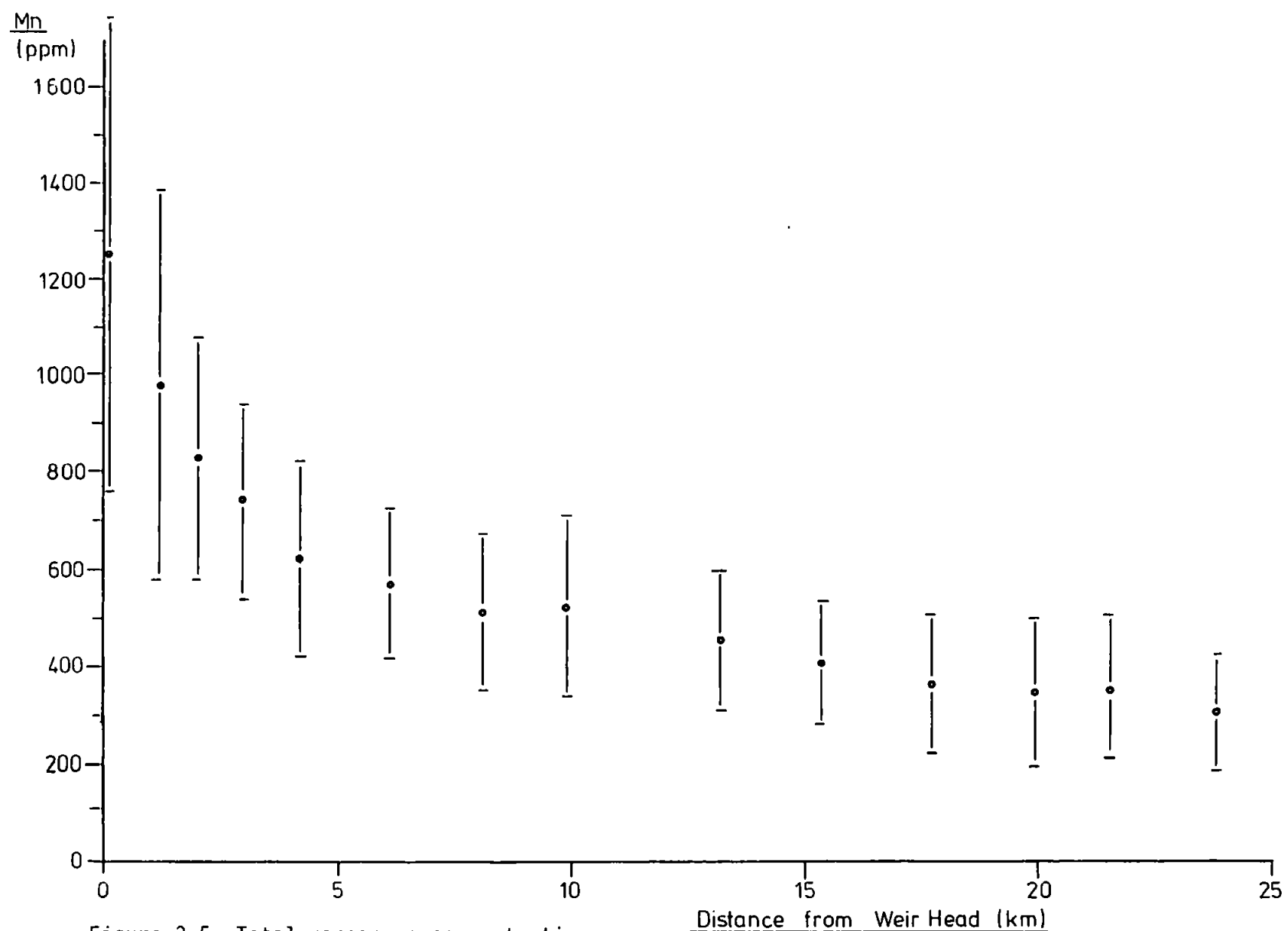
Figure 3.5   Total manganese concentrations
in Tamar sediments

only to be remobilised into the water column as divalent manganese during spring tides. Adsorption of manganese onto particulates in seawater is not favoured so the manganese could be flushed from the estuary in the dissolved phase. This results in a net loss to the sediment in the lower estuary, as shown by the sediment profile.

Lead (Figure 3.6) exhibited a similar profile to mercury. In the mid-estuarine region, the C.V. was in the range 30-35% with the exception of the site 16 km from the weir which had a C.V. of 45%. The lead at this site could have originated from a disused silver/lead mine. Other sources of input in the lower estuary could include sewage effluent and storm drains which contain lead associated with road run-off.

The zinc profile (Figure 3.7) was very similar to that of copper in that the main source of zinc input was the mine spoils region. Down-estuary of 6 km the mean and standard deviations were relatively constant, with a C.V. of 20%.

The axial profile of the grain-size analysis (Figure 3.8) showed the presence of three distinct regions; 0-5 km, 5-20 km and 20-24 km. The upper zone was characterised by a coarser-grained riverine sediment and also displayed high standard deviations. The mid-estuarine region was composed of finer material (80% < 63 µm) some of which could have been flocculants and showed minimal variation in composition. The lower estuary was characterised by high proportions of fine material (70-80% < 63 µm), but increased standard deviations. Due to the effect of grain-size variation on the metal content, statistical methods (see Section 3.1.3) were based on a metal content which was normalised to 100% fine material.
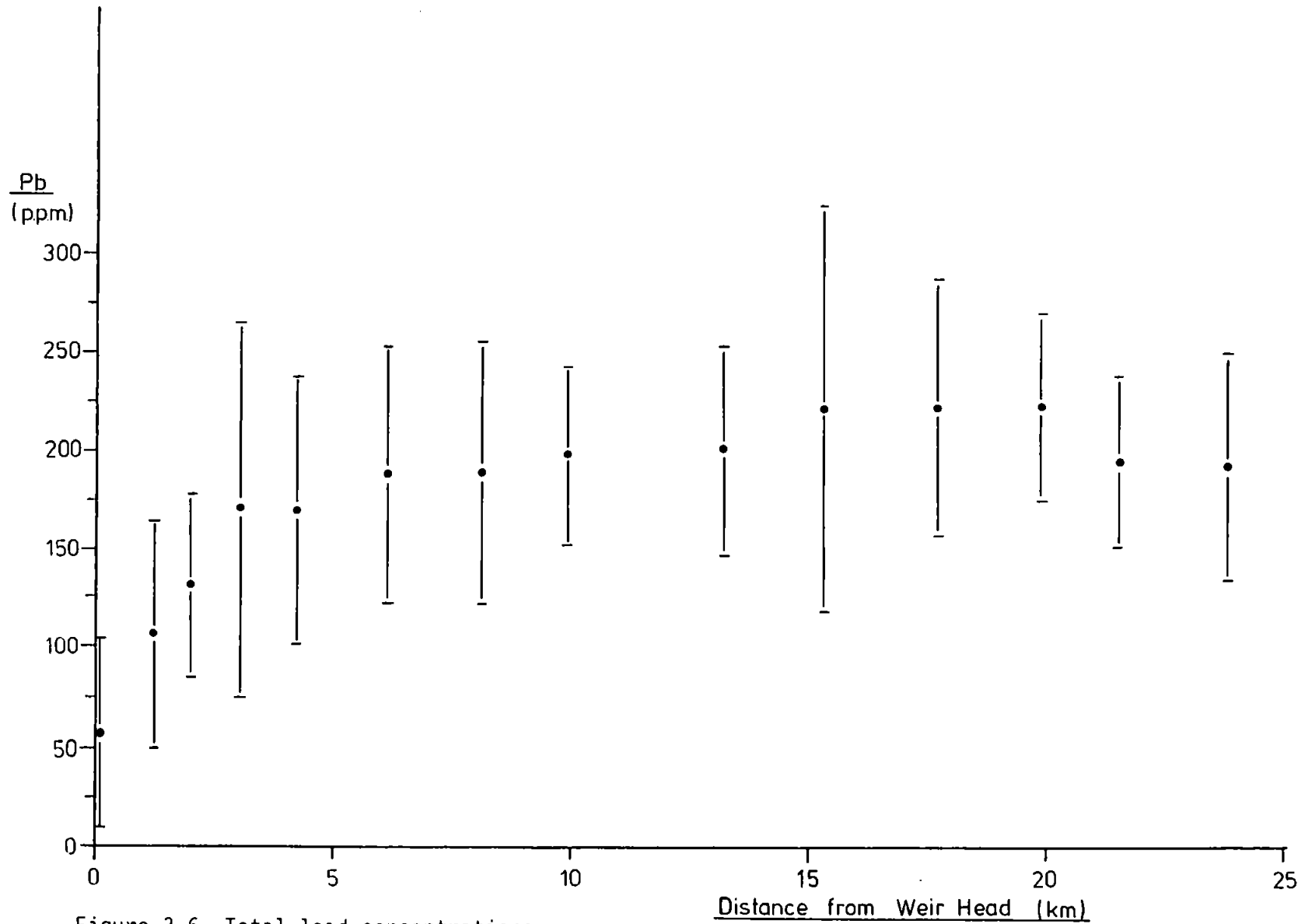
Figure 3.6   Total lead concentrations
            in Tamar sediments
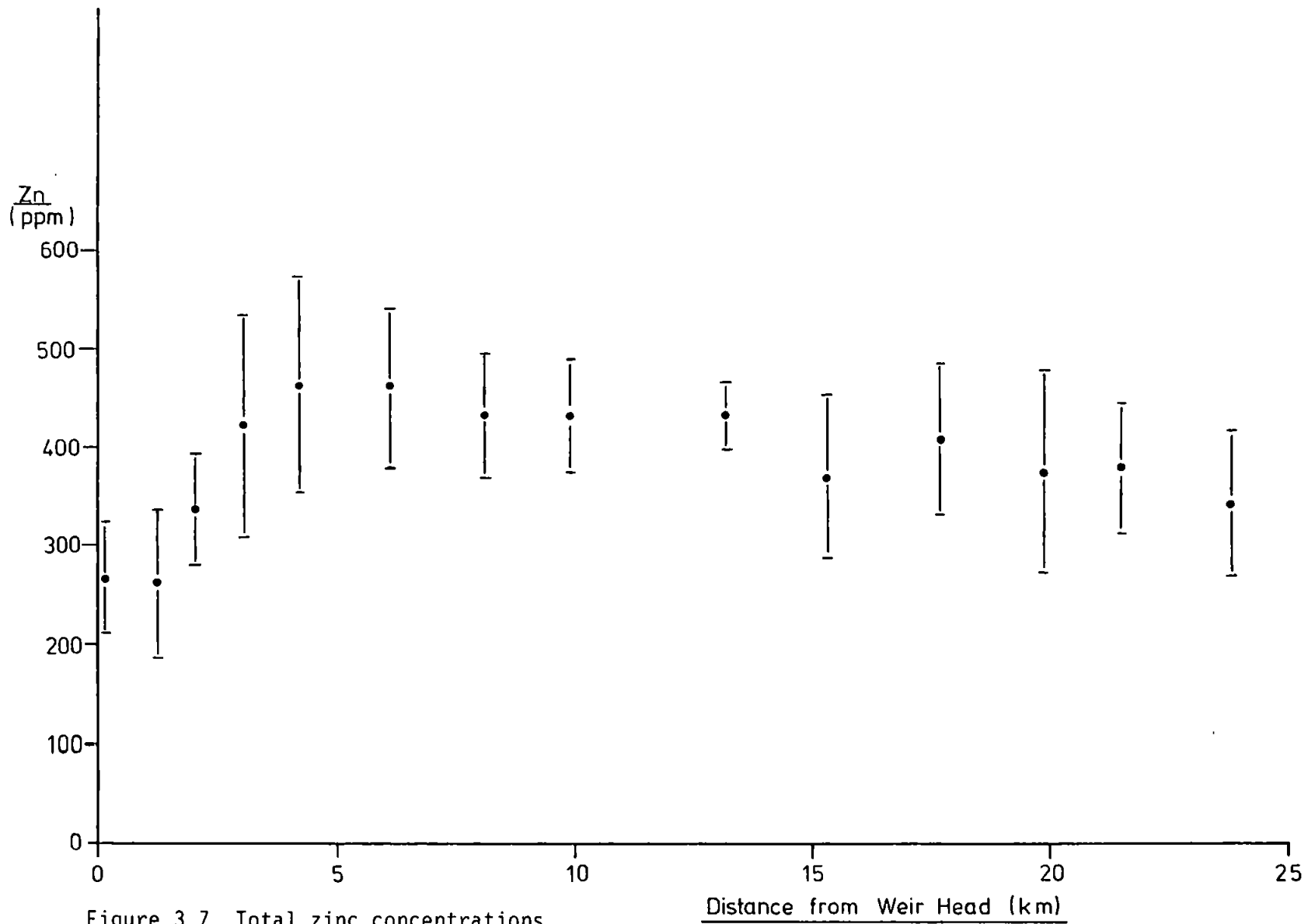
Figure 3.7   Total zinc concentrations
             in Tamar sediments
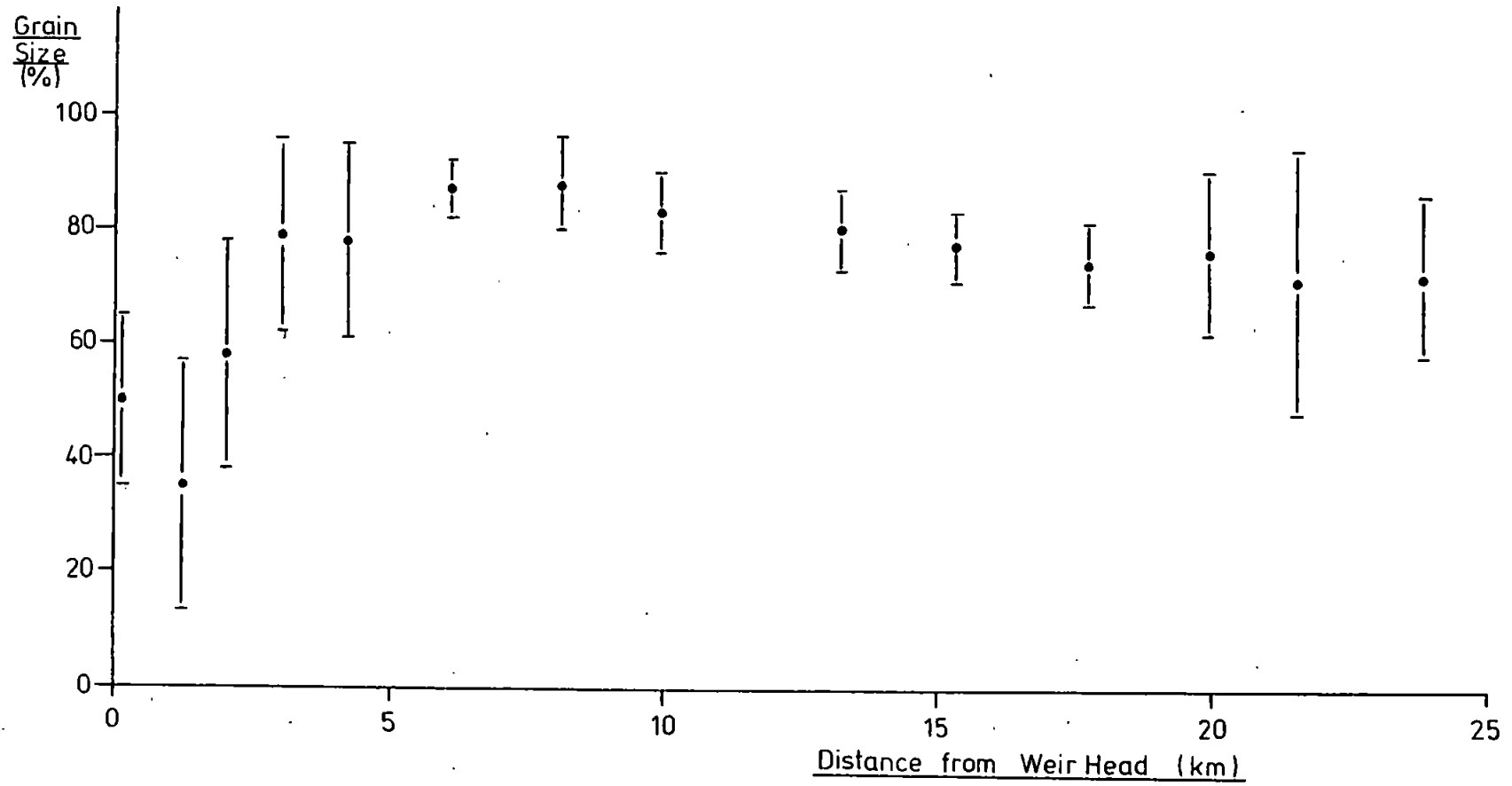
Figure 3.8   Grain size analysis of Tamar sediments

The sediment T.O.C. (Figure 3.9) showed marked similarities with the grain-size profile. The two parameters are of course inter-related; organic matter tends to be associated with the finer grain-size material. The profile however did not exhibit the same distinct sub-divisions of the grain-size data. T.O.C. values were low and variable (C.V. 60%) in the upper estuary; a second, smaller region 5-10 km downestuary showed the highest T.O.C. levels and also a low C.V. of 7%. Downestuary of 10 km the T.O.C. content decreased slightly, but with a corresponding increase in C.V. to 30%. This may be due to the influence of the Tavy Estuary or a transition to a more marine environment.

3.1.2.c Acetic Acid Digestions

The profiles for the acetic acid digestions were obtained from the summation of five surveys and indicate the mean and one standard deviation at each sample site. This selective leach may indicate areas participating in adsorption and desorption reactions which may be occurring in the estuary. This data is also indicative of the labile fraction which may be available to the biota, and which may be potentially harmful in high concentrations.

The copper profile (Figure 3.10) indicated that the estuary was reacting almost as two individual segments. The upper section (omitting the first two stations) had high metal levels, but also showed the largest C.V.s (80-90%), possibly associated with the mine spoil input. These decreased in amplitude to a minimum of 16% at approximately 10 km and downestuary of this point, although the mean levels decreased, the C.V.s increased. The results indicate variable inputs at the head of the estuary, but with consistently high mean values, thus a possible region of net accumulation to the sediment. The lower mean levels
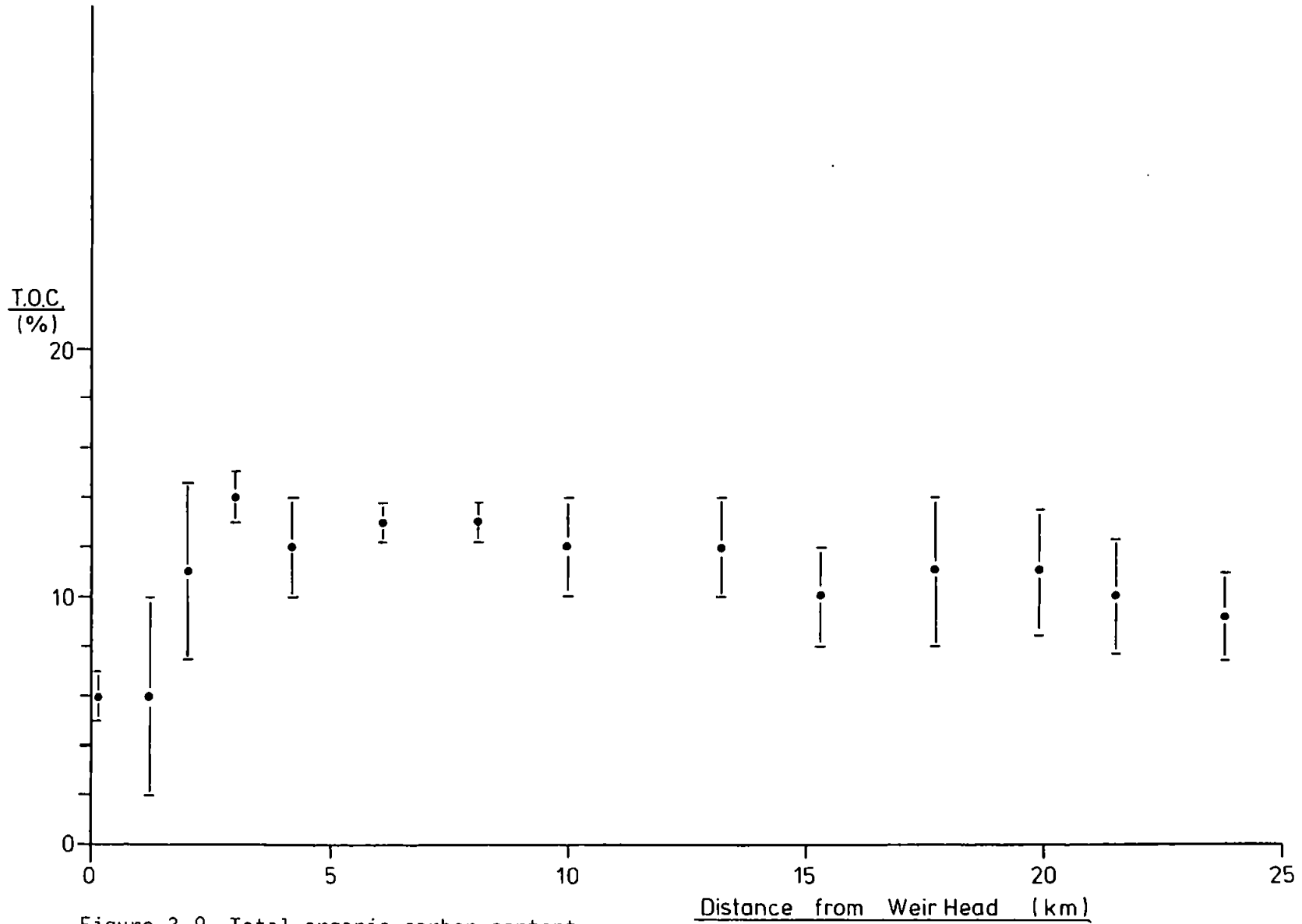
Figure 3.9   Total organic carbon content
             in Tamar sediments
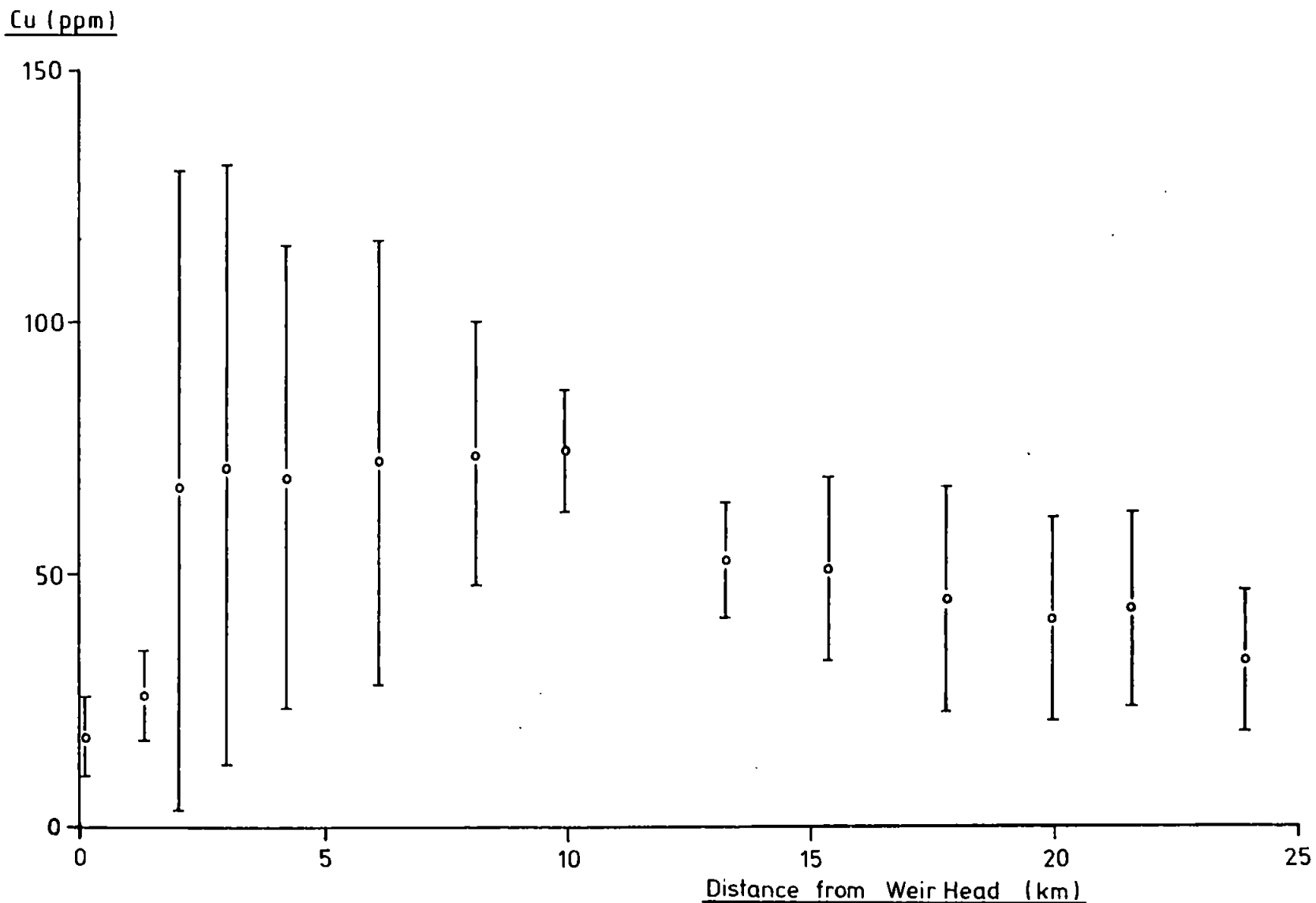
<u>Figure 3.10</u>   Non-detrital copper concentrations in Tamar sediments

downestuary of 13 km indicate a loss, possibly due to desorption at the approximate position of the F.B.I. or a dilution effect due to inputs of marine sediment.

The iron profile (Figure 3.11) showed that with the exception of the first three sites, the iron concentrations were fairly uniform through-out the estuary. The C.V. of the first two sites was approximately 70%, suggesting that the riverine input of non-detrital iron was very variable. The lack of any discernible pattern downestuary did not reflect the estuarine chemical behaviour of iron. One would have expected to see greater discrepancies between the acetic acid soluble metal and the total metal profiles, but as only 5-15% was available to acetic acid leach, any changes may not be noted experimentally.

The leachable manganese profile (Figure 3.12) showed striking similarities to the total levels with high but variable concentrations (C.V. 70%) in the upper estuary reflecting variable inputs from the riverine system. Concentrations decreased down the estuary as manganese was remobilised via liberation of the pore water due to tidal mixing and thus lost from the sediment fraction. The C.V. exhibited no readily identifiable pattern in mid-estuary, but showed increases to about 40% in the lower estuary, again due to possible effects from coastal regions.

The lead profile (Figure 3.13) indicated two possible regions of input; the mine spoils region (3-7 km) and the lower estuary (20-24 km). The minimum C.V. of 6% observed at 15-16 km in this profile coincided with a maximum value for the total lead levels (Figure 3.6). This difference may be due to the input of lead in the detrital (crystalline lattice) form as would be expected in an ore body. The higher values in the 20-24 km region may indicate the adsorption of anthropogenically
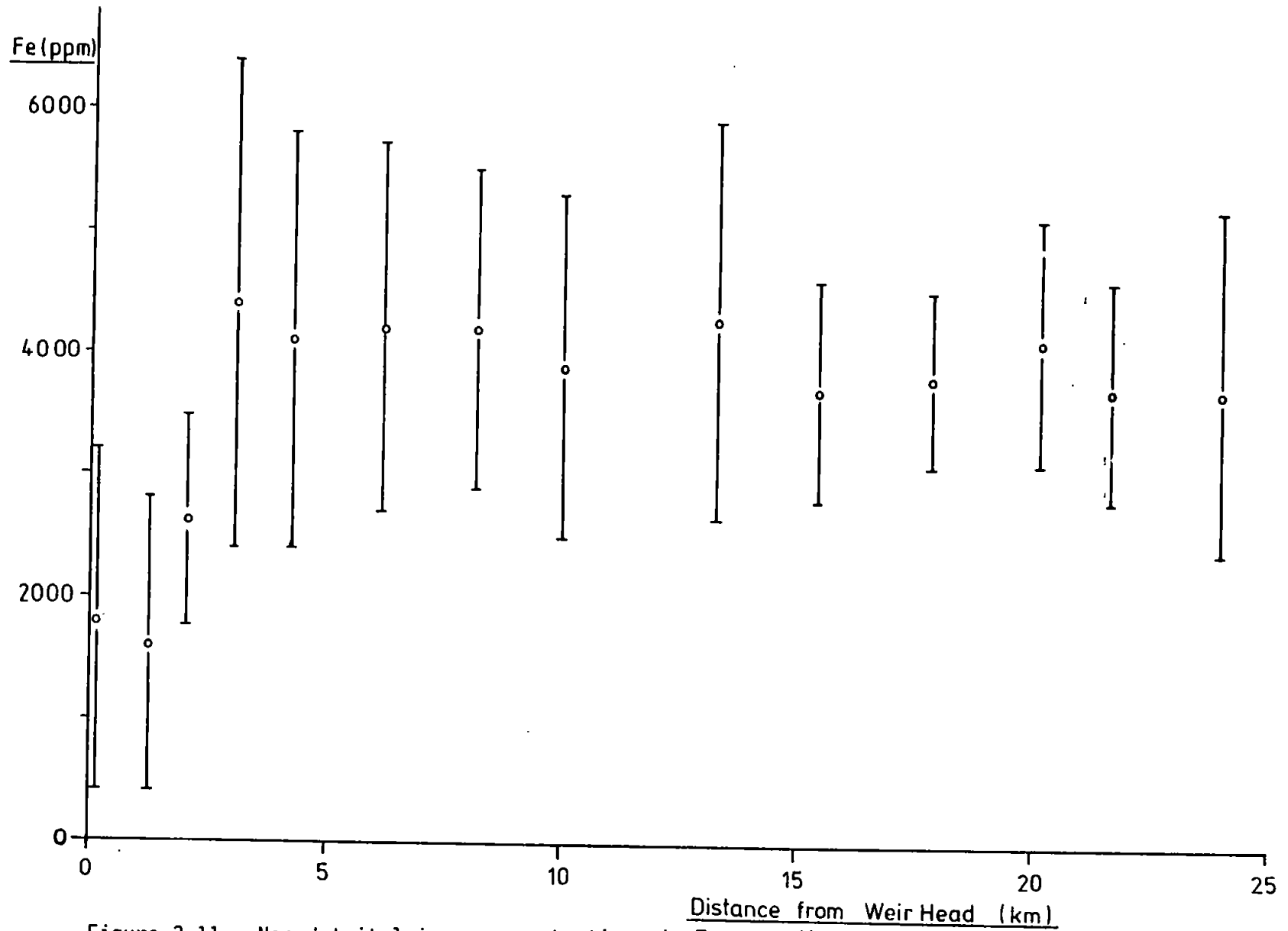
Figure 3.11   Non-detrital iron concentrations in Tamar sediments
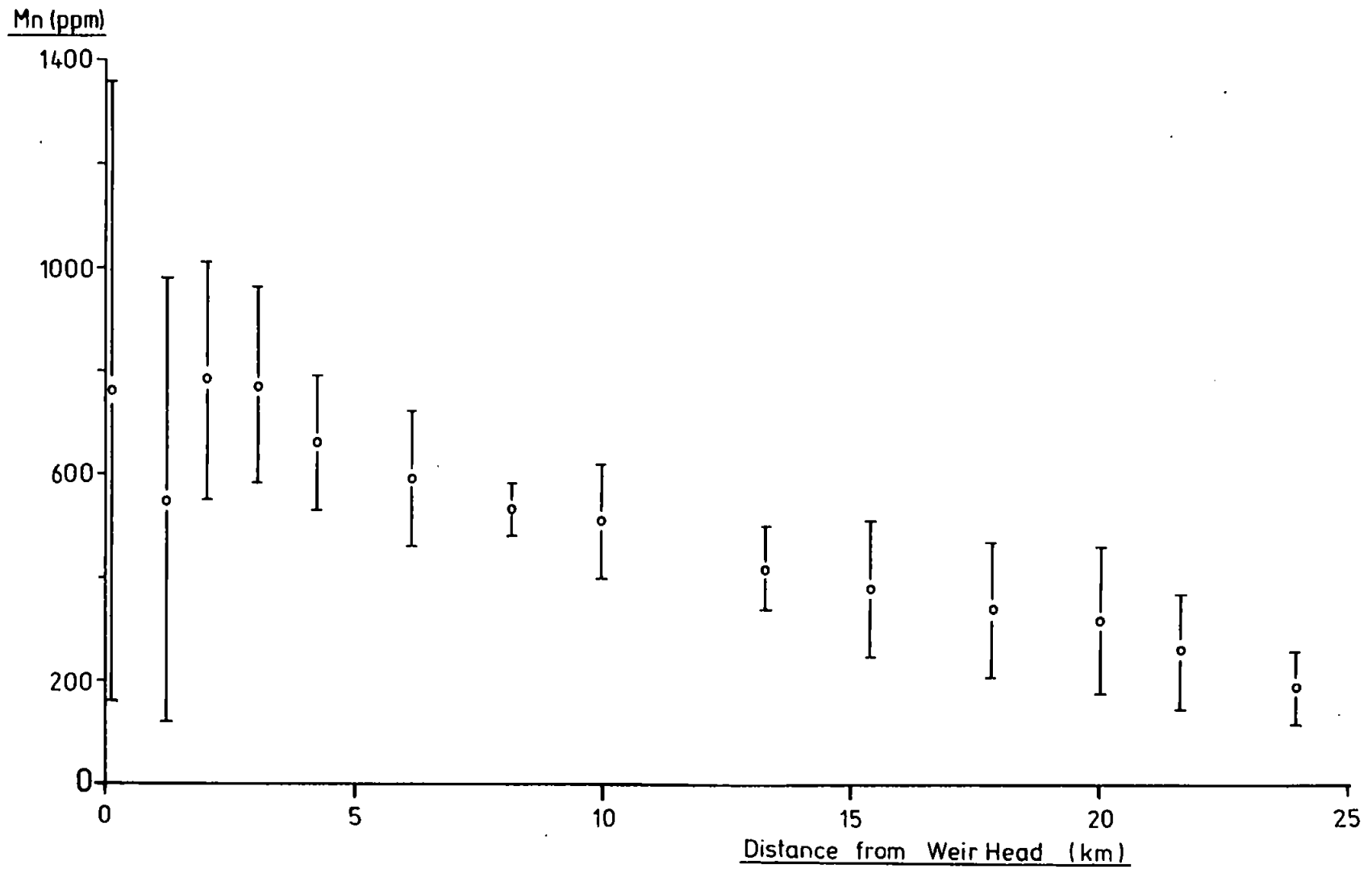
Figure 3.12   Non-detrital manganese concentrations in Tamar sediments
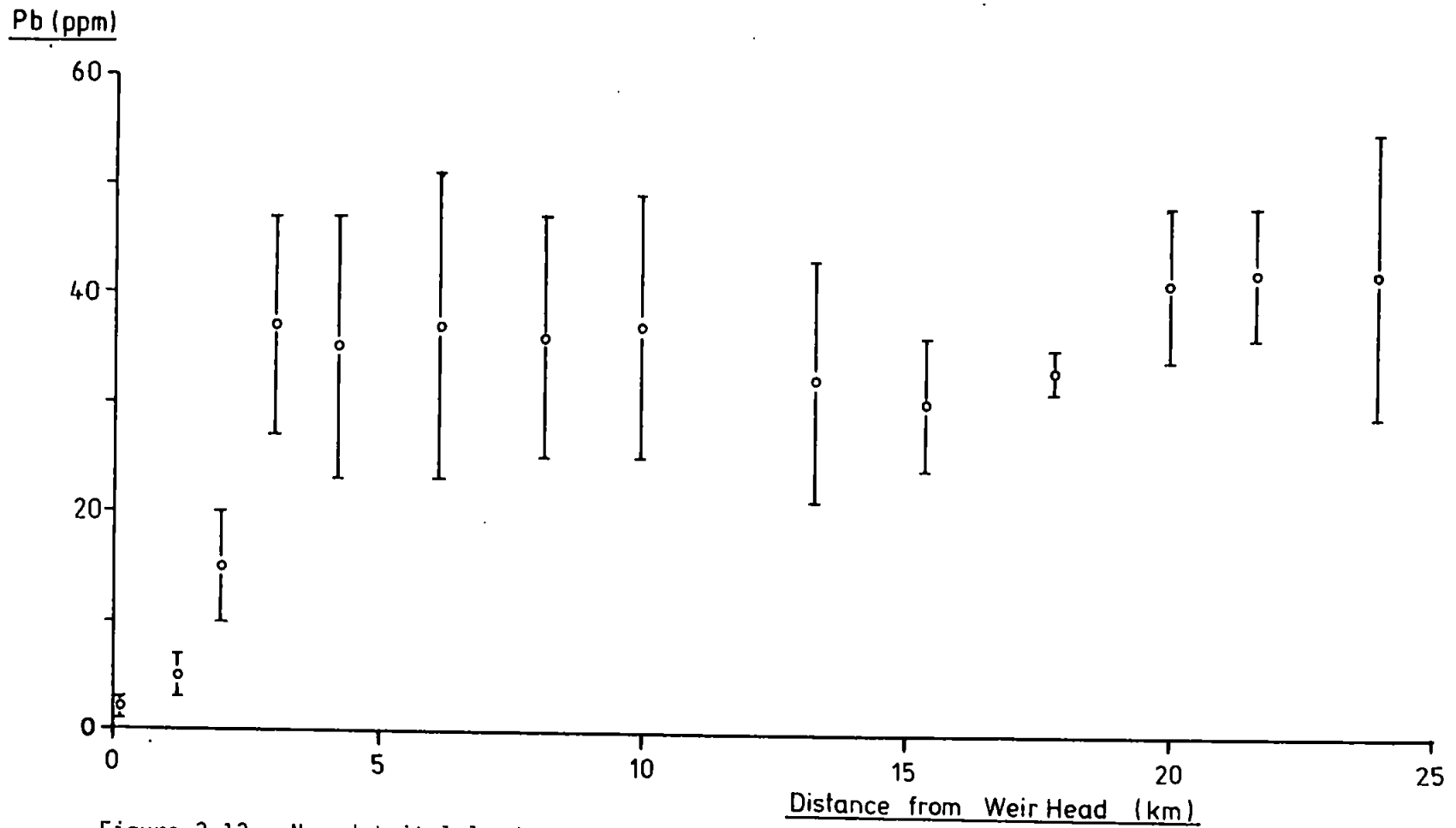
Figure 3.13   Non-detrital lead concentrations in Tamar sediments

introduced lead onto the estuarine sedimentary particles.

The zinc profile (Figure 3.14) showed the presence of a possible mid-estuarine maximum, not co-incident with the mine spoils region. This interesting feature may suggest the sedimentation of zinc-rich particles in this region, representing an input to the sediment from other estuarine phases. The C.V.s vary from 77% at the weir to 20% in the mid-estuarine region with higher values of about 30% in the marine end-member.

3.1.3   Sediment Data Analysis

The initial reduction of the data consisted of simple regression plots to establish any relationship between iron and the other heavy metals. The graphical comparisons were made by plotting the metal concentration against the corresponding iron value, as shown in Figure 3.15 which depicts the manganese-iron relationship for two summer and one winter survey. The plot shows that there are two distinct populations of data, one for the summer and one for the winter. This was the first evidence which suggested some seasonality in the sediment composition. However, whilst Figure 3.15 shows a clear difference, this was not the case for all the metal-iron plots. From this empirical regression study, full correlation matrices were calculated (Figure 3.16 shows a flow diagram of the calculation procedure) and examples are given in Tables 3.4 and 3.5. Matrices for each individual survey are contained in Appendix I.

Following this correlation analysis, it was acknowledged that problems had arisen associated with the data in its present form. Some of the
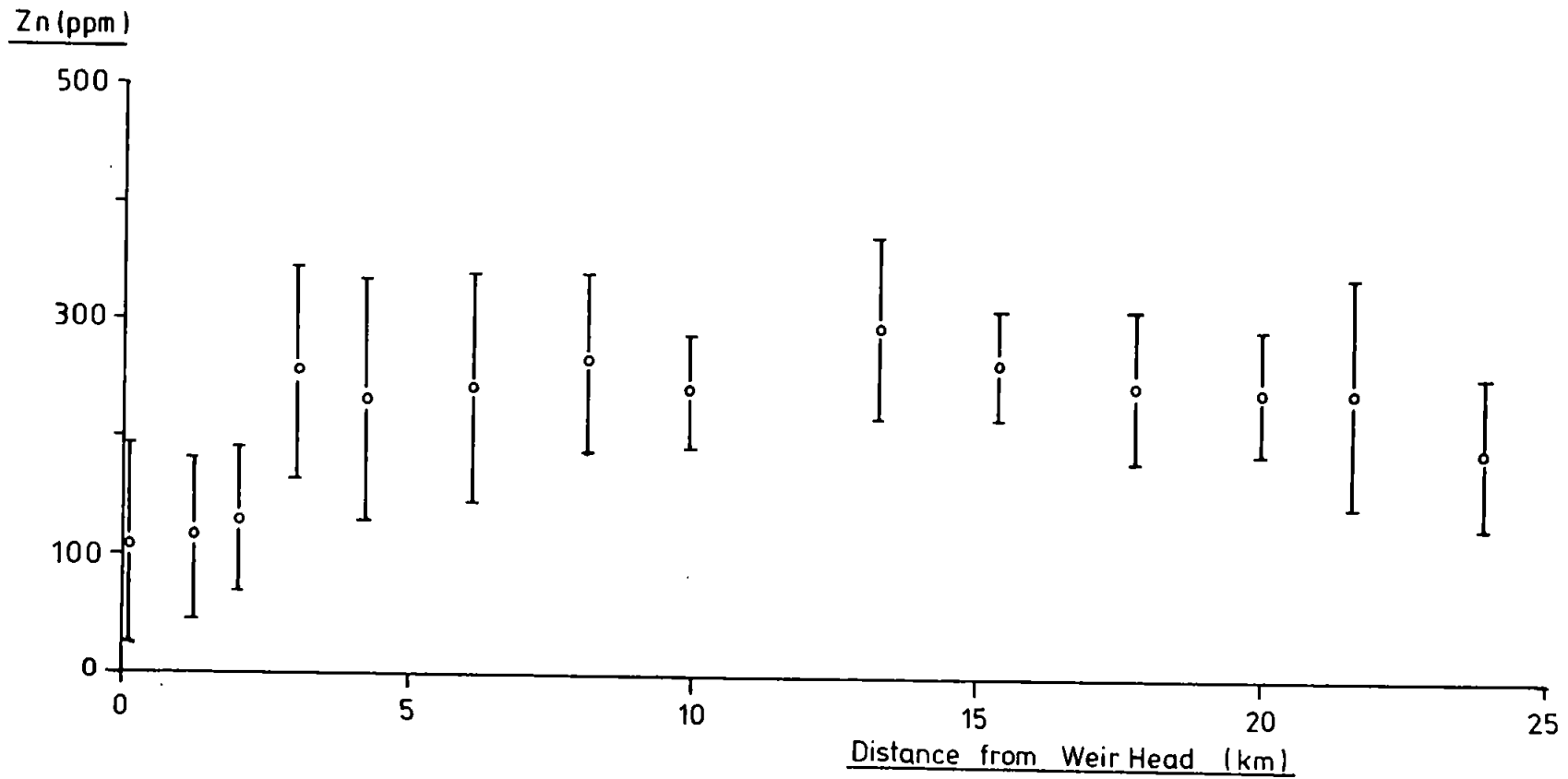
Figure 3.14   Non-detrital zinc concentrations in Tamar sediments .
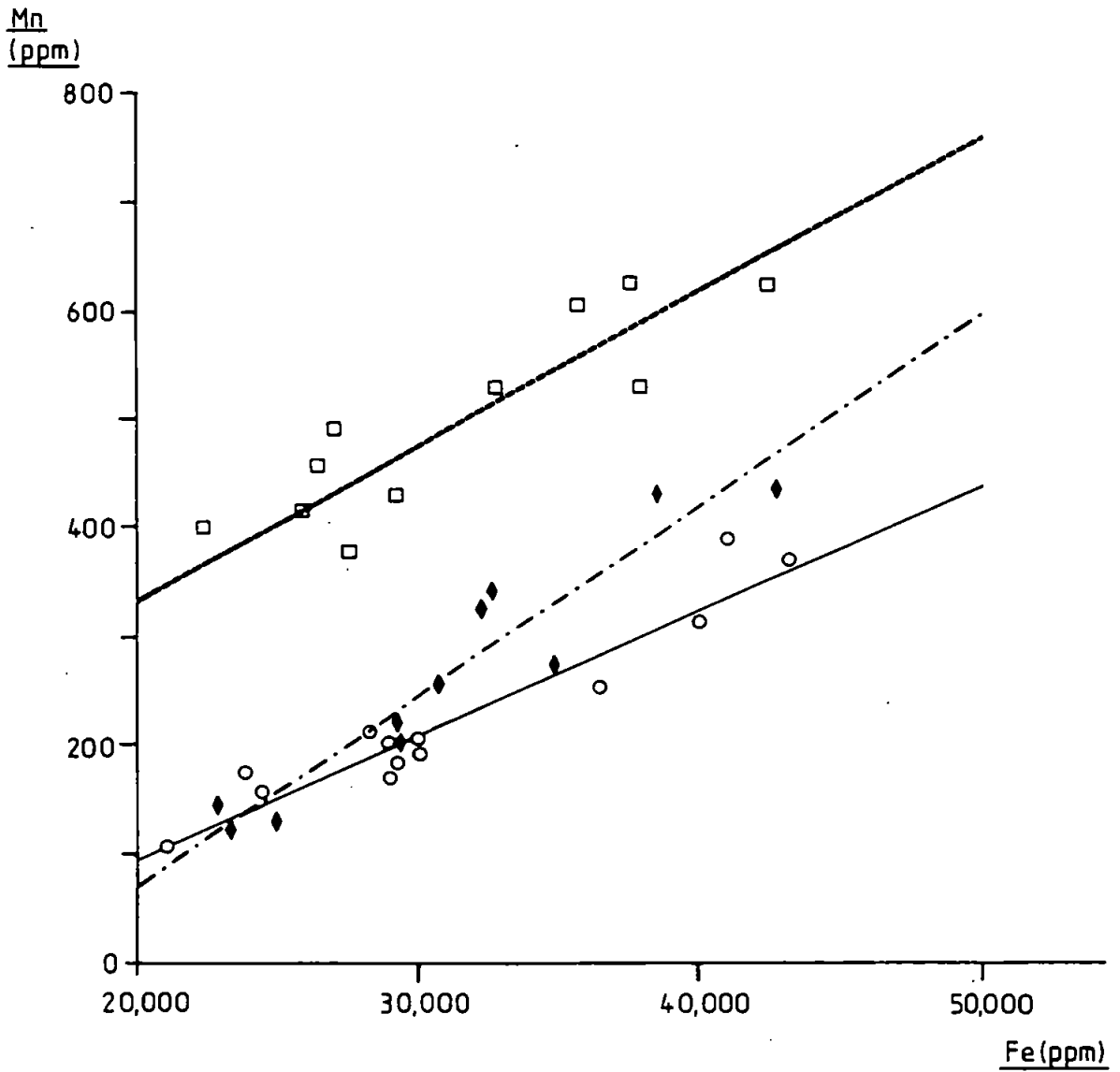
Figure 3.15 A preliminary study of manganese-iron relationships
showing apparent seasonality

□ - Survey for 04/02/81 (winter);
♦ - Survey for 17/06/81 (summer) and
○ - Survey for 26/08/80 (summer)

correlations produced were unexpected and possibly accidental, thus giving a distorted picture of inter-relationships in the matrix. For example, correlations between iron, manganese, copper and zinc could be expected to be significant but this was not the case in Tables 3.4 and 3.5. Having re-examined the axial profile for grain-size (Figure 3.9), it was decided to normalise the metal data to 100% fine (< 63 μm) grain-size. By normalising the data, the bias created by the variation in grain-size was eliminated (see Table 3.6 and 3.7) and thus the correlations obtained from this data would be more indicative of possible estuarine processes (De Groot, et al., 1976).

Conspicuous differences were observed between normalised and non-normalised correlation coefficients, particularly for manganese-iron, copper-iron and zinc-iron (for example compare the data in Table 3.4 with Table 3.6). Using the correlations from the normalised data it can be seen (Tables 3.6 and 3.7) that the relationships between almost all the metals are positive and significant at the 99% level. The correlation coefficients for lead are generally less than the 99% confidence level which may indicate a source of lead different to the other metals, as had been suggested earlier (Section 3.1.2.c). Interestingly, the metal-T.O.C. relationships are seasonally dependent with the correlation coefficients being significant at the 99% level in the summer, but not significant in the winter.

Due to the interdependence of the correlation coefficients, a test of statistical significance was necessary. This was achieved using a rank order correlation method (Figure 3.16). Initially, the normalised data was processed through the Pearson (Kendall and Stuart, 1961) correlation programme to produce a 'core' matrix. The correlation

89

STATISTICAL ANALYSIS

"TOTAL" METAL DATA   "NON-DETRITAL" METAL DATA

RAMDOMISED —————— CORRELATION ANALYSIS

DATA

PRODUCES CORRELATION COEFFICIENTS
AND SCATTER PLOTS.

RANK ORDER ANALYSIS

ORDERS THE CORRELATION
COEFFICIENTS

PRODUCES PLOTS.

PLUS 20 RANDOMISED PLOTS.
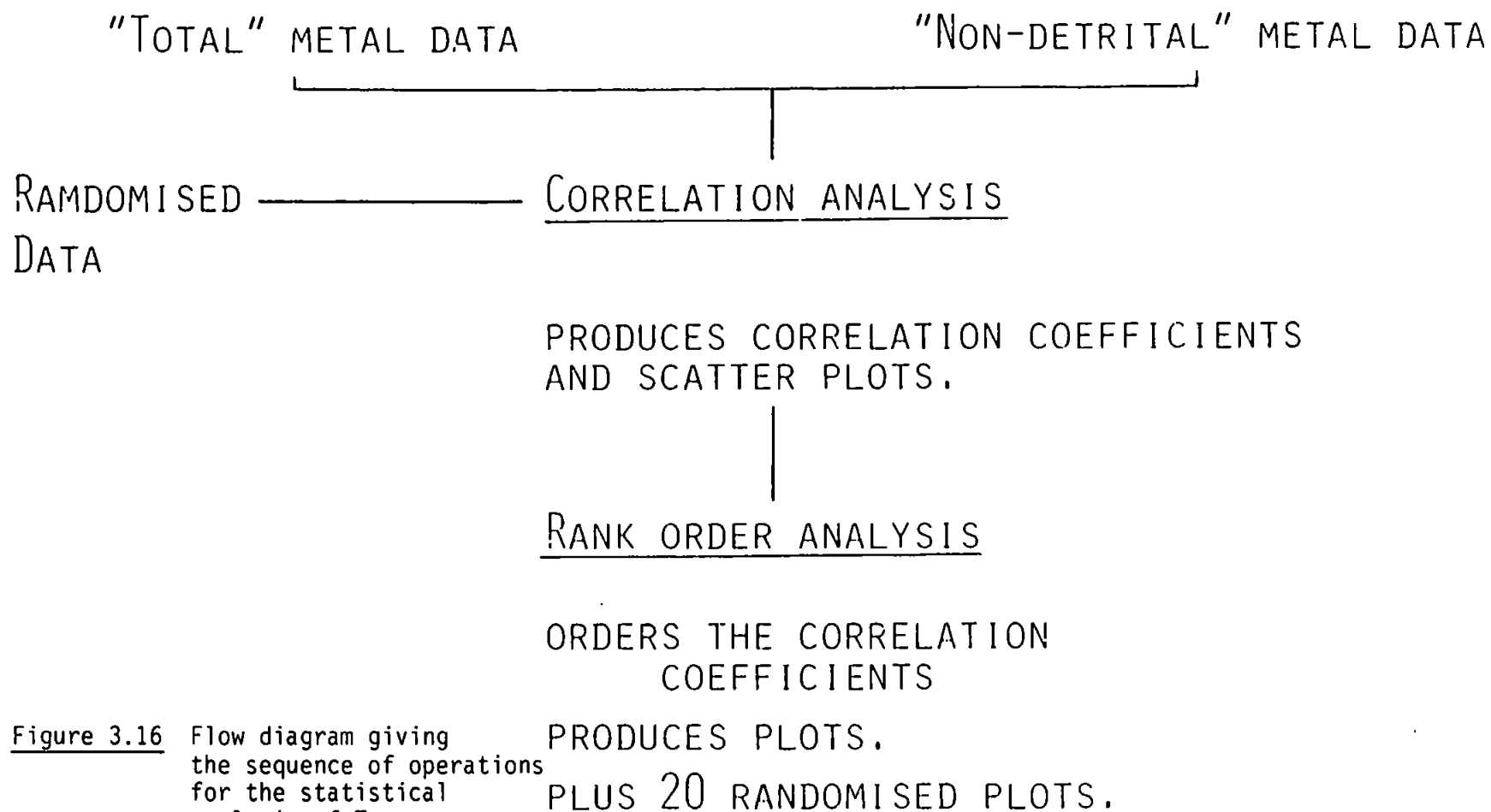
Figure 3.16 Flow diagram giving
the sequence of operations
for the statistical
analysis of Tamar
sediment results

Table 3.4 Correlation Matrix for 22/07/80
Hydrofluoric Acid Digestions

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Cd	Grain Size
Cu	-0.58							
Fe	0.28	0.58						
Zn	-0.54	0.98	0.61					
Pb	-0.78	0.93	0.34	0.90				
T.O.C.	-0.45	0.83	0.53	0.79	0.75			
Cd	-0.28	0.73	0.59	0.81	0.59	0.50		
Grain Size	-0.64	0.89	0.41	0.90	0.95	0.61	0.63	
Dist.	-0.71	0.05	-0.64	0.02	0.38	-0.08	0.27	0.36

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Table 3.5 Correlation Matrix for 04/02/81
Hydrofluoric Acid Digestions

	Mn	Cu	Fe	Zn	T.O.C.	Grain Size
Cu	-0.23					
Fe	0.69	-0.01				
Zn	-0.37	0.49	0.13			
T.O.C.	-0.69	0.32	-0.26	0.86		
Grain Size	-0.68	0.14	-0.23	0.82	0.96	
Dist.	-0.70	-0.43	-0.65	-0.10	0.34	0.45

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Table 3.6 Correlation Matrix for 22/07/80
Hydrofluoric Acid Digestions : Normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Cd
Cu	0.65						
Fe	0.93	0.87					
Zn	0.83	0.95	0.97				
Pb	0.13	0.81	0.48	0.63			
T.O.C.	0.78	0.96	0.95	0.98	0.71		
Cd	0.84	0.81	0.92	0.93	0.42	0.86	
Dist.	-0.61	-0.47	-0.53	-0.50	-0.00	-0.42	-0.61

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Table 3.7 Correlation Matrix for 04/02/81
Hydrofluoric Acid Digestions : Normalised

	Mn	Cu	Fe	Zn	T.O.C.
Cu	0.71				
Fe	0.98	0.80			
Zn	0.94	0.89	0.98		
T.O.C.	-0.36	0.07	-0.34	-0.18	
Dist.	-0.62	-0.54	-0.61	-0.66	-0.12

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

coefficients were then calculated and plotted graphically in ascending numerical order, most negative first and most positive last, against the total number of coefficients. The second phase of the method was to randomise the raw data matrix which consisted of columns of metal and T.O.C. concentrations as a function of site. The data in each column was reordered in a random way and the correlation programme was then re-run. The correlation coefficients from the randomised data were then plotted on the rank order graph. The random ordering process was carried out between 15 and 20 times and this method was adopted for each of the nine surveys for the normalised, total metal data.

Figure 3.17.a shows the rank order graph for the survey data of 22/07/80. The solid lines represent the correlation coefficients from twenty simulations in which the data set for 22/07/80 was randomised. It was observed that high correlations of up to r = 0.80 could still be obtained using the randomised data. The random profile would be symmetrical about the zero line if an infinite number of simulations were undertaken. The broken line represents the plot resulting from the matrix containing the real data. Since this line does not lie within the random plots, it demonstrates the existence of a significant number of non-random correlations in the data.

It was found that a summer profile (Figure 3.17.a) was different from a winter profile (Figure 3.17.b). The summer profile showed the real data was significantly removed from the random plots, in contrast the winter plot showed a greater proportion of real data to be much less removed from the random plots. The general transition from an ordered situation to a more random regime was observed as a progression
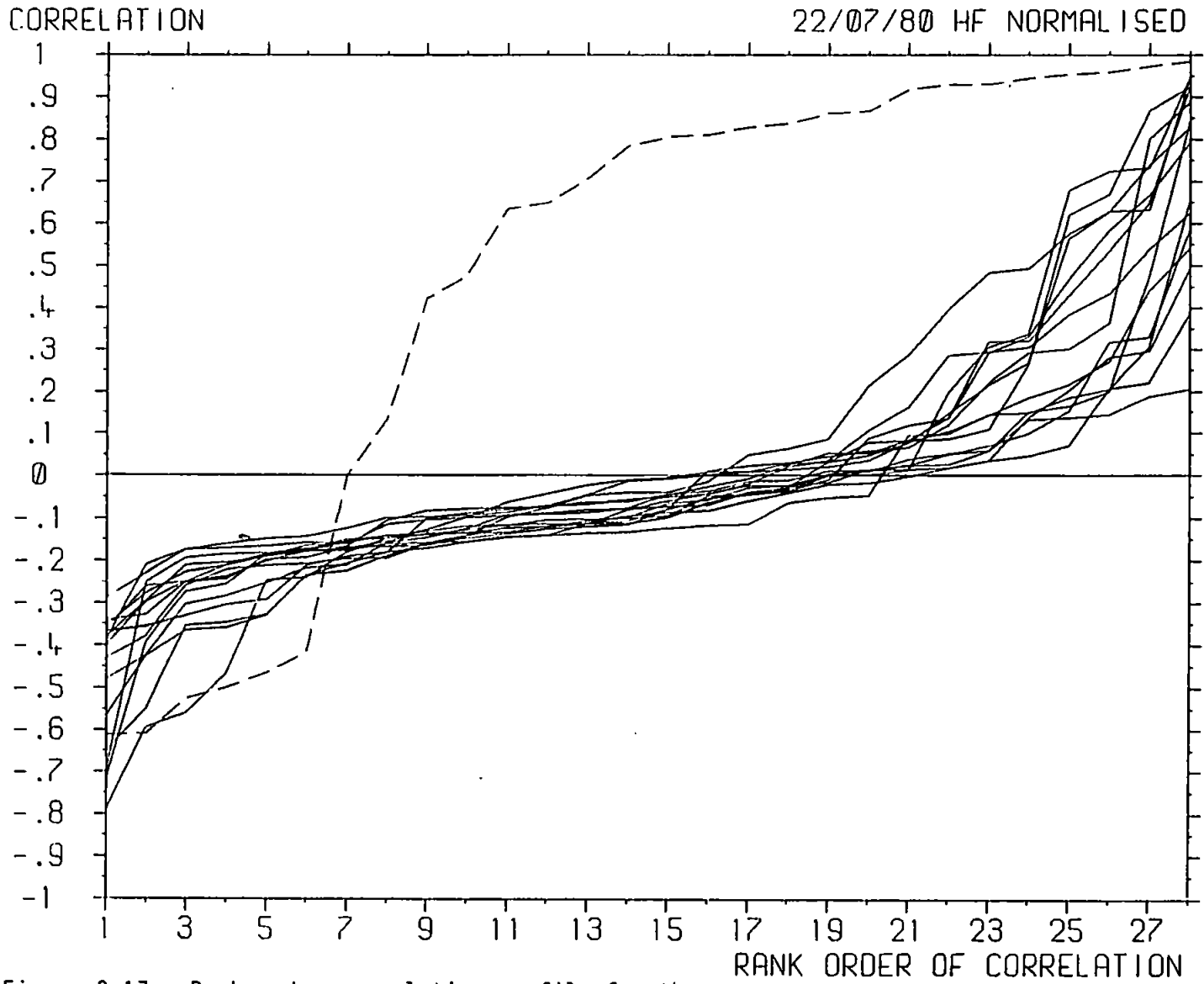
Figure 3.17a Rank order correlation profile for the
summer 1980, the real data is represented by the broken line
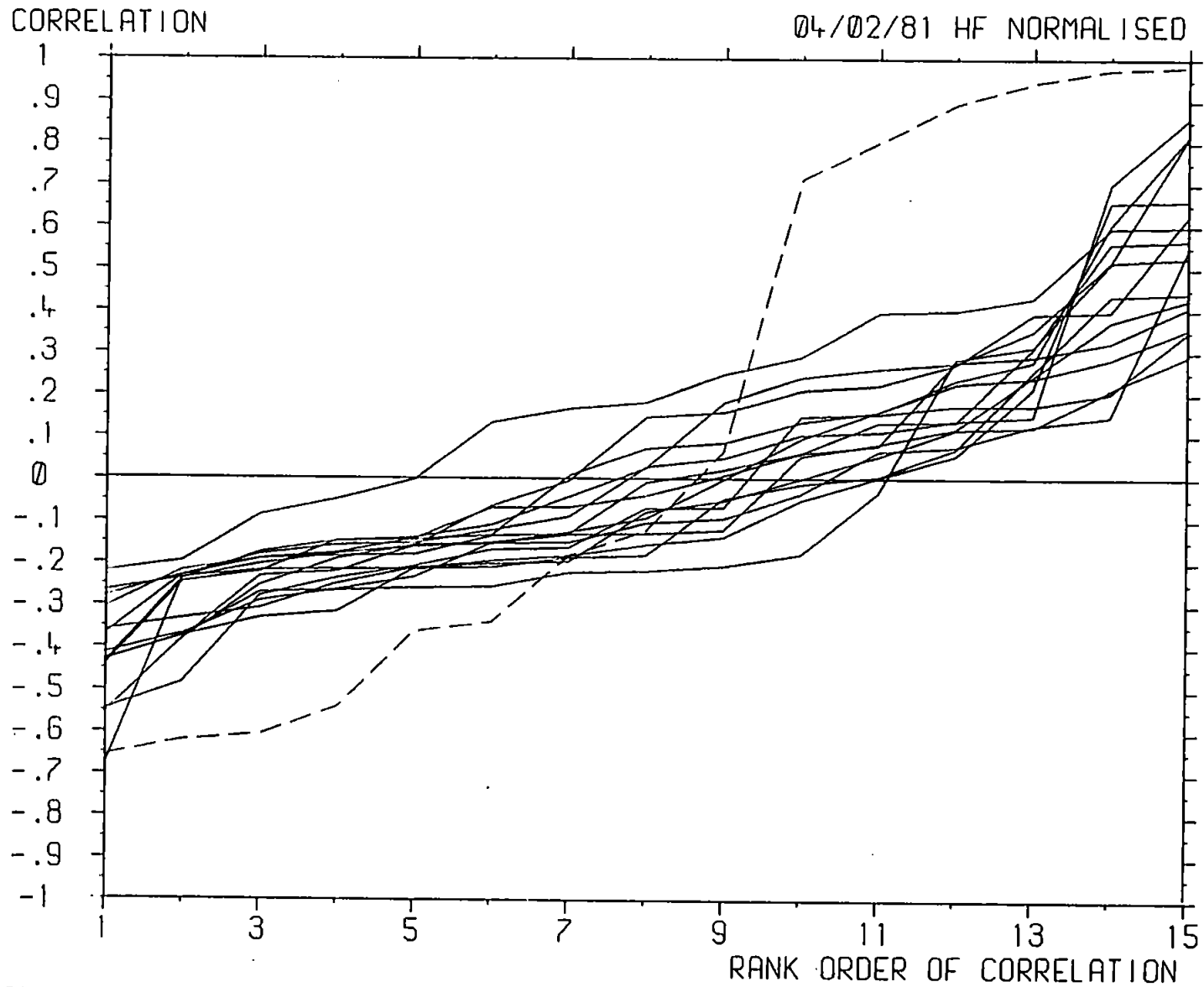
Figure 3.17b Rank order correlation profile for early
spring 1981, the real data is represented by the broken line

from summer to winter, where Figure 3.17.c shows the intermediate condition. The broken line (real data) was observed to approach the random 'envelope' of simulations in winter months, but become significantly removed in moving from winter to summer. By analysing the data in this manner, further evidence of seasonal variation in the metal-metal and metal-controlling variable relationships was established.

In order to rationalise this seasonal variation, a closer examination of the variables within the estuary, i.e. physico-chemical and possible biological processes, was undertaken. All the metals showed strong correlations with T.O.C. in the summer surveys. The variation may therefore be as a result of a biologically induced phenomenon caused possibly by seasonality in production or input. A more readily identifiable physical affector would be the variation in river flow. Seasonality induced by variation in precipitation and run-off produced extremes of high river flow in winter and low river flows in summer. As a consequence, high energy re-suspension and mixing of the estuarine sediment would occur in winter, whereas in summer with low flow rates and low energy re-suspension, a more quiescent sedimentary environment would prevail. The sediment would thus lie undisturbed and allow metal partitioning to occur, according to local conditions, between the various estuarine fractions. This process would persist in certain regions of the estuary until the initial spate conditions in autumn would disrupt any localised sites and restore a measure of homogeneity to the estuarine sediment.

Identical statistical analyses (using the method outlined in Figure 3.16) were carried out on the data from the acetic acid digestions
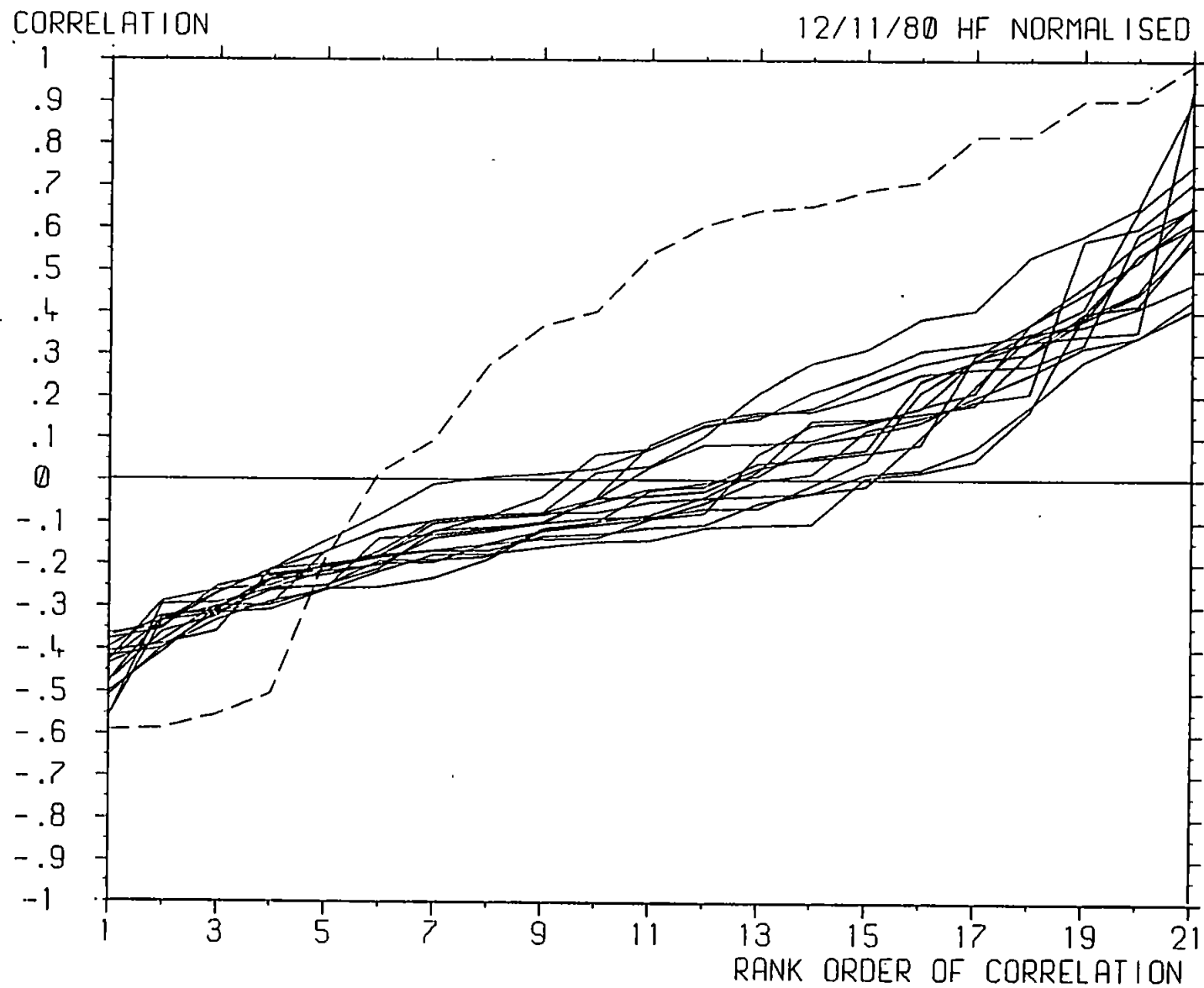
Figure 3.17c Rank order correlation profile for an intermediate position in
winter 1980, the real data is represented by the broken line

and correlation matrices were compiled. Table 3.8 gives the data for 22/07/80 and Table 3.9 the data for 04/02/81. No distinctive patterns in the correlations were observed for this data as is shown by the manganese values for summer and winter. Thus, the data was normalised to 100%, < 63 µm and the correlation programme re-run; the data is shown in Tables 3.10 and 3.11. The improvement in the metal inter-relationships was not as great as for the HF digests. It is particularly noticeable that the metal-T.O.C. relationships are not seasonally dependent and lead seems to behave independently of the other metals. To investigate the seasonality aspect further, the normalised data sets were used to create a rank order correlation plot and 20 random plots of the same data. Figures 3.18a and 3.18b show the rank order plots for a summer and winter profile and there is no strong indication of seasonal differences. As a consequence of the absence of definite seasonal changes in the acetic acid soluble fraction, changes must be occurring in the detrital (lattice-held) fraction of the sediment. The particulate surface chemistry must have remained relatively constant throughout the year, thus accounting for the lack of seasonality in the metal-metal correlations. The variability in total metal levels, therefore, must be primarily due to changes in the geological composition of the inputs, i.e. an influx of new material into the estuarine system.

Table 3.8 Correlation Matrix for 22/07/80
Acetic Acid Digestions

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Cd	Grain Size
Cu	-0.54							
Fe	-0.33	0.83						
Zn	-0.55	0.98	0.87					
Pb	-0.70	0.94	0.82	0.92				
T.O.C.	-0.27	0.77	0.76	0.78	0.68			
Cd	-0.19	0.73	0.62	0.74	0.64	0.52		
Grain Size	-0.57	0.93	0.86	0.92	0.94	0.61	0.67	
Dist.	-0.83	0.20	0.16	0.23	0.42	-0.08	-0.23	0.36

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Table 3.9 Correlation Matrix for 04/02/81
Acetic Acid Digestions

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Grain Size
Cu	0.78						
Fe	0.43	0.68					
Zn	0.11	0.36	0.88				
Pb	0.04	0.36	0.87	0.89			
T.O.C.	0.25	0.44	0.93	0.92	0.89		
Grain Size	0.16	0.30	0.87	0.91	0.89	0.96	
Dist.	-0.49	-0.38	0.23	0.50	0.62	0.42	0.52

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Table 3.10   Correlation Matrix for 22/07/80
Acetic Acid Digestions: Normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Cd
Cu	0.13						
Fe	0.91	0.39					
Zn	0.65	0.77	0.86				
Pb	-0.78	0.46	-0.52	-0.12			
T.O.C.	0.85	0.55	0.97	0.93	-0.39		
Cd	0.86	0.32	0.87	0.78	-0.55	0.85	
Dist.	-0.63	-0.16	-0.45	-0.34	0.50	-0.42	-0.62

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Table 3.11   Correlation Matrix for 04/02/81
Acetic Acid Digestions: Normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.
Cu	0.80					
Fe	0.45	0.82				
Zn	-0.35	0.12	0.51			
Pb	-0.28	0.27	0.62	0.74		
T.O.C.	0.30	0.58	0.86	0.46	0.52	
Dist.	-0.73	-0.56	-0.26	0.36	0.49	-0.12

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence
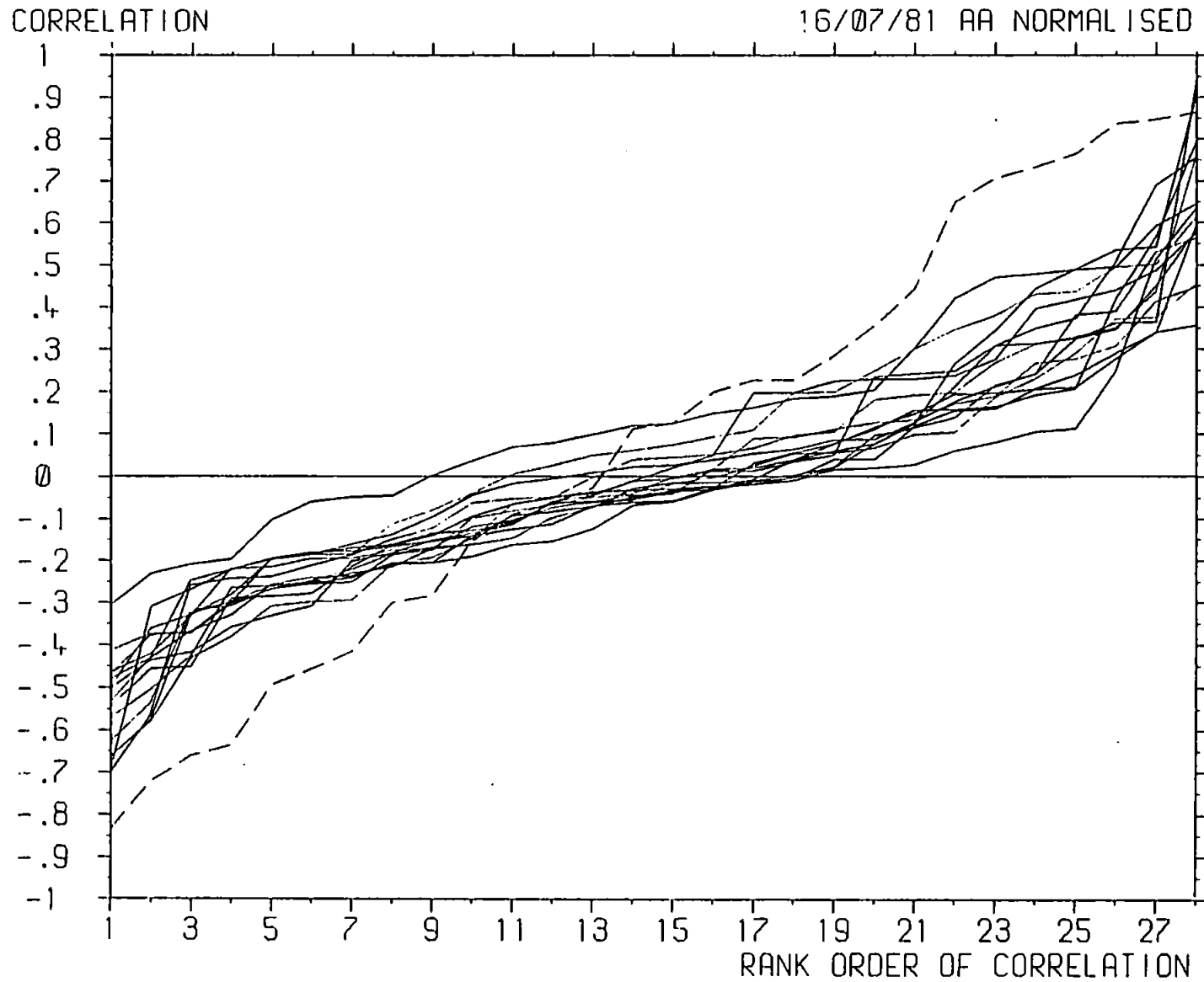
Figure 3.18a   Rank order correlation profile for the
summer 1981, the real data is represented by the broken line
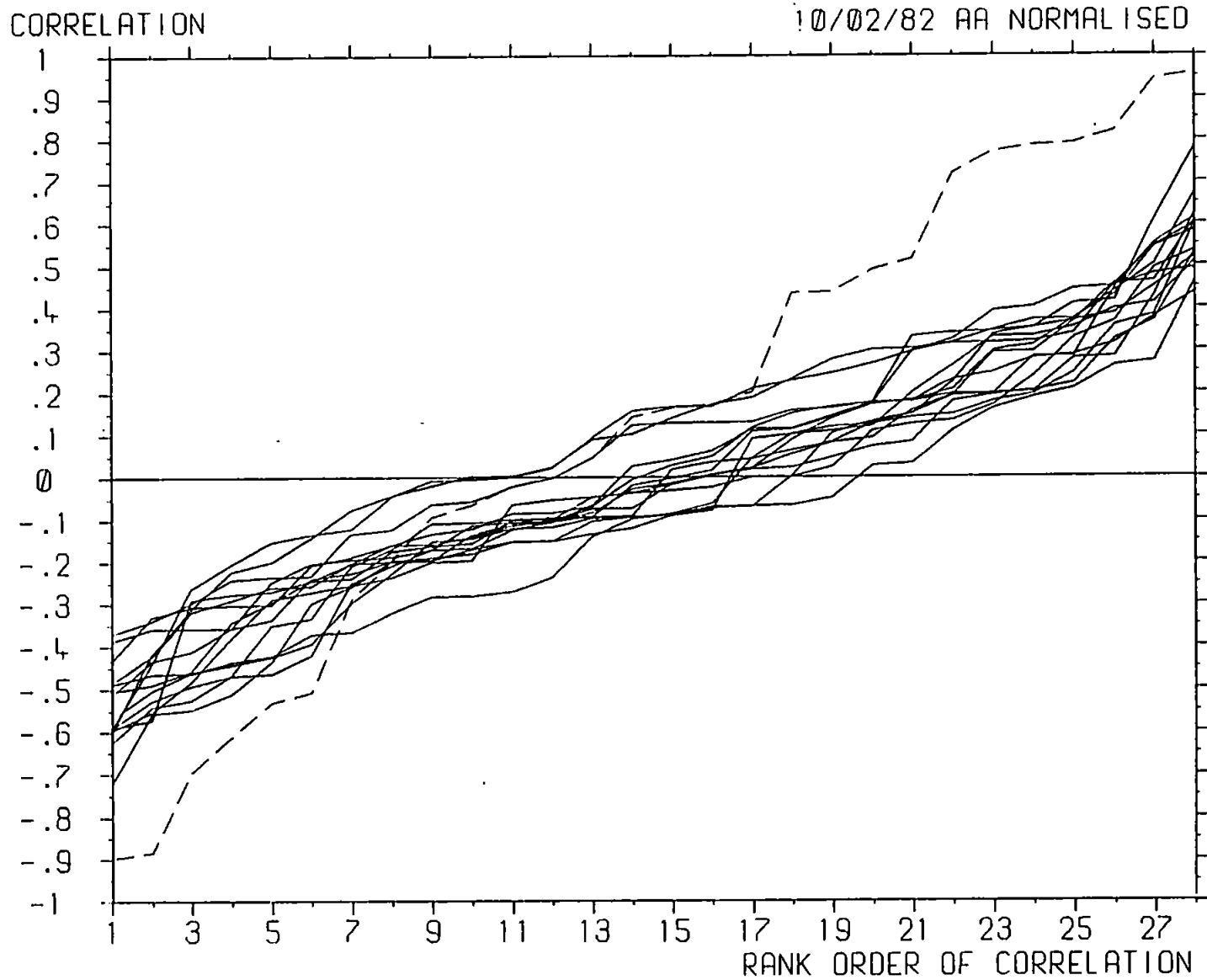
Figure 3.18b   Rank order correlation profile for the
              winter 1982, the real data is represented by the broken line

3.1.4   Time Series Analysis of Estuarine Sediment Data

Having established that a degree of seasonal variation was present,
this phenomenon was further investigated. The initial investigation
was to study the variation in grain-size as a function of time and
distance down the estuary (Figure 3.19). The diagram shows that
in periods of low river flow, a greater percentage of the fine-grained
material (<   63 μm) was found at the head of the estuary, for example
during 26/08/80 and 16/07/81. Under these conditions the sediment
composition in the lower estuary was coarser-grained in nature.
During the high river flows of 01/04/81, the upper estuary was com-
posed of mainly coarse-grained material, whereas the mid and lower
estuarine regions had relatively high levels of fine-grained material.
From this empirical analysis, it would appear that mass transport of
sediment was occurring upestuary in summer (low river flow) and
downestuary in winter (high river flow) to account for this variation
in grain-size. It would appear that the mass transport was mainly
associated with the fine material (<   63 μm).

This hypothesis was further substantiated by a seasonal study of actual
sediment elevations at various fixed stations throughout the estuary
(Bale, et al., 1983, unpublished data). This study ascertained that
an annual accretion/erosion cycle was prevalent in the estuary.

The tidal curve for the mid-estuarine region of the Tamar is
asymmetrical (George, 1975), with a long ebb period and short, high
energy flood, thus the flood period is characterised by high upestuary
current velocities which would move suspended sediment up the estuary.
Some of the suspended material would be deposited at slack water and
would only be partially re-mobilised by the weaker ebb currents, a

River Tamar Sediment Analysis

Grain Size Variation
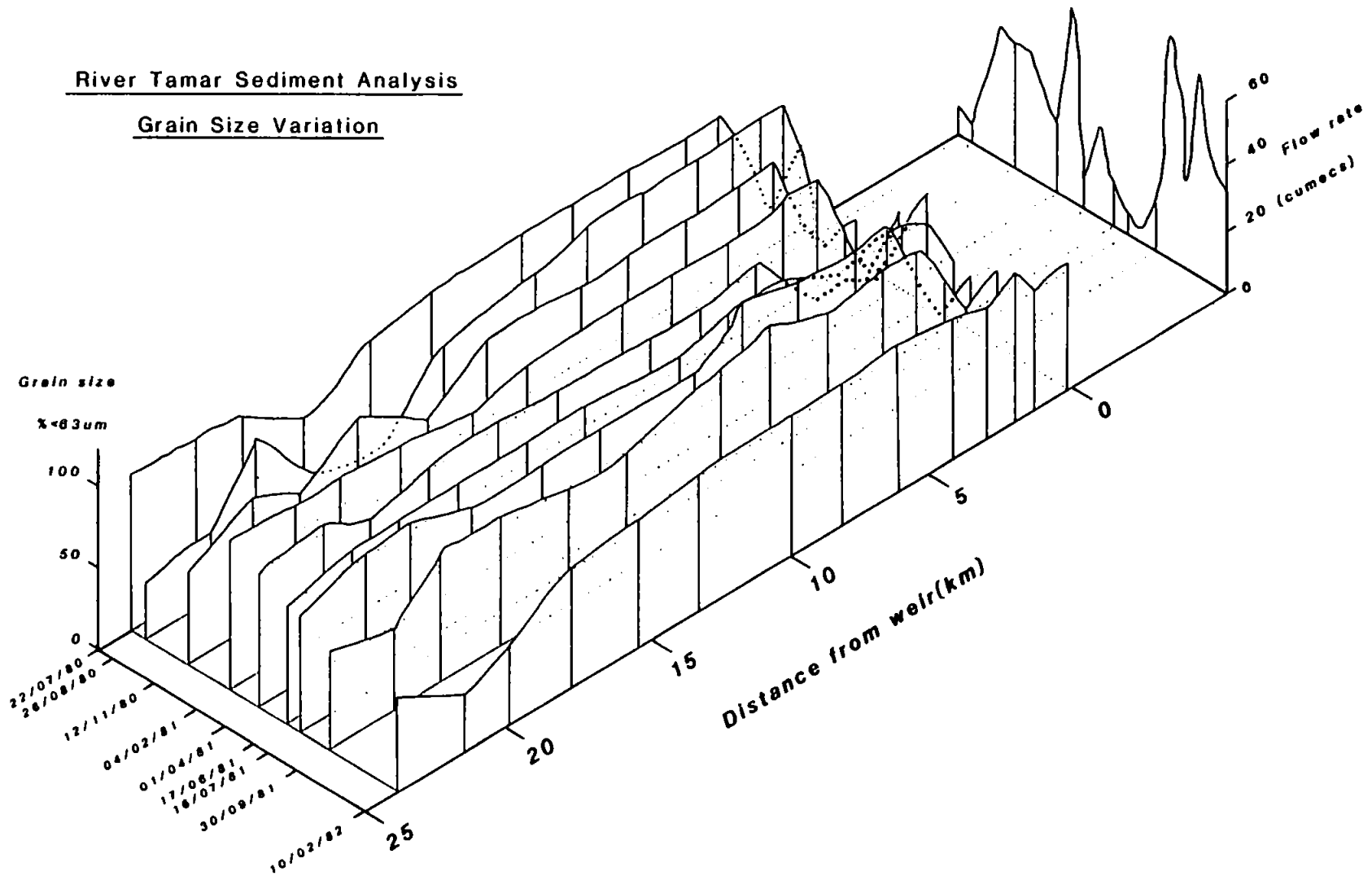
Figure 3.19   A 3-dimensional representation of the grain size composition
of the sediments in the Tamar Estuary

process known as tidal pumping. This mechanism would account for the accretion of sediment and also the increased percentage of fine material at the head of the estuary during low riverflow. At the end of the summer period, the quantity of erodable material would therefore be high. This mechanism of sediment transport has been observed in other estuaries (Allen, et al., 1980). During high riverflows, in winter, the converse would be true. The highest tidal velocities would occur on the ebb current, consequently tidal pumping through re-suspension would move sediment downestuary. This would account for the net loss of sediment at the head of the estuary and also the decrease in the percentage of fine material in this region. At neap tide, the tidal asymmetry is not so pronounced, so major transport would only occur during spring tides (Uncles, 1983, personal communication).

The Tamar Estuary was divided into 14 segments in such a manner that each sample site was approximately central in each segment (Figure 3.20). The area of each segment was calculated in km² and the depth of re-suspendable sediment, taken as 1 cm, was used to calculate the volume of mobile sediment in each segment. Using the normalised metal concentration and an average sediment density of 2.65 g cm^{-3}, the mass of metal in each segment could be calculated and thus the metal content per unit volume of sediment in kg m^{-3}. Employing this standard measurement, the variation in metal concentration as a function of time and distance down the estuary was plotted as a 3-dimensional diagram. Also included on these diagrams were the mean monthly riverflows (m^3 s^{-1}), for each survey date to emphasise the seasonal variability in the estuary.
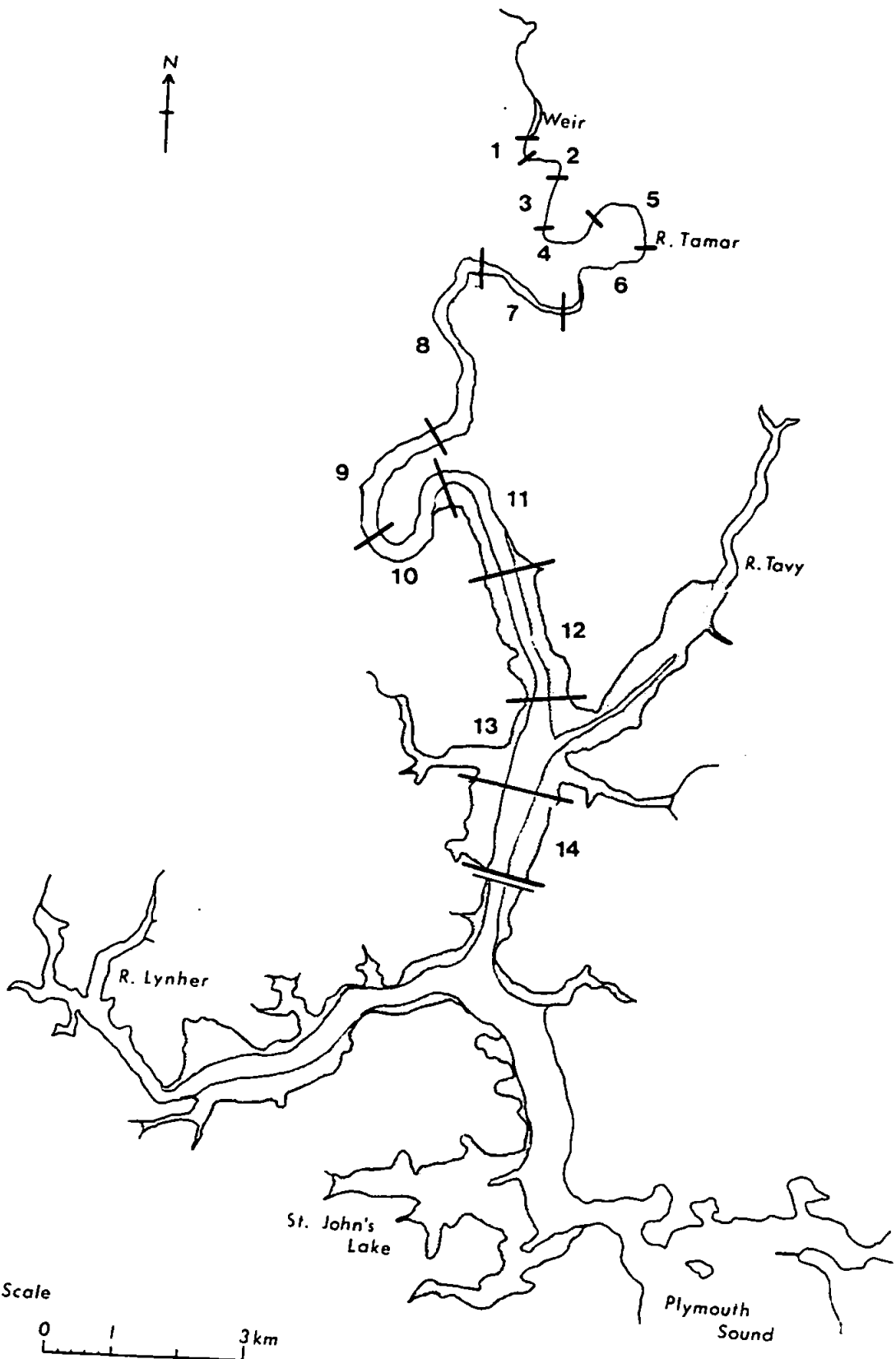
Figure 3.20   The Tamar Estuary divided into fourteen segments to
               determine total metal levels in each segment

106

3.1.4.a Copper

Figure 3.21 shows the variation of copper in the sediments as a function of time and distance along the estuary. There is evidence of copper inputs at the head and a general decrease in the total copper down the estuary. The segments in the 0-5 km region are subject to inputs of copper from the mine spoil tips at the sides of the estuary and it appears that the high river flow rates of the winter 1980/81 gave inputs of new copper-containing material into the upper segments. When the flow rates decreased the external supply decreased and metal levels fell accordingly. However, it is noted that during the low river flows experienced in summer of 1981 there was some accumulation of copper in the upper region which could be ascribed to the tidally induced upestuary movement of fine material. Following this the copper content decreased in this region as run-off increased and the metal-rich fines were moved downestuary. Conditions in the lower estuary appeared to complement processes at the head of the estuary. Under low flow conditions, there was a reduction in metal levels in the lower estuary, possibly due to the migration of the metal-rich fine sediment upestuary. Conversely, the copper levels in the lower segments were observed to increase slightly during the high river flows of winter 1981/82, possibly indicating the downestuary movement of copper-rich sediment.

3.1.4.b Iron

Figure 3.22 indicated a high degree of reactivity of the metal in the estuary. Iron may be more indicative of the physical, rather

Figure 3.21   A 3-dimensional representation of total copper content in the surficial sediment of each segment in the Tamar Estuary

Figure 3.22   A 3-dimensional representation of total iron content in the
surficial sediment of each segment in the Tamar Estuary

than chemical, processes affecting the estuarine sediment, as only 5-15% was found to be available to possible estuarine chemical changes. The estuary appeared to react as three distinct regions; upper (0-5 km), mid (5-15 km) and lower (15-24 km).

In the upper region, inputs were observed to be co-incident with increased run-off in the winter 1980/81. Iron levels were higher overall in this region when compared with the other two. In spring 1981, the metal levels decreased as the flow rate decreased, indicating that fresh inputs into the system emanated from a riverine source. A secondary input in summer 1981 was associated with low flow conditions, possibly indicative of the iron-rich sediment moving upestuary due to tidal pumping. The iron levels decreased with increasing river flow in winter 1981/82.

The mid-estuarine region was apparently fairly unreactive, it exhibited no pronounced addition or removal processes and appeared to be a transitional region between the two more reactive zones.

The lower estuary showed several interesting features; iron concentrations decreased from a peak in summer 1980 to a low in winter 1980/81. This was contrary to expectations, as an increase should have been observed in this region as iron-rich material was moved down the estuary due to high river flow. This low level of iron was maintained during the summer 1981, due to net movement upestuary of the sediment, therefore there was no supply of new material to the lower region. As run-off increased during winter 1981/82, iron levels increased in the lower region again. This

apparent bi-annual cycle may be due to intermittent reactivity in the region of possible sediment divergence at approximately 15 km. At this point, due to the shape of the estuary, tidal asymmetry becomes very pronounced so that sediment movement below this point is almost always seawards, whereas upestuary the movement can reverse depending on the prevailing river flow conditions previously discussed. One other possibility was that during the winter 1980/81, high flow conditions could have moved the iron-rich sediment into the mouth of the estuary, which has not been investigated in the scope of this study. Combined with high run-off from the river Tavy, this lower region may have been temporarily scoured of the metal-rich, fine-grained sediment.

3.1.4.c Manganese

The overall impression from Figure 3.23 was of inputs at the head of the estuary and a large decrease in manganese levels over the 0-5 km range. This was in good agreement with the axial profile (Figure 3.5). The uppermost two segments reacted differently in response to changes in river run-off. The first segment appeared to accumulate riverine inputs of manganese-rich particulates under both high and low flow conditions of summer and winter 1980/81. During low flow conditions of summer 1981, a secondary input was noted. This may again have been a result of the accretion of manganese-rich sediment in the upper estuary due to tidal pumping. This feature was recognisable in all the top four segments, the predominantly freshwater region.

The mid and lower-estuarine regions were relatively low in manganese
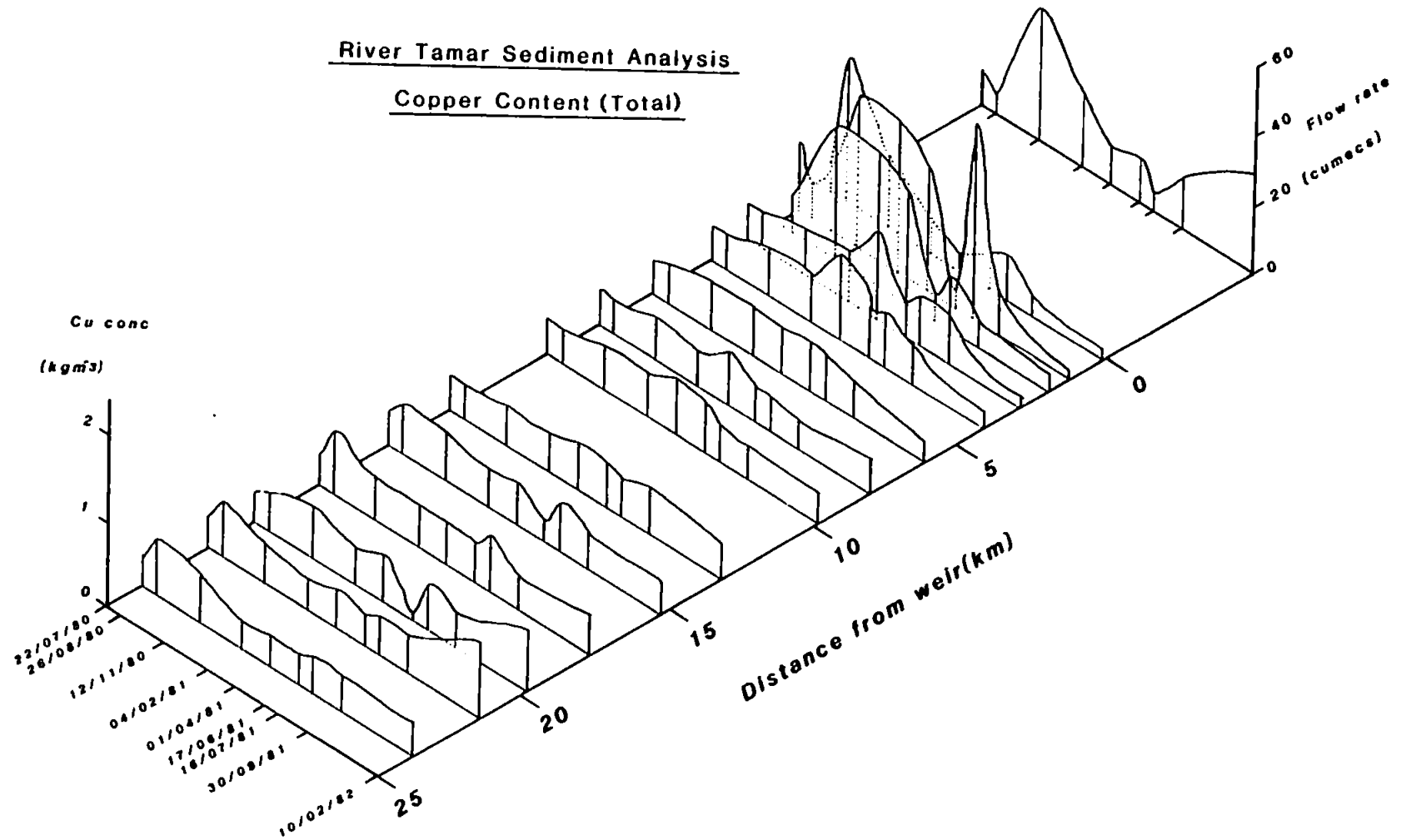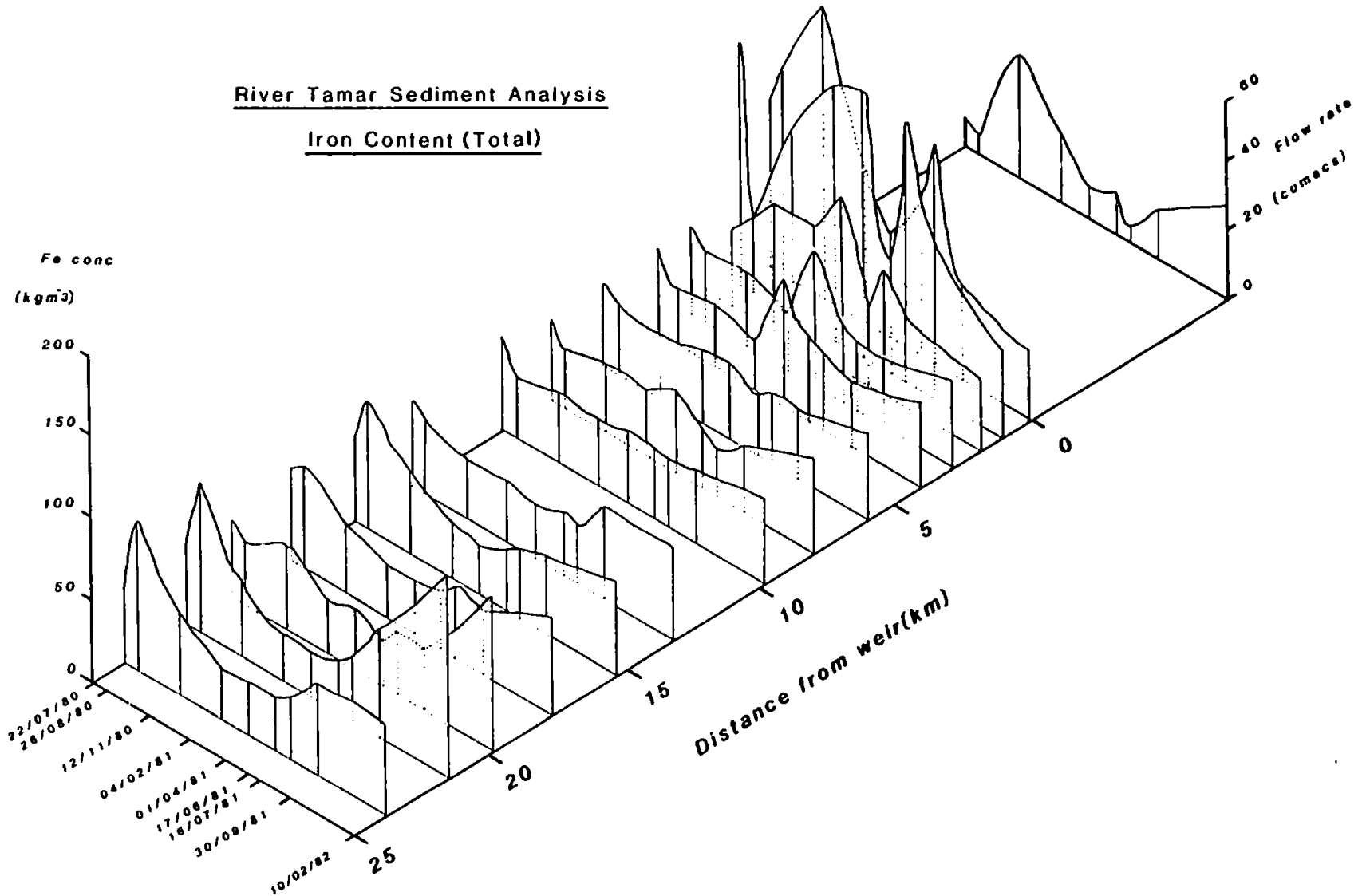
111

River Tamar Sediment Analysis

Manganese Content (Total)
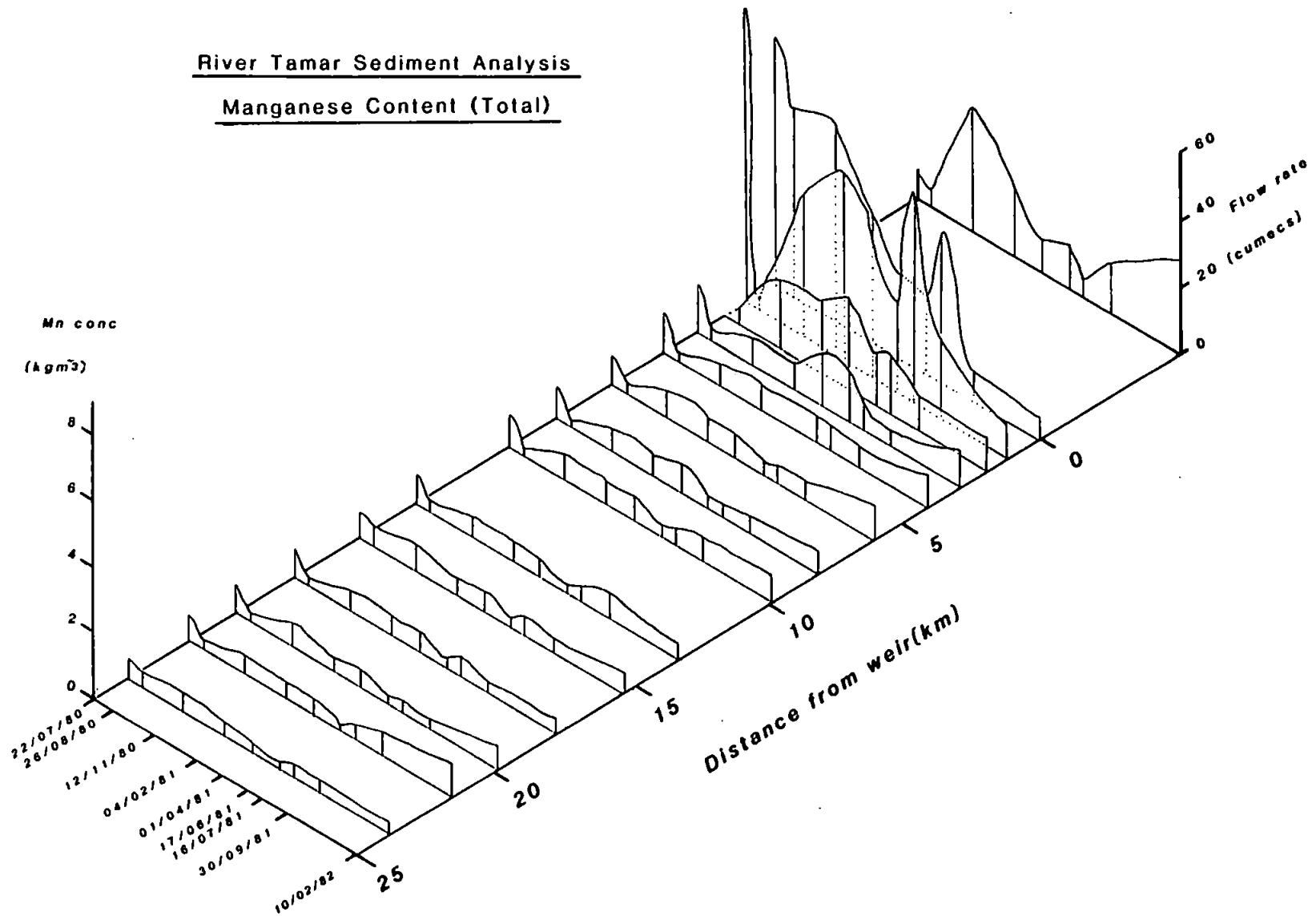
Figure 3.23 A 3-dimensional representation of total manganese content in the surficial sediment of each segment in the Tamar Estuary

levels. As the metal-rich sediment was re-mobilised by high winter flow conditions, manganese would be removed to the dissolved and particulate phases through the F.B.I. and thus removed from the general sedimentary reactions. Although the changes in the lower estuary were small, the reactivity was generally in agreement with the erosion/accretion cycle observed for the other metals.

3.1.4.d Zinc

In many respects, the behaviour of zinc (see Figure 3.24) was similar to that of iron. Three regions of varying reactivity were apparent, though not as distinct as in the case of iron. The upper region was characterised by zinc peaks in winter 1980/81 associated with the input of new zinc-rich material into the estuary under high flow conditions. As the flow rate decreased, the rate of input decreased and thus zinc levels in the sediment declined accordingly. A secondary peak was apparent, probably associated with zinc-rich sediment moving upestuary due to tidal pumping under the low river-flow conditions in summer 1981. This metal-rich reservoir was then dispersed downestuary as the flow rate increased in winter 1981/82. Small scale variation in zinc levels was a characteristic of the lower estuary. This may have been due to perturbations induced by the Tavy Estuary which may have produced subsidiary inputs into the lower Tamar.

River Tamar Sediment Analysis
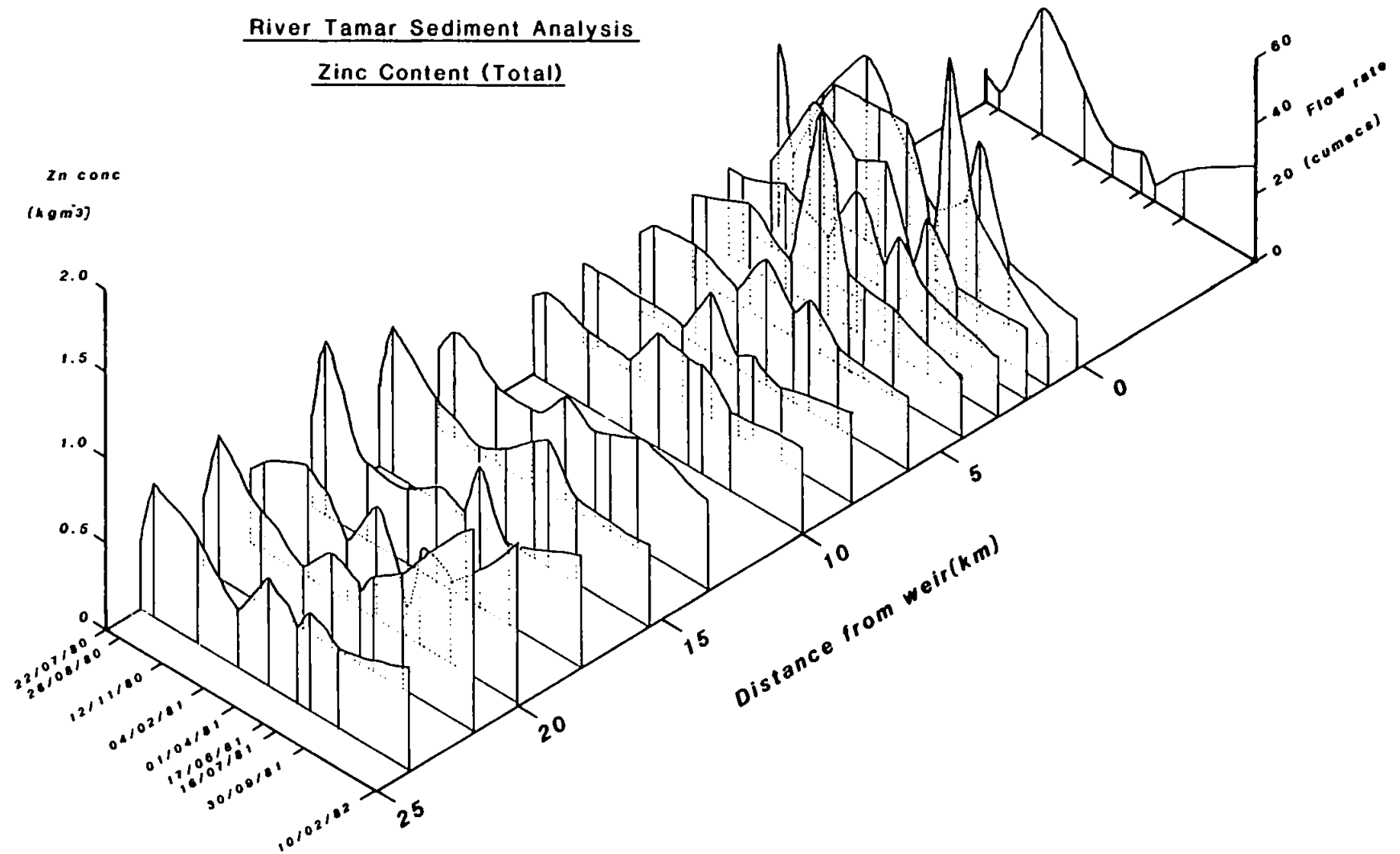
Zinc Content (Total)

Figure 3.24   A 3-dimensional representation of total zinc content in the
surficial sediment of each segment in the Tamar Estuary

3.1.5   Summary of Sediment Data

The large amount of information contained in this section may be
summarised as follows:-

(a) The HF digestions gave total metal analyses while the acetic acid
digestions gave reasonable estimates of the labile metals.

(b) The concentrations of heavy metals (non-normalised) in Tamar
sediments, summarised in Table 3.13 are significantly higher than
those obtained for contaminated coastal sediments from the North Sea
(Taylor, 1979) and those from Urr Water, which is considered to be an
unpolluted estuary. The results shown in Table 3.13 suggest that the
levels in the Tamar are influenced by inputs from a metalliferous
catchment area, although the contamination is not as acute as in the
case of Restronguet Creek (Aston, et al., 1975). Plots of sediment
metal concentration versus distance downestuary showed evidence of
estuarine geochemistry for Fe and Mn, both of which showed large
seasonal variations in river input. In other cases the metal-chemical
behaviour was complicated by anthropogenic inputs in the mine spoils
region of the upper estuary (Cu, Fe, Pb, Zn) and the more industrialised
lower estuary (Cd, Hg, Pb).

(c) A statistical analysis of the total metals showed that there were
seasonal differences in the chemical composition of the sediments.
These were thought to be linked to the tidal cycles and the annual
variation in river-flow. Similar statistical tests carried out on the
acetic acid digest data showed no evidence of seasonality which
suggested that the compositional changes in the sediments were in the
detrital form, i.e. an input of new material from the land.

Location	Cu	Zn	Pb	Cd	Mn	Fe	Hg	T.O.C. %	Reference
Tamar[a] (range)	585-60	640-130	335-19	4.3-0.2	3820-120	51,000-21,000	1.6-0.1	2.3-16.5	This Work
Lynher	274	317	150	-	289	23,120	2.1	10.5	Bland, et al., (1982)
Plym	-	256	-	9.3	171	12,100	0.35	4.1	Langston,(1980) Millward & Herbert,(1981) Bryan & Hummerstone, (1973)
Urr Water[a]	6.9	41.2	21.5	0.9	333	-	0.07	-	Taylor,(1976)
Tees Bay	8.0	74.1	45.4	0.2	242	-	0.1	-	Taylor,(1979)
Restronguet Creek	1690	1540	684	3	1030	54,000	-	-	Aston, et al., (1975)
Conwy	34	900	205	-	1500	-	-	-	Elderfield et al., (1971)

[a]The range of values is for samples collected throughout the whole estuarine regime.

Table 3.13 Heavy Metal Distributions in Estuarine Sediments (ppm, dry weight) for This Study and Others

(d) The temporal trends in the concentrations of Cu, Fe, Mn and Zn were further examined using 3-dimensional plots of distance, time and metal concentration for Cu, Fe, Mn and Zn. These plots showed the combined effects of river-flow and tidal pumping on the sediment metal levels.

3.2   ESTUARINE DISSOLVED METALS

3.2.1   Analytical Precision and Significance

The estuarine dissolved metal study proved difficult to quantify due to
a lack of comparison with dissolved metal standards. The contamination
during sample collection was known to be at a low level from a
comparison of bucket and pumped samples obtained simultaneously. A
possible source of error in the examination of the environmental
behaviour of dissolved copper and zinc occurred when attempting to
manipulate large volume (10 l) water samples without using 'clean room'
facilities. Contamination was observed in one of the surveys (see
Figure 3.28) but this was due to contamination of the filtering flasks
prior to use during the survey. The delay in filtration of the large
water volumes would have allowed chemical/biological modification of
the samples. On some occasions, filtration took up to five hours to
complete, particularly in samples with a high suspended particulate
load. The filters were not acid washed, but sample-rinsed, thus
extraneous material could still leach out of the filters. It was
thought that this contribution was small in comparison to other
potential sources, i.e. particles emitted from the 'Millipore' pumps.

The laboratory manipulations and 'Chelex-100' extraction would also be
open to sources of contamination, even though all possible measures
were taken to prevent contamination occurring. 'Chelex-100' efficiency
was found to increase in the order Zn > Mn > Cu in riverwater and the
extraction efficiency for copper was noticeably higher in seawater than
riverwater. It is thought that this was due to the increased competition
for the inorganic ligands by magnesium and calcium, thus leaving a
greater proportion of the dissolved metal available for ion exchange.

The pH of the environmental samples was well within the range of optimum extraction (pH = 5.0-9.1) for 'Chelex-100' quoted by Riley and Taylor, (1968) but the extraction efficiencies obtained by this work were generally lower than those of Riley and Taylor, (1968). The C.V. for the resin exchange procedure was in the order of 10% (Morris, personal communication), the manganese determinations had C.V.s of $< 5\%$, with a slight increase over the estuarine salinity range. The overall blank for the method was thought to be no more than 10% of the measured value.

The solvent procedure, after the incorporation of a back-extraction step, showed improved sample stability and C.V.s for replicate analyses of $< 5\%$. The major problem associated with the technique was the lack of consistency in results over a series of surveys, which is a prerequisite of any modelling study. The technique used for the adsorption/desorption study can be qualified in the following ways; artificial levels of dissolved copper and zinc nitrate were added to natural waters, but only allowed to equilibrate for 10 minutes, thus some of the initial measurements were taken when the dissolved metal was not at equilibrium with the model solution. Adsorption onto the container walls (Batley and Gardener, 1977) and uptake by natural humic material (Mantoura, et al., 1978) would account for some of the dissolved metal loss in the experiments at zero turbidity. It was not possible to condition the reaction vessels as they were acid-washed before each experiment to reduce contamination. Leakage around the membrane filter in the 'Swinnex' filter attachments occasionally proved problematical, as this allowed particulate matter to contaminate samples.

119

3.2.2   Estuarine Dissolved Metal Data : Results

3.2.2.a   Axial Profiles of the Estuarine Master Variables and Dissolved Copper, Manganese and Zinc

Five axial surveys of estuarine master variables and dissolved metals were undertaken over a period of eight months, but in this section only the salient features of the data will be discussed. Many of the changes observed were due to biological effects together with changes primarily due to chemical and physical activity. The biological study however is not within the scope of this work.

An axial survey was taken in July, under low river-flow conditions ($9 \text{ m}^3 \text{ s}^{-1}$) and two days after neap tide. Figure 3.25 showed the master variables-distance data and Figure 3.26 the corresponding dissolved metal-distance data. The gradient of the salinity profile steepens markedly at the F.B.I., indicating that this was a very stable interface with little turbulent mixing and thus well stratified (see Figure 3.25). The turbidity maximum was ill-defined and showed no pronounced peak, this again would be indicative of reduced tidal mixing and thus little re-suspension of the bed material. The water column was supersaturated with respect to dissolved oxygen throughout the whole length of the estuary. This was indicative that high primary productivity was occurring in the surface water which was not hindered by high turbidities reducing light penetration of the water column. At 5°/oo salinity there appeared to be an enhanced region of supersaturation, possibly due to an isolated phytoplankton bloom. A slight oxygen minimum was observed at the F.B.I., this was probably associated with microbial reduction of organic-rich material which was trapped at the F.B.I. (Morris, et al., 1982c). The pH levels were as expected with high (pH = 8.2) readings in the marine end-member. A pH minimum at the F.B.I. was observed (pH = 7.5), again

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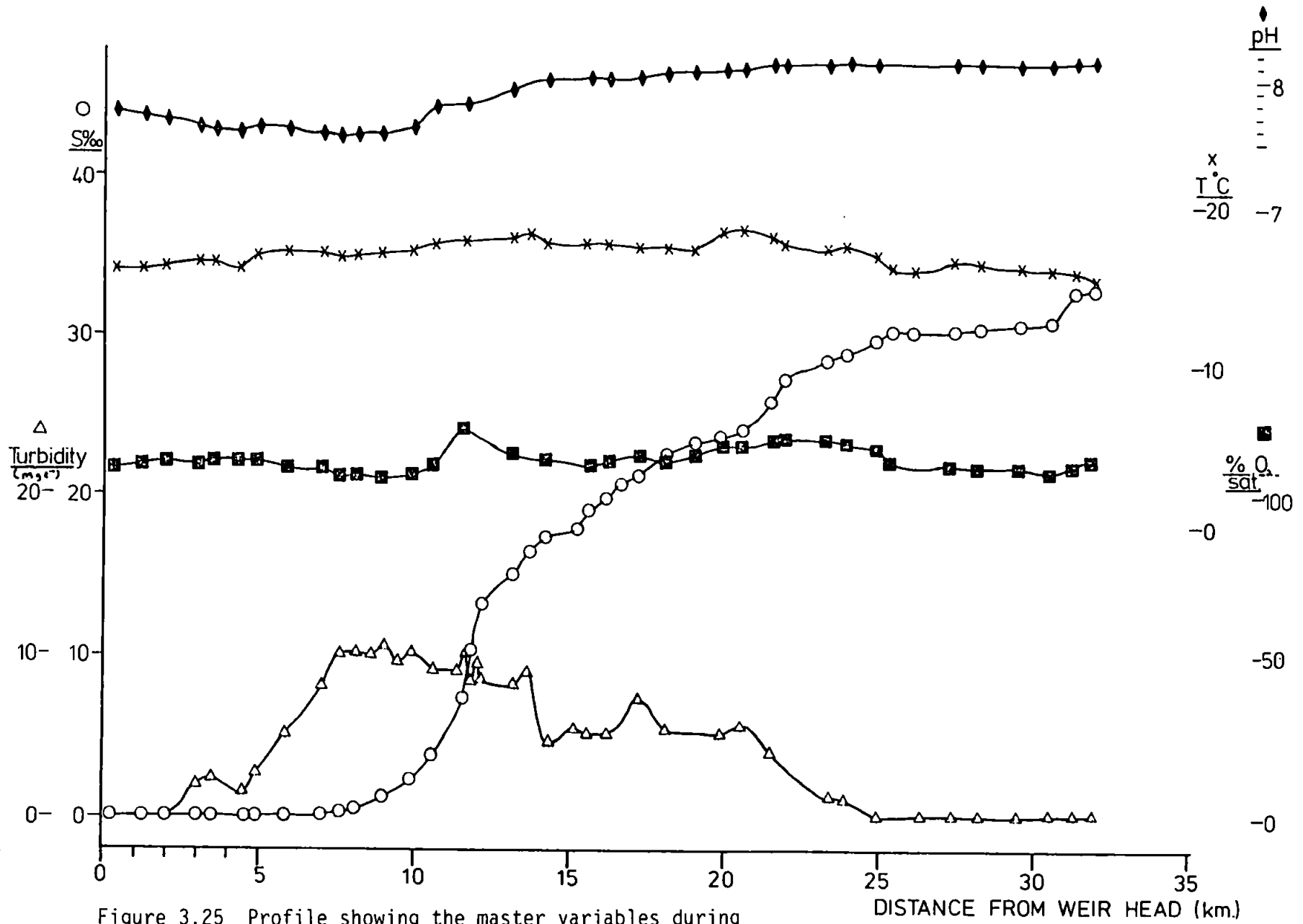
Figure 3.25   Profile showing the master variables during
an axial traverse of the Tamar Estuary, 24/07/80

Figure 3.26 Profile showing the dissolved metals during
an axial traverse of the Tamar Estuary, 24/07/80

122

probably due to biological activity. Riverine pH levels were slightly higher, pH = 7.8. The temperature profile exhibited a mid-estuarine maximum (18°C); the maximum was probably due to estuarine water moving over the shallow mud-flat regions previously exposed at low water and heated by solar radiation. As the incoming tide flooded onto the mud-flats, the water would be heated to an anomalously high temperature, thus producing this maximum.

Figure 3.26 shows the dissolved metal profiles for the same survey. The peaks in zinc and manganese profiles were concurrent with the position of the F.B.I. Upestuary of this point zinc exhibited a pronounced minimum, but with increased levels in the absolutely fresh riverwater. Manganese, however, showed low levels in the riverwater, but in all other respects followed the zinc profile. The behaviour of copper was conspicuously different to that of either manganese or zinc. Slight perturbations were observed at the F.B.I., but otherwise the profile indicated little reactivity.

This profile can be contrasted with Figure 3.27 which showed another summer profile in August, with low river-flow, but during a spring tidal regime. The F.B.I. had penetrated further upestuary to approximately 4 km from the weir, as opposed to 7 km in Figure 3.25. The spring tide, with its inherent higher flood current velocities, had created a turbidity maximum thirty times the magnitude of the previous survey. The turbidity maximum was landward of the F.B.I. which was the result of tidal pumping mechanisms and the momentum imparted to the fresh water by the flood tidal currents. In the previous survey, (Figure 3.25) the low turbidity maximum produced by the neap tide was probably the result of the weaker gravitational circulation, thus producing a lower suspended particulate load.

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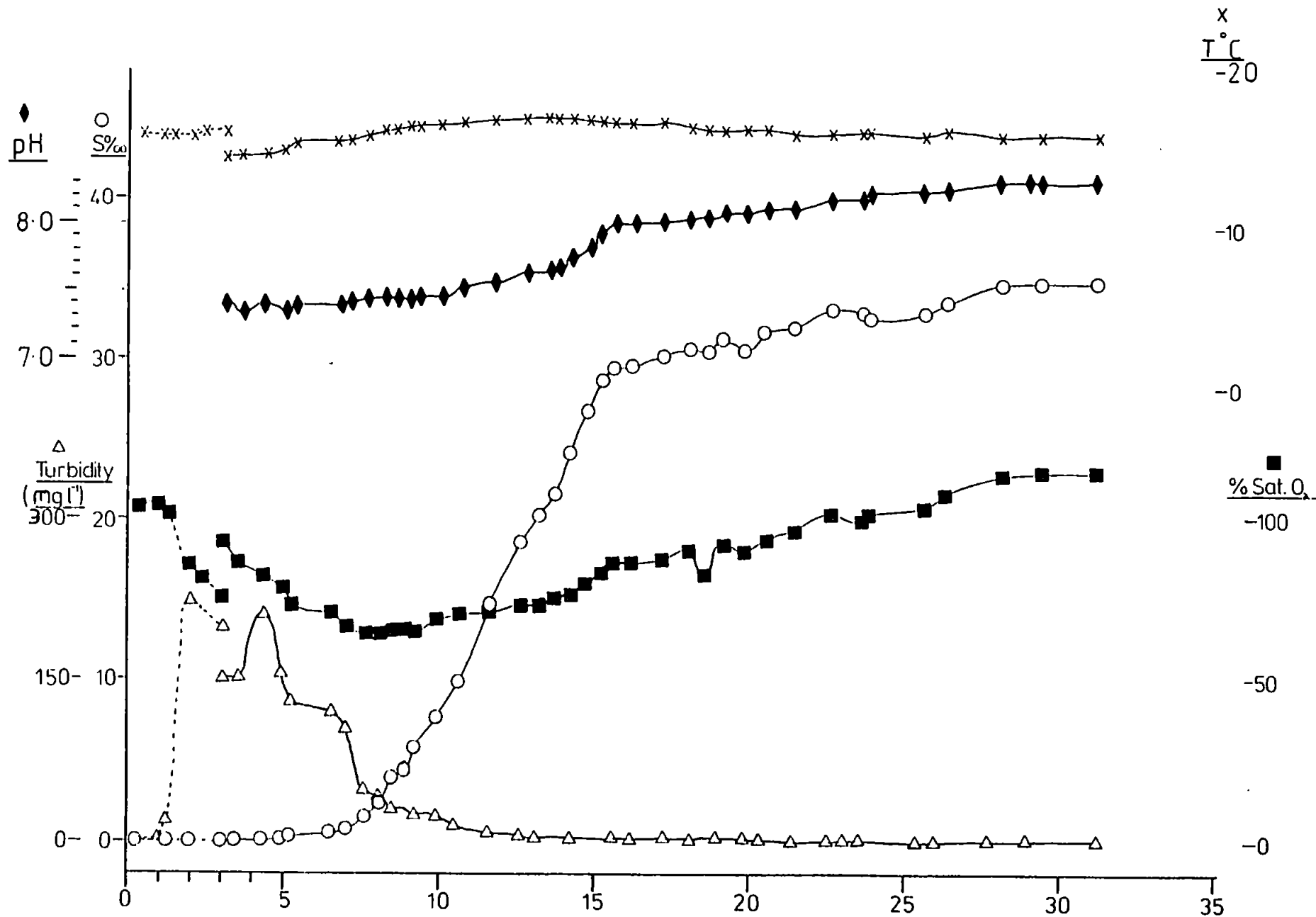
Figure 3.27 Profile showing the master variables during an axial traverse of the Tamar Estuary, 27-28/08/80

DISTANCE FROM WEIR HEAD (km.)

124

Another notable feature of the profile was the pronounced oxygen minimum associated with the F.B.I. which is suggested (Wellershaus, 1981; Morris et al., 1982c) to be associated with concentrations of organic-rich particles that were more or less permanently in suspension in the turbidity maximum. This material was readily degraded by endemic bacterial populations, thus producing a reduced dissolved oxygen concentration. For a chemical oxygen demand to produce a minimum on this scale was perhaps less likely, though chemical or bacterial oxidation of reduced species (e.g. ferrous iron, ammonia and divalent manganese) which had been generated in the anoxic sediments and released through re-suspension must provide some demand for dissolved oxygen. The pH profile showed a sharp decline at the F.B.I., consistent with an interface comprising seawater with a high pH (pH = 8.1) and riverwater of a lower pH (pH = 7.3). Minor variations in pH were invariably found to co-vary with salinity perturbations in accordance with general pH-salinity characteristics or associated with localised regions of enhanced primary productivity.

The dissolved metal profile (Figure 3.28) showed that manganese and zinc peaks were downestuary of the F.B.I. as the riverflow would displace the 'pulse' of dissolved metals liberated from the pore waters downestuary. Both zinc and copper showed pronounced removal in the turbidity maximum zone which was displaced upestuary of the F.B.I. Manganese levels decreased downestuary, whereas copper levels remained constant, zinc levels however increased. This was caused by contamination due to an experimental mishap which affected the samples from the five marine sites. This contamination could also have affected the copper results and accounted for the oscillations observed in estuarine profile.
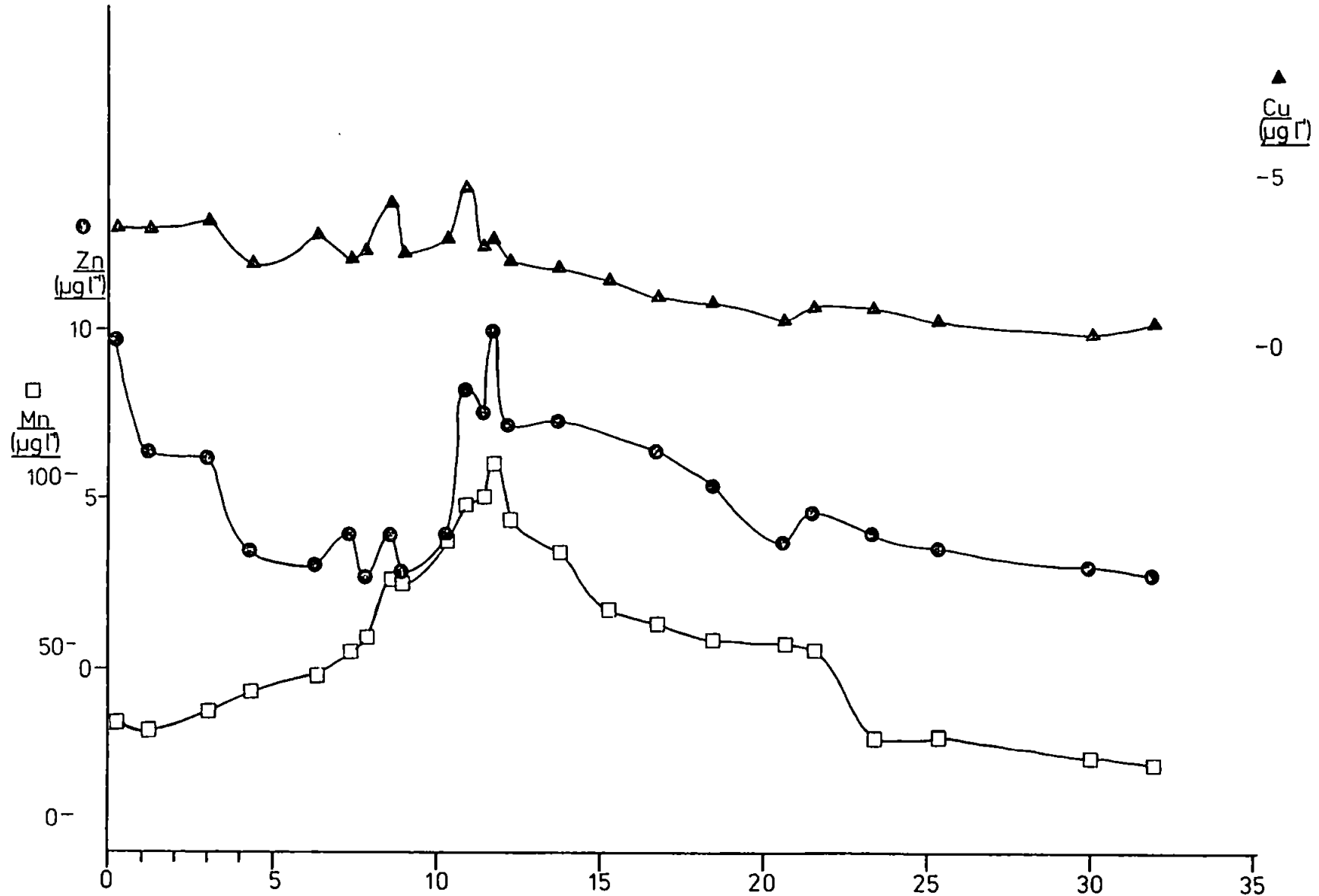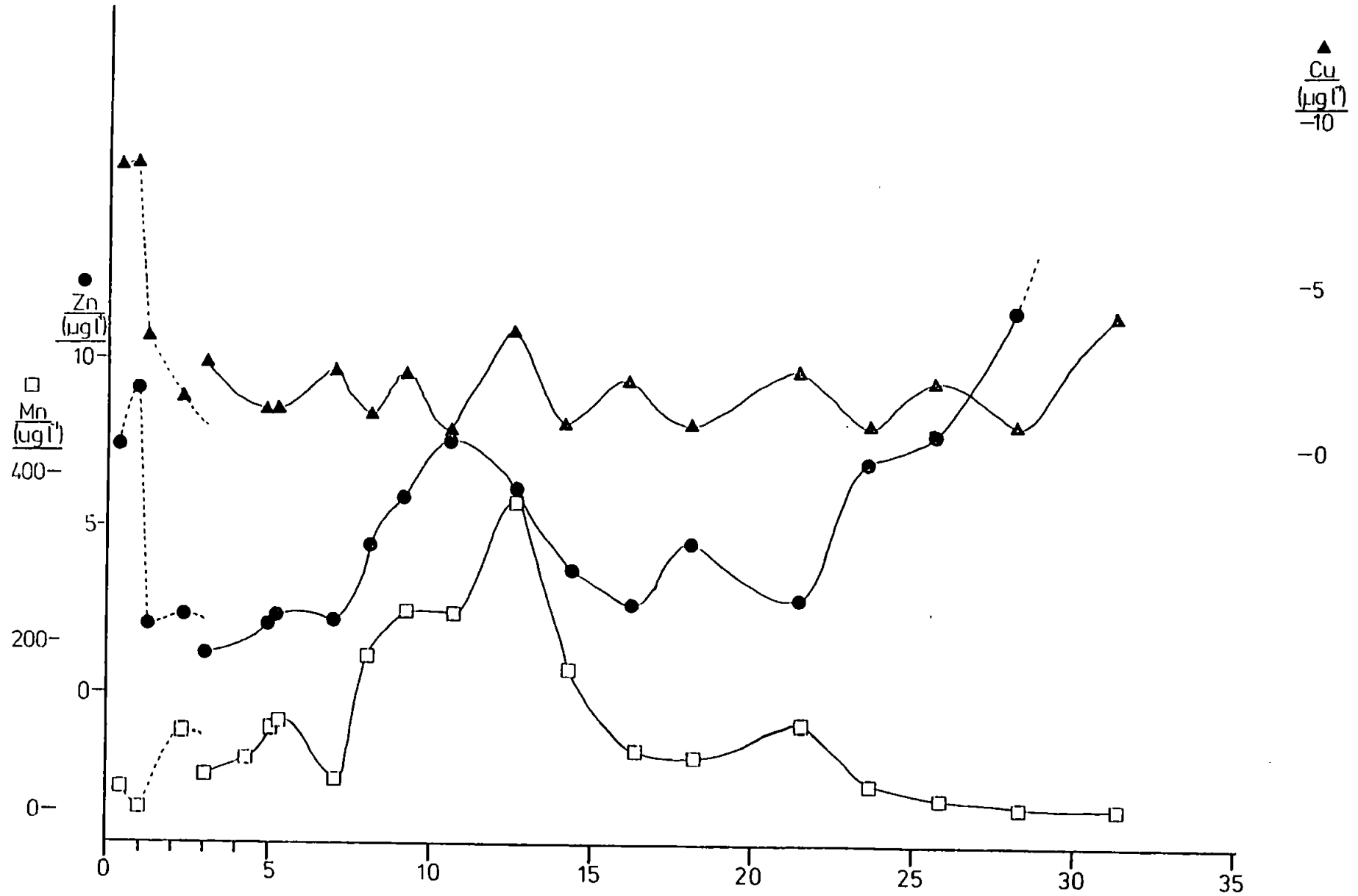
Figure 3.28 Profile showing the dissolved metals during
an axial traverse of the Tamar Estuary, 27-28/08/80

DISTANCE FROM WEIR HEAD (km.)

Figure 3.29 showed an axial profile taken in October under high river-flow conditions at a neap tide. By comparison with the previous neap profile (Figure 3.25), the F.B.I. had been displaced a considerable distance downestuary due to the high river run-off (29 m³ s^{-1}). The turbidity maximum was low and corresponding levels in seawater and freshwater were higher than the previous examples. During spate conditions, the contribution of riverine suspended material was greater than experienced under low flow conditions (see Figure 3.25) and formed an influx of new material into the estuarine system (see Section 3.1.4). Marine end-member turbidities were also higher, indicating possible migration of particulate material into or out of the estuarine system. The salinity measurements in this profile were erratic, possibly due to the influence of sharp bends on the tidal currents giving lateral salinity gradients; this is important at 15-16 km on the 'S' shaped loop of the Tamar, (see Figure 3.20). The perturbations at 20-30 km were probably caused by the Tavy Estuary. This region is characterised by a large area of mud-flats where water masses can be temporarily isolated due to incomplete mixing with the main stream. This can give rise to inhomogeneities in the regular mixing sequence. Tidal fronts and debris lines were often noticeable in this region and occasionally gave pronounced discontinuities. Perturbations in the pH profile were also consistent with the general pH-salinity trend, with a sharp decline in pH at the F.B.I. The oxygen minimum was less well defined. Under spate conditions, isolated bacterial populations and organic-rich particles would be dispersed and thus very little appreciable biological oxygen depletion would occur. Consistent with autumn conditions, seawater temperatures were higher than in the riverwater.

Figure 3.30 showed the corresponding dissolved metal profiles. The

Figure 3.29   Profile showing the master variables during an axial traverse of the Tamar Estuary, 30/10/80

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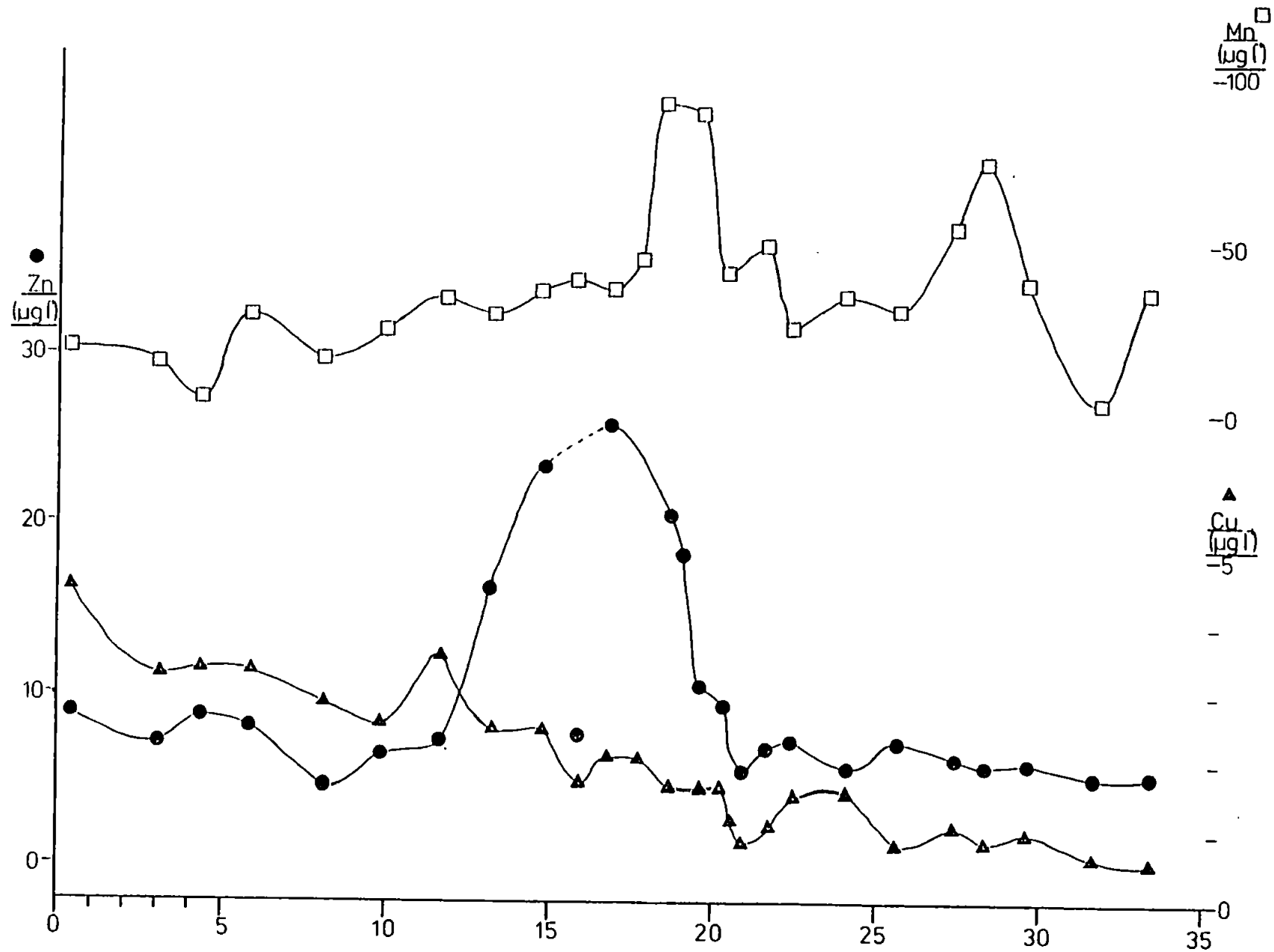
Figure 3.30   Profile showing dissolved metals during an
axial traverse of the Tamar Estuary, 30/10/80

most striking feature was the pronounced zinc maximum at the F.B.I., though the peak was in fact split by the intrusion of salt water at 16 km. The profile persisted as there was little suspended particulate material on which to adsorb (Grieve and Fletcher, 1977). The dissolved manganese profile exhibited two peaks, one co-incident with the F.B.I. and a second downestuary. The second peak could be associated with 'historical' effects of the previous tidal cycle with the 'pulse' of dissolved manganese persisting and gradually moving seaward (Morris, et al., 1982a). The magnitude of the dissolved manganese maximum was lower than on the previous survey (see Figure 3.28). The dissolved copper profile did not appear to exhibit any pronounced addition/ removal behaviour. The variations in levels appeared to coincide with changes in salinity, high levels were observed in riverwater and low levels in seawater.

Figure 3.31 showed a winter profile taken in February, a medium flow rate (13 m^3 s^{-1}) during a spring tide. The F.B.I. was again displaced well down the estuary (16 km) with a high turbidity maximum, double that shown in Figure 3.27. The dissolved oxygen profile showed supersaturation levels at the seaward end, but not in the freshwater. A reduced oxygen minimum was observed (in contrast to Figure 3.27), this could have been due to the small amount of available organic-rich particles, thus the oxygen minimum could have been primarily associated with the oxidation of reduced species of, for example, ferrous iron, ammonia and divalent manganese. These reduced species are generated within the anoxic sediment and released during sediment re-suspension (Knox, et al., 1981).

The profiles shown by Figure 3.32 were the dissolved metals for the same survey. The manganese peak was displaced upestuary of the F.B.I.

130

Figure 3.31   Profile showing the master variables during an
               axial traverse of the Tamar Estuary, 18/02/81

131
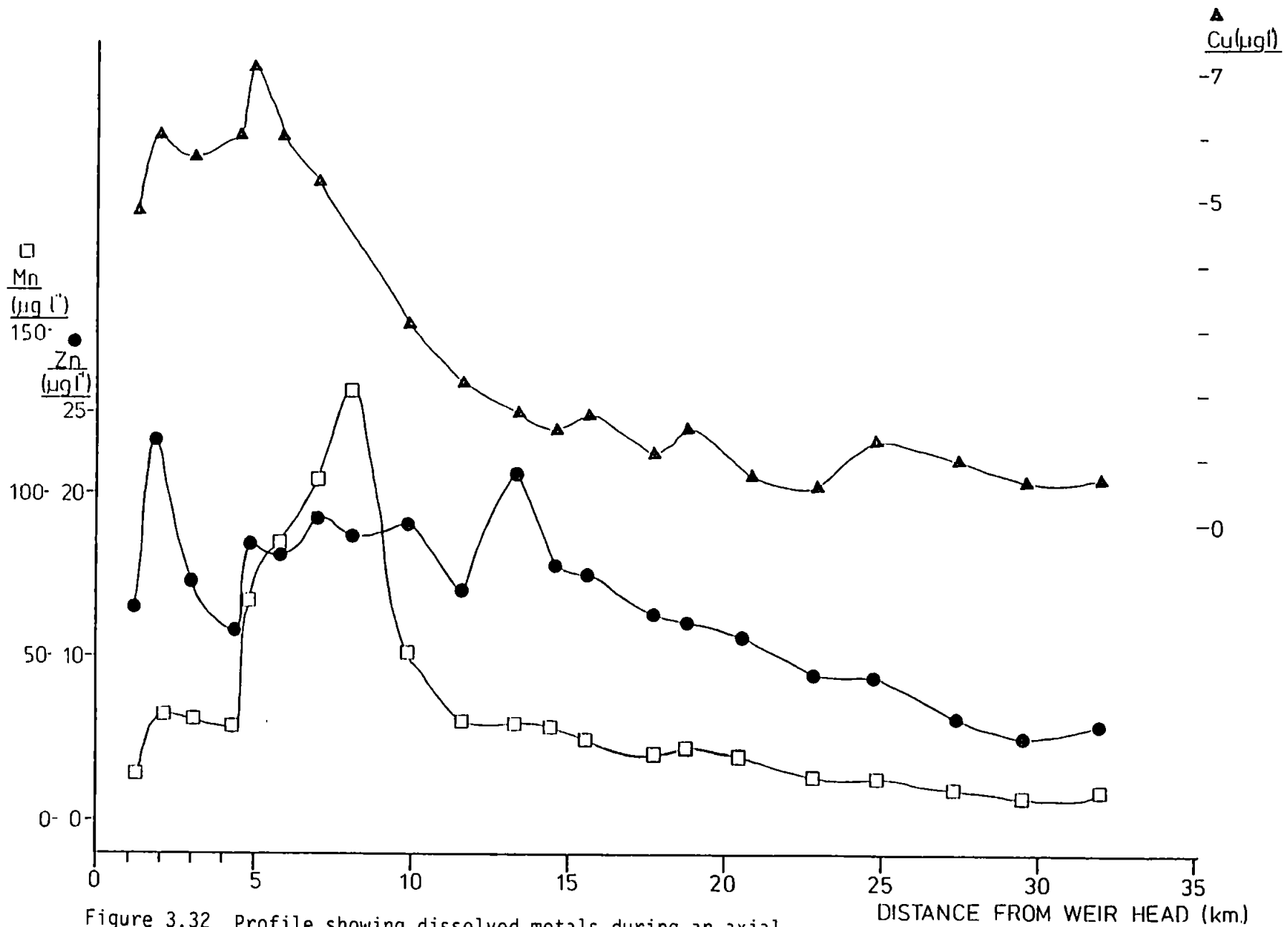
Figure 3.32   Profile showing dissolved metals during an axial
traverse of the Tamar Estuary, 18/02/81

132

and turbidity maximum. No appreciable zinc peak was observed, this could have been due to the delay in filtering the high turbidity samples, allowing some adsorption to take place and thus decreasing the dissolved zinc levels. The copper levels were high in the riverwater, a small peak was observed upestuary of the F.B.I. and the manganese peak, but the levels decreased rapidly at the F.B.I. with a more gradual reduction in the lower estuary.

Finally, Figures 3.33 and 3.34 showed results for a December profile, medium river-flow (17 m³ s^{-1}) and a tidal flow midway between springs and neaps. The results here are similar to the conditions in Figures 3.28 and 3.29 with the exception that the turbidity maximum was more prominent in Figure 3.33. Figures 3.25-3.34 could be summarised by concluding that the geographical position of the F.B.I. was a function of tidal regime and river flow. Both pH and dissolved oxygen showed non-conservative behaviour in the estuarine system, this was attributable to variations in marine and freshwater levels and also _in situ_ chemical and biological processes. Turbidity was the most variable component, with a range of 10-600 mg l^{-1}. Fluxes of suspended material from coastal waters and riverine input were, apart from during spate conditions, small relative to the quantity in suspension in the midestuary. The turbidity maximum was produced by a dynamic balance between re-suspension from and deposition to the estuarine sediment. The dissolved metal profiles were indicative of estuarine chemical processes and these are examined in the following section.

3.2.2.b Dissolved Metal-Salinity Profiles

A preliminary examination of the dissolved metal-distance profiles showed that significant chemical interactions were occurring in the
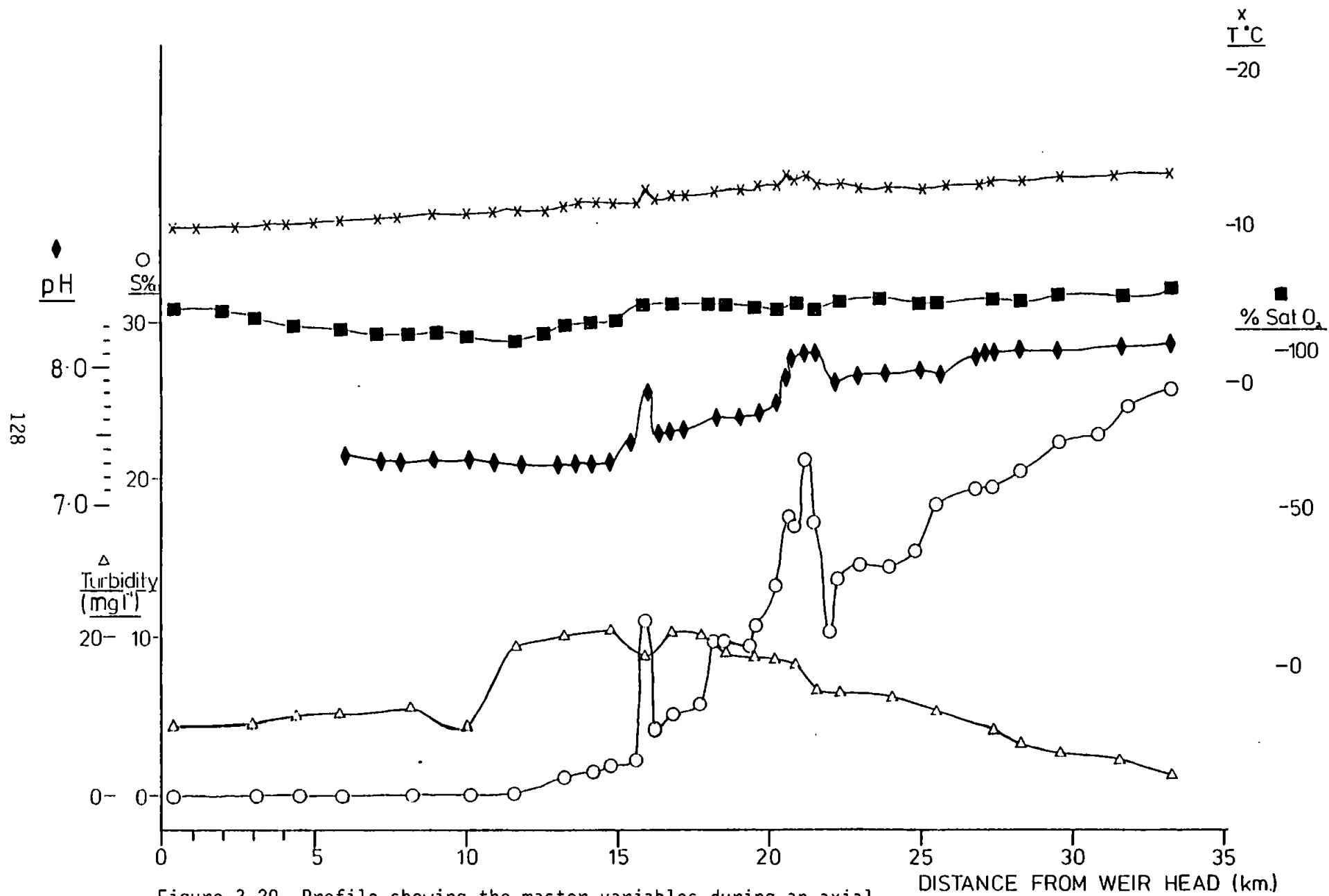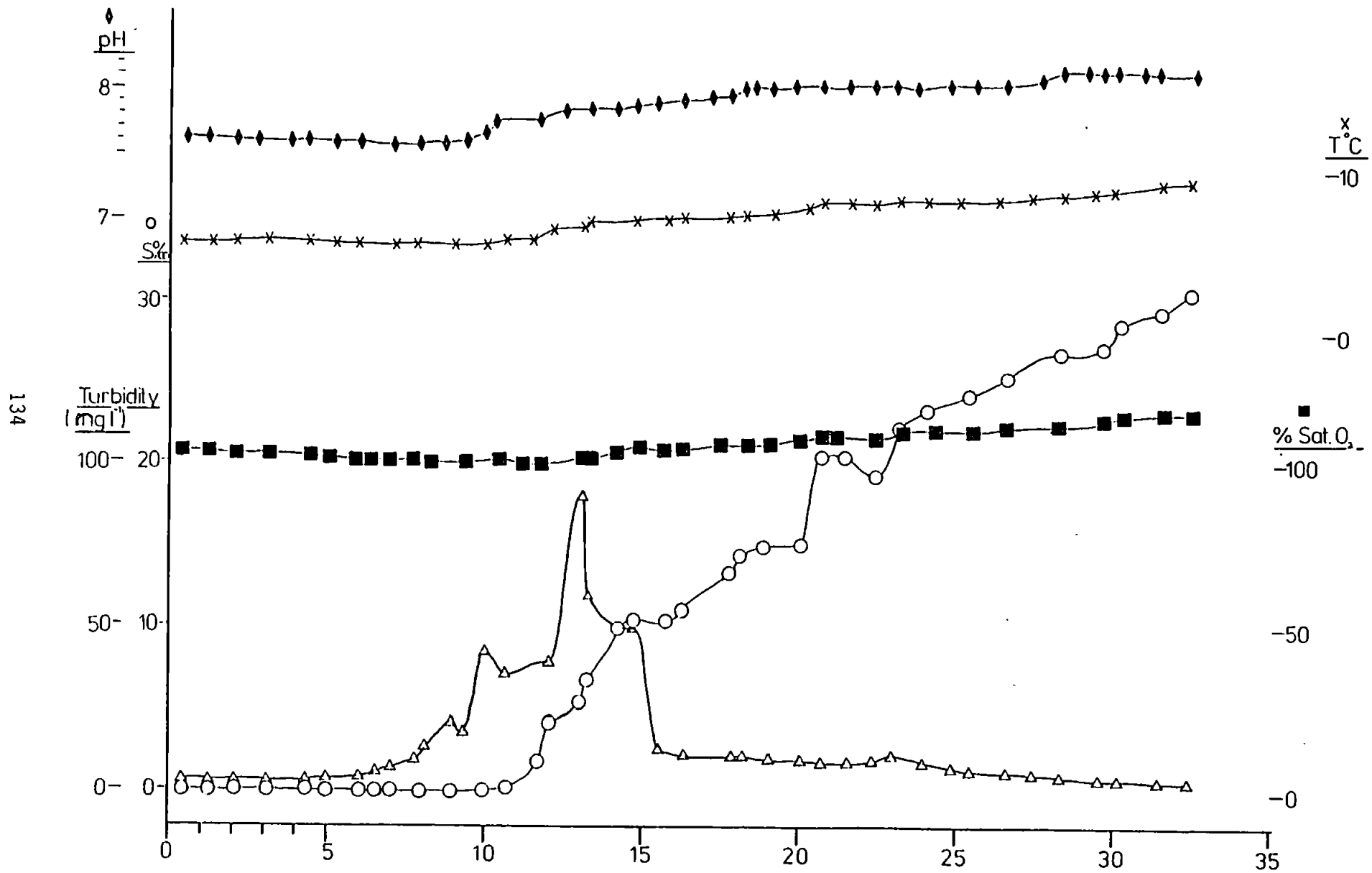
Figure 3.33   Profile showing the master variables during an
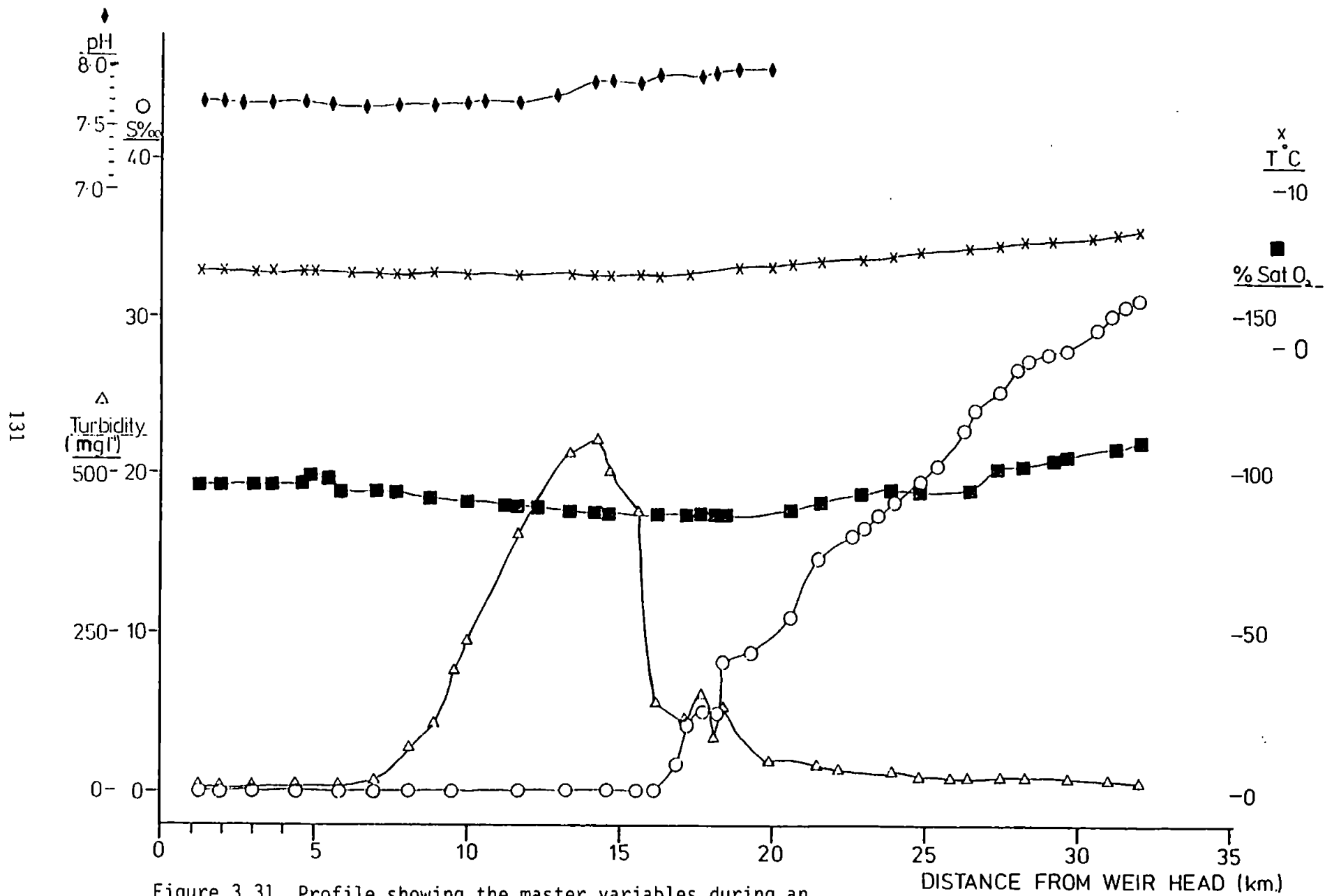axial traverse of the Tamar Estuary, 4/12/80

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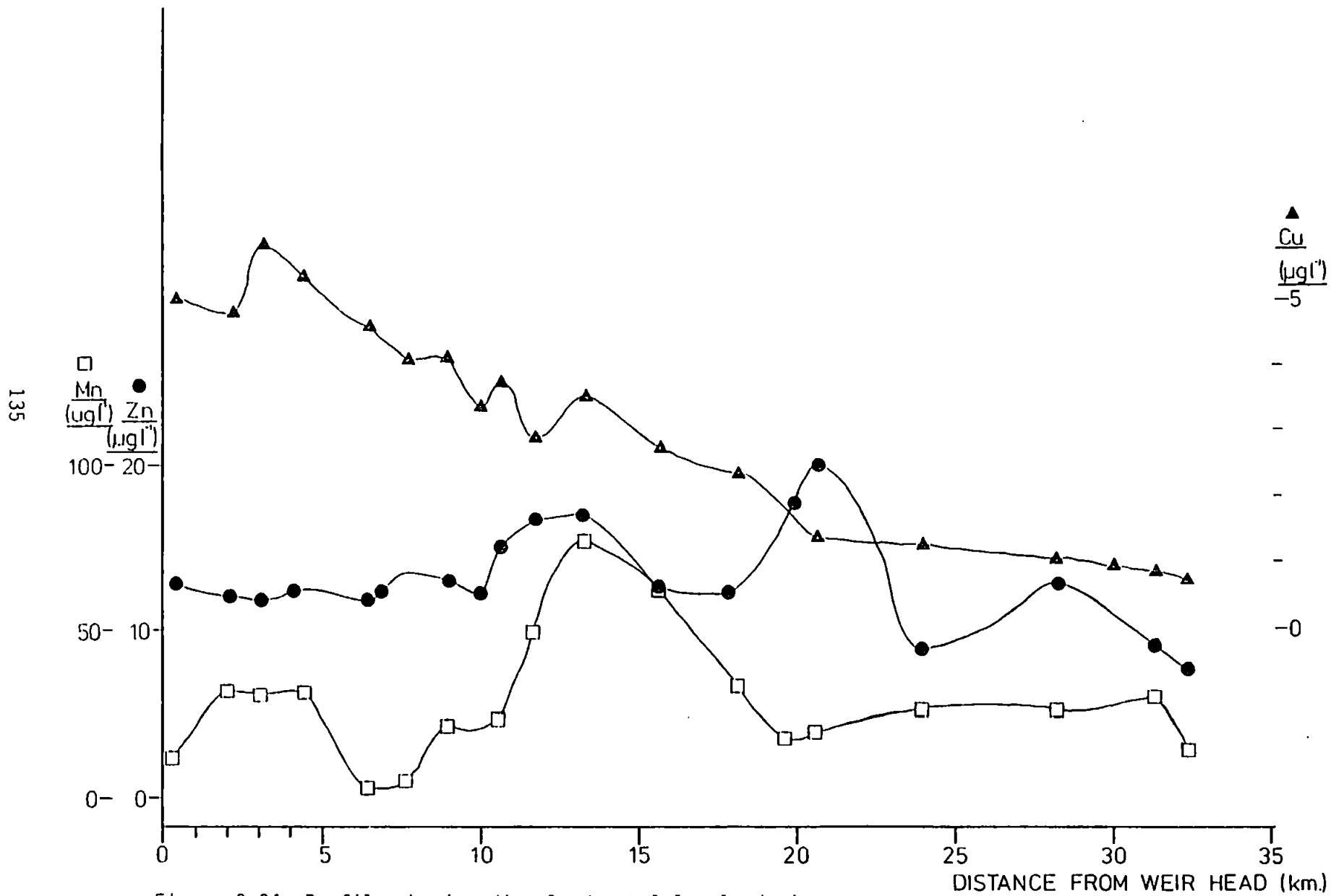
Figure 3.34   Profile showing dissolved metal levels during an
axial traverse of the Tamar Estuary, 4/12/80

region of the F.B.I. Because of the very low proportion of seawater represented at salinities < 1°/oo, this region has often been assumed to be insignificantly different from the riverwater. In the previous section it was observed that the sharpest and most extensive changes in estuarine master variables occurred within this region. This reaffirms the need to examine the low salinity region when attempting to rationalise dissolved metal-salinity relationships. This was a key aspect of the chemical analyses undertaken in this work.

The dissolved metal-salinity profiles for each of the five surveys are depicted in Figures 3.35-3.39. Conventionally, the salinity axis is linear with the changes in the low salinity region obscured. In these diagrams, the salinity axis was logarithmic to highlight the changes taking place in this important region. There is however, a distortion of the overall mixing profile. The data for each metal was tested against a linear function of salinity and the results were summarised as follows: the copper profiles at the higher salinities (> 5°/oo) were conservative, whereas the manganese and zinc profiles were apparently non-conservative. For example, in Figure 3.35 the non-conservative behaviour of manganese and zinc was evident from the co-incident metal peaks at a salinity 10°/oo, thereafter decreasing with increasing salinity. For zinc, with high levels in the freshwater, the very low salinity region exhibited some removal from the dissolved phase which was not observed for manganese. The copper in the low salinity region showed no overall trend, taking into account the scatter of the results, however removal has been observed (see Figure 3.38), but the concentrations decreased at higher salinities in a manner consistent with conservative mixing. These general conclusions for the data in Figure 3.35 can be extended to the other dissolved metal surveys.
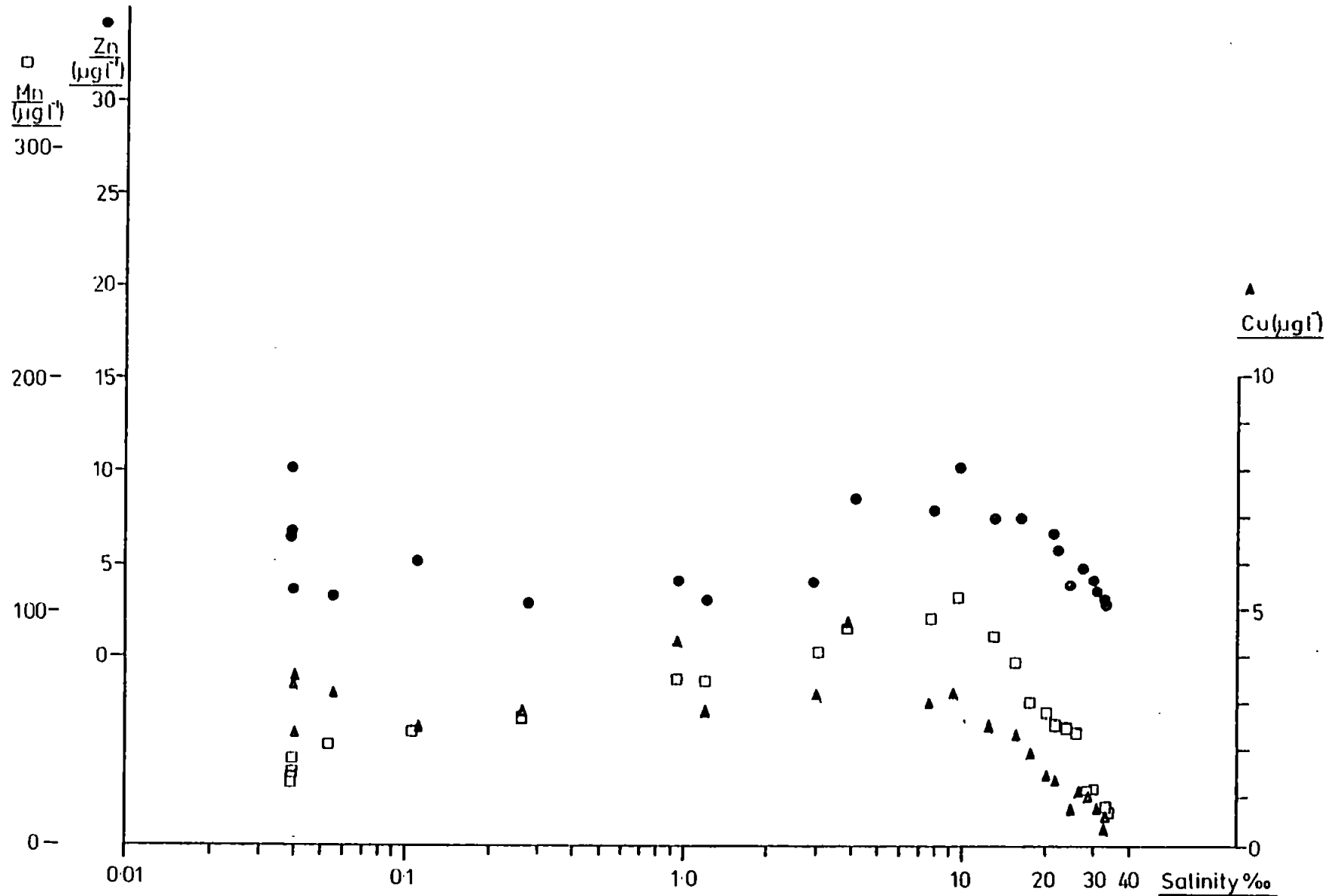
Figure 3.35   Dissolved metal-log. salinity profile for 24/07/80

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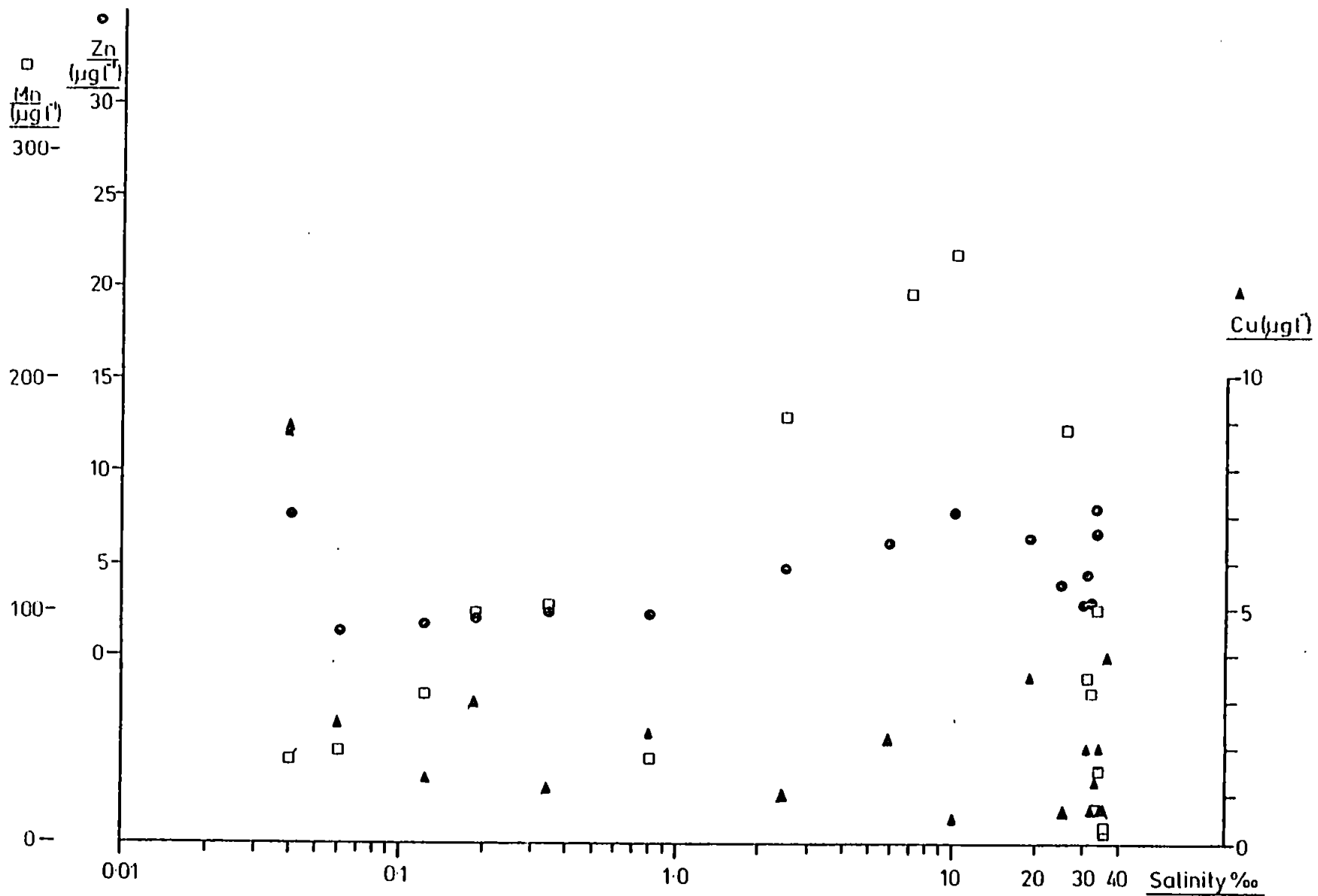
Figure 3.36   Dissolved metal-log. salinity profile for 27-28/08/80

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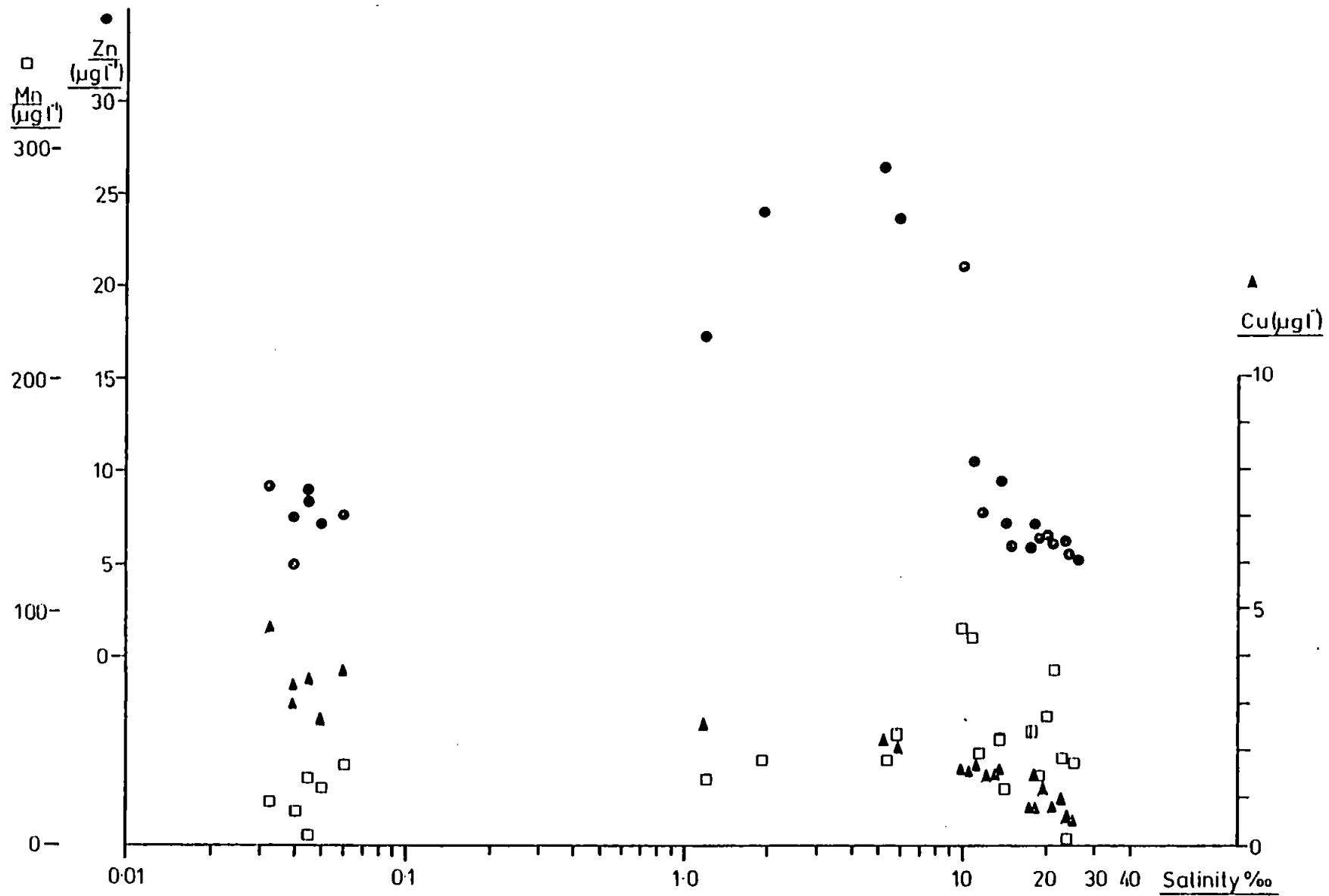
Figure 3.37   Dissolved metal-log. salinity profile for 30/10/80
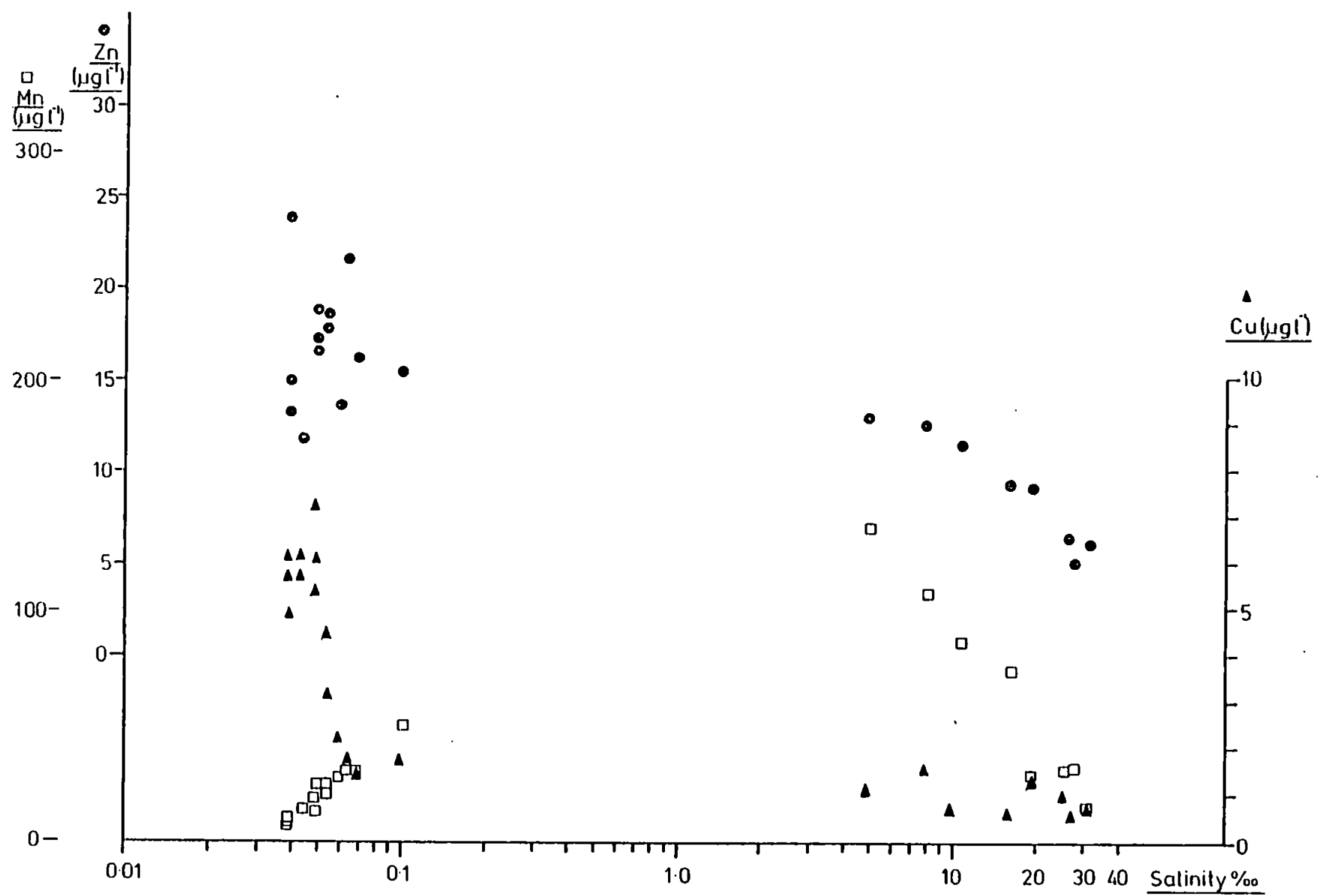
Figure 3.38   Dissolved metal-log. salinity profile for 18/02/81

140
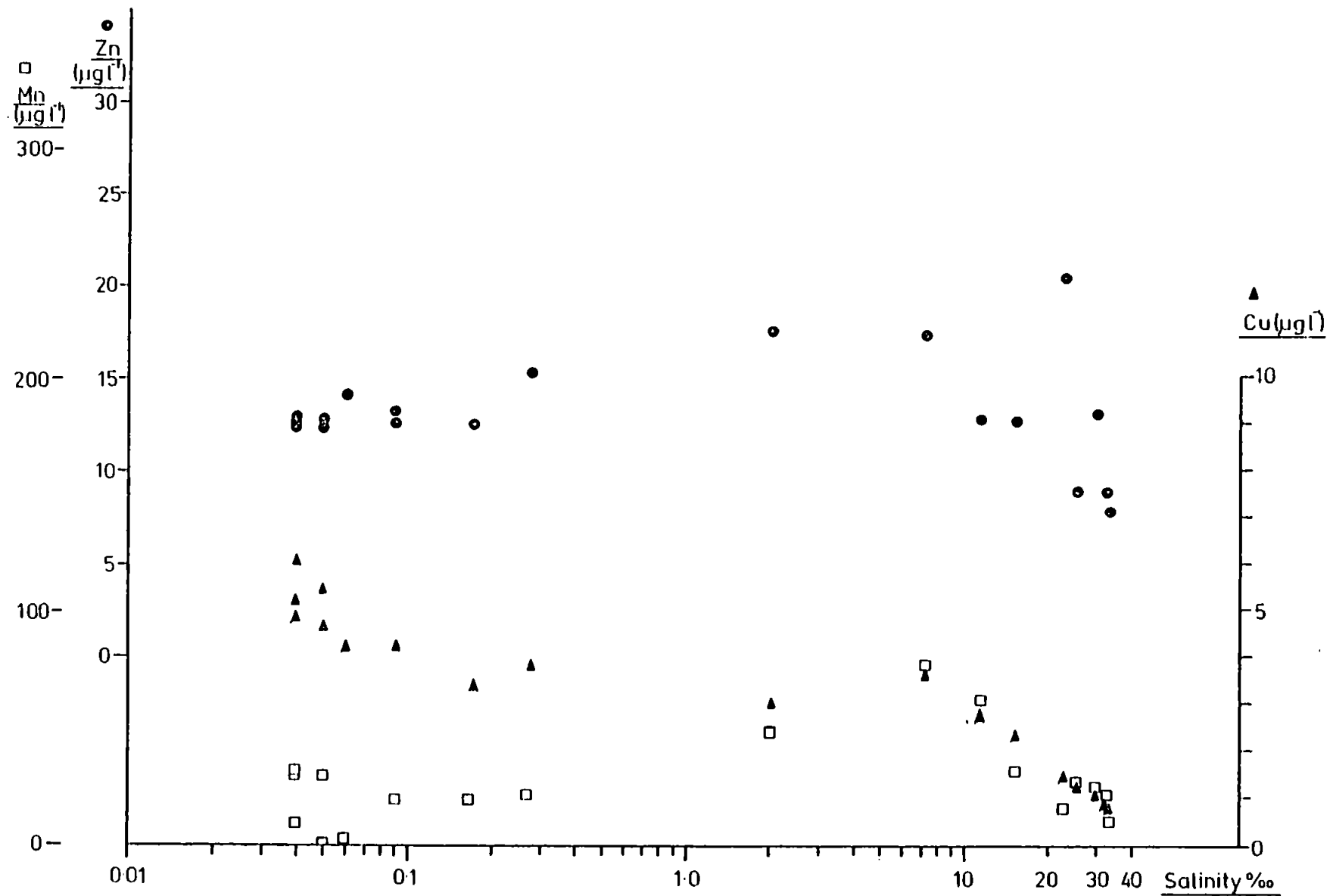
Figure 3.39   Dissolved metal-log. salinity profile for 4/12/80

In view of the apparent similarities in the metal behaviour, the data was summarised in the form of a composite graph for each metal. This was achieved by tracing the metal profiles (including unpublished data by Bale, et al., 1976-1979) onto a single diagram, thus highlighting the addition/removal behaviour in common for all the surveys.

The copper levels (see Figure 3.40) were generally very low, in the region of 2 µg l^{-1} and the relative changes were only by a factor of two. This made interpretation of these profiles difficult, but there was evidence of some removal in the low salinity region, (see also Morris, et al., 1978), with possible inputs at higher salinities (3-7°/oo). The general indication that the behaviour of copper in the Tamar is non-conservative was in agreement with work in the Zaire Estuary (Moore and Burton, 1978). The composite graph for manganese (see Figure 3.41) showed evidence of pronounced input in the low salinity region (3-10°/oo). A number of the profiles indicated removal of dissolved manganese in the very low salinity region, in agreement with Knox, et al., (1981), and Morris and Bale, (1979). The range of dissolved manganese levels in the riverwater was again much greater than the range observed in the marine end-member. The zinc profiles (see Figure 3.42) depicted striking variations in the absolutely fresh-water region. The principal feature borne out by the diagram was the presence of dissolved zinc maxima at 8-15°/oo, approximately co-incident with those of manganese. Zinc removal at the very low salinity region was observed on a number of surveys. The variation in riverine dissolved zinc levels was noticeably greater than either of the other two metals. The profiles indicated that zinc was behaving non-conser-vatively, in contrast to Elderfield, et al., (1979), and Holliday and Liss, (1976) who found conservative behaviour. However, zinc profiles at the higher salinities appeared to behave conservatively.

142
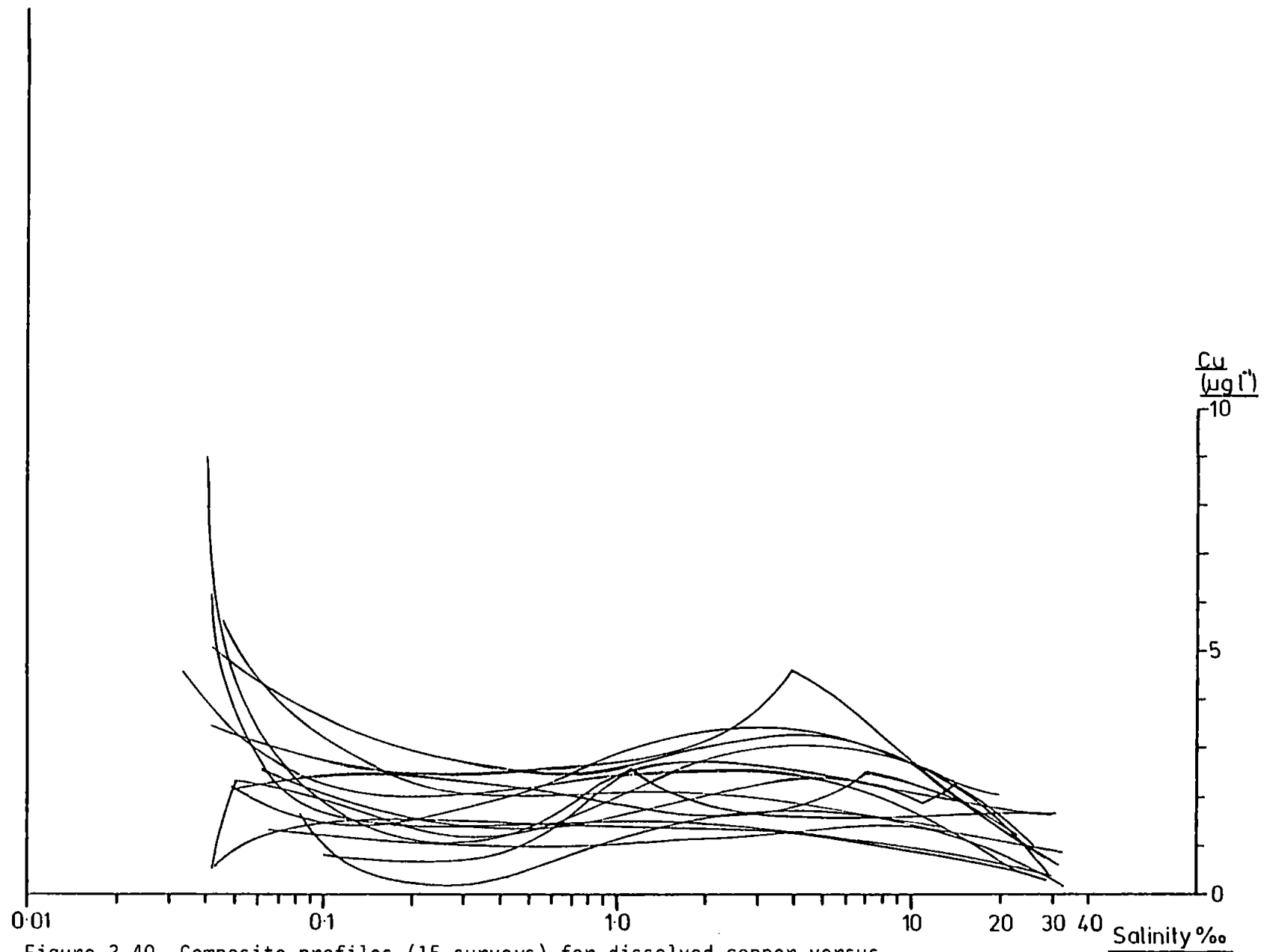
Figure 3.40   Composite profiles (15 surveys) for dissolved copper versus
              log. salinity in the Tamar Estuary, 1976-81
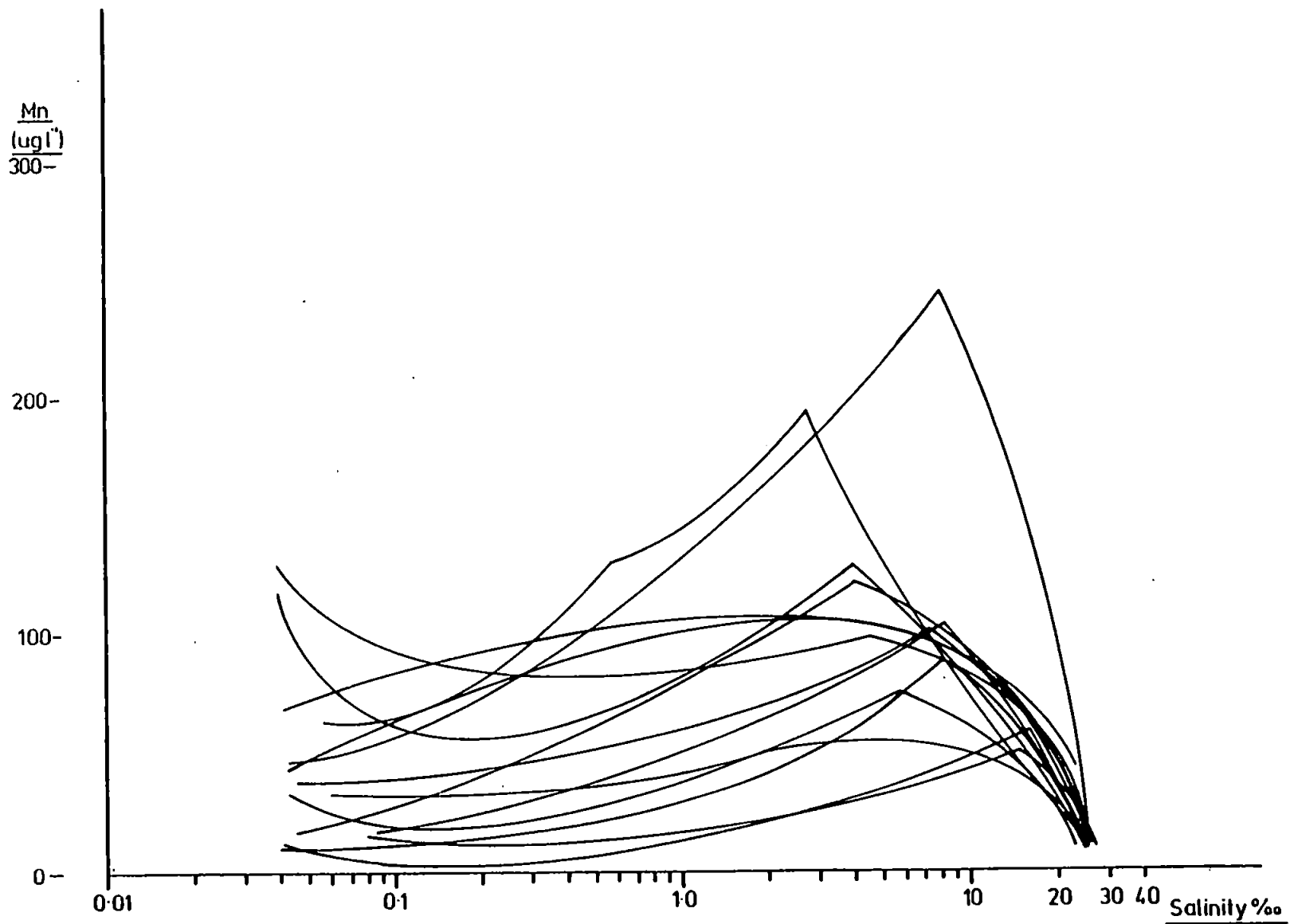
Figure 3.41   Composite profiles (15 surveys) for dissolved manganese versus
log. salinity in the Tamar Estuary, 1976-81
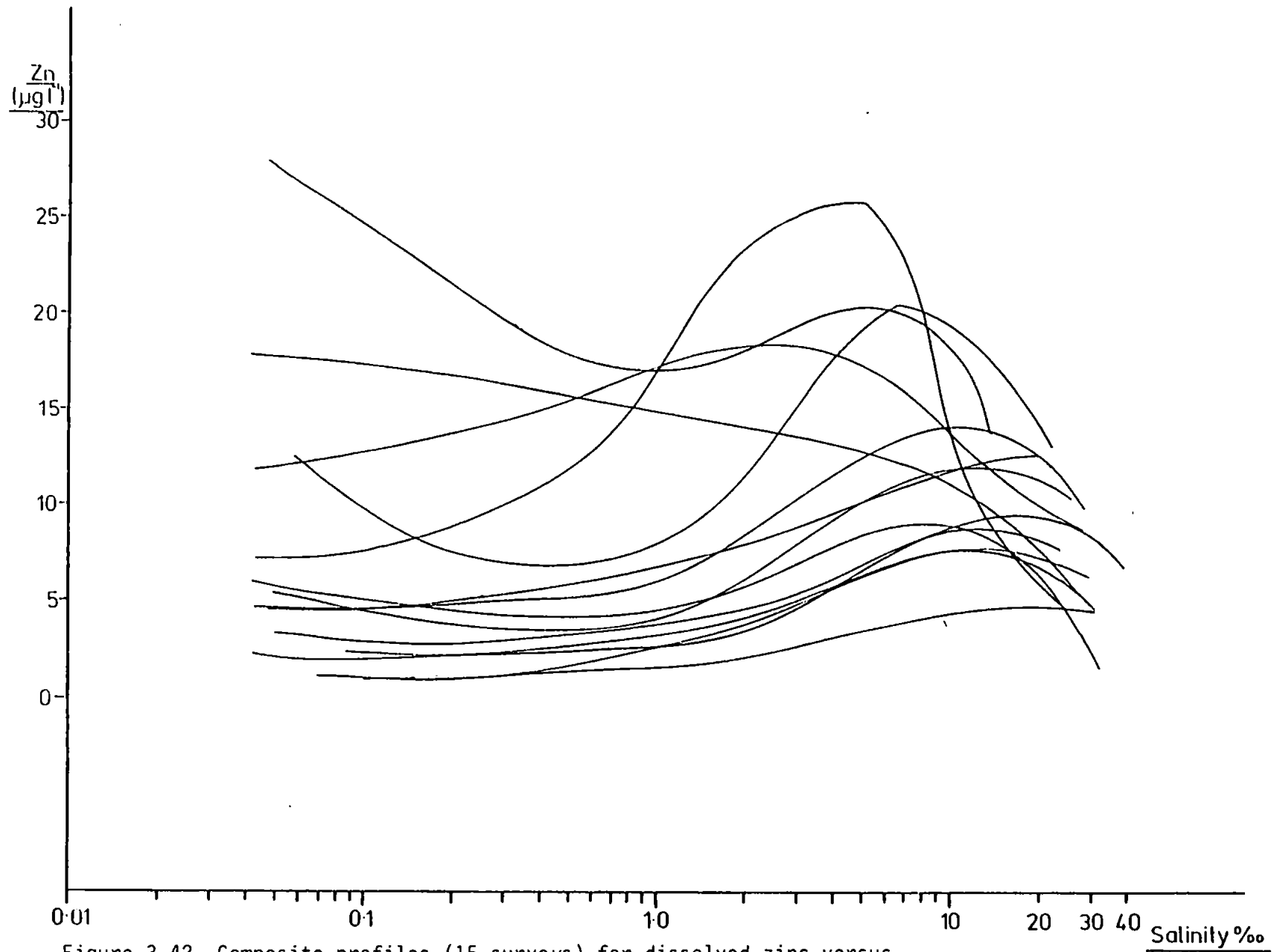
Figure 3.42 Composite profiles (15 surveys) for dissolved zinc versus log. salinity in the Tamar Estuary, 1976-81

Evidence for the input of dissolved manganese and zinc was gained from the examination of the dissolved metal-salinity profiles; it was found that the maxima for manganese and zinc were concurrent. As manganese inputs at the F.B.I. are largely a result of the influx of manganese-rich pore waters into the water column (Knox, et al., 1981; Morris, et al., 1982), it was presumed that zinc inputs were from the same source, rather than salinity-induced desorption from suspended particulates or additional land-derived inputs. This theme is discussed later in the text (see Sections 3.2.3 and 3.3.2).

3.2.3   Statistical Analysis

Statistical analyses of the data were undertaken in an attempt to establish whether the dissolved manganese and zinc were emanating from the same source, i.e. the metal-rich sediment pore waters. This was achieved using a modified computer programme previously used for manganese and ammonia in estuaries (Knox, et al., 1981). The statistical technique involved the use of F-ratios (Snedecor and Cochran, 1967) which were used to assess the significance of the association between copper, manganese, zinc and salinity. Two equations were used to test the behaviour of the components (the full derivation is given in Knox, et al., 1981);

a)   conservative mixing line

$$[A] = a_0 + a_1 S \qquad\qquad (1)$$

b)   that constituents [A] and [B] were originating from the same physical source

$$[A] = c_0 + c_1 S + c_2 [B] \qquad\qquad (2)$$

146

The following predictions could be made;

   (i)   all the data will fit equation (2) and

either (ii)   the fit to equation (2) will be significantly better

          than the fit to equation (1)

or   (iii)   the data will fit equation (1).

The statement (iii) allows for the possibility that the dissolved metal

maximum does not dominate the profile and thus the conservative mixing

line provides an adequate fit. The statistical tests were carried out

using F-ratio tables (Murdoch and Barnes, 1974) at the 95% confidence

level.

The F-ratio is defined as;

$$F = \frac{\text{improvement in residual sum of squares}}{\text{mean square of deviations from equation (2)}}$$

Predictions (i) and (iii) were tested using the F-ratios for the

regressions (2) and (1) respectively. Prediction (ii) was tested using

F-ratio for the addition of the variable [B] to the regression (1).

The data was analysed in two forms;

   I   with data collected above the F.B.I. omitted (as in

        Knox, et al., (1981), F.B.I. defined as salinities

        below $0.5^{o}/oo$) Table 3.15.

   II   containing all the data taken on the axial traverse

        Table 3.16.

Knox, et al., (1981) had used form I as they had found that dissolved

manganese was removed at the F.B.I. and this provided a more stable

freshwater end-member on which to base the statistical analysis. It

is suggested in this work that the inclusion of the data upestuary

	TMn/Sal[a]	TMn/Sal/Cu[b]	Cu/Sal[a]	Cu/Sal/TMn[b]	TMn/Sal/Zn[b]	Zn/Sal[a]	Zn/Sal/TMn[b]	Zn/Sal/Cu[b]	Cu/Sal/Zn[b]
Oct. 76	-	-	-	-	-	-	-	-	-
Jan. 77	+	-	-	-	+	-	-	+	+
Mar. 77	-	-	-	-	-	+	-	-	-
Apr. 77	+	-	-	-	+	+	+	+	+
May. 77	-	-	-	-	+	+	+	-	-
Jy. 77	-	-	-	-	+	+	+	-	-
Sep. 77	-	+	-	+	+	-	-	+	+
Oct. 77	-	-	-	-	+	+	+	+	+
Nov. 77	+	-	-	-	+	+	+	+	+
Jy. 80	-	+	-	+	+	-	+	+	+
Aug. 80	-	-	-	-	-	+	-	-	-
Oct. 80	-	-	-	-	-	-	-	-	-
Dec. 80	-	-	-	-	-	-	-	-	-
Feb. 81	-	-	-	-	-	-	-	-	-

[a] This represents the results for test (iii)

[b] This represents the results for tests (i) and (ii)

+ = above 95% confidence level

- = below 95% confidence level

Table 3.15 Statistical Analysis of Dissolved Metals; Data Above the F.B.I. Omitted (Case I)

	TMn/Sal[a]	TMn/Sal/Cu[b]	Cu/Sal[a]	Cu/Sal/TMn[b]	TMn/Sal/Zn[b]	Zn/Sal[a]	Zn/Sal/TMn[b]	Zn/Sal/Cu[b]	Cu/Sal/Zn[b]
Oct. 76	-	-	-	-	-	-	-	+	+
Jan. 77	-	-	-	-	-	-	-	+	+
Mar. 77	+	+	-	+	+	+	+	+	+
Apr. 77	+	-	-	-	+	+	+	+	-
May 77	-	-	-	-	+	+	+	-	-
Jy. 77	-	-	-	-	+	+	+	-	-
Sep. 77	-	-	-	-	-	+	-	+	+
Oct. 77	-	-	-	-	+	+	+	+	+
Nov. 77	-	-	-	-	+	+	+	+	+
Jy. 80	-	-	-	+	+	-	-	+	+
Aug. 80	-	-	-	-	-	+	-	+	+
Oct. 80	-	-	-	-	+	-	+	-	-
Dec. 80	-	-	-	-	-	-	-	-	-
Feb. 81	-	-	-	-	-	-	-	-	-

[a]This represents the results for test (iii)

[b]This represents the results for tests (i) and (ii)

+ = above 95% confidence level

- = below 95% confidence level

Table 3.16   Statistical Analysis of Dissolved Metals; Data Above the F.B.I. Included (Case II)

of the F.B.I. would reflect the important reactions taking place in the very low salinity region (0.04-0.5^o/oo) that have been observed in the metal-salinity profiles.

The implication from the results in Tables 3.15 and 3.16 was that for both edited and unedited data, the copper data does not fit the conservative mixing equation. Neither does the copper follow the behaviour of manganese which suggests that they are not emanating from the same source (manganese is presumed to be liberated from the pore waters). Copper, for example, probably has secondary inputs from the banks of the estuary and/or desorption from the suspended particulates entering saline waters. The zinc results showed that there were occasions when zinc appeared to behave conservatively, in good agreement with Elderfield, et al., (1979) and Holliday and Liss, (1976). There were, however, a significant number of occasions when zinc results could be fitted to equation (2) in association with manganese, which suggested non-conservative behaviour. By inference, the zinc in these cases could have been emanating from the pore waters. There was also an indication that on occasions the behaviour of copper and zinc was significantly related, which supports the notion of a secondary source for zinc as well as copper. This conflicting evidence suggests that statements about dissolved metal behaviour should not be made on the basis of one survey (as in Elderfield, et al., 1979 and Holliday and Liss, 1976) as the large variability in estuarine conditions appears to affect the chemical behaviour of the dissolved metals.

In order to examine further the possibilities of infusions from pore waters, first order calculations were made to assess the contribution

from this pore water reservoir to the overlying water column.

It was assumed that a mid-estuarine region from 10 to 20 km from Weir Head (usually the zone of the dissolved metal maxima) and a sediment depth of 5 cm was predominantly involved in the pore water infusion mechanism. This gave a total sediment volume of 8.5×10^4 m^3, it was assumed that 70% of this volume was occupied by pore water. The average depth of the water column in this region was taken as 2 m, resulting in a water volume of 2.7×10^9 litres. Sediment pore water analyses (Watson, personal communication) gave zinc ranges of 100-500 µg l^{-1}, thus the pore waters could contain between 2 kg and 9.3 kg of zinc. If all this were injected into the water column during tidal mixing, the concentrations in the mid-estuarine region could be enhanced by between 2 and 9 µg l^{-1}. This infusion could account for some of the zinc peaks observed in the estuary. Similar calculations for manganese, where pore water concentrations vary between 1500-2000 µg l^{-1} (Knox, et al., 1981) showed that the mid-estuarine concentrations could be enhanced by 26 to 35 µg l^{-1}. Although these estimates are formed on the basis of fairly crude assumptions, they do indicate that in some cases, the dissolved metal maxima observed in the estuary could be explained by this pore water infusion mechanism. However, the possibility of metal desorption still applies and this mechanism is considered in Section 3.3.

3.2.4 Summary of Dissolved Metal Data

The estuarine dissolved metal study is summarised as follows;

1. The dissolved copper, manganese and zinc showed differences in behaviour, metal-salinity profiles indicated essentially non-conservative behaviour in the very low salinity region (0.04-5°/oo), at higher salinities (10-30°/oo) the behaviour appeared to be conservative. The variability in dissolved metal levels is shown in Table 3.14 for the Tamar and other estuaries. Dissolved copper levels in the Tamar were similar to the levels in the Bristol Channel and Conwy, but lower than the grossly polluted Restronguet Estuary. Given the number of potential injection points for copper in the Tamar (see Figure 2.1), it is interesting that the dissolved copper levels were low, possibly due to the fact that up to 80% of the particulate copper is in the detrital form. The manganese levels were high in comparison to the other examples whereas the zinc levels were generally lower.

2. The variation in master variables had a major bearing on the behaviour of the dissolved and particulate metals. The changes in river-flow and tidal regime exerted a major influence on the dissolved metal profiles.

3. Statistical analysis suggested that the estuarine behaviour of manganese and zinc was similar, though not in all cases, and there was also some similarity in the behaviour of copper and zinc. By inference, dissolved manganese appeared to have one major source, namely sediment pore waters. In contrast, the statistical results suggested that

Location	Cu	Mn	Zn	Reference
Tamar	0.5-7.0	10-380	2-25	This work
Bristol Channel	0.71-5.45	0.45-4.14	3-25	Abdullah and Royle, (1974)
Restronguet and Helford Estuaries	16-26	36-112	150-300	Boyden, et al., (1979)
Conwy	1.2-6.4	0.8-172	-	Elderfield, et al., (1971)
Conwy	-	-	5-55	Elderfield, et al., (1979)
Beaulieu Estuary	-	20-120	7-45	Holliday and Liss, (1976)

Table 3.14 Dissolved Metal Levels ($\mu g \, l^{-1}$) for this Work and Others

copper and zinc have two possible sources which involve infusion from sediment pore water and desorption from suspended particulates entering the low salinity region. Calculations relating to pore water infusion and desorption from particulates, under certain conditions, could account for the copper and zinc peaks observed and the two processes are presumed not to be mutually exclusive. The relative magnitude of the pore water infusion compared to the desorption process could not be determined.

4. A comparison of the composite metal-salinity profiles (Figures 3.40-3.42) revealed several interesting features. The dissolved copper (Figure 3.40) peaks occurred consistently at $S = 4^o/oo$. This could be indicative of desorption reactions from estuarine particulates given the measure of salinity dependence. The dissolved manganese (Figure 3.41) peaks occurred over a range of salinities $S = 3-15^o/oo$, indicative of a geographically dependent input, i.e. liberation from the pore waters. The geographical position and magnitude of dissolved manganese peaks were observed to vary with the spring-neap tidal cycle (Morris, et al., 1982a) thus accounting for the range of salinities observed. Dissolved zinc (Figure 3.42) peaks were also found to occur over a range of salinities, the range was less than for manganese indicating some measure of salinity dependence for zinc, again support-ing the hypothesis of two potential sources of dissolved zinc. The evidence given here again highlights the differences between copper and manganese with zinc acting as an intermediary.

3.3 ADSORPTION BEHAVIOUR OF DISSOLVED COPPER AND ZINC USING SIMULATED ESTUARINE CONDITIONS

In an attempt to rationalise some of the questions posed by the field data, a series of laboratory-based experiments was undertaken to ascertain the influence of sorption characteristics as a function of key parameters, i.e. turbidity, pH and salinity and to try to relate the results to changes observed in the estuary.

3.3.1 Results and Analysis

The results are presented as the percentage of dissolved metal remaining in solution at successive time intervals. Figures 3.43 and 3.44 showed adsorption characteristics of dissolved copper and zinc under increasing turbidities at natural pH (pH = 7.6) and a salinity of $10^o/oo$. Many other adsorption profiles were undertaken but only the summary is reported here. Slight adsorption was observed for copper (Figure 3.43) at zero turbidity, this could have been due to the container walls or the effect of removal by colloidal humic substances which also offer adsorption or complexation sites for dissolved metals (Mantoura, et al., 1978). At the higher turbidities the dissolved metal uptake at equilibrium was increased. Zinc losses at zero turbidity were greater than copper but again the adsorption increased with higher turbidities. The adsorption was followed for two hours and quasi-equilibrium condition was reached after approximately twenty minutes in almost all cases. Extrapolation beyond twenty minutes indicated that a much slower uptake mechanism was prevailing. Figures 3.45 and 3.46 showed adsorption under the same S.P.M. loads.

155

156
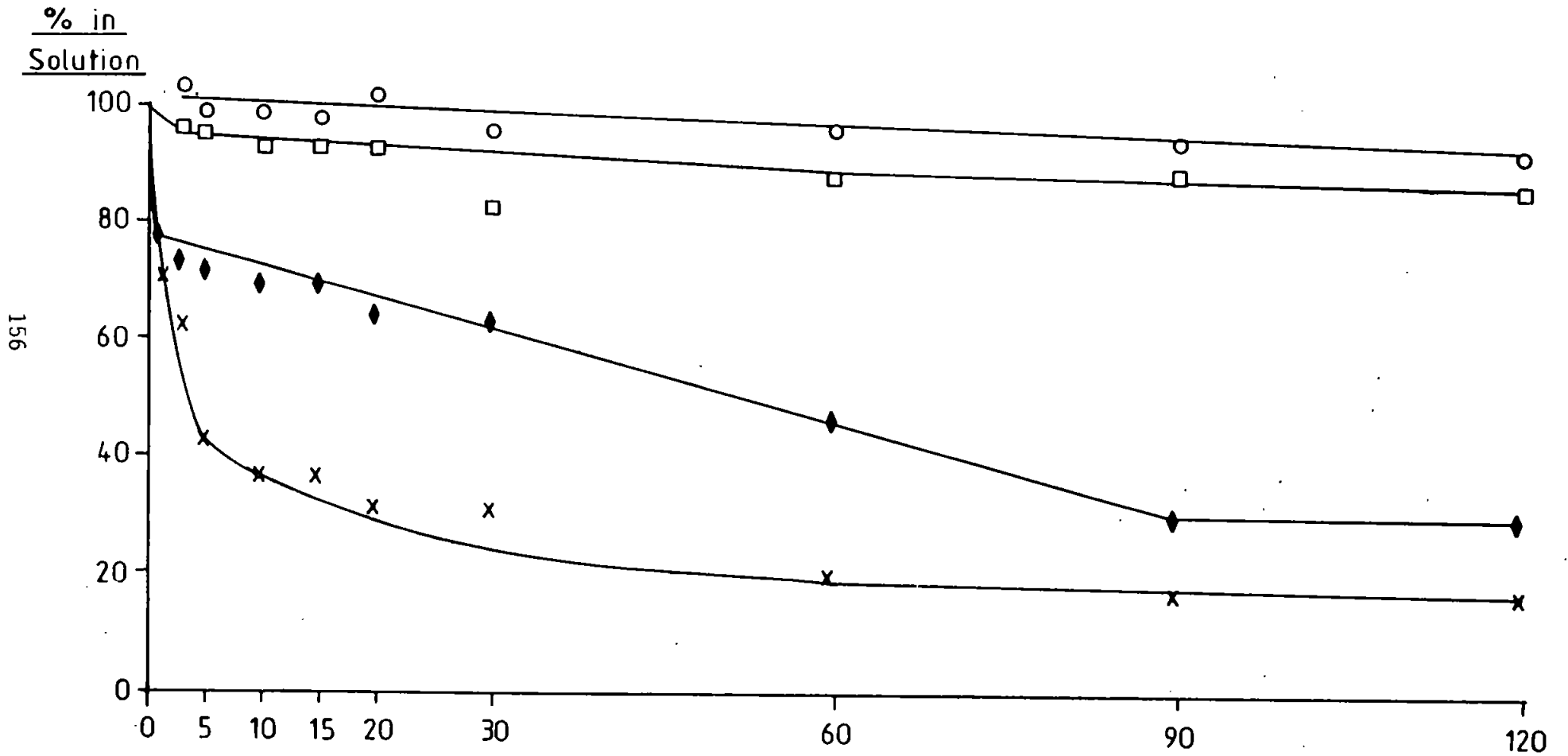
Figure 3.43 Adsorption profiles for dissolved copper with increasing turbidity
S = 10^0/oo, pH = 7.61.   O - 0 mg l^{-1}; □ - 10 mg l^{-1}; ♦ - 100 mg l^{-1} and x - 500 mg l^{-1}
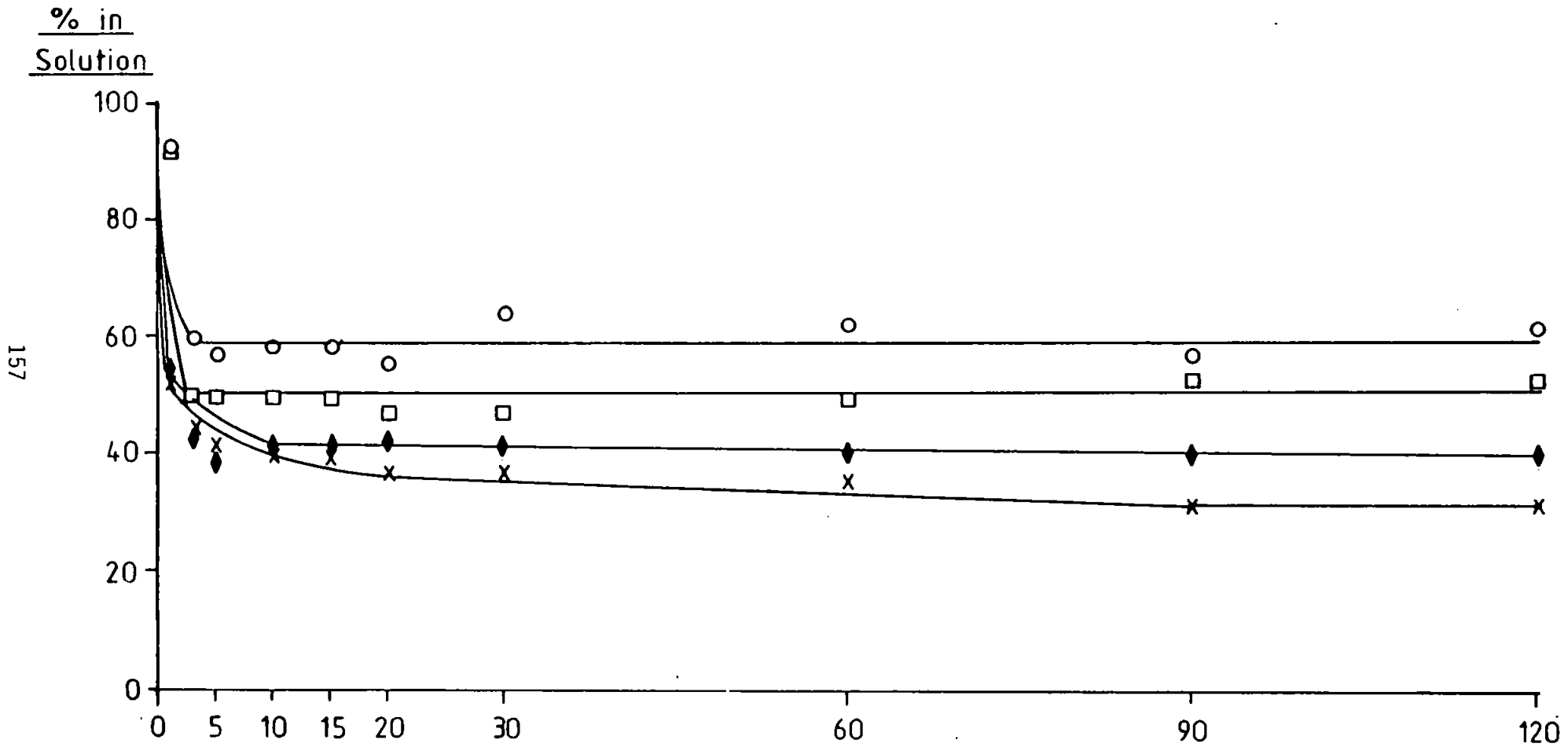
Figure 3.44   Adsorption profiles for dissolved zinc with increasing turbidity
S = 10^0/oo, pH = 7.61.   O- 0 mg l^{-1}; □- 10 mg l^{-1}; ♦- 100 mg l^{-1} and   x - 500 mg l^{-1}
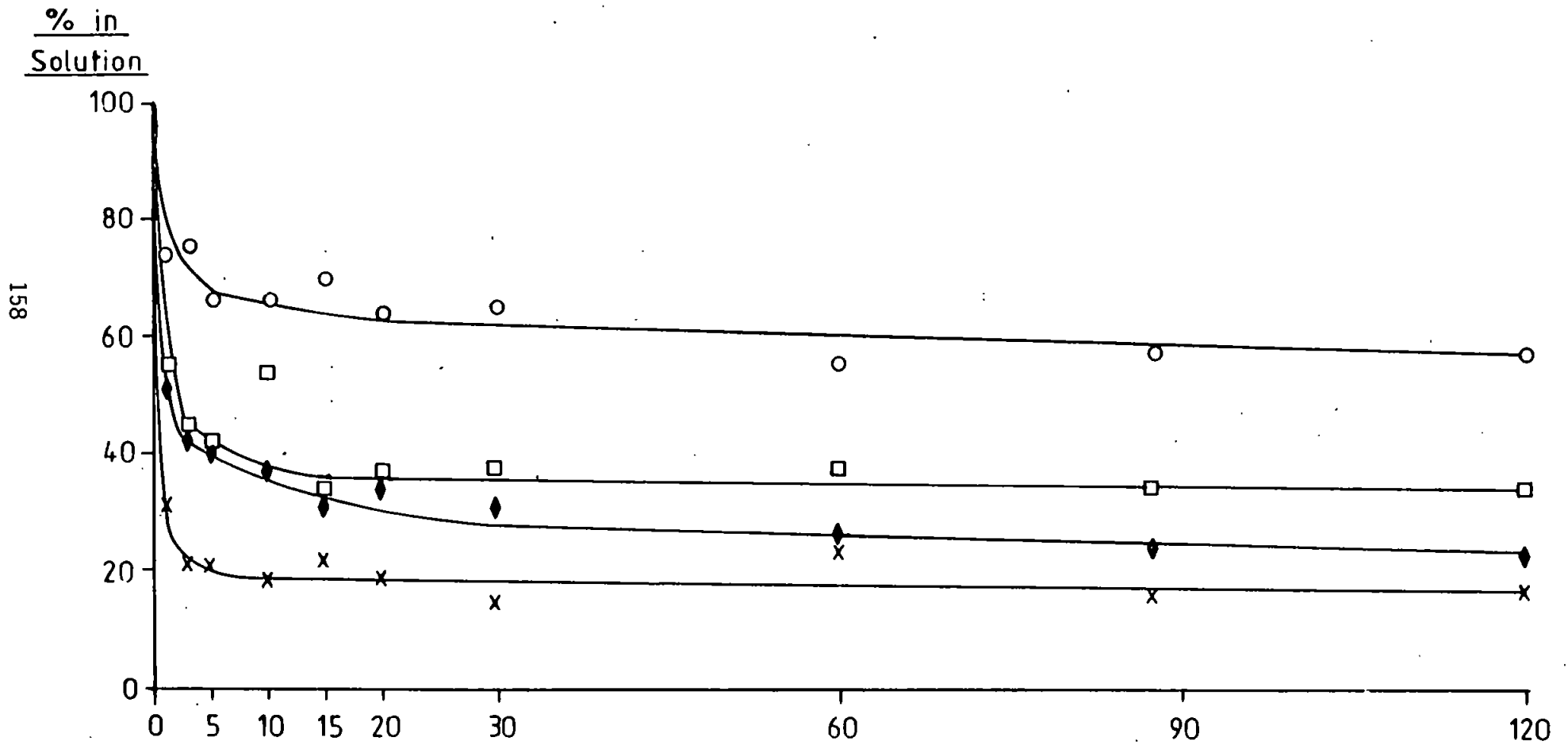
Figure 3.45   Adsorption profiles for dissolved copper with increasing turbidity
S = 1^0/oo, pH = 8.00.   O - 0 mg l^{-1}; □ - 10 mg l^{-1}; ♦ - 100 mg l^{-1} and x - 500 mg l^{-1}
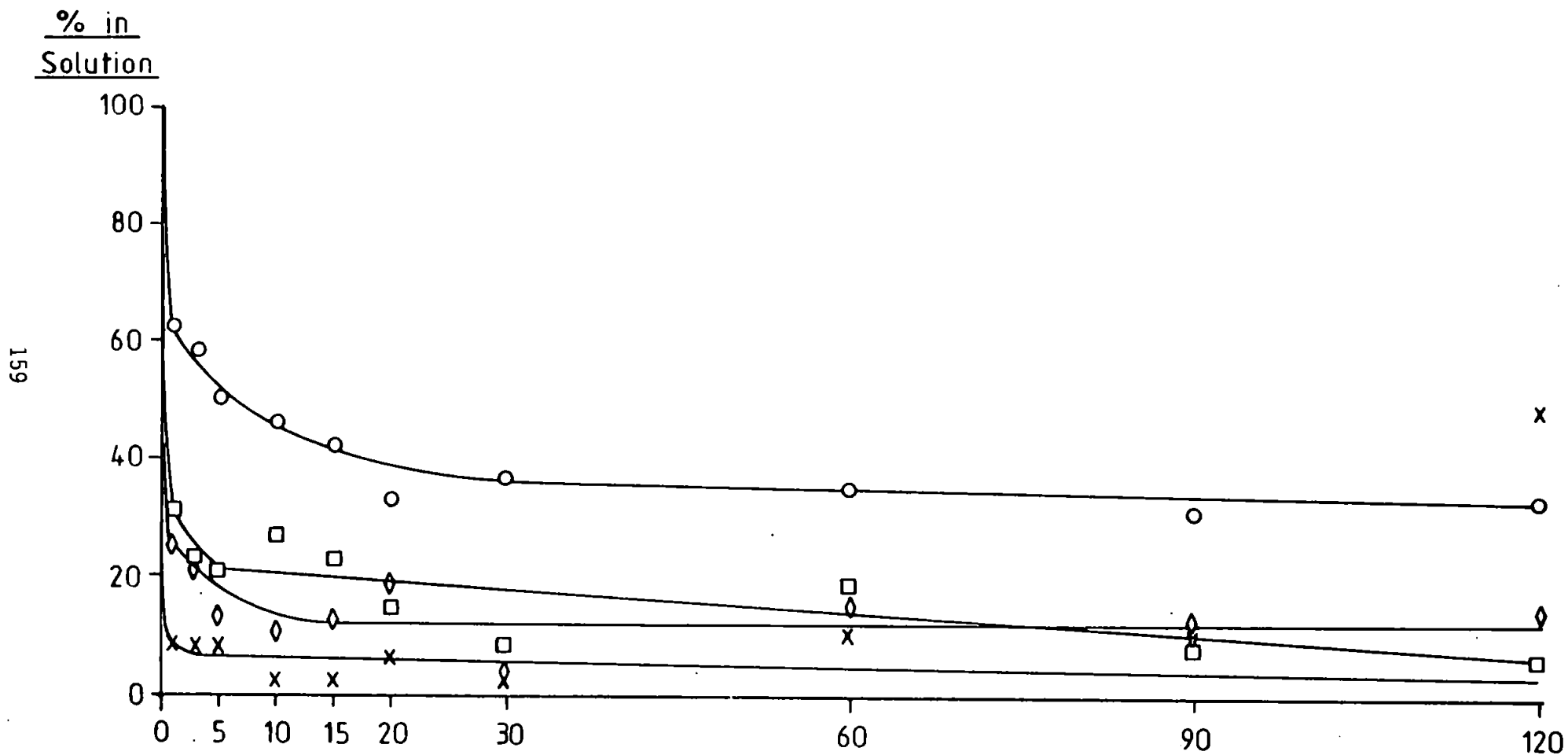
Figure 3.46 Adsorption profiles for dissolved zinc with increasing turbidity
S = 1^0/oo, pH = 8.00. O- 0 mg l^{-1}; □- 10 mg l^{-1}; ◊ - 100 mg l^{-1} and x- 500 mg l^{-1}

but at elevated pH values (pH = 8.0) and 1°/oo salinity. Both copper (Figure 3.45) and zinc (Figure 3.46) showed pronounced removal in the 0 mg 1^{-1} experiment. Again, this could be due to the presence of humic material removing the dissolved metals. Increasing adsorption was observed with increasing turbidity, but not by proportion.

As the results showed quasi-equilibrium conditions as a function of turbidity, the data was tested against three possible first and second order reversible reactions;

$$A \rightleftharpoons X$$
$$A + B \rightleftharpoons X + Y$$
$$A + B \rightleftharpoons X$$
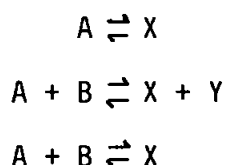
where A and B were species of copper and zinc in solution and X and Y were adsorbed forms of the metals. The integrated forms of the rate equation (Swinborne, 1971) were plotted as a function of time. In no case, for any of the above mechanisms, was linearity observed in these plots. These simple reactions, therefore, could not account for the observed data, which suggests the reaction was complex, possibly involving a multi-stage reaction. The value of this work was that time-scales of the adsorption could be estimated, and the quasi-equilibrium conditions assessed. As previously stated, initial adsorption was rapid, in the order of twenty minutes, this is comparable to mixing timescales in the low salinity region and therefore an important process in the cycling of copper and zinc through the F.B.I.

Figure 3.47 showed the adsorption of copper and zinc at equilibrium in the freshwater at natural pH (pH = 7.6) as a function of turbidity.

Figure 3.47   Profile showing the adsorption at equilibrium of
dissolved copper and zinc in the freshwater and
freshwater turbidity maximum conditions

●- dissolved copper and □- dissolved zinc

The zinc adsorption data was found to be compatible with that obtained by Salomons, (1980) who showed that 80-90% dissolved zinc was removed by a turbidity of 500 mg l^{-1} of natural particulates. A conspicuous difference was observed between the adsorption of copper and the adsorption of zinc. Copper was consistently adsorbed more than zinc over the range of turbidities at a fixed pH. This was due to the difference in the pH of onset of hydrolysis; copper hydrolysis begins at a lower pH than zinc. Work by Millward and Moore, (1982) on adsorption onto iron oxyhydroxides showed that at pH = 7.5 approximately 90% of the copper was adsorbed, in good agreement with the present work. Copper has a pH_{50} (pH for 50% retention) = 5.5 (Millward and Moore, 1982) whereas zinc has a pH_{50} = 6.3 so that copper adsorption would always be favoured.

Figure 3.48 depicts the percentage of copper adsorbed at equilibrium with increasing turbidity, pH and salinity. Above 100 mg l^{-1} turbidity, adsorption appeared to be independent of salinity and pH, in good agreement with some aspects of the study by Millward and Moore, (1982). There was some variation at low turbidities and natural pH for the range of salinities. The percentage adsorption was found to be much lower than in the high pH experiments except for at 10^{0}/oo. This remains an unresolved problem.

For zinc (Figure 3.49) adsorption was less at high salinities than in freshwater in all ranges of turbidity at the higher pH (pH = 8.0). The natural pH profiles appeared to be more complex. At high turbidities the salinity reflects similar behaviour to the high pH. However at lower turbidities these profiles appeared to be reversed. This also remains an unresolved problem.

Figure 3.48   Profile showing dissolved copper adsorption versus
turbidity with variation in salinity and pH.
Natural pH; ● - 0°/oo, ■ - 1°/oo and ◆ - 10°/oo
pH = 8.00;   ○ - 0°/oo, □ - 1°/oo and ◇ - 10°/oo

Figure 3.49   Profile showing dissolved zinc adsorption versus
turbidity with variation in salinity and pH.

Natural pH; ● - 0^0/oo, ■ - 1^0/oo and ◆ - 10^0/oo

pH = 8.00;   O - 0^0/oo and ◊ - 10^0/oo

Figure 3.50 shows the profile for the three copper desorption
experiments performed on suspended particulates at a turbidity of
500 mg l^{-1} with varying salinities and at the natural pH = 7.6 The
profiles for copper indicated that desorption appeared to be independent
of salinity, when considering the scatter of the data, desorption was
in the range 5-15% for the range of salinities. The copper desorption
appeared to be fairly independent of salinity in agreement with
Millward and Moore, (1982) who found no salinity variation.

Figure 3.51 shows zinc desorption was clearly salinity dependent, in
agreement with Grieve and Fletcher, (1977). This work, in agreement
with Millward and Moore, (1982) found that adsorption was also a
function of salinity, the adsorption therefore appears to be reversible
with changes of salinity and thus more open to addition/removal
reactions in the estuary. The desorption was found to vary from 5%
in freshwater to 18-20% in brackish water (10°/oo).

3.3.2   The Significance of the Adsorption/Desorption Studies

The adsorption of copper and zinc in freshwater was found to be
turbidity dependent. Removal must therefore occur in the freshwater
region of the turbidity maximum upestuary of the F.B.I., as reported
by Morris, et al., (1978) and Knox, et al., (1981). The zinc
adsorption characteristics were very similar to those found by Salomons,
(1980) and also for copper and zinc adsorption onto iron oxyhydroxides
(Millward and Moore, 1982). An attempt was made to rationalise the
adsorption/desorption processes occurring in the estuary, particularly
at the F.B.I. Assuming; a range of S.P.M. of 10-100 mg l^{-1}; a value
of 250 µg g^{-1} for non-detrital zinc levels, and a desorption level of
10%, the dissolved zinc concentrations in the region of the F.B.I.
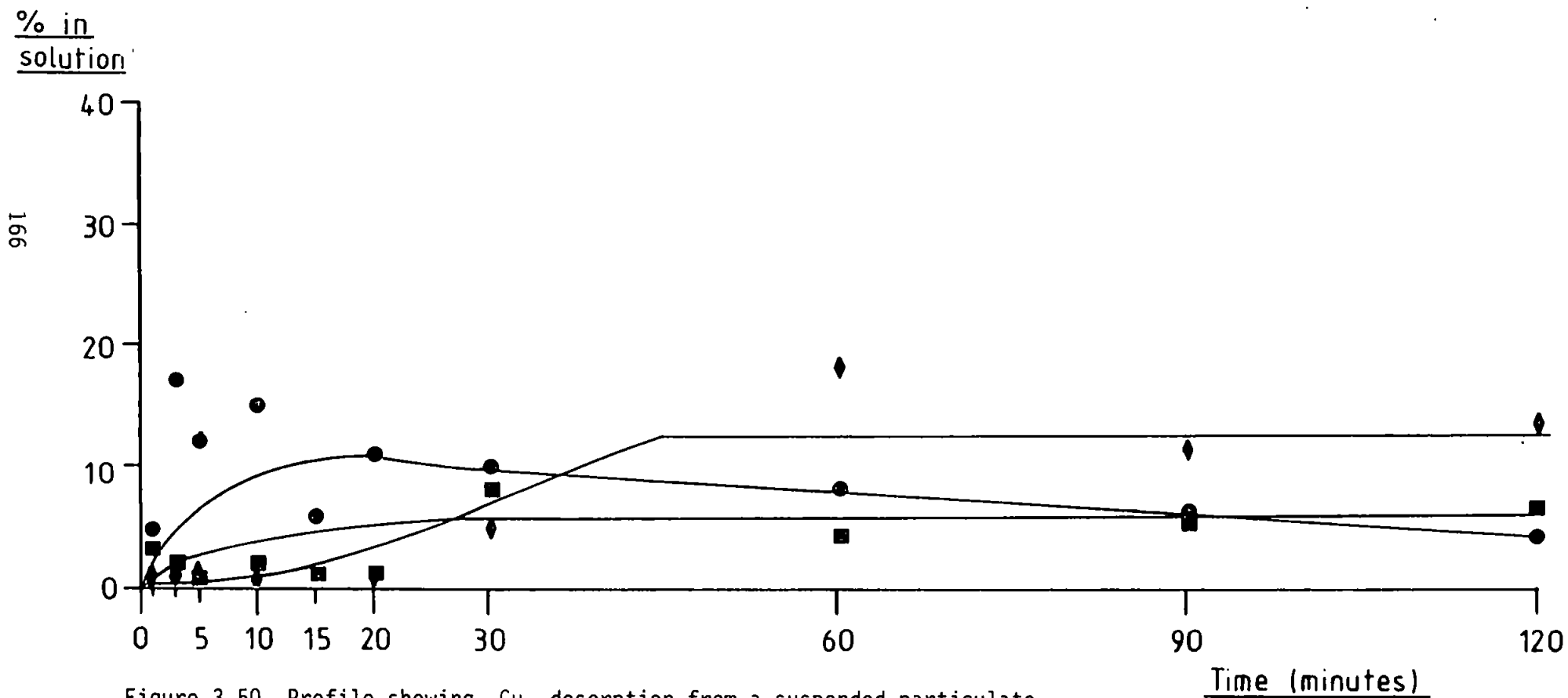
Figure 3.50   Profile showing Cu desorption from a suspended particulate
load of 500 mg 1^{-1} under varying conditions of salinity

■ - 0^0/oo,   ♦ - 1^0/oo and   ● - 10^0/oo
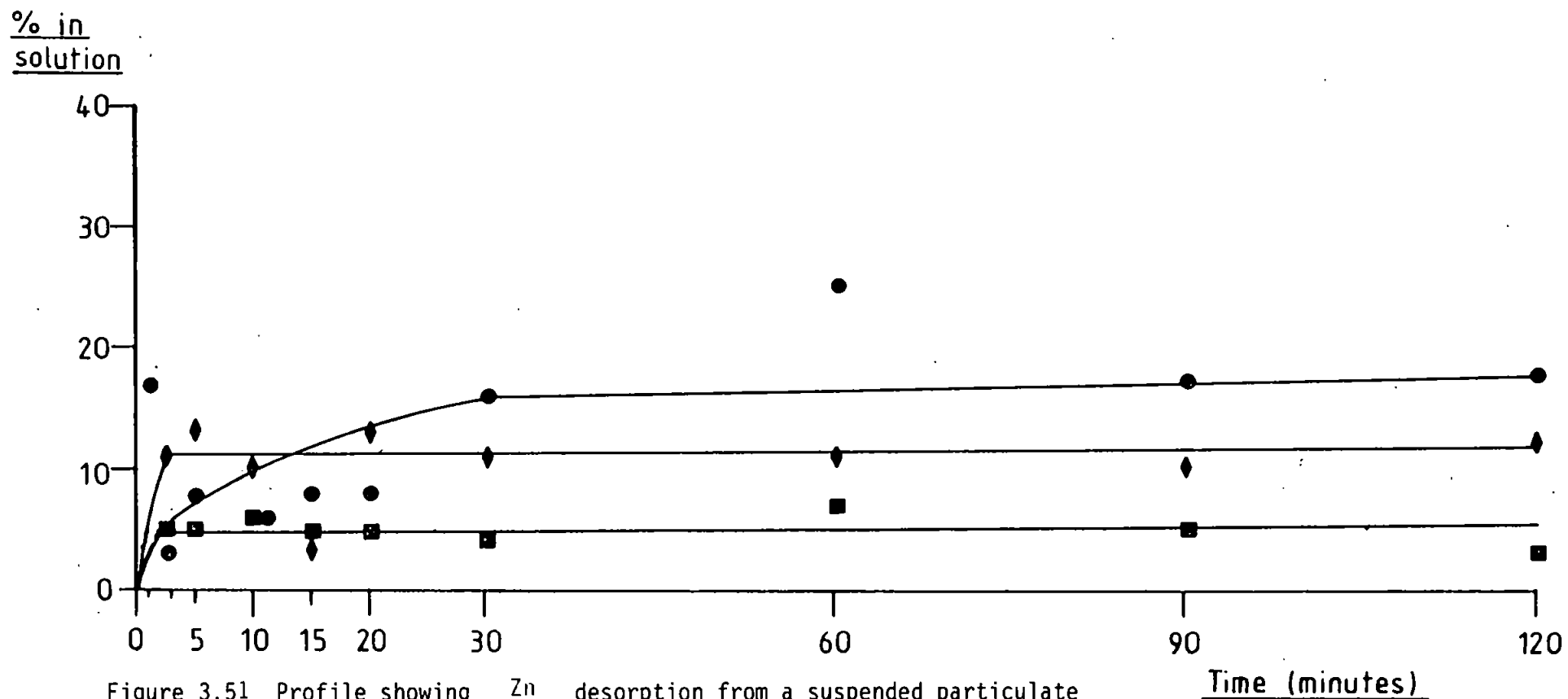
Figure 3.51 Profile showing ^{Zn} desorption from a suspended particulate load of 500 mg l^{-1} under varying conditions of pH and salinity

■ - 0^0/oo, ♦ - 1^0/oo and ● - 10^0/oo

could have been enhanced by 0.3 to 3 µg 1^{-1}, purely by a desorption process.

Assuming that the mechanisms of desorption from S.P.M. and pore water infusion are producing zinc peaks in the region of the F.B.I., the profiles depicting the master variables and dissolved metals (Figures 3.25-3.34) were re-examined to assess whether one or both of the processes could account for the dissolved zinc peaks observed at the time of the survey. Figures 3.27 and 3.28 showed conditions under a spring tide and low river flow giving a high turbidity maximum (and thus pore water release) together with an observed dissolved zinc peak of 9 µg 1^{-1}, at $S = 10^{0}$/oo. The calculations given in section 3.2 suggest that the pore waters could contribute between 2 and 9 µg 1^{-1} of zinc. Therefore under these flow conditions the pore waters alone could supply the additional zinc. In contrast, Figures 3.29 and 3.30 show a condition of high river flow and neap tide with a small turbidity maximum (therefore low pore water infusion), but high riverine particulate load. The dissolved zinc peak at the F.B.I. was of the order of 25 µg 1^{-1} at $S = 5^{0}$/oo. It is suggested that in this case contributions from both pore waters and desorption would be needed to account for the additional zinc. In this case the input from the pore waters may have been greater than anticipated, as the desorption process could only supply about 3 µg 1^{-1}.

Similar calculations were undertaken for copper desorption from suspended particulates containing 130 µg g^{-1} of non-detrital copper. A contribution of 0.1 to 1.3 µg 1^{-1} attributable to the desorption of copper from S.P.M. was obtained. Occasionally dissolved copper peaks of a few µg 1^{-1} were observed in the low salinity region

168

(see Figures 3.26; 3.30; 3.32) which could be explained by the desorption mechanism. However, further discussion of the dissolved copper data can only be achieved when reliable values for copper in pore waters are available.

In conclusion, both the pore water infusion and the desorption mechanisms could make important contributions to estuarine dissolved metal maxima, but further work is necessary to ascertain the relative importance of these two processes.

3.4   ESTUARINE SUSPENDED PARTICULATE MATTER

3.4.1   Behaviour of Non-detrital and Detrital Copper, Iron,
        Manganese and Zinc in the S.P.M.

Zones of turbidity maximum have been reported in many estuaries (Schubel,

1968; Sundby and Loring, 1978; Sholkovitz, 1979; Sholkovitz and Price,

1980; Loring, et al., 1982). Sholkovitz, (1979) discussed the chemical

and physical processes which might control the composition of suspended

particulate matter (S.P.M.) in estuaries. The purpose of the data

presented here is to assist in the general description of the estuarine

chemistry of the Tamar and also for inclusion into the two-box model

(see Section 4.1). Details of the variation in composition of S.P.M.

in the Tamar during individual surveys are discussed elsewhere (Loring,

et al., 1982). The results presented here are of data collected over

a number of surveys and presented in a manner that describes the

relationship between heavy metal content in the S.P.M. at increasing

turbidity levels in comparison to the average sediment metal levels,

thus indicating enrichment or removal behaviour in the two components.

The sediments and S.P.M. were analysed using similar digestion techniques

(see Section 2.3) thus enabling valid intercomparisons to be made.

Figures 3.52 to 3.55 depict the non-detrital and detrital composition

of the S.P.M. in the Tamar Estuary. Four distinct particle

sub-populations were recognised;

    (i)   particles of riverine origin (open circles,
       suspended load < 5 mg 1^{-1})

    (ii)   particles of immediate marine origin (closed circles,
       suspended load < 5 mg 1^{-1})

    (iii) particles re-suspended from the sediment (suspended
       load > 500 mg 1^{-1})
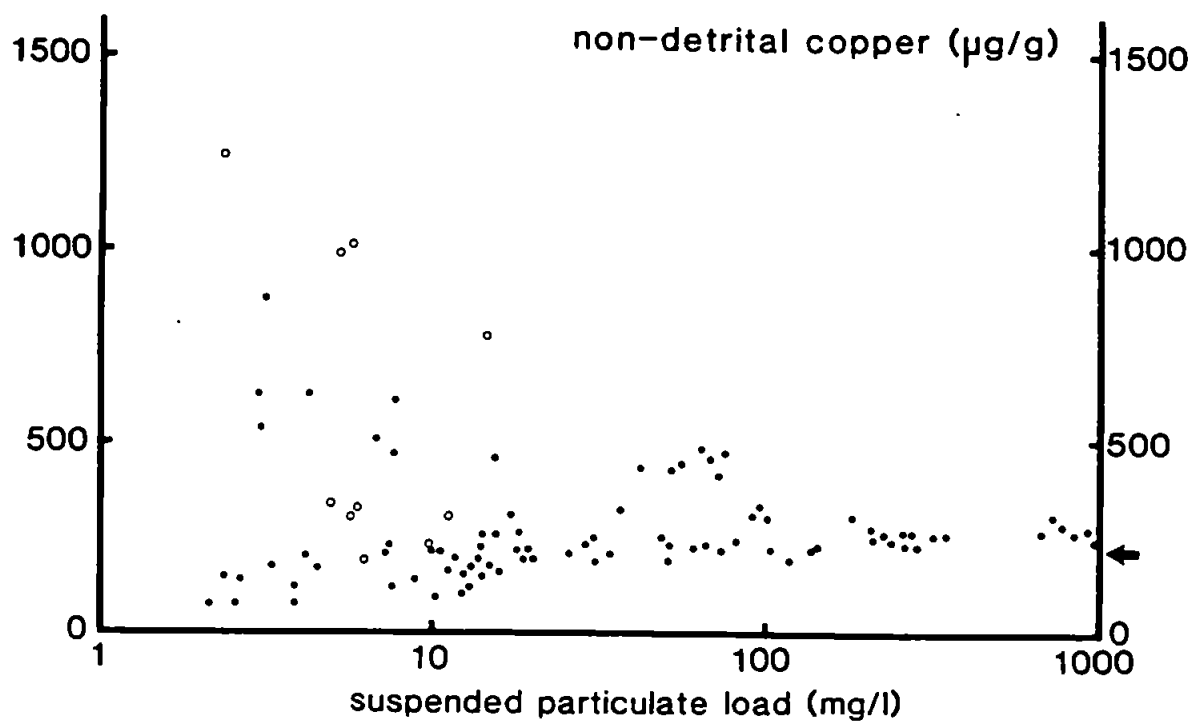
Figure 3.52a   Non-detrital copper in suspended particulates
as a function of turbidity
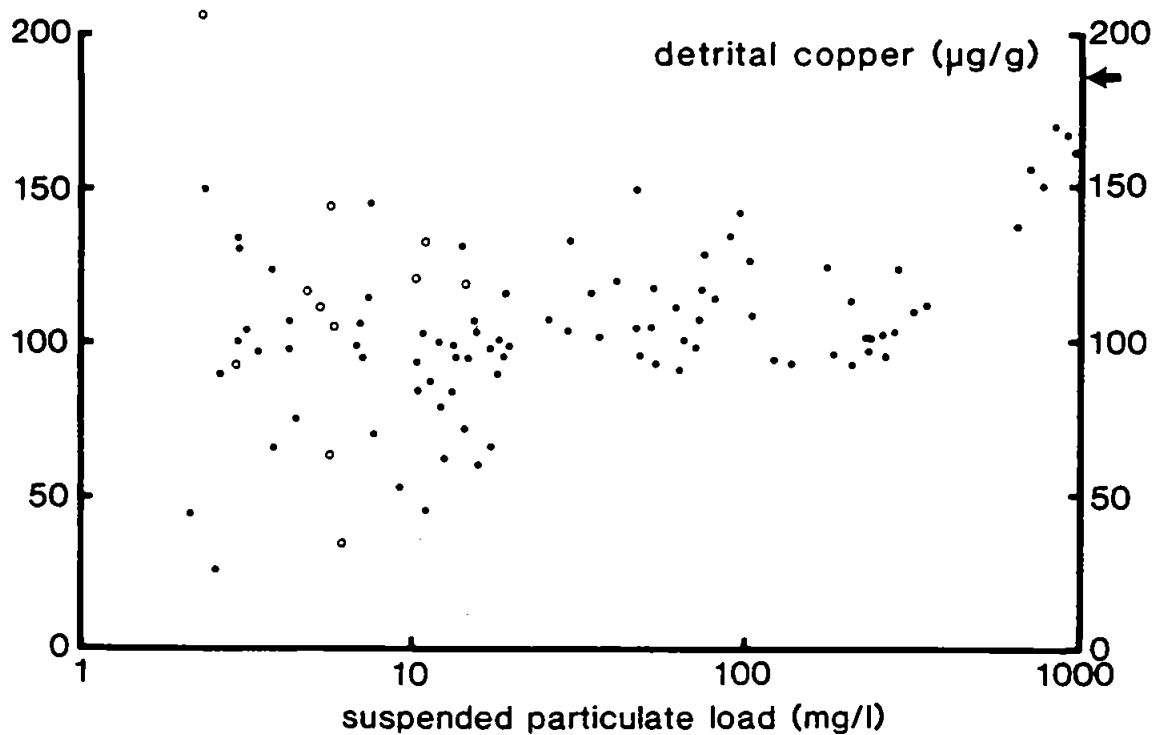
Figure 3.52b   Detrital copper in suspended particulates
as a function of turbidity
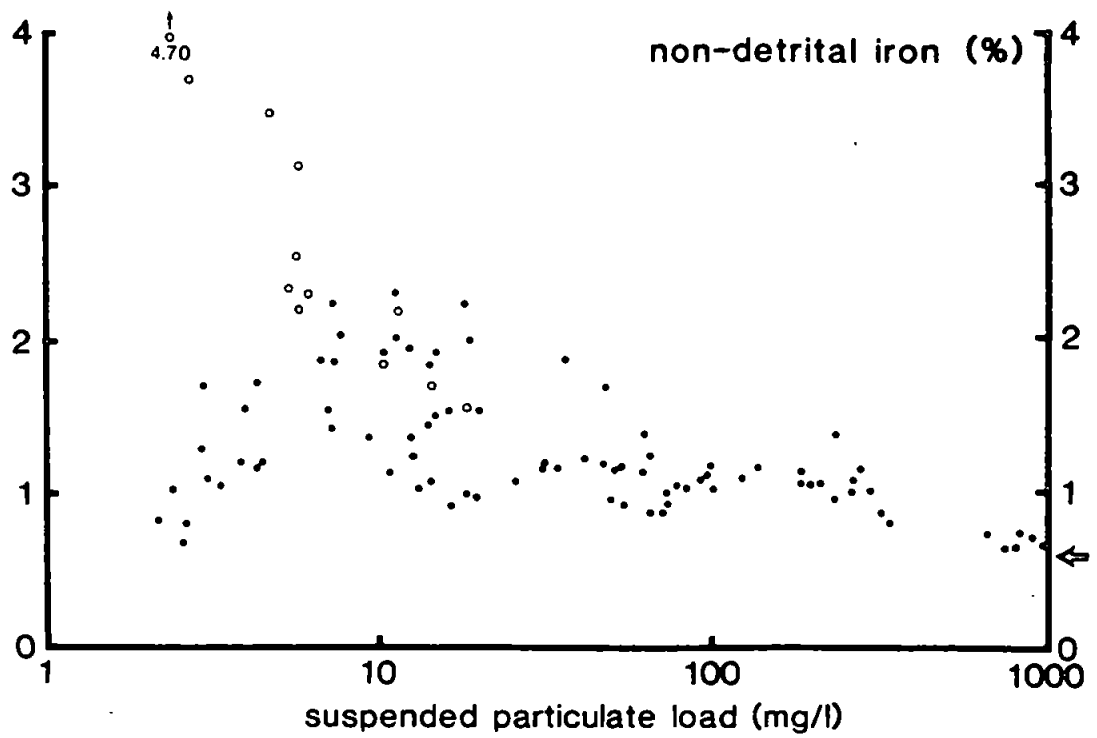
Figure 3.53a   Non-detrital iron in suspended particulates
as a function of turbidity
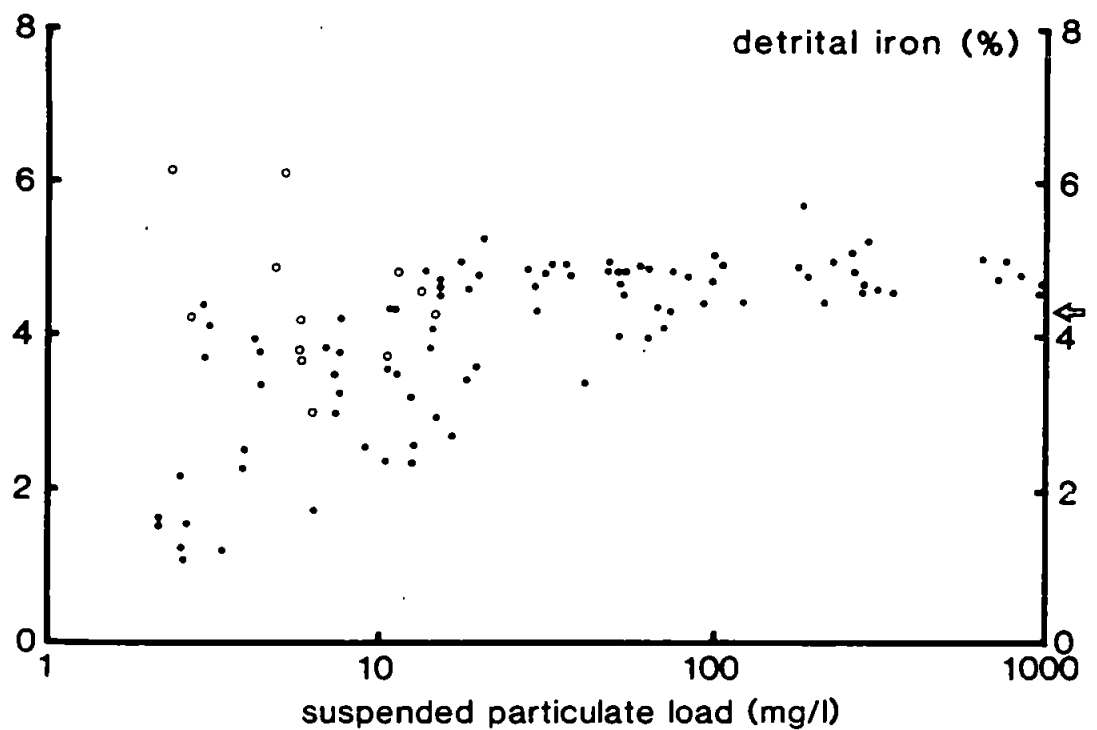
Figure 3.53b   Detrital iron in suspended particulates
as a function of turbidity
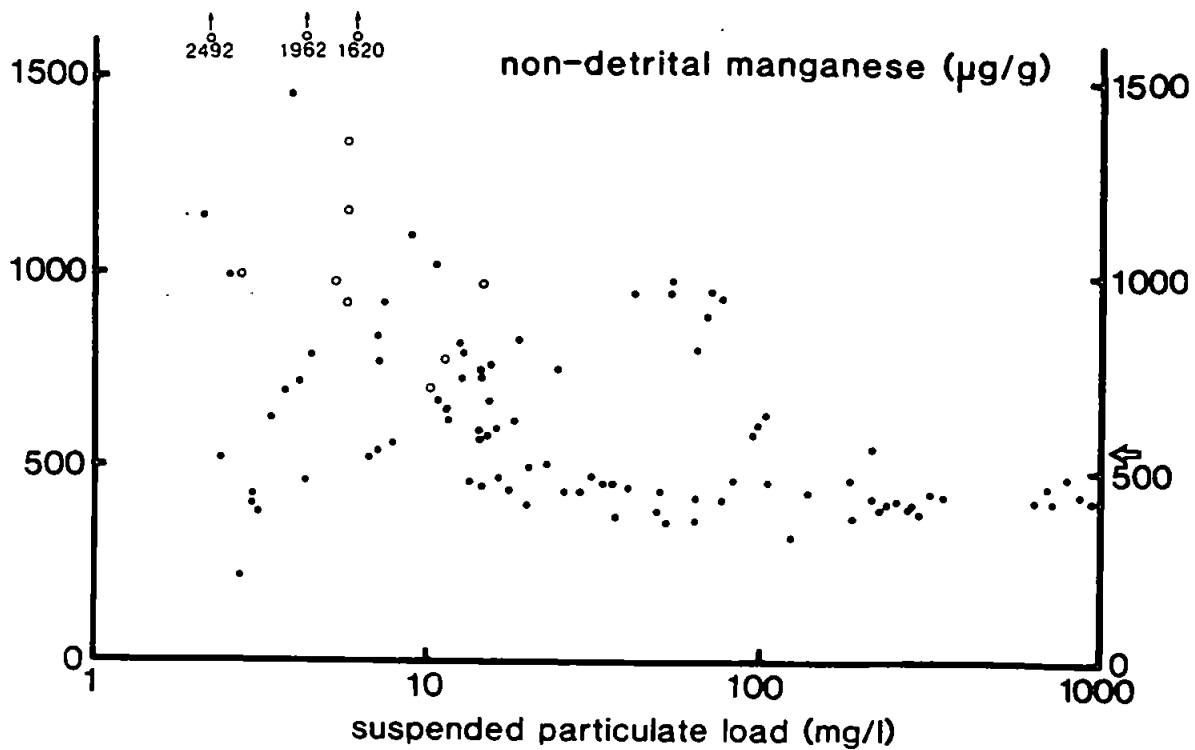
Figure 3.54a   Non-detrital manganese in suspended particulates
                as a function of turbidity
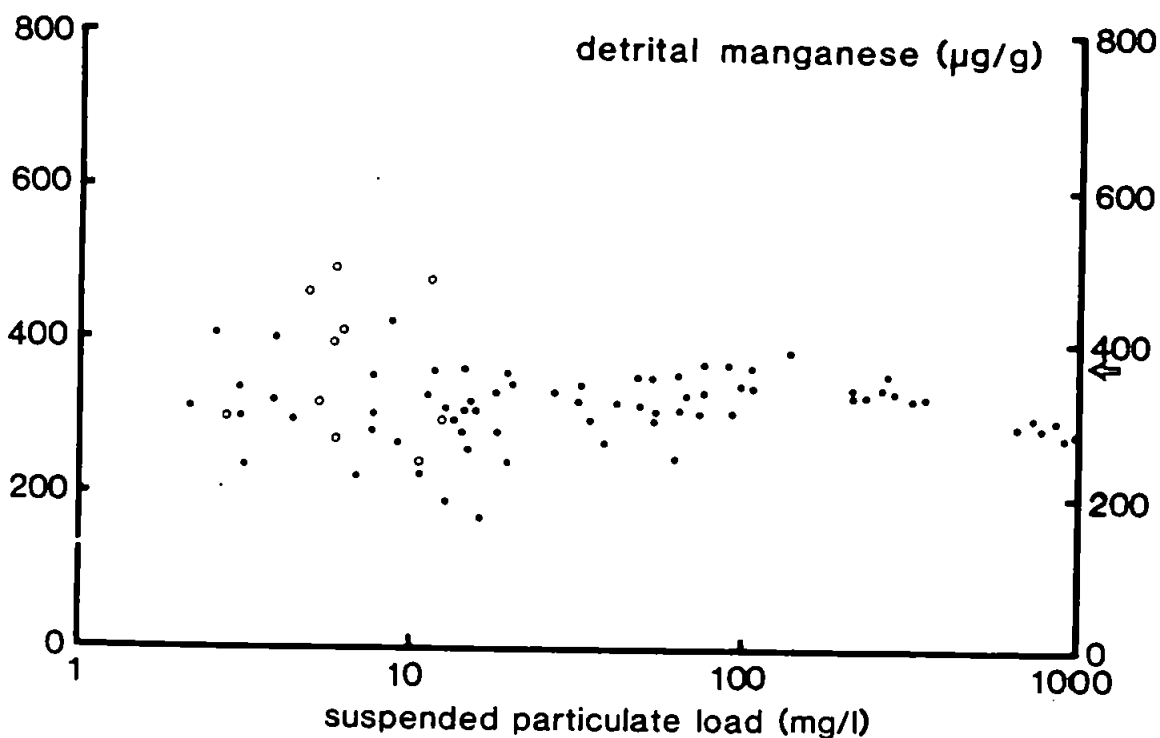
Figure 3.54b   Detrital manganese in suspended particulates
                as a function of turbidity

173
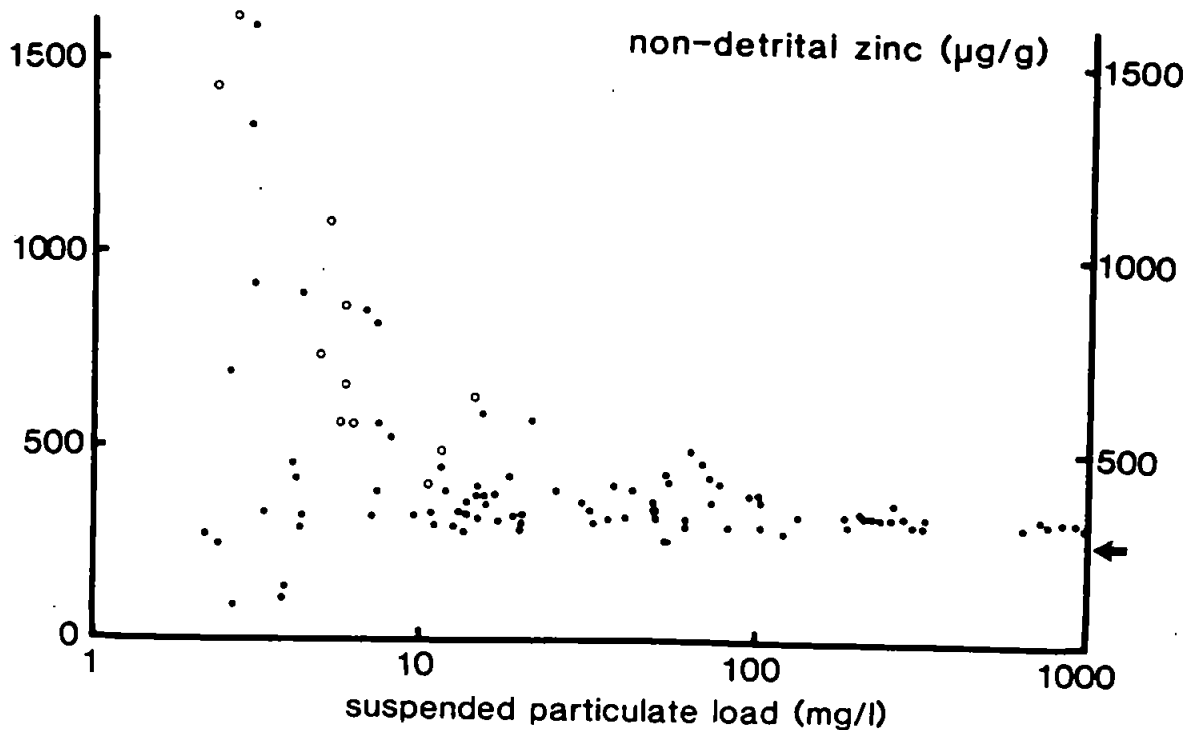
Figure 3.55a   Non-detrital zinc in suspended particulates
                as a function of turbidity
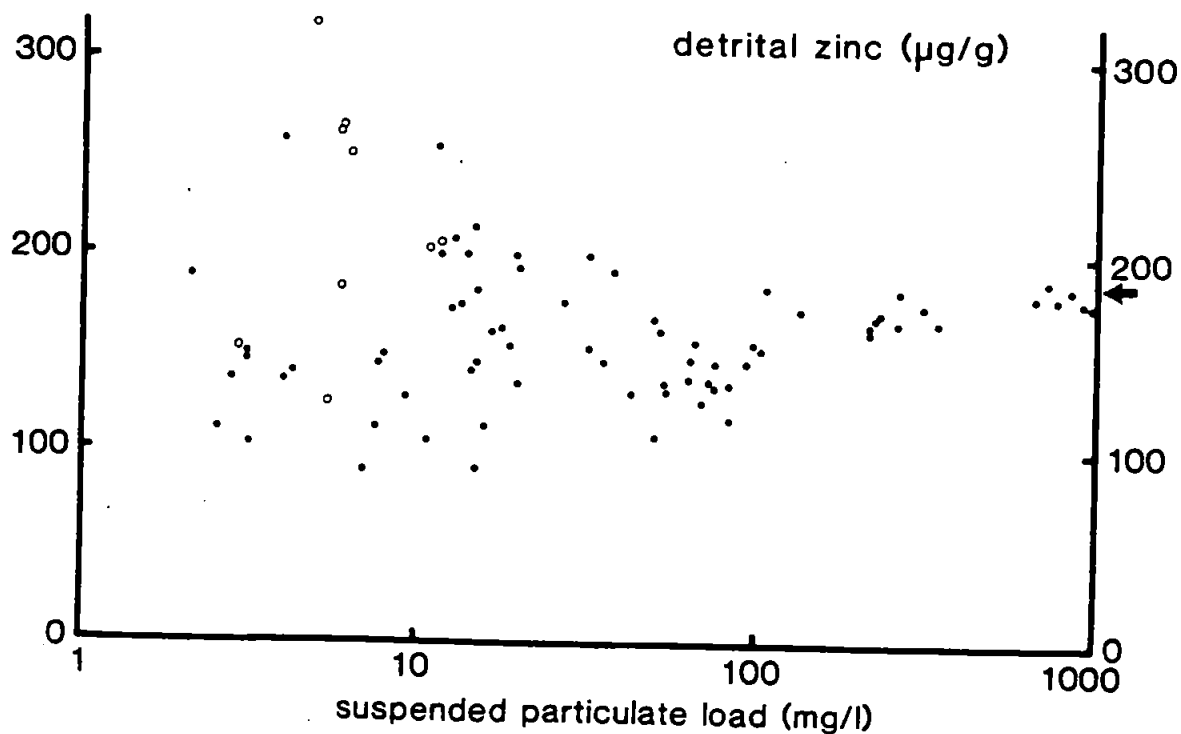
Figure 3.55b   Detrital zinc in suspended particulates
                as a function of turbidity

174

(iv)   more or less permanently suspended estuarine

particles (suspended load 5-500 mg l^{-1}).

The average estuarine sediment composition is indicated by the arrow

on the right-hand axis. The conclusions presented here are tentative

as the work is still under review.

Figure 3.52 showed the profiles for non-detrital (part a) and detrital

(part b) copper levels. The non-detrital freshwater levels were high

and variable, indicating inputs of fresh copper-rich particles into

the system. This information corroborates the hypotheses from Figure

3.21 where increased metal levels were observed at the head of the

estuary with high river-flow rates. Marine levels were also found to

be high and variable. The copper concentration of the high suspended

load was very closely related to the estuarine sedimentary levels.

Some enrichment could possibly be present in the estuarine S.P.M.,

but the evidence was not overwhelming. Part b showing the detrital

fraction indicated conspicuous differences to the non-detrital profile.

All the four sub-populations were depleted in copper with respect to

the sediment value. Conversely, the sediment was enriched in detrital

copper showing accumulation in the estuarine sediments. This part-

itioning could be due to the heavy mineral physically settling out

of the water column and remaining as a constituent part of the sediment.

Figure 3.53a showed the profile for non-detrital iron, again there

appeared to be inputs from the riverine system, in good agreement with

Figure 3.22. The iron levels in the S.P.M. were enriched in comparison

to the general sediment levels, this could be due to adsorption of diss-

olved iron from the estuarine water or, more likely, the formation of iron

colloidal material. The detrital levels (part b) tended to be variable in

freshwater and low in the marine particulates. The mid- and highest turbidity populations had levels which fell within the range of sedimentary values.

Figure 3.54 for the two manganese fractions depicted behaviour consistent with that discussed by Duinker, et al., (1979). The non-detrital (part a) riverwater fraction was high relative to the estuarine levels, indicating a source of input during spate conditions, a feature already described in Figure 3.23. The marine levels were low whereas the estuarine concentrations were elevated when compared with the superficial sediment. The detrital (part b) manganese levels in marine, riverine and mid-estuarine S.P.M. were similar and consistent with sediment levels.

Figure 3.55 showed non-detrital (part a) and detrital (part b) levels of zinc. The riverine non-detrital zinc was high, consistent with an input to the estuary (Figure 3.24), marine non-detrital inputs were variable. The estuarine levels were slightly enriched with respect to the surficial sediments, although there was no distinct trend. The higher turbidities had zinc levels consistent with those of the sediment. Both riverine and marine detrital (part b) values were highly variable, the estuarine S.P.M. showed levels which were similar to those in the surficial sediment.

In summary, non-detrital iron and manganese appeared to be accumulating in S.P.M., whereas detrital copper was accumulating in the sediment. Zinc in contrast showed a net loss of zinc-rich particles from the estuary.

176

CHAPTER FOUR

A TWO-BOX MODEL OF THE TAMAR ESTUARY

4.1 APPLICATION OF A TWO-BOX MODEL TO THE TAMAR ESTUARY

This section is concerned with an attept to rationalise the large amount
of field data by summarising it in the form of a two-box, steady-state,
model of the Tamar Estuary. This model is similar in conception to
that developed by Duinker, et al., (1979) and contains pathways of
importance to the model for the St. Lawrence Estuary (Sundby, et al.,
1981).

4.1.1. Construction of the Box Model

The estuary was divided into two with the upper box respresenting the
0-10°/oo salinity range. This division was made because, in general
terms, the chemical processes in the low salinity region were identified
with removal processes, whereas at higher salinities there was evidence
of remobilisation of the metals. An important feature of this two-box
model was to estimate the transfer of the metals between the upper and
lower estuary. The field data suggested that the hydrographic boundary
at S = 10°/oo would emphasise these transfers. The geographical
boundaries were; the weir at Gunnislake, 14 km from the weir (approxim-
ating to the position of the 10°/oo isohaline) and the bridges at
Saltash, 24 km from the weir. Ordnance Survey maps were used to deduce
the total area of sediment in each box.

The well-defined seasonality in the river-flow rate was obtained from
the South West Water Authority gauging station records taken at
Gunnislake Weir and the tidal influxes, Q, were obtained from a simple
diffusion model:-

$$QS + \frac{KA}{\Delta x} \, dS = 0$$

where at Saltash K (diffusion coefficient) = 100 m^2 s^{-1}; A (cross-sectional area) = 10^3 m^2; Δx (distance between the box mid-points = 15 x 10^3 m; S and dS (salinities determined from estuarine profiles). This gave a tidal flow of about 6 m^3 s^{-1} under neaps and about 10 m^3 s^{-1} during spring tidal regime.

Three surveys (July, October and December 1980) were selected for analysis since, on these occasions, there was a comprehensive data base of master variables and concentrations of copper, manganese and zinc were available for the dissolved and particulate phases. In the surveys selected, the sample collections were carried out simultaneously and the three occasions encompassed the ranges of both river-flow and tidal-flow rates.

Dissolved metal fluxes were calculated in kg $(month)^{-1}$ using mean monthly river-flows or appropriate tidal-flows and average dissolved copper, manganese and zinc concentrations. Subsidiary dissolved fluxes from sediment pore waters were calculated using published diffusion rates in the literature, with the understanding that these may not be strictly applicable to the Tamar Estuary (see discussion, Section 1.3.5). For Mn a value of 400 µg cm^{-2} yr^{-1} was used which had been deduced by Duinker, et al., (1979) for the Scheldt and represents a reasonable mid-point in the range of values available. A value of 2.6 µg cm^{-2} yr^{-1} was taken for Cu and 2.7 µg cm^{-2} yr^{-1} for Zn (Elderfield and Hepworth, 1975). The total pore water flux for each box was calculated using the values above and the total sediment area in each box.

The particulate metal fluxes were calculated from the mean monthly

river-flow or appropriate tidal-flow, the average suspended particulate load and the total metal content of the suspended particulate matter. Partitioning of the elements between the dissolved and particulate phases within each box was calculated by balancing the input/output budgets and assigning either adsorption or desorption fluxes for the dissolved phase and deposition or resuspension from the sediments to the particulate phase. It was thought that sediment transport (mainly as bed load) between the boxes could be important in the overall budget, however the sediment mass transport studies were not undertaken until two years after the 1980 surveys. These observations, as they were not concurrent with the fieldwork, could not properly reflect the conditions in the surveys discussed here. However, the sediment mass transport values given in Table 4.1 provide estimates which can be used together with sediment metal concentrations to calculate potential sediment metal fluxes. These can be compared with those determined for the box model.

Table 4.1 Observed Sediment Flux Calculations for the Tamar Estuary

Date	Upper Box kg (month)$^{-1}$	Lower Box kg (month)$^{-1}$	Average River Flow m^3 s^{-1}
July 1982	Gain 1.9 x 10^6	Gain 2.8 x 10^6	6.4
Oct 1982	Loss 7.7 x 10^6	Gain 1.3 x 10^5	51.5
Dec 1982	Loss 4.8 x 10^6	Gain 4.8 x 10^6	69.0

The magnitudes of the fluxes in the box models were examined and consideration was given to presentation of the data to two significant figures. This has not been done in thise case because of the need to preserve the numerical balance in the model. The dilemma is best

exemplified by Figure 4.4 where the fluxes cover approximately two orders of magnitude. Therefore, it should be noted that the values ascribed to the largest fluxes are not intended to reflect the analytical precision of the measurements.

4.2   BOX MODEL CALCULATIONS FOR COPPER, MANGANESE AND ZINC

4.2.1   Copper

Figure 4.1 shows the box model for a summer survey with low river-flow
and neap tide. The riverine input into the system was dominated by
the dissolved phase although the losses from the estuary were equally
divided between the dissolved and solid phases. Copper adsorption and
re-suspension in the upper box gave an increased particulate flux into
the lower estuary, where an additional adsorption onto the particulates
was important to the accumulation of 90 kg Cu $(month)^{-1}$ in the sediments.
The tidal incursion of both dissolved and particulate copper from the
lower box was < 10% of the downestuary flux. A general conclusion from
this model was that a loss in dissolved and particulate copper from the
upper box led to an accumulation in the sediments of the lower box. Data
from the 1982 sediment mass transport study and total copper concen-
trations from the July 1980 sediment survey showed that approximately
870 kg Cu $(month)^{-1}$ was deposited in the upper box, whilst 1000 kg Cu
$(month)^{-1}$ was deposited in the lower box.

At this point, note should be made of the large discrepancies between
the observed and calculated sediment movements. Three factors need
to be taken into account:

(i)   the sediment mass transport study (1982) was carried out under
different hydraulic conditions to the sediment sample collection (1980)

(ii)   no estimates were obtained for the injection of particulate
copper into either box from small tributaries or streams. In a
mineralised area such as the Tamar Valley these inputs could be important
but would warrant a separate study.

Upper Box　　　　　　　**Lower Box**

80　　　　　　　　　　80　　　　　　　30

20

30　　　　　　　　50

10　　　　　　　　70　　　　　　　20

10　　　　　20　　　　10

20　　　　　90

183

Weir

14 km

Saltash
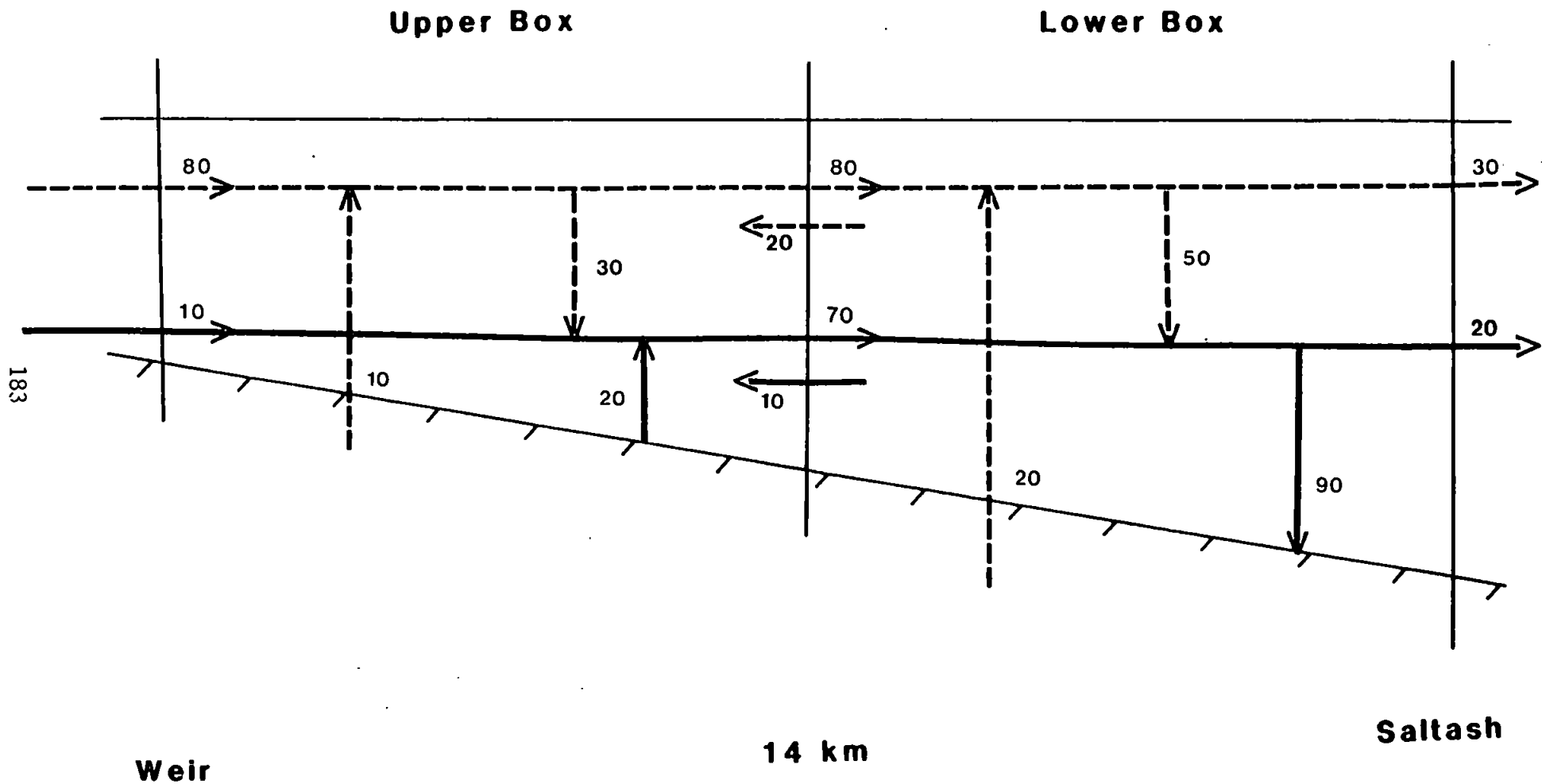
<u>Figure 4.1</u>　Box model for copper, July, 1980

River-flow rate = 9 m³ s⁻¹, neap tide. Fluxes in kg (month)⁻¹;—— dissolved flux, —— particulate flux

(iii) a problem existed with accurate determination of the particulate
flux. This stemmed from the fact that the suspended matter determin-
ations were made at the surface of the water, using the constant head
flow cell. Clearly, under certain flow conditions, there would be
large variations in suspended particulate concentrations with depth.
During stratified conditions in the summer it was quite possible that
considerable quantities of particulate material were moving as bed load.
In the case of high river-flow rates, with a more turbulent regime, the
water column could be well mixed and thus this problem would diminish
in importance. In the summer condition therefore, the particulate
fluxes obtained were probably underestimates and comparison of the
model sediment flux data with the experimental values could be improved
if the total particulate flux in the water column were available.
Nevertheless, the one notable feature of Figure 4.1 is that the estuary
appeared to be a trap for particulate copper during conditions of low
river-flow.

The summer model can be contrasted with Figure 4.2 which corresponds
to conditions of high river-flow and neap tide. Although the dissolved
phase input was of major importance, an increase in both dissolved and
particulate copper was associated with the increased river-flow, a
feature which was previously examined using the 3-dimensional profiles
(see Section 3.1.4). Adsorption onto the particulates was again an
important process in the upper box, with an increased re-mobilisation
from the sediment. Movement into the lower box was influenced by
particulate input, due to high turbidities generated in the upper box.
Movement upestuary due to the tidal incursion was approximately 20% of
the downestuary fluxes in both fractions. In the lower box, over 50%
of the dissolved input was adsorbed onto the particulates, the remainder

184

Upper Box

Lower Box

370

240

110

160

20

130

270

530

290

10

60

40

20

330
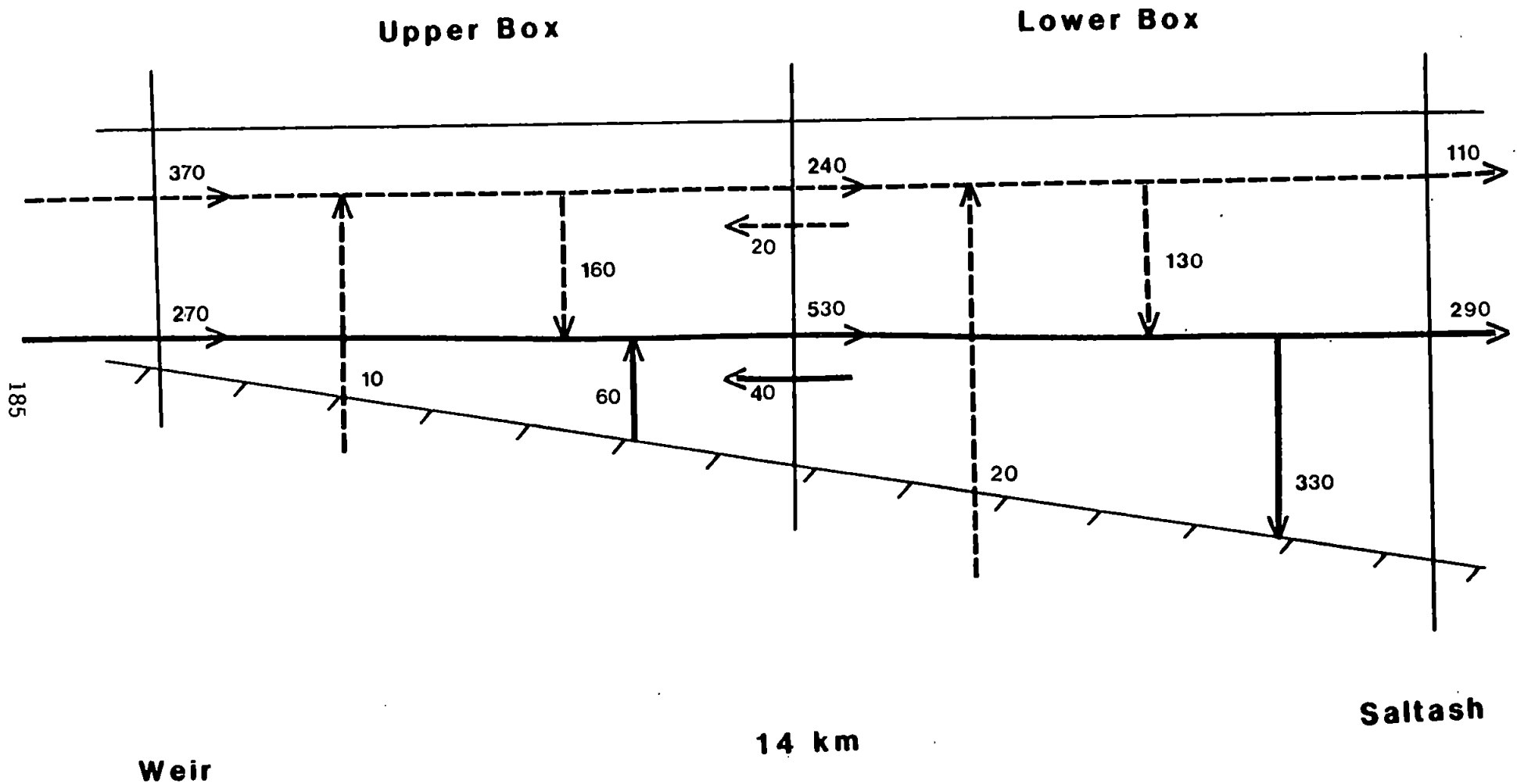
Saltash

14 km

Weir

Figure 4.2   Box model for copper, October 1980

River-flow rate = 40 m³ s^{-1}, neap tide.   Fluxes in kg(month)$^{-1}$; — — dissolved flux, —— particulate flux

was lost from the estuary, together with half the particulate input. A large proportion of the copper in the suspended particulate phase was removed to the sediment. The overall impression was of a particulate dominated model as a result of increased river-flow. A net loss of 60 kg Cu $(month)^{-1}$ from the sediment in the upper box was observed with a gain of 330 kg Cu $(month)^{-1}$ in the lower box, in agreement with the 3-dimensional profiles. The calculated sediment flux data indicated a loss of 3300 kg Cu $(month)^{-1}$ from the upper box with a gain of only 50 kg Cu $(month)^{-1}$ in the lower box. The imbalance could be accounted for by an absolute loss from the estuary into the coastal regions which were not within the scope of this study.

Figure 4.3 shows a winter profile with high river-flow, but with a mid-tidal range. Inputs to the upper box were dominated by the dissolved phase, with the highest input of the three examples chosen, the part-iculate input however was slightly lower than the previous example, probably due to the reduced flow rate. The particulate budget was enhanced by adsorption from the dissolved phase and re-suspension from the sediment (see also Figure 4.2). The particulate flux to the lower box increased nine-fold due to the high turbidity maximum generated with the increased tidal flow. An increased flux was observed from the lower to the upper box also as a result of this increased tidal incursion. In the lower box, the net flux was into the sediment showing deposition. In contrast to the input into the upper box, the output from the estuary was dominated by the particulate phase. Calculations for the sediment fluxes indicated a loss of 2060 kg Cu $(month)^{-1}$ from the upper box and a gain of 1720 kg Cu $(month)^{-1}$ in the lower box, although these figures are twice the fluxes observed in the model, the ratio of loss and gain is in good agreement and reinforces the

186

Upper Box

Lower Box

510 →

380 →

140 →

170

← 30

230

170 →

1280 →

620 →

10

810

← 130

20

760

187
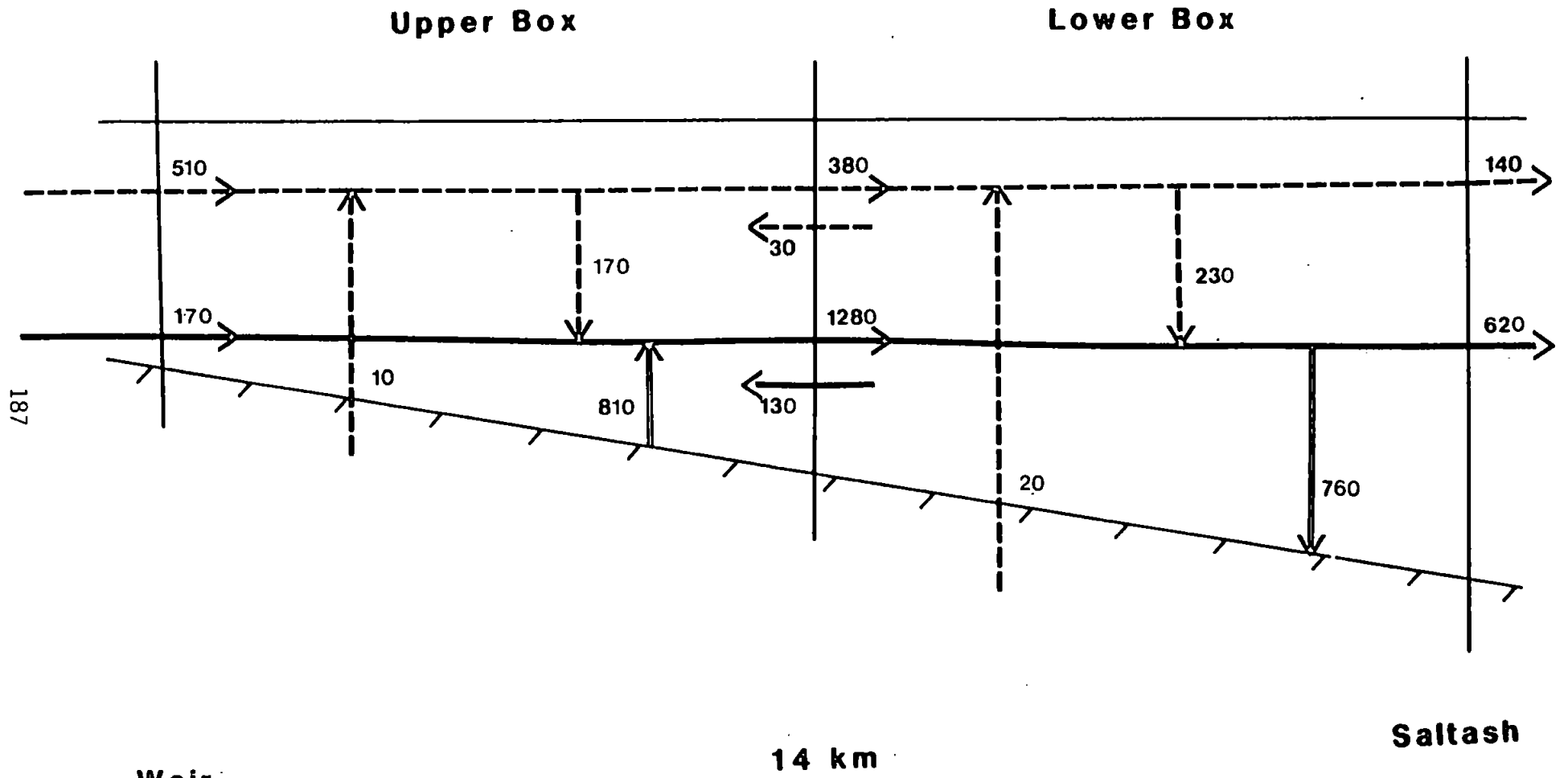
Saltash

14 km

Weir

Figure 4.3   Box model for copper, December 1980
River-flow rate = 37 m³ s^{-1}, mid-tidal range. Fluxes in kg (month)$^{-1}$; — — dissolved flux, — particulate flux

suppositions discussed in Section 3.1.4. In this case, a more turbulent regime was prevalent. Under these conditions the water column was well mixed and the vertical S.P.M. variations were less important, thus the measured sediment mass fluxes would be more likely to agree with the model values.

4.2.2   Manganese

Figure 4.4 depicts the box model for summer conditions, the out-standing feature of this particular model and the manganese results in general, was the dominance of the dissolved phase with respect to the particulate phase. Input into the estuary was predominantly in the dissolved form where adsorption onto the S.P.M. was observed, in good agreement with results from the fieldwork. For manganese, pore water infusion formed a significant input to both upper and lower boxes. The adsorption led to an increased S.P.M. flux to the lower box and resultant sedimentation. The return flow due to tidal incursion also provided significant contributions to the upper box (40% of the dissolved and particulate output). The net movement in the lower box was ultimately sedimentation via adsorption from the dissolved phase onto the S.P.M. but with a large loss from the estuary, predominantly via the dissolved phase. The observed sediment fluxes showed a gain in both boxes, in the upper box of 5190 kg Mn $(month)^{-1}$, a ten-fold increase on the model and in the lower box of 2240 kg Mn $(month)^{-1}$ which was in excellent agreement with the amount calculated by the model.

The calculation given in Figure 4.5, under high run-off conditions, showed a large increase in the particulate contribution by the riverine

189

Upper Box

Lower Box

700

1700

1100

730

650

2290

50

200

120

920

580

2420

2290

80

Saltash

14 km

Weir
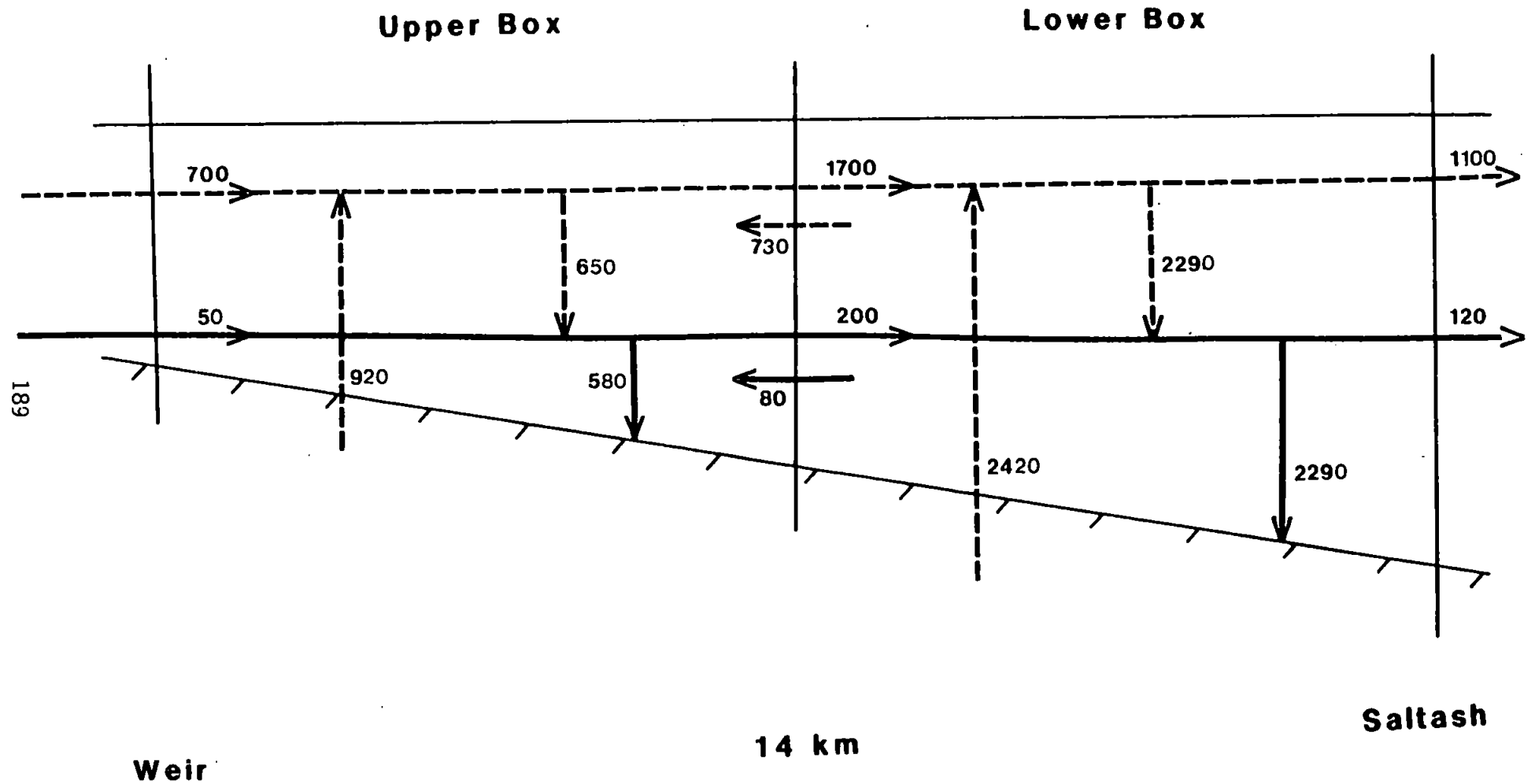
Figure 4.4   Box model for manganese, July 1980

River-flow rate = 9 m³ s^{-1}, neap tide.   Fluxes in kg (month)$^{-1}$;— — dissolved flux, —— particulate flux

Upper Box

Lower Box

1630

4310·

4520

680

1080

1530

1370

1200

670

920

810

100

1530

2420

1960

190

Weir

14 km

Saltash
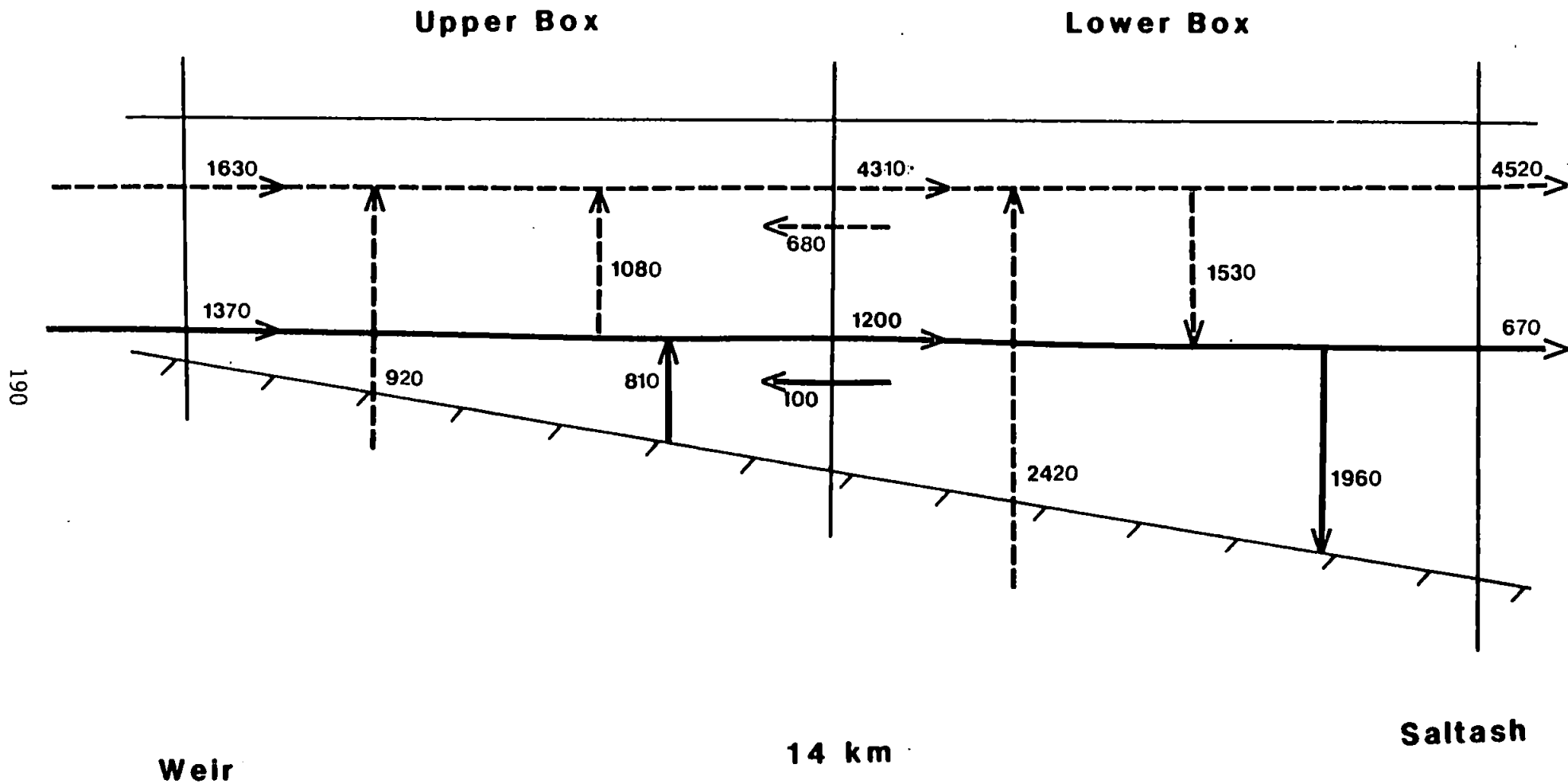
Figure 4.5 Box model for manganese, October 1980

River-flow rate = 40 m³ s⁻¹, neap tide. Fluxes in kg (month)⁻¹;— — dissolved flux, —— particulate flux

input into the upper box in comparison to Figure 4.4, together with a smaller increase in the dissolved input. A large demand for dissolved manganese was evident in the upper box to balance the four-fold increase in dissolved flux to the lower box. This increase would presumably be emanating from an enhanced influx from the pore water, but due to the limitations in this model the pore water infusion was constant, thus the dissolved input was accounted for by desorption from the S.P.M. The fluxes, due to tidal incursion to the upper box, were approximately 10%. The fluxes in the lower box were dominated by the dissolved phase. Approximately 30% of the input into the lower box was removed from the dissolved phase by adsorption onto the S.P.M. The particulate manganese loss from the estuary was approximately 30% of the amount deposited in the sediment. The general trends from this model were of removal in the upper estuary and deposition in the lower estuary, but with considerable loss from the estuary in the dissolved form. The sediment flux observations showed a loss of 6160 kg Mn $(month)^{-1}$ from the upper box with a net gain of only 60 kg Mn $(month)^{-1}$ in the lower box, indicating a massive loss to either the S.P.M. or dissolved phase. It is presumed that the loss was predominantly in the dissolved phase because the figures do not corroborate with those in the model, although the removal in the upper box and accretion in the lower box was still evident.

Figure 4.6 shows a winter condition under a slightly lower river-flow than Figure 4.5 but during mid-tide conditions. The inputs to the upper box and outputs from the lower box were again dominated by the dissolved phase, but the particulate phase was dominant at the boundary between the two boxes as a result of the sediment re-suspension

191

Upper Box **Lower Box**

2210

2580

2560

550

1100

1890

420

3380

410

920

1770

90

2420

4770

192

Saltash

14 km
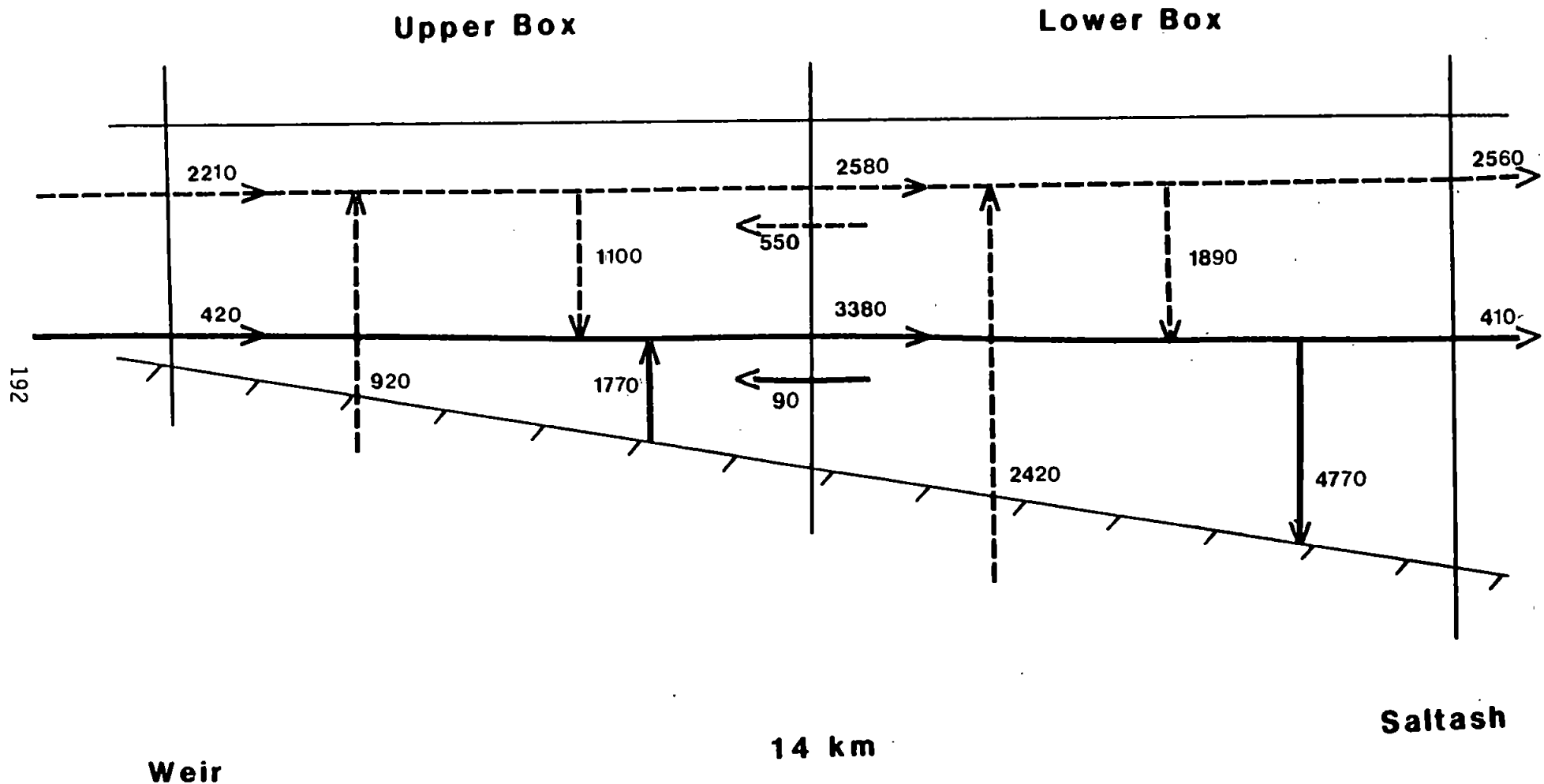
Weir

<u>Figure 4.6</u> Box model for manganese, December 1980

River-flow rate = 37 m³ s⁻¹, mid-tidal range. Fluxes in kg (month)⁻¹; — — dissolved flux, — particulate flux

produced by the increased tidal mixing. The input from the sediment therefore was a two-fold increase on the previous example (see Figure 4.5). The large S.P.M. levels at the boundary were reduced in the lower box by the increased deposition, giving a net balance between input into and output from the estuary in both particulate and dissolved phases. The overall cycling was however in reasonable agreement with the calculated sediment flux data which gave a loss of 3830 kg Mn $(month)^{-1}$ from the upper box and a gain in the lower box of 220 kg Mn $(month)^{-1}$.

4.2.3   Zinc

Figure 4.7 shows a summer profile, low river-flow and under neap tide conditions. Inputs to the upper box were predominantly in the dissolved form, although adsorption onto the S.P.M. led to net deposition of zinc to the sediments in the upper box. The transfer to the lower box was equally divided between the dissolved and particulate phases, whereas the return flow due to tidal incursion was dominated by the dissolved phase. Mobilisation from the sediment to the S.P.M. and desorption to the dissolved phase was maintained. The loss from the lower box was primarily in the dissolved phase. The observed sediment fluxes showed a gain in the upper box of 1080 kg Zn $(month)^{-1}$, which although greater, was in agreement with the general movement in the model. A gain was also recorded for the lower box of 1270 kg Zn $(month)^{-1}$, whereas a small loss was indicated by the model, this exemplifies the problems inherent in using data which was not strictly compatible.

Figure 4.8 depicts the fluxes for a high river-flow and neap tide.

193

Upper Box   Lower Box

194

Weir

14 km

Saltash
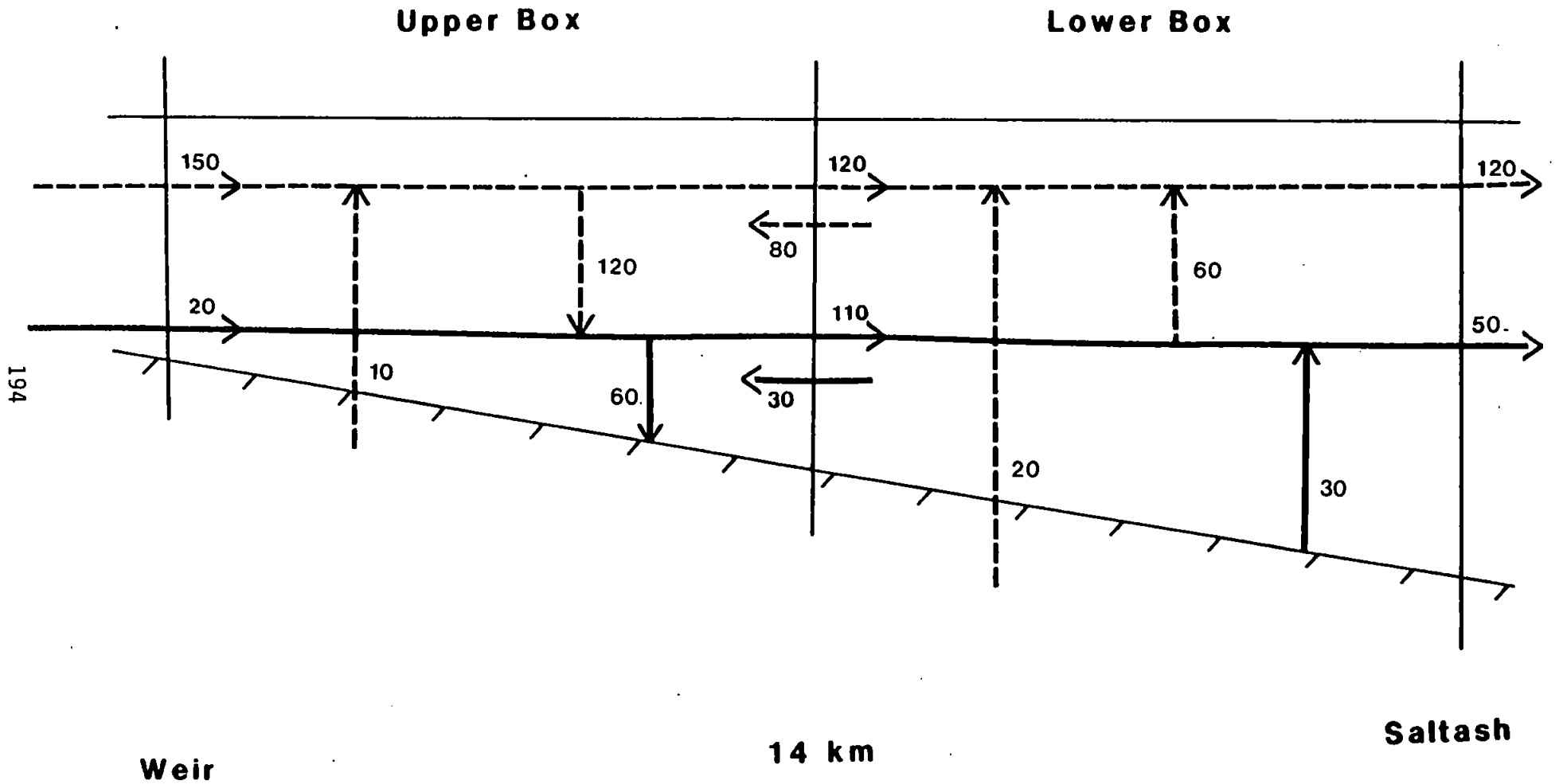
Figure 4.7 Box model for zinc, July 1980

River-flow rate = 9 m³ s⁻¹, neap tide. Fluxes in kg (month)⁻¹; ▬▬ dissolved flux, ▬▬ particulate flux

Upper Box

Lower Box

780 →

1730 →

700

← 100

520 →

840

790 →

460 →

950

10

1040

70

1210

20

Saltash

14 km

Weir
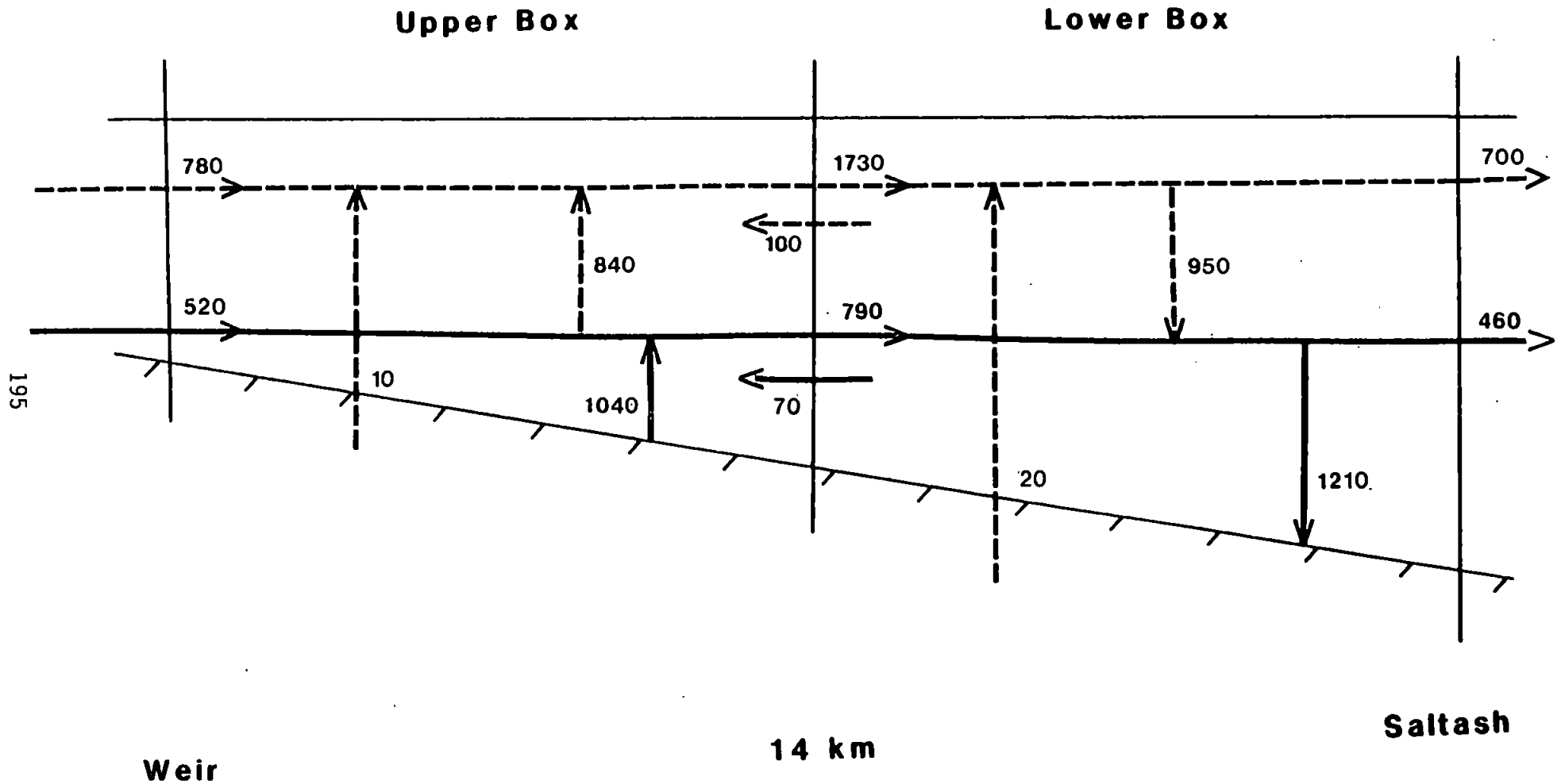
Figure 4.8 Box model for zinc, October 1980

River-flow rate = 40 m³ s⁻¹, neap tide. Fluxes in kg (month)⁻¹; ━ ━ dissolved flux, ━━ particulate flux

Both the dissolved and particulate inputs into the upper box had increased markedly due to the influence of high river-flows. As a result of the increased dissolved zinc flux into the lower box, an input to the S.P.M. from the sediment and consequent desorption from the S.P.M. was required to balance the fluxes in the upper box. The return fluxes, due to tidal incursion, were below 10% for both dissolved and particulate phases. The increased dissolved fluxes in the lower box were reduced by adsorption onto the S.P.M. and ultimate deposition to the sediment. The outputs from the lower box were slightly lower than the inputs into the upper box, apparently indicating a net retention of zinc in the estuary, although a large degree of internal cycling was taking place. The observed sediment fluxes showed a 3120 kg Zn $(month)^{-1}$ loss in the upper box, but only a 50 kg Zn $(month)^{-1}$ gain in the lower box, implying net loss from the estuary. The box model however indicated an approximate internal balance within the two boxes.

Figure 4.9 shows the model under a winter condition, the input into the upper box and outputs from the lower box were dominated by the dissolved phase. A large S.P.M. flux into the lower box produced a large demand for re-suspension of the sediment, thus resulting in the fluxes of dissolved and particulate zinc to the lower box being similar in magnitude. The increased tidal incursion resulted in increased movement from the lower to the upper box, approximately 20% for the dissolved phase and 25% for the particulate phase. Desorption from the S.P.M. in the lower box maintained a high dissolved zinc flux out of the estuary. The S.P.M. flux out of the lower box was reduced in comparison to that received from the upper box, requiring net deposition to the sediment to balance the fluxes. The overall model sediment movement

Upper Box   Lower Box

1180   1340   1140

250

100   30

110   1330   280

10

1060   60

20   960

197

14 km

Weir   Saltash
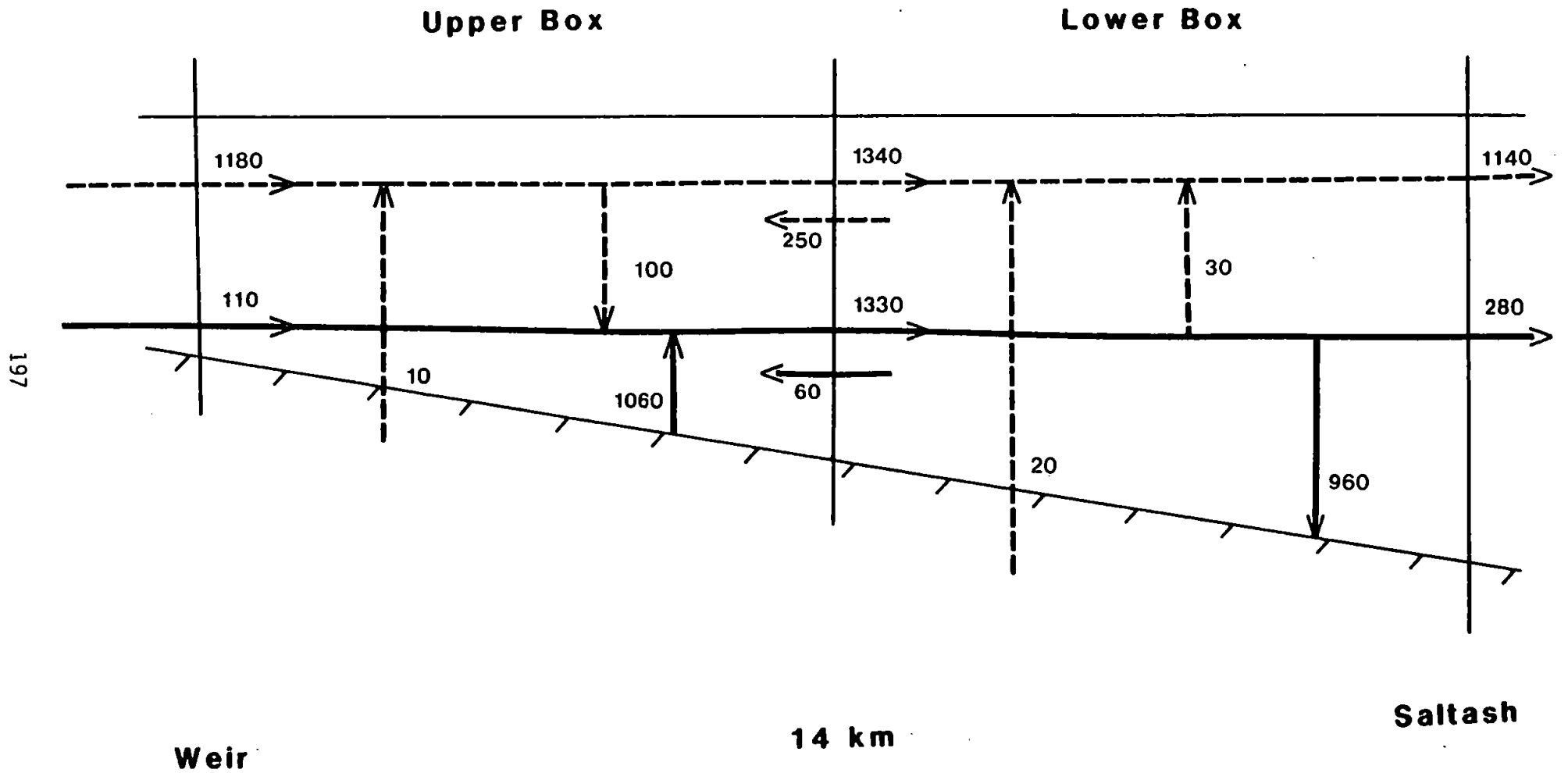
Figure 4.9   Box model for zinc, December 1980

River-flow rate = 37 m³ s^{-1}, mid-tidal range.   Fluxes in kg (month)$^{-1}$;━━ dissolved flux, ━━ particulate flux

was of a loss in the upper and a net gain in the lower box. The observed sediment movement gave a loss of 1940 kg Zn $(month)^{-1}$ from the upper box with a net gain of 1810 kg Zn $(month)^{-1}$ in the lower box, in reasonable agreement with the model results. The overall pattern of sediment movement was in agreement with the model.

4.3   CONCLUSIONS FROM THE TWO-BOX MODEL

4.3.1   Observations on the Evidence for Removal and Remobilisation of Copper, Manganese and Zinc

This particular method of examining the removal and remobilisation behaviour in an estuary has been validated. Of particular interest was the seasonal variation in fluxes, for example the seasonal differences are highlighted by Figures 4.1 and 4.2. The dissolved Cu flux increased five-fold in the winter profile, but more importantly, the particulate flux (new material into the estuary) showed a thirty-fold increase. Thus the high river-flows were instrumental in supplying the input of new, copper-rich particulates into the upper estuary. Increases were also observed in the output to the coastal region, again by a factor of five for dissolved and by a fourteen-fold increase in particulate material, indicating a loss from the lower estuary. This dominance of the particulates in the lower estuary is accounted for by the fact that 80% of the Cu is bound up in the crystalline lattice of the matrix, with only 20% in a labile form.

The behaviour of Cu (Figures 4.1-4.3) showed that whilst it entered the estuary in predominantly the dissolved form, adsorption onto particulates in the upper estuary and subsequent remobilisation from the sediment meant that loss from the estuary was predominantly in the particulate form. The combined dissolved and particulate flux out of the estuary was equalled by the flux into the sediment in the lower box, indicating an accumulation of Cu in the sediment of the Tamar.

The behaviour of Mn was such that the dominant input phase was as dissolved metal (see Figures 4.4 and 4.6) but up to 90% of the particulate

Mn was in a labile form. The dissolved phase remained important throughout the upper and lower estuary and formed the major output pathway from the estuary. The particulate flux became of importance during high river-flows, due to resuspension from the sediment at the 14 km boundary, but generally this led to increased deposition in the lower estuary. Duinker, et al., (1979) stated that Mn escaped from the lower Scheldt Estuary in predominantly the particulate form, in contrast to this work. It is interesting to note, however, that the lower boundary in their study was truly marine (North Sea) whereas in the present study it was estuarine. The Mn in the marine condition could be composed of manganese-rich particulate matter of the sort observed by Eisma, et al., (1980) in the low salinity mixing regime of the Rhine Estuary and during laboratory simulations in the S = 2 to 4°/oo range. The Mn fluxes into the Scheldt Estuary were one hundred times greater than in the Tamar, presumably this difference in magnitude is related to the higher river discharge in the Scheldt Estuary and its associated oxygen sag at low salinity. Sundby, et al., (1981) also found that Mn escapes the St. Lawrence Estuary in the form of manganese-enriched, fine-grained particles.

The Zn models formed an intermediate case, between that of Cu and Mn. Zinc particulates have 40 to 60% Zn in a labile form which is greater than that for Cu, but less than Mn. Although the dissolved phase Zn fluxes were generally higher than the particulate fluxes, the discrepancy was not as great as in the case of Mn. Zinc also displayed some of the characteristics of the Cu fluxes. During high river-flows, a large proportion of the downestuary flux was due to sediment remobilisation. The S.P.M. flux to the sediment in the lower estuary was equal to the sum of the dissolved and particulate fluxes leaving

the lower estuary. This was indicative of a large degree of internal cycling for Zn between the upper and lower boxes, but inputs into the system generally balanced the loss from the lower estuary.

In some of the models, there are discrepancies between the sediment fluxes derived from the 1982 sediment mass transport study and the values estimated by the model. Particularly large differences were observed in the gain of trace metals in the sediments of the lower box, e.g. the July cases for Cu and Zn. The question arises as to whether this is a result of the use, in the model, of a fixed pore water diffusion rate when, in reality, it is a function of both the hydro-dynamic conditions near the bed and the concentration of the metal in the pore waters. Changes in the diffusive flux can be examined but the nature of the cycle in the model is such that any increase in dissolved metals from the pore waters would have to be deposited in the sediment of the same box. This arises because the dissolved and particulate outputs from the box are fixed by field measurements. Thus, they constrain any additional input to be recycled internally within a box. An examination of the influence of the pore water flux was made by comparing the calculated rates of sediment trace metal accretion and erosion with those obtained from the sediment mass transport study (see summary Table 4.2). In the July case, the observed sediment deposition rates were almost always larger than the calculated one. This discrepancy could be explained by enhanced pore water fluxes. Thus, for Cu and Zn the pore water fluxes would have to increase by between 50 and 100 to account for the observed sediment deposition. For Mn, which had a relatively large pore water flux anyway, the calculated and observed sediment sediment deposition rates for the lower box are in excellent agreement but for compatability in the upper box the Mn pore

Month	Metal	Upper [a]		Lower [a]	
		Calculated	Observed	Calculated	Observed
July	Cu	-20	+870	+90	+1000
	Mn	+580	+5190	+2290	+2240
	Zn	+60	+1080	-30	+1270
October	Cu	-60	-3300	+330	+50
	Mn	-810	-6160	+1960	+60
	Zn	-3120	-1040	+1210	+50
December	Cu	-810	-2060	+780	+1720
	Mn	-1770	-3830	+4770	+220
	Zn	-1100	-1940	+1810	+1270

[a] A positive value indicates a gain and a negative value a loss

Table 4.2 Summary of Calculated and Observed Trace Metal Sediment Deposition and Erosion in the Upper and Lower Estuary, kg (month)$^{-1}$

water flux would need to be increased by a factor of 5.

The summer condition can now be contrasted with that for autumn and winter. In the latter cases the model predicts losses of all three metals from the upper box, in line with the anticipated erosion during periods of high river-flow. For this situation an enhanced pore water flux would tend to widen the gap between the calculated and observed sediment trace metal fluxes. Furthermore, in the lower box the calculated sediment metal fluxes are generally larger than the observed ones. Thus, for Cu and Zn the selected value for the flux (~ 2.5 µg/cm^2/yr) seems to be reasonable, but for Mn, if the flux were reduced by a factor of 10, to 40 µg/cm^2/yr, then the results would become more compatible.

Whilst the data in Table 4.2 does not always consistently support the above remarks, the general conclusion is that the pore water fluxes appear to be higher in summer than in winter. The values for the summer would appear to be in the range 125-250 µg/cm^2/yr for Cu; 400-2000 µg/cm^2/yr for Mn and 125-250 µg/cm^2/yr for Zn, where the upper limit of the range is applicable to the more dynamic low salinity region (i.e. S = 0 to 10°/oo). In the winter time the fluxes would seem to be much smaller, with values of about 2.5 µg/cm^2/yr for Cu and Zn and 40 µg/cm^2/yr for Mn. This seasonality in the pore water fluxes is in line with the observations of Elderfield, et al., (1981) in Narragansett Bay. The present study would seem to support the contention that increased pore water fluxes would be a feature of the quiescent summer time conditions in the estuary, with an extended period of benthic anoxia during the period of sediment accretion.

It is implied in this analysis that the additional trace metal input

into the water column emanates solely from the pore waters. However, there is also the possibility that lateral inputs from tributaries and streams could be significant. Unfortunately, these did not come within the scope of this study and this is where the two-box model presented here differs from that developed by Duinker, et al., (1979). The modified pore water fluxes discussed above should therefore be regarded as upper limits. Despite the lack of field data on estuarine pore water inputs, it is clear from this model that they are an important component and that future experimental work should be directed towards better quantification of their magnitudes.

CHAPTER FIVE

CONCLUSIONS AND FUTURE WORK

5.1 CONCLUSIONS TO THE STUDY

In this final chapter, the key areas of this study will be drawn together to obtain an overview of the complete work. There will also be an examination of the interrelationships between the separate aspects of the investigations. An attempt will be made to assess the value of the work as a contribution to the knowledge of estuarine chemical processes. The possible application of the box model as a predictive tool will be discussed together with recommendations regarding aspects for further study.

5.1.1 Estuarine Particulates

The chemical fractionation of the sediments and S.P.M. into the two components, total and non-detrital metal, was important in identifying the sources of heavy metal input and the potential for sorption reactions in the Tamar Estuary. The major source region for cadmium, copper, iron, manganese and zinc was at the head of the estuary in the region of historical mining activity (see Figure 2.1). However, mercury and lead were found to have inputs predominantly in the lower estuary, probably associated with present day anthropogenic inputs in this region. The non-detrital fraction of copper in sediments showed desorption losses taking place to account for the decreased concentrations observed at the approximate geographical position of the F.B.I. Manganese was dominated by the behaviour of the non-detrital phase showing a loss from the sediments throughout the estuary. The behaviour of the non-detrital zinc fraction indicated possible adsorption onto sediments giving the mid-estuarine maximum observed. Iron and lead sediment profiles were dominated by the detrital fraction.

206

The important feature exemplified by the sediment study as a whole, particularly by the 3-dimensional grain size diagram (see Figure 3.20), was the concept of seasonality in the distribution of the fine-grained (< 63 μm) fraction. This showed accretion at the head of the estuary in summer and removal to the lower estuary in winter. This movement was accomplished by the action of tidal pumping which acted upestuary in low flow conditions and downestuary under spate conditions. The seasonality in the total metal-metal and metal-grain size/T.O.C. correlations was also a result of the sediment transport resulting in the conclusion that most of the seasonal variation in the correlation coefficients was due to a change in the geochemistry of particulates in the estuary, related to the seasonal migration of the sediment. A major conclusion drawn from this work was the real need to undertake physical measurements of the estuarine environment in collaboration with the chemical study. This point was emphasised when attempting to rationalise relationships between the sediment analysis carried out in 1980 and the sediment flux study undertaken in 1982. An analysis of the S.P.M. data identified inputs of new material into the estuary in the form of metal-rich particulates. This supply was observed to increase with increased river-flow in winter, corroborated by the evidence of increased particulate metal fluxes observed in the upper box of the two-box model (for example compare Figures 4.1 and 4.2). This input was predominantly in the non-detrital form (see Section 3.4.1) and represented an input into the system which could undergo removal to the sediments and/or sorption processes in the water column.

The chemical fractionation of the sediment into total and non-detrital components showed a gradation in the labile component as follows; Cu = 20%, Zn = 60% and Mn = 100%. This must reflect the ability to

participate in estuarine chemical transformations. The two-box model
(see Section 4.1) exemplified the dominance of the differing phases
for each metal. Copper was found to be recycled within and transported
from the estuary mainly in the particulate phase and predominantly in
the detrital fraction. In contrast, manganese cycling was clearly
dominated by the dissolved phase, whereas zinc showed an intermediate
behaviour as it was transported in both particulate and dissolved
phases. These findings were in agreement with the field data for the
dissolved and particulate results.

5.1.2   Estuarine Dissolved Metals

The dissolved metal field surveys indicated evidence of non-conservative
behaviour in the very low salinity regions (see Figures 3.40-3.42) for
copper, manganese and zinc. The importance in measuring the master
variables was highlighted by the large changes observed at the F.B.I.
and consequent effects on the behaviour of the dissolved and particulate
metals. The effects of biological/biochemical parameters such as
bacterial and phytoplanktonic modification (both in situ and on samples
collected in the field) were outside the scope of this study, although
evidence for these effects has been discussed (see Section 3.2.2.a).
Attempts to account for the dissolved manganese peaks by considering
a sediment pore-water infusion mechanism have been discussed by Knox,
et al., (1981) and Morris, et al., (1982a). First order calculations
carried out here showed that, under the assumed conditions, pore-water
infusion could account for some of the dissolved manganese and zinc
maxima observed in the water column (see Section 3.2.4). The results
from the statistical analysis (see Section 3.2.3) indicated that
dissolved copper and manganese were not emanating from the same source,

i.e. the pore waters. Furthermore, dissolved zinc could have two sources, infusion from the pore waters and/or desorption from the particulates. Evidence from the desorption studies (see Section 3.3.1) was that up to 15% of the exchangable particulate copper and 5-20% for particulate zinc could be remobilised to the dissolved phase at the F.B.I. The crude calculations have shown that a significant contribution to both dissolved copper and zinc peaks observed in the estuary could be attributable to desorption from riverine particulates at the F.B.I., although the relative importance of the desorption process compared to the pore water infusion process was not established.

5.1.3   Two-Box Model of the Tamar Estuary

The primary objective of the model was to examine the interrelationships between dissolved and particulate metals. The most interesting result was that transport by the dissolved phase was in the order Mn > Zn > Cu which was indicative of the reactivity of the labile fraction of the particulates. Manganese was lost from the estuary primarily in the dissolved phase, copper appeared to be concentrating in the sediments of the lower estuary which could ultimately be lost to coastal sediments. Zinc showed a high degree of internal cycling via sorption reactions, though losses were primarily in the dissolved phase. The seasonal accretion-erosion cycle indicated by the sediment pole survey was substantiated to a large degree by the model, particularly under high river flow conditions. Under low flow conditions, the model under-estimated the sediment metal flux, probably due to the inhomogeneity of the S.P.M. with depth in the stratified water column. There would be potential for an order of magnitude change between surface

209

and bed turbidities. The measurements taken at the surface were therefore underestimates of the total particulate flux. There appeared to be an improvement in the agreement between the model and observed sediment fluxes during spate conditions. This could be due to the greater degree of mixing resulting in a more homogeneous water column, thus the surface turbidity was more representative of the whole water column and gave improved compatability.

The model could be used in a simple predictive capacity, to estimate the effects of increasing or decreasing inputs into the estuary due to variations in the river-flow. Thus, on progressing from summer to winter (or at times of expected high or low river-flow) the budgets of metals in the estuary can be roughly estimated.

When the river-flow increases by a factor of approximately 4, the copper flux into and out of the estuary increases. The dissolved input exceeds the particulate input, but the output from the estuary remains predominantly in the particulate phase which increases by a factor between 15 and 30. The particulate flux from the upper estuary to the lower estuary is supported by sediment mobilisation in the upper estuary. The deposition of particulate copper to the sediment in the lower box will increase by a factor of between 5 and 10.

The changes for manganese are less dramatic than copper. For the same increase in river-flow, manganese will have its input into the system dominated by the dissolved form. The losses in this form from the estuary will increase by a factor of 3 to 5. Whilst there is some increased particulate flux due to sediment remobilisation in the upper box, the particulate deposition in the lower box only increased by a

factor of 2 at most. This could indicate a loss from the estuary to the coastal waters.

In the case of zinc the amount coming into the estuary is approximately equal to that going out in both dissolved and particulate phases, under any river-flow conditions. It can also be observed that the recycling of sediment metal flux is approximately in balance, in that the amount remobilised in the upper estuary is equal to that deposited in the lower estuary.

5.2   RECOMMENDATIONS FOR FUTURE WORK

1. A mineralogical analysis, possibly using S.E.M. and X-ray microprobe

analysis of both the sediment and the S.P.M., would pinpoint subsidiary

inputs into the estuary. This input could also be quantified chemically.

This information together with an examination of particulate flux as a

function of depth would be used to modify the box model, possibly by

dividing the mox model vertically, thus resulting in a two-layer, two-

box system. This would result in an improved assessment of the

particulate flux.

2. The box model could also be refined to examine the role of the

non-detrital fraction, (as opposed to the total fraction) which would

give a greater insight into the cycling of the reactive fraction.

This study would increase the knowledge of potentially harmful deposits

in a form available to the biota.

3. A closer examination of the composition of estuarine pore-waters

would aid in the separation of the relative importance of the pore-

waters as a potential source of dissolved copper and zinc. The field/

laboratory studies of estuarine sorption reactions need to be refined

using an improved analytical technique, possibly using a flow injection

system coupled with an atomic absorption spectrophotometer, or a

polargraphic method to give greater analytical precision and reliability.

4. A priority in future modelling work would be to investigate the

effects of organic complexation on the sorption reactions in the estuary.

Comparisons of the metal behaviour in irradiated samples with the

behaviour observed in natural samples would provide evidence of these

potential differences. The use of organic-free particulates
(particulates could be treated with NaOH or H_2O_2 to remove organic
coatings) would also provide information on the effect on adsorption
sites on the particulates when compared to the results using natural
particles. This study would provide information on the potential for
biological modification of estuarine chemical processes. The
evaluation of the kinetics of the sorption reactions is vital to the
interfacing of the timescales of the physical processes with the
chemical processes.

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214

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APPENDIX I

Correlation Matrices for Non-normalised Data: Hydrofluoric Acid Digestions

Correlation coefficients for 22/07/80 - see Table 3.4

Correlation coefficients for 26/08/80, non-normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	0.27							
Fe	0.01	0.54						
Zn	-0.06	0.89	0.57					
Hg	-0.43	-0.50	0.42	-0.30				
Pb	-0.73	0.40	0.45	0.63	0.21			
T.O.C.	-0.21	0.77	0.78	0.85	-0.00	0.79		
Cd	-0.22	0.11	-0.15	0.10	0.02	0.08	-0.05	
Dist.	-0.59	-0.71	-0.48	-0.58	0.51	0.07	-0.48	0.22

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 12/11/80, non-normalised

	Mn	Cu	Fe	Zn	T.O.C.	Cd
Cu	-0.20					
Fe	0.61	-0.04				
Zn	-0.24	0.69	0.33			
T.O.C.	-0.56	0.48	0.26	0.82		
Cd	-0.64	0.43	0.02	0.68	0.87	
Dist.	-0.76	-0.32	-0.33	-0.07	0.37	0.48

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 04/02/80, non-normalised – see Table 3.5

Correlation coefficients for 01/04/81, non-normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd	Grain Size
Cu	-0.70								
Fe	0.74	-0.22							
Zn	-0.60	0.59	-0.11						
Hg	-0.73	0.31	-0.75	0.47					
Pb	-0.81	0.46	-0.80	0.53	0.96				
T.O.C.	-0.55	0.65	-0.15	0.48	0.29	0.36			
Cd	-0.47	0.12	-0.38	0.21	0.54	0.48	0.03		
Grain Size	-0.42	0.17	-0.30	0.62	0.68	0.63	0.54	0.05	
Dist.	-0.75	0.15	-0.85	0.36	0.87	0.85	0.25	0.36	0.65

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 17/06/81, non-normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd	Grain Size
Cu	-0.32								
Fe	0.89	0.04							
Zn	-0.18	0.97	0.18						
Hg	-0.60	0.82	-0.37	0.77					
Pb	-0.73	0.68	-0.49	0.65	0.85				
T.O.C.	0.62	0.45	0.82	0.57	0.03	-0.04			
Cd	0.29	-0.21	0.21	-0.25	-0.29	-0.45	-0.19		
Grain Size	-0.45	0.41	-0.30	0.42	0.46	0.68	0.18	-0.85	
Dist.	-0.78	-0.06	-0.89	-0.15	0.45	0.55	-0.70	-0.43	0.41

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 16/07/81, non-normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd	Grain Size
Cu	-0.32								
Fe	0.58	0.15							
Zn	-0.57	0.78	0.09						
Hg	-0.86	0.53	-0.33	0.70					
Pb	-0.84	0.69	-0.23	0.84	0.93				
T.O.C.	-0.62	0.75	0.05	0.85	0.73	0.88			
Cd	-0.30	0.10	0.04	0.33	0.54	0.40	0.32		
Grain Size	-0.78	0.45	-0.04	0.80	0.80	0.84	0.72	0.38	
Dist.	-0.74	-0.00	-0.64	0.70	0.70	0.58	0.37	0.25	0.39

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 30/09/81, non-normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd	Grain Size
Cu	-0.07								
Fe	0.30	0.84							
Zn	-0.17	0.98	0.80						
Hg	-0.58	0.76	0.48	0.80					
Pb	-0.37	0.87	0.59	0.84	0.88				
T.O.C.	0.17	0.92	0.89	0.88	0.58	0.69			
Cd	-0.17	0.87	0.77	0.89	0.81	0.82	0.80		
Grain Size	-0.20	0.85	0.67	0.84	0.80	0.77	0.82	0.75	
Dist.	-0.76	0.03	-0.09	0.14	0.56	0.30	-0.21	0.29	0.04

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 10/02/82, non-normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd	Grain Size
Cu	-0.63								
Fe	0.23	0.51							
Zn	-0.61	0.97	0.56						
Hg	-0.64	0.89	0.44	0.91					
Pb	-0.66	0.74	0.21	0.67	0.62				
T.O.C.	-0.03	0.58	0.85	0.71	0.56	0.33			
Cd	0.30	-0.03	0.52	0.14	0.22	-0.25	0.53		
Grain Size	0.68	-0.14	0.40	-0.20	-0.30	-0.25	0.20	0.11	
Dist.	-0.92	0.66	-0.11	0.67	0.67	0.68	0.20	-0.16	-0.28

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation Matrices for Normalised Data: Hydrofluoric Acid Digestions

Correlation coefficients for 22/07/80 - see Table 3.6

Correlation coefficients for 26/08/80, normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	0.95							
Fe	0.74	0.84						
Zn	0.85	0.96	0.89					
Hg	-0.11	0.05	0.50	0.17				
Pb	-0.40	-0.15	0.25	0.08	0.70			
T.O.C.	0.65	0.77	0.89	0.80	0.52	0.35		
Cd	0.62	0.80	0.86	0.91	0.30	0.33	0.72	
Dist.	-0.35	-0.11	0.19	0.08	0.63	0.88	0.27	0.30

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 12/11/80, normalised

	Mn	Cu	Fe	Zn	T.O.C.	Cd
Cu	0.64					
Fe	0.99	0.61				
Zn	0.90	0.82	0.90			
T.O.C.	0.27	0.02	0.37	0.40		
Cd	0.65	0.71	0.69	0.82	0.54	
Dist.	-0.59	-0.55	-0.50	-0.59	0.10	-0.19

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 04/02/81 - see Table 3.7

Correlation coefficients for 01/04/81, normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	0.68							
Fe	0.95	0.85						
Zn	0.44	0.78	0.64					
Hg	-0.21	-0.03	-0.18	-0.01				
Pb	-0.03	0.42	0.10	0.40	0.83			
T.O.C.	0.59	0.88	0.76	0.58	-0.22	0.18		
Cd	0.76	0.63	0.78	0.45	0.37	0.42	0.49	
Dist.	-0.72	-0.54	-0.73	-0.48	0.63	0.40	-0.57	-0.32

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 17/06/81, normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	-0.17							
Fe	0.92	0.04						
Zn	0.17	0.91	0.38					
Hg	-0.53	0.75	-0.36	0.59				
Pb	-0.76	0.54	-0.61	0.33	-0.82			
T.O.C.	0.85	0.30	0.83	0.56	-0.23	-0.47		
Cd	0.59	0.05	0.80	0.31	0.14	-0.33	0.42	
Dist.	-0.78	-0.22	-0.76	-0.45	0.41	0.56	-0.91	-0.40

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

A 7

Correlation coefficients for 16/07/81, normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	0.80							
Fe	0.99	0.76						
Zn	0.92	0.93	0.90					
Hg	-0.04	0.44	-0.09	0.24				
Pb	0.32	0.78	0.28	0.61	0.84			
T.O.C.	0.77	0.91	0.76	0.91	0.38	0.76		
Cd	0.76	0.50	0.76	0.69	0.08	0.20	0.54	
Dist.	-0.57	-0.37	-0.59	-0.47	0.54	0.16	-0.30	-0.28

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 30/09/81, normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	0.32							
Fe	0.90	0.38						
Zn	0.55	0.81	0.74					
Hg	-0.70	0.25	-0.47	0.04				
Pb	0.65	0.60	0.81	0.79	-0.01			
T.O.C.	0.63	0.73	0.53	0.63	-0.30	0.41		
Cd	0.47	0.76	0.63	0.84	0.18	0.77	0.60	
Dist.	-0.54	0.02	-0.20	0.10	0.86	0.13	-0.47	0.24

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 10/02/82, normalised

	Mn	Cu	Fe	Zn	Hg	Pb	T.O.C.	Cd
Cu	-0.38							
Fe	0.05	0.87						
Zn	-0.21	0.97	0.96					
Hg	-0.19	0.94	0.92	0.96				
Pb	-0.40	0.89	0.79	0.87	0.83			
T.O.C.	-0.08	0.88	0.91	0.92	0.86	0.77		
Cd	0.25	0.65	0.87	0.79	0.82	0.54	0.81	
Dist.	-0.67	0.84	0.63	0.80	0.74	0.87	0.68	0.42

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation Matrices for Non-normalised Data: Acetic Acid Digestions

Correlation coefficients for 22/07/80 - see Table 3.8

Correlation coefficients for 04/02/80 - see Table 3.9

Correlation coefficients for 16/07/81, non-normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Grain Size
Cu	0.17						
Fe	-0.12	0.73					
Zn	-0.19	0.59	0.46				
Pb	-0.45	0.58	0.80	0.62			
T.O.C.	-0.13	0.66	0.74	0.77	0.74		
Grain Size	-0.03	0.75	0.84	0.63	0.85	0.72	
Dist.	-0.74	-0.12	0.40	0.22	0.72	0.37	0.39

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 30/09/81, non-normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Grain Size
Cu	0.41						
Fe	0.06	0.77					
Zn	0.13	0.83	0.70				
Pb	-0.58	0.15	0.58	0.27			
T.O.C.	0.38	0.85	0.76	0.76	0.15		
Grain Size	-0.01	0.56	0.77	0.53	0.44	0.80	
Dist.	-0.80	-0.13	0.21	0.21	0.80	-0.22	0.04

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 10/02/82, non-normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.	Grain Size
Cu	0.08						
Fe	-0.36	0.37					
Zn	-0.08	0.53	0.73				
Pb	-0.64	0.35	0.84	0.71			
T.O.C.	0.54	0.52	0.50	0.61	0.17		
Grain Size	0.61	0.29	-0.61	-0.25	-0.61	0.20	
Dist.	-0.60	0.19	0.87	0.65	0.96	0.20	-0.71

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation Matrices for Normalised Data: Acetic Acid Digestions

Correlation coefficients for 22/07/80 - see Table 3.10

Correlation coefficients for 04/02/81 - see Table 3.11

Correlation coefficients for 16/07/81, normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.
Cu	0.23					
Fe	-0.09	0.11				
Zn	0.44	0.65	-0.06			
Pb	-0.83	-0.49	0.23	-0.66		
T.O.C.	0.29	0.73	0.20	0.85	-0.46	
Dist.	-0.72	-0.64	0.13	-0.41	0.84	-0.30

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 30/09/81, normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.
Cu	0.66					
Fe	0.09	0.59				
Zn	0.29	0.79	0.59			
Pb	-0.55	-0.12	0.57	0.08		
T.O.C.	0.74	0.86	0.33	0.71	-0.40	
Dist.	-0.68	-0.21	0.36	0.19	0.86	-0.47

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

Correlation coefficients for 10/02/82, normalised

	Mn	Cu	Fe	Zn	Pb	T.O.C.
Cu	0.10					
Fe	0.23	0.66				
Zn	0.27	0.71	0.91			
Pb	-0.06	0.67	0.92	0.88		
T.O.C.	0.51	0.62	0.93	0.89	0.76	
Dist.	-0.17	0.56	0.80	0.81	0.92	0.68

Significance level 0.46 at 90% confidence; 0.66 at 99% confidence

APPENDIX II

PUBLISHED WORK

HEAVY METAL CONTENT OF OYSTERS FROM THE LYNHER ESTUARY, U.K.

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ABSTRACT

The concentrations of As, Cd, Cu, Hg, Pb and Zn have been determined in oysters and sediments from the Lynher Estuary, U.K. The sediments contained high levels of Cu, Fe, Pb and Zn probably associated with run off from a metalliferous catchment area and high Hg associated with a local sewage input. In contrast, the analyses of the oyster tissue showed that only Cu and Zn were concentrated in the flesh. The majority of samples contained coliform bacteria in excess of 1000 organisms per ml of tissue. It is concluded that the quality of the oysters from this fishery was limited by the bacteriological cleanliness rather than toxic metal content.

INTRODUCTION

The consequences of marine pollution are most evident in estuaries, which are under considerable pressure from human activities (Olausson and Cato, 1980). The contamination of the estuarine environment often results from industrial activity and inputs of sewage waste. This may well conflict with the use of estuarine waters as breeding grounds for commercial shellfish (Metcalf and Stiles, 1965, 1968; Thornton et al., 1975; Topping, 1976). Such breeding grounds are present at the confluence of the Tamar and Lynher Estuaries in S.W. England, where a traditional oyster fishery has been in existence for about 700 years. This fishery has had a troubled history which in more recent times has been complicated by the fact that Lynher oysters have been associated with occurrences of gastroenteritis, despite the fact that the shellfish had undergone an approved cleaning procedure (Wood, 1969). The fishery has been closed since 1966 but recently the possibility of reopening the fishery has been raised.

Despite the obvious commercial importance of the fishery, there is only limited information on the condition of these oysters and others in Cornwall

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(Barrow, 1973; Barrow and Miller, 1969). In this study we have examined one aspect of possible contamination, namely that from heavy metals. These shellfish are found in an estuary which drains a mineralised catchment area, where until the turn of the century metals, including As, Cu, Pb and Zn were mined. Drainage from this region and areas of secondary contamination continue to constitute an active input of metals into these estuaries, in addition to localised inputs of domestic sewage. Previous studies on oysters in Cornwall have shown that the general metal accumulation in these shellfish reflect the geochemical status of the estuary (Thornton et al., 1975). Thus, the results from the present work will contribute to the information on the distribution of heavy metals in a particular species of oyster for which there is a lack of data.

EXPERIMENTAL

Oysters of commercial size and sediment samples were collected by diver in August 1980 from positions between Henn Point and Wearde Quay, see Fig. 1. Nine oyster samples were taken to the laboratory for immediate bacteriological analysis of the tissue. The oysters were prepared using methods described by Harrigan and McCance (1976) using a mechanical stomacher. Presumptive coliform counts were then carried out using the
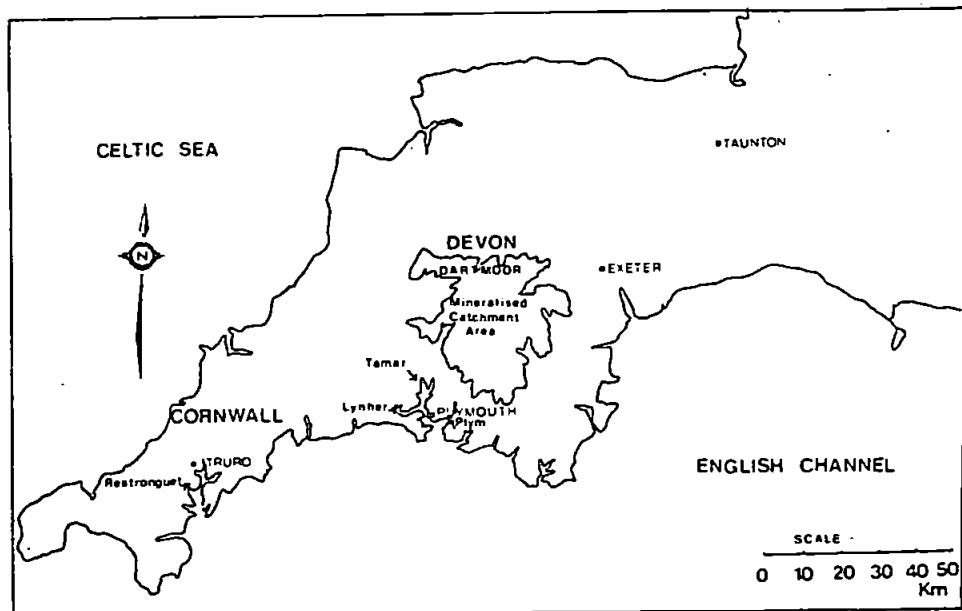

Fig. 1. The south-west peninsula of England showing the location of the Tamar and Lnyher Estuaries and the mineralised catchment area of Dartmoor. Restronguet Creek, Cornwall, also receives acid mine waste.

multiple tube technique (Thatcher and Clarke, 1968). A total of 81 culture media were used with dilutions of 10^{-1}, 10^{-2} and 10^{-3}.

The oysters for metal analyses were shucked, washed and weighed and were then kept for 3 days in diluted, clean seawater to allow the removal of ingested food particles. The tissue was then removed and freeze dried for 48—72 h after which no further weight loss was observed. Each dried tissue was ground into an homogeneous powder and 2 g were used for each of the digestions. Super pure acids were used for the digestions and all other reagents were of 'Analar' grade. Eleven samples were selected for As analyses using an ashing slurry which was dry-ashed at 500°C in a muffle furnace (Penrose et al., 1975; Langston, 1980). A total of twenty samples for Cd, Cu, Hg, Pb and Zn analyses were allowed to stand overnight in concentrated HNO_3 and then digested under reflux for 2 h at 50°C. A 10-ml aliquot of a 50% v/v mixture of concentrated HNO_3 and H_2SO_4 was then added to the digest and heated for a further 3 h at 60°C. After cooling 10 ml of H_2O_2 were carefully added and the mixture heated for a futher 1 h at 80°C. The final solution was washed into a 250-ml volumetric flask which was made up to the mark with double distilled, deionised water.

Sediment samples were washed with distilled water and digested using an aqua regia/HF digestion mixture in a teflon digestion vessel heated at 100°C for 1 h (Loring and Rantala, 1977). The dry weight of the sediment was determined after drying at 60°C and the organic carbon was determined as weight loss on ashing at 670°C for 6 h in a muffle furnace.

Analyses for Cd, Cu, Pb and Zn were carried out using conventional flame atomic absorption spectrophotometry. Total arsenic was determined by hydride generation atomic absorption spectrophotometry with an Ar/H_2 flame. The samples were made up in 5M acid with 0.1% KI added (Pahlavan-pour et al., 1980).

RESULTS AND DISCUSSION

Table 1 shows the results for the heavy metal content of sediments from the oyster fishery. The concentrations are significantly higher than those obtained for contaminated coastal sediments from the North Sea (Taylor, 1979) and those from Urr Water, which is considered to be an unpolluted estuary (Taylor, 1976). The values obtained in the present work are probably enhanced by inputs from the metalliferous catchment area. Analyses of heavy metals in Tamar sediments, obtained during several surveys of 14 sites in the estuarine zone, have shown that the levels of the metals As, Cu, Fe, Mn, Pb and Zn are elevated, although the contamination is not as acute as in the case of Restronguet Creek (Aston et al., 1975). The Tamar results show that the highest concentrations of As, Cu, Fe, Mn and Zn tend to be found in the upper low salinity region of the estuary whereas elevated levels of Hg and Pb are found near the seaward limit of the survey at the Tamar Bridge. There are not significant sources of Hg in the catchment area (Perkins, 1971)

TABLE 1

HEAVY METAL DISTRIBUTIONS IN SEDIMENTS (ppm, dry weight) FOR THIS STUDY AND OTHERS

Location	Cu	Zn	Pb	Cd	Mn	Fe	As	Hg	% Organics	Reference
Lynher	274	317	150	—	289	23,120	50.7	2.1	10.5	This work
Tamar[a] (range)	545—154	605—221	239—19	—	1500—105	49,000—21,000	25—236	1.5—0.2	2.3—16.5	Ackroyd & Marsh (1981)
Plym	—	256	—	9.3	171	12,100	41	0.35	4.1	Langston (1980) Millward & Herbert (1981) Bryan & Hummerstone (1973)
Urr Water	6.9	41.2	21.5	0.9	333	—	—	0.07	—	Taylor (1976)
Tees Bay	8.0	74.1	45.4	0.2	242	—	—	0.1	—	Taylor (1979)
Restronguet Creek	1690	1540	684	3	1030	54,000	1080	—	—	Aston et al. (1975)

[a] The range of values is for samples collected throughout the whole estuarine regime.

TABLE 2
ANALYSES OF THE COLIFORM COUNT FOR SAMPLES OF OYSTER TISSUE

Sample No.	No. of positive tubes at 3 dilutions			Most probable No. of coliforms per gram
	10^{-1}	10^{-2}	10^{-3}	
1	3	3	2	1,100
2	3	3	3	>1,100
3	3	3	2	1,100
4	3	3	2	1,100
5	3	3	1	500
6	3	3	2	1,100
7	3	3	2	1,100
8	3	2	3	210
9	3	3	1	500

and this suggests that the high concentrations at the site and in the Tamar are associated with sewage inputs, as has been found in the Plym Estuary (Millward and Herbert, 1981).

The results of the bacteriological analyses are shown in Table 2 from which it is clear that the majority of the samples have a high coliform count. The presence of *Escherichia coli* in the tissue is indicative of faecal contamination from local outfalls and the high counts make these shellfish unsuitable for direct human consumption (Wood, 1969).

The analyses of the oysters did not show high levels of Hg as might have been expected, although some mercury species could have been lost during the cleaning procedure. Only Cu and Zn were significantly concentrated compared to the sediment, although it should be noted that Cu can be metabolised and forms haemocyanin (Phillips, 1976). Whilst the levels of Cu and Zn reported here are greater than average concentrations (Bryan, 1976), they are less than those obtained for the Tamar and Derwent, Tasmania (Ayling, 1974; Bloom and Ayling, 1977) which have given rise to nausea and vomiting. In general the metal levels are more compatible with other oyster species (see Table 3).

In conclusion, the heavy metal content is not significant even though the shellfish are found in sediments that are contaminated. However, the high coliform count of these samples suggests that the oysters require further treatment prior to consumption.

TABLE 3

HEAVY METAL DISTRIBUTION IN OYSTERS (ppm, dry weight) FOR THIS STUDY AND OTHERS

Species and location	Cu	Zn	Pb	Cd	As	Hg	Reference
O. edulis[a,b] Lynher, U.K.	610 (115—1840)	3280 (690—9150)	0.6 (0.15—5.0)	7.4 (3.5—29.7)	9.1 (6.9—10.7)	0.23 (0.17—0.31)	This work
Oysters[a] (Overall)	100	1700	3.0	10	10	0.4	Bryan (1976)
C. commercialis N.S.W. Australia	20	227	0.8	0.2	1.2	—	Mackay et al. (1975)
C. gigas Helford, U.K.	273	1640	—	6.0	8.2	0.76	Thornton et al. (1976)
C. gigas Tamar, Tasmania	691	7227	0.82	33.2	—	—	Ayling (1974)
C. virginica San Antonio Bay, U.S.A.	161	322	0.8	3.2	1.3	0.05	Sims & Presley (1976)

[a] Geometric means.
[b] Bracketted values are the ranges.

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