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THE REMOVAL OF ARSENIC FROM AQUATIC

SYSTEMS BY IRON OXYHYDROXIDES

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ABSTRACT

Surveys of dissolved Fe, Mn and As in the River Tamar, Devon, indicated general removal from the water column at low salinities. Manganese and As showed evidence of remobilisation at higher salinities. Total and non-detrital sediment extracts confirmed a remobilisation chemistry for Mn and non-detrital As, and a redox couple between Mn and As was considered. Spatial-temporal analysis of sediment data indicated both physical and chemical processes were involved in the estuarine transport of these elements.

Studies of synthetic and natural Fe precipitates indicated that speciation of the Fe source and temperature of formation influenced the surface area and nature of the precipitate formed. The presence of non-authigenic Fe coatings on sedimentary particles was demonstrated.

Chemical models of synthetic and natural Fe oxyhydroxides were used to study As adsorption as a function of pH, temperature and precipitate age. Uptake of As (V) onto fresh Fe (III)-derived material was rapid and related to precipitate formation. Adsorption by fresh Fe (II) precipitates was pH dependent in freshwater and in seawater followed two kinetic regimes. Adsorption was 1st order at pH < 7.6, dependent on the slow oxidation of Fe (II), and 2nd order at pH > 7.6, where the adsorption process was rate determining. General agreement was found with natural precipitates.

The overall adsorption behaviour of aged Fe (II) and Fe (III) precipitates suggested a physical process and an electrostatic adsorption model was proposed. Aged Fe (II) material did not adsorb As (III) and an Fe (III)-As (III) redox model was developed to account for the general slowness of As (III) adsorption. Natural aged precipitates showed complex adsorption behaviour, confirmed by precipitate characterisation studies which indicated a mixed oxide composition.

The estuarine behaviour of As was interpreted in terms of the adsorption models and estuarine surveys. A model illustrating the timescales of As adsorption and desorption within an estuary was developed, and used to elucidate the anomalous behaviour of dissolved Fe, Mn and As in the River Carnon, Cornwall.

CONTENTS

CHAPTER ONE

INTRODUCTION

1.1   Overview

In the last two hundred years the previously small settlements around
the estuaries and coasts of Britain and other maritime countries have
greatly enlarged, due to the development of ports, shipping-related
industry and the proliferation of residential suburbs. In addition,
chemical industries, oil refineries and nuclear and oil-fired power
stations have all increasingly concentrated in these coastal regions.
This has been largely due to the saving of transportation costs and the
availability of large amounts of cooling water, required by modern
plant. Furthermore, estuaries are vital in the life-cycle of many
commercially important fish, as shellfish breeding grounds, for sport-
fishing and as recreational facilities. These factors resulted in
population relocation towards coastal areas, such that today some 30%
of the U.K. population live adjacent to estuaries.

This in turn has brought increasing pressure on estuaries and coastal
waters in terms of land reclamation projects and the discharge of
industrial and urban wastes. In the south-west of England, for example,
there is a considerable seasonal pressure on sewage discharges associated
with tourism and an additional factor is the input of wastes from
current and past metalliferous mining activities (Hamilton-Jenkin, 1974).

Any attempt to formulate management policy for regulating the use of
estuaries must recognise the importance of even small modifications to
the estuarine environment. Estuaries are complex systems in which the
mixing of two very different water masses takes place, to produce a wide
range of biogeochemical interactions. Whilst these systems have been
intensively investigated over the last decade (Olausson & Cato, 1980),

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little is known of the detailed interactions that take place. The chemical composition of estuarine waters and the reactivity of elements are important components of water quality models. This work concentrates on the chemical behaviour of As in estuarine waters with particular emphasis on the heterogeneous reactivity of the element.

The adsorption of trace elements onto the solid phase, which includes Fe oxyhydroxides, is an important control on the composition of the dissolved phase and on the precipitates which deposit as sediment. Of particular interest are the low salinity regions of estuaries where the rapidly changing pH and ionic strength of the medium may significantly affect adsorption equilibria (Morris, 1977; Morris, et al., 1978).

The quantitative information derived from studies of adsorption behaviour is of value in the development of precise biogeochemical models of estuarine systems. These models are of importance in the management of estuaries and inland waters, which requires a greater understanding of trace element behaviour, so that the fate of potentially toxic wastes in these waters may be accurately predicted.

1.2   The Estuarine Environment

1.2.1   Physical Processes in Estuaries

1.2.1.1 Definitions

An estuary may be defined by common usage as an area where river water comes into contact with, and is mixed with, seawater. There is a variety of more precise definitions which tend to reflect the academic specialities of the authors.

Geographers and geomorphologists would define an estuary (e.g. Dionne, 1963) as an inlet of the sea reaching into a river valley as far as the upper limit of tidal incursion. Chemists, however, would define the upper limit of an estuary as the innermost boundary of freshwater and saltwater mixing, as in the definition of Pritchard (1967). This definition, although commonly used, would appear to be incomplete, for all areas of fresh and saltwater mixing are not necessarily estuaries (see e.g. Caspers, 1967).

It would therefore seem necessary to incorporate hydrodynamic, as well as hydrochemical, factors in a basic definition of estuaries. This has been attempted by Fairbridge (1980) as follows :

'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, and

iii)   an upper or fluvial estuary, characterised by freshwater but subject to daily tidal action.'

The delineation of these sectors will vary from estuary to estuary and from day to day within a particular estuary.

The classification of estuarine types has also varied with the authors' own specialisations and they have been defined physiographically by Pritchard (1967) and Fairbridge (1980). Stratification parameters have also been used (Ketchum, 1951; Hansen & Rattray, 1966). The most widely used classification is a stratification/hydrochemical system first developed by Cameron & Pritchard (1963):

i)   Salt-wedge estuaries, in which the freshwater, being less dense than saltwater, flows outwards over the seawater surface, forming a saltwater wedge along the bottom of the estuary.

ii)   Fjords are a special case of salt-wedge estuary with a 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 effectively than entrainment. Surface salinity increases more slowly down the estuary than in salt-wedge types.

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

1.2.1.2 Flushing Parameters

An overall view of estuarine mixing properties can be provided by the estimation of an estuary's flushing time, which has a major influence on the timescales of the physical processes operating, and indirectly, the chemical processes. Arons & Stommel (1951) developed a one-dimensional model which defined the flushing number (F) of an estuary. The magnitude of F can be used to relate the estuary to the classification of Cameron & Pritchard (1963), described above. In its simplest form, however, flushing time (t_1) can be calculated using freshwater as a tracer (Bowden, 1980). Assuming that freshwater is removed at the same rate as river discharge adds it to the estuary, t_1 is given by;

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$$t_1 = F_T/R \tag{1.1}$$

where R is the rate of influx of freshwater and F_T is the total volume of freshwater present in the estuary. To calculate F_T, the estuary is divided into segments of volume δV and the appropriate freshwater fraction f assigned to each. F_T is then given as;

$$F_T = \sum_{n=1}^{n=N} f \, \delta V \tag{1.2}$$

$$\text{where} \quad f = \frac{S_o - S_n}{S_o} \tag{1.3}$$

and S_o is the salinity of open seawater available for mixing, S_n is the time-averaged salinity of the segment and N is the total number of segments.

1.2.1.3 Sediment Transport

The other major physical process which indirectly affects the chemical processes in an estuary is that of sediment transport, deposition and resuspension. Estuaries characteristically carry a large and variable suspended particulate load (Sholkovitz, 1979; Morris, et al., 1982; Loring, et al., 1983) which results primarily from land inputs (Holeman, 1968) or resuspension from mud banks (Biggs, 1970) and the sediment boundary layer during tidal stirring. A further input may be seaward sources (Gorsline, 1967).

The bulk of this sedimentary input, which is sand and gravel-sized material, is deposited around the tip of the seawater intrusion. The finer (< 2 μm) material, composed largely of clay minerals and metal oxyhydroxides, is in almost permanent suspension within the upper estuary,

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and will only flocculate in the more saline reaches (Dyer, 1979). This process of flocculation is dependant on a number of factors, including particle and electrolyte concentrations (Dyer, 1979). A portion of this material may undergo exchange between the colloidal and dissolved phases (Duinker, et al., 1974) and the prolonged residence time of these particles within the water column increases the likelihood of adsorption and precipitation reactions occurring.

Particle size fractionation can also occur in the region of the turbidity maximum of an estuary, due to the sorting action of tidal currents in the upper and middle estuary (Schubel, 1969).

1.2.2   The Chemical Composition of Estuaries

1.2.2.1 Elemental Distribution

The chemical composition of an estuary depends on a number of inputs to and outputs from the system and on the various interactions between elements and their compounds within the estuarine environment. This general interchange is shown in fig. 1.1 superimposed on the physical processes described in the previous section.

An estuary may receive inputs of allochthonous material from the litho-sphere as run-off, from the atmosphere in precipitation and gaseous exchange, and from the adjoining fresh and saltwater hydrospheres. There will also be inputs from the estuarine sediments due to resuspension and redissolution. Similarly, materials may be lost to the surrounding environments via evaporation, sedimentation and discharge into the ocean.
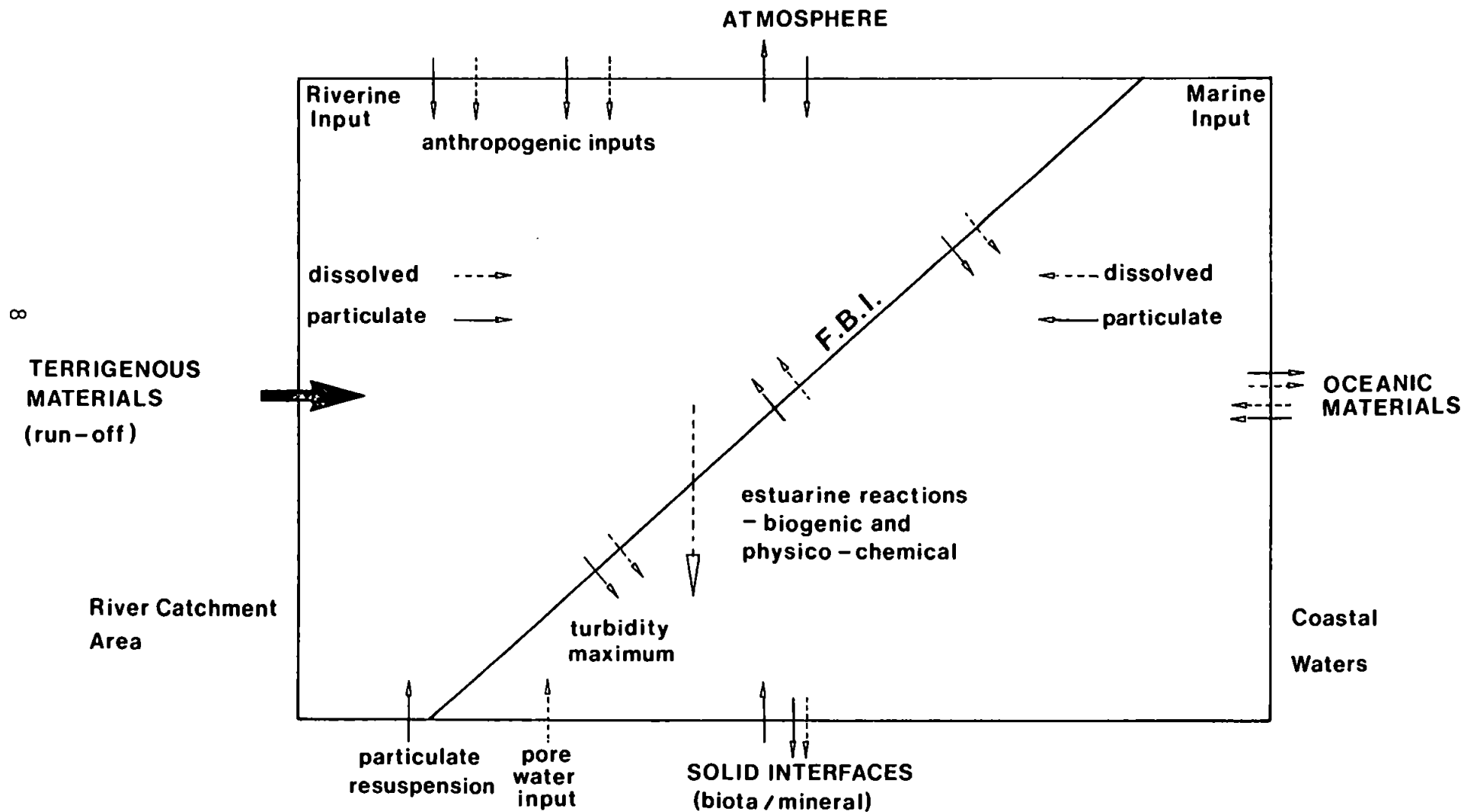
Figure 1.1 Physical and chemical processes occurring in the estuarine system

All these processes are in turn subject to diurnal and seasonal fluctuations such as variations in precipitation and tidal cycles. It is therefore possible to generalise to a degree regarding the elemental composition of river, estuarine and seawater; but the wide variations incurred by the action of individual combinations of factors must be borne in mind (Livingstone, 1963 ; Martin & Meybeck, 1979). Data for the average composition of fresh and saltwater have been compiled by Livingstone (1963) and Turekian (1969 & 1971), and these are presented in table 1.1. It is reasonable to assume that levels in a particular estuary will normally fall somewhere between these figures. This data indicates that in river waters the dominant species are Ca^+ and HCO_3^-, whereas in seawater Na^+, Mg^{2+}, Cl^- and SO_4^{2-} predominate. Trace elements such as Pb and Zn also show marked contrasts between riverwater and seawater levels, although some, such as As, show little apparent variation. All the major constituents of fresh and seawater show an increase in concentration with increasing salinity. They occur in seawater in quantities several orders of magnitude in excess of the freshwater values, with the exception of HCO_3^- ion. The minor elements display individual trends, with Sr, B and F enhanced in seawater and the more reactive elements, such as Fe, Mn, Cu and Zn, showing the reverse trend. Marked variations, of an order of magnitude, have been found among minor element concentrations between different freshwater sources (Kharkar, et al., 1968).

The amount of suspended material transported by rivers is generally greater than the amount of dissolved material, although this is not always the case. The world average particulate load in freshwater systems, 400-560 mg/L (Holeman, 1968; Turekian, 1971), is in marked contrast to the load in seawater, 100 µg/L (Chester & Stoner, 1972). The particulate load of a system is an important factor in the transport of some metals,

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Table 1.1 Comparison of Element and Species Levels in Freshwater and Seawater. (Adapted from Livingstone (1963) and Turekian (1969 & 1971))

Species	Freshwater (mg/L)	Seawater (mg/L)
Cl^-	7.8	19×10^3
Na^+	6.3	10.5×10^3
Mg^{2+}	4.1	1.3×10^3
SO_4^{2-}	11.2	2.65×10^3
K^+	2.3	3.8×10^2
Ca^{2+}	15	4.0×10^2
HCO_3^-	58.4	1.4×10^2
SiO_2	13.1	6
Br^-	0.02	65
CO_3^{2-}	?	18
Sr^{2+}	0.07	8
Al^{3+}	0.4	0.1×10^{-2}
B^-	0.02	4.5
F^-	0.1	1.3
Mn	7×10^{-3}	0.4×10^{-3}
Cu	7×10^{-3}	1×10^{-3}
Zn	20×10^{-3}	2.5×10^{-3}
As	2.0×10^{-3}	2.6×10^{-3}
Se	0.2×10^{-3}	0.09×10^{-3}
Sb	?	0.81×10^{-3}
Sn	2.0×10^{-3}	0.33×10^{-3}

especially Fe, Mn, Ni and Co (Gibbs, 1973; Martin & Meybeck, 1979).

The use of salinity as a conservative mixing index is widespread although some workers have preferred chlorinity (e.g. Carpenter, cited in Warner, 1972). Studies have shown that the major constituents of seawater behave conservatively (Hosokawa, et al., 1970; Carpenter, cited in Warner, 1972), although Carpenter (cited in Warner, 1972) found removal of Mg in the Potomac estuary. It has been suggested that this is due to uptake by ion exchange sites on clay minerals (Russell, 1970; Sayles & Mangelsdorf, 1979). Of the riverwater dominant elements, removal has been observed for Al (Hosokawa, et al., 1970), Fe (Coonley, et al., 1971; Yeats & Bewers, 1976; Holliday & Liss, 1976; Boyle, et al., 1977) and SiO_2 (Hosokawa, et al., 1970). Contrary evidence has been supplied for SiO_2, however, by Park, et al. (1970) and Boyle, et al. (1974). As the interpretation of mixing curves is not always easy, Boyle, et al. (1974) have proposed a mathematical model to aid in this interpretation.

1.2.2.2 Chemical Speciation

The composition of riverwater varies widely, depending on the major source of dissolved salts. There are two major sources; sea salts cycled to the river via precipitation and the weathering of rocks by rain water, which is the predominant source (Burton, 1976). The sea, in contrast, is of relatively constant composition. The main ionic constituents of river and seawater, and their concentrations, are shown in table 1.2.

The dramatic increase in ionic strength from virtually zero in riverwater

Table 1.2 Ionic Concentrations (in moles/L, M) of the Main Constituents of Standard Sea Water (SSW), High and Low Alkalinity (HARW/LARW) River Water. (Adapted from Dyrssen & Wedborg, 1980)

Constituent	SSW	HARW	LARW
CO_3^{2-} alkalinity (A_c)	2.4×10^{-3}	1.4×10^{-3}	0.1×10^{-3}
$[HCO_3^-]_t$	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

to 0.7 M in seawater, together with the changes in composition, cause

changes in the speciation of elements present and their possible removal

via flocculation and coagulation, or changes to their dissolved chemical

form. Biological activity may also affect the speciation of particular

elements (Morris, et al., 1978). The forms in which metal species can

occur in natural waters have been summarised by Stumm & Brauner (1975).

Figure 1.2 is adapted from their work.

It is operationally difficult to distinguish between dissolved and

colloidal dispersed forms of an element. For example, α-FeOOH(s)

(Goethite) or $Fe(OH)_3$ (s) (amorphous) may occur with particle sizes of

< 10 nm, therefore passing through a 0.45 μm filter. Organic substances

can assist greatly in the formation of stable colloidal dispersions.

The use of equilibrium models in determining the species composition of

natural waters has been developed by a number of workers, including

Sillen (1961), Garrels & Christ (1965), Zirino & Yamamoto (1972) and

Dyrssen & Wedborg (1974 & 1980). More recently, an improved specific

interaction model has been developed by Whitfield (1975). Turner, et al.,

(1981) have developed an equilibrium speciation model utilising a

recalculated data base, in order to elucidate some of the general

principles governing the speciation of elements in natural waters and

relating this to their periodicity.

1.2.2.3 Organic Processes - Humic Substances

The addition and removal of organic matter to and from the estuarine

environment is, as elsewhere, a biologically mediated process. Primary

production, respiration and other biological processes affect the Eh

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Size range

membrane filterable

true soln.

$-$ 1 nm

$-$ 10 nm

$-$ 100 nm

Free metal ions — Cu^{2+} aq./Fe^{3+} aq./Pb^{2+} aq.

Inorganic ion pairs;

inorganic complexes — $Cu_2(OH)_2{}^{2+}$/$Pb(CO_3)^0$

Organic complexes;

chelates — M – SR/M – OOCR/

porphyrin ring

Metal spp bound to

high MW. Organic — M – lipids/M – humic acid/

material lakes/M – polysaccharides

Metal spp in form

of highly dispersed

colloids — $FeOOH$/$Fe(OH)_3$/Ag_2S/$Mn(IV)$ oxides

Metal spp sorbed on

colloids — $Mx[OH]y$/MCO_3/$FeOOH$/$Mn(IV)$ oxides

Precipitates, org.

particles, biotic debris

Figure 1.2 The forms of metal species occurring in natural waters. (Adapted from Stumm & Brauner (1975))

and pH of systems due to their alteration of the levels of O_2 and CO_2. This will in turn affect the speciation of elements within the system. Biological processes are particularly important in estuaries due to the naturally large inputs of inorganic and organic matter to these systems.

The amounts of particulate organic matter (POM) (> 0.45 µm) and dissolved organic matter (DOM) (< 0.45 µm) in freshwater are usually smaller than the corresponding amounts of inorganic matter. Beck, et al. (1974) gave 120 mg/L inorganic matter for world riverwater, against 10 mg/L for DOM. For seawater the DOM content is usually in the range 0.5-5.0 mg/L, compared to a typical dissolved inorganic content of around 35 g/L (Head, 1976).

The concentration of total organic carbon (TOC) in estuaries tends to lie between the levels found in river and seawater. The distribution of TOC between the dissolved and particulate phases is, however, often different to that of the surrounding environments. DOC levels of 20 mg/L may be reached (Riley & Chester, 1971), although these levels are probably associated with pollution. Average levels are around 1-5 mg/L, similar to the POC levels in estuaries, which are around 0.5-5.0 mg/L for the Bristol Channel and Severn Estuary (Abdullah, et al., 1973).

The organic matter of an estuarine system is composed of an autochthonous fraction, derived from primary production and an allochthonous fraction contributed from adjacent environmental systems. Apart from the effect on Eh and pH parameters mentioned earlier, the main role of organic matter in influencing the behaviour of trace metals in estuaries is thought to be via complexation mechanisms with humic compounds. Humic substances, which constitute a large proportion of riverwater DOM, are

complex phenolic carboxylic acid macromolecules. They may be present in true solution or as hydrophilic colloids. Their anionic character enables them to react with trace metal cations to form chelation complexes. They are also thought to be important in the chemistry of Fe oxyhydroxide interactions in estuaries (Sholkovitz, 1976 & 1978; Boyle, et al., 1977; Senesi, et al., 1977; Sugimura, et al., 1978; Moore, et al., 1979; Sholkovitz & Copland, 1981; Tipping, 1981). Their stability is higher than that of corresponding inorganic-metal complexes (Reuter & Perdue, 1977). The solubility of humic acids is affected by salinity, those derived from land and river sources precipitating out with increasing salinity (Eckert & Sholkovitz, 1976). Organic and humic substances are also known to form coatings on solid surfaces, e.g. clay minerals. Mantoura, et al. (1978) computed speciation models for a number of metals, taking into account metal-humic interactions. In freshwater they found that > 90% of Cu and Hg were complexed, but < 11% of the other metals studied. In seawater > 99% of the humic material was complexed with Ca and Mg, only Cu was otherwise chelated to any significant degree (10%).

1.2.2.4 Clay Sorption

The cation exchange capacity of clays is considerable (Sayles & Mangelsdorf, 1979). This represents, however, only a small fraction of the total sorption capacity for metals of particulate matter in rivers and estuaries. It is therefore unlikely that direct adsorption is important with regard to trace metals, especially as they would have to compete with the major bulk species (Ca^{2+}, Mg^{2+}, Na^{+}) for exchange sites (Duinker, 1980). Clay minerals may, however, be important in their role as nucleation centres for Fe and Mn

oxyhydroxides in freshwater environments (Förstner, 1977) and during estuarine mixing (Aston & Chester, 1973). They may also serve as centres for the flocculation and precipitation of dissolved and colloidal organic matter during the estuarine mixing process (Rashid, et al., 1972; Sholkovitz, 1976; Liss, 1976).

1.3   The Aquatic Chemistry of Iron
1.3.1   The Colloid Chemistry of Iron

The behaviour of Fe in aquatic systems is largely related to its colloid chemistry. Colloidal dispersions are thermodynamically unstable due to their high surface free energy and are irreversible. Fe (III) oxy- hydroxides are therefore unstable in aqueous solution, with a tendency to flocculate, coagulate and precipitate. There is, however, a potential energy barrier which must be overcome before coagulation can occur (Shaw, 1970). Repulsive forces are due to like charge repulsion at the elect- rical double layer and attractive forces are Van der Waals-London based.

The Stern Plane of the electrical double layer is situated at around an hydrated ion radius from the particle surface, so that ions are not specifically adsorbed. If an electrolyte of opposite charge is added to the colloidal system, however, it will have the effect of compressing the double layer. This will cause the particles to approach close enough to each other that the Van der Waals forces will create attraction, leading to flocculation and precipitation.

The major factor which affects the coagulating power of an electrolyte is its oxidation state. The oxidation state of the co-ion and its

concentration have no effect. This gives rise to the Hardy-Schultze Rule which states that the coagulating power of an ion increases rapidly with its oxidation state. NaCl is the most concentrated electrolyte in the estuarine environment and is therefore likely to be the most important coagulating agent present. The much lower concentration of SO_4^{2-} ion present, however, which is divalent and will therefore precipitate Fe oxyhydroxides at lower concentrations, is probably sufficient in most cases to have an effect (Glasson, 1980, personal communication).

Complicating factors which affect the colloidal chemistry of Fe oxyhydroxides in estuaries include the preferential adsorption of SO_4^{2-} ions, which cause the oxyhydroxide to become negatively charged (Parks, 1975). A pH of zero point charge (pH_{zpc}) has been established for Fe (III) oxyhydroxide of 7.9 in 10^{-3}M $NaNO_3$ (Davis & Leckie, 1978a). This means that the adsorption of Cl^- or SO_4^{2-} from seawater would lower the pH_{zpc}, bringing it down to a value where it would exhibit a negative charge in the pH range normally associated with seawater.

Other factors which may influence the precipitation of Fe oxyhydroxides are the formation of inorganic and organic complexes, which may play a role in controlling the solubility and stabilisation of Fe compounds (Sillen, 1961). Aston & Chester (1973) have found that the presence of inorganic suspended particles increases the rate and extent of Fe precipitation in seawater and Perdue, et al. (1976) showed that dissolved organic matter forms complexes with Fe, thus affecting precipitation concentrations and rates. Sholkovitz (1976) found that this association was an important factor in the removal behaviour of Fe from the water

column. The effect of individual electrolytes present in seawater upon the flocculation of Fe, Al and humates was investigated by Eckert & Sholkovitz (1976), who found adherence to the Hardy-Schultz Rule stated earlier. Moore, et al. (1979) studied the in situ flocculation of Fe with organic matter during estuarine mixing and found evidence of colloidal Fe, stabilised by DOM, in the dissolved fraction. Evidence of organically complexed Fe in marine anoxic pore waters has been presented by Lyons, et al. (1979).

1.3.2   The Distribution and Speciation of Iron in Aquatic Systems

The levels of dissolved Fe found in natural water environments vary by several orders of magnitude. Levels found in riverwater include those of 670 µg/L (Livingstone, 1963), where filtration of the samples was not specified, 104 µg/L Fe in the Luce (Sholkovitz & Copland, 1981) and 0.3-8.8 µg/L Fe found in low flow filtered samples of several North Californian rivers (Jones, et al., 1974).

Seawater levels of Fe are consistently lower; 1.1 µg/L dissolved (Chester & Stoner, 1974) and 0.17 µg/L particulate (Betzer & Pilson, 1970). Other workers have found levels of 0.86-1.1 µg/L dissolved Fe throughout the water column (Kremling & Peterson, 1978), 1.6 µg/L in the North Atlantic and 1.3 µg/L in the Gulf of St. Lawrence (Bewers, et al., 1974 and 1976). Sugimura, et al. (1978) found 2.2-3.8 µg/L dissolved Fe in Japanese coastal waters. Higher levels have, however, been reported in seawater. Head (1971) found a mean dissolved concentration of 9.1 µg/L Fe in Southampton Water, which he compared to levels of 2.5-50 µg/L Fe in the North East Atlantic.

Estuarine levels of Fe fall naturally between those found in riverwater and seawater. The following have been reported; 167 µg/L dissolved Fe at 1^0/oo S and 33.5 µg/L at 20^0/oo S (Boyle, et al., 1974), while Elderfield & Hepworth (1975) found an average of 10 µg/L in the Conway Estuary.

Elderfield & Hepworth (1975) also found that sediment pore waters of the Conway Estuary contained 520 µg/L Fe with a flux between sediment and water column of 643 x 10^{-8} g/cm^2/yr. They concluded that organic matter was an important control of Fe chemistry in the anoxic estuarine environment. Sugimura, et al. (1978) found, using Amberlite XAD-2 macro-reticular resin to preferentially adsorb organically associated Fe, that 80-90% of the Fe in Japanese coastal waters was organic bound. Koenings (1976) showed that non-reactive Fe, e.g. $Fe(OH)_3$, was a minor component of North Gate Lake, an acid bog lake and that the majority of Fe (III) present was complexed to organic acids by peptised sol formation (Stumm & Morgan, 1981). Other studies (Riley & Taylor, 1969; Stuermer & Harvey, 1974 & 1977; Stuermer & Payne, 1976) have also concluded that organic acids (humic and fulvic) are the organic ligands binding Fe.

Organically-bound Fe was found to comprise 74-84% of the total Fe concentrations present in the pore waters of Loch Duich, Scotland (Krom & Sholkovitz, 1978). The levels measured greatly exceeded the levels found in the overlying sea, and also the calculated solubility of Fe in equilibrium with its least soluble species FeS (Brooks, et al., 1968; Duchart, et al., 1973; Elderfield & Hepworth, 1975). It was therefore concluded that, in agreement with the findings of Nissenbaum & Swaine (1976) and others (section 1.3.1), complexation of Fe with dissolved organic matter (DOM) was taking place.

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Fe (II) is more soluble than Fe (III), but will normally only exist in significant quantities in the anoxic environment of the sedimentary layers or in the inputs of acid mine streams. The complexation. of Fe (II) with humic and fulvic acids is known, however, to retard the oxidation process to Fe (III) (Theis & Singer, 1973), with the result that higher than expected levels may arise in the water column. Kremling & Peterson (1978) found, though, that the vertical distribution of Fe (III) was homogeneous in the water column, indicating that oxidation of Fe (II) from the sediment is complete very near to the oxic boundary layer.

Work by Sung & Morgan (1980) has shown that the oxidation of Fe (II) is dependant on temperature, pH and ionic strength and that the precipitates formed are crystalline (lepidocrocite: γ-FeOOH), unlike the amorphous precipitates of Fe (III) oxyhydroxide.

The principal speciation of Fe in aqueous solution is due to its hydrolysis and the main species are believed to be $[FeOH]^{2+}$, $[Fe(OH)_2]^+$, $[FeOH_4]^-$ and $Fe(OH)_3$ (Bryne & Kester, 1976). Hsu (1973) aged solutions of $Fe(ClO_4)_3$ through slow hydrolysis and determined that the initial reaction products were true solutions and the secondary reaction products colloidal (e.g. $Fe(OH)_3$). He suggested the existence of a dimeric soluble species which had been postulated by Mulay & Selwood (1955) from the following reaction, first proposed by Hedstrom (1953) (cited in Mulay & Selwood, 1955);

$$Fe^{3+} + H_2O \rightleftharpoons [FeOH]^{2+} + H^+ \quad K_{11} = 9.0 \pm 1.0 \times 10^{-4} \quad (1.4)$$

$$Fe^{3+} + 2H_2O \rightleftharpoons [Fe(OH)_2]^+ + 2H^+ \quad K_{12} = 4.9 \pm 1.0 \times 10^{-7} \quad (1.5)$$

$$2Fe^{3+} + 2H_2O \rightleftharpoons [Fe_2(OH)_2]^{4+} + 2H^+ \quad K_{22} = 1.22 \pm 0.1 \times 10^{-3} \quad (1.6)$$
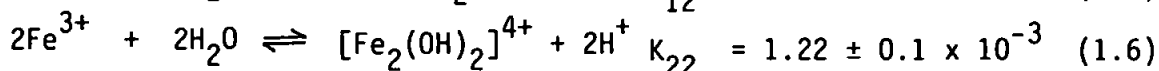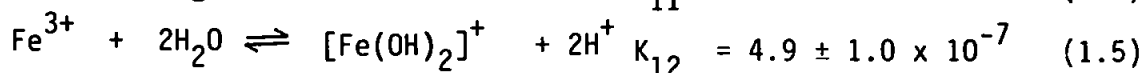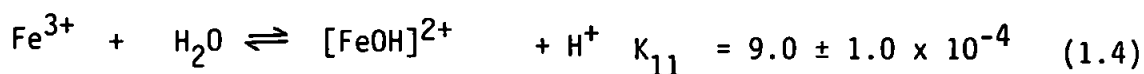
The existence of polymeric forms of Fe, in aqueous solution, of up to

50 Fe atoms length has also been proposed (Spiro, et al., 1966; Hsu,

1972 & 1973). Spiro, et al. (1966) carried out the hydrolysis of Fe

(III) NO_3 with HCO_3^- ion to produce an Fe polymer of average molecular

weight 1.4×10^5 and empirical composition $Fe(OH)_x (NO_3)_{3-x}$; x = 2.3-2.5.

Hem (1972) has produced a series of Eh-pH diagrams depicting the speciation

of Fe in natural waters under a variety of concentrations and co-species.

1.4   The Aquatic Chemistry of Arsenic

Arsenic is a group V B element of the periodic table. Under normal

conditions the trivalent and pentavalent ions are the most commonly

occurring oxidation states (Stark & Wallace, 1970). In natural environ-

ments, however, As can exist in several oxidation states, both as inorganic

and organometallic species, in both the dissolved and gaseous phases

(table 1.3). The most common species found are arsenate, arsenite,

methanearsonic acid (MMAA) and dimethyl arsenic acid (DMAA). These species

possess different chemical properties which will affect their relative

mobilities in a given environment. In the aqueous environment, dissolved

As species may absorb to suspended solids and be carried down to the

sediment. Since reduced gaseous As compounds can form, they may be

removed from the sediments as dissolved gas or in gas bubbles (e.g. CH_4).

Arsenic may thus cycle within the aquatic environment (Ferguson &

Gavis, 1973).

Studies of dissolved As in the Pacific Ocean have found a range of 1.4-

1.8 µg/L As (Crecelius, et al., 1975; Andreae, 1978; Sanders, 1980).

Similar studies in the Atlantic Ocean show slightly lower concentrations

of around 1.0-1.5 µg/L As (Waslenchuk, 1978). Levels of As in river

and estuarine systems may, however, vary over a greater range due to the

great variation in general composition of freshwater environments. Levels

Table 1.3   Arsenic Species Commonly Found in Natural Environments
          (Adapted from Holm, et al., 1979)

Species	Name(s)	Oxidn. State
AsO_4^{3-}	Arsenate	+5
AsO_3^{3-}	Arsenite	+3
$CH_3AsO(OH)_2$	Methanearsonic acid (MMAA)	+3
$(CH_3)_2AsOOH$	Dimethyl Arsenic acid (DMAA)[a]	+1
As°		0
AsH_3	Arsine[b]	-3
$(CH_3)_2AsH$	Dimethyl Arsine[b]	-3
$(CH_3)_3As$	Trimethyl Arsine[b]	-3

[a] IUPAC name = Hydroxydimethyl Arsine Oxide

[b] Gaseous

ranging from 0.2-1.0 µg/L As were found in the Ogeechee River estuary by
Waslenchuk & Windom (1978). Silker (1965) reported levels in the Columbia
River of between 0.45-4.9 µg/L As and a world average river burden of
1.7 µg/L was calculated by Boyle & Jonasson (1973). Martin & Meybeck
(1979) have suggested that As transport through the estuarine system is
predominantly in the dissolved phase; using an average dissolved river
concentration of 1.7 µg/L As and an average particulate concentration
of 5 µg/g produced a relatively high Dissolved Transport Index of 44.

The addition of anthropogenic As, especially from areas of mining and
smelting of arsenical ores, may result in river levels much greater than
those above. Portmann, cited in Aston, et al. (1975) reported levels of
5.5-10 µg/L As for samples of water (unfiltered) from the Lynher, Tamar
and Tavy rivers and Aston, et al. (1975) themselves reported levels
ranging from 10-250 µg/L As for rivers in South West England, an area of
past and present metalliferrous mining operations. Levels of As in
estuarine sediments have been reported from 2 µg/g in Morecambe Bay to
2500 µg/g in Restronguet Creek, a branch of the Fal estuary contaminated
by mining wastes (Langston, 1980). In many cases Langston (1980) found
strong positive correlations in estuarine systems between As and Fe in
the 1 N HCl extractable fraction of sediment. Arsenic/iron ratios of
190×10^{-4} were found in estuaries with a source of FeAsS, compared to
11×10^{-4} in unpolluted estuaries. Similar ratios to the latter figure
were obtained by Neal, et al. (1979) for sediments of the North Atlantic.
It appears that the Fe and As in the deep sea sediments are of authi-
genic origin and, due to the similarity in As/Fe ratios, such a source
for the extractable As and Fe in estuarine sediments cannot be discounted.

Arsenic occurs naturally in the marine environment in several different
oxidation states. Arsenate (AsO_4^{3-}) is the stable oxidation state,
the predominant dissolved form being $HAsO_4^{2-}$ (Ferguson & Gavis, 1972;

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Lowenthal, et al., 1977). The reduced, As (III) form, arsenite (AsO_3^{3-}) is sometimes found in significant quantities (Johnson & Pilson, 1975; Waslenchuk, 1978; Andreae, 1978 & 1979), even though it is unstable thermodynamically in oxic-marine environments (Ferguson & Gavis, 1972; Johnson & Pilson, 1975). Organoarsenic compounds, such as MMAA and DMAA may also be present, probably as a result of biological activity (Andreae, 1978; Waslenchuk, 1978; Sanders & Windom, 1980). AsO_4^{3-} enters into biological reactions due to its similarity to PO_4^{3-} (Andreae & Klumpp, 1979; Sanders & Windom, 1980).

Eh-pH diagrams for the aqueous speciation of As have been produced by several authors, including Bostrum (1967), Ferguson & Gavis (1972) and Hem (1977). More recently, Wagemann (1978) has examined a number of different metals to determine their possible effect on As speciation. He found that Ba, Cr, Fe and Cu were possible candidates, Ba being the most likely in freshwater environments.

1.5 The Removal of Arsenic from Aqueous Solution by Iron Oxyhydroxides
1.5.1 Trace Element Adsorption by Iron Oxyhydroxides

Fe (III) oxyhydroxide is slightly positive in distilled water and in NaCl solutions up to 1.0 M. It specifically adsorbs SO_4^{2-} ion from dilute SO_4^{2-} solutions and becomes negatively charged (Parks, 1975). In fresh water, Fe (III) oxyhydroxide is thus an anion adsorbant, but in seawater, due to the presence of SO_4^{2-} which lowers its pH_{zpc} (Davis & Leckie, 1978a), it will adsorb cations.

The origin of charge on oxides in aqueous systems results from interaction with water which hydroxylates the oxide surface. Solid hydroxides likewise have this hydroxylated surface (Parks, 1967). These surface MOH groups have Brønsted acidity, and charge can develop by amphoteric dissociation or hydrolysis (equivalent to H^+ desorption and adsorption);

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$$MOH \rightleftharpoons MO^- + H^+ \tag{1.7}$$

$$MOH^+ \overset{H^+}{\rightleftharpoons} MOH_2^+ \tag{1.8}$$

(MOH_2^+ is equivalent to hydrated M^+).

This is probably the principle mechanism of charge development on insoluble oxides and hydroxides (Healy & Fuerstanau, 1965; Parks, 1967).

Goldberg (1954) and Krauskopf (1956) were among the first to indicate that Fe oxyhydroxides might influence heavy metal concentrations in seawater by adsorption processes. Since then, numerous studies have been made of the role of Fe oxyhydroxides in trace metal adsorption (James & Healy, 1972; Gadde & Laitinen, 1974; Hem, 1977; Vuceta & Morgan, 1978; Kremling & Peterson, 1978; Davis & Leckie, 1978b; Venkataramani, et al., 1978; Millward, 1980). Whilst most of the work on Fe oxyhydroxides prior to 1980 was concerned with the adsorption behaviour of Fe (III), some studies of Fe (II) were made (e.g. Stumm & Lee, 1961). Little work was carried out, however, on the chemistry of Fe in systems directly comparable to those found in the natural environment (Crosby, 1982).

More recently the situation has changed somewhat, with the appearance of a number of studies on the behaviour of Fe in lake waters (Hoffman & Eisenreich, 1981; Tipping, et al., 1982; Adams, et al., 1982), including several studies of Fe (II) (Adams, et al., 1982; Davison, 1982; Macalady, et al., 1982).

1.5.2 The Reactivity of Arsenic in Estuaries

A study of several South Eastern U.S. rivers by Waslenchuk & Windom (1978) has found As to be unreactive and to produce a conservative mixing curve

along the estuary. This behaviour seems unexpected considering the potential removal mechanisms present in the estuary. It is well known the Fe precipitates as $Fe(OH)_3$ at the freshwater-brackishwater interface (F.B.I.) (Windom, 1975; Boyle, et al., 1977), producing a non-conservative mixing curve within an estuary. It is also known that AsO_4^{3-} ion is actively scavenged by $Fe(OH)_3$ (Crecelius, et al., 1975). If AsO_4^{3-} were present as the free ion, co-precipitation should occur. The findings of Waslenchuk & Windom (1978) therefore suggest that, at least in some cases, complexation of As with other ligands may take place.

Arsenic shows no significant complexation with inorganic radicles other than OH^- (Ferguson & Gavis, 1972), but organoarsenic complexes do exist (Waslenchuk & Windom, 1978), and therefore the majority of the As present may be rendered non-reactive. An alternative possibility, that organic matter complexes with and reduces the surface activity of $Fe(OH)_3$, has been proposed (Waslenchuk & Windom, 1978) and Koenings & Hooper (1976) have found evidence of this with regard to $Fe(OH)_3$-PO_4 interactions.

Removal of As by sedimentation of the organoarsenic complexes proposed above might also be expected, but it has been shown by Waslenchuk & Windom (1978) that As associates only with the lighter organic material, which remains suspended.

Several studies of As adsorption onto amorphous Fe oxyhydroxides have been made by Pierce & Moore (1980 & 1982), but as yet, no studies of Fe (II) derived precipitates have been made. The study of As adsorption is complicated by the existence of As (III) and As (V) species. Pierce & Moore (1982) studied both species, but only in low ionic strength media (0.01 M $NaNO_3$), and over ill-defined ageing times.

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1.6   Aims of the Present Work

The aim of this research was the investigation of the removal of As by Fe oxyhydroxides from aquatic systems. The specific objectives were as follows:

1.   To carry out environmental studies of water samples from the River Tamar, Devon and the River Carnon, Cornwall, together with sediment samples from the River Tamar, in order to investigate the estuarine behaviour of Fe, Mn and As. To develop a semi-quantitative picture of the estuarine partitioning of these elements between the water column and sedimentary phase.

2.   To carry out identification and characterisation of Fe precipitates on materials derived from both synthetic and natural sources, using a suite of techniques.

3.   To carry out an investigation of River Tamar sediments using scanning electron microscopy and X-ray microprobe analysis, in order to obtain evidence for the coating of sedimentary particles by Fe.

4.   To carry out laboratory experiments using an established chemical modelling procedure (Millward & Le Bihan, 1978; Millward, 1980; Crosby, 1982) in which the equilibration of As with the Fe solid phase could be followed in solutions of varying pH, ionic strength and temperature. To carry out similar modelling experiments on natural waters from areas of the Rivers Plym, Tavy and Carnon in Devon and Cornwall, which drain from mineralised catchment areas.

5.   To use the data from the laboratory models to further elucidate the kinetics and mechanisms of As uptake onto Fe oxyhydroxides and to extract rate constants and activation energies from these reactions wherever possible.

CHAPTER TWO

EXPERIMENTAL METHODS

2.1   Analytical Methods

The analytical methodology used in this work can be divided into two
main areas, although some of the techniques used were mutual to both.
The first area involved the analysis of environmental samples from
the water column and sediments, obtained on the estuarine surveys.
It also included the analysis of laboratory models used to determine
the adsorption behaviour of As onto Fe oxyhydroxides (sections
2.1.1 - 2.1.3).

The second area of investigation was concerned with the surface
characterisation of precipitates, both synthetically produced and
naturally occurring (sections 2.1.4 and 2.1.5). Electron microscopy
(section 2.1.4) was also used in the investigation of sediment
particles obtained on the estuarine surveys.

2.1.1   Flame Atomic Absorption Spectrophotometry

Aqueous acidified samples or sediment extracts (diluted as necessary
with 10% v/v HCl or distilled water) were aspirated directly into an
I.L. 151 atomic absorption spectrophotometer. An air-acetylene flame
was used for atomisation and Fe (initially) and Mn were detected at
their appropriate wavelengths using background correction. Output
was directly as absorbance units or via a Perkin-Elmer 101 chart
recorder. Standard operating conditions were used (I.L. AAS Methods
Manual, 1975). The detection limits (2 x blank value) were 200 µg/L Fe
and 10 µg/L Mn, with R.S.D.s (6 injections of 1 mg/L) of ± 2.7% and
± 0.9% respectively. Sediment extracts were also analysed for Cu, Zn

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and Pb using flame AAS and standard operating conditions. Hg was analysed in sediment extracts using a flameless cold vapour fluorescence method (Thompson & Reynolds, 1971; Thompson & Godden, 1975), applied to sediment analysis by Millward & Herbert (1981). Cd was determined using the Delves Cup method (Delves, 1970 & 1977).

2.1.2   Hydride Generation Atomic Absorption Spectrophotometry

Arsenic was analysed by the detection of its gaseous hydride, arsine (AsH_3). Two hydride-generating systems were utilised; a discreet sample method and a more sensitive continuous-flow method developed at a later date.

In the discreet sample method AsH_3 was generated in a closed reaction vessel (fig. 2.1) by the addition of 4% w/v sodium borohydride ($NaBH_4$) in aqueous 0.1 M NaOH to an aliquot of sample made up to a concentration of 6 M with HCl. The AsH_3 generated was swept into an argon-hydrogen flame by an auxiliary argon supply and detected at a wavelength of 193.7 nm using an I.L. 151 spectrophotometer. Nitrogen was substituted for argon at a later date because it was less expensive and made no difference to the conditions of analysis or sensitivity of the method. Output was via a Perkin-Elmer 101 chart recorder. The detection limit (2 x blank value) for the method was 6 µg/L As and the R.S.D. (10 injections of 100 µg/L) ± 1.4%.

The advantages of the continuous-flow system developed were an increased detection limit, a lower sample volume requirement (< 2ml) and the ability to speciate As into inorganic As (III) and As (V).
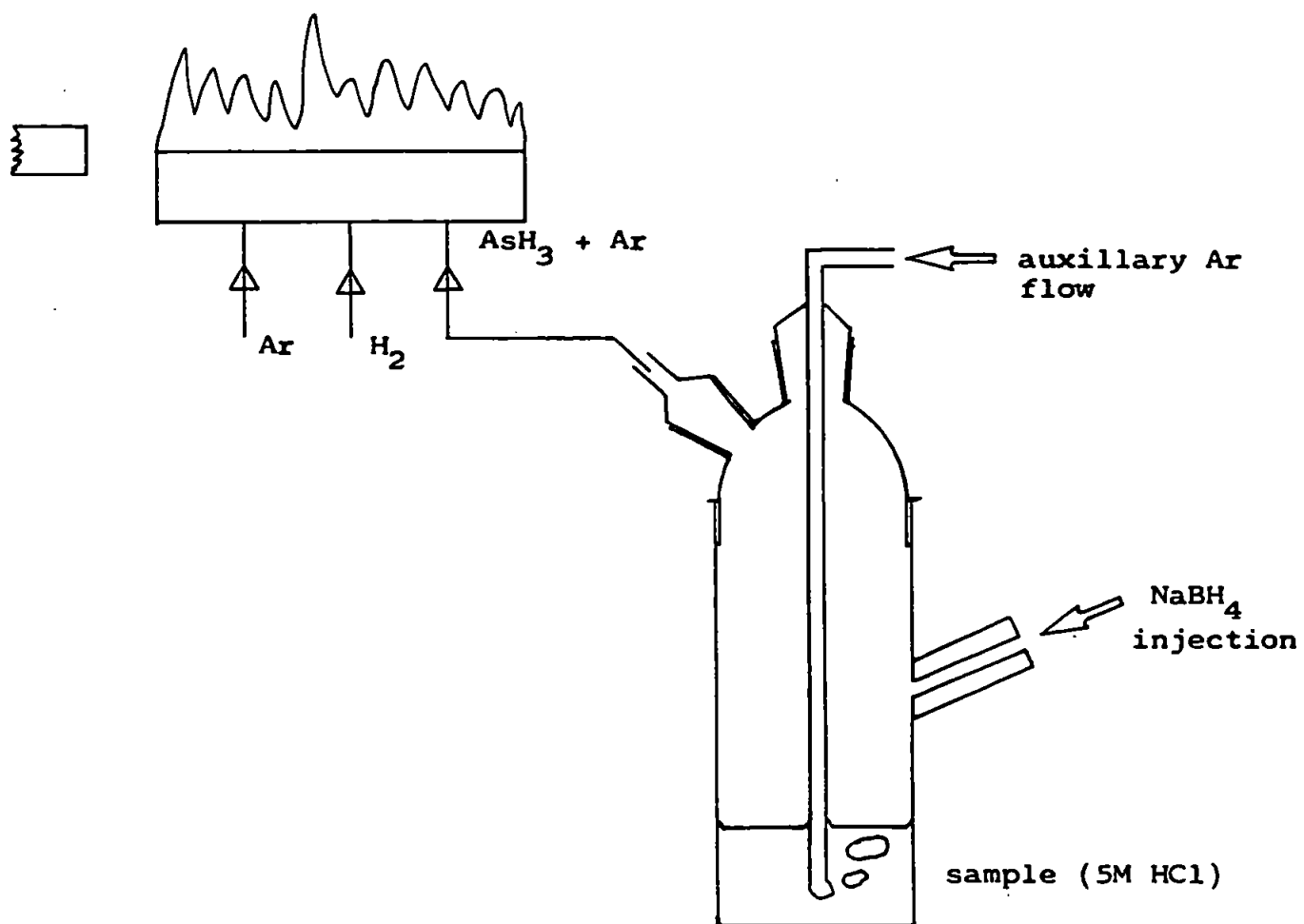
Figure 2.1   Discreet sample hydride generation system for the
determination of As using flame AAS

The differentiation of 'inorganic' As (III) and As (V) is achieved by exploiting the pH dependence for reduction of As compounds by $NaBH_4$ (Aggett & Aspell, 1976). It has been widely reported that As must be in the trivalent form to evolve a hydride (Fernandez & Manning, 1971; Chu, et al., 1972; Braman & Foreback, 1973) and consequently a highly acidic sample matrix is required for the determination of total As, in order that As (V) is reduced to As (III) at a similar rate to that of the formation of AsH_3 from As (III). Buffering the hydride-generating system to pH 5 with a sodium acetate-acetic acid buffer slows the reduction of As (V) to As (III) sufficiently that AsH_3 is generated only from the As (III) present (Howard & Arbab-Zavar, 1981). The subsequent determination of total As at an acid concentration of 6 M HCl allows the determination of As (V) in the sample by difference.

In the continuous-flow system (fig. 2.2) the aqueous sample was introduced using a peristaltic pump operating at 8.2 ml/min. Two Y-joints connected in tandem entrained either sodium acetate buffer (pH 5) or 6 M HCl and 4% w/v $NaBH_4$ (in 0.1 M NaOH) sequentially with the sample flow, supplied by a dual-channel peristaltic pump at 1.6 ml/min. The mixture was then passed through a 10 loop mixing coil before being transferred to a gas/liquid separator. The separated AsH_3 was then swept by an auxiliary nitrogen supply into a silica atomisation tube, based on the design of Thompson & Thomerson (1974) and heated by an air-acetylene flame mounted in a Pye-Unicam SP9 spectrophotometer. Detection was at 193.7 nm and output was via a Perkin-Elmer 101 chart recorder. The detection limit (2 x baseline noise) was 0.5 µg/L As and the R.S.D. (10 replicates of 5 µg/L As) was ± 4.9%.

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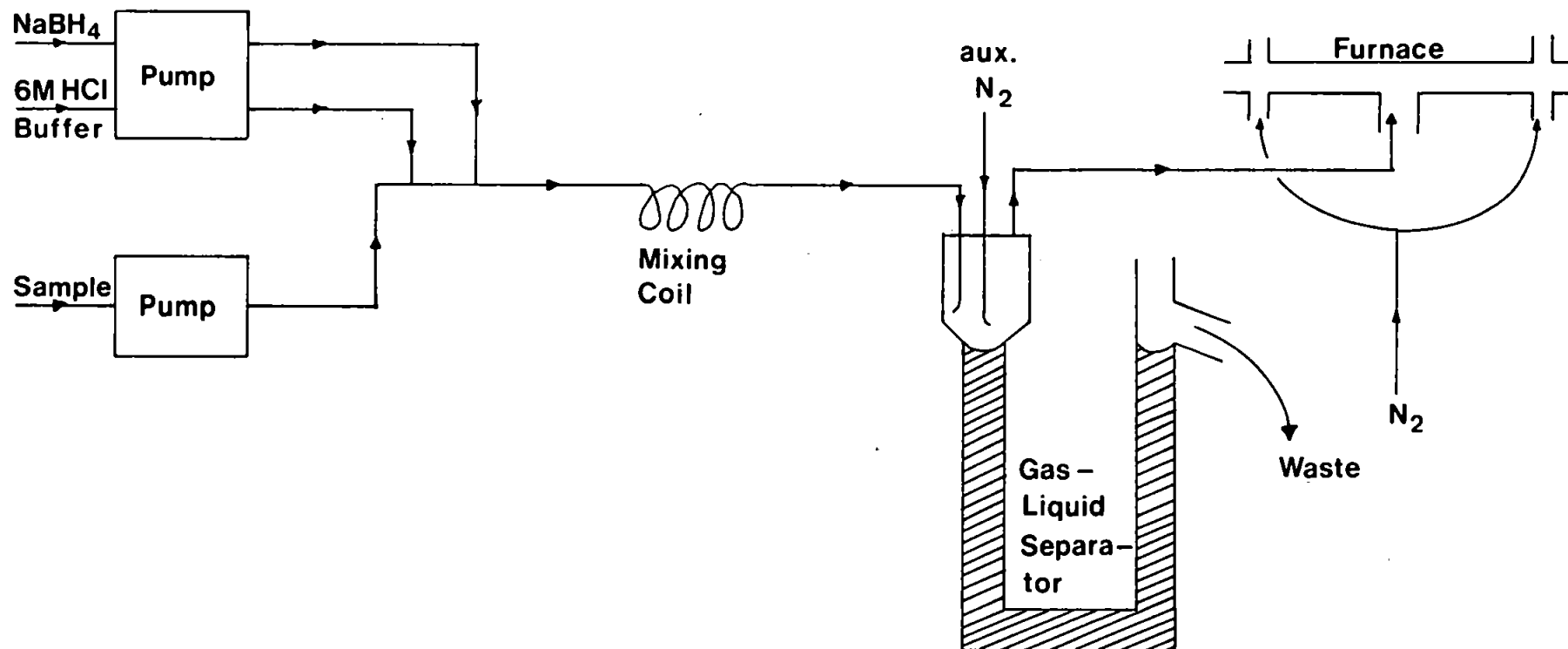
Figure 2.2   Continuous flow hydride generation system for the
determination of As

2.1.3   Spectrophotometric Analysis

Natural water samples from the water column surveys and for use in the model runs were analysed colorimetrically for Fe using the Ferrozine® reagent method (Stookey, 1970), modified by Gibbs (1979) and further modified by omitting the addition of acid to the Fe (II) sample (Crosby, 1982). The advantages of the Ferrozine method are twofold; it is very sensitive to Fe, with a molar extinction co-efficient of 27900 (Stookey, 1970) and it does not form a coloured complex with Fe (III) (Attari & Jaselskis, 1972). It may therefore be used to speciate Fe into Fe (II) and Fe (III) by difference, having reduced the Fe (III) in the sample to give a total Fe measurement.

Measurements were made using a Pye-Unicam model SP 500 spectrophotometer with 1 cm cells at a wavelength of 562 nm. Measurements were made within 5 minutes of complex formation and deoxygenated water was used for all necessary dilutions to minimise any equilibrium changes due to the slow oxidation of Fe (II) to Fe (III). Analyses of natural waters for the model studies were carried out immediately prior to each run for the same reasons.

2.1.4   Electron Microscopy

The laboratory prepared Fe precipitates (section 2.3.1) were examined using transmission electron microscopy. A Philips E.M. 300 microscope was used with an accelerating voltage of 80 kV. Several methods of sample mounting were tried, including wet loading and drying, but it was found that the most satisfactory results were obtained by spraying the dry precipitate directly onto Formovar coated copper grids using

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an air-brush.

Scanning electron microscopy was used to examine individual sediment particles (see section 2.2.2.4). These were mounted on aluminium stubs and sputter-coated with gold (12 μm). They were examined using a JOEL 35 scanning electron microscope coupled to a Link model 860 x-ray spectrum analyser. X-ray spectra were output via an X, Y plotter.

2.1.5   Surface Characterisation Studies

The laboratory prepared precipitates were also examined using additional techniques in order to further characterise their properties.

The surface areas and porosity of the prepared precipitates were measured using a gravimetric B.E.T. nitrogen adsorption technique. A C.I. mark 2B vacuum microbalance was used and the samples (~0.1 g) were degassed under vacuum on the balance for 24 h before analysis. Adsorption of nitrogen at -196°C was measured in steps of known volume until complete adsorption had taken place, in order to establish the surface area of the precipitate. Desorption was then measured over time to produce a hysteresis curve, from which the extent and nature of the precipitate's porosity could be determined.

Samples (10-20 mg) of the precipitates were mounted between poly-ethylene discs and their Mössbauer spectra recorded at room temperature (20°C) and at the temperature of liquid nitrogen (-196°C) using a Mössbauer spectrophotometer based on the design of Clark et al. (1967). A ^{57}Co source was used, of 25 mCi activity, in a rhodium matrix and

measurements were carried out over a period of 24 h. The resolution
of the isomer shifts (δ), measured against Fe metal as zero
velocity standard, was ± 0.1 mm/s, with a resolution of ± 0.05 mm/s
for quadrapole splitting. Output was via an X, Y printer/plotter.

X-ray diffraction analysis was carried out using a Hilger-Watts Y90
X-ray generator with Solus-Schall diffractometer and a Berthold scaler-
timer. Precipitate samples were placed in aluminium mounts and a
Mo-K$_\alpha$ source with Zr filter was used, generating at 36 kV and 18 mA.
The count rate was set at 3×10^2 counts/s with a 3 s time constant.
The d-spacings were calculated for all peaks produced and compared
to standard d-spacing values for Fe oxyhydroxides.

Infra-red spectra were also produced for all the precipitates. These
were recorded on a Perkin-Elmer 257 double-beam spectrophotometer
over the range 4000-400 wavenumbers. Samples were prepared as KBr
discs and the resultant spectra compared to IR standard spectra.

2.2   Environmental Studies

This section deals with the sampling and preparation procedures
followed during the estuarine surveys, the collection of natural water
samples for the modelling experiments and the analyses performed on
both the water and sediment samples. It also details the calibration
study carried out on the sediment extraction procedures used in this
work. The sampling and survey areas are shown in fig. 2.3
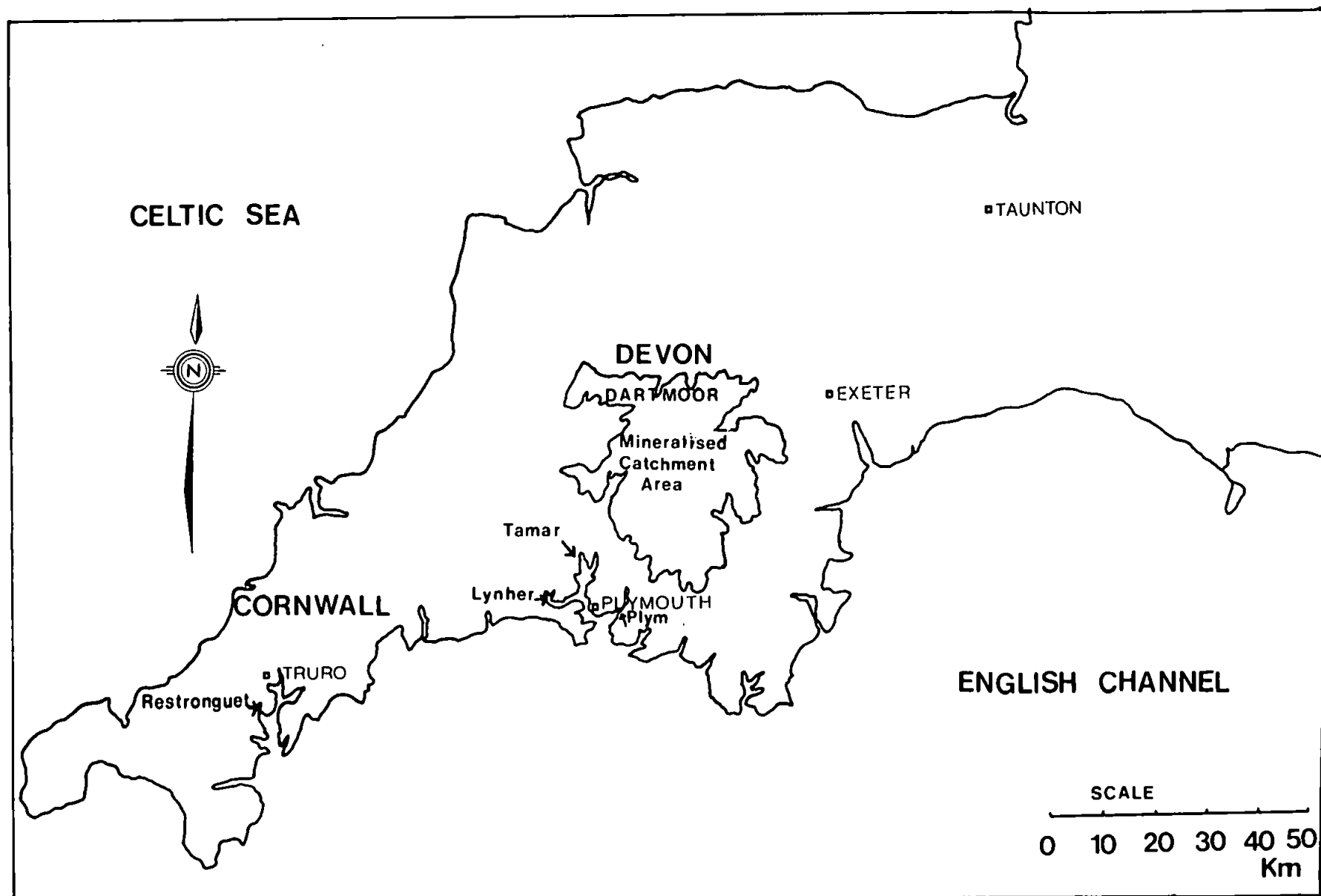
Figure 2.3   Collection areas for estuarine surveys, natural water samples and natural precipitates

2.2.1   Water Samples

Water samples for the estuarine surveys were collected from the River
Tamar estuary, Devon and the Fal estuary and its inlet, the River
Carnon, Cornwall.

Surface waters were collected either onboard R.V. Catfish or rubber
inflatable dinghy, if in shallow water, and using salinity as an
indicator of tidal incursion.   They were immediately filtered (0.45 µm
Millipore® cellulose acetate filters) in situ into acid-washed glass
bottles, containing sufficient HCl to bring the pH < 2.0.   The
dilution factor was negligible.   Surface temperatures and salinities
were determined for all samples using a pre-calibrated MC5 Mk II T/S
bridge and for selected surveys dissolved oxygen and suspended
particulate load were also determined using a Partech Dissolved
Oxygen Meter and a Partech Suspended Solids Monitor, calibrated with
Formazin standards.

Fe and Mn were analysed directly on these samples (diluted if
appropriate) using spectrophotometric analysis (section 2.1.3) and
flame AAS (section 2.1.1) respectively.   Arsenic was determined using
hydride-generation AAS (section 2.1.2).

Natural water samples were collected, for use in the laboratory
modelling studies (section 2.3.2) and precipitate studies (section
2.3.1), from ferrigenous acid mine streams situated on the mineralised
catchment area of Dartmoor, Devon and from the River Carnon, Cornwall.
The acid mine streams sampled in Devon were at Cadover Bridge on the

River Plym, Lady Bertha mine on the River Tavy and Wheal Franco mine on the River Walkham.

The water was collected and prefiltered (Whatman GF/C) into acid-washed polythene containers, filled to over-flowing and sealed to exclude air. These containers were packed in ice to retard oxidation of the Fe, returned to the laboratory immediately and stored at 4°C. These samples were refiltered (0.45 µm) immediately prior to use.

Interstitial water samples were collected from the acid mine stream at Cadover Bridge using in situ dialysis. Cellulose acetate dialysis bags were mounted in specially constructed perspex holders (Knox, et al., 1981). The dialysis bags contained approximately 20 ml of deoxygenated distilled water and were immersed in the anoxic layer of the stream sediment for 8 days (Benes & Steinnes, 1974). The samples were retrieved with an amount of the surrounding sediment intact to minimise the intrusion of air. They were placed in a glove bag previously flushed with nitrogen and returned to the laboratory immediately.

2.2.2   Sediment Samples

Sediment samples were collected from the upper section of the River Tamar, Devon (fig. 2.4). A total of 14 sample sites were chosen geographically and samples were collected in a rubber inflatable dinghy during low tide. Samples were collected by a surface scoop of the oxic top 1 cm of newly exposed sediment near the tidal edge. The samples were stored in sealed, acid-washed polythene containers,
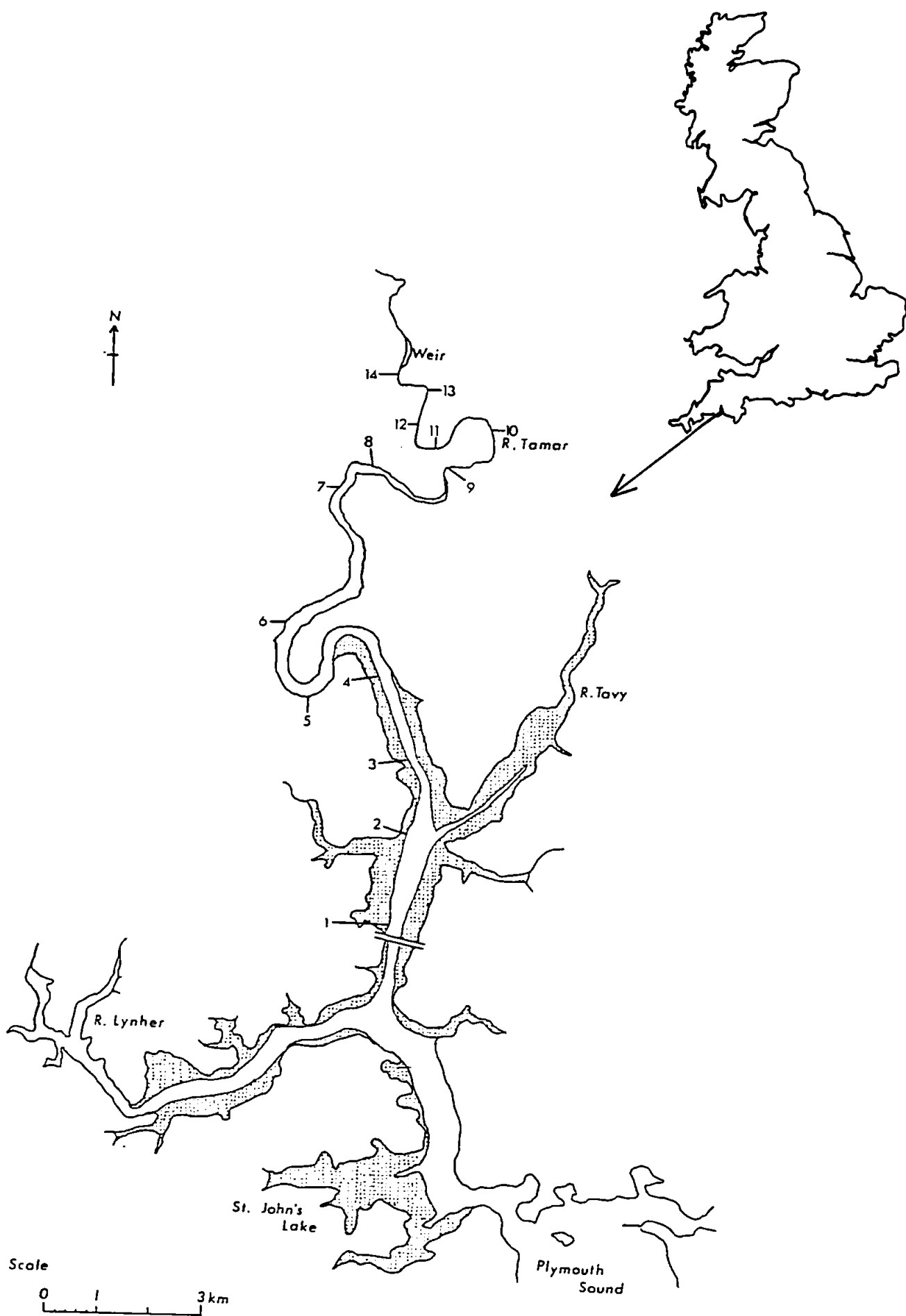
Figure 2.4   River Tamar - estuarine survey sample sites

returned to the laboratory and immediately washed several times with distilled water to remove salt. They were dried in an oven at 60°C for approximately 48 h, to constant weight. This procedure results in no metal losses on drying (Loring, 1982, personal communication). The samples were then cooled under vacuum to minimise readsorption of moisture, homogenised by light grinding and stored in plastic sample pots.

2.2.2.1 Sediment Extracts

A total digest of each sediment was prepared by treating an homogenised 1 g sub-sample with hydrofluoric acid/aqua regia at 100°C for 1 h in a sealed teflon bomb (Loring & Rantala, 1977). The resultant digest was washed into a 250 ml polythene volumetric flask containing 4.5 g boric acid to neutralise excess fluorides, and made up to volume with distilled water.

An 'available-metal' (non-detrital) leach was prepared by treating a further 10 g homogenised sub-sample with 50 ml of 25% v/v aqueous acetic acid at room temperature for 12 h on an orbital shaker (Chester & Hughes, 1967; Loring & Nota, 1973). This leachate was then filtered (0.45 μm) and the filtrate made up to 100 ml in a volumetric flask with 25% v/v aqueous acetic acid.

Both sediment extracts were analysed directly (with appropriate dilutions using distilled water) for Fe, Mn, As, Cu, Zn, Pb, Hg and Cd (see section 2.1.1).

In order to establish the validity of the HF sediment extraction procedure, triplicate analyses were carried out on two standard certified sediments, M.E.S.S.-1 and B.C.S.S.-1 (N.R.C. Marine Sediment Reference Materials). The identical procedure was followed and the results are given in table 2.1. The mean and standard deviations obtained for Cd, Cu, Hg, Mn, Pb, As and Zn were within the standard specification and showed good consistency. The results for Fe were low, especially for sample B.C.S.S.-1. The standard specifications given for Fe are, however, only semi-quantitative MS results. The results obtained for Al were very low compared to the standard values. This was considered to be due to the presence in the sample extracts of a gelatinous silica precipitate, which was particularly noticeable in two of the replicates made up in more concentrated form. Although Loring (1982, personal communication) has stated that this precipitate does not affect the analyses, such a precipitate might have a particular affinity for Al and would explain the anomalous results obtained.

In general, however, the consistency of results for the standard sediments was considered sufficient to validate the extraction procedure.

Acetic acid leaches of the standard sediments were also carried out and the results are shown in table 2.2. As no standard specifications are available for this extraction procedure, the results obtained in this work have been compared to other values obtained for sediments using the same extraction procedure (table 2.3).

It can be seen that the results obtained for the standard sediments

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Table 2.1 Analysis of N.R.C. Standard Sediments by Hydrofluoric Acid Digestion

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
As M.E.S.S.-1	9.2 ppm	7.8 ppm	9.5 ppm	8.8 ± 0.91 ppm	10	10.6 ± 1.2 ppm
B.C.S.S.-1	7.5 ppm	8.8 ppm	10.1 ppm	8.8 ± 1.3 ppm	15	11.1 ± 1.4 ppm
Al M.E.S.S.-1	6.24 ‰	0.93 ‰	0.83 ‰	2.67 ± 3.10 ‰	116	11.03 ± 0.38 %
B.C.S.S.-1	6.87 ‰	1.07 ‰	0.95 ‰	2.96 ± 3.38 ‰	114	11.83 ± 0.41 %

* C.V. of two results only

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Table 2.2 Analysis of N.R.C. Sediment Standards by Acetic Acid Leach

Element	Analysis	% of H.F.
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
As M.E.S.S.-1	0.939 ppm	10
B.C.S.S.-1	0.671 ppm	9

Table 2.3 A Comparison of the Acetic Acid Leach as a Percentage of the
Total Metal Level in Various Sediments

| Element | This Work | Loring (1980)[a] | Luoma and Bryan (1981) | | | Loring (1981) | |
	Tamar	Tamar	Tamar	Restronguet	Looe	Upper St. Lawrence Estuary	Saguenay Fjord
Cd	-	70-80	-	-	-	-	-
Cu	20	50-60	34	54	14	17-20	14-21
Fe	5-15	10-15	11	22	3	-	-
Mn	70-100	40-60	-	-	-	-	-
Pb	10-15	30-40	54	39	62	17-26	12-25
Zn	50-70	50-60	61	74	35	17-39	14-29

[a] Personal Communication

are low relative to the values for Tamar sediments. This is thought to be due to the different sediment mineralogies involved, the importance of which has been discussed by Loring (1976). Table 2.3 also shows that differences exist between this work and others on the River Tamar. This is again probably due to differences in mineralogical composition, temporally and spatially, within the same estuary. Luoma & Bryan (1981) have demonstrated the strong positive correlation between acetic acid extractable and total metal concentrations in a variety of sediments, indicating that the amount of non-detrital metal is largely determined by the total concentration present.

With these points in mind, it is possible to conclude that the HF digestion procedure has been established as a generally good indication of the total metal content of sediments. The acetic acid leaching procedure can be endorsed as an operational measure of the non-detrital metal present, being no less consistent than the majority of other non-detrital metal leaching procedures presented in the literature (table 2.4). It is important, however, when assessing non-detrital metal data, that the limitations of the particular extraction procedure utilised are accepted.

2.2.2.2 Total Organic Carbon

A 1 g sub-sample of the dried homogenised sediment was ashed at 670°C for 6 h in a muffle furnace. The percentage total organic carbon (TOC) was calculated from the weight loss.

Although this technique has been widely used (Holme & McIntyre, 1971;

Table 2.4 Comparison of Available Metal as a Percentage of Total Metal for a
Variety of Extraction Methods (after Luoma & Bryan, 1981)

Method of Extraction	% of Total Metal Concentration				
	Cu	Fe	Mn	Pb	Zn
Conc. Nitric Acid	100	100	100	100	100
1 M Hydrochloric Acid	38.1-91.0	7.5-39.6	15.3-78.1	51.9-92.0	35.1-92.3
25% Acetic Acid	5.5-90.0	3.9-25.3	10.7-100	20.0-73.6	29.0-91.1
Acid Ammonium Oxalate	0.1-62.5	7.9-63.9	14.1-67.7	0.7-42.5	24.1-83.4
Hydroxylamine HCl/HNO_3	0.1-48.8	0.7-14.4	8.3-66.5	0.8-70.8	10.6-70.1
Ammonium Acetate	0.4-4.9	0.005-0.40	2.4-21.6	0.4-7.3	1.0-10.7
Pyro-Phosphate	0.4-9.7	0.4-4.5	3.5-27.2	0.8-11.7	3.8-27.2
Ammonia	0.02-0.9	0.1-1.2	0.1-7.6	-	-
Sodium Hydroxide	0.004-1.27	0.05-1.04	0.17-2.30	-	-

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Millward & Herbert, 1981), comparison with more accurate methods
(Watson, et al., 1982) and the analysis of the N.R.C. standard
sediments indicate that the values obtained are high. Weight losses
on ignition, of up to 20%, after oxidation of the organic matter with
10% sodium hypochlorite, have been found (Mook & Hoskin, 1982).
These are presumed to be due to the loss of structural water from
within the clay mineral lattice. Weighed samples of both Tamar and
standard sediments were therefore treated with hydrogen peroxide
ANALAR. The samples were then filtered, dried at 50°C and reweighed.
Weight losses of between 5-15% were found, with a maximum loss due
to the procedure of 2%. On ashing the organic-free samples at 670°C
for 6 h, a further loss of 4-6% was found, presumed to be due to the
loss of structural water and the carbonate fraction of the sediment.

The corrected results thus obtained (table 2.5) were found to be in
good agreement with certified values for the standard sediments and
other work on the Tamar.

2.2.2.3 Grain Size Analysis

Particle size is well established as an important factor affecting
trace metal concentrations within samples (Thorne & Nickless, 1981).
Grain size analysis was therefore carried out in order to normalise
the sediment data and allow for grain size variation between samples.

A 10 g sub-sample of the dried homogenised sediment was wet-sieved
(63 μm). The ≤ 63 μm and > 63 μm fractions were retained, dried and
reweighed. The silt (≤ 63 um) fraction was calculated as a percentage

Table 2.5   Results of T.O.C. Analyses of Standard and River Tamar
Sediments Corrected for Structural Water Loss

N.R.C. Standard Sediments	T.O.C. (%)	
	This Work (corrected values)	N.R.C. specification
M.E.S.S.-1	4	2.99 ± 0.09
B.C.S.S.-1	5	2.19 ± 0.09
River Tamar Sediments (km from weir)	T.O.C. (%)	
	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

of the total. Losses were < 10%, the main source of experimental error being incomplete disaggregation of the sediment sample.

2.2.2.4 Scanning Electron Microscopy Studies

Homogenised sub-samples of selected sediments were separated into mineral fractions using a flotation method. A heavy mineral fraction was obtained using tetra-bromoethane (T.B.E.) which has a density (ρ) of 2.964 g/cm^3 at 20°C

Other intermediate fractions were obtained using mixtures of T.B.E. and acetone (ρ = 0.7899 at 20°C). These separated fractions were examined under an optical microscope and individual particles removed for S.E.M./ microprobe analysis (Loring, 1982, personal communication). These particles were mounted on aluminium stubs, sputter-coated with gold and examined under the scanning electron microscope. X-ray dispersive spectra were obtained in order to establish evidence of Fe coatings on these sediment particles (section 2.1.4).

2.3   Laboratory Studies

This section describes the procedures used in the preparation of the synthetic and natural Fe precipitates studied, and in the modelling experiments carried out.

2.3.1   Precipitate Preparation

20-30 L bulk natural water samples collected for precipitate preparation

were refiltered (0.45 μm) and stood for 24-48 h to allow precipitation to occur. The resultant precipitate was then concentrated on a high-speed centrifuge (6 x 250 ml aliquots) at 3000 rpm for 10 min. The supernatant was discarded and the precipitate washed thoroughly with acetone to remove gel water and arrest the ageing process (Glasson, 1960) before transfer to a suitable container. The collected precipitate was then dried at room temperature under vacuum and stored in plastic containers.

Natural flocs collected in a large volume of supernatant were immediately filtered (Whatman No. 45), on return to the laboratory, through a Büchner funnel and washed thoroughly with acetone. The collected precipitate was then dried at room temperature under vacuum and stored in plastic containers.

A synthetic Fe (II) derived oxyhydroxide was prepared at 2°C in a cold room by adding 0.05 M $FeCl_2$ to 20 L of $NaHCO_3$ buffered distilled water to give a final concentration of 1 x 10^{-4} mol/L. The precipitate was aged for 24 h and then collected and stored as above.

Surface characterisation studies were carried out on these prepared precipitates (section 2.1.5).

2.3.2   Adsorption Models

Adsorption studies were carried out in the laboratory using an established chemical modelling procedure (Millward & Le Bihan, 1978; Millward, 1980; Crosby, 1982) in which the equilibration of As with

the solid phase was followed in solutions of varying pH, ionic strength
and temperature. The analysis of the As remaining in the dissolved
phase after filtration was obtained by hydride-generation AAS (section
2.1.2). Similar modelling experiments were carried out on natural
waters from acid mine streams in the areas of the rivers Plym, Tavy,
Walkham and Carnon in Devon and Cornwall (section 2.2.1).

Models were run under carefully controlled conditions of pH, ionic
strength and temperature for both synthetic fresh and seawater solutions
and natural water samples.

The species Fe (II)/Fe (III) and As (III)/As (V) were studied.

2.3.2.1 Modelling Reagents

Synthetic freshwater solutions were prepared by dissolving 1.8 g
$NaHCO_3$ ANALAR in 10 L of distilled water and aerating the solution
overnight. This was carried out to increase the buffering capacity of
the medium. Seawater solutions were prepared using filtered (0.45 µm)
seawater collected from the area of the English Channel off Plymouth
Sound, Devon. Natural freshwaters were filtered (Whatman GF/C) in situ
and stored at 4°C. They were refiltered (0.45 µm) immediately prior
to use. Sewater analogues were prepared by the addition of a concentrated
solution of NaCl and $MgSO_4$ in the correct ratio, to the natural water
immediately prior to a model run, which brought the salinity of the
bulk solution to 34°/oo. All model solutions were stored in polythene
containers.

Arsenic stock solutions (100 mg/L) were prepared using sodium arsenite ANALAR (As (III)) and sodium arsenate ANALAR (As (V)). 1 ml of stock solution was injected into 1 L of the model solution to give a final concentration of 100 µg/L As.

Iron stock solutions (0.05 M) were prepared from Fe (II) and Fe (III) chlorides ANALAR. The Fe (II) stock solution was prepared in 0.01 M HCl to prevent hydrolysis. 1 ml of Fe stock solution was injected into 1 L of the model solution to give a final concentration of 5×10^{-5} M Fe (2.8 mg/L Fe).

2.3.2.2 Modelling Procedure

A 1 L glass reaction vessel was used to contain the model solution, thus giving the optimum practical volume/surface area ratio (Crosby, 1980). The reaction vessel walls were conditioned using an Fe solution and subsequently washed with distilled water only. This minimised the adsorption of Fe and As onto the container walls. A blank run of As (V) without the addition of Fe showed no adsorption onto the container walls over a period in excess of 2 h. The reaction vessel was held at a constant temperature in a thermostatted waterbath or in a constant temperature room and stirred throughout the model run. The pH of the model solution was controlled by the dropwise addition of either 10% aqueous HCl or NaOH and maintained at ± 0.05 pH units for seawater and ± 0.10 pH units for fresh and natural waters throughout the run. The volume change due to these additions was insignificant ($\ll$ 0.1%).

In the fresh precipitate studies Fe was injected simultaneously with the As, while for the aged precipitate studies Fe was injected and the bulk solution aerated for 24 h prior to the model run and the injection of As.

Twenty-five ml aliquots were then removed at specific time intervals over a 2 h period and immediately filtered (0.45 μm) into 50 ml volumetric flasks containing 25 ml of concentrated HCl to quench the reaction. These samples were subsequently analysed for As using hydride-generation AAS (section 2.1.2).

Natural water model solutions were analysed for Fe (II)/Fe (III) immediately prior to each run using the Ferrozine®reagent method (section 2.1.3).

CHAPTER THREE

ENVIRONMENTAL STUDIES

3.1   Water Column Analysis

A series of four surveys for the River Tamar and four surveys of the
River Carnon were carried out during this study. Water samples for
metal analysis were collected as detailed in section 2.2.1 and analysed
in the laboratory for Fe, Mn and As (section 2.1).

3.1.1.   River Tamar Surveys

The results of the dissolved metal surveys carried out in the River
Tamar during 1982/83 are summarised in figures 3.1-3.4. Figure 3.4
also shows the results of an As speciation study carried out on the
survey of 1/6/83. In general the profiles obtained from all the
surveys for Fe show removal from the water column occurring between
salinities of 0 and 5°/oo. This is in agreement with the findings of
Boyle, et al. (1977) for Fe concentrations in this range, and
contrasts with the freshwater removal of soluble Fe at riverine
concentrations of < 0.03 µg/L Fe observed by Eaton (1979) in the
Potomac Estuary.

The last three surveys were analysed for Fe using the Ferrozine®
reagent method, which is both more sensitive and less prone to matrix
interferences than the AAS method. In each case the expected smooth
non-conservative behaviour of dissolved Fe, from high freshwater
levels to low seawater levels, was not observed. A peak in the
dissolved Fe concentrations was often seen between 5 and 10°/oo S.
Although suspended solids were not measured on these surveys, this is
the region in which under certain tidal and river flow conditions the

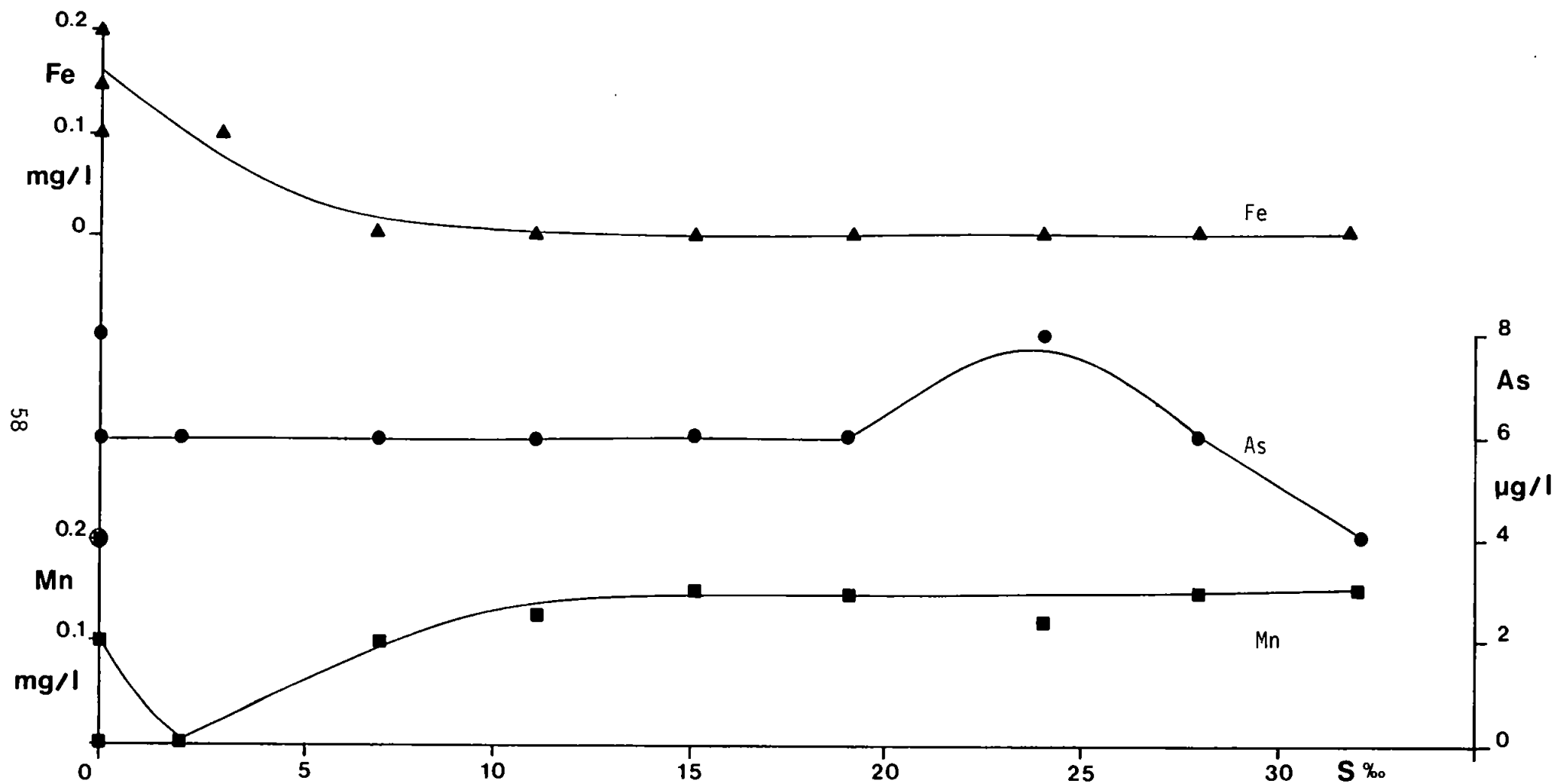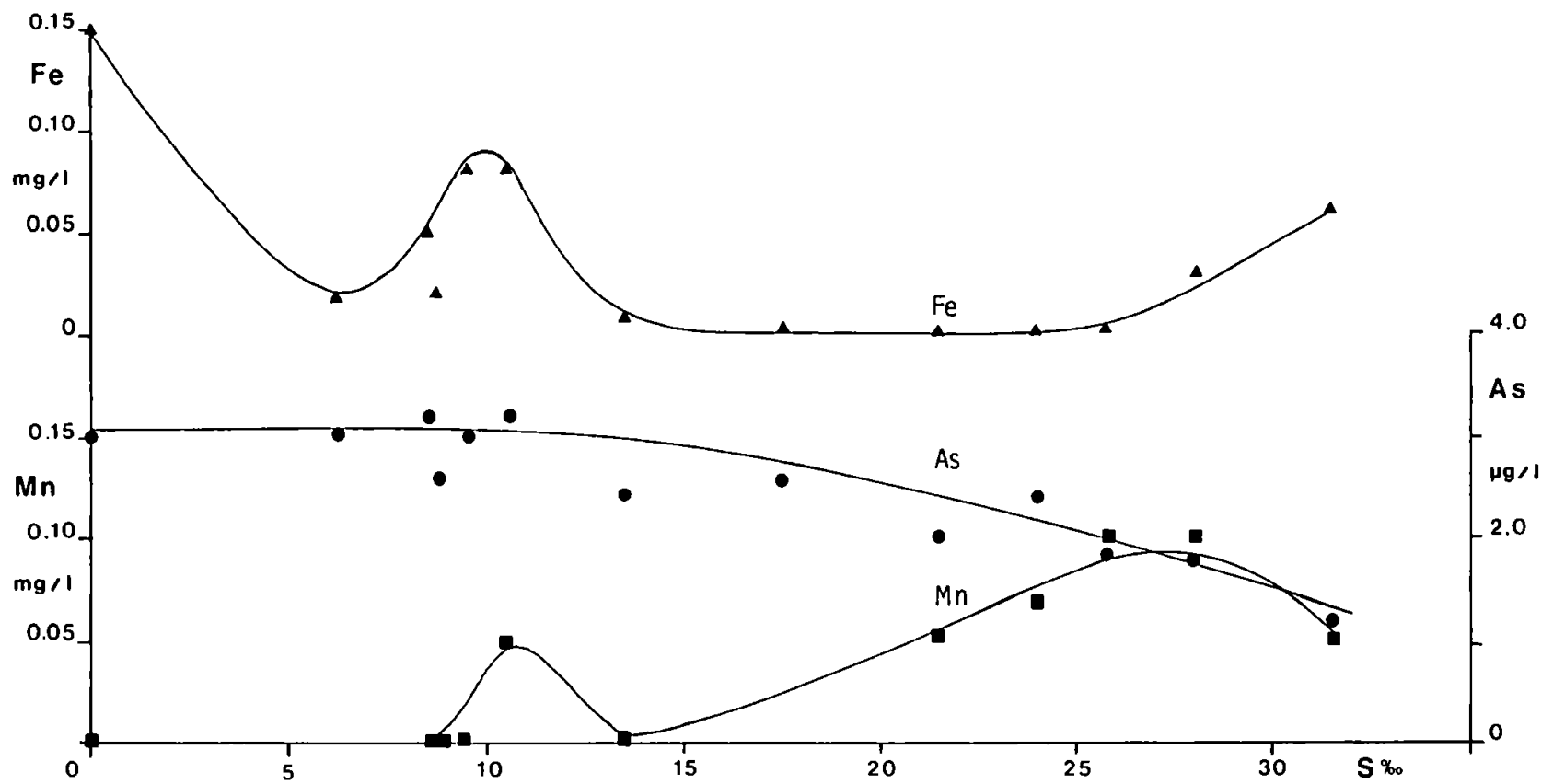Figure 3.1   River Tamar - dissolved metal survey (10/2/82)

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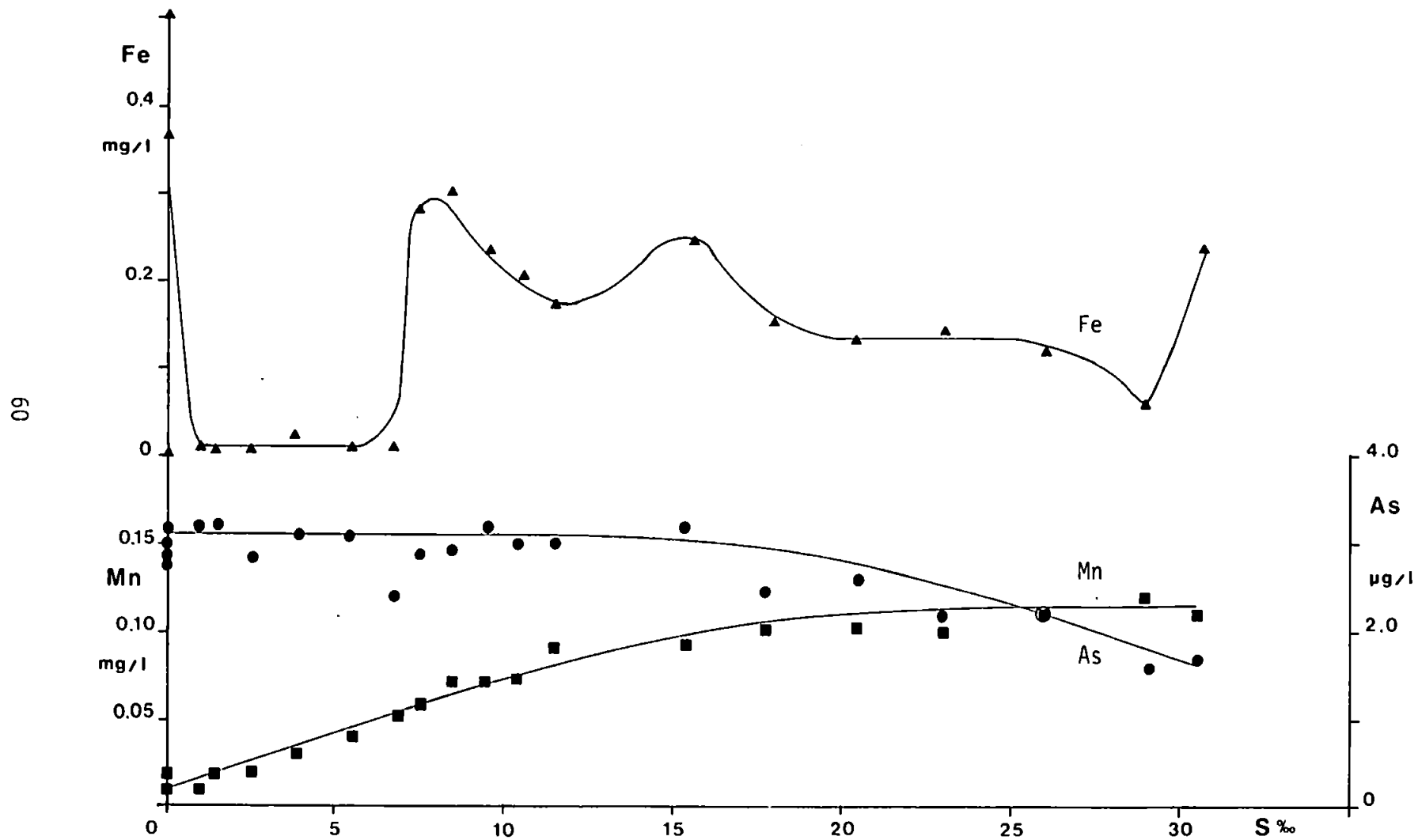
Figure 3.2   River Tamar - dissolved metal survey (9/3/83)

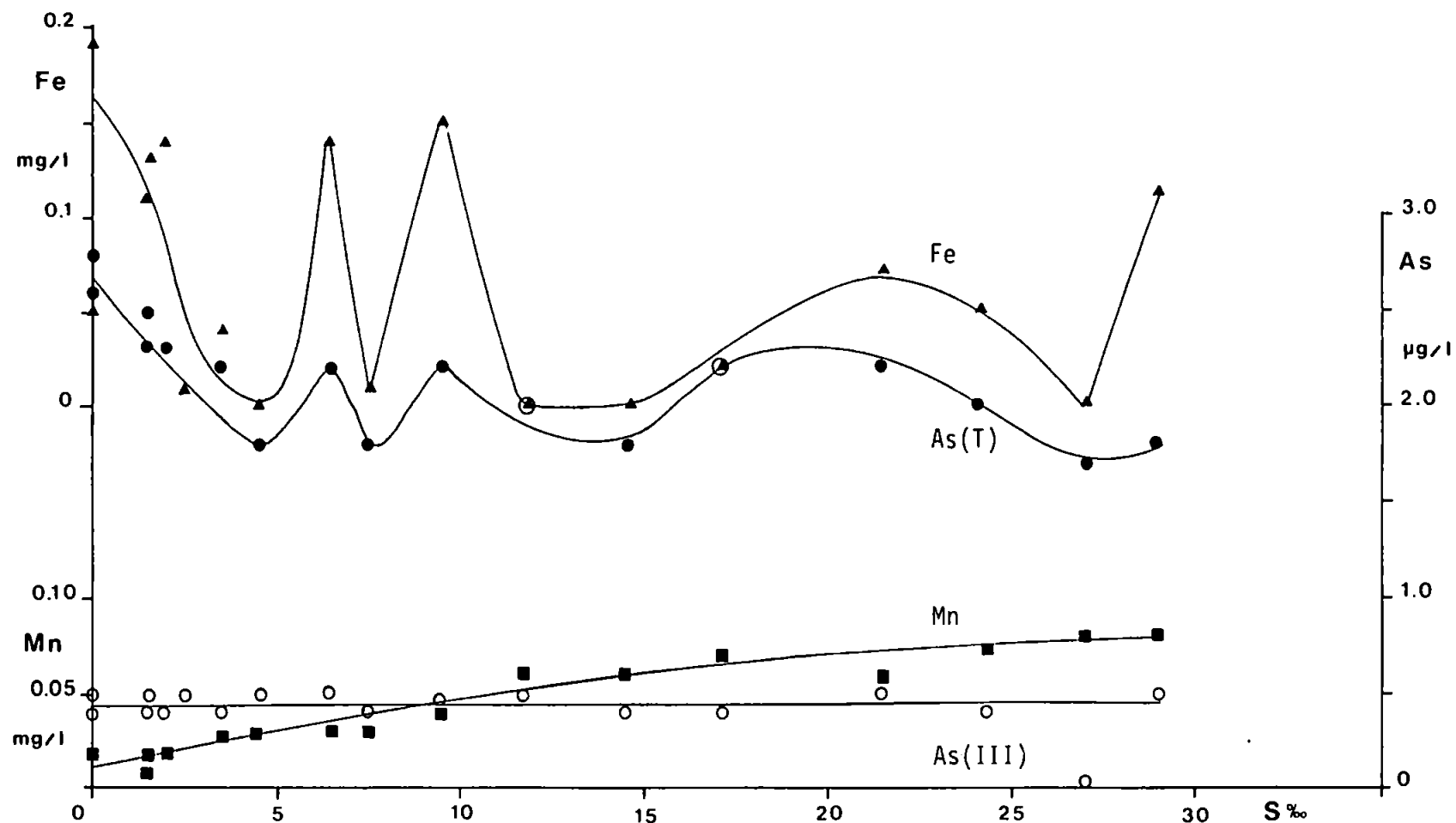Figure 3.3   River Tamar – dissolved metal survey (14/4/83)

Figure 3.4   River Tamar - dissolved metal survey (1/6/83)

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turbidity maximum can be found (Ackroyd, 1983; Morris, et al., 1982).
It is likely that this increase in dissolved Fe concentration is
due to the resuspension of Fe from the sediments, in the reduced,
soluble Fe (II) form which has a half-life ($t_{\frac{1}{2}}$) of 5 min in seawater
at pH 8.0 and 15°C (Murray & Gill, 1978). This accounts for the
subsequent removal of dissolved Fe downestuary.

A further peak in dissolved Fe concentrations was observed in these
surveys, in the saline end of the estuary, at around 30°/oo S. These
samples correspond with an area of anthropogenic input into the
estuary; comprising the City of Plymouth and its Naval Dockyard and
the town of Saltash. Other work by this author (Marsh & Evens,
unpublished) has shown that intermittent peaks in dissolved Fe
concentrations can occur in this area, associated with sewage and
industrial waste inputs into the estuary.

The results for dissolved Mn show that the concentrations are very
low at S < 3°/oo, suggesting removal in the turbid waters upestuary
of the salt wedge, in keeping with the findings of other workers
(Morris, et al., 1978; Knox, et al., 1981; Langston, 1983, personal
communication). This removal could be the result of biological
oxidation processes (Wollast, et al., 1979) or heterogeneous reactions
within the suspended matter (Morris & Bale, 1979; Knox, et al., 1981).

In contrast to Fe, Mn shows an increase in the dissolved phase between
5-15°/oo S in all the surveys, with occasionally well-defined maxima.
Although Sholkovitz (1976) and Boyle, et al. (1977) showed that Mn is
bound to the Fe precipitate and should therefore exhibit removal

within an estuary, they suggest that this may be overwhelmed by the dominance of the element's soluble form. This is also in keeping with observations in the River Tamar by other workers (Morris, et al., 1978 & 1982; Knox, et al., 1981), the Beaulieu estuary (Holliday & Liss, 1976) and the Rhine and Scheldt estuaries (Wollast, et al., 1979; Duinker, et al., 1979). It is widely believed that this maximum is due to the remobilisation of sediments during tidal mixing, which releases Mn in the soluble Mn (II) form from sediment pore waters into the water column (Graham, et al., 1976, Evans, et al., 1977; Knox, et al., 1981; Morris, et al., 1982). Further adsorption onto particulates is kinetically inhibited in saline conditions (Morris & Bale, 1979).

It is possible that the decrease in dissolved Mn concentration down-estuary observed is due to the slow oxidation of Mn (II) to Mn (IV). The appearance of particulate Mn has been shown in the Scheldt estuary (Duinker, et al., 1979) and the Rhine estuary (Eisma, et al., 1980); both having a long flushing time (t_f). Uncles (1983, personal communication) has indicated that t_f for the River Tamar varies between 7-12 d. This variation in t_f, coupled with the tidal conditions pertaining to an individual survey, may offer an explanation for the shape of the resuspension curves observed for Mn. For example, the survey of 9/3/83 (fig. 3.2) carried out during conditions of high flow (short t_f) and neap tides, shows resuspension occurring around 15-17°/oo S, with a well defined peak around 27°/oo S. Under these circumstances, tidal stirring would tend to be localised within the middle to lower regions of the estuary, in keeping with the observed Mn profile.

In contrast to this behaviour, the survey of 1/6/83 (fig. 3.4) was

carried out during summer low flow rates (long t_f), on the turn of the spring tide. Under these conditions, successively rising tides leading up to the spring tide will inject repeated slugs of dissolved Mn into the water column, which combined with the low flow rate within the estuary, will create the smearing out of the resuspended Mn profile observed.

The data obtained for dissolved As suggests that a complex chemical reactivity is involved in the case of the River Tamar. The results indicate variations in the nature of the As profiles between surveys. The surveys illustrated in fig.s 3.2 and 3.3 show an apparently conservative, unreactive profile, whereas the profile of fig. 3.4 and the additional survey of 19/8/81 (fig. 3.5) indicate that resuspension of As is occurring. This contrasts with the conservative behaviour of As in estuaries of the S.E. United States (Waslenchuk & Windom, 1978). These workers related the non-reactive behaviour of As to its association with low molecular weight organic matter, preventing its adsorption and removal by precipitating Fe oxyhydroxides. Elsewhere in this study it is proposed that, while the presence of organic matter may inhibit the precipitation of Fe in freshwater, it has no observable effect on the adsorption of As onto Fe oxyhydroxides in natural waters once precipitation has been initiated by increasing salinity (section 4.2.2.2.c). An alternative mechanism is therefore proposed here to explain the behaviour of dissolved As in the River Tamar.

It is suggested that the variations in As behaviour observed could be due to the chemistry of As (III) in the estuary. Although As (III) (fig. 3.4) was only analysed in one summer survey, where it was found to be unreactive and present at levels of about 0.5 µg/L throughout the
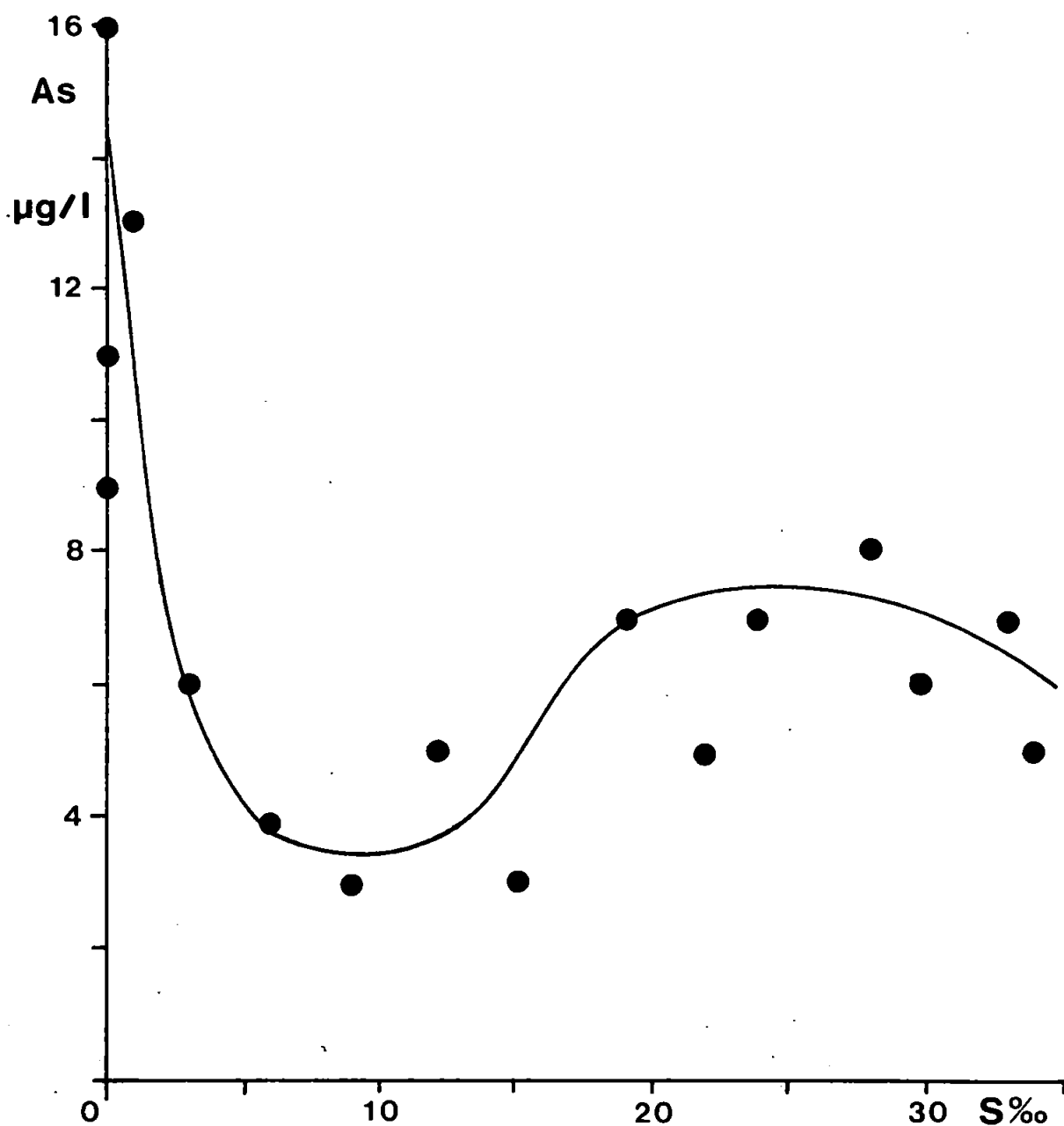
Figure 3.5   River Tamar - dissolved As survey (19/8/81)

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estuary, Howard, et al. (1982) have shown that in the Beaulieu, thermo-dynamically unstable As (III) is present in the water column during the summer months at levels of 0.1-0.3 µg/L when temperatures are around 12-15°C, comparable to the Tamar summer surveys (12-14°C). This presence of As (III) is probably due to phytoplankton metabolism (Johnson & Burke, 1978). Howard, et al. (1982) also found that As (III) was absent in the water column during the winter months at temperatures < 10°C, again comparable with those of the Tamar (7-8°C). If this situation pertains to the Tamar estuary, then the mid-estuarine maxima of As seen in some of the surveys could be due to the oxidation of sediment deposited As (III) and its subsequent remobilisation as As (V). This oxidation could be brought about by a redox couple between sedimentary Mn (IV) and As (III), as described by Oscarson, et al. (1981 & 1983). The redox couple ;

$$HAsO_2 \ + \ MnO_2 \ + \ 2H^+ \rightarrow H_3AsO_4 \ + \ Mn^{2+} \qquad \log K = 23.1 \qquad (3.1)$$
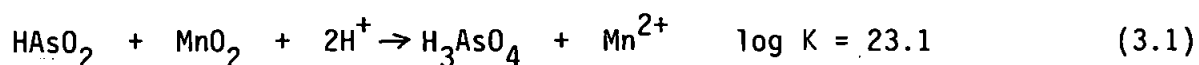
has been shown (Huang, et al., 1982) to be more favourable than the Fe-As redox couple;

$$HAsO_2 \ + \ 2Fe^{3+} \ + \ 2H_2O \rightarrow H_3AsO_4 \ + \ 2Fe^{2+} \ + \ 2H^+ \quad \log K = 7.5 \quad (3.2)$$
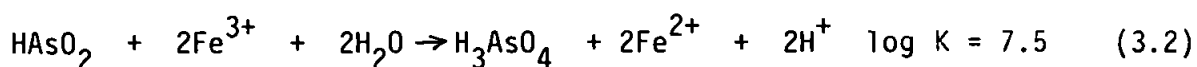
presumably because of the slower reaction kinetics of the latter couple. However, the view taken in this present study (section 4.2.2.1.b) suggests that the Fe-As redox couple cannot be completely discounted over the timescales involved in estuarine physical processes. The speciation study carried out on the River Tamar (fig. 3.4) indicates that the peaks observed for dissolved As in the water column are due to As (V), which is in agreement with a Mn-As redox couple.

In addition, the dissociation of the H_3AsO_4 (formed in equation 3.1) within the sedimentary environment will form an excess of H^+ ions;

$$H_3AsO_4 \rightleftharpoons H_2AsO_4^- + H^+ \qquad\qquad (3.3)$$

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+ \qquad\qquad (3.4)$$

and it is likely that these excess H^+ ions will attack the surfaces of ferromanganese oxides, partially dissolving them (Oscarson, et al., 1983). This could contribute to the dissolved Fe peak found in some of the estuarine profiles and also expose fresh Lewis acid sites on the MnO_2 particles, promoting the As oxidation process.

In order to test the feasibility of the hypothesis that the As (V) peaks observed in the water column were due to sediment pore water resuspension, a first-order calculation was carried out using pore water data supplied by Langston (1983, unpublished data). The mid-estuarine region (10-20 km downestuary) was chosen and a total sediment volume for the segment calculated, based on its area and an assumed depth of resuspended sediment of 5 cm. A pore water content for the sediment of 70% was also assumed. The water column volume of the segment was calculated assuming an average water depth of 2 m. This gave a range of pore water contribution to the water column of 0.12-0.26 µg/L As. This range is low compared to the observed range of peak values, which was 0.5-3.0 µg/L As. While the assumptions made in this calculation were considered reasonable, it must be stressed that they only represent an approximation and contrast with an average figure of 3.0 µg/L obtained by Langston (1983, personal communication) himself.

3.1.2   River Carnon Surveys

The four dissolved metal surveys of the River Carnon were carried out during 4/83 (T ~ 9-12°C) and 6/83 (T ~ 13-16°C). The results of these

surveys are shown in fig.s 3.6-3.9. Considerably higher concentrations
of Fe, Mn and As were observed, compared to the Tamar, together with
a wide range in pH from 5.0-8.0.

The data for the initial two surveys, on the 11-12/4/83, suggest that
dissolved Fe was behaving conservatively on these occasions. In the
light of Fe's widely established removal at the freshwater-brackish
water interface (Coonley, et al., 1971; Boyle, et al., 1974; Holliday
& Liss, 1976; Boyle, et al., 1977; Sholkovitz, 1978), these results
were initially thought to be due to a sampling artefact, whereby Fe (III)
particulates of colloidal dimensions were passing through the 0.45 µm
filter, used for the operational definition of 'dissolved' metal. To
test this hypothesis, duplicate samples were taken at some stations on
the subsequent surveys and filtered through 0.22 µm filters. No
significant differences in dissolved metal concentrations were found
for these sites between the 0.22 µm and 0.45 µm filtered samples
(table 3.1). On the second two surveys, however, Fe exhibited a removal
profile in the estuary. The possibility therefore remains that
colloidal Fe was responsible for the apparently conservative behaviour
of the Fe. Because of the particular topography of this estuary, which
results in an extensive, shallow mid-section, it was not possible on
falling tides to approach the freshwater end-member from the estuary
itself. Freshwater samples had, therefore, to be taken at land-based
stations some distance upriver from the estuary. An alternative
hypothesis for the conservative behaviour of Fe found in the initial
two surveys, suggested by this sampling regime, is that the removal
of Fe had taken place in the freshwater region (Eaton, 1979), or in the
low salinity region of the estuary, upstream of the saline survey area;
and that a quasi-conservative Fe profile was produced due to the
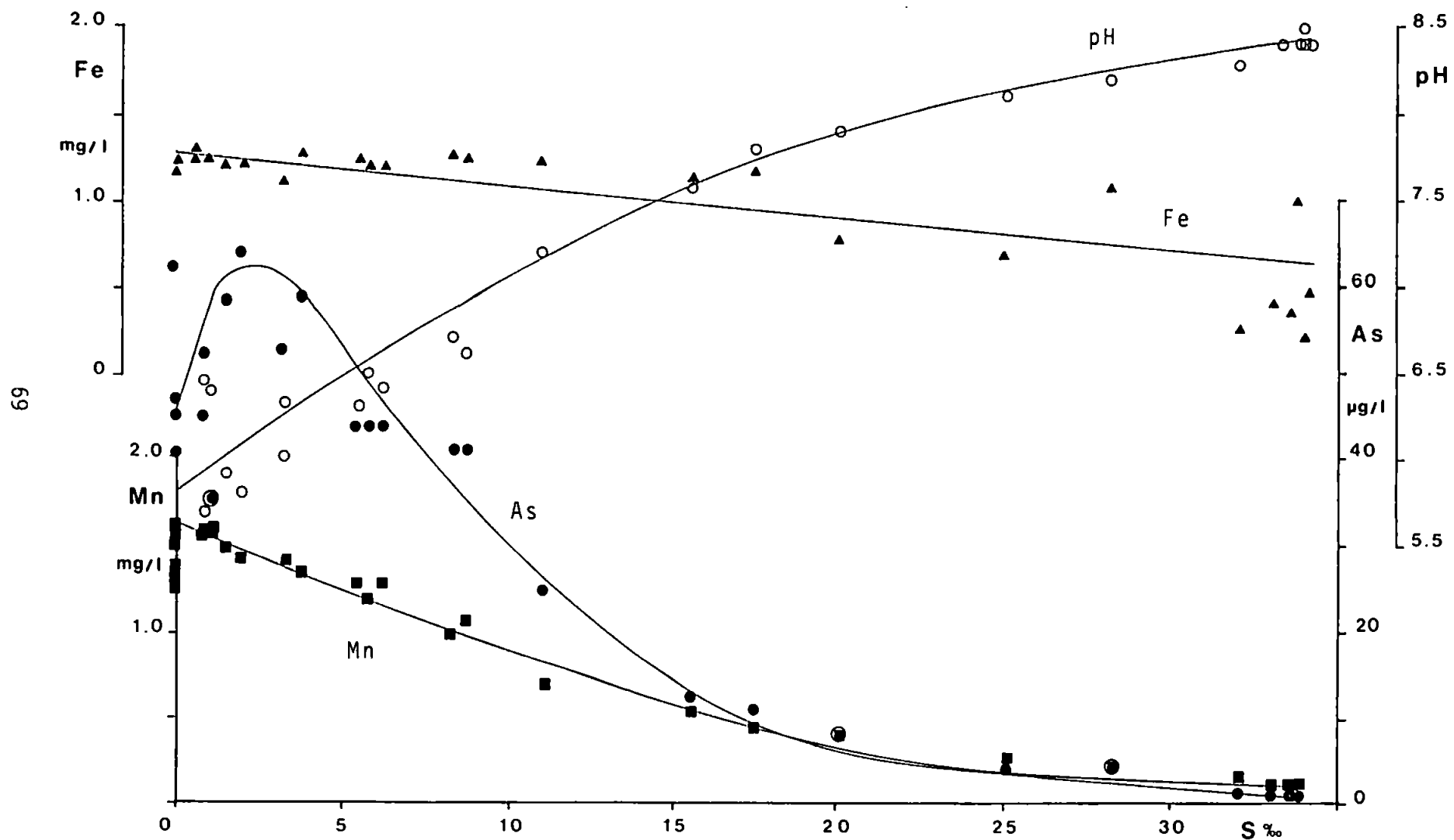
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Figure 3.6   River Carnon - dissolved metal survey (11/4/83)

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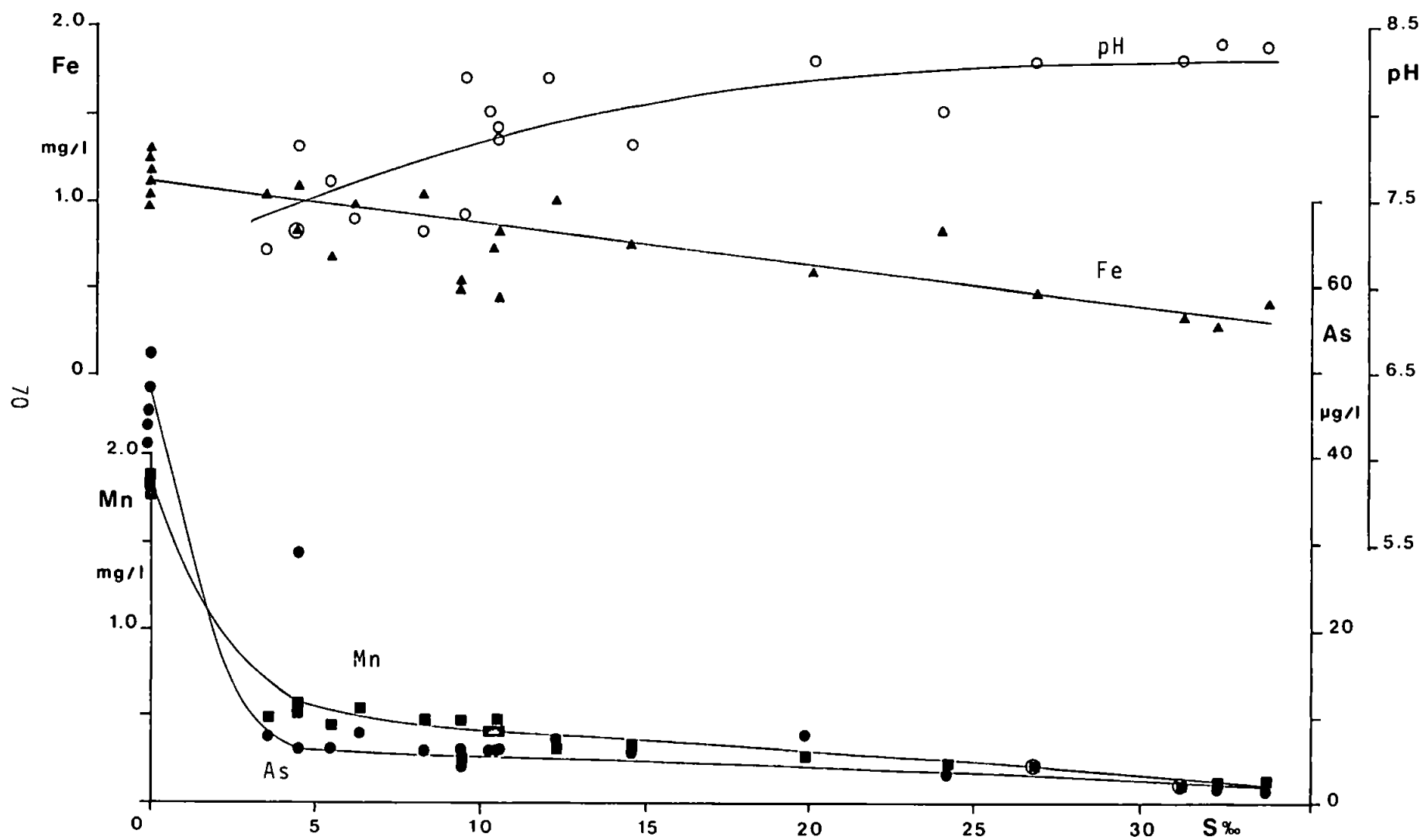
Figure 3.7   River Carnon - dissolved metal survey (12/4/83)
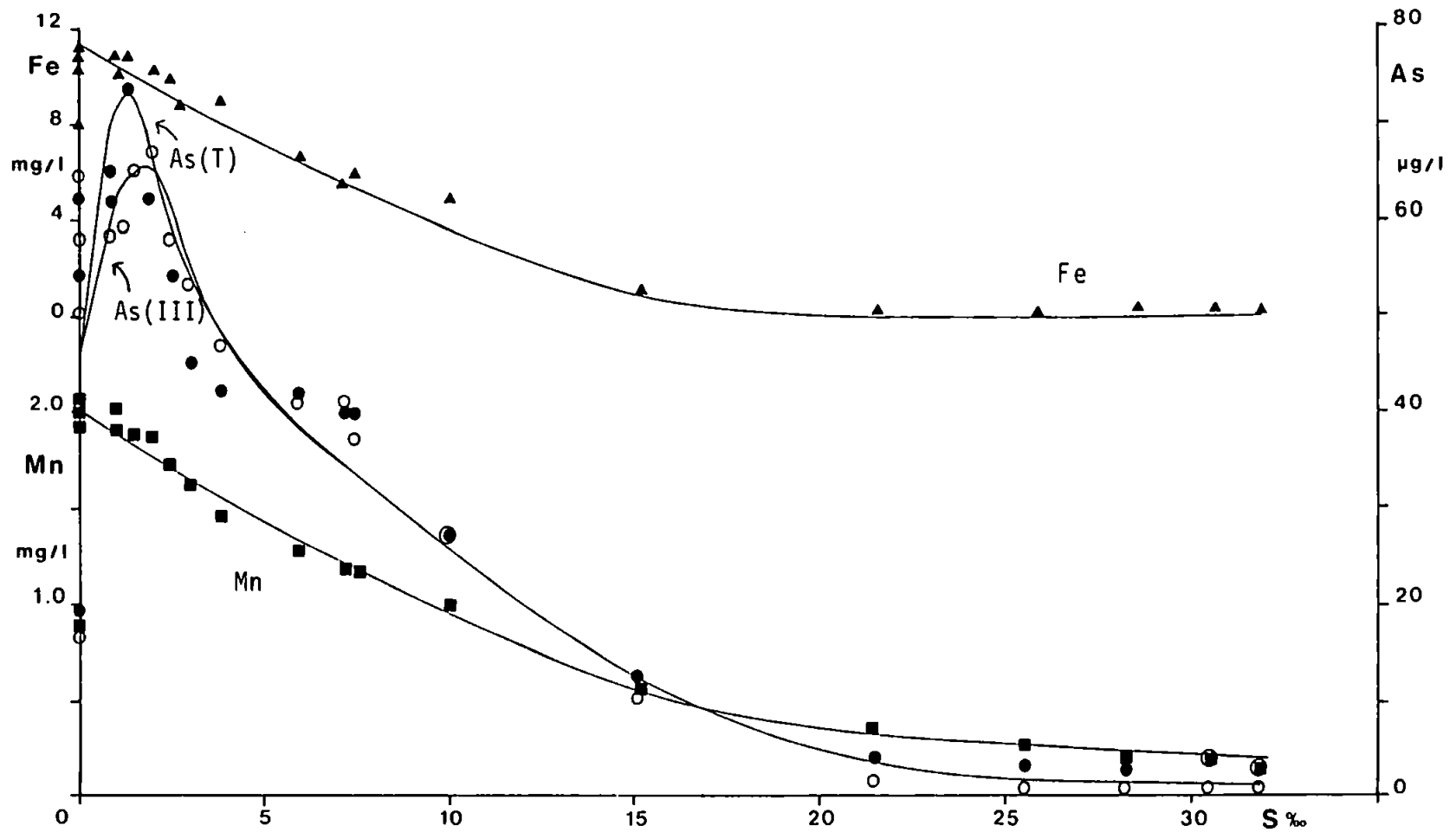
Figure 3.8   River Carnon - dissolved metal survey (6/6/83)

71
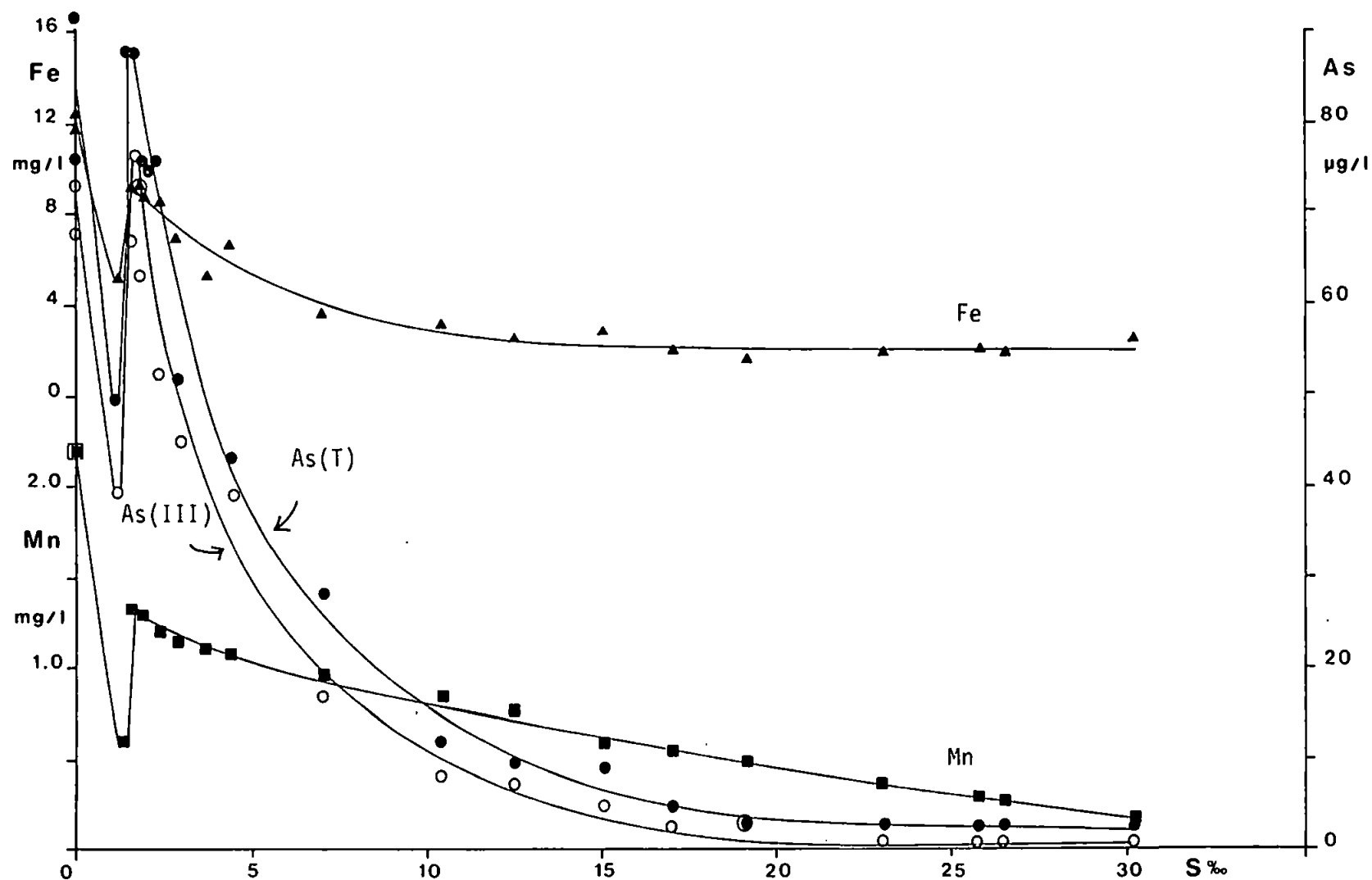
Figure 3.9   River Carnon - dissolved metal survey (7/6/33)

Table 3.1 Comparison of 0.45 µm and 0.22 µm Filtered
Samples from River Carnon Surveys (6-7/6/83)

Sample No. / Filter size (µm)		S‰	Fe (mg/L)	Mn (mg/L)	As (µg/L)
71	0.45	< 0.5	10.3	2.0	54
	0.22		10.4	2.0	54
63	0.45	< 0.5	10.7	2.0	63
	0.22		10.7	2.0	62
20	0.45	1.0	10.7	2.0	65
	0.22		10.4	2.0	62
35	0.45	1.8	9.1	1.3	76
	0.22		9.1	1.2	88
15	0.45	2.7	9.7	1.7	54
	0.22		9.7	1.7	50
30	0.45	2.9	6.9	1.1	52
	0.22		8.0	1.2	55
11	0.45	5.8	6.7	1.3	42
	0.22		7.1	1.3	42
6	0.45	21.5	0.04	0.4	3.8
	0.22		0.1	0.4	4.0
41	0.45	25.8	1.9	0.3	2.9
	0.22		1.9	0.3	2.5
3	0.45	28.2	0.1	0.2	3.2
	0.22		0.1	0.2	3.2

remobilisation of reduced Fe, either by tidal stirring or by drainage
from the extensive mud-banks of the estuary in the region of Restronguet
Creek.

The behaviour of dissolved Mn in the River Carnon appeared to differ
significantly from that of the River Tamar and other estuaries. In the
surveys conducted during high tides, Mn exhibited quasi-conservative
behaviour in the estuary, which is in agreement with the data of other
workers for this estuary (Langston, 1983, personal communication). In
the low tide surveys, Mn showed removal in the 0-5°/oo S range. This
behaviour may be an artefact caused by dilution in the main estuary,
brought about by riverine inputs from the nearby Rivers Fal and Perran.
Such an effect would be predominant in conditions of low tide. Alter-
natively, this removal may be a real phenomenon due to the slow oxidation
of Mn to particulate Mn (IV). However, in the light of the previous
discussion (section 3.1.1) of the time scales involved in this process,
this does not seem likely.

In contrast to the River Tamar, no resuspension of dissolved Mn was
detected in any of the surveys conducted. As the concentrations of
dissolved Mn in the Carnon, however, are an order of magnitude greater
than those of the Tamar, remobilisation of Mn of the same order
(0.1-0.2 mg/L) would tend to be masked by the overall conservative/
removal profile of the element.

Dissolved As showed a removal profile in the survey of 12/4/83 (fig.
3.7) (low tide falling), except for one site, which exhibited an elevated
level. This site also exhibited an anomalous T/S relationship,

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probably due to an input of solar-warmed interstitial water from the surrounding mud banks. In the other three surveys, the dissolved As profiles indicated remobilisation (rising or high tides) between 0-5°/oo S, probably due to pore water infusion and the effects of tidal stirring. The speciation surveys carried out for As on the 6-7/6/83 indicate that As is present predominantly as As (III) through-out the salinity range of the estuary. Klumpp & Peterson (1979) have stated that As input into the River Carnon is largely as As (III) and biological reduction, aided by the low freshwater pH ($\sim$3.5) of the river may be responsible for its predominance in the upper estuary. If, as has been previously suggested, the Mn-As redox couple is important in the oxidation of As (III) to As (V), the lack of evidence of Mn remobilisation in the River Carnon estuary, plus the high total levels of As, may explain the relative dominance of As (III), even in the high salinity region of the estuary.

The pH was recorded on several of the River Carnon surveys and the profiles are shown in fig.s 3.6 and 3.7. On one survey the scatter of points makes quantification difficult, but in the second a distinct removal of H$^+$ ions is observed. This removal has been observed more recently in the River Carnon (Russell, 1983, personal communication) and has also been observed in the River Tamar by Morris, et al. (1982). The short-term pH control in estuaries is governed by the inorganic carbonate system and Mook & Koene (1975) have developed an equilibrium pH model where total alkalinity is preserved. Morris, et al. (1982) attempted to fit non-conservative pH data obtained in the Tamar to this model and found there was little agreement. In the light of this evidence, it must be concluded that the removal of H$^+$ ions in these estuaries is due to a complex system of reactions which are yet to be elucidated.

3.1.3   River Carnon Adsorption/Desorption Model

In order to further test the validity of the proposed As reactivity
model, incorporating the Mn-As redox couple, an adsorption/desorption
model was carried out on natural water from the River Carnon. The
natural concentrations of Fe, Mn and As were used and the adsorption
model was carried out on site using a portable version of the
laboratory modelling system. Temperature was maintained at 10°C using
a cool-box and ice-packs,and the pH of 6.0 monitored and controlled as
for the laboratory models. Seawater concentrate (200 ml) was added to
the prefiltered (0.45 μm) freshwater bulk solution (800 ml) to initiate
the model run at 34°/oo S. The bulk solution was stirred throughout by a
portable battery-operated stirrer. Aliquots were removed at specific time
intervals, filtered (0.45 μm) and transferred to acid solution to
quench further reaction. The samples were returned to the laboratory
for analysis.

The desorption model was carried out in the laboratory utilising the
particulates collected during filtering of the adsorption model bulk
solution. Prior to the experiment the filters and particulates were
carefully washed with 2 ml of distilled water and dried at room
temperature. The filters and particulates were suspended in standard
seawater (35°/oo S) and stirred at a constant temperature of 20°C and
pH 8.1. Aliquots were removed at specific time intervals, filtered and
transferred to acid solution prior to analysis.

The results of both experiments are presented in fig. 3.10. The
adsorption model indicates that As was removed from solution along with
the Fe, whereas the concentration of dissolved Mn remained constant
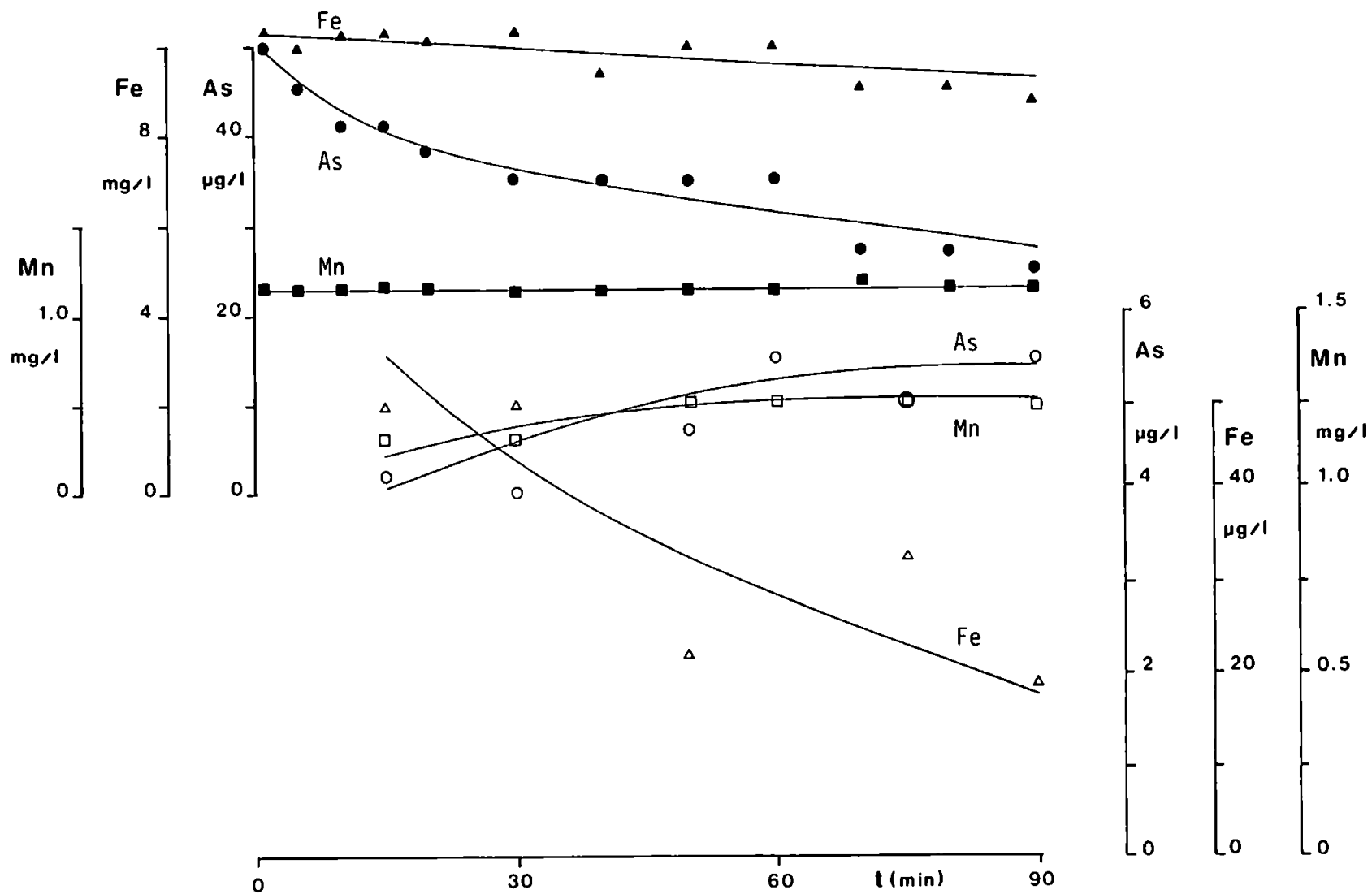
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Figure 3.10   River Carnon - adsorption/desorption model

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over the time period of the model. This result, using natural concentrations of the elements present, strongly implies that the removal of As from the water column is related to the removal of Fe.

The desorption model, in contrast, shows that both dissolved As and Mn increase over the time period of the run, providing strong evidence that the chemistry of these two elements is linked. The dissolved Fe which could have originated from the filters or been a component of the seawater is apparently removed from solution over the same period. The dissolved Fe is almost certainly taken up onto the particulates by adsorption processes. This experiment indicates that some As may have been readsorbed from solution by the precipitating Fe, depressing the As desorption profile and leading to an underestimate of the true amount of As released.

These models offer strong evidence for the Fe related adsorption and Mn related desorption of As, as proposed in the previous sections.

3.2   Sediment Analysis

A total of five sediment surveys of the River Tamar was carried out during 1981/82, as described in section 2.2.2. The removal of Fe from the water column via precipitation would result in the coating of sedimentary particles by this Fe and an initial study was carried out in order to obtain evidence of this process (section 3.2.1). Subsequently a detailed analysis of the distributions of Fe, Mn and As within the sediments was carried out in terms of their variations on a site to site basis with time (section 3.2.2),and their inter-correlation within the total and non-detrital fractions analysed

(section 3.2.3). Finally a spatial/temporal analysis of both the total and non-detrital data was conducted (section 3.2.4).

3.2.1 S.E.M. Analysis of Sediments

Samples from selected sites in several of the Tamar surveys were fractionated as described in section 2.2.2.4. The results of this fractionation study are presented in table 3.2, as a percentage of total sediment. This method was not, however, considered reliable, due mainly to problems of particle aggregation and difficulty in accurate recovery of the various fractions. This table should then only be taken as a rough guide to the actual sediment density fractions present, and the procedure served mainly to simplify visual identification of suspected coated particles under the optical microscope (section 2.2.4).

Plate 3.1 shows the heavy mineral fraction ($\rho > 2.96$) of station 13 for the survey of 1/4/81. A wide range of particle sizes is present, including particles of quartz and what appears to be tourmaline. Particles to the upper left of the plate appear to have a rust-like coating. Plate 3.2 shows several such particles in greater detail and it can be seen that several of these particles are coated. Plate 3.3 shows detail of the light mineral fraction ($\rho < 2.96$) of station 13 from this survey. The sample appears to be largely composed of quartz, with some flint present. There is apparent evidence of Fe staining on several of the particles in the centre of the photograph. Plate 3.4 shows the light mineral fraction ($\rho < 2.72$) of station 14 from the same survey and indicates the predominance of clay particles in this site at the head of the estuary. The presence of this clay fraction made the identification of minerals or their Fe coatings impossible at this site.

Table 3.2   River Tamar Surveys - Sediment Density Fractions (%)

Density Fraction (ρ)	River Tamar Survey (1/4/81) - Station No.			
	1	7	13	14
> 2.96	< 0.1	< 0.1	17	< 0.1
< 2.96 / > 2.72				41
< 2.96 / > 2.68	1			
< 2.96 / > 2.59		9		
< 2.96			83	
< 2.72	·			59
< 2.68	99			
< 2.59		91		

Density Fraction (ρ)	River Tamar Survey (16/7/81) - Station No.			
	1	7	13	14
> 2.96	< 0.1	< 0.1	< 0.1	2
< 2.96 / > 2.64	7			
< 2.96 / > 2.58		2		
< 2.96			100	98
< 2.64	93			
< 2.58		98		

Plate 3.1   Heavy mineral fraction of station 13 for
            the survey of 1/4/81

Plate 3.2   Detail of heavy mineral fraction of station 13
            (1/4/81), showing Fe coating on several particles

Plate 3.3 Detail of light mineral fraction of station 13
          (1/4/81), showing Fe staining on particles

Plate 3.4 Light mineral fraction of station 14 (1/4/81),
          showing predominance of clay material

To complement this subjective analysis, various particles, both coated
and uncoated, were mounted and examined under a scanning electron
microscope (section 2.2.2.4). Plate 3.5 shows a typical particle from
the heavy mineral fraction ($\rho <$ 2.96; $>$ 2.68) of station 7 for the
survey of 16/7/81. No Fe oxide coating was apparent on this particle
upon visual examination and the accompanying X-ray dispersive analysis
(fig. 3.11) indicates an absence of Fe in the surface layers
penetrated by the probe. Plate 3.6 is a surface detail of this particle,
showing the presence of clay platelets and a slightly porous nature,
but no evidence of Fe or other metal coating.

The particle shown in Plate 3.7 is part of a larger, very crumbly, rich
rust-coloured particle. The detail in Plate 3.8 indicates a very
different surface to that of the previous particle (Plate 3.6), with
the presence of a large number of pores. The X-ray dispersive analysis
of this particle (fig. 3.12), shows that its surface is entirely
composed of Fe and it is probably a solid hydrous Fe oxide particle.
This represents one of the first observations of such particles in an
estuary.

Finally, Plate 3.9 shows an alumino-silicate particle, which upon
examination under the S.E.M., was found to have patches of surface
coating present. The X-ray analysis of one such area of coating (fig.
3.13) indicates that this coating is largely composed of Fe, and in
fact is probably a patch of Fe oxyhydroxide, as the X-ray analysis
would also pick up the alumino-silicate matrix beneath the coating.

The importance of this study, apart from its identification of sediment
particles coated with Fe and the observation of a solid particle of

Plate 3.5   Electron micrograph of heavy mineral particle from
             station 7 for the survey of 16/7/81, showing no
             evidence of Fe coating.

Plate 3.6   Electron micrograph detail of particle in plate 3.5

25KV   0101   100.0U PPEMU

25KV   0104   10.0U PPEMU
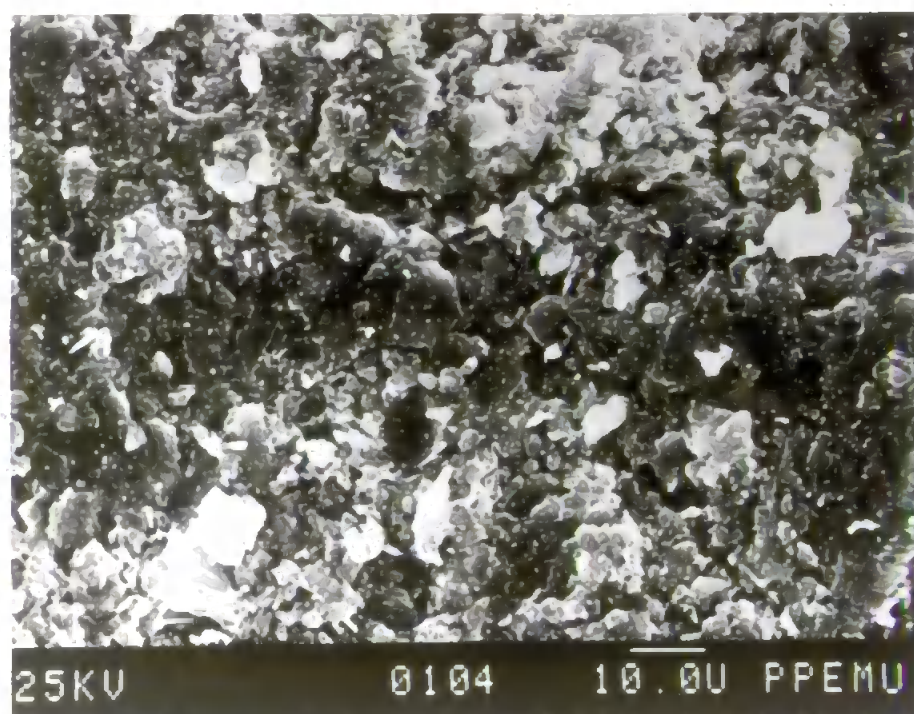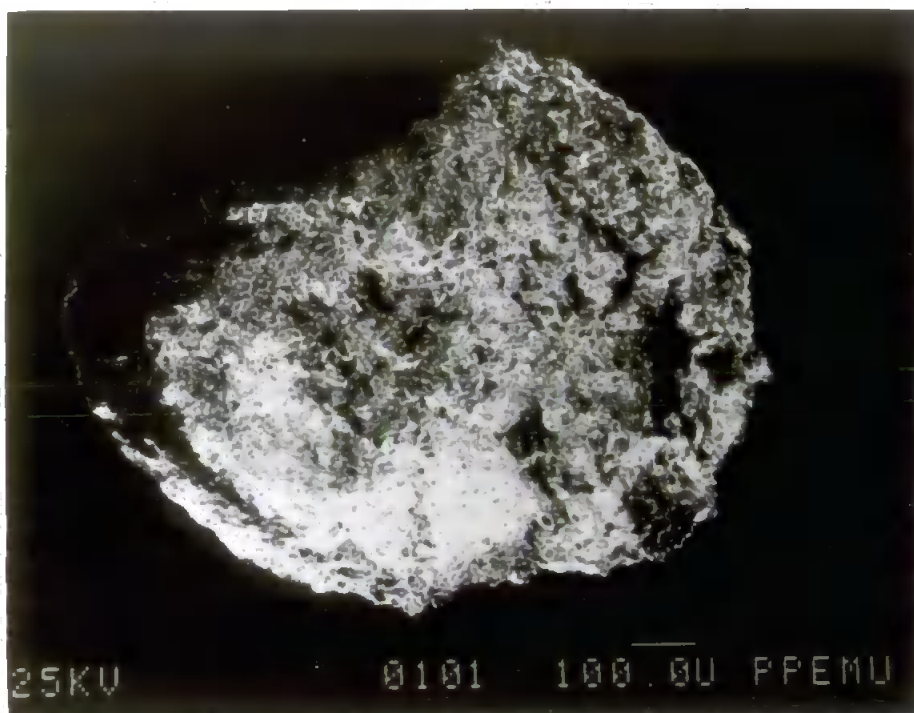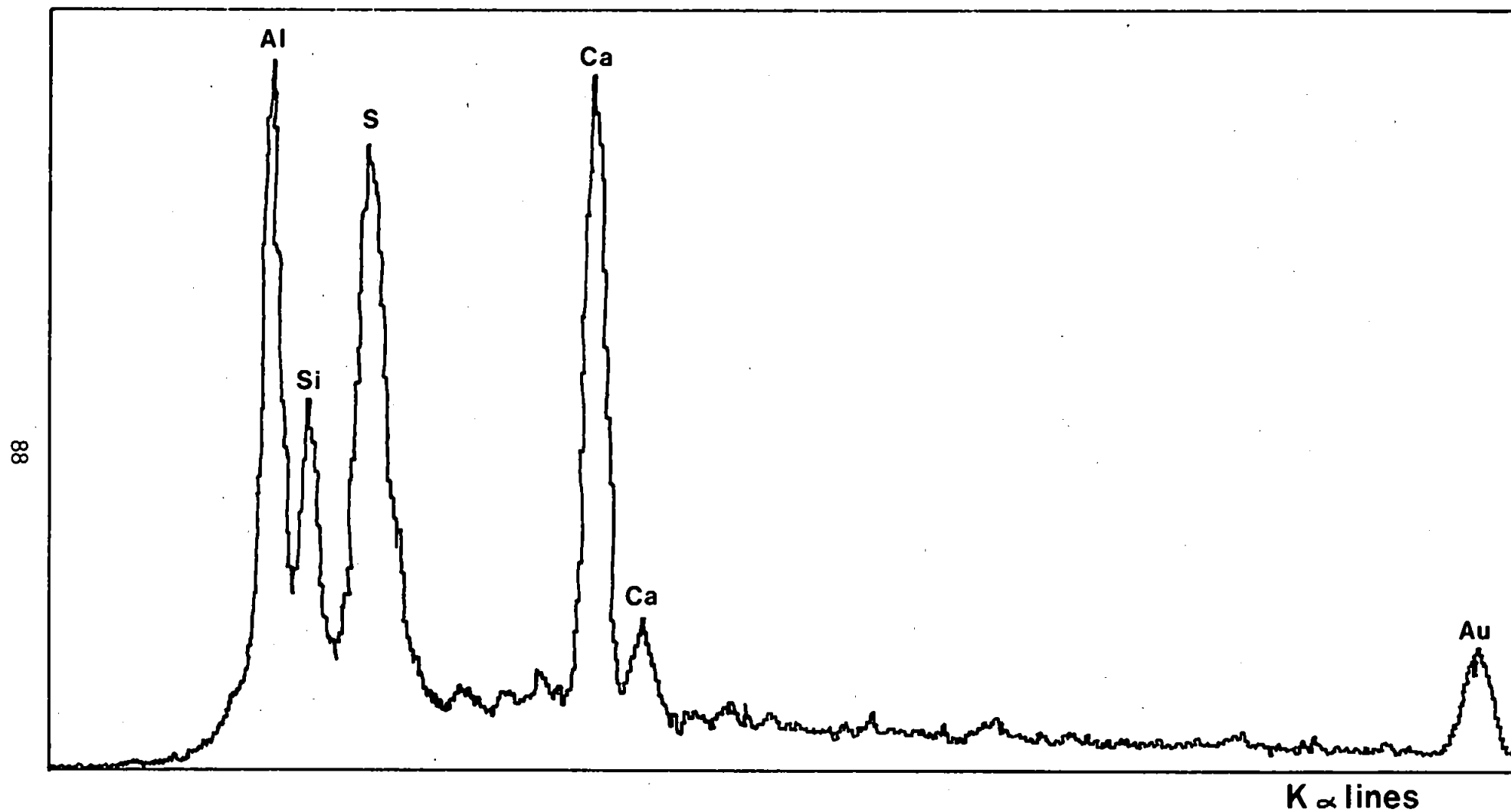
Figure 3.11   X-ray dispersive analysis of sediment particle showing no evidence of Fe coating (plate 3.5)

Plate 3.7 Electron micrograph of Fe oxyhydroxide particle
from station 7 (16/7/81)

Plate 3.8 Electron micrograph detail of particle in plate 3.7

25KV 0106 100.0U PPEMU

25KV 0107 10.0U PPEMU
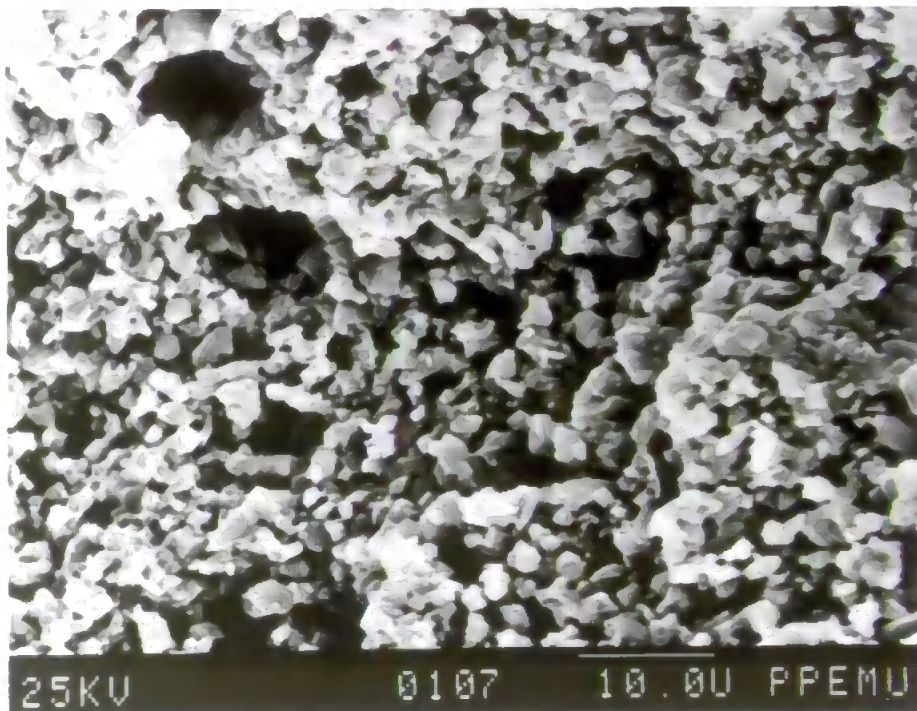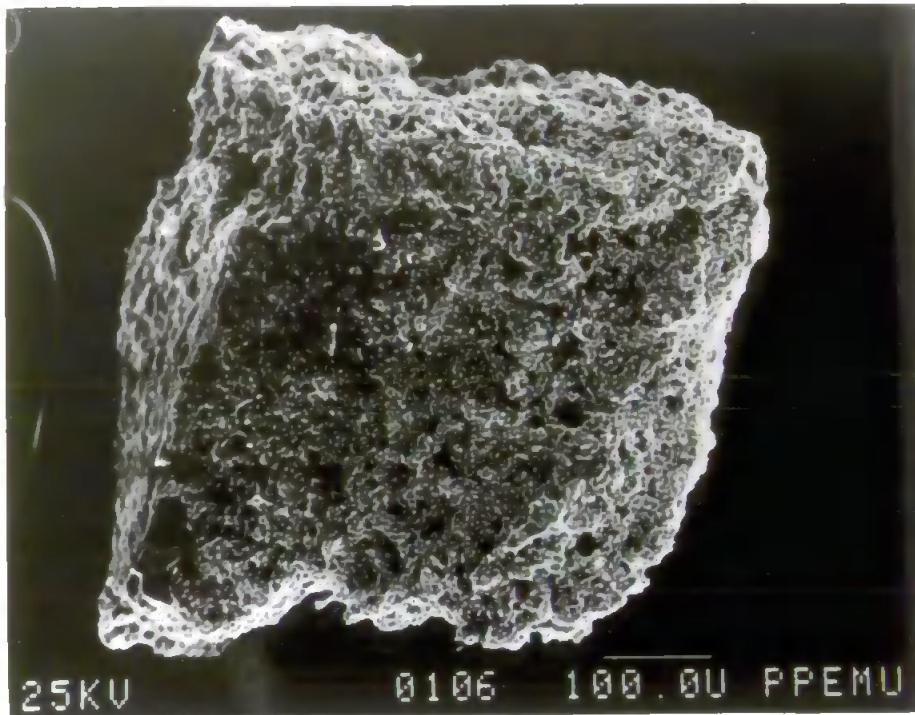
Figure 3.12   X-ray dispersive analysis of solid Fe oxide sediment particle (plate 3.7)

Plate 3.9   Electron micrograph of particle from station 7
            (16/7/81), showing evidence of Fe oxyhydroxide
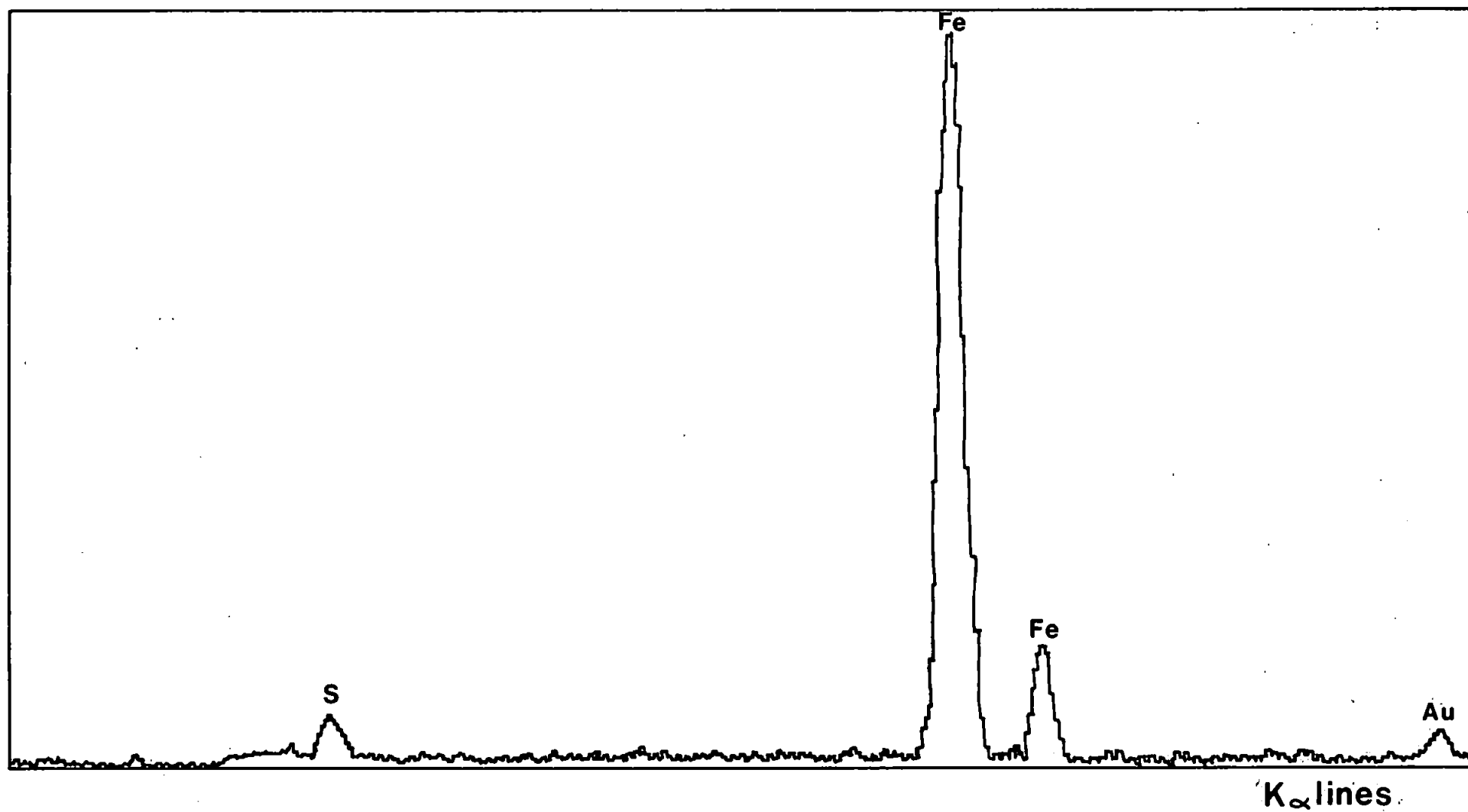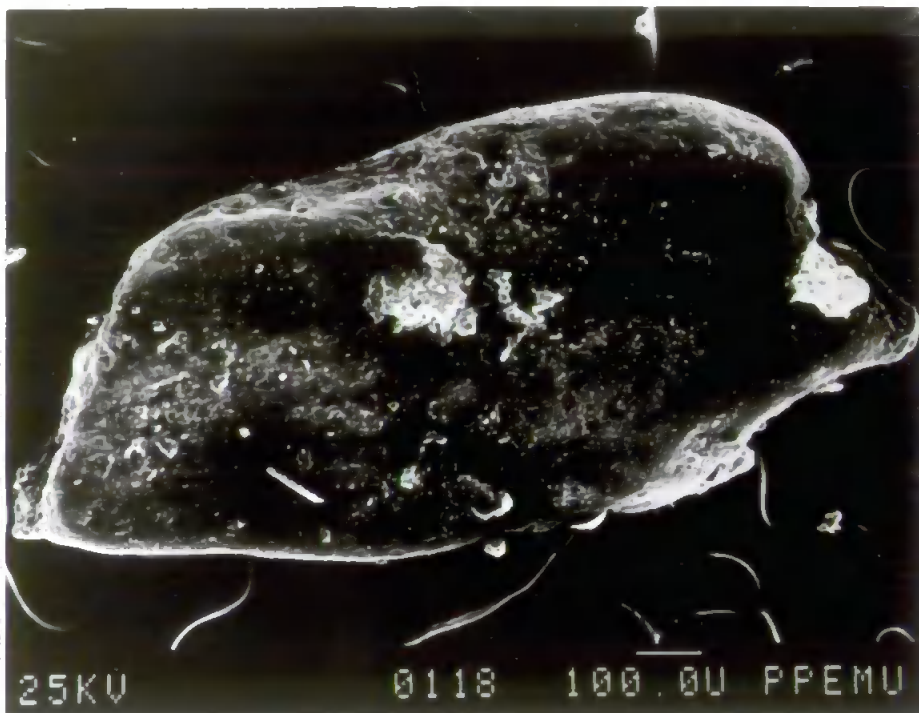   patches on surface
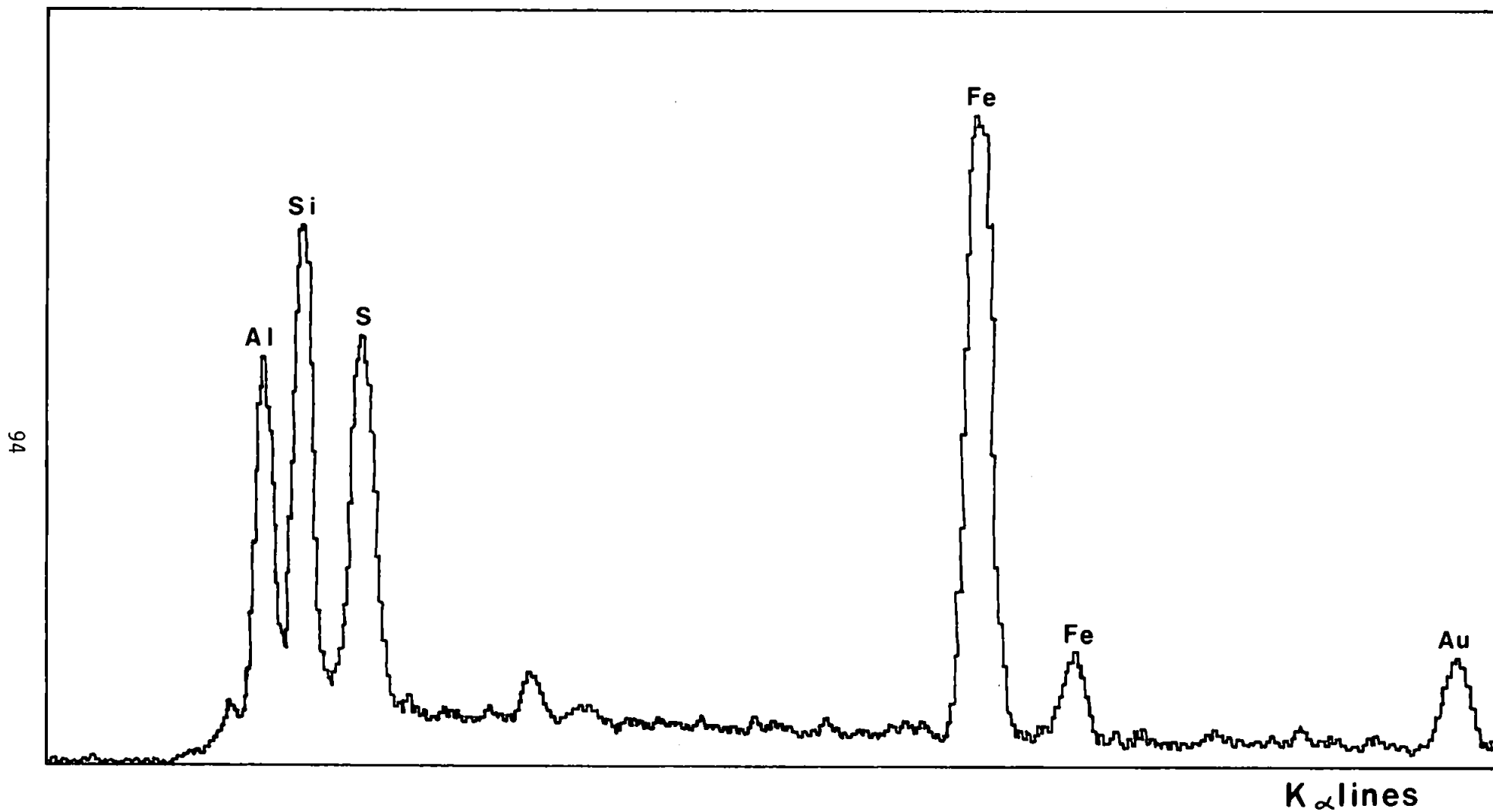
25KV   0118 100.0U PPEMU

Figure 3.13   X-ray dispersive analysis of sediment particle showing patches of
Fe oxide coating (plate 3.9)

Fe oxyhydroxide, is that only a small fraction of the sediment particles was found to be coated. This strongly implies that the coating is not a process of authigenic formation, but is probably taking place in the water column, either subsequently to, or associated with, the initial formation of the Fe precipitate. This leads to the possibility that these sedimentary particles are directly involved as nucleation sites for the formation of the oxyhydroxide and are thus intimately involved in the removal process of Fe from the water column.

3.2.2   Sediment Metal Distributions

A total of five sediment surveys of the River Tamar was carried out during 1981/82 (fig. 2.4), as described in section 2.2.2. Total and available metal digests were obtained for the prepared samples and these were analysed for Fe, Mn and As (sections 2.1.1, 2.1.2 and 2.2.2.1). The metal data obtained from these surveys are plotted against distance from the hydrodynamically defined head of the estuary in fig.s 3.14-3.19. Mean concentrations are plotted with bars denoting ± 1 standard deviation. In addition, data were obtained for total organic carbon (section 2.2.2.2) and grain size (section 2.2.2.3), and these are plotted as fig.s 3.20 and 3.21.

The total concentrations of sediment Fe (fig. 3.14) vary little with distance downstream. The mean values are lower in the upper, fresh-water section of the estuary and show a slight increase at around 3-5 km downstream with a low coefficient of variation (C.V.), dropping off again with increasing distance, to reach their lowest values around 25 km from the head of the estuary. The variation in total Fe

Figure 3.14   River Tamar sediments - Fe (total component)

Figure 3.15   River Tamar sediments - Fe (non-detrital component)

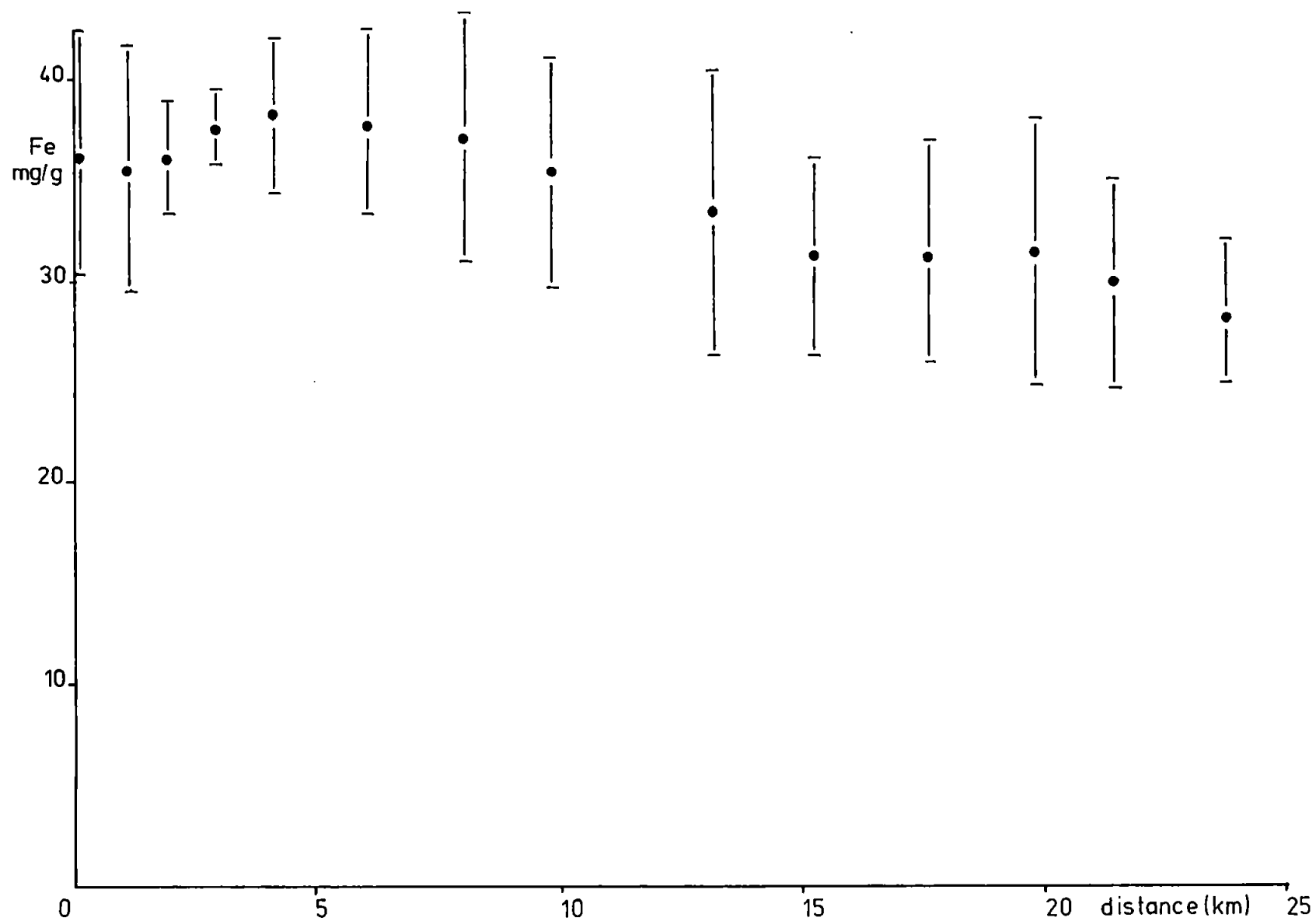Figure 3.16   River Tamar sediments - Mn (total component)
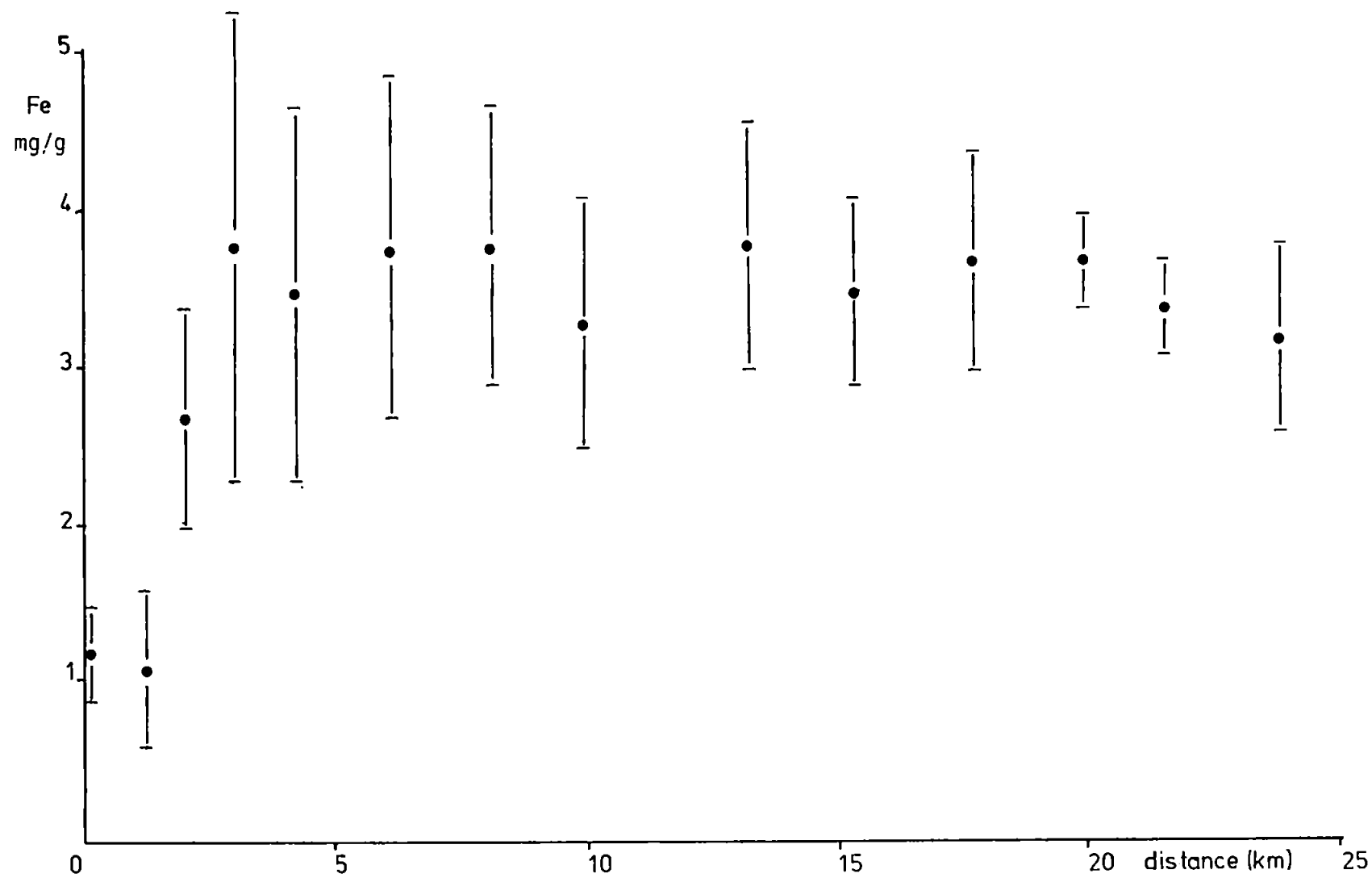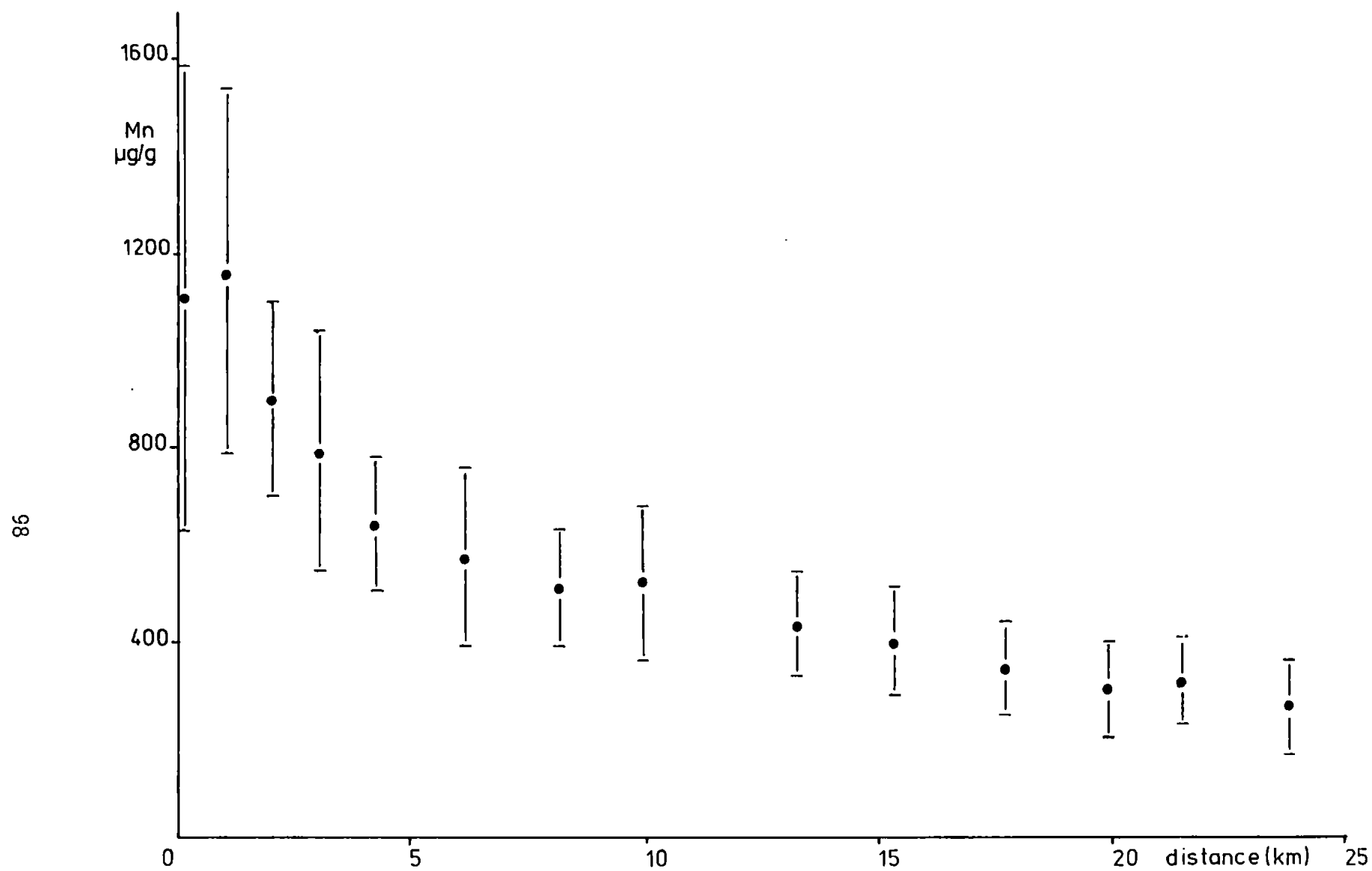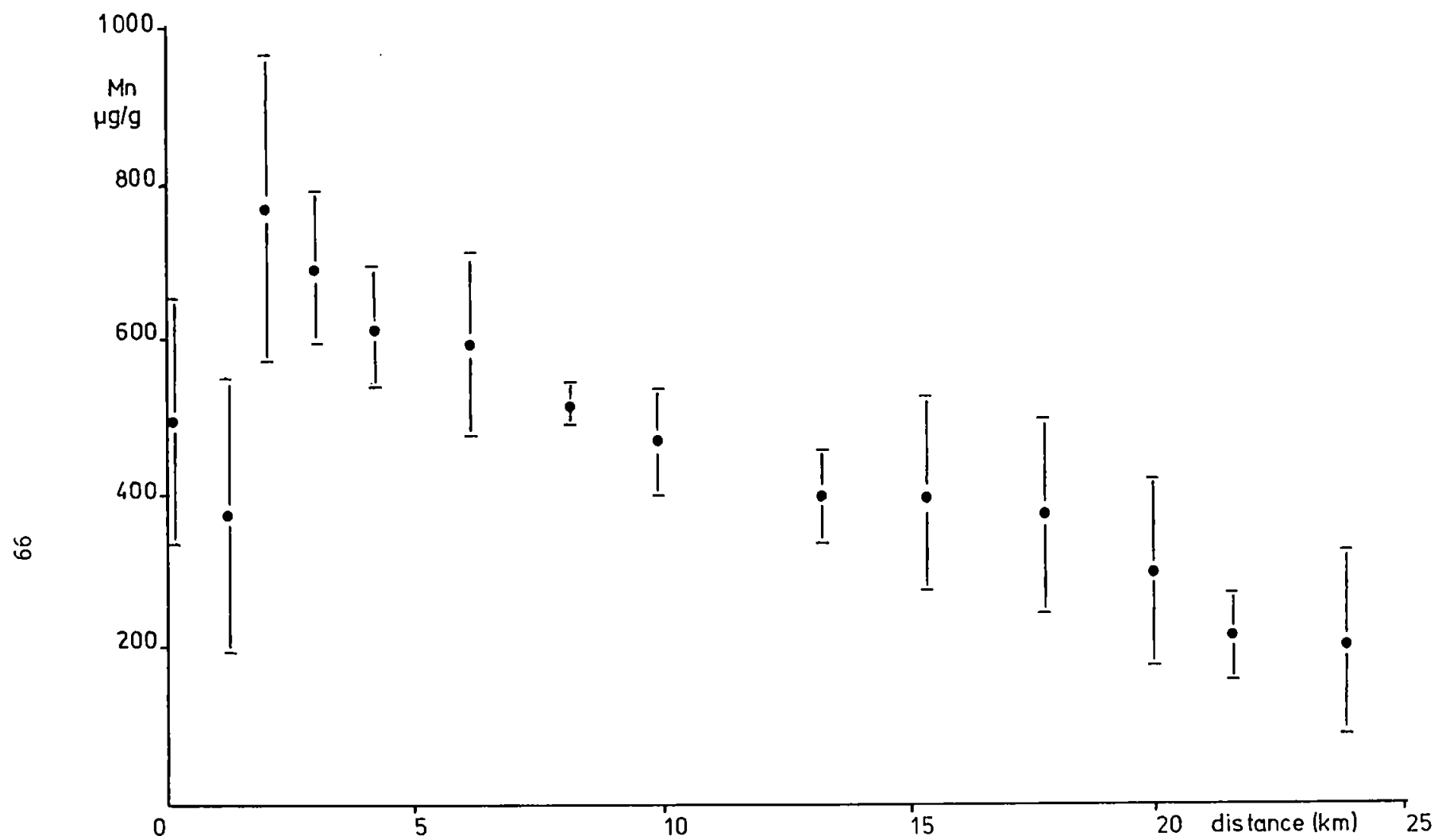
Figure 3.17   River Tamar sediments - Mn (non-detrital component)
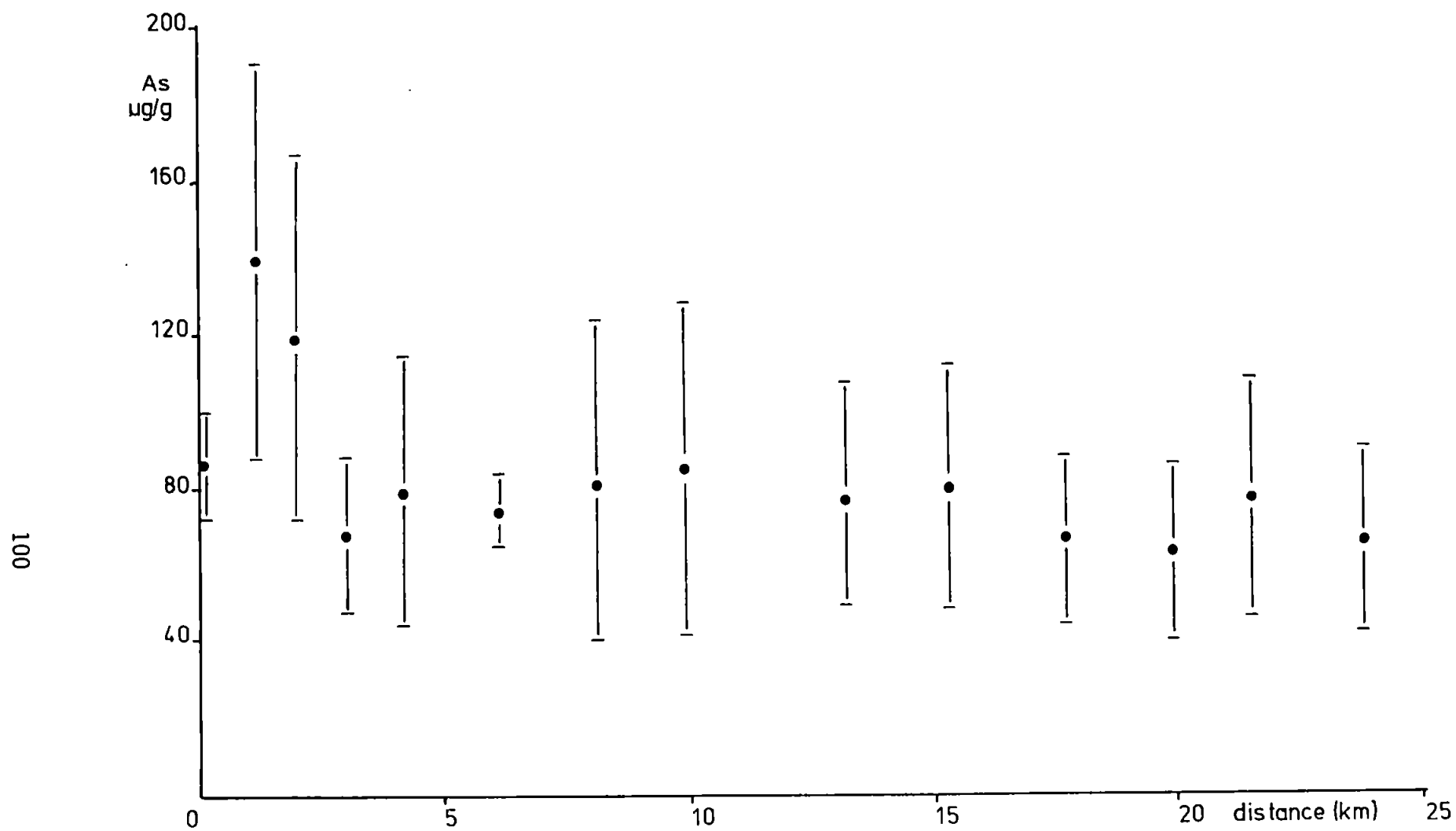
Figure 3.18   River Tamar sediments - As (total component)
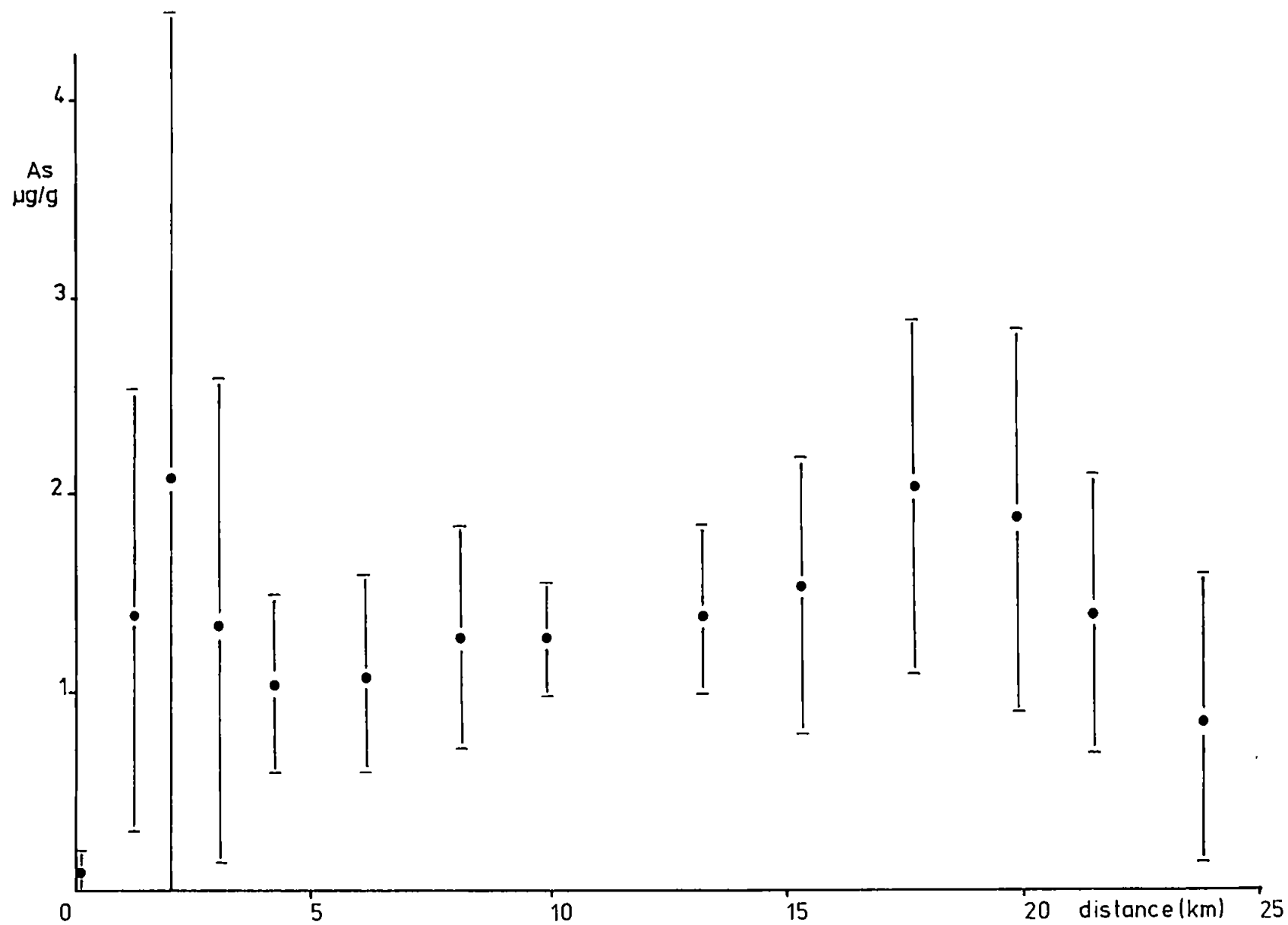
Figure 3.19   River Tamar sediments - As (non-detrital component)

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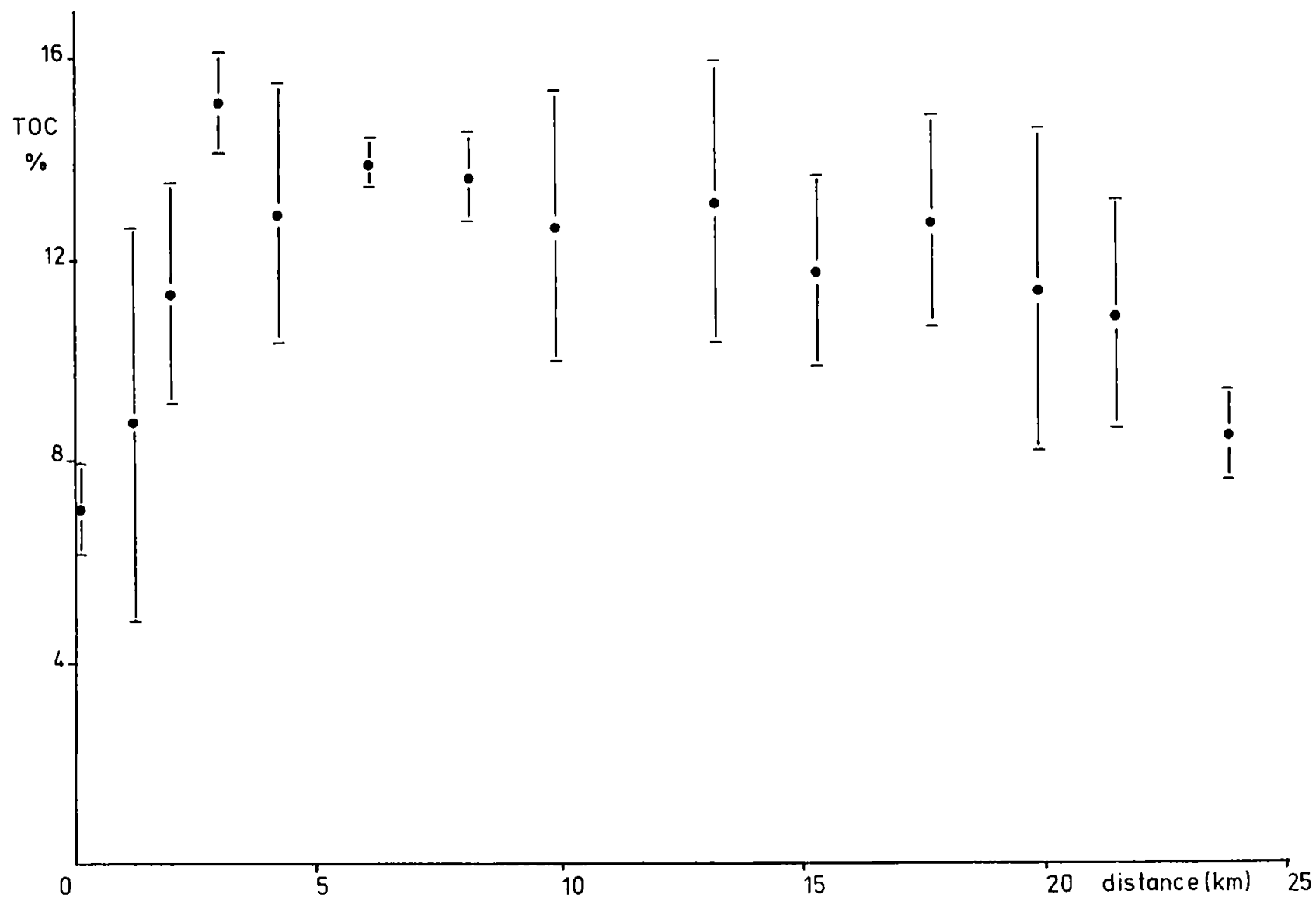
Figure 3.20   River Tamar sediments - total organic carbon (TOC)
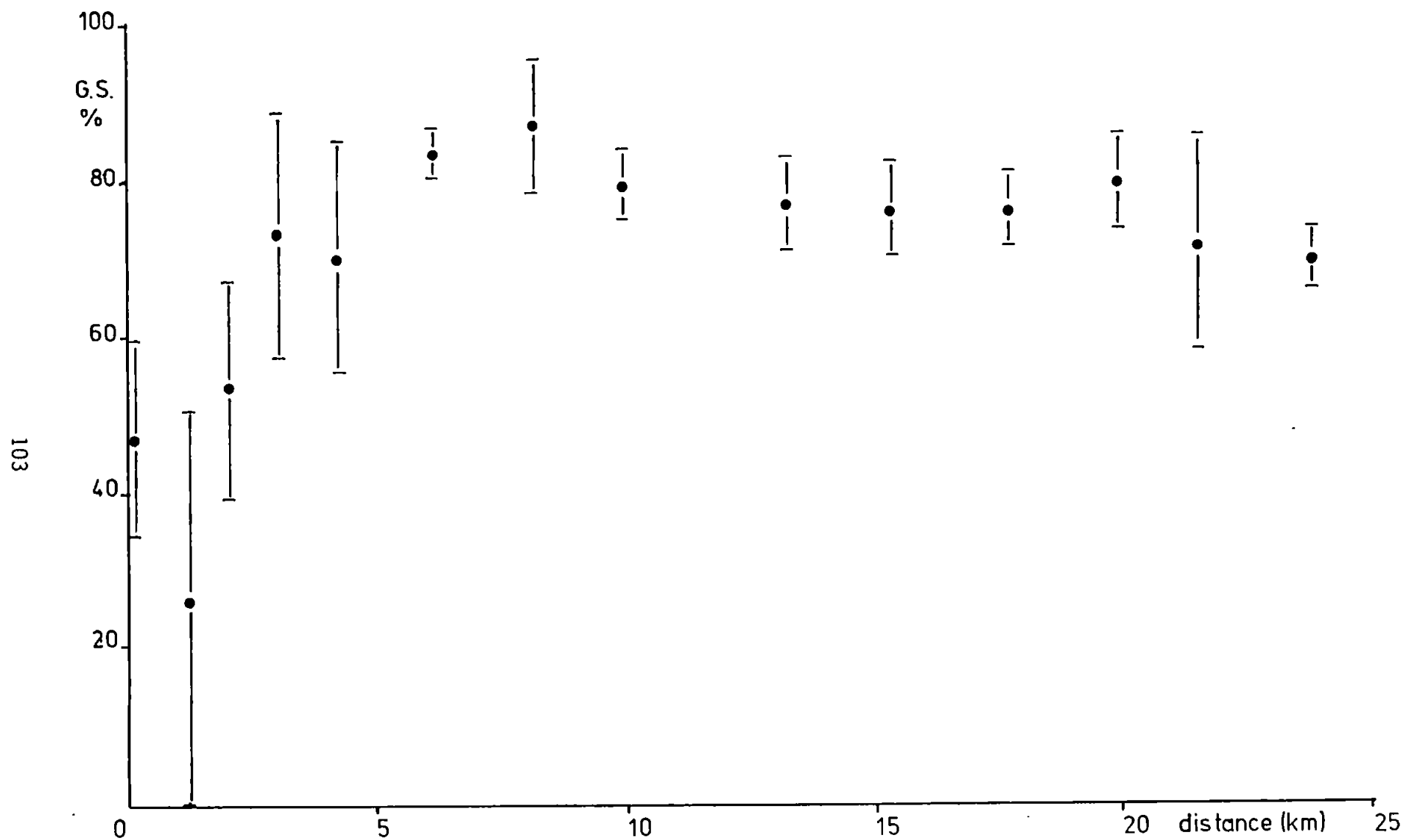
Figure 3.21   River Tamar sediments - grain size (G.S.) (< 63 μm, as %)

concentrations increases again beyond 5 km along the length of the estuary. The area between 0-5 km downestuary shows a predominance of larger particle sizes in the sediment (fig. 3.21) and is in a part of the estuary associated with past metalliferous mining activity.

These factors together suggest that the elevated levels of Fe in this region are related to a mineralogical input from the mine tailings in the area, rather than oxide coatings of Fe on sedimentary particles (section 3.2.1). The most likely mineral input from these mine tailings, which were latterly reworked for As, is arsenopyrite (FeAsS), known to occur in pneumatolytic veins (Sn and Cu) from this area (Read, 1970). This is further confirmed by low levels of non-detrital Fe in the uppermost section of the estuary.

The non-detrital metal data for sediment Fe (fig. 3.15) shows an increase around 3-4 km downstream with a large C.V. This fraction of the total sedimentary Fe relates largely to oxide coatings on sediment particles and reflects either the removal of dissolved Fe from the water column at low salinities, which is deposited in the sediment, or other inputs of Fe available to the acetic acid leach.

Total Mn levels in the sediments (fig. 3.16) peaked around 1-2 km downestuary, with a gradual decrease in concentration into the lower estuary. Variations in the mid and lower estuary were relatively small and uniform. Coefficients of variation in the upper, freshwater section of the estuary (to approximately 4 km downestuary) were greatest, reflecting the variability of inputs into this area. The decrease in Mn is related to its reduction and remobilisation occurring in this region of the estuary and resulting in inputs of dissolved Mn to the

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water column at low salinities (Morris, 1978 & 1982; Knox, et al., 1981). The non-detrital metal concentrations of Mn enhance this profile (fig. 3.17) and along with the high percentage non-detrital to total metal found for this element, typically 80-100% (section 2.1.2.1), indicate that Mn is found in the estuarine sediments predominantly as coatings on other lithogenic particles. The non-detrital values of Mn in the upper, freshwater region of the estuary (0-4 km) closely follow those of the silt fraction (fig. 3.21), which is in agreement with other work on the River Tamar (Morris, 1978 & 1982; Knox, et al., 1981), which has shown that Mn is found in freshwater predominantly in the particulate phase.

The data for total As in the sediments (fig. 3.18) show an input at around 2-3 km downstream of Weir Head, with concentrations falling again between 4-5 km downstream. The seasonal variation from station to station is reasonably uniform. The elevated sediment concentrations of As around 2-3 km downstream are probably related to the inputs of arsenopyrite from mine tailings in this area, as referred to in the previous discussion of Fe. However, the very large coefficient of variation for non-detrital As observed at these stations (fig. 3.19), indicates that As is also input into sediments in this region in the form of non-mineral surface coatings, probably via co-precipitation with dissolved Fe, as shown by the correspondingly elevated levels of non-detrital Fe in this area (fig. 3.15). This input of non-detrital As into the sediments is presumably related to the seasonal mobilisation of As from the mine tailings. In summer, as the water table falls, arsenopyrite is increasingly exposed to an oxidising environment (Rose, et al., 1979). The oxidation of this arsenopyrite releases As from the mineral lattice, which is then mobilised by subsequent precipitation

(Levinson, 1980) and input into the estuary via run-off from the tailings. Acidification of the run-off, due to the presence of reducing sulphide minerals, would assist in the mobilisation process and elevated levels of both Fe and As have been found in mine tailing adits in this and other regions of the catchment area during the summer months (this work). The data for Fe and As, however, did not show discernably elevated levels in the sediments during the summer months. This could be due to the relative immobility and moderate mobility of Fe and As respectively in an oxidising environment (Andrews-Jones, 1968: cited in Levinson, 1980), which may result in only a localised dispersion of these elements. Alternatively, the apparent anomaly might be associated with the seasonal transport of sediment within the estuary (see section 3.2.4). The total organic carbon profile (fig. 3.20) closely followed that of the grain size distribution (fig. 3.21). The greatest seasonal variation was again found around 2-3 km downstream, associated with the largest variation in grain size. This is also the region with the lowest percentage fine grain sediment. This positive relationship between decreasing grain size and increasing T.O.C. is expected, as organic matter is likely to be present largely as coatings on, or associated with coatings on, sediment particles. The finer sediments will have a correspondingly greater surface area and therefore a greater organic matter content.

Finally, a comparison was made between the range of concentrations found for the whole suite of metals analysed and those of other sediment surveys (table 3.3). 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 this work

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Table 3.3 Heavy Metal Distributions in Sediments (ppm, dry weight) for This Study and Others

Location	Cu	Zn	Pb	Cd	Mn	Fe	As	Hg	T.O.C. %	Reference
Lynher	274	317	150	-	289	23,120	50.7	2.1	10.5	Ackroyd, et al. (1982)
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	This work
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

for the additional metals cited are probably also related to the inputs from the metalliferous catchment area (Bland, et al., 1982).

3.2.3   Correlation of Sediment Data

Statistical analysis of the sediment data from the Tamar surveys was carried out, to determine the extent of correlation between Fe, Mn, As, T.O.C. and grain size (G.S.), for both the total and non-detrital fractions. The normalised sediment data was also analysed. This was the original data which had been recalculated as if it were composed entirely of the < 63 μm fraction, to allow for grain size variation, spatially and temporally, between the samples.

A summary of the correlation coefficients is presented in tables 3.4 and 3.5. A significance level of 1% (P = 0.01) is assumed in this discussion. That is, correlation coefficients (r) of > ± 0.66 are considered significant for the 14 data pairs examined (Murdoch & Barnes, 1970) and values > ± 0.78 very significant (P = 0.001).

No significant correlation was observed between Fe and As in the non-normalised total fraction (table 3.4). Significant positive correlations (P = 0.001) were found in the non-detrital leach data for the surveys of 30/9/81 and 10/2/82, but were apparently independent of season. This may indicate a similar estuarine chemistry for the non-detrital components of these elements over this period, which is associated with a period of increasing river flow rate following the summer of 1981 (section 3.2.4), and may be related to the mechanism of Fe/As mobilisation discussed previously (section 3.2.2).

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Table 3.4 River Tamar Sediments –
Correlation Coefficients (r) for Non-Normalised Data

Correlation	River Tamar Surveys - total extract				
	1/4/81	17/6/81	16/7/81	30/9/81	10/2/82
Fe/Mn	0.74	0.89	0.58	0.30	0.23
Fe/As	0.04	0.42	0.34	- 0.01	0.09
Mn/As	0.35	0.15	0.83	0.42	0.19
Fe/T.O.C.	- 0.15	0.82	0.05	0.89	0.85
Mn/T.O.C.	- 0.55	0.62	- 0.62	0.17	- 0.03
As/T.O.C.	- 0.58	0.35	- 0.64	- 0.22	- 0.17
Fe/G.S.	- 0.30	- 0.30	- 0.04	0.67	0.40
Mn/G.S.	- 0.42	- 0.45	- 0.78	- 0.20	0.68
As/G.S.	- 0.68	- 0.43	- 0.78	- 0.17	0.28

Correlation	River Tamar Surveys - non-detrital extract			
	4/2/81	16/7/81	30/9/81	10/2/82
Fe/Mn	0.43	- 0.12	0.06	- 0.36
Fe/As	- 0.18	0.38	0.84	0.93
Mn/As	0.25	- 0.48	0.16	- 0.57
Fe/T.O.C.	0.93	0.74	0.76	0.50
Mn/T.O.C.	0.25	- 0.13	0.38	0.54
As/T.O.C.	- 0.43	0.35	0.68	0.26
Fe/G.S.	0.87	0.84	0.77	- 0.61
Mn/G.S.	0.16	- 0.03	- 0.01	0.61
As/G.S.	- 0.57	- 0.01	0.27	- 0.71

Table 3.5   River Tamar Sediments -
            Correlation Coefficients (r) for Normalised Data

Correlation	River Tamar Surveys - total extract				
	1/4/81	17/6/81	16/7/81	30/9/81	10/2/82
Fe/Mn	0.95	0.92	0.99	0.90	0.05
Fe/As	0.87	0.85	0.96	0.90	0.73
Mn/As	0.88	0.60	0.97	0.85	0.14
Fe/T.O.C.	0.76	0.83	0.76	0.53	0.91
Mn/T.O.C.	0.59	0.85	0.77	0.63	- 0.08
As/T.O.C.	0.53	0.59	0.84	0.31	0.52

Correlation	River Tamar Surveys - non-detrital extract			
	4/2/81	16/7/81	30/9/81	10/2/82
Fe/Mn	0.45	- 0.09	0.09	0.23
Fe/As	0.36	0.36	0.44	0.98
Mn/As	0.76	- 0.03	- 0.27	0.13
Fe/T.O.C.	0.86	0.20	0.33	0.93
Mn/T.O.C.	0.30	0.29	0.74	0.51
As/T.O.C.	0.09	0.86	- 0.01	0.88

These positive correlations are similar to those observed by Langston (1980) for estuarine sediments, and Neal, et al. (1979) for deep sea sediments.

The lack of significant correlations for Fe and As in the non-normalised total extract data is surprising in the light of the likely mineralogical association between these elements discussed in section 3.2.2. When the total metal data normalised for G.S. distribution is considered, however, (table 3.5) strong correlations are found in all the surveys (P = 0.001), confirming the association of these elements in the < 63 μm fraction. The relationship between As and Fe is not found in three of the four normalised non-detrital correlation coefficients, indicating that the association between the elements is strongest in the detrital fraction of the sediment. This implies the association is largely mineralogical, which is presumably due to the presence of weathered Fe AsS.

The As/Fe ratios found in these sediments were 20×10^{-4} - 38×10^{-4} for the non-normalised total data and 5×10^{-5} - 5×10^{-4} for the non-normalised non-detrital data. The total extract ratio is in good agreement with an average estuarine value of 32×10^{-4} found by Langston (1980) for a 1 N HCl extract, but the non-detrital leach ratio is low compared to this figure. This can be accounted for by the average 60% of total As extracted by the 1 N HCl, making it much closer to a total extract when compared to the average 22% of total As extracted by 25% acetic acid also used in this study.

However, there is also the suggestion that scavenging of As by surface

active Fe precipitates may not be occurring with the magnitude observed for deep sea sediments (Neal, et al., 1979). These workers observed a reverse situation to that found here, in that only 8% of the As was of detrital origin, compared to 90% in this case. Nevertheless, the majority of the As in these deep sea sediments is associated with an Fe phase, and both elements have an authigenic origin, possibly from hydrothermal vents. The implication of this observed behaviour in the Tamar sediments is that in some estuaries, at least, the association of Fe and As is dominated by lithogenous inputs, compared to the deep ocean where authigenic processes are more important.

Strong positive correlations (P = 0.001) were found between non-normalised total Fe and Mn in several of the surveys and in all but one of the surveys normalised for grain size (table 3.5). This is surprising considering the previously established differences in behaviour of these two metals in the sediment environment and the large proportion of Mn in the non-detrital fraction. There did not appear to be any seasonal bias in these correlations. These correlations were not repeated in the non-detrital data however, implying again that the association is mineralogical. This seems likely as Fleischer (1955) has observed that Mn is found as a trace element in 98% of the FeAsS, at levels of up to 3000 µg/g.

Several strong correlations (P = 0.001) were also found in the normalised total data for Mn and As. This was again probably due to this mineralogical association, as correlations were not found (with one exception) in the non-detrital data, either normalised or non-normalised. The lack of significant correlations between Mn and Fe

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or As (with one exception in the normalised data for the survey of 4/2/81) in the non-detrital data for these elements, is in good agreement with the proposed behaviour of these elements.

In general, little correlation was found between Fe and G.S. in the total data, compared to strong positive correlation (P = 0.001) in three out of four non-detrital surveys. This ties non-detrital Fe in with its presence as coatings on other sediment particles, the finer grain fraction comprising the larger surface area. Little correlation of Mn with G.S. was observed and no consistent trends were found, with one strong positive correlation found in a total metal summer survey and a negative correlation (P = 0.01) found in one winter survey.

No consistent trends were observed between As and G.S. for either the total or non-detrital data, although negative correlations (P = 0.01) were found in several of the total metal data sets and one of the non-detrital surveys. This appears to contradict the relation of As, in the form of FeAsS, to the finer-grained fractions of the sediment discussed earlier, and is difficult to explain. It is considered that a larger data base is required in order to attempt an explanation of this correlation.

Strong positive correlations (P = 0.001) were found for total Fe and T.O.C. in the non-normalised data, which were generally strengthened in the normalised data. This indicates that the association is probably related to the surface coating of Fe minerals with organic matter. Strong correlations were also found in the non-detrital surveys, but were not generally strengthened by the normalisation of the data. This suggests general association of Fe and T.O.C. as coatings on sedimentary

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particles, but does not imply any chemical association. As with G.S., little correlation was observed between Mn and T.O.C. in any of this data, barring two of the normalised total summer surveys. This is not, however, sufficient evidence to draw any conclusions on seasonality (see last paragraph).

No strong correlations were found between total As levels and T.O.C., in either normalised or non-normalised data, except for one survey. This is in keeping with the suggested mineralogical association of the detrital As. A significant positive correlation (P = 0.01) was observed between non-detrital As and T.O.C. in one non-normalised survey and in several of the normalised surveys. This could be related to the coating of sediment particles with As and organic matter, but does not necessarily imply any chemical complexation.

Finally, it must be concluded that although individual correlations have been observed and discussed in relation to the proposed behaviour of Fe, Mn and As in the Tamar estuary, there is insufficient data to form any firm conclusions regarding the seasonal behaviour or association of these elements. To establish this, a larger number of specifically designed surveys would be required. A discussion of the seasonally related behaviour of Fe, Mn and As must be approached, using this limited data base, from a different perspective, as described in the next section.

3.2.4   Spatial-Temporal Analysis

The variations observed in both total and non-detrital sediment levels of Fe, Mn and As (section 3.2.2) were further elucidated by the

application of spatial-temporal analysis to the data, using the method
described in Ackroyd (1983). The purpose of this analysis is to relate
sediment metal levels to the transport of sediment within the estuary
as a result of hydrodynamic factors. This is important in explaining
the temporal differences of metal distributions in the sediments and
may explain some of the possible inconsistencies found in the data.

The correlation of the normalised and non-normalised metal data within
the estuary, examined in section 3.2.3, has established the relationship
between metal levels and grain size. It is therefore necessary, in
order to understand the transport of sediment held metals, to analyse
the movement of sediment on a seasonal basis. Fig. 3.22 depicts the
variation of grain size in the estuary as a function of time and distance.
Monthly averaged river flow is also plotted, as this is the main factor
affecting the transport of sediment on a seasonal basis. From this
analysis, it can be seen that under conditions of low river flow, for
example on 26/8/80 and 16/7/81, the upper and middle sections of the
estuary contained the majority of the fine grained (< 63 μm) sediment,
while the lower estuarine sediments were largely composed of coarser
grained material. In contrast, during the high river flows associated
with the surveys of 12/11/80 and 4/2/81, the upper estuarine sediments
were composed largely of coarser grained material, while the mid and
lower sections were relatively high in finer grained material.

The implications of this analysis are that sediment mass transport is
occurring upestuary during periods of low river flow (summer) and
downestuary with high river flows (winter). Intermediate situations
exist, in both the summer and winter, for example the surveys of 30/9/81
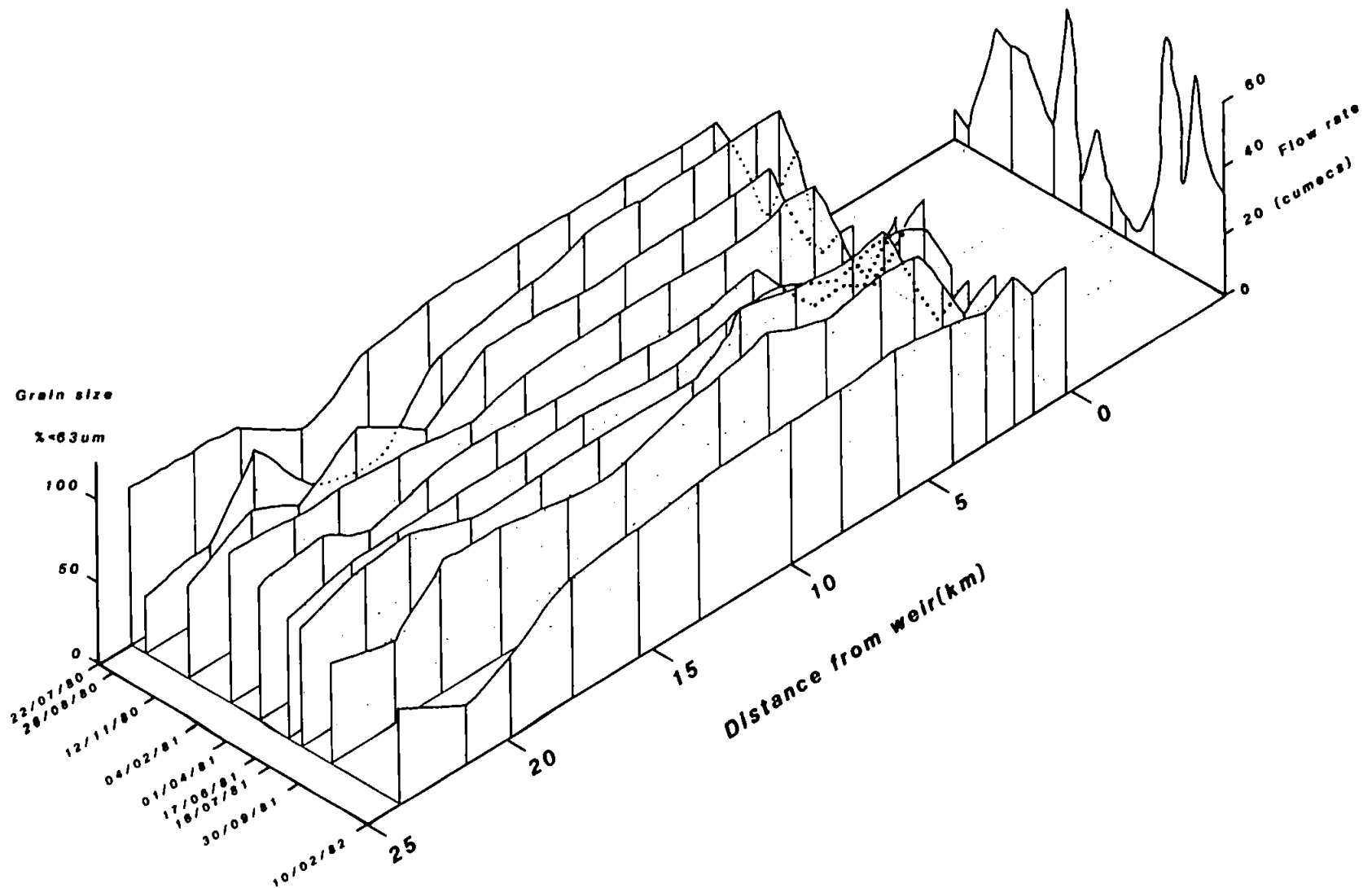
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Figure 3.22   River Tamar sediments - spatial/temporal analysis of grain size distribution

and 10/2/82. These correspond to situations of relatively rapid changes in river flow condition, indicating that comparatively long periods of flow stability are required to enable equilibrium to be achieved. The data from an unpublished study by Bale, et al. (cited in Ackroyd, 1983) has shown an annual accretion/erosion cycle taking place in the Tamar estuary, which supports these conclusions.

Further support for this model comes from the work of George (1975), which has established an asymmetrical tidal curve for the mid estuarine region of the Tamar, associated with a long ebb period and short, high energy flood. Sediment would therefore be resuspended and moved upestuary by the high upstream current velocities of the flood period. Material redeposited upstream at slack water would only be partially remobilised by weaker ebb currents, accounting for the accretion of sediment, especially the finer material, upestuary during the periods of low river flow. This process involving the tidal pumping of sediment has been observed in other estuaries (Allen, et al., 1980). During the high river flows associated with the winter months, the highest tidal velocities would be associated with the ebb periods, resulting in the reverse transport of fine grained sediment downestuary.

For the purpose of relating this model of sediment transport within the estuary to the observed levels of metals occurring there, the Tamar estuary was divided into 14 segments, in which the appropriate sample site was approximately centralised (fig. 3.23). In order to calculate a metal content per unit volume of sediment, several assumptions had to be made. This was acceptable because the spatial-temporal analysis is largely a comparative exercise. The area of each segment was calculated in km^2 and a depth of 1 cm for resuspendable sediment assumed to
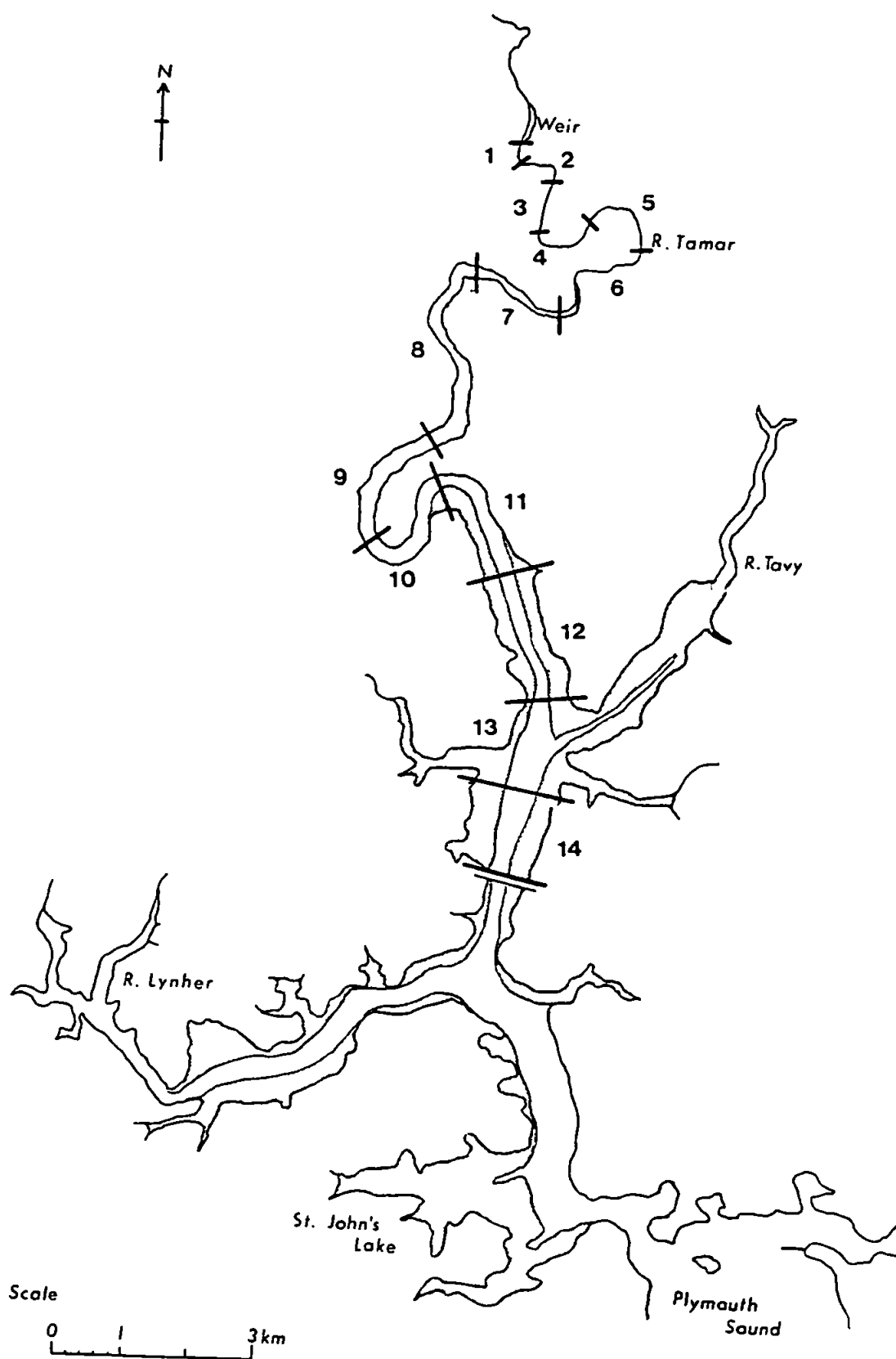
Figure 3.23   River Tamar sediments - estuarine segments used in spatial/temporal analysis

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calculate the volume of mobile sediment in each segment. The average

metal concentration in each segment was calculated using an average

sediment density[a] of 2.65 g/cm³ and the normalised metal concentration

of each sample site, because of the established association of metal

with fine grain fraction. This standardised value was used to plot the

variation in metal levels temporally and spatially, within the estuary.

Mean monthly river flow was also plotted to establish its influence on

the metal levels.

3.2.4.1 Iron

The analysis of total Fe (fig. 3.24) shows that this metal is highly

reactive within the estuarine sediments. The time period covered, of

18 months, includes data obtained from earlier surveys (Ackroyd, 1982),

not included in the present work.

In the upper estuary, downstream to a distance of around 5 km, Fe

levels are at their highest, compared to the rest of the estuary. Peak

levels of Fe occur at the head of the estuary during periods of high

river flow in the winter months of 1980/81. These are probably

associated with increased run-off from the mineralised catchment area.

The diagram shows this peak moving downstream in the succeeding months,

during the period of continuing high river flow rates.

The levels of total Fe in the top segment of the estuary decreased with

decreasing river flow rate during the spring of 1981, associated with

an expected decrease in run-off levels from the surrounding mine

tailings. A second upper estuarine peak occurred, however, in the

summer of 1981, during conditions of low river flow. This may have

[a] This is probably an overestimate due to the relatively large volume of
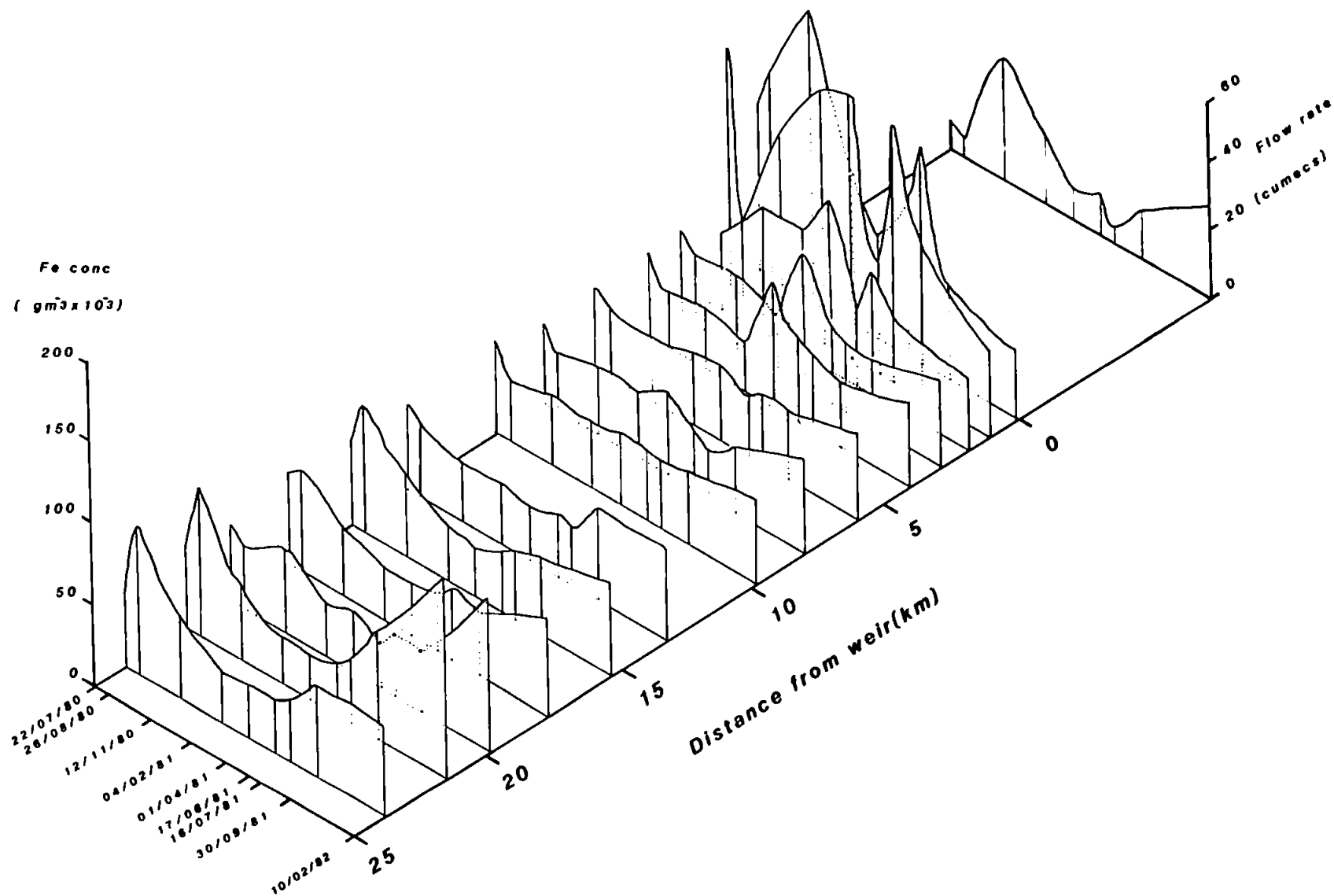pore water at the near sediment-water interface

Figure 3.24   River Tamar sediments - spatial/temporal analysis of total Fe distribution

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been due to the upestuary transport of sediment during this season mentioned previously. An alternative explanation for this peak in total Fe levels is the mobilisation of Fe brought about by the oxidation of arsenopyrite during periods of low run-off referred to in section 3.2.2. This Fe would be present in the sediments as particle coatings, however, and should therefore show a peak in the non-detrital levels of Fe during this period. Although a peak is observed at this time (fig. 3.25), suggesting that this process may be occurring, it only accounts for less than 10% of the total Fe content, therefore indicating that the peak levels observed are largely due to physical processes. This strongly favours the first mechanism.

The metal content of the mid-estuarine region from 5-15 km downstream showed relatively little change, with no significant addition or removal of Fe occurring over the period of study. The lower section of the estuary (15-25 km downstream) again exhibited a high degree of variability in metal content. In the lower section Fe levels decreased from a peak in the summer months of 1980 to low levels in the winter of 1980/81. The high river flows associated with this period should have led to high levels in this region of the estuary, due to the downstream transport of sediment. These low levels persisted throughout the summer of 1981, probably due to the net upstream movement of sediment over this period, resulting in no new material reaching this region. During the winter of 1981/82 increased run-off in the upper estuary led to increasing levels in the lower estuary again.

The profile for non-detrital Fe in the estuary (fig. 3.25) appears to follow the total Fe profile over this period, depicting high upper estuarine levels coupled with low levels in the lower estuary, in the
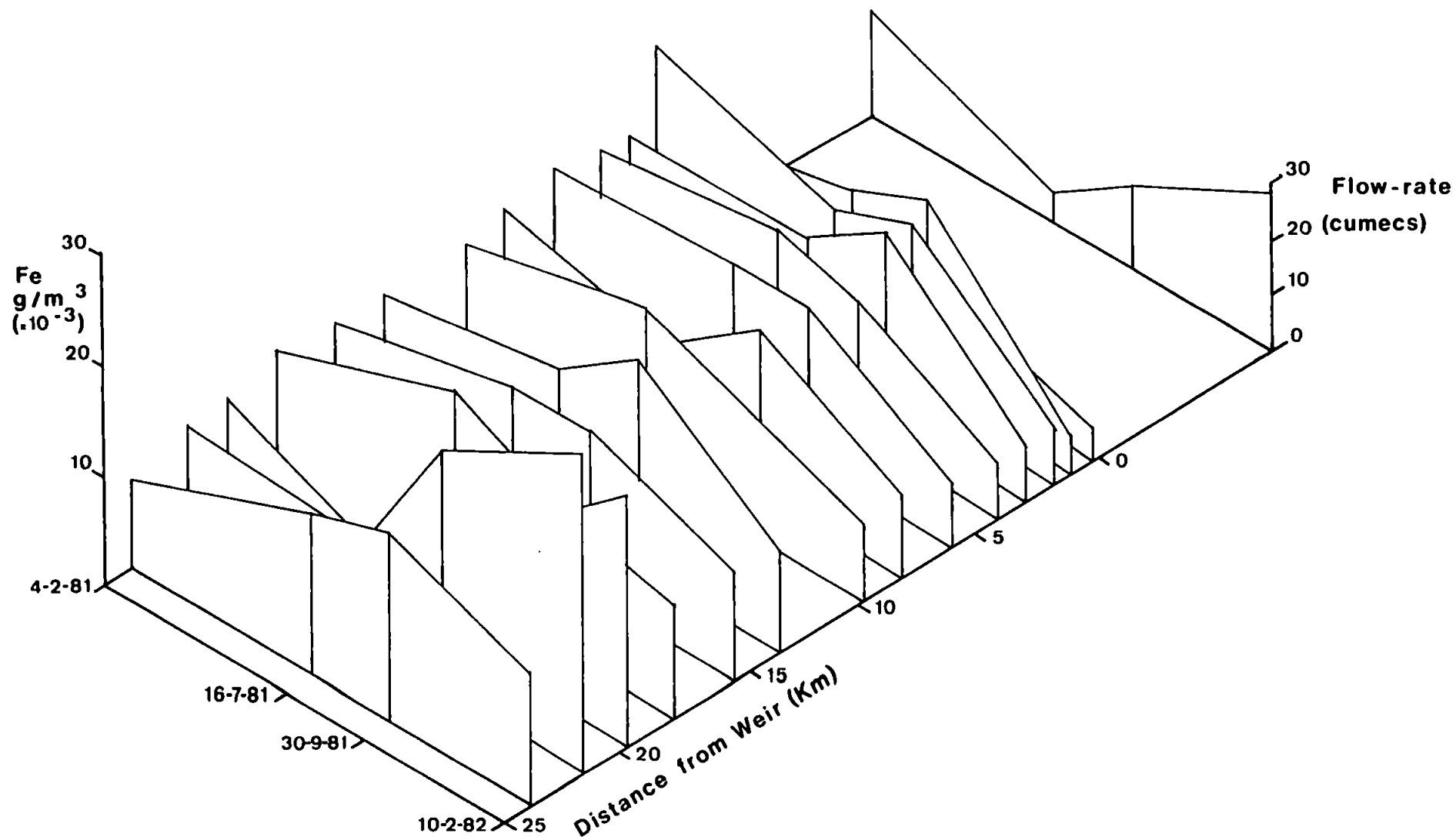
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Figure 3.25   River Tamar sediments - spatial/temporal analysis of non-detrital Fe distribution

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winter 1981 period. The reverse pattern occurs during the summer of 1981 to the winter of 1981/82. The mid-estuarine region again shows little change. This therefore implies that the chemically reactive fraction of the sediment is closely bound to the mineral, largely chemically unreactive fraction. As the overall range of non-detrital metal to total metal levels is $\sim$5-15%, the behaviour of Fe in the sediments appears to be related mainly to the physical processes occurring within the estuary.

Several possibilities exist to explain the apparent inconsistency in behaviour between the upper and lower estuarine regions of the Tamar during the winter months of 1980/81. The previously mentioned tidal assymetry of the mid-Tamar region (George, 1975) may result in sediment divergence at this point, sediment transport below this being largely seaward, while above this region transport reversal may occur. It is also possible that the very high river flows of the winter of 1980/81 (cf, winter 1981/82) resulted in a net seaward transport of sediment outside the region of the survey, leading to a depletion of Fe-rich fine grained material in this section of the estuary. A third possibility, related to the first, is that the apparently unaltered mid-estuary may act as a buffer zone, the summer Fe peak of 1981 relating to transport reversal from mid-estuary as described above, while the lower estuary peak of summer-winter 1981/82 may relate to the buffered transport into the lower estuary of the winter 1980 upstream sediment load.

3.2.4.2 <u>Manganese</u>

The temporal-spatial profile for total Mn within the Tamar estuary

(fig. 3.26) indicates large inputs of Mn in the top 2 km of the estuary during the autumn and winter of 1980/81, associated with concurrent high river flows. This Mn load can be observed moving downestuary in the subsequent months. In common with total Fe, a second total Mn peak was observed during the summer of 1981, under conditions of low river flow. This may likewise be due to the effects of tidal pumping, as described for Fe. The most notable feature of the total Mn profile, however, is the rapid removal of Mn from the sediment, which has occurred in the top 5 km of the estuary. This Mn does not reappear in subsequent sections of the estuary and the mid and lower estuarine segments show little sign of addition or removal processes operating. This implies that, unlike Fe, the behaviour of sedimentary Mn is controlled largely by chemical processes, rather than physical ones. This is borne out by the non-detrital Mn data (fig. 3.27), which shows that Mn is present largely (80-100%) in a chemically reactive form, probably as surface coatings on sediment particles. The profile mirrors that of the corresponding section of the total Mn profile, indicating rapid removal within the top few km of the estuary. A relatively small amount of addition is seen in the lower estuary during the winter of 1981/82, showing that the physical processes of sediment transport described for Fe play a small part in the estuarine transport of sediment Mn. The overwhelming mechanism of Mn control in the sediments, however, is plainly that of chemical reactivity, and this is in good agreement with the mechanism of reduction and subsequent remobilisation in the dissolved phase, into the water column, described in section 3.1.1.

3.2.4.3 Arsenic

In contrast to Fe and Mn, the spatial-temporal profiles for As in Tamar
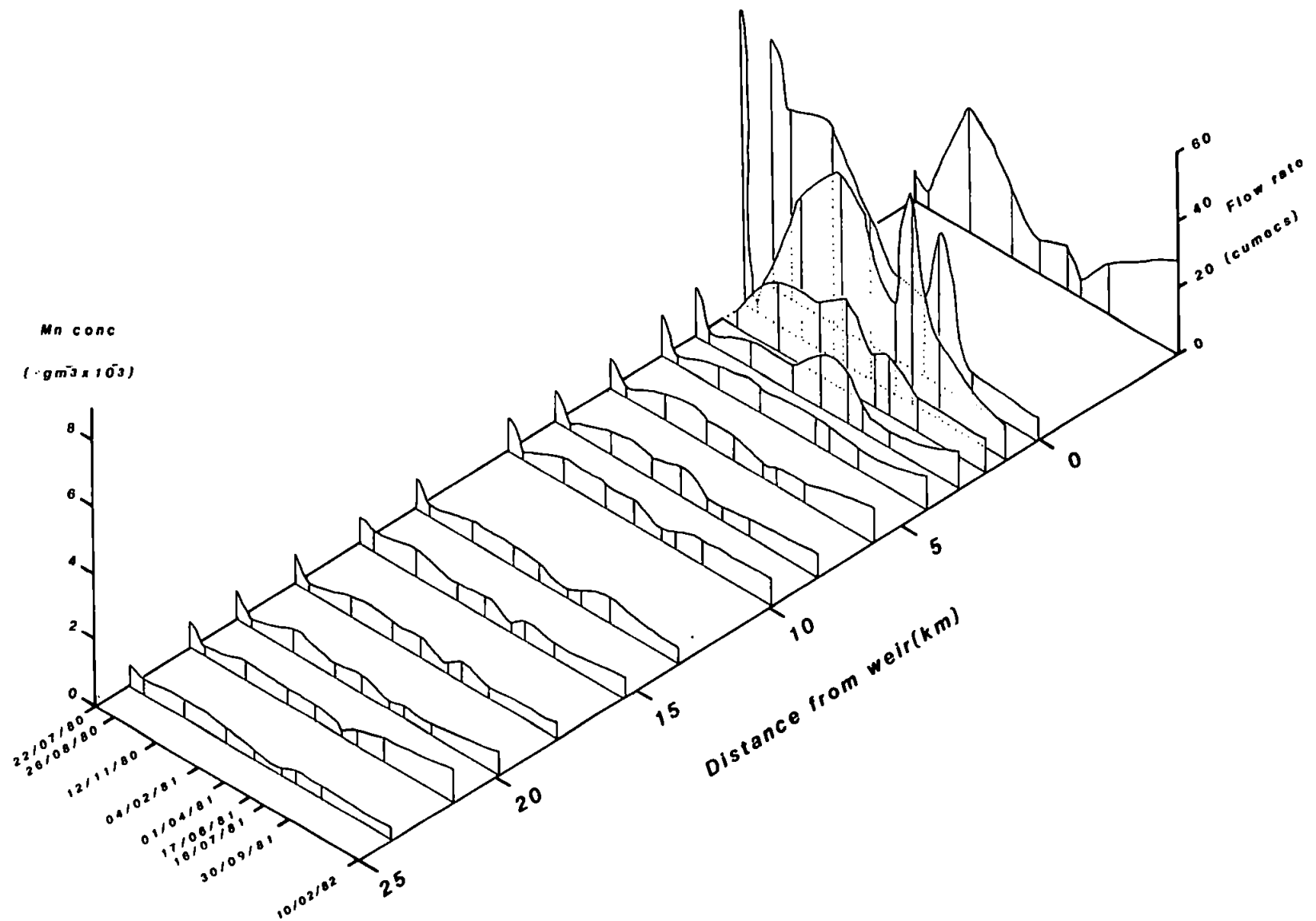
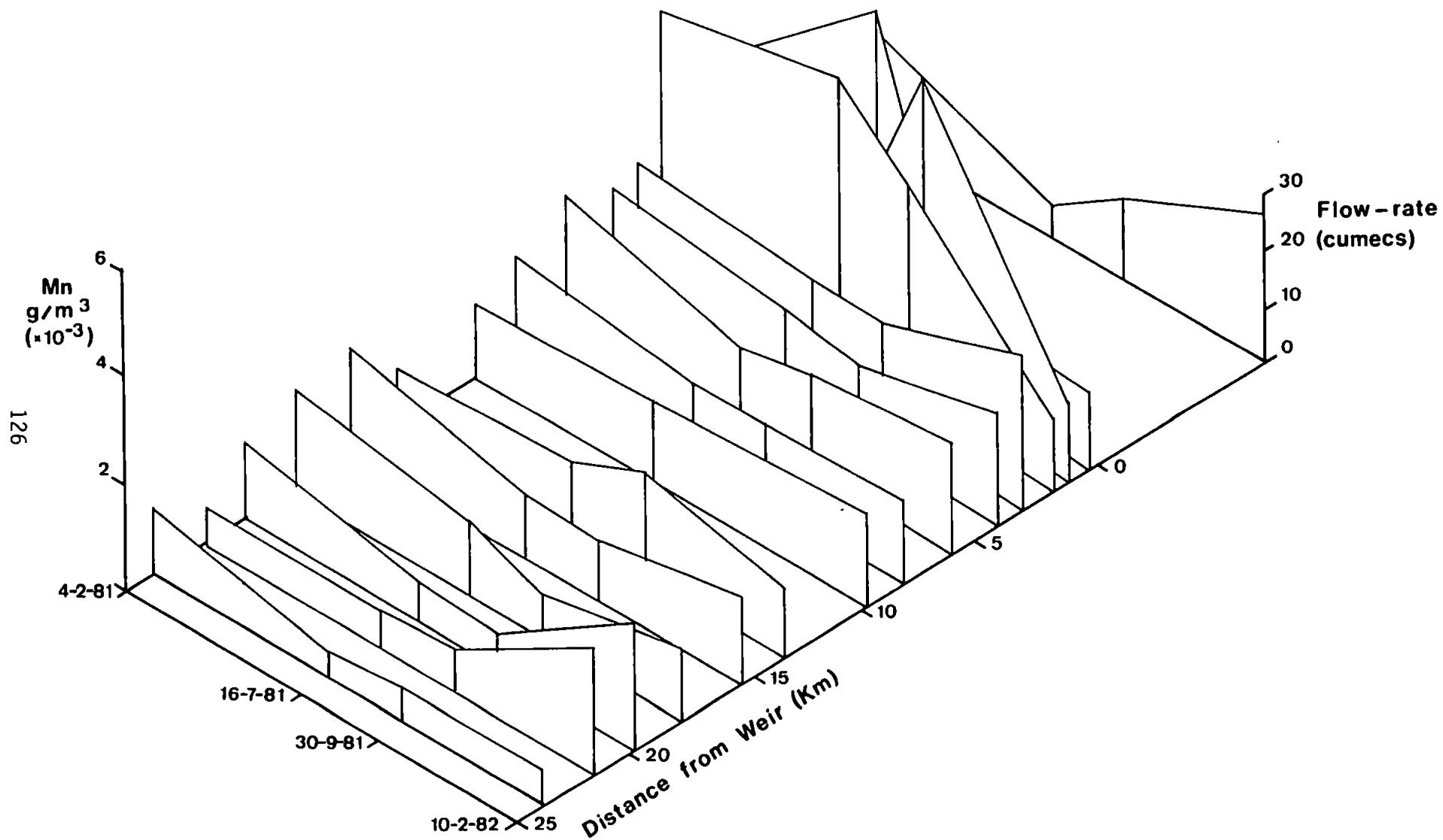Figure 3.26   River Tamar sediments - spatial/temporal analysis of total Mn distribution

Figure 3.27   River Tamar sediments - spatial/temporal analysis of non-detrital Mn distribution

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sediments indicate that its mobility depends on both chemical and physical processes affecting the sediments. The profile for total sediment As (fig. 3.28) is similar to that for total Fe over the same time period (fig. 3.24). A peak in As levels in the top few segments of the estuary is observed, associated with the high river flows in the winter 1981 period. A similar peak is observed during the low river flow of summer 1981, as with Fe and Mn, probably associated with processes of tidal pumping. The mid-estuarine region is again relatively unchanged. Evidence of addition into the lower estuary is seen during the winter period of 1981/82, associated with high river flows, and presumably due to downestuary sediment transport. This is in agreement with the physical processes of sediment mobilisation described for Fe, and is also in keeping with the low levels of non-detrital As ($\ll 5\%$) found throughout the period of the surveys.

Although physical processes are likely to be the predominant forces influencing the sediment transport of As because of the high detrital As content overall, the non-detrital profile for As (fig. 3.29) has more in common with that of Mn, indicating a largely chemical dominated transport. Peak levels of As occur in the upper estuary during the winter of 1981. A second, low flow, summer peak is not observed however. The levels of As drop off rapidly and are at a minimum within 3 km of the estuary head. Some addition of As is apparent in the lower estuary during the winter of 1981/82, but this is not of the magnitude or extent of that observed for total As in this region. It is probably indicative of some influence by physical processes on the behaviour of non-detrital As, but the main processes involved appear to be chemical. This agrees well with the hypothesis stated in section 3.1.1, relating to the behaviour of dissolved As in the water column, and reflecting a similar
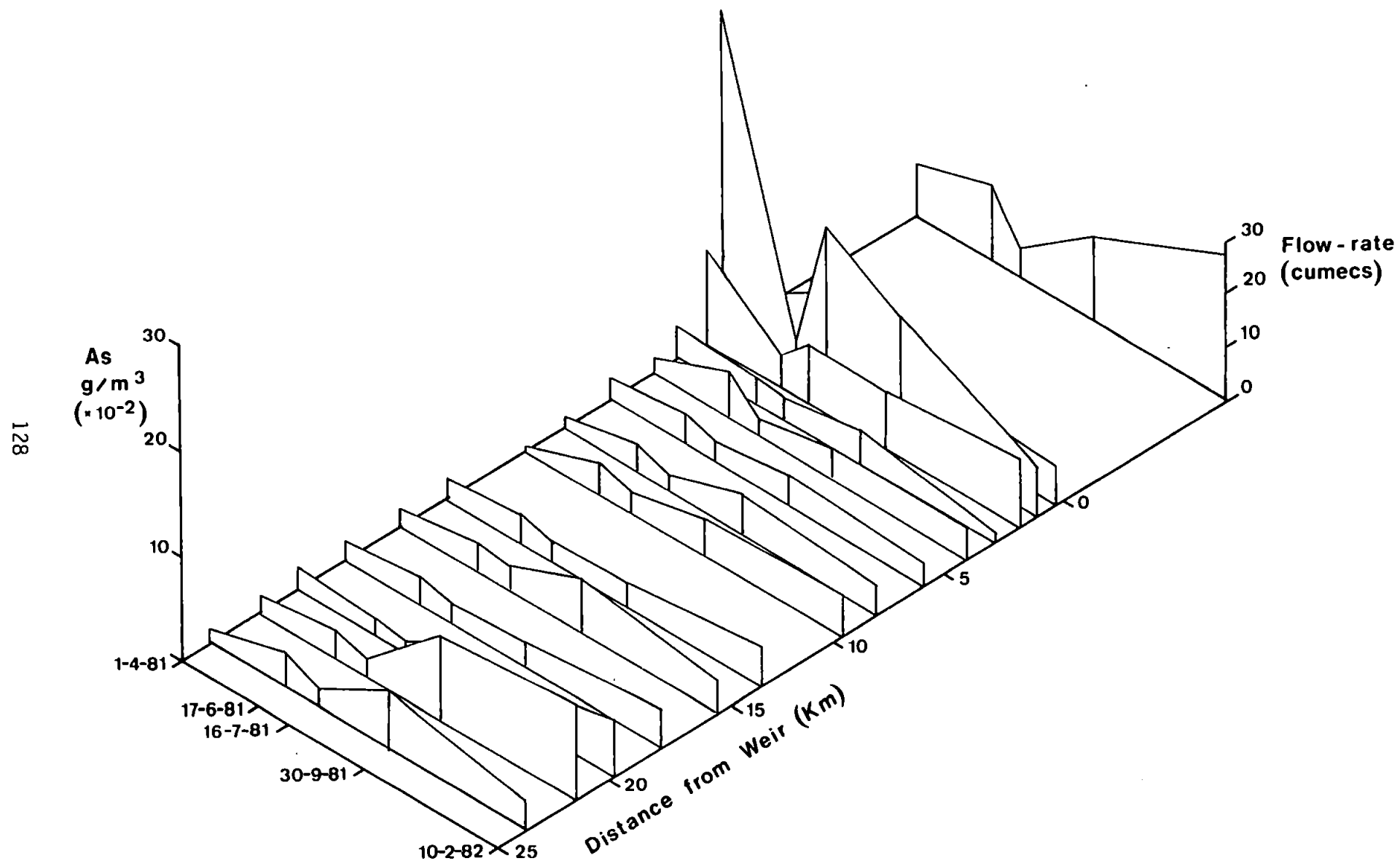
Figure 3.28   River Tamar sediments - spatial/temporal analysis of total As distribution
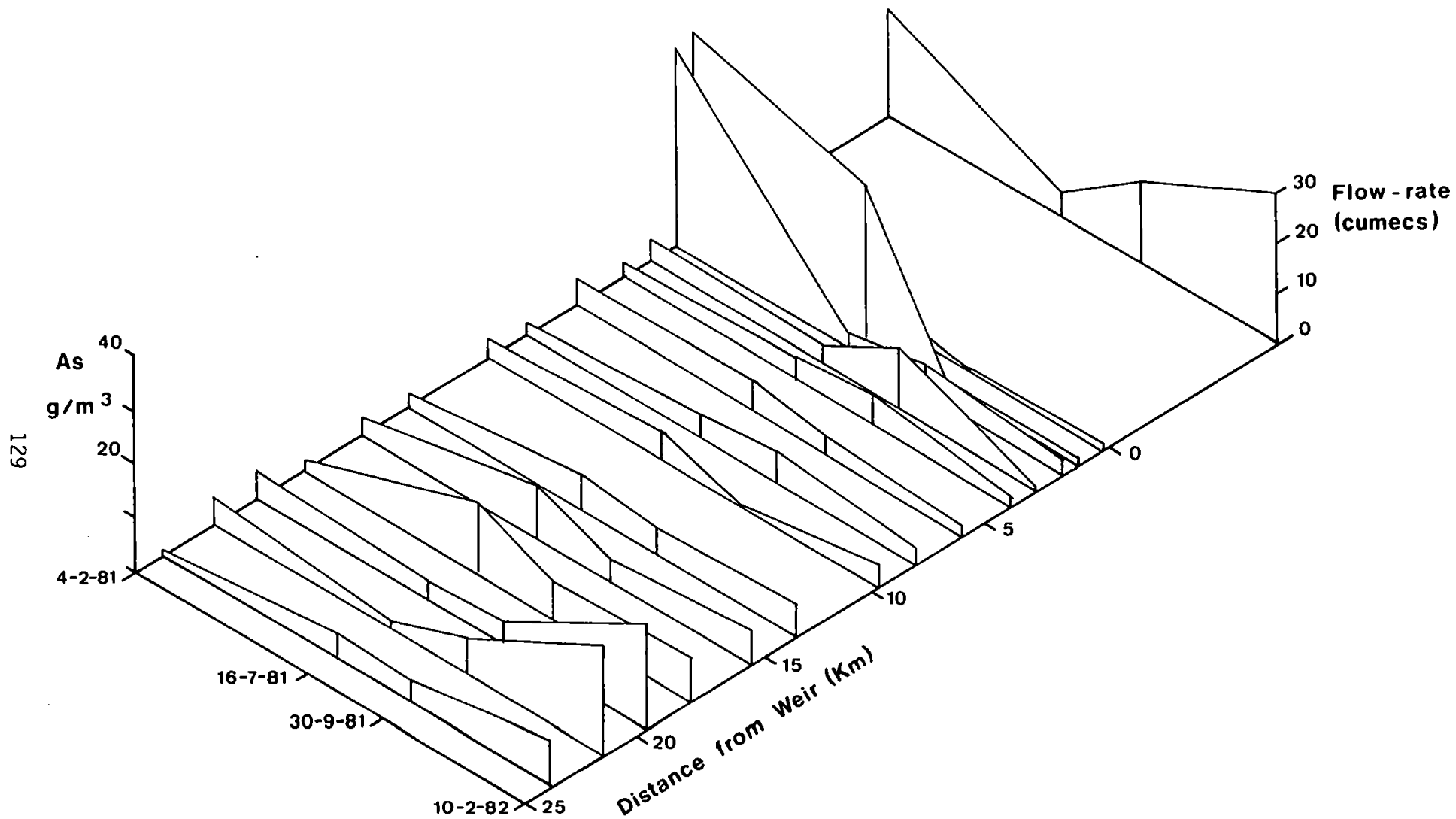
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Figure 3.29   River Tamar sediments - spatial/temporal analysis of non-detrital As distribution

remobilisation chemistry. It can also be noted that the lower estuary addition of non-detrital As occurs during the winter months, associated with the loss of a well defined dissolved As remobilisation profile in the water column.

CHAPTER FOUR

LABORATORY STUDIES

4.1   Precipitate Studies

An understanding of the surface properties of freshly precipitated or aged Fe oxyhydroxides is a vital aid to the interpretation of adsorption behaviour at the solid-solution interface (Stumm & Morgan, 1981). Much recent work has been carried out evaluating the surface characteristics of natural and synthetic Fe oxyhydroxides (e.g. Schwertmann & Fischer, 1973; Schwertmann & Taylor, 1979; Carlson & Schwertmann, 1980 & 1981; Crosby, 1982). The surface area of the solid phase is of major importance in the adsorption process, as is the shape and size of the pores present; for these may control the reversibility of this process (Crosby, et al., in press). Many of the earlier studies of synthetic Fe precipitates, however, used a wide range of preparative techniques (e.g. Davis, 1977; Evans, et al., 1979; Davis & Leckie, 1980; Tipping, 1981), making definitive comparisons between precipitates difficult. In addition, these studies have frequently been based on conditions not directly comparable with those found in the natural environment. For example, hydrous Fe oxides have been precipitated by direct hydrolysis of Fe (III) salts, whereas under natural conditions they are more commonly precipitated by the oxidation and hydrolysis of Fe (II) compounds, resulting from the input of acid mine streams (Singer & Stumm, 1970; Thornton, et al., 1975) or from the remobilisation of anoxic pore waters at the oxic/anoxic boundary of sediments during tidal stirring (Troup, et al., 1974; Lyons, et al., 1979). Also the Fe concentrations used have often been much higher than those found in natural systems and pH and ageing times have been poorly defined.

In this research group (Crosby, 1982) we have attempted to overcome these inconsistencies by investigating the surface area and porosity

of both Fe (II) and Fe (III) derived oxyhydroxides, precipitated under controlled conditions of pH, temperature and ageing time, using Fe concentrations similar to those found in natural water systems. Additionally, we have compared precipitates of Fe oxyhydroxides from both synthetic and natural sources.

The surface areas and porosities of the precipitates were determined using a gravimetric B.E.T. nitrogen adsorption technique (section 2.1.5) and identification of the precipitates was attempted using XRD, IR spectroscopy and Mössbauer spectroscopy (section 2.1.5). Ideally, such surface area studies should be carried out in solution, utilising the adsorption of the appropriate ion (Greg & Sing, 1967; Everett & Ottewill, 1969; Anderson & Malotky, 1979). Some of these in situ techniques, such as negative adsorption (Avotins, 1975; Davis, 1977), however, must be used with care as they only apply to non-porous surfaces (Van den Hul & Lyklema, 1968) and so cannot be applied to the study of Fe oxyhydroxides. The major advantage of the vacuum microbalance technique is that the adsorption/desorption hysteresis curves yield information on both the pore shape and size of the precipitate. Comparable hysteresis experiments using an appropriate dissolved ion would be difficult to perform in solution.

The method of precipitate preparation used here retains the reticular structure of the original matrix (Glasson, 1960), although it must be borne in mind that drying procedures have been shown to affect the surface area obtained (Egashira & Aomine, 1974) and that surface areas determined on dried samples are normally lower than those determined in solution. The surface area data presented should therefore be taken as a probable underestimate, although comparability between samples is retained.

4.1.1   Synthetic Precipitates

A comparison of the IR spectra for synthetic Fe (II) derived precipitates formed at 15°C and 2°C with that of a Lepidocrocite (γ-FeOOH) standard (fig. 4.1) indicates that both materials have a similar structure, that of partially crystallised γ-FeOOH.

Figure 4.2 shows the isotherms obtained for these Fe (II) precipitates, which were formed from 10^{-4}M Fe (II) at pH 7.0, over an ageing period of 48 h. The 15°C isotherm was shown by Crosby (1982) to have a surface area of 121 m^2/g, the hysteresis indicating open, randomly orientated slit-shaped pores with an almost unrestricted mesopore size range of 2-50 nm. The XRD diffractogram for this precipitate gave good agreement with that of the crystalline Fe oxide γ-FeOOH. The Mössbauer spectrum merely confirmed that this was an Fe (III) oxyhydroxide, which did not contradict the identification as γ-FeOOH.

Referring to the 2°C isotherm in fig. 4.2, it can be seen that while the pore structure of this precipitate was similar to that of the 15°C derived material, the surface area was some three times greater at 299 m^2/g. This indicates that the temperature of formation has an important effect on the activity of the precipitate formed, which would be significant in the natural environment, where a wide range of temperatures is encountered. This would lead to increased surface areas during the winter months, at a time of increased groundwater flow and higher dissolved metal concentrations.

Although this result appears anomalous at first, due to an expected decrease in oxidation rate at the lower temperature, its consequent
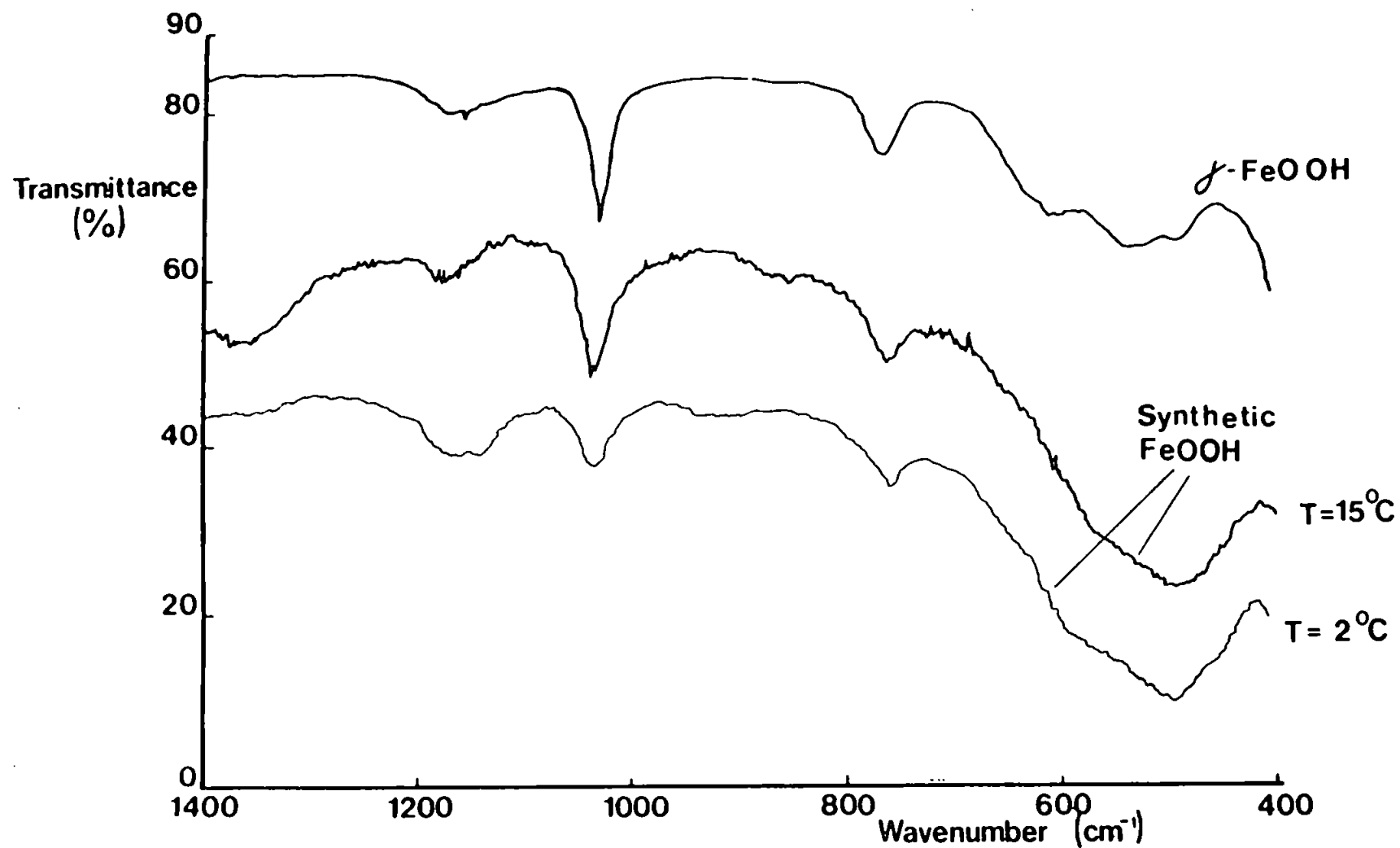
Figure 4.1   IR spectra of synthetic Fe oxyhydroxides prepared at 15°C and 2°C, compared to a γ-FeOOH standard
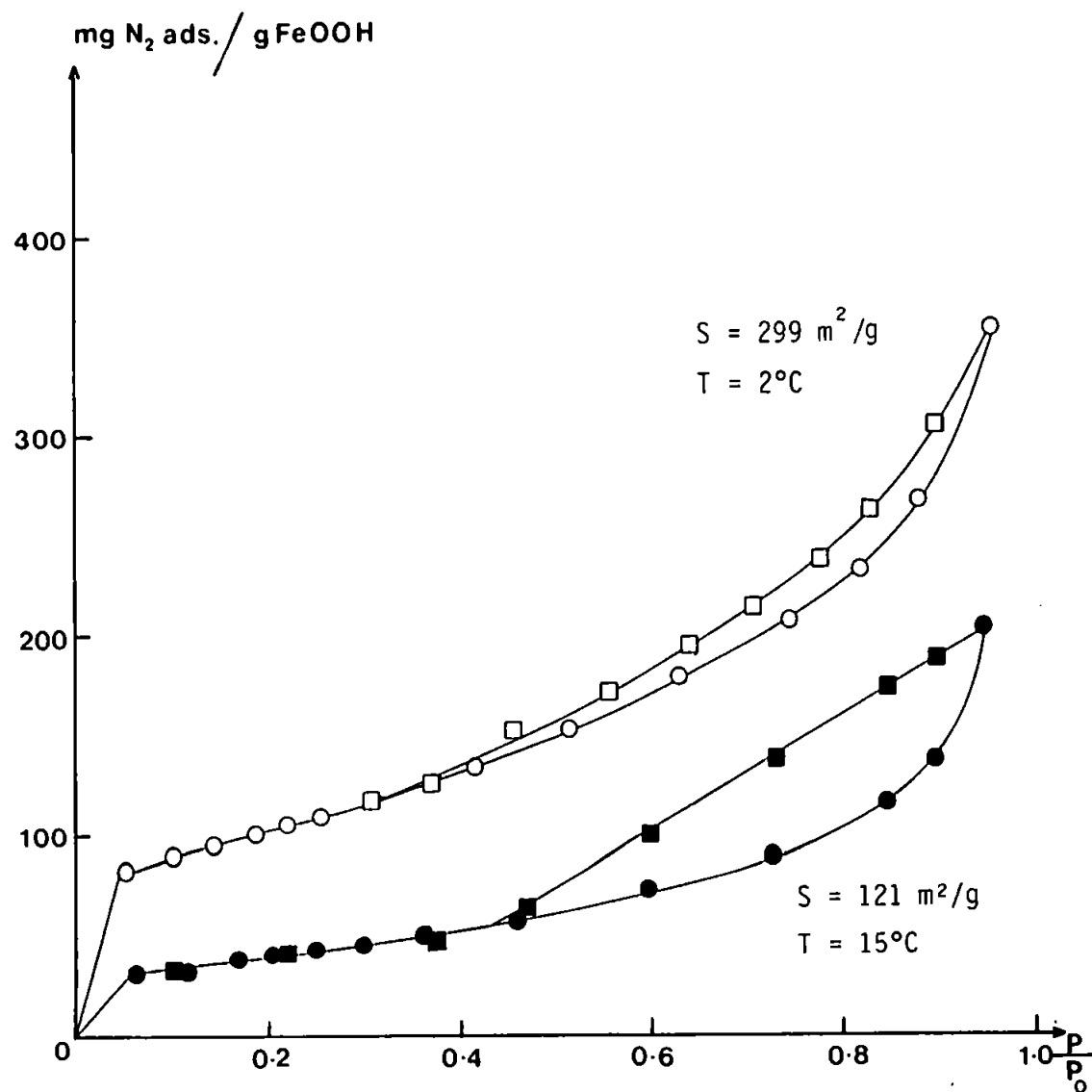
135

Figure 4.2   Comparison of adsorption hysteresis curves for Fe oxyhydroxides prepared at 15°C and 2°C

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effect is to decrease the rate of nucleation of the oxyhydroxide. This leads to a more finely divided precipitate with a consequently greater surface area.

The Mössbauer spectrum (fig. 4.3) again indicated that the 2°C derived Fe (II) precipitate was an Fe (III) oxyhydroxide, but no definitive crystallinity was observed.

The nature of the Fe (II) derived precipitates described above contrasts sharply with that of oxyhydroxides derived from synthetic Fe (III) sources. Crosby (1982) has shown that Fe oxyhydroxides derived from Fe (III) sources tend to yield amorphous oxides (am-FeOOH) over ageing times of 48 h. Over long periods of several days the presence of goethite (α-FeOOH) can be detected. It was shown that the Fe (III) derived material had a surface area of 234 m²/g, double that of the Fe (II) derived material, with a hysteresis of the type associated with narrow-necked, wide-bodied, 'ink bottle' pores (Lowell, 1979). The pore size range was 1-4 nm, well within the mesopore size range and far more restricted than that of the Fe (II) material.

The differences observed between the Fe (III) and Fe (II) derived materials are due largely to differences in the mechanism of precipitate formation. The development of a colloid from Fe (III) salts at 15°C and pH 7.0 occurs in < 10 s (Crosby, 1982). With Fe (II) salts there is initial oxidation of Fe (II) to Fe (III) before hydrolysis and formation of a colloid. The appearance of a colloid can take several minutes, depending on the conditions of formation. For example, the homogeneous oxidation half-life of Fe (II) at pH 6.9 is 63 min at 15°C and 315 min at 5°C (Sung & Morgan, 1980).
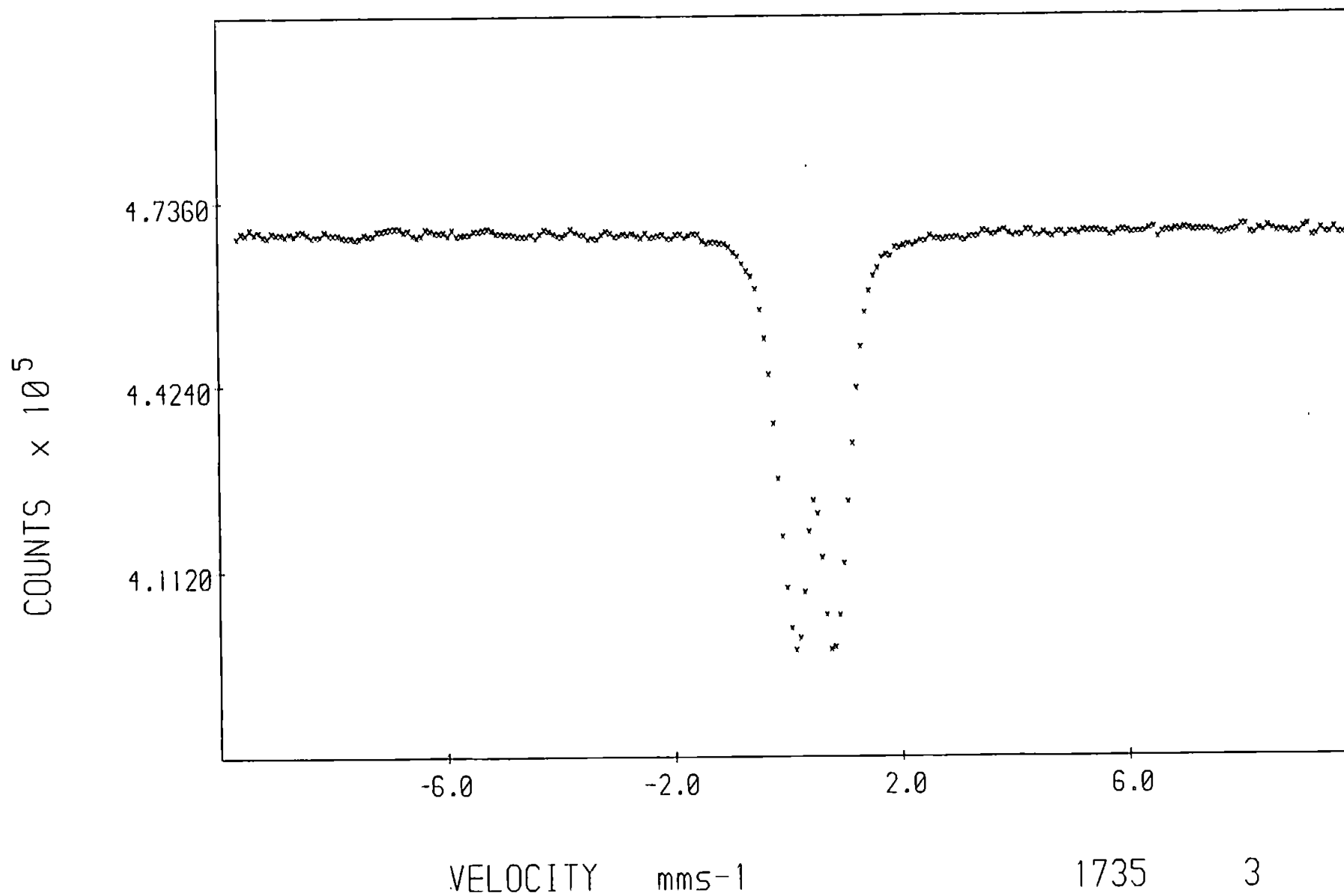
Figure 4.3   Mössbauer spectrum of Fe oxyhydroxide prepared at 2°C

4.1.2   Natural Precipitates

The isotherm for a natural acid mine stream precipitate, from Herodsfoot, Cornwall (fig. 2.3) derived entirely from Fe (II) shows a hysteresis (fig. 4.4) very similar to that of the synthetically derived Fe (II) precipitate, indicating the same slit-shaped pore structure and wide mesopore size range.   The X-ray diffractogram for this precipitate did not yield the d spacings of γ-FeOOH, however, and the IR spectrum was inconclusive, indicating a possible mixture of γ-FeOOH and Ferrihydrite (table 4.1).   The Mössbauer spectrum of the precipitate gave little information, showing only that the material was 100% Fe (III) oxyhydroxide.   This precipitate therefore appeared to be a mixed oxy-hydroxide, making positive identification difficult and indicates some of the problems involved in identifying natural precipitates.   Crosby (1982) found evidence of a mixed oxyhydroxide in sediment floc from the Lady Bertha minestream, although, as here, identification was not conclusive.   He also studied a naturally derived precipitate from an acid minestream containing 37% dissolved Fe (III), and found its hysteresis loop resembled that of an Fe (III) derived material, while the surface area (141 m^2/g) and pore size range (1.5-10 nm) were more indicative of a crystalline oxide.   Characterisation studies, however, yielded no evidence of crystallinity.

The character of the precipitate in this case appears to be determined by the dissolved Fe (III) present.   The almost immediate formation of an Fe oxyhydroxide from the Fe (III) component would provide active sites for the rapid heterogeneous oxidation of Fe (II) (Sung & Morgan, 1980).   This would tend to confer an Fe (III)-like character on the precipitate.   The low surface area is probably due to the coprecipitation

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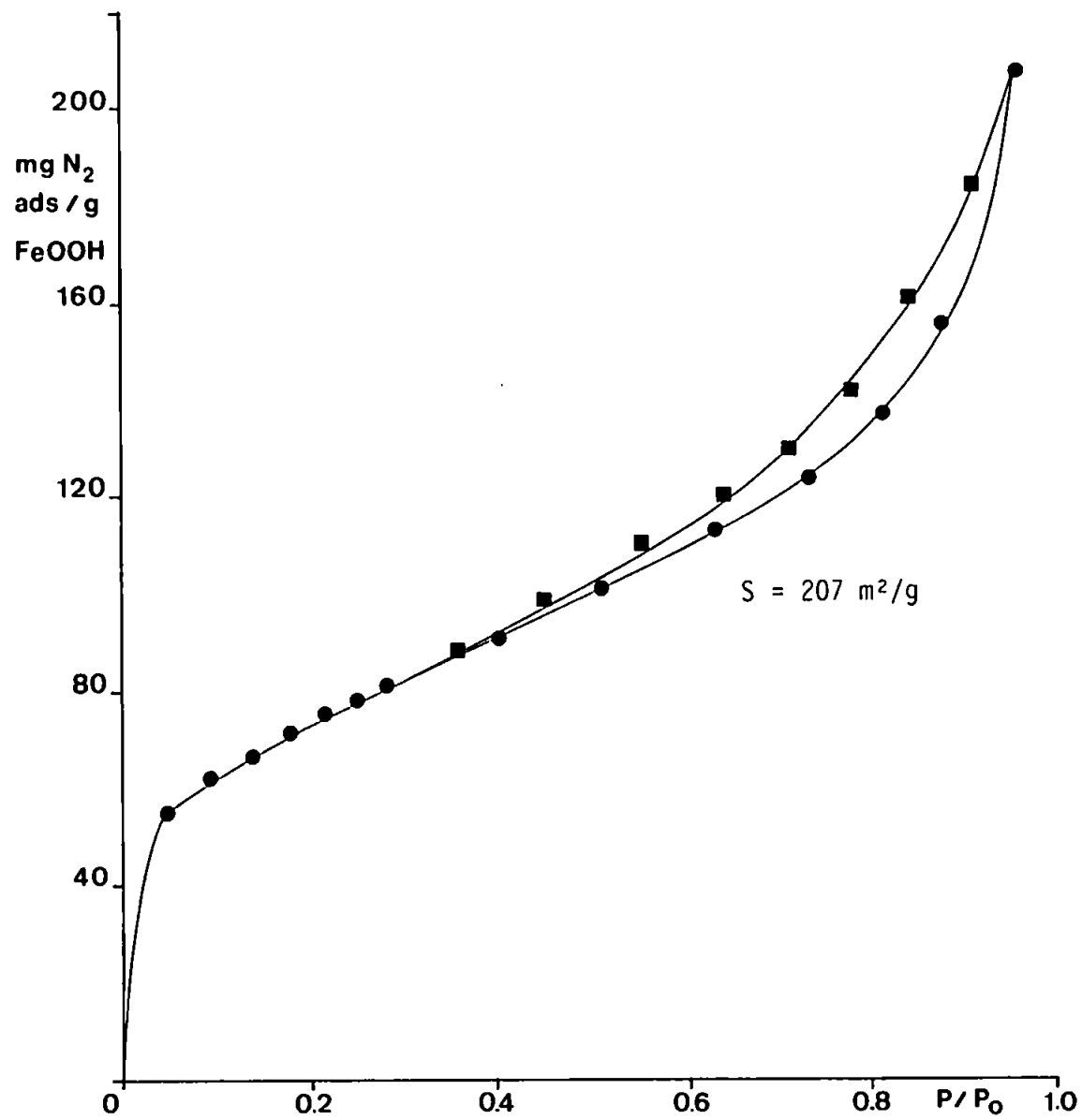
Figure 4.4   Adsorption hysteresis curve for natural Fe oxyhydroxide from Herodsfoot, Cornwall

Table 4.1   Comparison of IR Spectra Peak Values for Natural
Precipitate from Herodsfoot with Standard Peak Values
for Lepidrocrocite (γ-FeOOH) and Ferrihydrite

Herodsfoot Precipitate (cm^{-1})	γ-FeOOH (cm^{-1})	Ferrihydrite[a] (cm^{-1})
3400		3400
1610		1625
1380		
1020	1020	
	750	
480		

[a] from Schwertman & Fischer (1973)

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of organic matter in the natural environment, which is known to reduce the surface areas of natural hydrous Fe oxides (Schwertmann & Taylor, 1979).

Differences were also examined between Fe flocs precipitated naturally in situ and therefore of indeterminate age, and those precipitated in the laboratory over a relatively short ageing period (48 h). Figure 4.5 shows a comparison between two such materials, both from the Wheal Franco acid minestream, situated on the River Walkham, Devon (fig. 2.3). The upper isotherm is that of the naturally precipitated particulate. The shape of the hysteresis curve indicated the presence of slit-shaped pores typical of Fe (II) derived precipitates. The high surface area of the material, compared to that of the synthetic precipitate, may reflect the effect of a low formation temperature ($\sim 6°C$) on its activity, as shown earlier for the synthetic precipitates. The lower isotherm is that of the laboratory formed precipitate and this showed a generally similar hysteresis loop, but with a reduced surface area. This precipitate was formed at a temperature of 18°C, and although previous work (Crosby, 1982) has shown that there is an initial increase in the surface area of Fe (III) derived precipitates over an ageing period of around 48 h, no such increase has been observed for Fe (II) precipitates and the general trend for both Fe (II) and Fe (III) derived materials is one of decreasing surface area with age. The most likely explanation of the differences in surface areas therefore remains the effect of precipitation temperature. The characterisation studies for these precipitates proved inconclusive and these materials were not identified.

4.1.3   Natural Particulates

The suspended particulate material from a river high in dissolved iron;
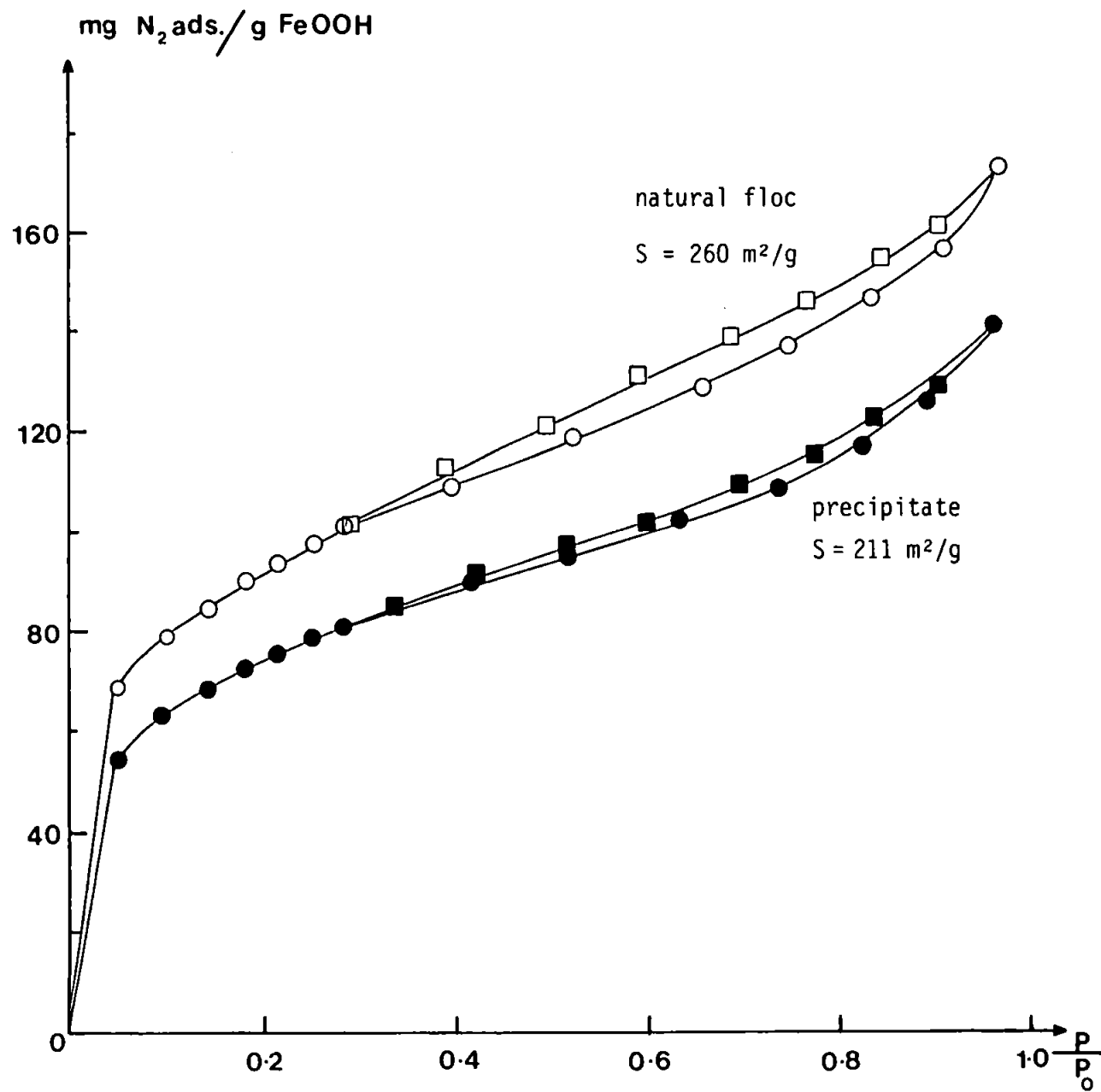
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Figure 4.5   Adsorption hysteresis curves for natural floc and precipitated Fe oxyhydroxides
from Wheal Franco, Devon

the River Carnon, Cornwall (fig. 2.3), was investigated. This river has known inputs from active mine workings (Thornton, et al., 1975; Boyden, et al., 1979) with 4-6 mg/L dissolved Fe present. The sample was collected by large volume filtration, at 9°C, pH 5.0, and contained 4 mg/L Fe. The characterisation studies of this clay-like particulate confirmed a complex composition with a non-detrital Fe content of 0.6%, estimated by a 25% v/v acetic acid leach (section 2.2.2.1). The isotherm of this material (fig. 4.6) is interesting because it shows that, despite the complexity of the particulate, its adsorption behaviour is typical of an iron (II) precipitate, although with a significantly lower surface area. The Fe-like adsorption behaviour of this material suggests that the Fe is present as a surface coating on the clay matrix, reducing the clay's adsorption capacity and thereby causing the material to behave as an Fe-like particulate. The low surface activity is difficult to explain, but presumably some of the Fe's surface is involved in binding with the clay matrix. It is also possible that the association of individual clay particles with one another would further reduce the available Fe surface area.

4.2   Modelling Studies

4.2.1   Approach to Chemical Modelling

As indicated in chapter 1, the speciation of As in natural waters is complicated, compared to that of P (Crosby, 1982), by the existence of the As (III) and As (V) forms. This results in a proportionally greater number of model variations requiring consideration. In order to limit the total number of experiments required, only the estuarine end-members were modelled. Seawater has a relatively constant composition away from riverine inputs and anthropogenic influences in coastal waters and
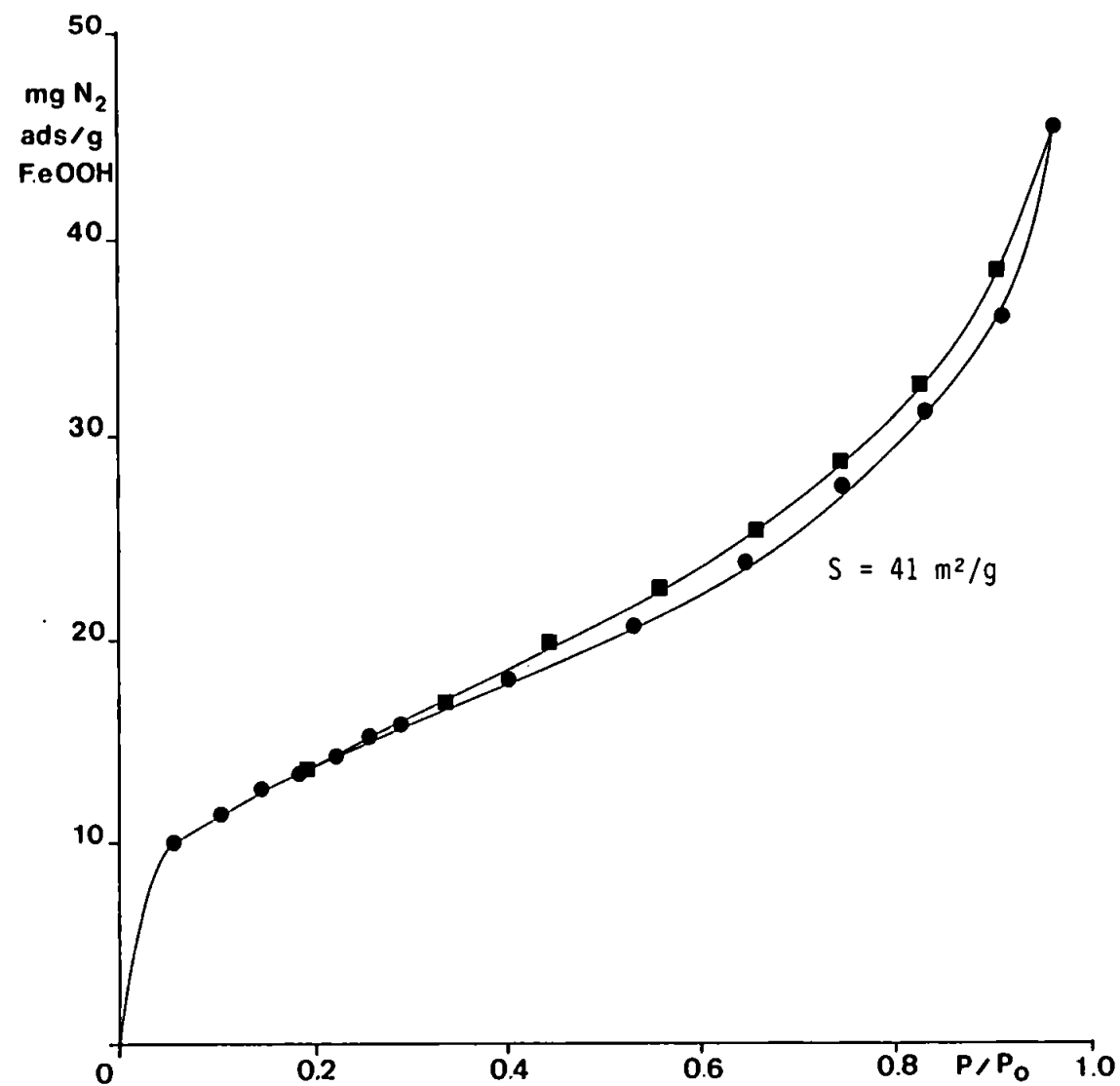
Figure 4.6   Adsorption hysteresis curve for natural suspended particulate from the River Carnon, Cornwall

estuaries. Filtered seawater was therefore used to model the saline end-member, although some of the earlier models exhibited an unacceptable degree of variability in results. This was traced to a high and variable dissolved organic content in the seawater and subsequently only relatively organic free seawater (<1 mg/L) from the English Channel was used, which proved to be an acceptable analogue.

Distilled water buffered with 2 mM $NaHCO_3$ was used as a matrix for the riverine end-member, but this was considered a less acceptable analogue because of the wide variations in freshwater composition, especially with regard to the minor elements (Kharkar, et al., 1968). However, it was felt necessary to simplify the analogue in this way, in order to standardise the modelling procedure.

The importance of the low salinity region of estuaries has been reported by Morris, et al., (1978), but nephelometric studies by Crosby (1982) have shown that the rate of precipitate formation is not significantly altered at pH 7.9 and $> 10^o/oo$ S for Fe (II), and that the rate of precipitation of Fe (III) is relatively constant throughout the natural pH range in both seawater and freshwater. The end-member approach is therefore considered viable as it enables the acquisition of mechanistic information about the adsorption processes under investigation at the extremes of the natural aquatic environment.

Fresh and aged precipitates were studied in the models because these reflect different types of input into natural water systems. Fresh Fe precipitates will be formed from dissolved Fe inputs related to acid minestreams, industrial effluents and pore water infusions at the sediment-water interface. Aged Fe precipitates are analogous to inputs

from crustal weathering, the solid phases resulting from mining activity, or to suspended precipitates formed and aged during transport through the estuarine system.

The models were run at temperatures of either 20°C or 2°C. Two temperatures were again chosen to limit the number of experimental runs required and these represent the approximate limits of seasonal temperatures in aquatic systems, and the temperature difference chosen was also useful as each difference of 10°C should lead to a factor of two change in the reaction rate (Laidler, 1965), which is thus of value in the kinetic analysis.

The pH ranges chosen, pH 6.0-7.5 for freshwater models and pH 7.0-8.5 for seawater models reflect a reasonable range either side of the average pH values for these media. Although seawater is a relatively buffered system, wide ranges of pH far outside those covered in the modelling can occur in freshwater systems due to the input of mine wastes or other industrial effluents. It was not considered feasible to model such an extreme range, and therefore extrapolation of the experimental data is made, as appropriate, in the discussion.

Other factors, such as the presence of organic matter, variation in dissolved O_2 content and the influence of other solid phases, such as clay particles, were excluded from the modelling studies. This was done in order to retain a simple, well defined matrix which could be relatively easily quantified, and also enabled comparison of this work with that of Crosby (1982). The effects of such potentially important components can, however, be studied by the modification of such a modelling system (Millward & Burton, 1975; Millward & LeBihan, 1978).

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The majority of the modelling work was carried out on the uptake of As (V) onto Fe (II) derived precipitates. This is because As (V) as the arsenate ion (AsO_4^{3-}) is the predominant thermodynamically stable species in oxic aqueous environments (Ferguson & Gavis, 1973), and Fe (II) is potentially more significant than Fe (III) (see chapter 1).

4.2.2 Mechanisms of Arsenic Removal
4.2.2.1 Aged Precipitates
4.2.2.1.a Fe (III) derived precipitates

A number of models were carried out on the adsorption of As (V) and As (III) onto aged Fe (III) precipitates. Figure 4.7 shows the profiles for As (V) and As (III) at 2°C and pH 7.1 in freshwater. The profile for As (V) uptake onto aged Fe (III) indicates that the rate of adsorption is quite slow, having a time to equilibrium (t_e) of 55 min, with 80% of the As adsorbed at equilibrium. In contrast, the adsorption of As (III) is considerably slower, with only 20% As adsorbed after 2 h and with final equilibrium still to be reached. The rapid initial adsorption seen within the first minute is difficult to explain, but is thought to be the result of instrumental error in this particular case, the true profile being a steady decrease from 100 µg/L As.

The adsorption of As (V) and As (III) onto aged Fe (III) in seawater is shown in fig.s 4.8 and 4.9 respectively. The adsorption of As (V) at 20°C is slow (t_e = 40 min) with about 55% As adsorbed at equilibrium. At 2°C the adsorption is at a similar rate, although equilibrium has not been reached at 2 h when some 70% As has been adsorbed. This implies a more active precipitate has been formed at this temperature (all
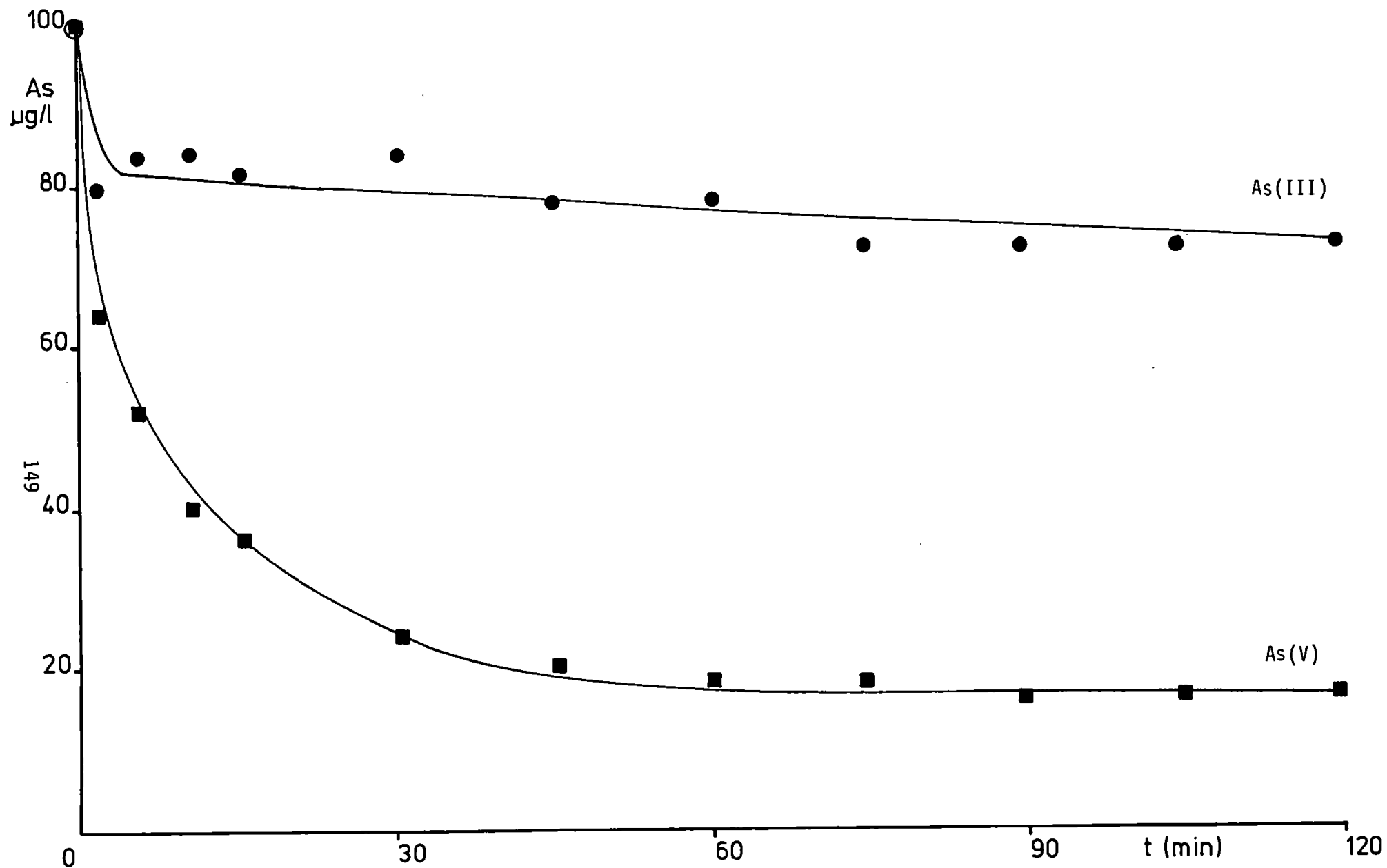
Figure 4.7   Adsorption profiles for As (V) and As (III) onto aged Fe (III) precipitates in freshwater at pH 7.1 and 2°C
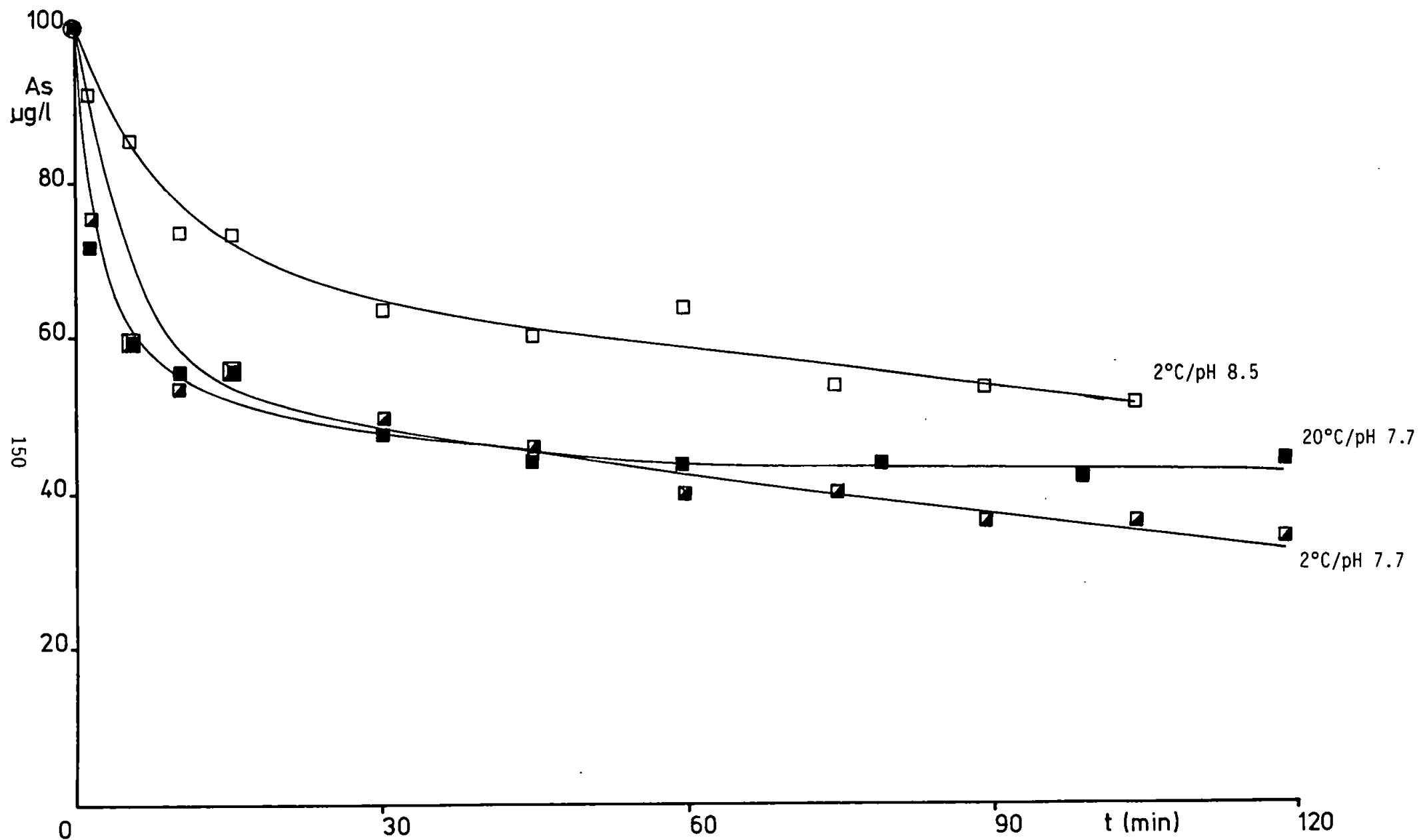
Figure 4.8   Adsorption profiles for As (V) onto aged Fe (III) precipitates in seawater
at various pH and T

Figure 4.9   Adsorption profiles for As (III) onto aged Fe (III) precipitates in seawater
at various pH and T

precipitates were aged at the temperature of the model run), analogous to the increased activity seen in the Fe (II) precipitates aged at lower temperatures and discussed in section 4.2.1. No formal investigation of variation in surface activity with temperature, however, was carried out for Fe (III) derived precipitates, although Sylva (1972) has shown that the hydrolysis of Fe (III) is temperature dependant. In the case of As (III) in seawater at 20°C, the adsorption rate is slower (t_e = 60 min) compared to As (V). The equilibrium concentration value is also lower, at around 25%. The 2°C profiles indicate a slightly faster initial adsorption rate, with a greater equilibrium value; although this was reached more slowly (t_e > 90 min), again suggesting a more active precipitate. An important point here is the apparent pH independence of the adsorption reaction at this temperature, which may be related to the increased surface area. This will be discussed further in connection with the Fe (II) derived precipitates.

4.2.2.1.b Fe (II) derived precipitates

The adsorption of As onto aged Fe (II) derived precipitates was investigated in some detail for the reasons stated earlier. Consistent trends were observed for the adsorption of As (V) in both freshwater and seawater at 20°C. These trends were related to the pH and ionic strength of the model medium (fig.s 4.10 and 4.11). The rate of As (V) adsorption and the equilibrium value of the reaction was found to increase with decreasing pH in both media. The adsorption behaviour of As in these cases may be related to chemical or physical processes, or perhaps a mixture of both. The use of adsorption isotherms can give insights into the nature of the processes taking place during uptake, and three derived

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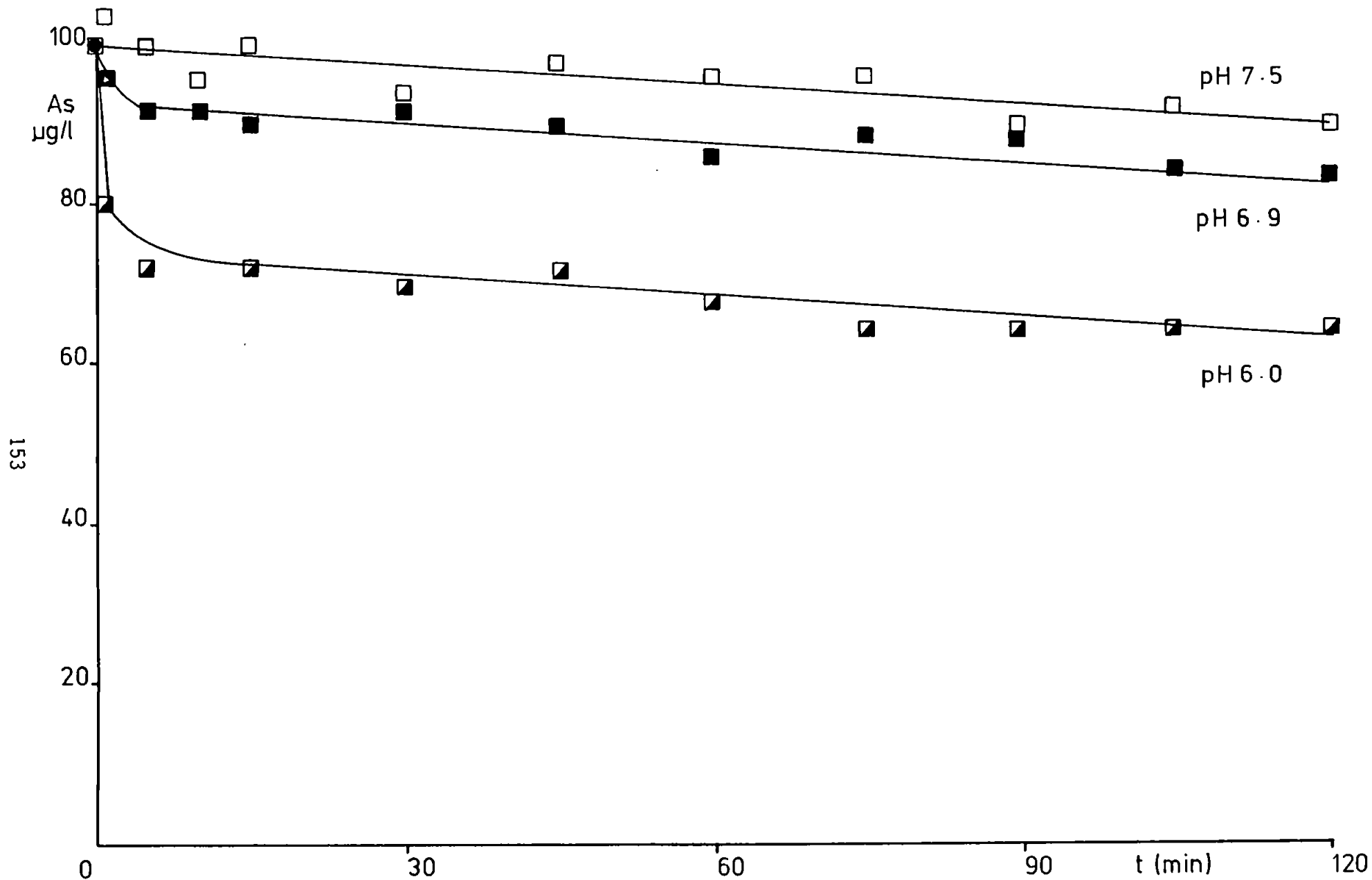
Figure 4.10   Adsorption profiles for As (V) onto aged Fe (II) precipitates in freshwater at 20°C and various pH

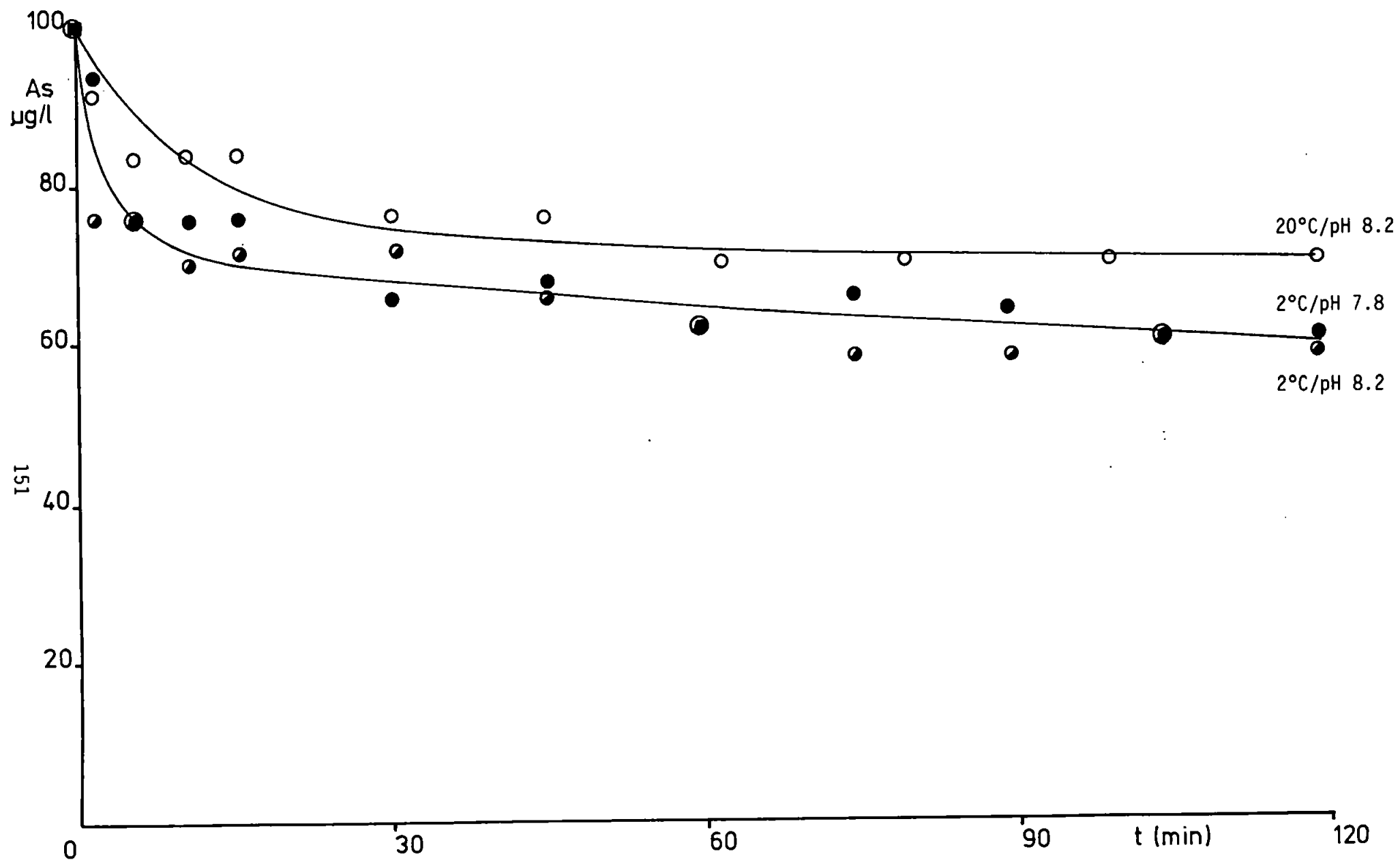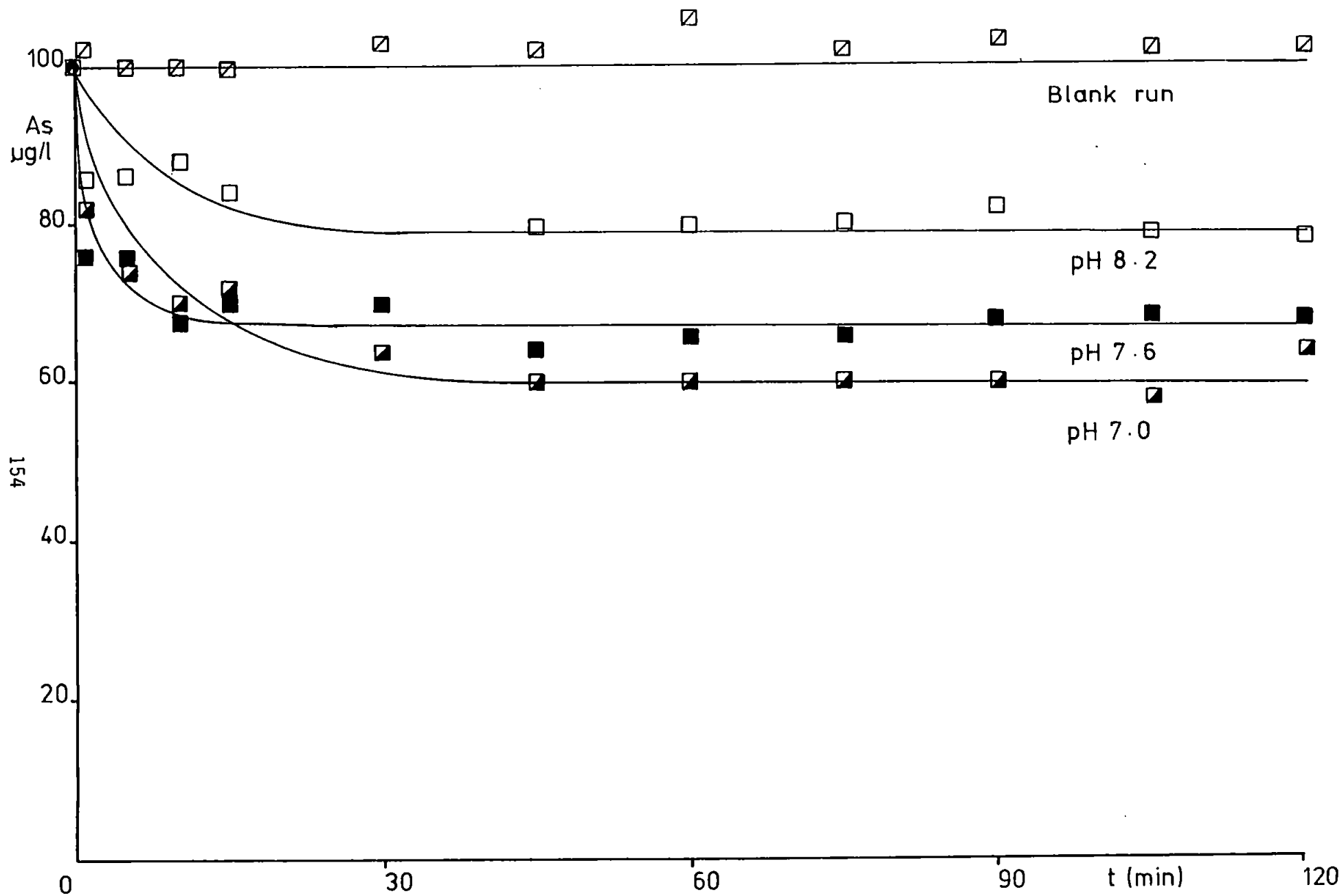Figure 4.11 Adsorption profiles for As (V) onto aged Fe (II) precipitates in seawater
at 20°C and various pH

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isotherm equations are in common use. The Brunauer, Emmett and Teller (B.E.T.) isotherm was utilised in section 4.1 in the evaluation of the precipitate surface areas. This isotherm is not applicable here as it only applies to non-porous surfaces (Brunauer, et al., 1938). Likewise, the Langmuir isotherm equation is probably not of use in this instance because no interaction between the adsorbed species is permitted (Posner & Bowden, 1980). Crosby (1982) has shown that the Langmuir isotherm is not applicable to the adsorption of PO_4^{3-} onto Fe precipitates.

The third common isotherm, that of Freundlich, was applied to the adsorption of As (V) onto Fe (II) for a series of As concentrations. This isotherm assumes an exponential decrease in adsorption as uptake of the adsorbed species continues, and implies a physical process of adsorption. For adsorption in solution, the Freundlich isotherm takes the form:

$$x/m = k c^{1/n} \qquad (4.1)$$

where x is the amount of solute adsorbed by mass m of solid, c is the equilibrium concentration of adsorbate and k and n are constants, which are functions of the sorption process. The logarithmic form of this equation:

$$\log x/m = 1/n \log c + \log k \qquad (4.2)$$

can be plotted to give a straight line of slope $1/n$ and intercept $\log k$ (fig. 4.12). The values of n and k were calculated as 0.88 and 223.9 respectively. Although the points plotted clearly fit the equation perfectly, there is not enough data from which to draw conclusions about adsorption mechanisms, and no isotherms were plotted for freshwater adsorption. The differences in uptake between the two media, however, implies a more physical type of adsorption, as chemisorption could not
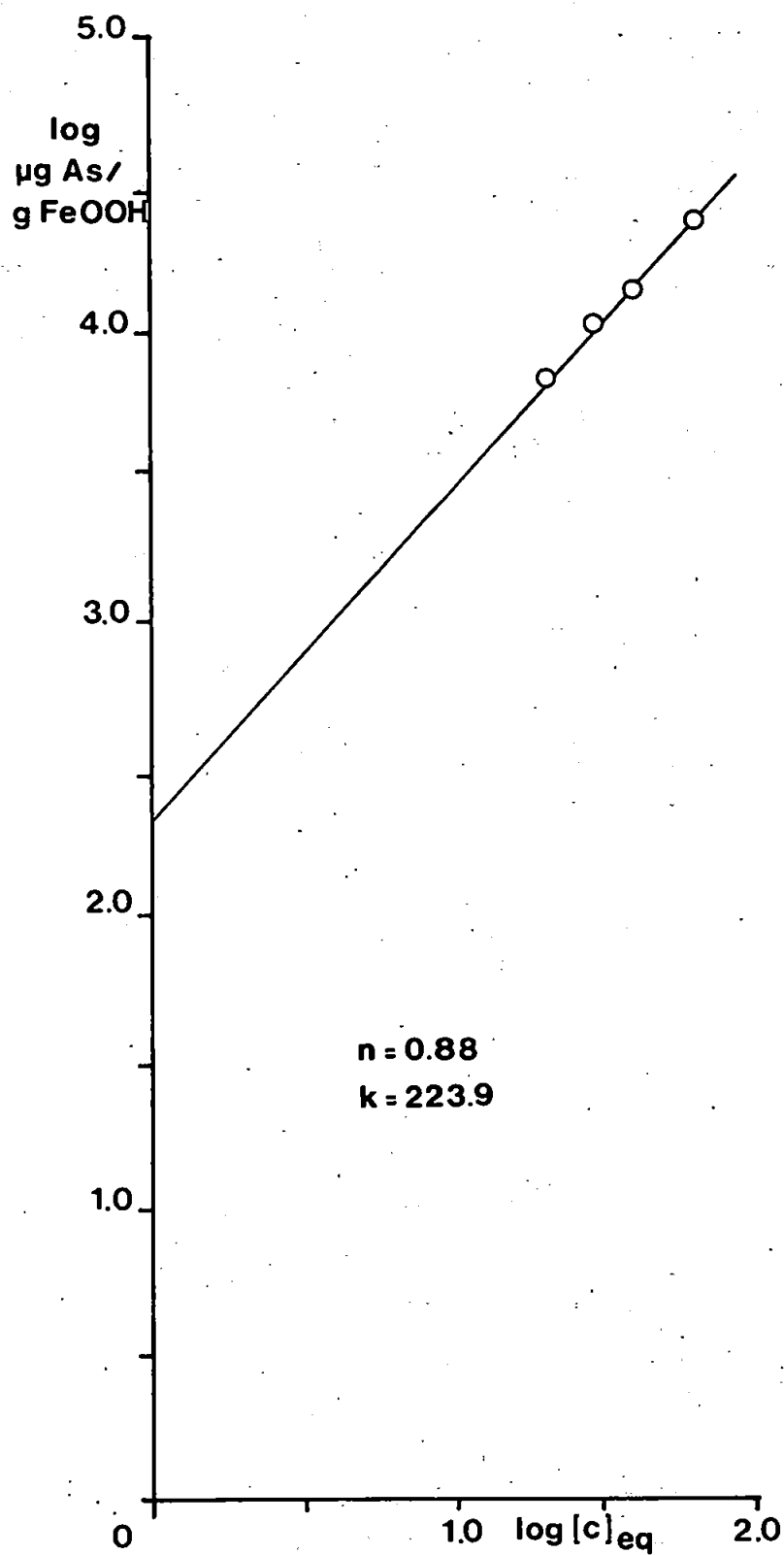
Figure 4.12   Plot of Freundlich isotherm for As (V) adsorption onto
              aged Fe (II) precipitates in seawater at 20°C and
              pH 7.9 - 100, 200, 500 & 1000 µg/L As

readily account for this. The extent of any chemisorption will depend on the relative affinity of Fe for As (V) compared to the OH$^-$ ion. Semiquantitatively, this can be examined by reference to the appropriate solubility products of the competing reactions :

$$Fe^{3+} + AsO_4^{3-} \rightleftharpoons FeAsO_4 \qquad \log k = -20.2 \qquad (4.3)$$

$$Fe^{3+} + 3(OH^-) \rightleftharpoons Fe(OH)_3 \qquad \log k = -38.7 \qquad (4.4)$$
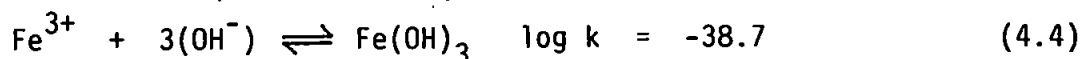
It can be seen that OH$^-$ has a stronger affinity for Fe (III) than As (V), although this will depend on the relative concentrations of AsO_4^{3-} and OH$^-$, according to the ratio $[AsO_4^{3-}]/[OH^-]^3$. For example, at pH 7.0 the OH$^-$ ion concentration in equation 4.4 is 10^{-21} mol/L. The Fe^{3+} concentration required to meet the solubility product is $10^{-17.7}$ mol/L. Applying this to equation 4.3 results in an $[AsO_4^{3-}]$ requirement of $10^{-2.5}$ mol/L. For an initial AsO_4^{3-} concentration of 100 µg/L, the maximum $[AsO_4^{3-}]$ is 1.33×10^{-6} mol/L, and the solubility product is therefore not met.

In the light of the above discussion, an electrostatic physical adsorption model has been proposed to account for the behaviour of As (V) uptake onto aged Fe (II) precipitates (fig. 4.13). The speciation of As (V) presented in this model has been calculated for the pH range 5-9, in both freshwater and seawater, using the data of Turner, et al. (1981). The data is presented graphically in fig. 4.14.

The speciation of As (III) was not attempted as there appears to be disagreement in the literature as to the As (III) species present in natural waters. The corresponding arsenious acid species; H_3AsO_3, $H_2AsO_3^-$ and $HAsO_3^{2-}$ are generally considered present in reducing conditions (N.A.S., 1977), but disagreement exists over the speciation in oxic waters.
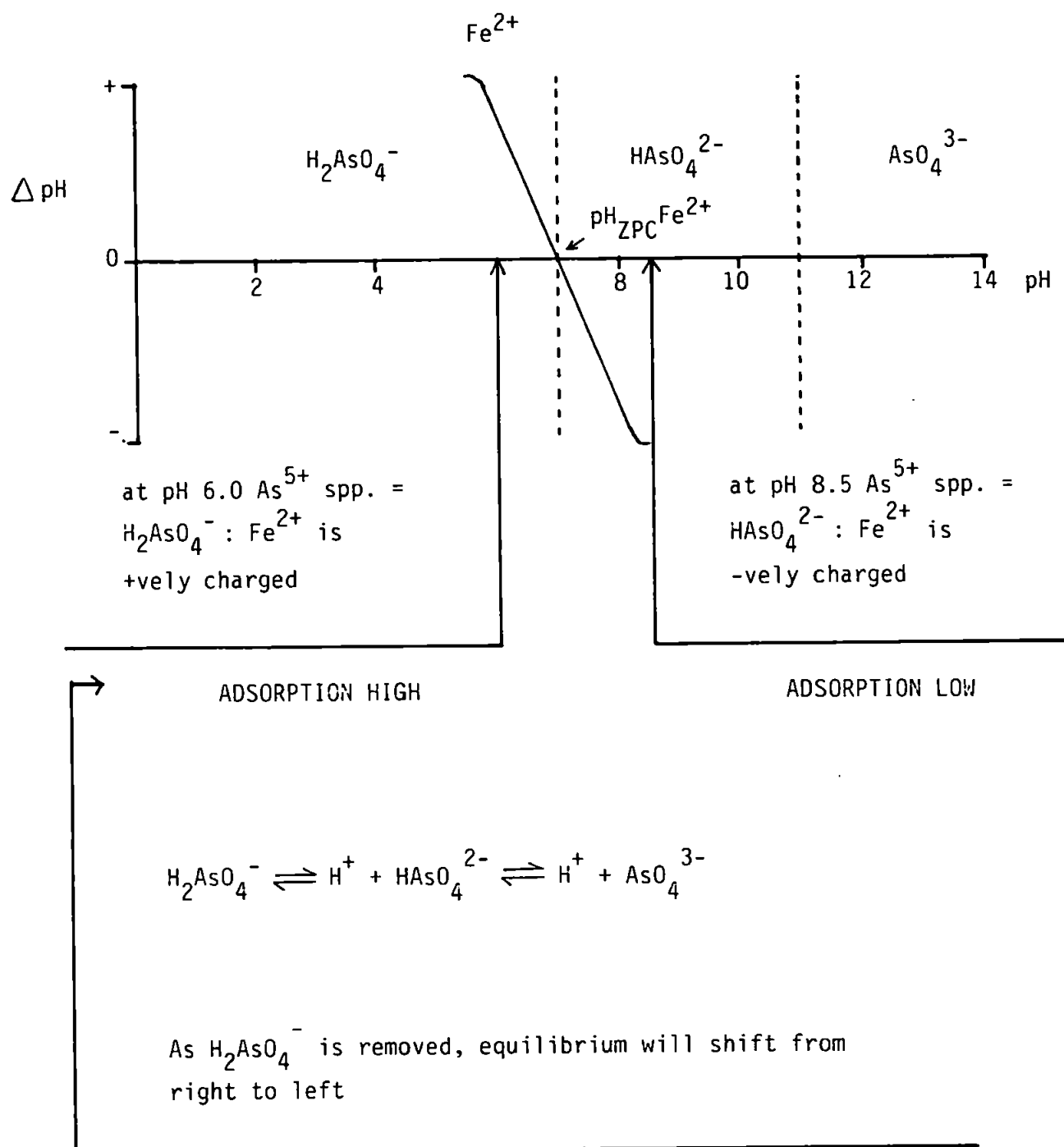
Figure 4.13 Proposed electrostatic adsorption model for As (V) onto aged Fe (II) precipitates
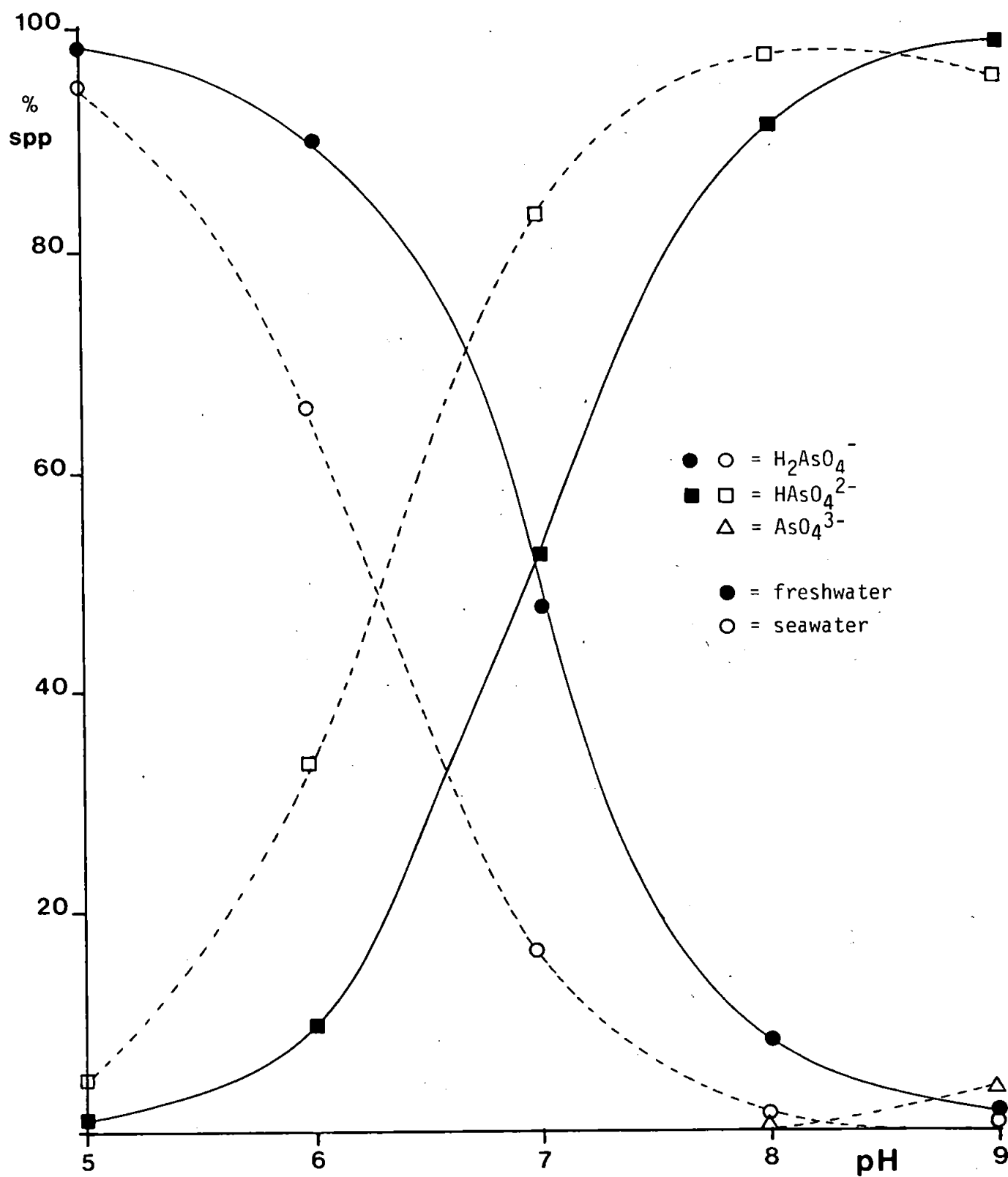
Figure 4.14   Speciation of As (V) in freshwater and seawater
over the range pH 5.0 - 9.0

Faust & Aly (1981) state that the associated form $HAsO_2$ is the predominant species occurring over the entire pH range of pH - 0.9 to 9.2, with AsO^+ existing at pH < - 0.9 and AsO_2^- at pH > 9.2. However, two species $As(OH)_3$ and $As(OH)_4^-$ are described by Turner, et al. (1981), presumably on the assumption that As (III) behaves more like $Sb(OH)_3$ than AsO_4^{3-} or PO_4^{3-}.

The pH_{zpc} of γ-FeOOH is not well documented, but literature values of 6.2 (Cabrera, et al., 1977) and 6.9 (Sung & Morgan, 1981) have been reported. This is lower than the pH_{zpc} of Fe (III), which is around 7.9 (Hingston, et al., 1972).

The enhanced uptake of As (V) in seawater, which does not fit a chemisorption model, may be explained as follows. Seawater major cations (Ca^{2+}/Mg^{2+}) are adsorbed onto Fe (II) oxyhydroxides, which are negatively charged in seawater (Balistrieri & Murray, 1979 & 1981). This will have the effect of altering the pH_{zpc}. For example, the normal pH_{zpc} of Goethite is 7.8-8.3 (Hingston, et al., 1972), and this is depressed to around 6.7-7.6 by the coprecipitation or specific adsorption of Cl^- or SO_4^{2-} from the seawater (Parks, 1975). This would make the electrostatic attraction of negatively charged As species less favourable compared to the freshwater situation. However, the opposite is observed. This can be explained in terms of the coprecipitation of Ca and Mg with the As (V). A model proposed by Balistrieri & Murray (1979 & 1981) predicts that at pH 8.0, 37% of the sites on the Fe (II) oxyhydroxide will be neutral, 36% will be positively charged by $MgOH^+$, Mg^{2+} and Ca^{2+} and 27% negatively charged by SO_4^{2-} and Cl^-. So although a pH_{zpc} of around 7.0 indicates that the oxide will be negatively charged at pH > 7.0, the adsorption of Ca and Mg will increase the number of positive sites

available. Also possible complexes of Ca and Mg - AsO_4 may be produced which can be adsorbed, although Turner, et al. (1981) calculated the abundance of analogous PO_4^{3-} species to be < 1%.

The aged Fe (II) precipitates at 2°C in both freshwater and seawater (fig. 4.15) showed a similar maximum equilibrium value compared to the 20°C models (~40%). The equilibrium value, however, appeared to be pH independent in both media. It was initially thought that this might be due to a shift in the equilibrium of the As (V) species with temperature:

$$H_2AsO_4^- \rightleftharpoons H^+ + HAsO_4^{2-} \rightleftharpoons H^+ + AsO_4^{3-} \qquad (4.5)$$
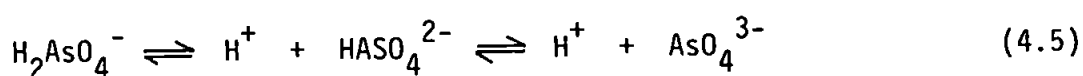
At 2°C the equilibrium would shift to the left, i.e. the associated form would be preferred. However, thermodynamic data (Stumm & Morgan, 1981) suggests that any shift would be of minor importance.

The other possibility was that the precipitate formed at 2°C had different surface charge characteristics, such that the pH_{zpc} < 7.0. A precipitate prepared at this temperature was nevertheless found to be poorly crystallised γ-FeOOH (section 4.1), but the increased surface area found would mean an increase in the adsorption sites available and might alter the effective pH_{zpc}. This would account for the bunching together of the profiles, but the apparent maximum capacity of ~40% is more difficult to explain.

The profiles for As (III) uptake onto aged Fe (II) in freshwater and seawater at both 20°C and 2°C are shown in fig. 4.16. It can be seen that no adsorption occurred in either media, and this was also found after periods in excess of 4 h. This behaviour is analogous with that

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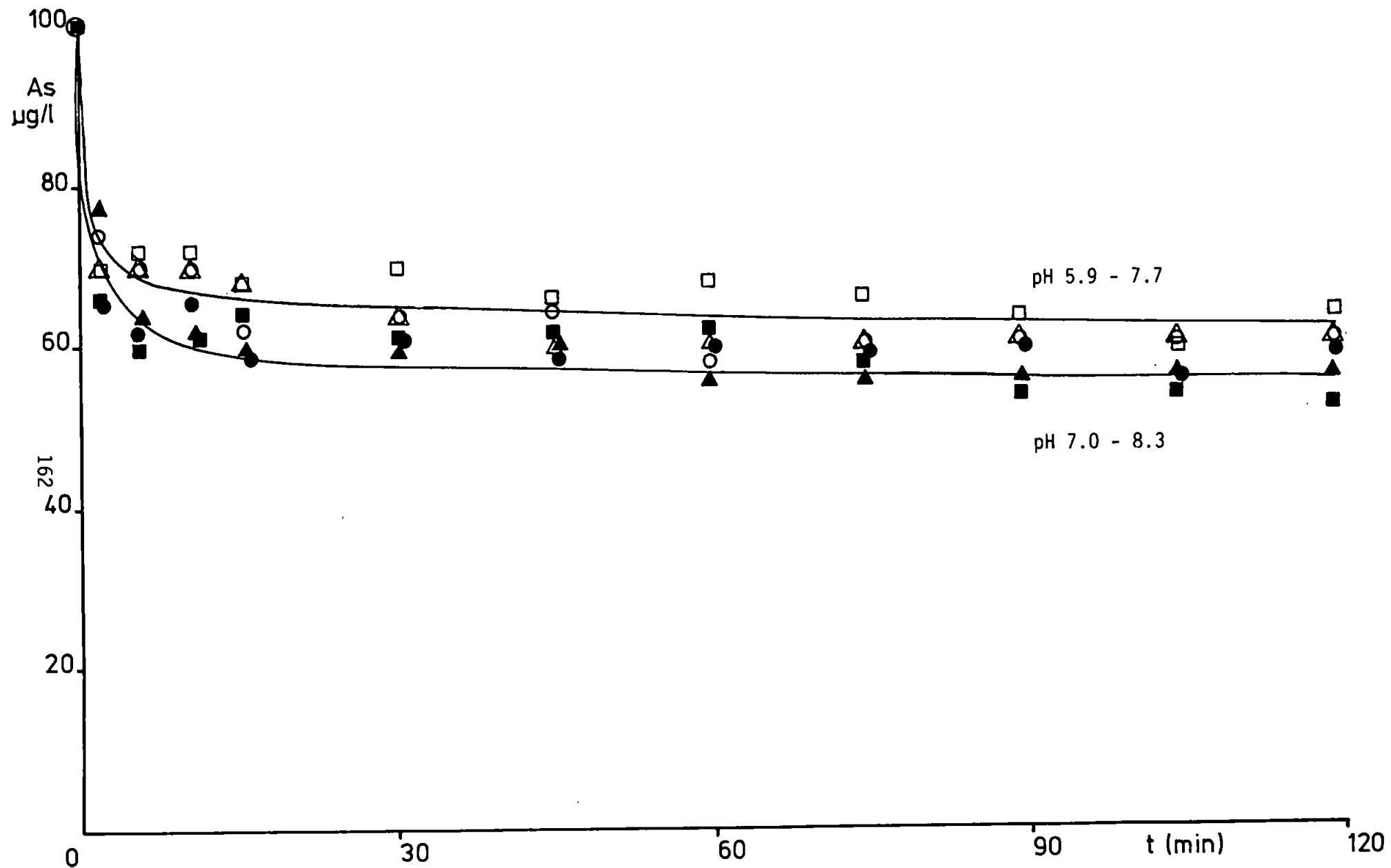
Figure 4.15   Adsorption profiles for As (V) onto aged Fe (II) precipitates in
freshwater and seawater at 2°C and various pH
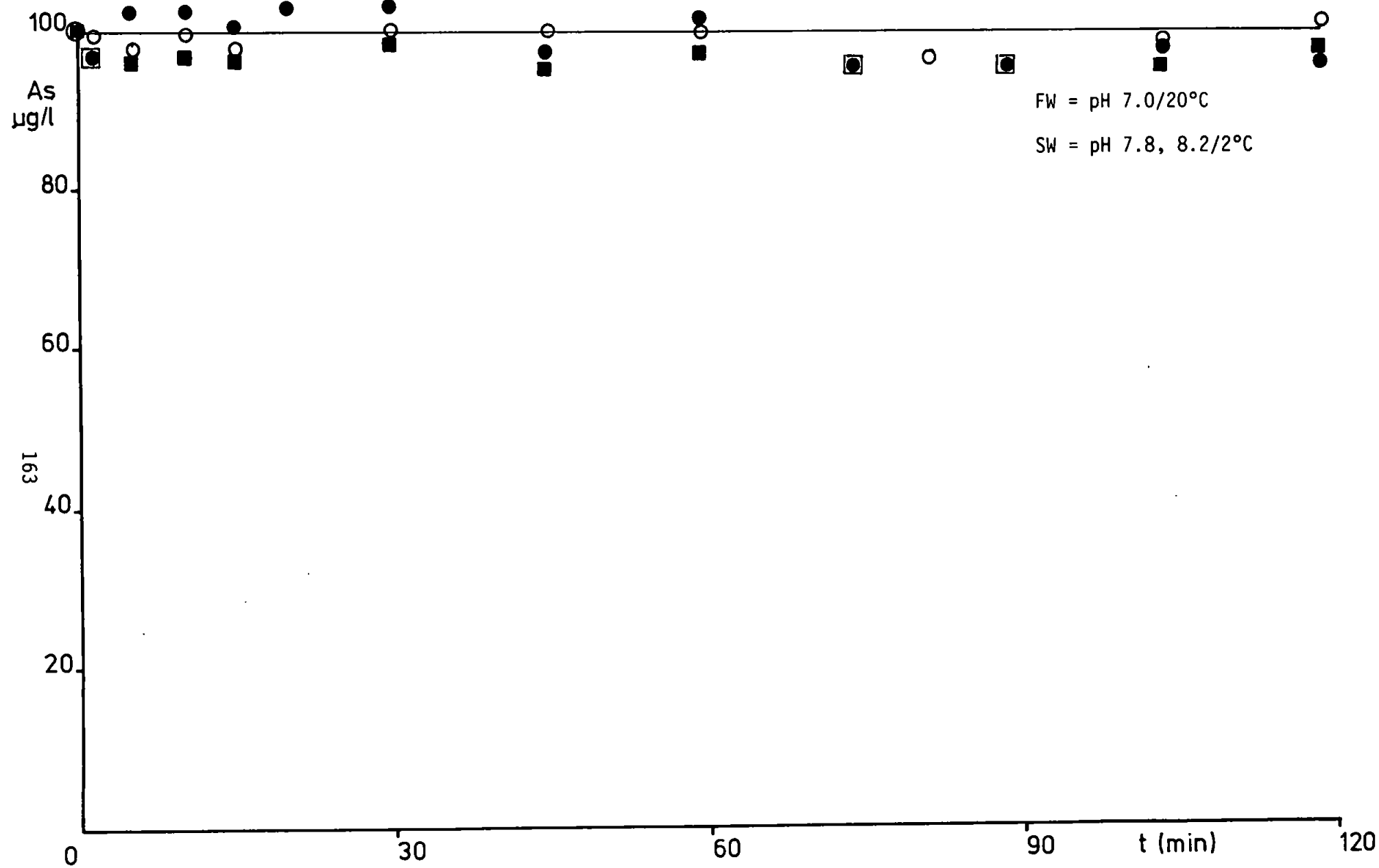
Figure 4.16   Adsorption profiles for As (III) onto aged Fe (II) precipitates in freshwater and seawater at various pH and T

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of PO_4^{3-} onto aged Fe (II) precipitates (Crosby, 1982) and offers an explanation of the generally observed slowness of As (III) adsorption onto both Fe (II) and Fe (III) precipitates when compared to As (V). Little is known about the oxidation-reduction behaviour of redox sensitive anions, such as AsO_4^{3-}, in natural waters. It is therefore difficult to determine the speciation of the elements involved, but for Fe and As at a pH within the range of natural waters the reaction might be:

$$2Fe^{3+}(aq.) + H_2AsO_3^-(aq.) + H_2O = 2Fe^{2+}(aq.) + H_2AsO_4^-(aq.) + 2H^+$$
$$\Delta G = -37.32 \text{ kJ/mol} \qquad (4.6)$$
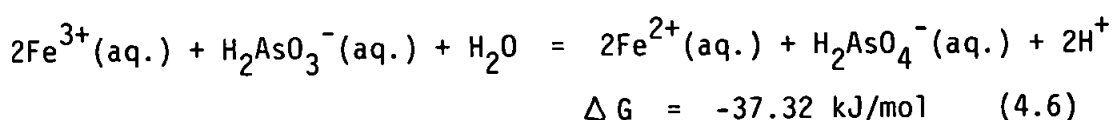
This work and others (Oscarson, et al., 1981 & 1983) have shown no experimental evidence of a redox reaction between Fe (III) and As (III), although Oscarson, et al. (1981) have stated that it is thermodynamically favourable. However, it is proposed that such a reaction does, in fact, take place. The model presented suggests that As (III) is not adsorbed as such by either Fe (II) or Fe (III) oxyhydroxides, but that a redox reaction, as depicted in fig. 4.17, takes place at the solid-liquid interface. This could well be an intimate surface phenomenon, occurring within the particle boundary layer of the oxyhydroxide particle. This would explain why the redox cannot be detected by sampling of the bulk solution. The diffusion of As (III) to the boundary layer of the particle is required for the redox to take place. The oxidised As (V) produced is either then adsorbed by Fe (III) surface groups or taken up by the oxidising Fe (II) (fig. 4.17) and subsequently adsorbed. This is a complex set of processes, and although nothing is known of the reaction rates of the processes involved, any of the steps could be rate limiting. It is therefore perfectly feasible that this would be an overall slower process compared to the one or two step process of As (V) adsorption. This model would also explain the reduced rate of

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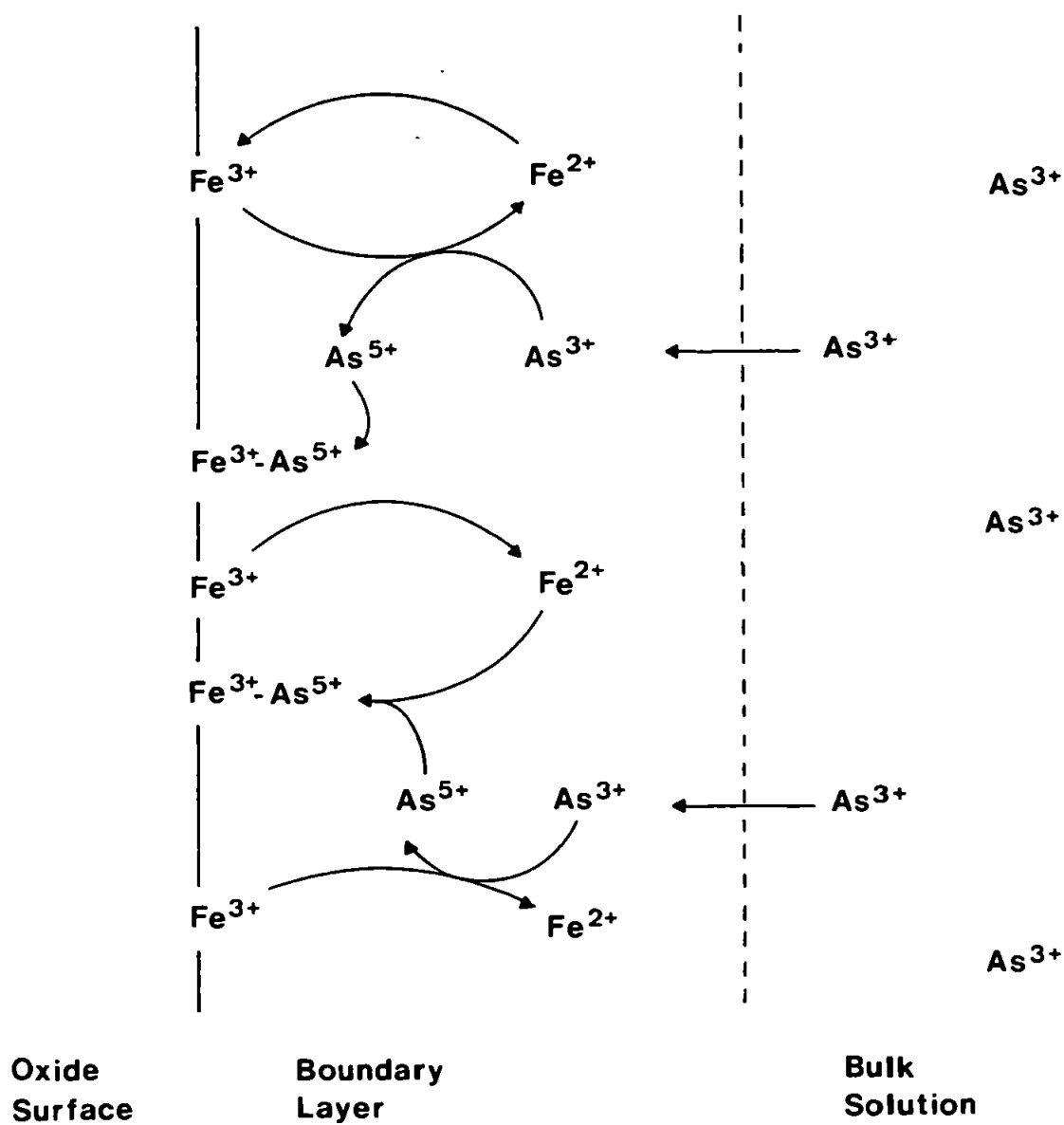
Figure 4.17   Proposed mechanism for the surface redox of
As (III) on Fe (III) oxyhydroxide colloids

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uptake of As (III) in fresh precipitate models, as the uptake would depend on the initial formation of a solid surface prior to adsorption.

4.2.2.1.c Natural Precipitates

The models produced using aged precipitates from natural water sources did not show good agreement in most cases with the synthetic models. This was probably due to the mixed nature of the oxyhydroxides formed, as discussed in section 4.1, which would result in a variety of competing adsorption behaviours.

The profiles for natural water at 20°C from the Lady Bertha minestream, situated on the banks of the River Tavy, Devon, are closer to those found for seawater (fig. 4.18). In addition, the adsorption is apparently pH independent. This may be explained by the co-precipitation of some unidentified cation or cations present in the natural matrix, which is depressing the pH_{zpc} of the oxyhydroxide. The relative scatter of the data points may be due to the presence of organic matter or analytical error.

For the 2°C profiles shown in fig. 4.19 natural water samples from the Lady Bertha minestream were collected after a long dry spell followed by heavy rain. The consequent oxidation and leaching of arsenical pyrites resulted in high natural levels of As in the water. The initial concentrations of As present in these runs were not known, but the profile at pH 6.0 indicates that As was still present in the bulk solution, in addition to the 100 µg/L injected, after equilibrium had been reached during the ageing process. The profiles presented then, reflect the
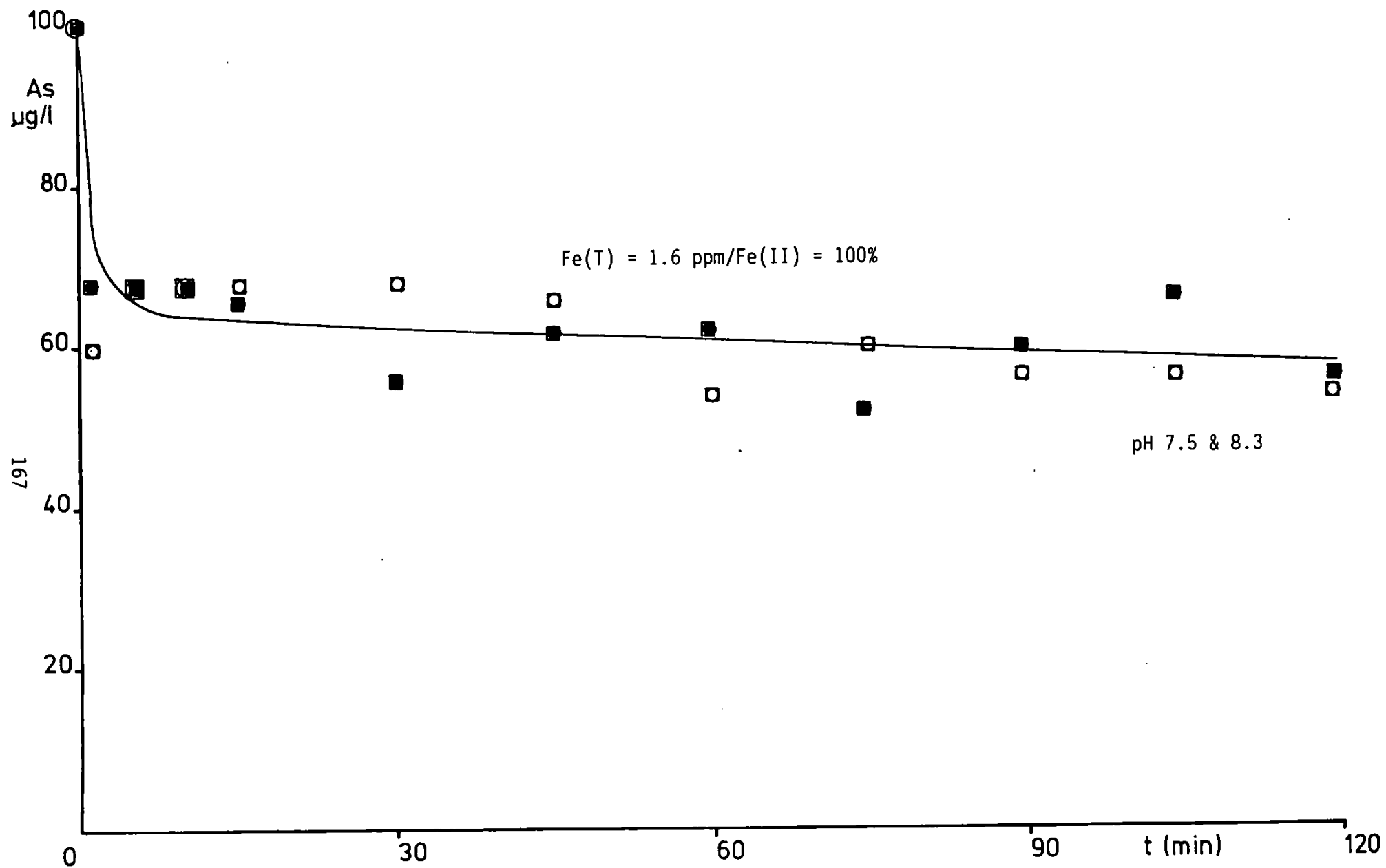
Figure 4.18   Adsorption profiles for As (V) onto natural aged Fe precipitates from the Lady Bertha minestream, Devon, at 20°C in freshwater analogue
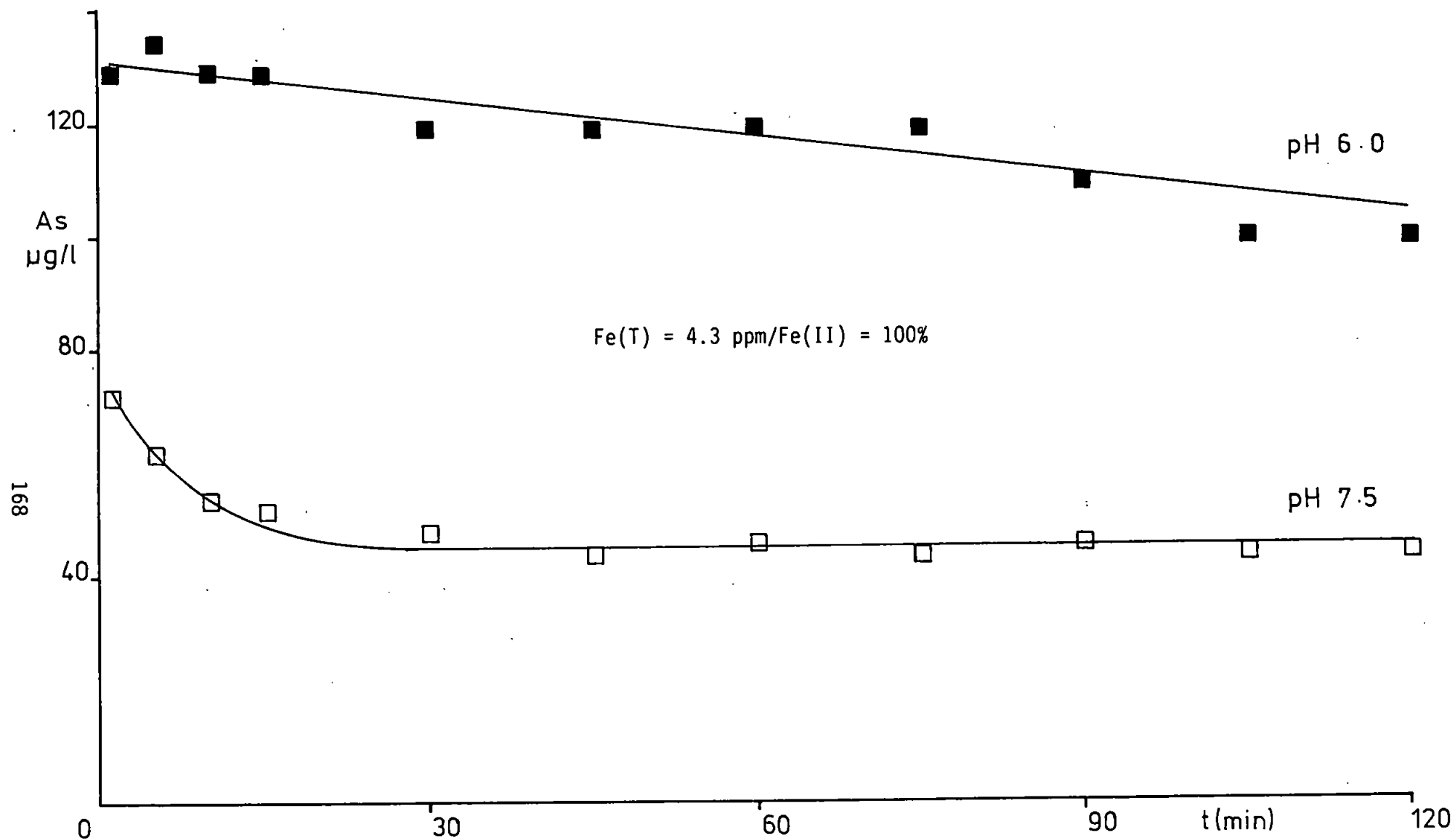
Figure 4.19 Adsorption profiles for As (V) onto natural aged Fe precipitates from the Lady Bertha
minestream, Devon, at 2°C in freshwater analogue

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additional adsorption of As brought about by the adjustment of the pH of the bulk solution. This obviously complicates the adsorption process and may explain the anomalous profiles obtained. The profile at pH 7.5 had a t_e ~30 min, whereas the pH 6.0 profile was still not at equilibrium after 2 h. It is therefore possible that the final equilibrium value for the pH 6.0 model would have been greater than that of the pH 7.5 model, substantiating the proposed electrostatic adsorption mechanism. The slowness of the reaction rate could be due to the already largely saturated state of the precipitate, although in analogy to the case of PO_4^{3-} (Lijklema, 1980), the capacity of the precipitate would be expected to be high.

Finally, in the case of water from the Wheal Franco minestream, on the River Walkham, Devon, the profile for As (V) gave good agreement with the synthetic models in seawater at 2°C (fig. 4.20). However, the As (III) profile showed that some 20% adsorption had taken place. This is probably not as anomalous as it seems, as the 6% dissolved Fe (III) initially present amounted to 0.5 mg/L at the high dissolved Fe concentrations found in this particular sample. This would probably be sufficient to account for the adsorption of As (III) observed in this model.

It must be concluded, however, that the adsorption behaviour of aged natural Fe (II) precipitates in particular requires further investigation, with regard to the uptake of As (V) and As (III).

4.2.2.2. Fit Precipitates

4.2.2.2.a Fe (III) derived precipitates

The fresh precipitates derived from Fe (III) salts were very efficient
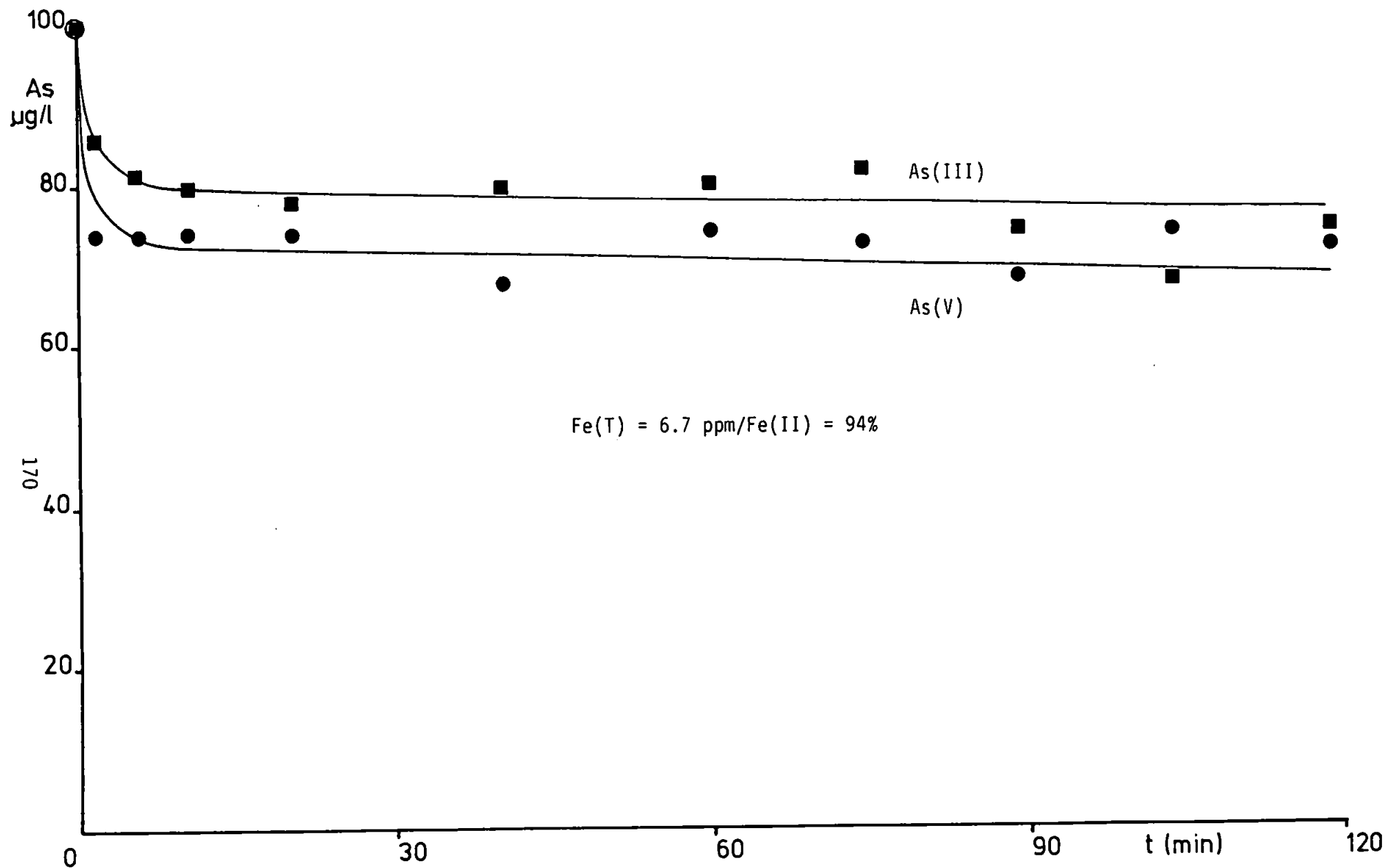
Figure 4.20 Adsorption profiles for As (III) and As (V) onto natural aged Fe precipitates from the Wheal Franco minestream, Devon, at 2°C and pH 7.8 in seawater analogue

removers of As (V) in both freshwater and seawater. As (V) was removed very rapidly (t_e = < 30s) from freshwater at both 20°C and 2°C (fig. 4.21), all the detectable As being lost within 1 min. The reaction appeared to be independent of pH and temperature, as was found for PO_4^{3-} by Crosby (1982). The rate of removal of As (V) by Fe (III) in seawater was slightly slower (fig. 4.21), with t_e ~10 min. This indicated a small ionic strength effect. The rapid removal of As from solution was due to the extremely rapid formation of an active surface by the Fe (III), which takes < 10s at 15°C (Crosby, 1982). This tends to mask the effect of variables such as pH, temperature and ionic strength. The temperature dependence of this active surface formation was not investigated by Crosby, but the hydrolysis of Fe (III) has been shown to be temperature dependent by Sylva (1972). This will exert a control on nucleation rate and hence surface area. The fast uptake rates of these processes makes kinetic analysis impossible using the methods applied in this study and they give little evidence as to the mechanisms involved. These mechanisms may be of a physical or chemical nature. $FeAsO_4$ may be precipitated, depending on the conditions of pH and As concentration. A number of forms of $FeAsO_4$ have been prepared under various conditions, including one of formula $FeAsO_4-4H_2O$ by the addition of Fe_2O_3 to arsenic acid in solution (Mellor, 1947). The stability of such a complex is obviously important, but the solubility product of Fe (III) AsO_4 has been reported as log K = -20.2 (Sillen & Martell, 1964; Smith, 1973). This makes it very insoluble, in common with the other heavy metal arsenates. However, the low concentrations of AsO_4^{3-} used in the models means that the amount of $FeAsO_4$ present will be negligible compared to the amount of $Fe(OH)_3$ formed (section 4.2.2.1.b). This would make detection of $FeAsO_4$ almost impossible. The possibility of such a complex being present, however, does not affect the removal of As from the
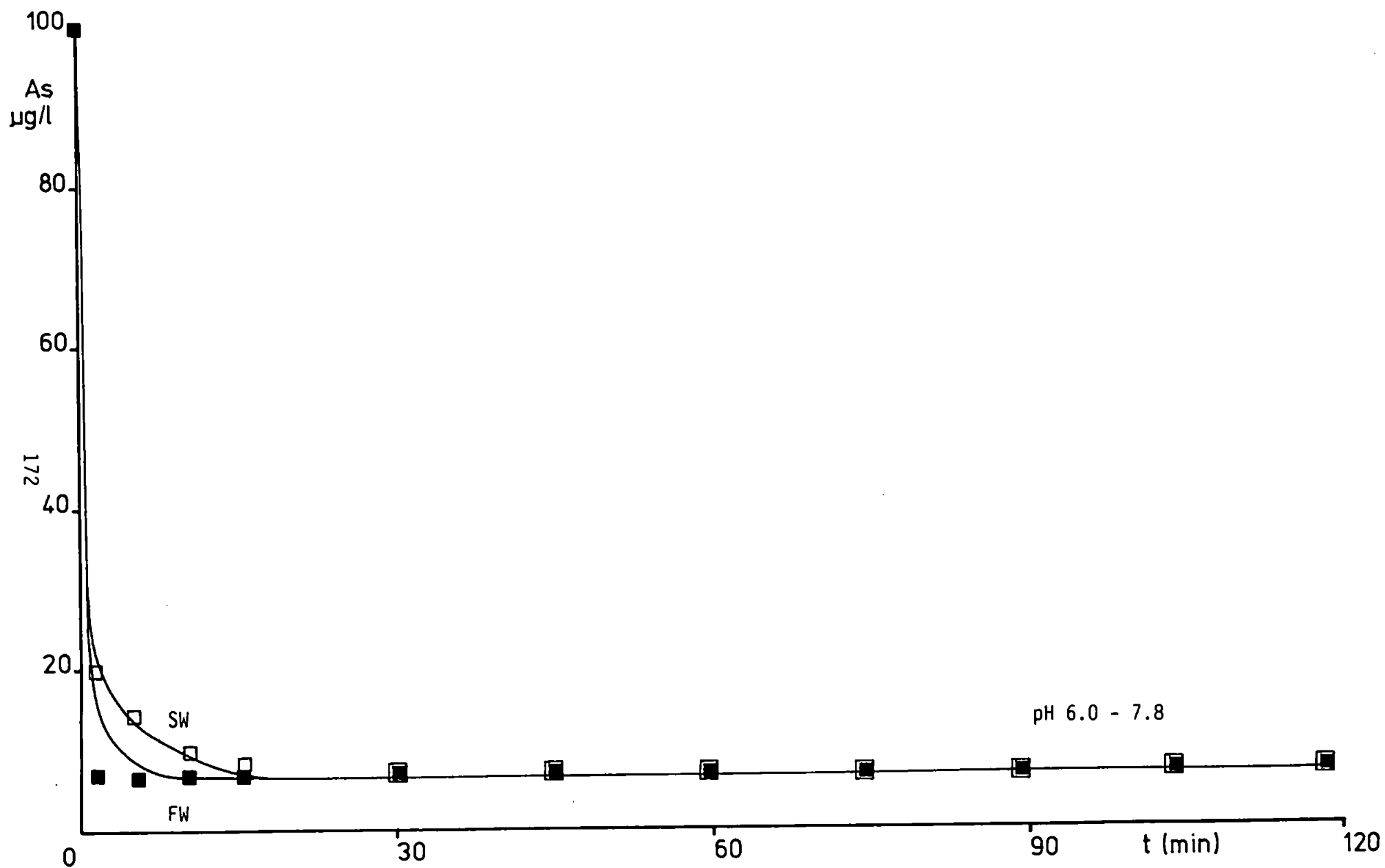
Figure 4.21 Adsorption profiles for As (V) onto fresh Fe (III) precipitates in freshwater
and seawater, at various pH and T

dissolved phase and in fact the rate of formation is not affected by the identity of the ligand (Cotton & Wilkinson, 1980). The possible mechanisms of physical adsorption are discussed in detail elsewhere. The only conclusion that can be drawn from this analysis of the adsorption of As (V) onto Fe (III) precipitates is that uptake is dependent on the rate of precipitate formation.

The adsorption of As (III) onto freshly precipitated Fe (III) was generally slower than that of As (V) under the same conditions. The adsorption profile for As (III) onto Fe (III) precipitates is shown in fig. 4.22, for freshwater at pH 7.1, 20°C and 2°C. The 2°C profile at the same pH shows a slight increase in adsorption rate over the 20°C profile (t_e = 60 min cf, t_e = 90 min), which can be explained in terms of an increased nucleation rate at the lower temperature. The seawater 2°C profile (fig. 4.23) shows a slower rate of adsorption for As (III), analogous to the ionic strength effect seen in the As (V) profiles. This result seems anomalous in terms of the predicted increase in particle coagulation resulting from the increase in ionic strength. It may, however, be related to competition for active sites on the Fe particles from other ions or to complexation of the As with other ions present prior to adsorption, as discussed previously for aged precipitates (section 4.2.2.1.b).

The overall relative independence on temperature shown by the adsorption profiles for As (V) and As (III) onto fresh Fe (III) precipitates is suggestive of a physical adsorption process or processes.

4.2.2.2.b Fe (II) derived precipitates

For fresh precipitates of Fe (II) in freshwater at 20°C (fig. 4.24), the

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Figure 4.22   Adsorption profiles for As (III) onto fresh Fe (III) precipitates in
freshwater at pH 7.1 and various T

Figure 4.23 Adsorption profiles for As (III) onto fresh Fe (III) precipitates
in seawater at 2°C and various pH

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Figure 4.24   Adsorption profiles for As (V) onto fresh Fe (II) precipitates in freshwater
at 20°C and various pH

adsorption behaviour of As (V) was significantly different. Although the equilibrium concentration of As was pH independent, with no detectable dissolved As (V) present after periods of 5-30 min, the rate of adsorption was related to pH. At pH 7.5 adsorption of As was very rapid, with a t_e of between 1-5 min after injection. As pH decreased, the rate of adsorption decreased significantly, and at pH 6.6 a lag time was observed of ~5 min before any adsorption occurred. The initiation of adsorption could be related to the formation of a visible precipitate, and therefore once again the rate of As adsorption could be related to the rate of precipitate formation. However, for Fe (II) this is a two step process, involving the initial oxidation of Fe (II) to Fe (III) and subsequent hydrolysis of Fe (III) to form a precipitate. It is the initial, slower oxidation step which determines the overall rate of precipitate formation. This is pH dependent and is considerably slower in seawater.

The oxidation step is also temperature dependent, as can be seen in fig. 4.25, showing the profiles for Fe (II) and As (V) in freshwater at 2°C. Here the rate of adsorption at a given pH is significantly retarded compared to the 20°C profile (t_e = 70 min at pH 7.5). The anomalous rapid initial adsorption of ~20% seen at pH < 7.5 was observed on several repeat runs and is thought to be due to the adsorption of As onto the rapidly nucleating Fe (III) particles. The major part of the adsorption curve at pH 7.1, occurring at around t = 90 min, coincided with the formation of a visible precipitate. Conversely, the run at pH 6.0 showed no visible precipitate formation over a period in excess of 120 min.

The profiles for As (V) adsorption in seawater at 20°C (fig. 4.26)
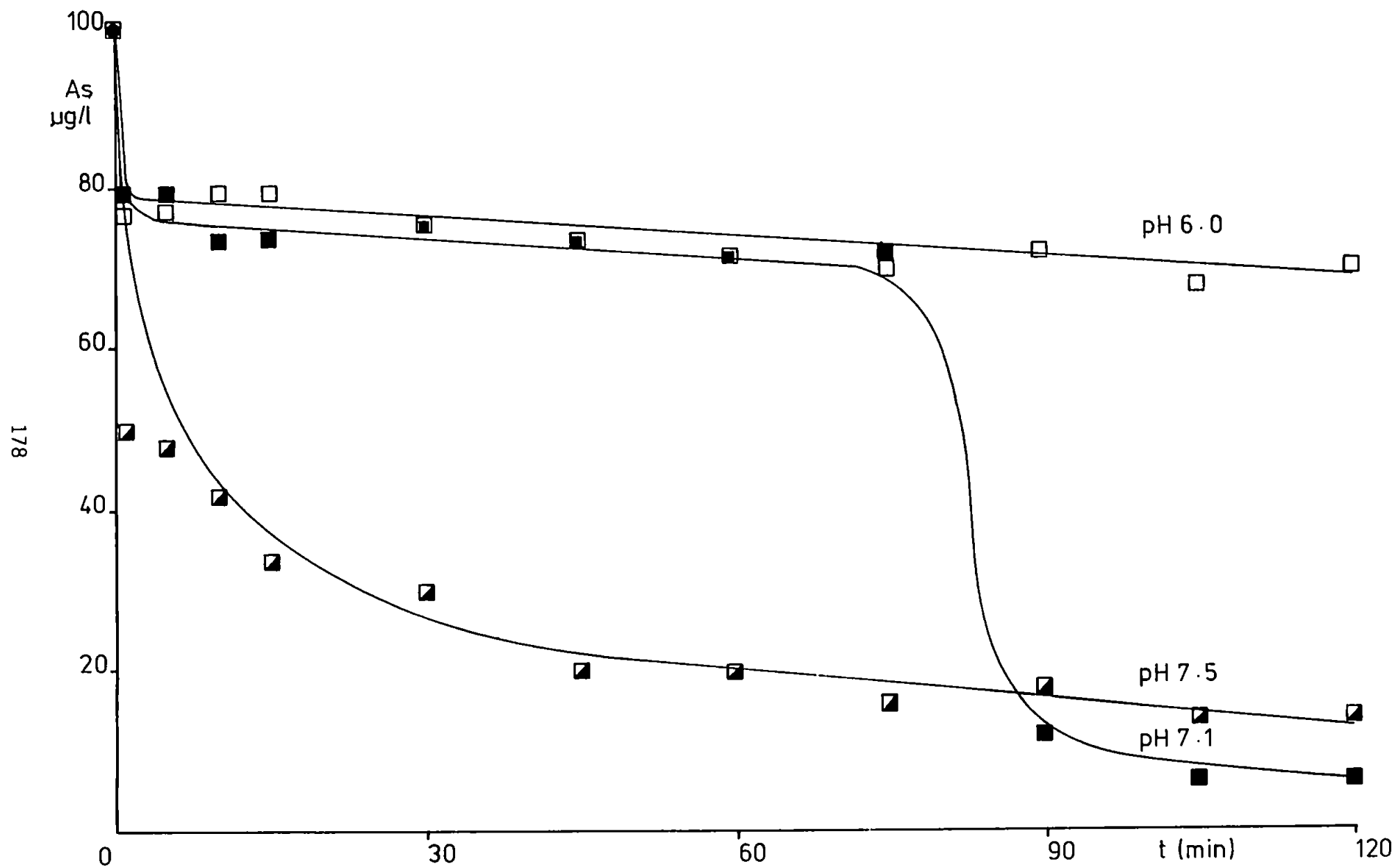
Figure 4.25   Adsorption profiles for As (V) onto fresh Fe (II) precipitates in
freshwater at 2°C and various pH

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indicate that in this medium the equilibrium values above pH 7.6 become
pH dependent, while the adsorption rates are slower, compared with freshwater
(t_e = 25 min at pH 7.4). This trend is emphasised in the 2°C profiles
(fig. 4.27) where the rates of adsorption are still slower (t_e = > 120 min
at pH 7.0).

At both temperatures, two distinct processes appear to be occurring.
At pH 7.6 and above the rate of adsorption is relatively fast and the
equilibrium value reached is pH dependent. A slight slowing in the
reaction rate is seen at pH 7.8 and 2°C. At pH < 7.6, however, the
rate is significantly slower, more obviously in the 2°C profiles, and
there is a suggestion of the equilibrium value becoming pH independent.
It is also noticeable that the equilibrium values are enhanced at the
lower temperature, again probably associated with the increased surface
area discussed in section 4.1. The adsorption at pH < 7.6 appears to
be related to the formation of the solid phase, while at pH > 7.6 the
adsorption itself appears to be rate determining. This will be
discussed in detail in the section on kinetic analysis (section 4.3).

The adsorption of As (III) onto freshly precipitated Fe (II) in seawater
(fig. 4.28) is once again much slower at 20°C compared to As (V)
(t_e = 60 min at pH 7.7), a trend that is emphasised in the 2°C profile
(t_e = > 120 min at pH 7.7).

4.2.2.2.c Natural precipitates

A number of model runs were carried out on Fe-rich natural waters from
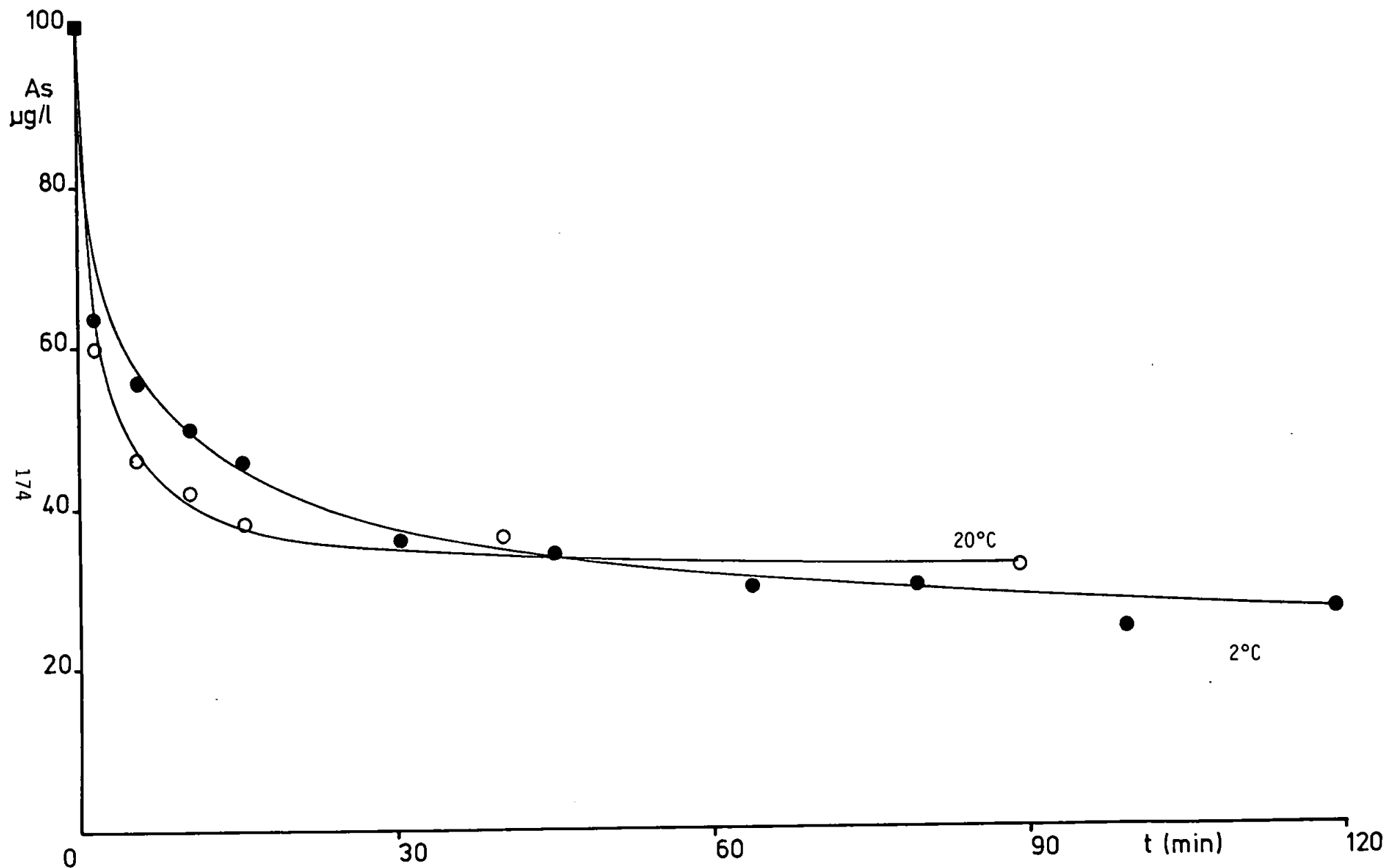several sites in the Devon and Cornwall area (see fig. 2.3). Only a
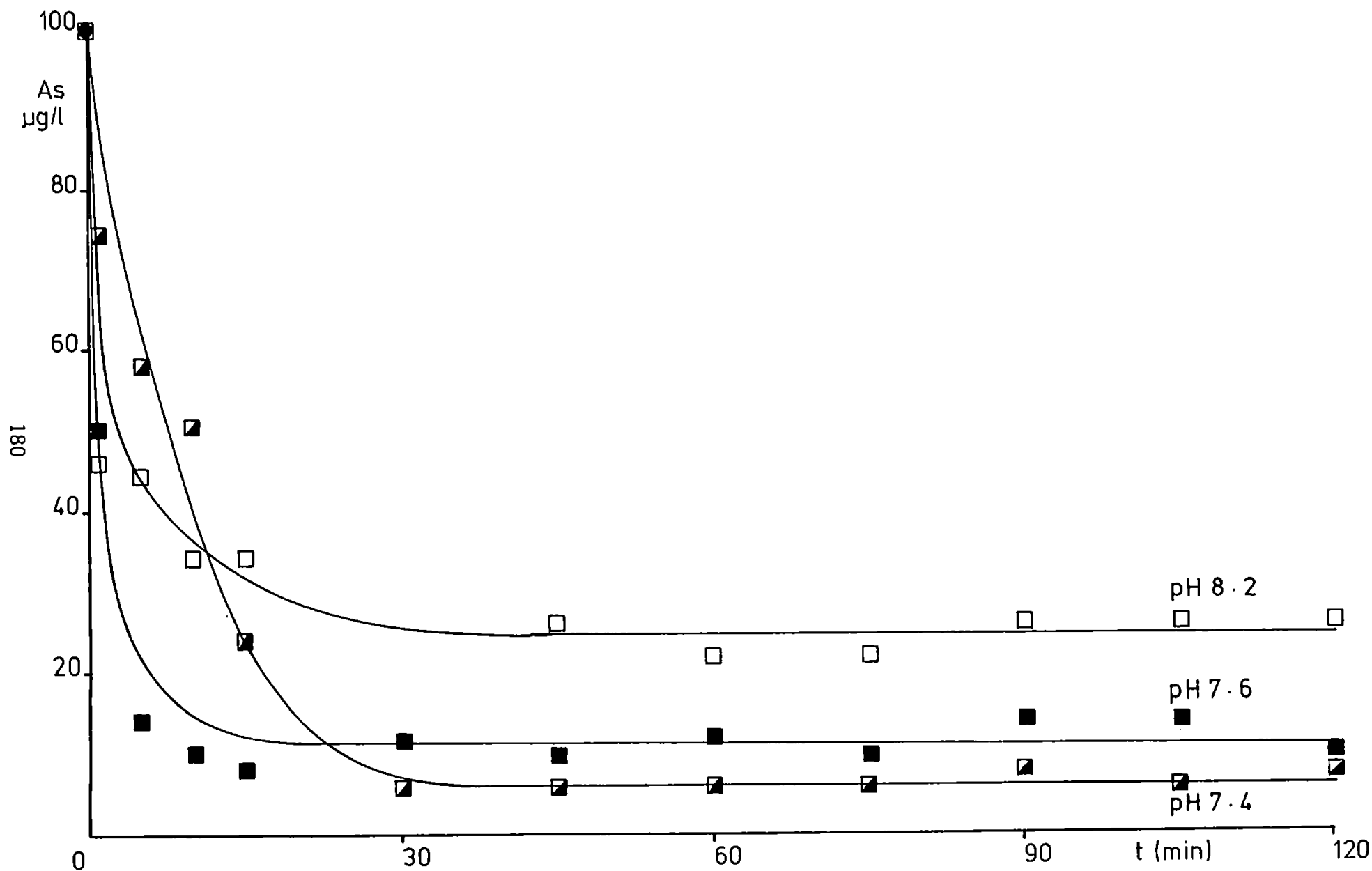
Figure 4.26   Adsorption profiles for As (V) onto fresh Fe (II) precipitates in seawater, at 20°C and various pH
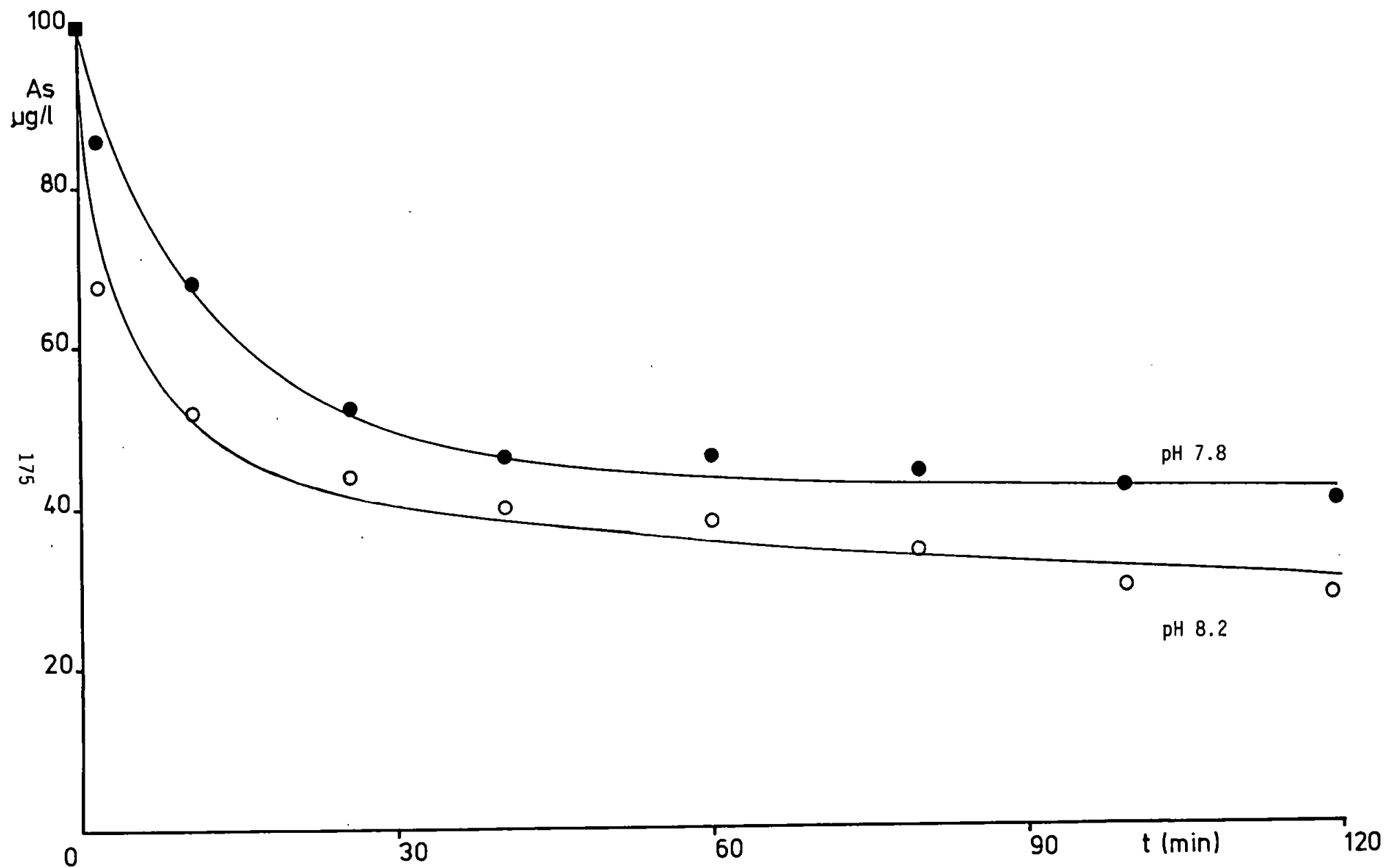
181
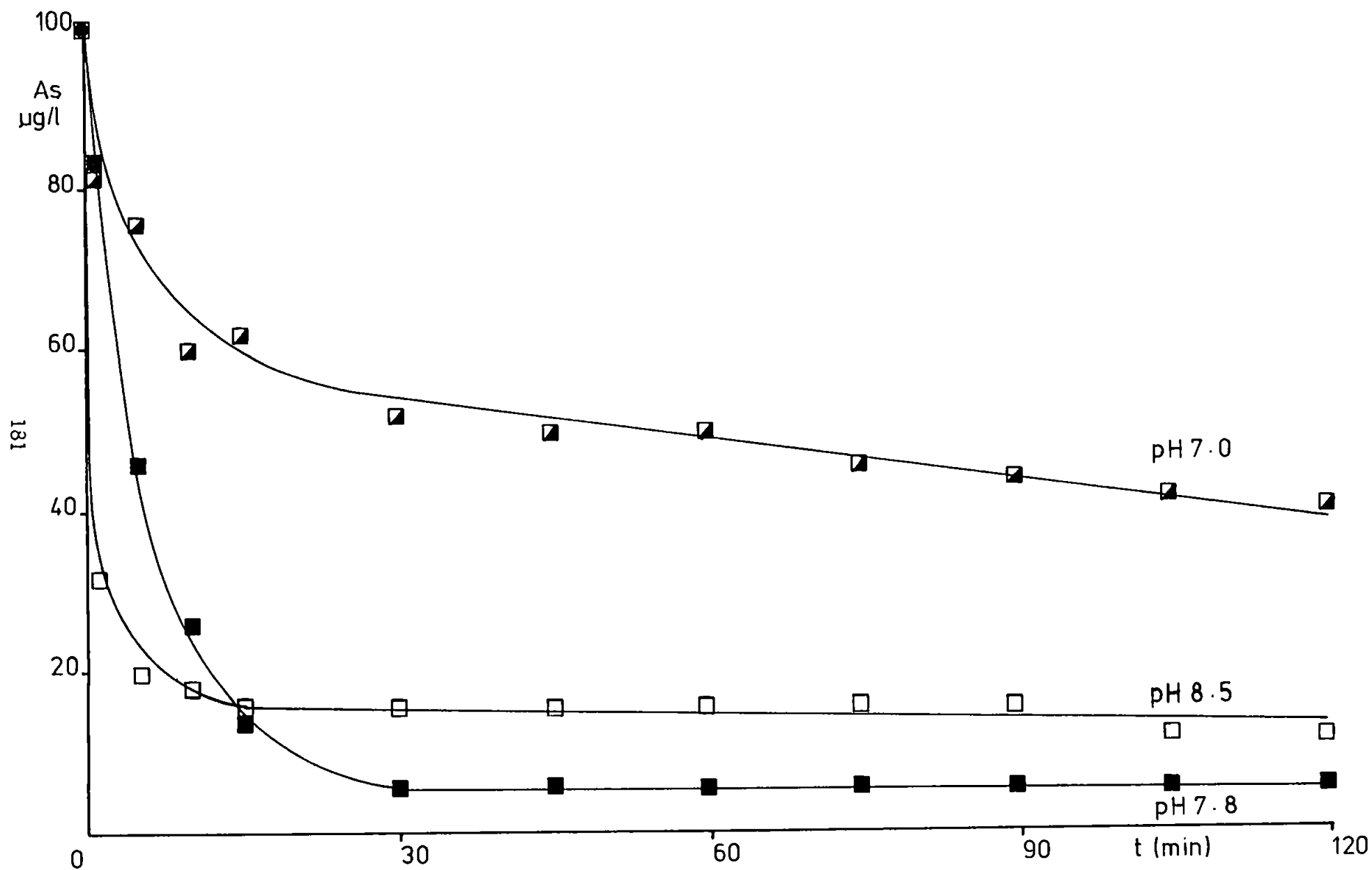
Figure 4.27 Adsorption profiles for As (V) onto fresh Fe (II) precipitates in seawater,
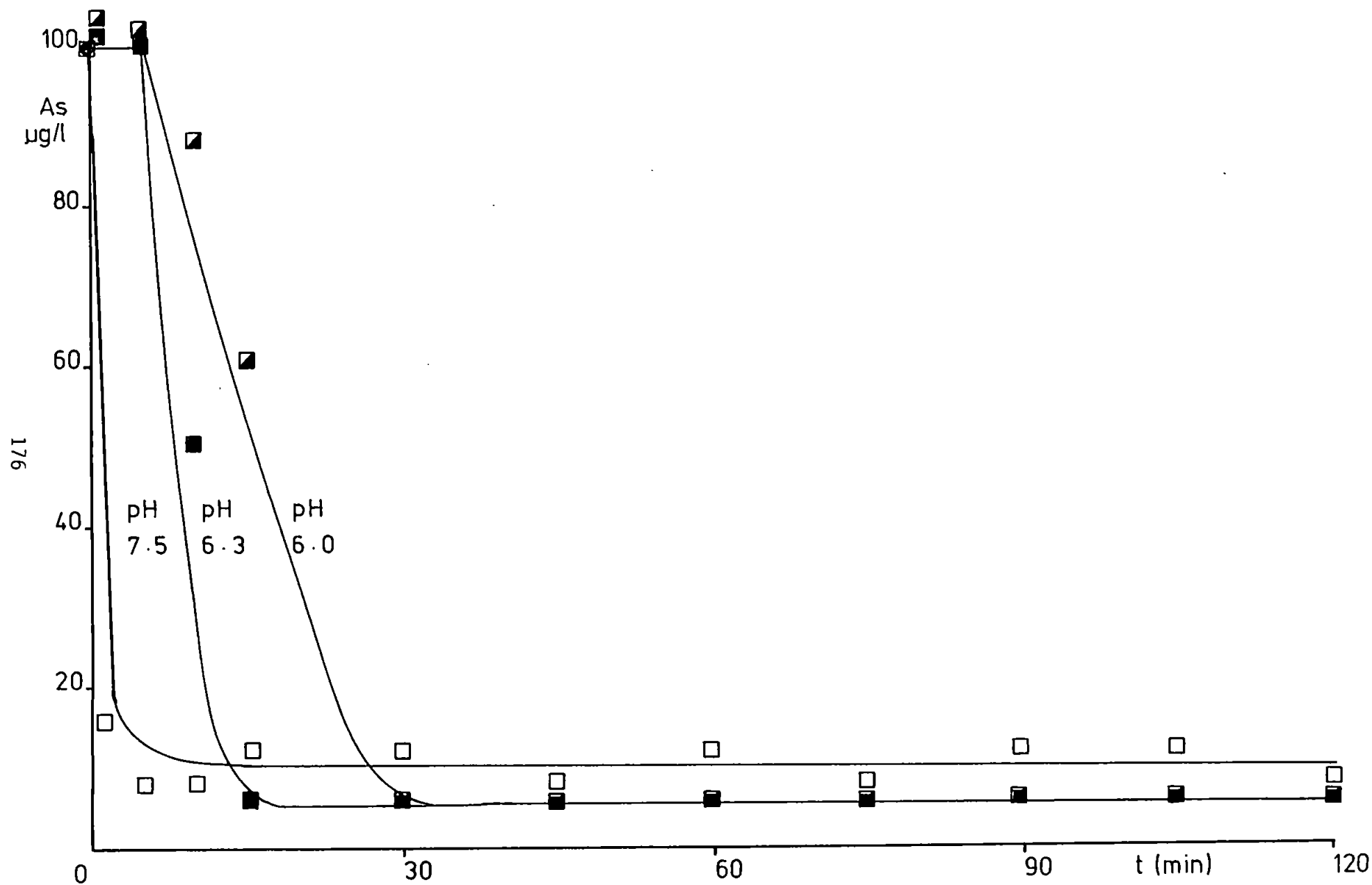   at 2°C and various pH
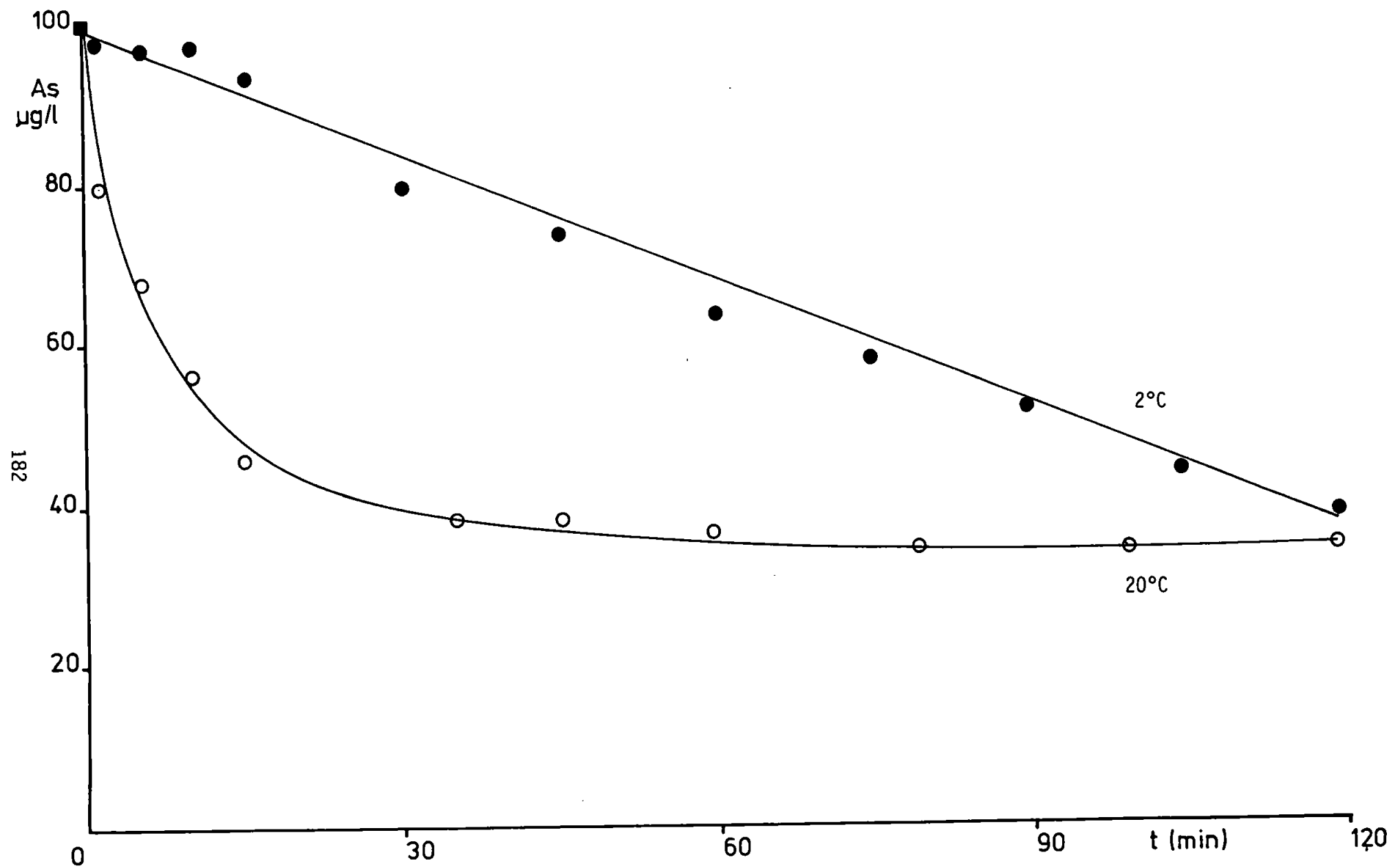
Figure 4.28 Adsorption profiles for As (III) onto fresh Fe (II) precipitates in seawater
at pH 7.1 and various T

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selection of runs are presented here in order to simplify the discussion. In general, the behaviour of the natural waters was in reasonable agreement with the synthetic runs. A few observed anomalies will also be discussed.

Natural water models run using freshwater from Cadover Stream, Devon, at 20°C, showed initially no adsorption of As (V) at pHs as high as pH 8.0, over a period in excess of 24 h . This was related to the absence of visible precipitate formation and was thought to be due to the presence of organic matter inhibiting oxidation (Theis & Singer, 1973 & 1974). The addition of a mixture of NaCl and $MgSO_4$, in the correct seawater proportions, to a level of $3^o/oo$ allowed precipitation to proceed.(fig. 4.29).

Differences in the equilibrium values obtained for these runs, compared to the synthetic freshwater models, may be related to the presence of the major seawater ions or possibly the organic matter and the presence of small amounts of dissolved Fe (III). The overall similarity of the profiles to those of Fe (II)/As (V) in seawater at 20°C suggest that the seawater ions are the major influence and that therefore salinities as low as $3^o/oo$ may alter the adsorption behaviour of the precipitates, compared to the freshwater regime. The absence of any significant slowing in the rate of adsorption below pH 7.6 may be related to the Fe (III) component present. The adsorption of As (V) in Cadover water at 20°C and S^o/oo of $34^o/oo$ (fig. 4.29) gave similar profiles, in agreement with the synthetic models, but the profile at pH 6.5 also showed the rate reduction observed in the initial models (fig. 4.26) at lower pHs. The profiles at 2°C (fig. 4.30) showed the trends of reduced adsorption rate and enhanced equilibrium value observed in the

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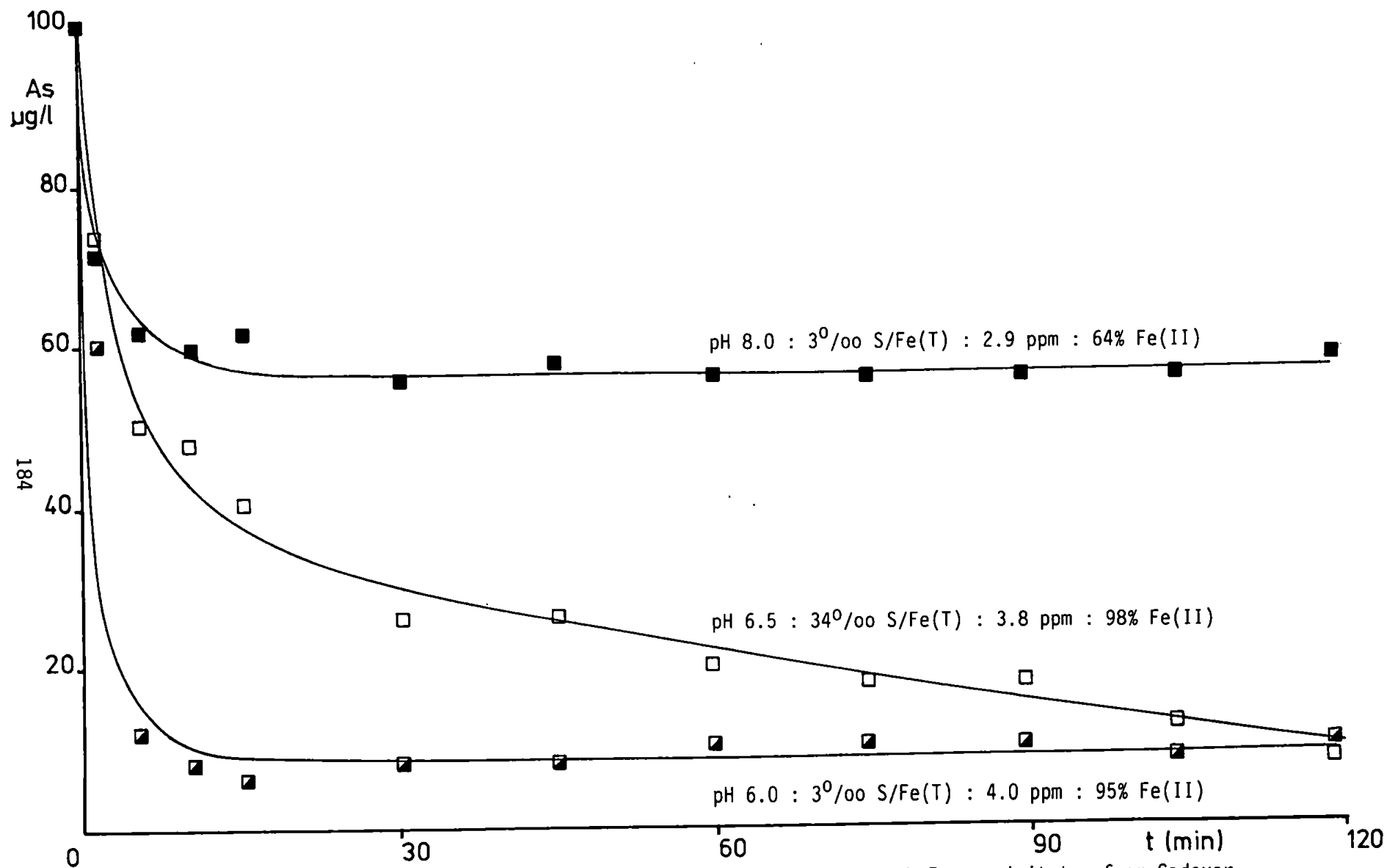
Figure 4.29   Adsorption profiles for As (V) onto natural fresh Fe precipitates from Cadover Stream, Devon, at 20°C and various pH and S°/oo

pH 8.0 : 3°/oo S/Fe(T) : 2.9 ppm : 64% Fe(II)

pH 6.5 : 34°/oo S/Fe(T) : 3.8 ppm : 98% Fe(II)

pH 6.0 : 3°/oo S/Fe(T) : 4.0 ppm : 95% Fe(II)

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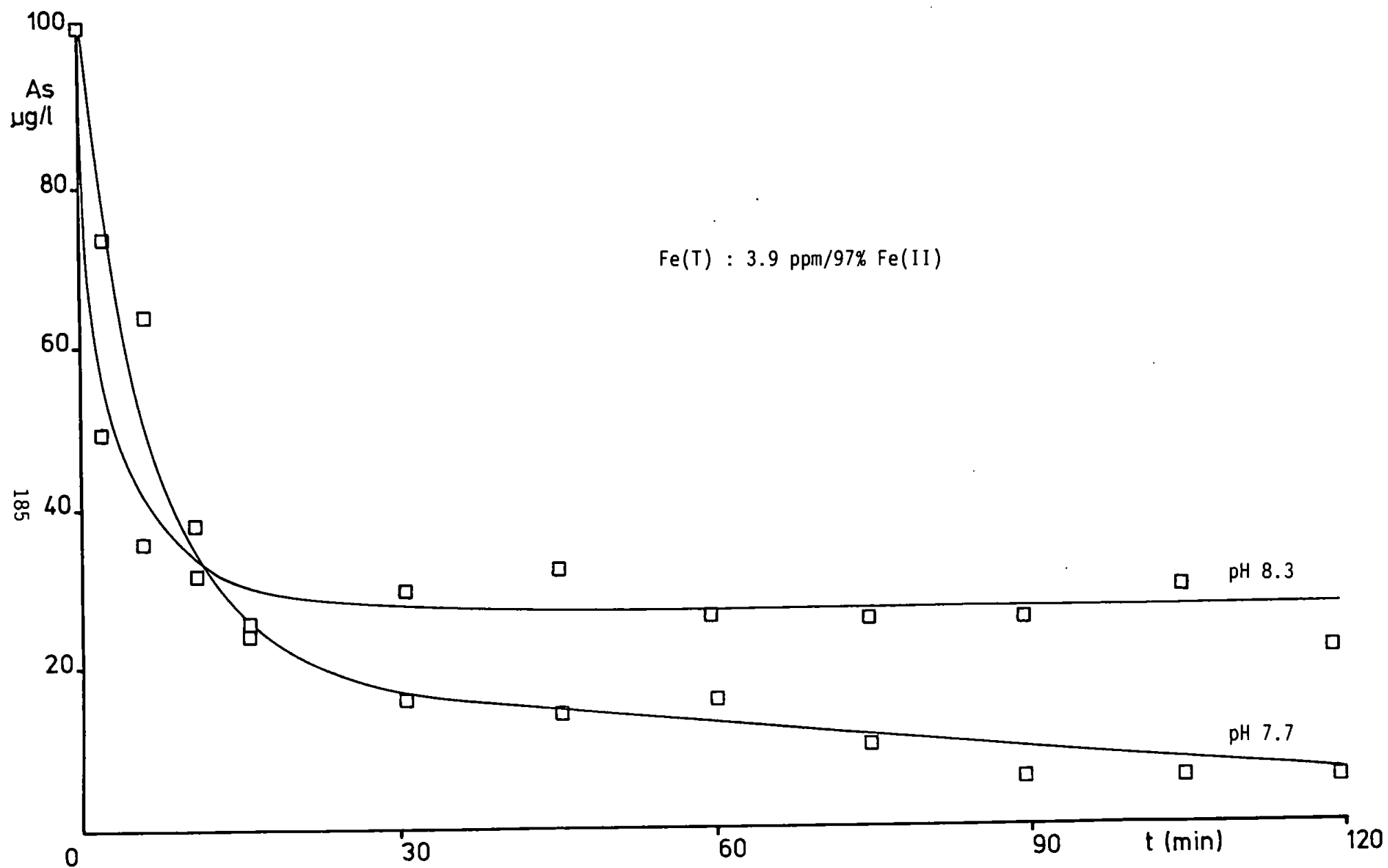
Figure 4.30 Adsorption profiles for As (V) onto natural fresh Fe precipitates from Cadover Stream, Devon at 2°C and various pH, in seawater analogue

synthetic models.

Figure 4.31 shows the profiles for Lady Bertha minestream at 2°C for the adsorption of As (V). The profiles at pH 6.1 and 7.4 are in close agreement with the synthetic profiles at around these pHs. The lag time in adsorption at pH 6.1 could be due to the presence of small quantities of organic matter, but is more likely to be due to the large natural content of As in this water, which is of unknown speciation. The rapidity of uptake at pH 6.9, compared to the synthetic models, is difficult to explain.

A seawater analogue using an iron-rich pore water, collected by membrane dialysis, which contained 100% dissolved Fe (II) (2.4 mg/L), was run with As (V) at 2°C and pH 8.0. It showed very close agreement with the synthetic models run under these conditions.

Model runs carried out on the natural water from the River Carnon, Cornwall, and which contained 100% dissolved Fe (II) (3.7-4.8 mg/L), in both freshwater and seawater, showed uptake of As (V) that was very rapid over a range of pH values (t_e = < 1 min). This behaviour was more akin to that of a freshly derived Fe (III) precipitate and was also observed in the freshwater and seawater profiles obtained for the uptake of As (III) onto Fe (II) in a natural water from the Wheal Franco minestream (fig. 4.32).

This anomaly is difficult to explain, but may be due to several factors. It is possible that the method used to estimate the Fe (II) content of the samples is inhibited by the presence of organic matter in the waters. This organic matter may be complexing with Fe (III) present and preventing

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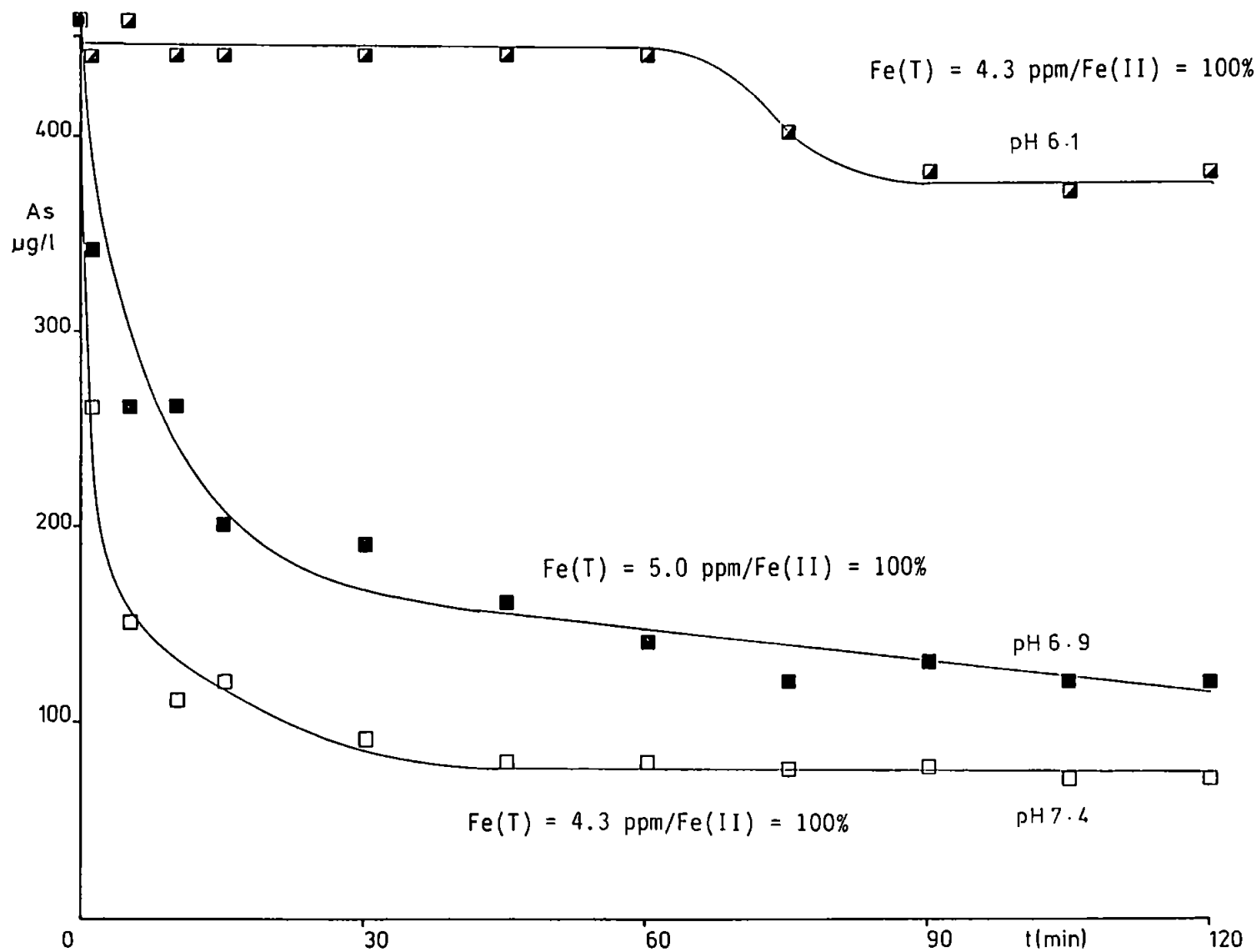
Figure 4.31 Adsorption profiles for As (V) onto natural fresh Fe precipitates from the Lady Bertha mine-stream, Devon, at 2°C and various pH, in freshwater analogue
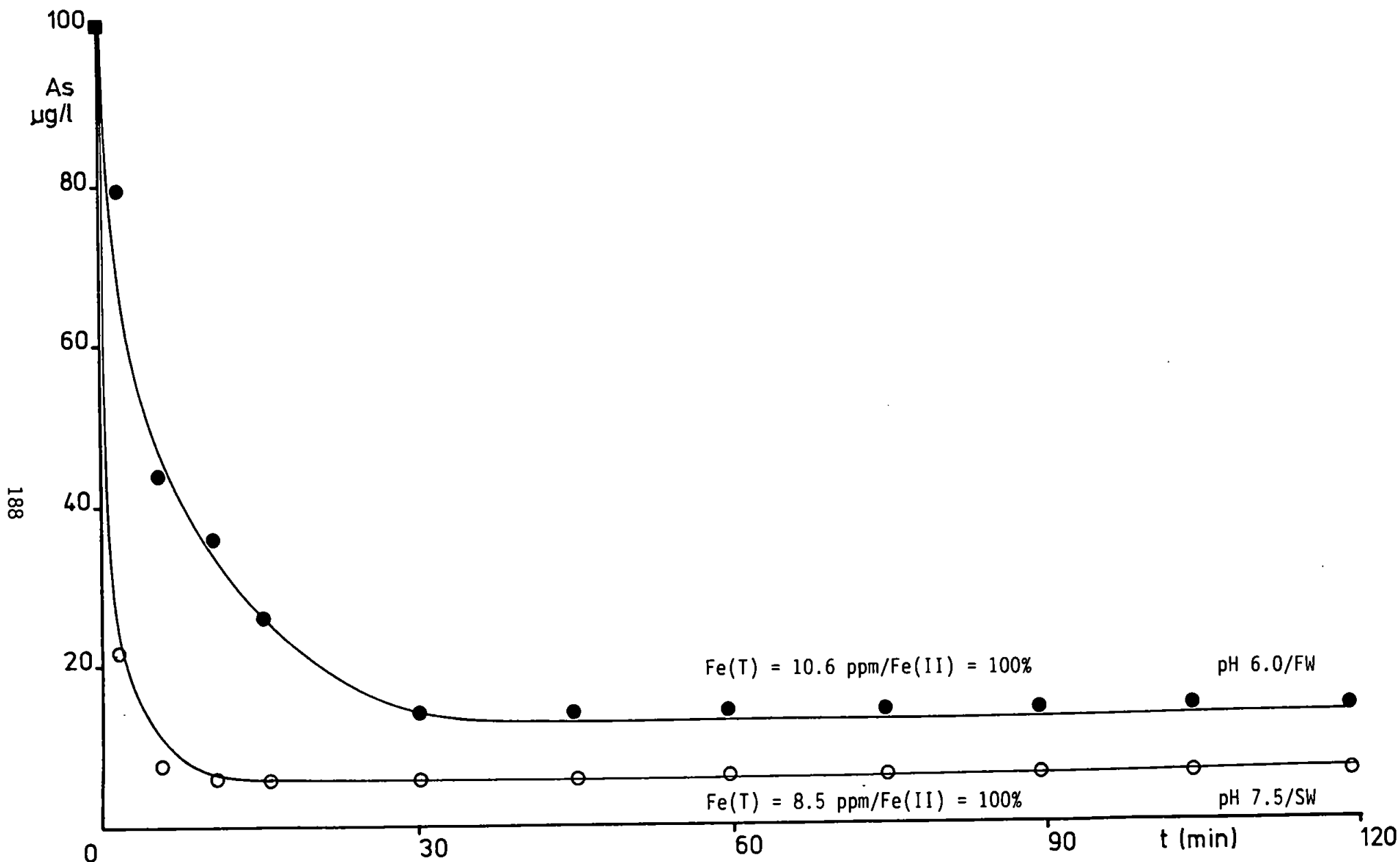
Figure 4.32 Adsorption profiles for As (III) onto natural fresh Fe precipitates from the Wheal Franco minestream, Devon, at 2°C and various pH, in freshwater and seawater analogues

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its detection. An alternative explanation is that the pH of the water from both these sources is very low (pH < 3.5). It is therefore necessary to rapidly raise the pH of the model solution immediately prior to the initiation of a run. This is turn may result in the formation of a very finely divided precipitate, with a consequently high surface area at the beginning of the run. It is this precipitate that may be responsible for the rapid uptake profile in these models.

4.2.3 Kinetics of Arsenic Removal

The quality of the adsorption data obtained from the modelling studies was such that it lent itself to quantitative kinetic analysis, which complements the earlier qualitative mechanistic information discussed in section 4.2.2. An evaluation of the chemical timescales involved is required in order to apply the data obtained to predictive models, which combine both chemical and physical processes over the timescales of natural systems. Kinetic analysis of the data will yield rate constants and the rate of a reaction as a function of temperature can be used to calculate the activation energy of the reaction.

A number of the models did not lend themselves to quantitative analysis for several reasons. Many of the Fe (III) fresh precipitate runs were too rapid (t_e = < 1 min) for kinetic analysis using the methods adopted in this study. Secondly, the uptake of As (III) onto aged Fe (II) derived precipitates could not be analysed as no adsorption took place. Also, a number of the natural water models did not yield data precise enough to attempt analysis. Finally, the majority of the freshwater models were too rapid (t_e = < 5 min) to analyse successfully.

The mechanistic analysis of As discussed in the preceeding section and previous work on the adsorption of PO_4^{3-} (Crosby, 1982) has shown that the processes involved are complex. The approach adopted was similar to that of Crosby (1982), involving trial and error methods which attempt to find the best fit for the adsorption data using a variety of possible reactions. In this section the analysis of fresh precipitates will be discussed first, for reasons of clarity.

4.2.3.1   Fresh Precipitates

4.2.3.1.a Arsenate adsorption behaviour

From the mechanistic analysis discussed in the previous section it can be seen that for fresh precipitates of Fe (II) in seawater, at both 20°C and 2°C, two distinct regimes were present, with slow uptake at pH < 7.6.

At both 20°C and 2°C with pH < 7.6 the adsorption was relatively slow and the removal of As (V) appeared to relate to the appearance of the Fe precipitate. It is argued that the rate determining step in this case is the relatively slow oxidation of Fe (II) to Fe (III) :

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{slow} 4Fe^{3+} + 2H_2O \qquad (4.7)$$
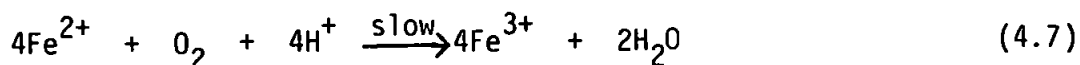
This would be followed by the hydrolysis and precipitation step, which is more rapid :

$$Fe^{3+} + 3H_2O \xrightarrow{fast} Fe(OH)_3 + 3H^+ \qquad (4.8)$$
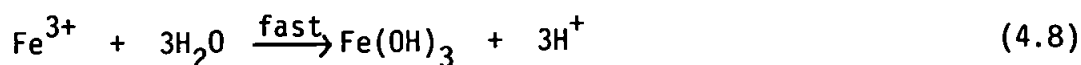
Under these conditions, the adsorption process itself is assumed to be relatively fast (as in the case of the rapid uptake of As (V) onto fresh Fe (III) precipitates). To test this hypothesis, the rate of

uptake of As (V) was equated to the rate of removal of Fe (II) by oxidation, i.e.

$$\frac{-d\,[Fe\,(II)]}{dt} = \frac{-d\,(AsO_4{}^{3-})}{dt} \tag{4.9}$$

The general rate law for the oxidation of Fe (II) (Pankow & Morgan, 1981; Tamura, et al., 1976; Sung & Morgan, 1980) has been established as :

$$\frac{-d\,[Fe(II)]}{dt} = k\,[OH^-]^2\,P_{O_2}\,[Fe(II)] \tag{4.10}$$

where k is the homogenous constant of units $M^{-2}\,atm^{-1}\,min^{-1}$, and P_{O_2} the partial pressure of O_2. At constant pH and P_{O_2} this reduces to the first order equation :

$$\frac{-d\,[Fe(II)]}{dt} = k_1\,[Fe(II)]_0 \tag{4.11}$$

where $k_1 = k\,[OH^-]^2\,P_{O_2}$. This equation integrates to :

$$[Fe(II)]_t = [Fe(II)]_0\,exp\,(-k_1 t) \tag{4.12}$$

and by the analogy above :

$$[AsO_4{}^{3-}]_t = [AsO_4{}^{3-}]_0\,exp\,(-k_1 t) \tag{4.13}$$

Therefore a plot of log $[(X)_t/(X)_0]$ against time should be linear, where (X) is equal to $[AsO_4{}^{3-}]$. Hence k can be calculated, with $[OH^-]$ from the pH and K_w (T), P_{O_2} = 0.21 atm, and k_1 from the slope of the plot.

Figure 4.33 shows first order plots using equation (4.12) for several of the model runs and the rate constants are summarised in table 4.2.

The analysis of $AsO_4{}^{3-}$ adsorption at 20°C and pH 7.4 gave a value for the rate constant $k = 1.3 \times 10^{13}\,M^{-2}\,atm^{-1}\,min^{-1}$. This figure compares well with other data from the literature (table 4.3).
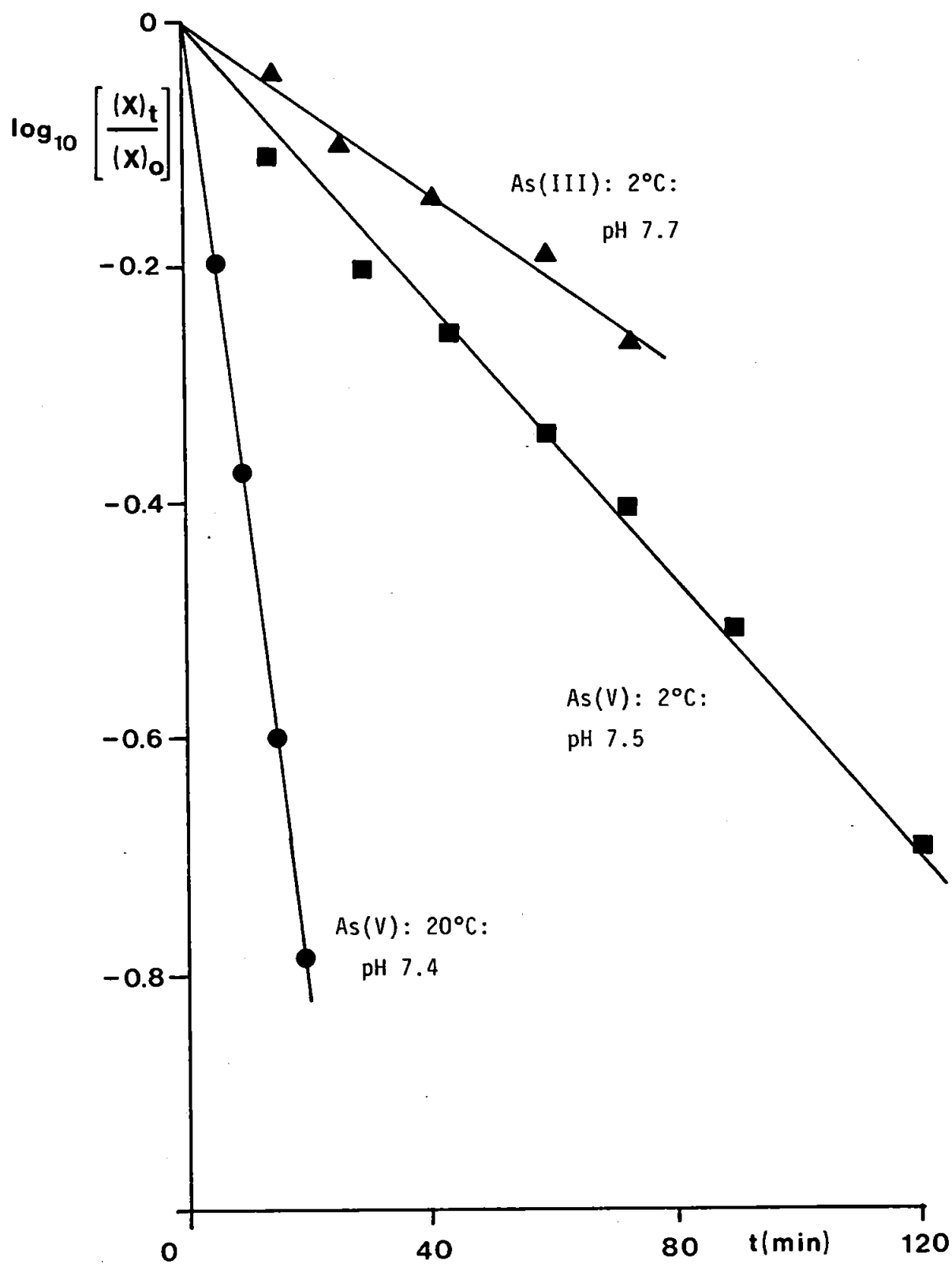
Figure 4.33   1st order kinetic plots for AsO_4 and AsO_3 adsorption onto fresh Fe (II) precipitates in seawater, $S = 34^o/oo$

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Table 4.2 Variation of k values for 1st order reactions in seawater, $S = 34^O/oo$ (fresh precipitates) - Fe (II)

Solution Composition[a]	pH	T(°C)	k (M^{-2} atm^{-1} min^{-1})	$t_{1/2}$(min)
1.33 µM AsO_4	7.4	20	1.3×10^{13}	8
1.33 µM AsO_4	7.5	2	2.5×10^{13}	52
1.33 µM AsO_3	7.7	2	5.4×10^{12}	95

[a] All solutions contained 50 µM/L Fe

Table 4.3 Comparison of k values for 1st order reactions in seawater analogues - Fe (II)

Solution Composition[a]	pH	T(°C)	k (M^{-2} atm^{-1} min^{-1})	Authors
$34^O/oo$ S : AsO_4	7.4	20	1.3×10^{13}	this work
0.5 M NaCl	7.2	25	1.8×10^{12}	Sung & Morgan (1980)
Puget Sound Seawater	8.0	~15	8.9×10^{11}	Murray & Gill (1978)
Various	var.	var.	$1.5\text{-}3 \times 10^{13}$	Davison & Seed (1983)
$34^O/oo$ S : PO_4	7.3	15	1.2×10^{13}	Millward, et al. (1983)
$34^O/oo$ S : AsO_4	7.5	2	2.5×10^{13}	this work
0.11 M $NaClO_4$	6.76	5	9.2×10^{13}	Sung & Morgan (1980)
$34^O/oo$ S : PO_4	7.9	2	2.9×10^{13}	Millward, et al. (1983)

[a] [Fe(II)], [AsO_4] and [PO_4] varies

A model carried out at 2°C and pH 7.5 for As (V) also fitted the first order rate law, giving a value of $k = 2.5 \times 10^{13} \ M^{-2} \ atm^{-1} \ min^{-1}$. The closest comparisons that could be found in the literature are given in table 4.3. A value of $k = 5.4 \times 10^{12} \ M^{-2} \ atm^{-1} \ min^{-1}$ for As (III) at 2°C and pH 7.7 was obtained using the first order rate equation. This was lower than might be expected at this pH, and may reflect the complexity of the adsorption reaction postulated in section 4.2.2. The reasonable agreement between rate constants determined directly from Fe (II) oxidation and those determined indirectly from AsO_4^{3-} adsorption indicate that there is a strong coupling between the Fe (II) oxidation process and the adsorption of AsO_4^{3-}, and indirectly, AsO_3^{3-} at pH < 7.6.

The half-lives of these reactions can be calculated from the expression :

$$t_{\frac{1}{2}} = \ln 2 / k_1 \tag{4.14}$$

The half-life of the AsO_4^{3-} adsorption varied from 8 min at 20°C and pH 7.4, to 52 min at 2°C and pH 7.5, being pH and temperature dependent. The half-life for AsO_3^{3-} adsorption at 2°C and pH 7.7 was 95 min, indicating the comparative reduction in reaction rate compared to AsO_4^{3-} adsorption.

As the pH values of the two AsO_4^{3-} adsorption models at 20°C and 2°C are so close (virtually within experimental error), we can calculate the activation energy of the reaction utilising the Arrhenius equation :

$$k = Ae^{-E/RT} \tag{4.15}$$

where A is a constant characteristic of the reaction, E is the activation energy, R the molar gas constant and T the temperature in K. Given the values of k_1 at two temperatures, equation (4.15) can be rearranged to give :

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$$\log_{10} k_{1_a} - \log_{10} k_{1_b} = E/2.3R \ [1/T_b - 1/T_a] \qquad (4.16)$$

from which E can be calculated. This gave an activation energy of 70.1 kJ/mol. This situation is complex, but almost all of the activation energy could be ascribed to the oxidation step. This does not then, necessarily imply a chemisorption process.

The second kinetic regime observed was that of Fe (II) precipitates for pH > 7.6 at 20°C and pH > 7.9 at 2°, under which circumstances the above first order equation was not adequate. Under these conditions the oxidation of Fe (II) is rapid and the newly formed Fe (III) surface has an autocatalytic effect on the oxidation of Fe (II). This results in a complicated kinetic regime where the adsorption reaction itself becomes rate determining. Attempts to fit the integrated rate equation for the heterogeneous oxidation of Fe (II) (Sung & Morgan, 1980) to the adsorption of PO_4^{3-} have proved unsuccessful (Crosby, 1982). It is therefore unlikely that simple kinetics can be successfully applied to such a situation (Laidler, 1965). It was therefore decided that, as a working predictive model was the main requirement, a set of standard integrated rate equations for several reversible reactions would be applied to the data (Swinbourne, 1971), in order to obtain a best-fit. These equations and the ln(f) functions of their integrated forms are summarised in table 4.4. Analysing the data using these equations showed that equation 4 gave the best fit in these cases. This rate equation may also be applied to reactions involving equal concentrations of two separate reactants; however, this would involve the reaction of the active sites on the oxyhydroxide surface. Even if this was the case, or if a binuclear complex was formed (Lijklema, 1980), the number of sites occupied by the AsO_4^{3-} would be small compared to the total number

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Table 4.4   ln(f)s of the integrated rate equations for several reaction mechanisms examined (from Swinbourne, 1971)

Reaction Mechanism	ln(f)
1. $X \rightleftharpoons A$	$\dfrac{[X]_0 - [X]_\infty}{[X] - [X]_\infty}$
2. $X \rightleftharpoons A+B$	$\dfrac{[X]_0^2 - [X]_\infty [X]}{([X] - [X]_\infty)\,[X]_0}$
3. $2X \rightleftharpoons A$	$\dfrac{([X]_0 - [X]_\infty)\,([X][X]_0 + [X]_0 [X]_\infty - [X][X]_\infty)}{[X]_0^2\,([X] - [X]_\infty)}$
4. $2X \rightleftharpoons A+B$	$\dfrac{[X]_0 [X]_\infty - 2[X][X]_\infty + [X][X]_0}{[X]_0\,([X] - [X]_\infty)}$

$[X]_0$ =   Initial concentration of AsO_4

$[X]_\infty$ =   Equilibrium concentration of AsO_4

$[X]$ =   Concentration of AsO_4 at time t

A; B   =   Adsorbed AsO_4 species, possibly bound to the surface on different sites

of sites present. This would result in pseudo-first order kinetics, as would the case of other similar reactants such as the OH^- group, since these models were carried out at a constant pH. The favoured mechanism is therefore :

$$2X \rightleftharpoons A + B \qquad\qquad (4.17)$$

where X is the AsO_4^{3-} and A, B the adsorbed species.

Despite the uncertainty surrounding the exact mechanism, the use of this equation allows the determination of conditional rate constants. Its integrated form is :

$$K_2 t = \left[\frac{X_0 - X_\infty}{2X_0 X_\infty}\right] \ln \left[\frac{X_0 X_\infty - 2X_\infty + X_t X_0}{X_0 (X_t - X_\infty)}\right] \qquad (4.18)$$

where X is the concentration of AsO_4^{3-} at time (t) = 0, t and ∞ (equilibrium) respectively.

This equation was applied to the data for As (V) adsorption onto Fe (II) at pH > 7.6 in seawater and the results are plotted in fig. 4.34 as the function ln (f) against time for synthetic precipitates. The half-lives for these reactions can be calculated from the derived equation :

$$K_2 t_{\frac{1}{2}} = \left[\frac{X_0 - X_\infty}{2X_0 X_\infty}\right] \ln \left[\frac{X_0}{(X_0 - 2X_\infty)}\right] \qquad (4.19)$$

The rate constants and half-lives are summarised in table 4.5.

The synthetic precipitates show rapid uptake at 20°C and pH 7.8, with a half-life of < 1 min. At 2°C the half-life increases to 4 mins, indicating the reduced rate of reaction with decrease in temperature.
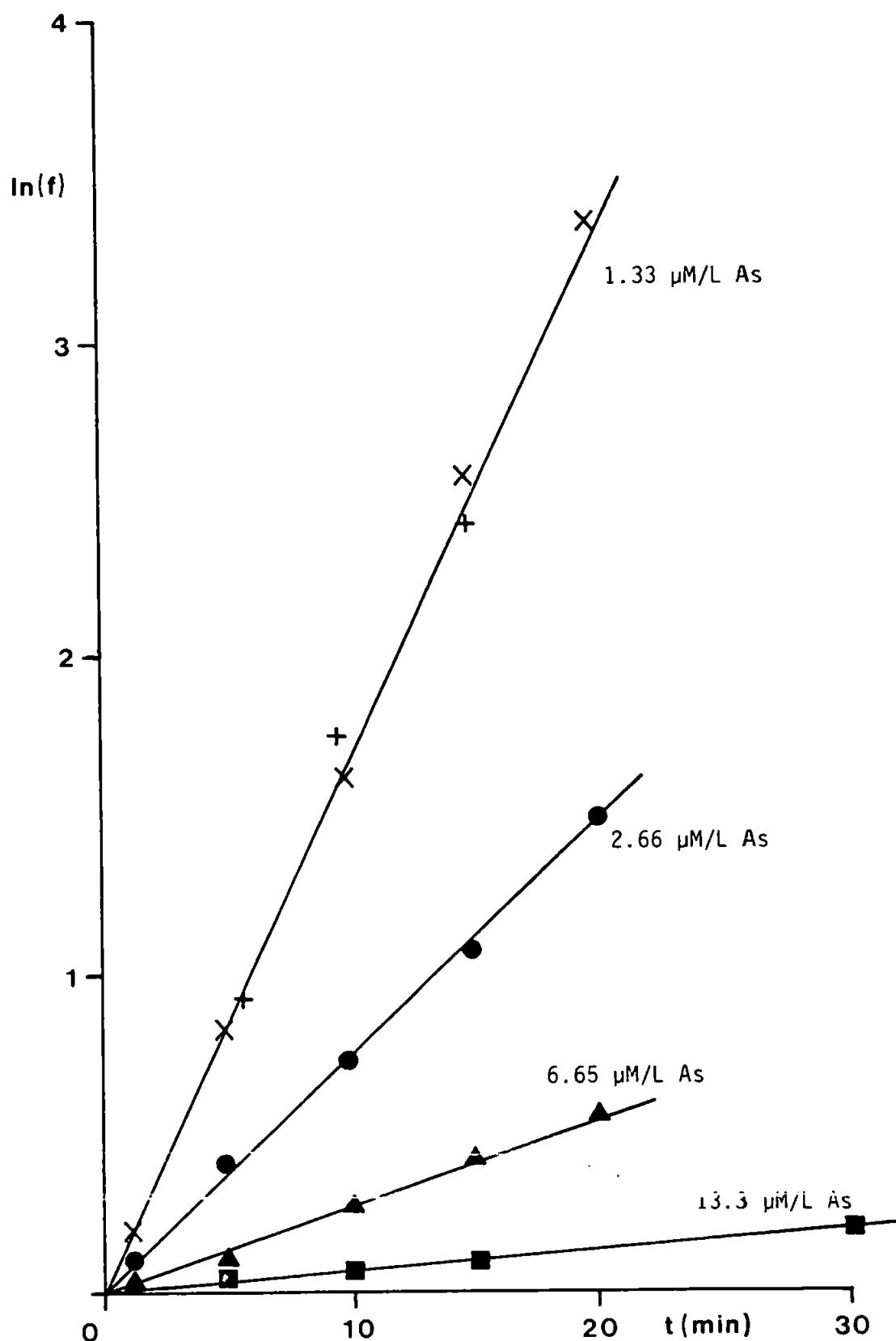
Figure 4.34   2nd order kinetic plots for AsO_4 adsorption onto fresh Fe (II) precipitates in seawater, $S = 34^0/oo$, at pH 7.8 and 2°C.   + = fresh Fe (III) precipitate at same pH and T, $[AsO_4]$ = 1.33 μM/L.   Fe (II) at pH 8.0 and 20°C are not plotted because of scale differences

Table 4.5 Summary of k_2 and $t_{1/2}$ values for synthetic and natural models in seawater, $S = 34^0/oo$ (fresh precipitates) - AsO_4

Solution Composition	pH	T(°C)	k_2 (L M^{-1} min^{-1})	$t_{1/2}$ (min)
Synthetic[a]:				
Fe^{3+} : 1.33 µM/L AsO_4	7.8	2	8.0×10^5	< 1
Fe^{2+} : 1.33 µM/L AsO_4	8.0	20	9.5×10^5	< 1
Fe^{2+} : 1.33 µM/L AsO_4	8.0	2	1.7×10^5	4
Fe^{2+} : 2.66 µM/L AsO_4	8.0	2	1.2×10^5	3
Fe^{2+} : 6.65 µM/L AsO_4	8.0	2	3.2×10^4	5
Fe^{2+} : 13.3 µM/L AsO_4	8.0	2	6.9×10^3	11
Natural :				
Fe^{2+} : 1.33 µM/L AsO_4[b]	7.7	20	9.8×10^5	< 1
Fe^{2+} : 1.33 µM/L AsO_4[b]	7.7	2	1.2×10^5	6
Fe^{2+} : 1.33 µM/L AsO_4[c]	8.0	2	1.9×10^5	4
Fe^{2+} : 1.33 µM/L AsO_4[b]	8.3	2	1.9×10^5	4

[a] All solutions contained 50 µM/L Fe.

[b] Minestream water Fe (T) = 65 µM/L, Fe (II) = 95%.

[c] Interstitial water Fe (T) = 45 µM/L, Fe (II) = 100%.

The activation energy of this reaction was calculated as 64.0 kJ/mol. This can only be regarded as an apparent activation energy (Laidler, 1965) since :

$$E \text{ (true)} = E \text{ (apparent)} + \text{heat of adsorption} \qquad (4.20)$$

A lower limit of approximately 40 kJ/mol can be assumed for the heat of reaction. This is close to the heat of formation of hydrogen bonds, which could be involved in the bonding of AsO_4 ions to surface $-OH_2^+$ and $-OH$ groups. This means that the true activation energy could be as high as 104 kJ/mol, indicating that this is a chemisorption process.

Under these conditions of pH and temperature, a slow increase in the half-life of the reaction is observed with increasing concentration of AsO_4^{3-}, and this may be related to the increasing competition for surface sites.

The data for natural precipitates is plotted in fig. 4.35, and the rate constants listed in table 4.5. The rate constants for these reactions are in good agreement with those of the synthetic sources, with half-lives of the same order. The exception to this is the precipitate derived from an acid mine water at 20°C, 34°/oo S and pH 7.7. Although the rate constant is comparable with that of the synthetic precipitate at similar pH and temperature, in this case only 50% of the original AsO_4^{3-} was removed from solution at equilibrium, compared to the synthetic precipitate which removed around 90%. Under these conditions the natural water appeared to be behaving more like an aged Fe (II) precipitate and this result appears anomalous. The apparent activation energy of this reaction was high at 77.7 kJ/mole, indicating a process of chemisorption, for the reasons discussed earlier.
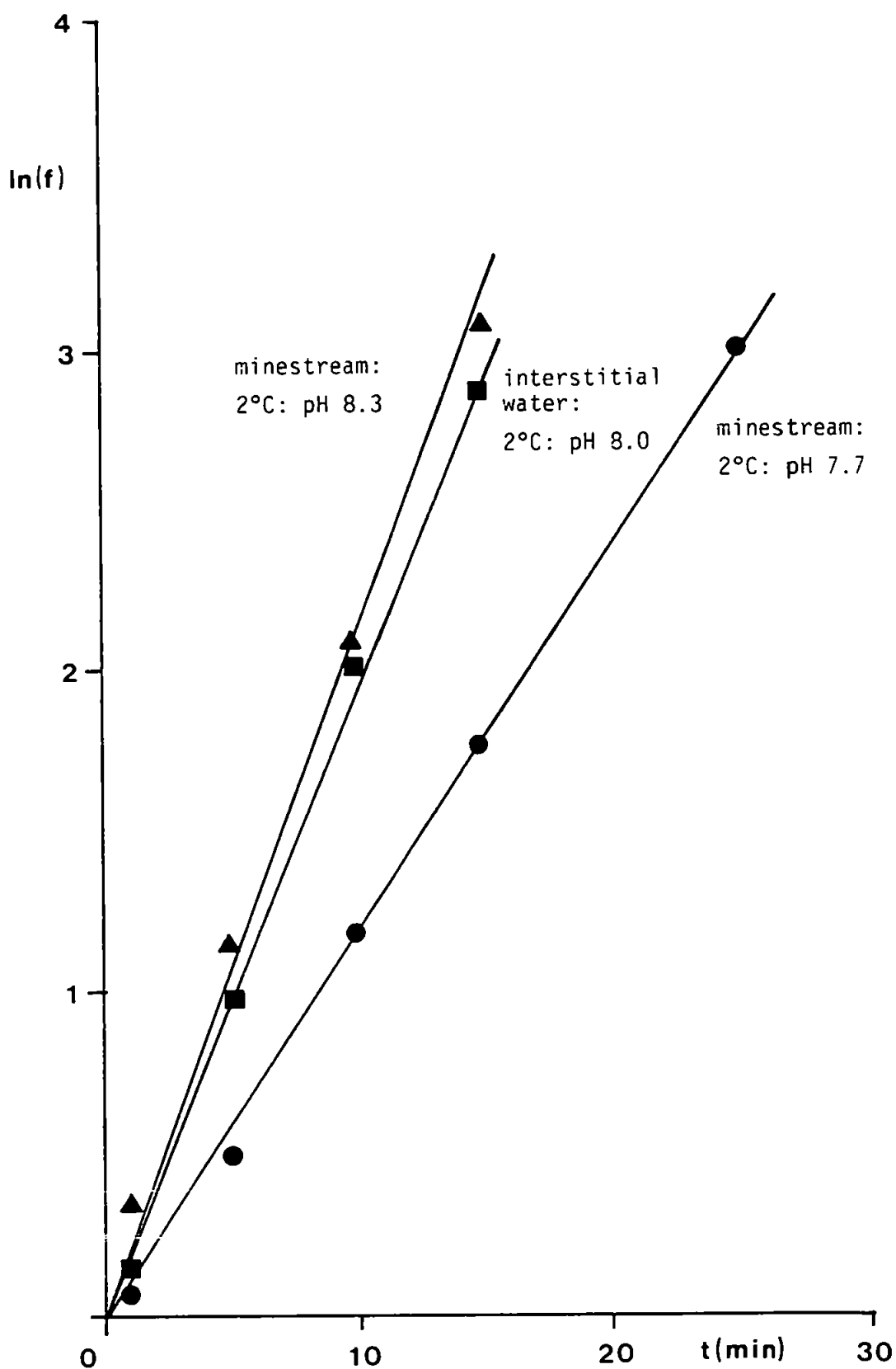
Figure 4.35   2nd order kinetic plots for AsO_4 adsorption onto natural, fresh Fe (II) precipitates in seawater, S = 34°/oo. Fe (II) from minestream at pH 7.7 and 20°C are not plotted because of scale differences

Despite the very rapid adsorption of As (V) by fresh Fe (III) precipitates in seawater, one profile was found to be amenable to analysis and gave a value of $k_2 = 8.00 \times 10^5$ L M^{-1} min^{-1} with a half-life of <1 min, at 2°C and pH 7.8.

The general agreement between the precipitates formed from synthetic and natural sources shown above, indicates that possible interferences in the natural samples, such as the presence of organic matter, appear to exert a minor influence on the processes of As removal by Fe in these media. The comparison is summarised in table 4.6.

Table 4.6   Comparison of k_2 values for synthetic and natural models (fresh precipitates) in seawater, S = 34°/oo

Solution Composition[a]	pH	T(°C)	k_2 (synthetic)[b]	k_2 (natural)[b]
Fe^{2+} : As^{5+}	7.8	20	9.5×10^5	9.8×10^5
Fe^{2+} : As^{5+}	7.8	2	1.7×10^5	1.2×10^5

[a] All solutions contained 50 μM/L Fe and 1.33 μM/L As
[b] k_2 values in L M^{-1} min^{-1}

4.2.3.1.b Arsenite Adsorption Behaviour

The relatively fast adsorption of As (V) by freshly derived Fe (II) and Fe (III) precipitates from freshwater at both 20°C and 2°C (see section 4.2) made kinetic analysis largely impossible. However, the generally slower adsorption of As (III) enabled several profiles to be evaluated.

The results of trial and error analysis indicated that the kinetic behaviour generally followed that of the reaction utilised in the second order analysis of the previous models, i.e.

$$2X \rightleftharpoons A + B \qquad\qquad (4.21)$$

The data is plotted in fig. 4.36 and summarised as table 4.7.

Table 4.7 Summary of k_2 and $t_{\frac{1}{2}}$ values for synthetic and natural models in freshwater (fresh precipitates) - AsO_3

Solution Composition[a]	pH	T(°C)	k_2 (L M^{-1} min^{-1})	$t_{\frac{1}{2}}$ (min)
Synthetic :				
Fe^{3+} : 1.33 µM/L AsO_3	7.1	20	8.4×10^4	9
Fe^{3+} : 1.33 µM/L AsO_3	7.1	2	6.7×10^4	11
Fe^{3+} : 1.33 µM/L AsO_3	6.6	2	6.1×10^4	16
Natural :				
Fe^{2+} : 1.33 µM/L AsO_3[b]	6.0	2	2.4×10^5	3

[a] All solutions contained 50 µM/L Fe (III) except;
[b] Minestream water Fe (T) = 10.6 mg/L, Fe (II) = 100%

The adsorption of As (III) onto Fe (III) precipitates at pH 7.1 again showed a decrease in reaction rate at 2°C compared to 20°C and an apparent activation energy of 20.4 kJ/mol was calculated. This is on the low side, but is still greater than the heat of formation and implies a possible chemisorption mechanism. The adsorption at pH 6.6 and 2°C was slower by an order of magnitude and illustrated the pH dependence of the reaction. The adsorption of As (III) onto Fe (II) from a natural water source at 2°C and pH 6.0 was analysable and gave $k_2 = 2.42 \times 10^5$ L M^{-1} min^{-1} with a half-life of 3 min. This appears
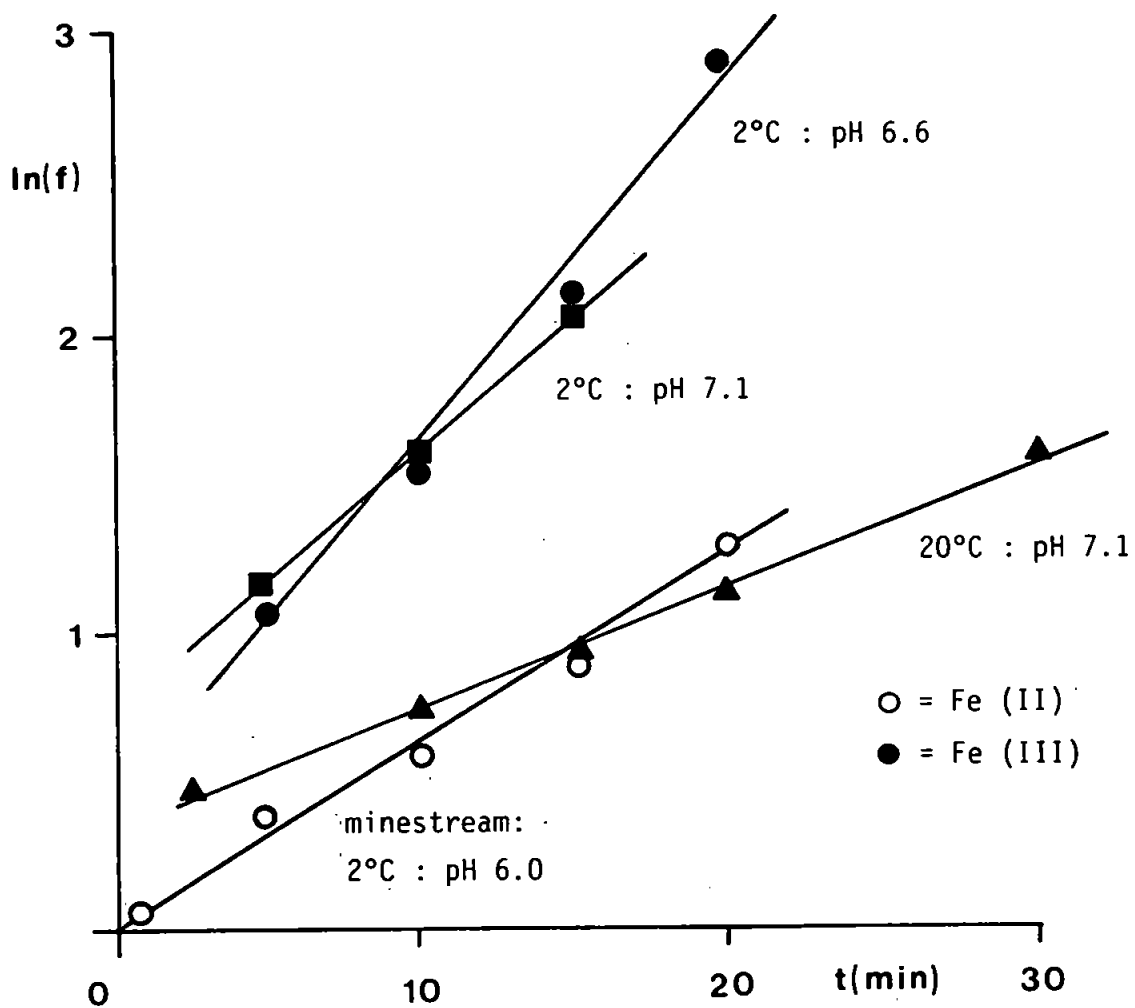
Figure 4.36   2nd order kinetic plots of AsO_3 adsorption onto fresh
Fe (III) and natural Fe (II) precipitates in freshwater

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anomalously fast and does not fit the general trend expected as the uptake of As (III) by Fe (II) should be slower, compared to that of Fe (III). A possible explanation is that this natural water source was of low pH ($<$ 3.0) and the adjustment of pH prior to the model run may have resulted in the formation of an initial active Fe (III) precipitate preceeding the addition of As (III), as detailed in section 4.2.2.2.c).

The adsorption of As (III) onto Fe (II) and Fe (III) derived precipitates in seawater was found to be amenable to analysis, due to the generally slower uptake observed. One model was found to be first order and this was described in the previous section for the sake of convenience. The remaining profiles fitted the second order equation utilised and these are discussed here.

The adsorption of As (III) onto Fe (II) derived precipitates gave a value of k_2 = 5.38 x 10^4 L M^{-1} min^{-1} and a half-life of 15 min, at 20°C and pH 7.7. This compares to a half-life of $<$ 1 min for As (V) at similar pH and temperature and reflects the general reduction in rate of adsorption observed for As (III) discussed in section 4.2.2.1.b. At 2°C and pH 8.3 k_2 = 1.17 x 10^5 L M^{-1} min^{-1} with a half-life of 7 min. This increase in reaction rate is probably due to the formation of a more active precipitate at the lower temperature.

The adsorption of As (III) onto Fe (III) at 2°C and pH 7.8 gave k_2 = 1.79 x 10^4 L M^{-1} min^{-1} and half-life 48 min. This value is not directly comparable with the other data obtained, but seems rather slow considering the enhanced activity of Fe (III) precipitates compared to those of Fe (II). The data for the above reactions is summarised as table 4.8, and is plotted as ln(f) against time in fig. 4.37.
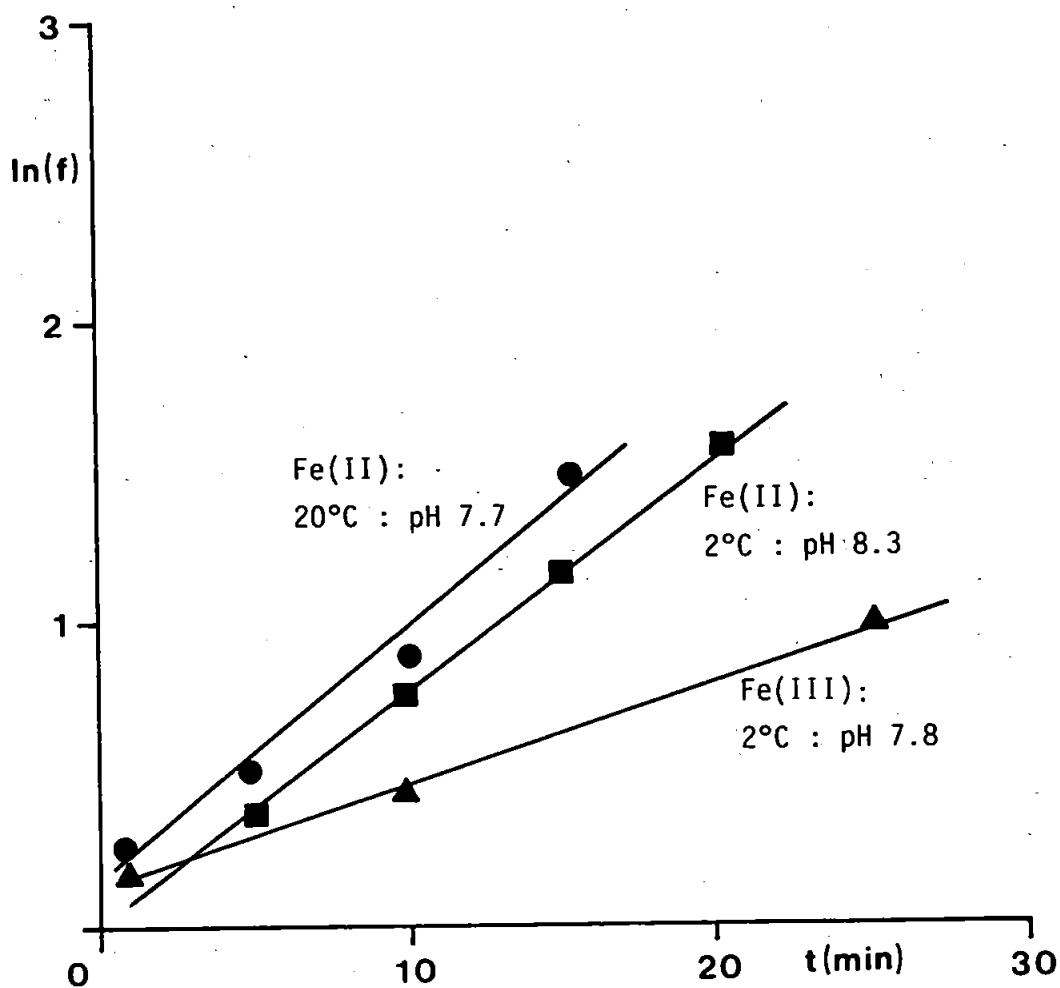
Figure 4.37　2nd order kinetic plots of AsO_3 adsorption onto fresh Fe (II) and Fe (III) precipitates in seawater, $S = 34^o/oo$

Table 4.8   Summary of k_2 and $t_{\frac{1}{2}}$ values for synthetic models in
seawater, S = 34°/oo (fresh precipitates) - AsO_3

Solution Composition[a]	pH	T(°C)	k_2 (L M^{-1} min^{-1})	$t_{\frac{1}{2}}$ (min)
Fe^{3+} : 1.33 µM/L AsO_3	7.8	2	1.8×10^4	48
Fe^{2+} : 1.33 µM/L AsO_3	7.7	20	5.4×10^4	15
Fe^{2+} : 1.33 µM/L AsO_3	8.3	2	1.2×10^5	7

[a] All solutions contained 50 µM/L Fe

Comparison of the rate constants for As (V) and As (III) obtained here

for the second order kinetics with other work is very difficult as

little work has been carried out on the kinetics of As adsorption onto

Fe oxyhydroxides. Other studies have tended to concentrate on the

mechanisms of As adsorption by investigating the isotherm behaviour

derived from equilibrium data (Pierce & Moore, 1980 & 1982) or on kinetic

studies only indirectly related to Fe oxyhydroxides (Oscarson, et al.,

1983). This data can, however, be compared to kinetic data for the

adsorption of PO_4^{3-} onto Fe oxyhydroxides studied by Crosby, et al.

(in press) who postulated similar reaction processes. The comparison

gives quite good agreement, as can be seen from the summary provided in

table 4.9.

4.2.3.2 Aged Precipitates

Only a limited kinetic analysis of the uptake of As (V) and As (III)

onto aged Fe oxyhydroxides was possible. This was due to several factors.

Firstly, a number of the reactions were too rapid to allow analysis and

Table 4.9   Comparison of k_2 values for As and P data in seawater, $S = 34^o/oo$ (fresh precipitates) - Fe (II)

Solution Composition	pH	T(°C)	k_2 (L M^{-1} min^{-1}) AsO_4	k_2 (L M^{-1} min^{-1}) PO_4	T(°C)	pH	Solution Composition
Synthetic[a] :							Synthetic[b] :
	7.8	20	9.5×10^5	2.0×10^5	15	7.7	
	7.8	2	1.7×10^5	5.6×10^4	2	7.9	
Natural[c] :							Natural[d] :
	7.7	20	9.8×10^5	5.6×10^5	15	7.6	

a   All solutions contained 50 µM/L Fe and 1.33 µM/L AsO_4

b   All solutions contained 50 µM/L Fe and 1.00 µM/L PO_4

c   Minestream water Fe (T) = 65 µM/L, Fe (II) = 95%

d   Minestream water Fe (T)/Fe(II) levels not stated

secondly a number of the profiles did not fit any of the rate equations attempted and remain unresolved. In particular, none of the aged precipitates from natural water sources was analysable and this indicates that this area especially, requires further study. The remaining profiles which were amenable to analysis were found to conform to the second order rate equation utilised in the analysis of fresh precipitates.

The adsorption of As (V) onto Fe (III) at 20°C and pH 7.7 was slow at $k_2 = 4.46 \times 10^4$ L M^{-1} min^{-1} and $t_{\frac{1}{2}} = 22$ min, compared to the relevant Fe (II) profile. However, the rate constants were of the same order of magnitude and the equilibrium value for the Fe (III) reaction at around 60% was higher than that of the Fe (II) at 35% and indicates a greater surface area (section 4.1). The adsorption of As (III) onto Fe (III) at 20°C and pH 8.2 was slower, with $k_2 = 1.03 \times 10^4$ L M^{-1} min^{-1}, in keeping with the proposed redox requirement of this reaction. Less than 50% As (III) was adsorbed at equilibrium, preventing the calculation of $t_{\frac{1}{2}}$. The data for these reactions is plotted in fig. 4.38.

The case of As (V) adsorption onto aged Fe (II) precipitates (fig. 4.39) is interesting because it is in complete contrast to the behaviour of PO_4^{3-} in this pH range, which shows no adsorption (Crosby, et al., 1981). For AsO_4^{3-} the adsorption is inversely proportional to pH, and an explanation for this behaviour has been proposed in section 4.2.2.1.b. In the case of PO_4^{3-}, at pH 8.2 for example, the species composition would be 70% HPO_4^{2-} and 30% PO_4^{3-}, resulting in considerable electro-static repulsion which would prevent adsorption. The adsorption profiles for As (V) uptake were found to obey a linear relationship, which could be described by the equation :

$$\log_{10} k_2 = 6.99 - 0.37 \text{ pH} \qquad r^2 = 0.91 \qquad (4.22)$$
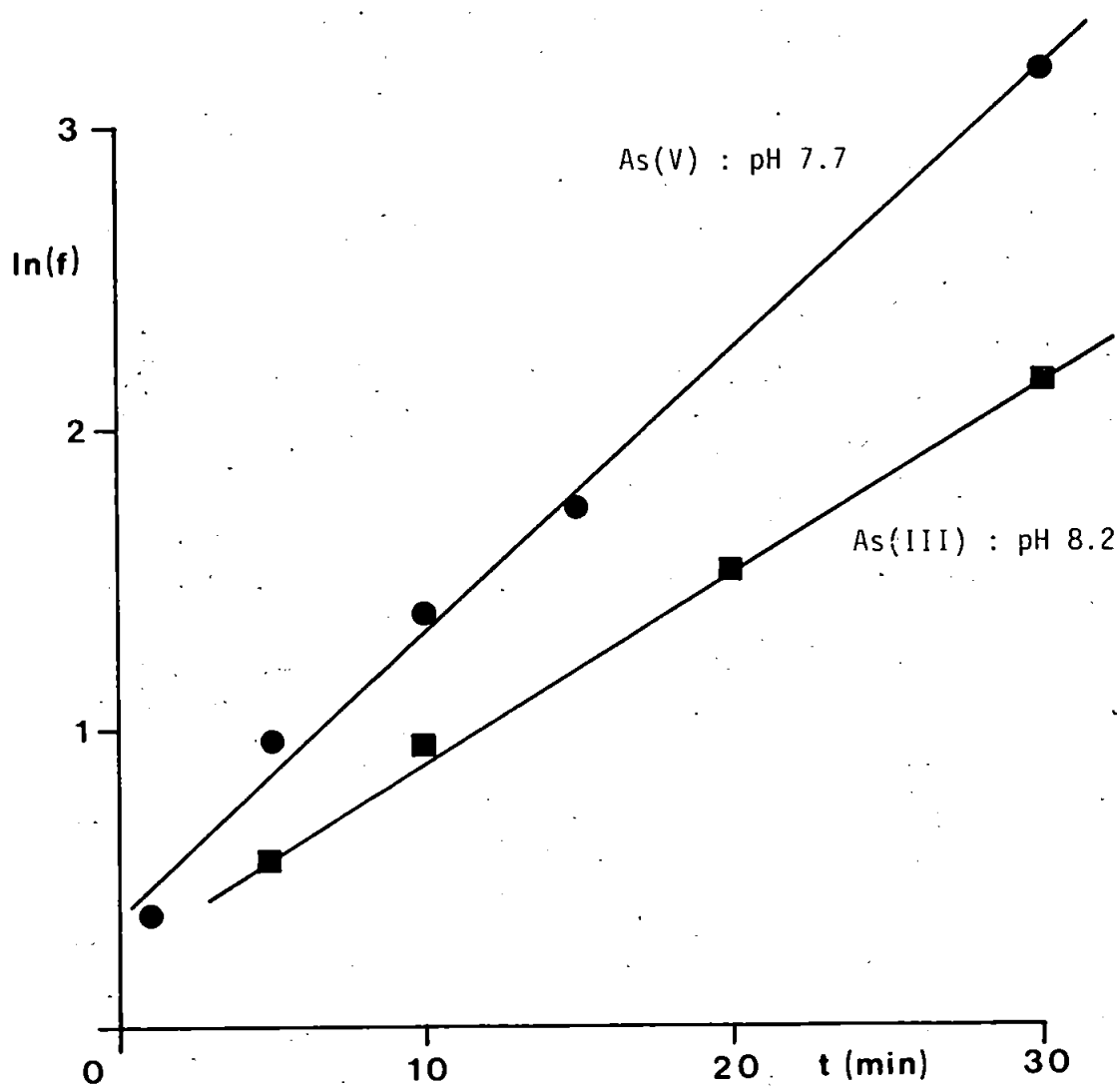
Figure 4.38   2nd order kinetic plots of AsO_4 and AsO_3 adsorption onto aged Fe (III) precipitates in seawater, $S = 34^o/oo$ at 20°C
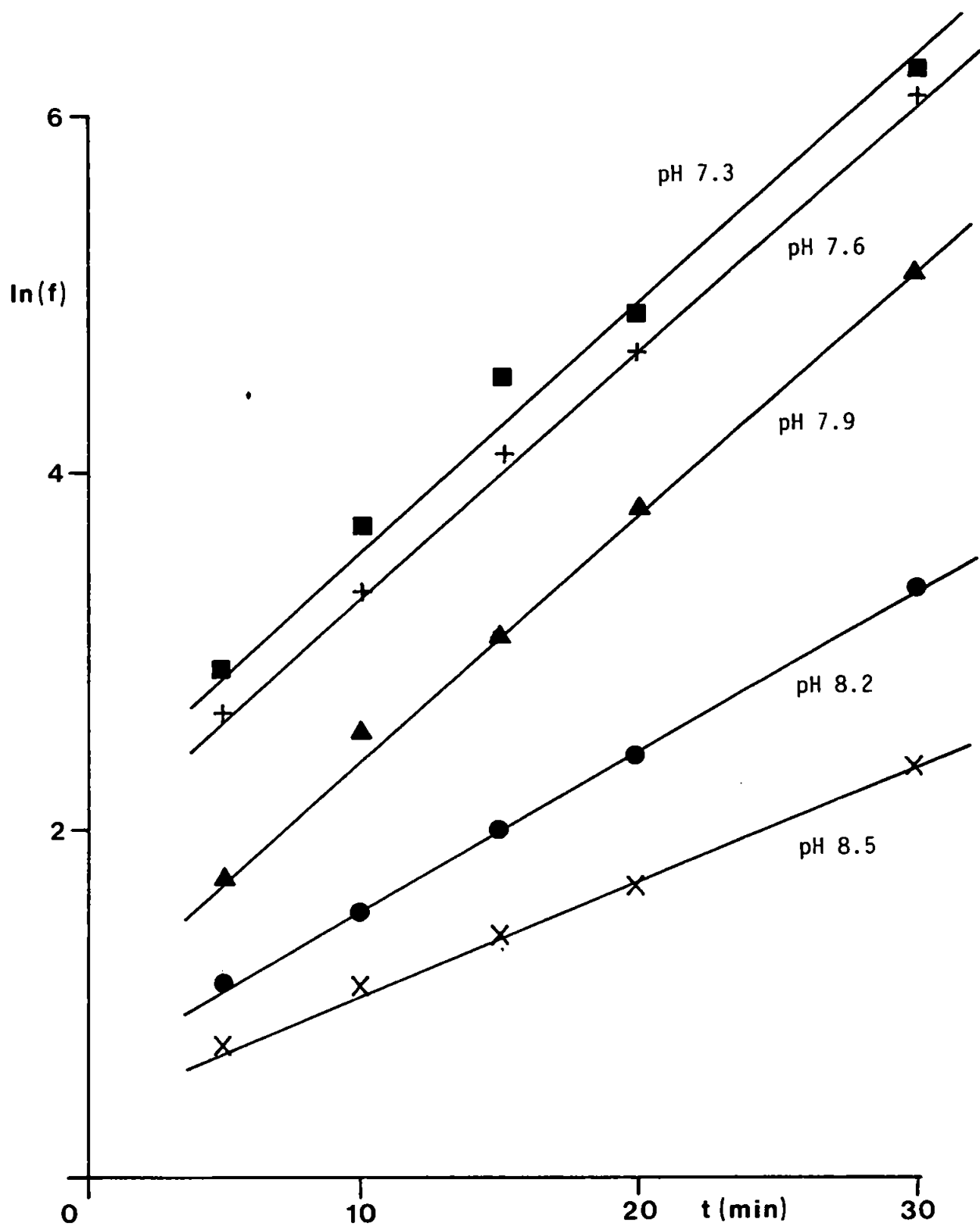
Figure 4.39   2nd order kinetic plots for AsO$_4$ adsorption onto aged
Fe (II) precipitates in seawater, S = 34^0/oo at 20^{0}C

The variation of rate constant with pH is summarised in table 4.10.

Table 4.10   Variation of k_2 value with pH for AsO_4 adsorption in seawater, $S = 34^{\circ}/oo$ (aged precipitates) - Fe (II)

Solution Composition[a]	pH	T(°C)	k_2 (L M^{-1} min^{-1})
Fe^{2+} : As^{5+}	7.3	20	1.8×10^4
	7.6	20	1.6×10^4
	7.9	20	1.5×10^4
	8.2	20	9.6×10^3
	8.5	20	6.3×10^3

[a]   Initial concentrations : 50 μm/L Fe and 1.33 μM/L As

Finally, only one profile for aged precipitates in freshwater was analysable and this gave $k_2 = 7.50 \times 10^4$ L M^{-1} min^{-1} and $t_{\frac{1}{2}} = 10$ min for As (V) uptake onto aged Fe (III) at 20°C and pH 7.1 (fig. 4.40).

Comparison of the aged precipitate rate constants produced here with other work is virtually impossible for the reasons stated earlier. In addition, comparison with values obtained for PO_4^{3-} by Crosby (1982) is limited because aged Fe (II) did not adsorb PO_4^{3-} and Crosby did not study adsorption onto aged Fe (III) at 2°C. There is, however, relative agreement between values for the adsorption of AsO_4^{3-} and PO_4^{3-} onto aged Fe (III) precipitates in seawater, allowing for the temperature difference (table 4.11).
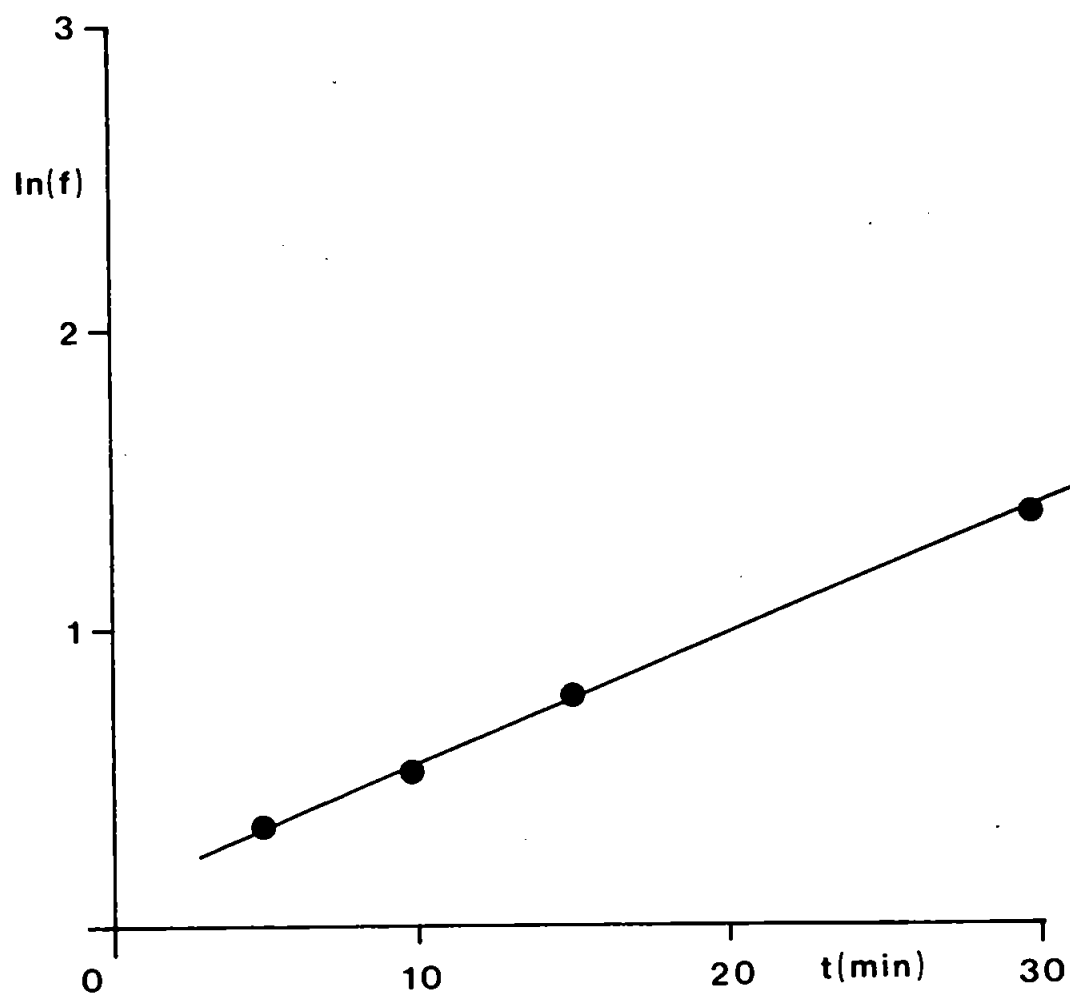
Figure 4.40   2nd order kinetic plot for AsO_4 adsorption onto aged
Fe (III) precipitate in freshwater, at pH 7.1 and 2°C

Table 4.11 Comparison of k_2 values for As and P data in seawater, $S = 34^o/oo$ (aged precipitates) - Fe (III)

Solution Composition[a]	pH	T(°C)	k_2 (L M^{-1} min^{-1}) AsO_4	k_2 (L M^{-1} min^{-1}) PO_4	T(°C)	pH	Solution Composition[b]
Fe^{3+} : As^{5+}	7.7	20	4.5×10^4	7.9×10^4	15	7.7	Fe^{3+} : P^{5+}
	8.2	20	1.0×10^{4}[c]	6.3×10^4	15	8.2	

[a] All solutions contained 50 µM/L Fe and 1.33 µM/L As

[b] All solutions contained 50 µM/L Fe and 1.00 µM/L PO_4

[c] Solution contained 1.33 µM/L $As=_3$ (As (III))

CHAPTER FIVE

CONCLUSIONS

5.1   General Discussion

In this section the data obtained from the environmental and laboratory studies will be assessed in relationship to the physical and chemical processes operating within the aquatic environment. The results of the laboratory modelling and kinetic analysis of As adsorption onto Fe oxyhydroxides will be integrated with an analysis of the estuarine surveys in order to draw conclusions regarding the behaviour of Fe, Mn and As in aquatic systems. Finally, an attempt will be made to assess the timescales of these processes with reference to aquatic environments.

5.1.1   Short-Term, Localised Processes

The short-term processes are defined as those occurring over timescales of seconds to hours and are best illustrated by the laboratory models. These laboratory modelling studies indicated the rate and extent of As adsorption onto Fe oxyhydroxides, under a variety of conditions.

5.1.1.1 Fresh Precipitates

Studies of fresh Fe precipitates, analogous to Fe inputs from acid minestreams, industrial effluents and pore water infusions at the sediment-water interface within an estuary, indicated that the speciation of Fe was important. Precipitates derived from Fe (III) sources were fast and efficient removers of As (III) and As (V), such that in both freshwater and seawater complete adsorption had occurred in < 1 min. This was related to the rapid nucleation of colloidal Fe to produce highly active

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porous precipitates with surface areas $> 200 \ m^2/g$. The temperature independence of these reactions (i.e. a zero activation energy) suggests a physical process of adsorption, and they were also found to be pH independent.

For inputs of Fe (II),,the situation was complicated by the fact that oxidation of Fe (II) to Fe (III) must take place before precipitation. In freshwater, the amount of As adsorbed at equilibrium was independent of pH, although the rate of adsorption was pH dependent. This was related to the influence of pH on the initial oxidation step, prior to the hydrolysis and formation of a precipitate. In seawater, two distinct adsorption regimes were observed. Kinetic analysis showed that at pH < 7.6 1st order adsorption kinetics were obeyed and the rate of uptake was related to the relatively slow appearance of the solid phase. The adsorption process itself was thought to be of a physical nature, being pH independent. The magnitudes of the 1st order rate constants obtained were similar to those obtained from studies of the oxidation of Fe (II). At pH > 7.6, the reactions were 2nd order, pH dependent and related to the adsorption process itself. The apparent activation energies involved were in the range 64-78 kJ/mole, which indicated a chemisorption process.

The fresh precipitate studies of natural waters showed good agreement with the synthetic models, indicating that the chemical analogues are probably a reasonable representation of the actual processes occurring in aquatic systems. The only discrepancies involved natural waters with a known high organic matter content. This had the effect of retarding formation of a precipitate and hence adsorption. The adjustment to $3^o/oo$ S of the model, however, enabled adsorption to proceed, although the profiles

obtained-were of the type associated with seawater models. This indicates both that the presence of organic matter does not affect the rate of As adsorption, only its initiation, and also that salinities of as low as $3^o/oo$ S will lead to adsorption behaviour akin to the seawater environment.

The rate constants calculated for some of these reactions gave half-lives in the range < 1-95 min, those exhibiting 1st order kinetics and those involving the adsorption of As (III) being significantly slower. The effect of lowering the temperature of these reactions was to decrease the rate of adsorption, as would be expected for a process with a measurable activation energy. This temperature effect is of potential significance in the estuarine environment, as it will lead to reduced adsorption rates in the colder, winter months, at a time when the dissolved As burden is potentially at its peak.

A further value of the kinetic data is that it can be used in a predictive capacity to evaluate the removal of As by Fe (II) precipitates in seawater. In this context the data can be of practical use in predicting the fate of arsenical wastes which are dumped at sea. In the case where AsO_4^{3-} wastes are disposed of in warm ($\sim$20°C) temperature ocean waters with a pH in the range 7.9-8.1, the interactions with freshly precipitating Fe (II) derived oxyhydroxides will take place with a $t_{\frac{1}{2}}$ of 1-3 min. Advective current velocities of the order of 0.1-1.0 m/s will result in a maximum transport from the dump site of only $\sim$200 m. Thus, the dispersion of AsO_4^{3-} wastes under these conditions will be limited to the vicinity of the dump site. Where the wastes are disposed of in cold ($\sim$2°C) polar ocean waters of pH 7.9-8.1, 1st order adsorption half-lives of $\sim$5 min

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and 2nd order adsorption half-lives of ~45 min are predicted. Given the same advective water movements, there is a greater potential for the lateral transport of As, which at its maximum would extend to about 2500 m from the dump site.

A further use of the predictive capacity of this kinetic analysis would involve the determination of the dispersion potential of estuarine dumped wastes, such as the Fe (II) waste resulting from the cleaning of titanium ores. The half-lives calculated show, however, when considered in relationship to the potential concentrations of Fe and As and the dilution factors involved in the riverine or estuarine environment, that the adsorption of As is effectively a localised phenomenon, the bulk of As being removed from the water column close to source.

This interpretation is supported by evidence from the S.E.M. studies, which indicated that only a small proportion of sediment particles was coated with Fe precipitates. This does not tie in with the authigenic formation of Fe coating within the estuarine sediments, but suggests that the process was allochthonous. This is also supported by the analysis of sediment metal distributions, which showed non-detrital Fe and As peaking close to the head of the estuary, during periods of high river flow and hence input, associated with the winter months. This is backed by a lack of discernably elevated levels during the low-flow, summer months, indicating a relatively localised dispersion. This can be linked to the relatively low geochemical mobilities of Fe and As (Levinson, 1980). It may also be influenced by the seasonal transport of sediment as described in the next section.

5.1.1.2 Aged Precipitates

In the case of aged Fe precipitates, the situation is somewhat different. These precipitates are analogous to inputs from crustal weathering, the solid phases resulting from mining activity and suspended particulates formed and aged during transport through an aquatic system. Their relevance to the adsorption of As, then, is largely their potential for removing As from an aquatic environment in situations remote from the source of input. This contrasts with the case of fresh precipitates, which, for the reasons stated above, are more relevant to the removal of locally input As.

The overall adsorption behaviour of aged Fe (II) and Fe (III) precipitates indicated a physical-type process and an electrostatic adsorption model was proposed to elucidate this behaviour with reference to Fe (II) and As (V). This physical adsorption behaviour was further supported by the apparent Freundlich-type isotherm derived for As adsorption onto Fe (II) precipitates. The equilibrium value for adsorption of As (V) onto aged Fe (II) precipitates was found to be inversely dependent on pH, which was related to the electrostatic interactions resulting from the speciation of the As (V). The enhanced uptake of As (V) onto aged Fe (II) precipitates observed in seawater was related to the co-precipitation of Ca and Mg under these conditions. Aged Fe (II) precipitates generally removed < 50% of dissolved AsO_4^{3-} in around 20 min, and in this case there exists the possibility for considerable transport and mixing in the dissolved phase.

The rate of As (III) adsorption onto aged Fe (III) precipitates was again found, as in the case of fresh Fe precipitates, to be slow compared to

As (V). This led to the proposal of a surface related Fe (III)/As (III) redox model (fig. 5.1), based on the observed non-adsorption of As (III) onto aged Fe (II) precipitates. A k_2 value of 1.0×10^4 L M^{-1} min^{-1} was found for As (III) adsorption onto an aged Fe (III) oxyhydroxide at 20°C and pH 8.2, virtually identical to that of As (V) adsorption onto an aged Fe (II) precipitate under the same conditions (9.6×10^3 L M^{-1} min^{-1}). This model is also relevant to the fresh participate case, as it requires the formation of a solid phase before the redox can commence. Here, a typical k_2 value of 9.5×10^5 L M^{-1} min^{-1} for As (V) adsorption onto a fresh Fe (II) precipitate at 20°C and pH 7.8, is reduced to $k_2 = 5.4 \times 10^4$ L M^{-1} min^{-1} for As (III), with a corresponding increase in $t_{\frac{1}{2}}$ from < 1 min to 15 min.

The other important aspect of the adsorption of As onto aged Fe precipitates was the observation of enhanced uptake at lower temperatures. Surface area studies of Fe (II) precipitates formed at 2°C demonstrated that the surface area was greatly increased, compared to those formed at 15-20°C, although the precipitates were still identified as γ-FeOOH. The formation of the less active γ-FeOOH precipitate from Fe (II) sources, compared to am-FeOOH derived from Fe (III) has been previously demonstrated (Crosby, 1982), and is related to the kinetics of their formation. The environmental significance of this increase in surface area with decrease in temperature is that the more active precipitate will be formed during the winter months, at a time of increased ground-water flow and higher dissolved metal concentrations. This will have the effect of increasing the potential removal capacity of the Fe precipitates at a time when the dissolved As concentrations will be greatest.

A natural particulate sample from the River Carnon, showed an Fe-like

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Oxide Surface	Boundary Layer		Bulk Solution
Fe^{3+}	Fe^{2+}		As^{3+}
	As^{5+} As^{3+}		As^{3+}
Fe^{3+}-As^{5+}			
Fe^{3+}	Fe^{2+}		As^{3+}
Fe^{3+}-As^{5+}			
	As^{5+} As^{3+}		As^{3+}
Fe^{3+}	Fe^{2+}		As^{3+}
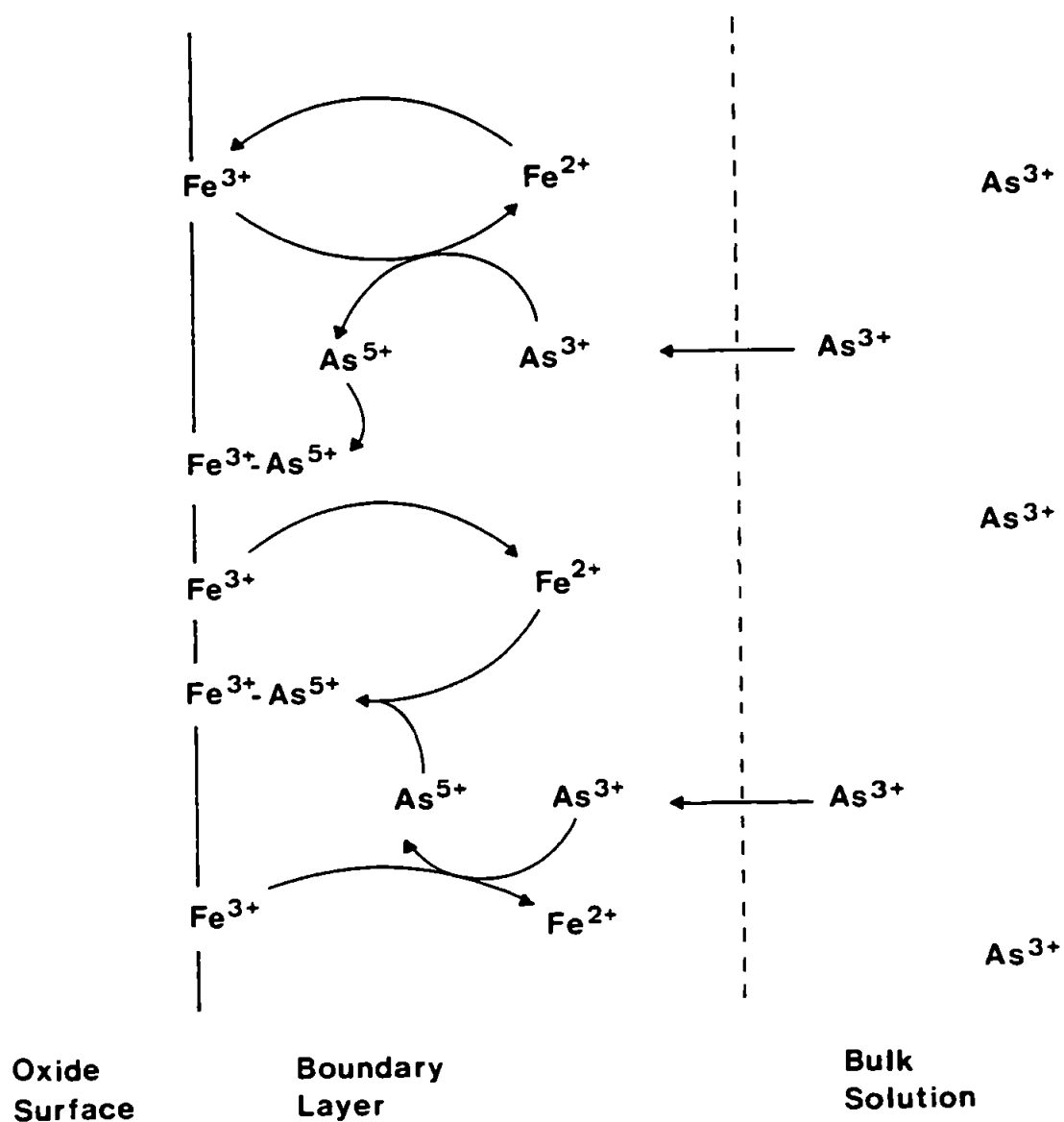
Figure 5.1   Proposed mechanism for the surface redox of As (III) on Fe (III) oxyhydroxide colloids

adsorption character, probably due to the presence of Fe coatings on the clay matrix. The analysis of Fe precipitates from natural sources indicated the presence of a mixture of oxides, making positive characterisation impossible. This mixture of oxides emphasised the complexity of factors affecting precipitate formation in the natural environment and explained the general lack of agreement between the adsorption behaviour of the synthetic and natural water models of aged Fe precipitates.

The kinetic analysis of these aged Fe precipitate reactions indicated that they were generally, but not significantly, slower than the corresponding fresh precipitate reactions. The adsorption capacity of these precipitates was, however, limited, with few adsorbing > 50% of the As available. It can therefore be concluded that although the potential exists for these precipitates to be carried into the estuary for some distance, the timescales of the adsorption reactions, compared to the timescales of estuarine processes, make them a relatively localised phenomenon (table 5.1).

5.1.1.3 A comparison of the Short-Term Adsorption Behaviour of P and As

The adsorption behaviour of P, another Group (V) element, onto Fe oxyhydroxides has been extensively studied by Crosby (1982). The uptake of these two elements onto fresh Fe (II) and Fe (III)-derived precipitates was found to be very similar, with similar kinetic regimes being identified, leading to half-life values of the same order of magnitude in freshwater and seawater. The adsorption behaviour of As is complicated by the existence of the two species As (V) and As (III). The behaviour of As (V) uptake was generally comparable with that of P (as PO_4^{3-}), with

Table 5.1   Summary of the short-term As adsorption processes occurring in the estuarine environment

Fe species	As species	T (°C)	$t_{\frac{1}{2}}$ (min)
Fresh precipitates:			
Fe(II)	As(V)	20	< 1
	As(III)	20	7 - 15
	As(V)	2	3 - 95
	As(III)	2	3^{a}
Fe(III)	As(V)	20	< 1
	AS(III)	20	9 - 48
	As(V)	2	< 1
	As(III)	2	1 - 16
Aged precipitates:[b]			
Fe(II)	As(V)	20	~20
Fe(III)	As(V)/As(III)	20	~ 5

[a] One natural water sample only - minestream water
Fe(T) = 10.6 mg/L, Fe(II) = 100%

[b] Estimates only, $t_{\frac{1}{2}}$ could not be calculated using methods employed here

As (III) reactions being mainly slower, due to the reasons outlined in the last section.

A distinct contrast, however, is found between the uptake of P and As onto aged Fe precipitates. Whilst similarities were observed for the uptake of these elements onto aged Fe (III) precipitates, in the case of aged Fe (II) precipitates AsO_4^{3-} was adsorbed whereas PO_4^{3-} showed no adsorption under the same conditions. This can be explained in terms of the different species composition of the two elements under similar conditions of temperature and pH. The pH_{zpc} of γ-FeOOH is around 6.2-6.9. For AsO_4^{3-} in seawater at pH 7.0 the major species are $HAsO_4^{2-}$ (83%) and $H_2AsO_4^{-}$ (16%) and at pH 8.2 there is 98% $HAsO_4^{2-}$ and ~1% AsO_4^{3-} (Turner, et al., 1981). If electrostatic interactions are important, as proposed, then increases in the fraction of species with higher negative charges would lead to increases in the electrostatic repulsion and a decrease in adsorption with pH increases. In contrast, the speciation of PO_4^{3-} is such that at pH 8.2 there is 70% HPO_4^{2-} and 30% PO_4^{3-}, so that considerable electrostatic repulsion exists between the anion and the oxide surface and no adsorption takes place.

5.1.2 Processes Occurring on the Estuarine Timescale

In the previous section it was concluded that the adsorption of As by Fe oxyhydroxides was a relatively localised phenomenon, occurring near to source in the case of fresh Fe inputs, or within a restricted area in the case of aged Fe precipitates, over timescales of minutes or hours. Evidence from the estuarine surveys conducted during this study, however, indicates that Fe-As interactions and pathways through the estuarine environment are influenced by other factors over the greater timescales

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associated with estuarine processes, such as seasonal variations in river flow rates and the transport of sediment within the estuary.

The estuarine surveys carried out on the River Tamar indicated that Fe was removed from the water column in the upper section of the estuary. This is consistent with the timescales proposed in the previous section for the precipitation of Fe and corresponds with peak concentrations of Fe observed in the non-detrital sediment component in this region. This is also the region of As removal from the water column in the majority of the surveys and a related peak in the non-detrital sediment. There is some evidence for seasonal variations in these levels, which was linked to the variations in ground-water levels in section 5.1.1. Significant correlations were found between Fe and As in the non-detrital sediment data. However, the non-detrital fractions of Fe and As were only ~10% of the total sediment burden and the major portion of these elements was present in the sediments in the detrital phase. The detrital levels of both Fe and As peaked in the uppermost region of the estuary, associated with mineralogical inputs of FeAsS from the mine tailings in the area. Strong correlations were found between Fe and As in the G.S. normalised sediment data, confirming their association in the weathered, silt fraction.

The spatial-temporal analysis of the River Tamar indicated that under conditions of low-flow, the fine grain material was concentrated in the upper and mid-sections of the estuary and at times of high-flow, it was concentrated in the middle and lower sections. This results in mass transport of sediment upestuary in summer and downestuary in winter. The analysis of Fe showed it to be highly variable in the upper and lower

sections of the estuary, linked to this sediment transport regime. This was true of both the detrital and non-detrital components, indicating that they are closely bound. The behaviour of sedimentary Fe within the estuary was therefore found to be largely dominated by physical processes.

The spatial-temporal analysis of As indicated that physical processes also dominated the detrital form of this element, due to its association with mineralogically derived Fe, but that the non-detrital phase was dominated by chemical processes. The non-detrital component of As was found to be removed from the sediment in the upper to middle region of the estuary, and this was reflected in a peak in the dissolved As concentrations in the water column in this region. Although peaks of dissolved Fe were observed in the high salinity regions of the estuary, which may have been due to resuspension of sediment reduced Fe, these did not correspond with the dissolved As peaks, and could be due to localised inputs of dissolved Fe associated with industrial sources in the area. Such localised Fe peaks were observed during other surveys of the River Tamar at high salinities (Marsh & Evens, unpublished data).

The resuspension of As did, however, more closely follow the observed resuspension of Mn within the estuary. This previously reported phenomenon (Morris, et al., 1978) is due to the reduction of sedimentary Mn (IV) to Mn (II), with its subsequent remobilisation. The work of Oscarson, et al. (1983) has shown the viability of a redox couple between Mn (IV) and As (III), and it is believed that this is the process operating here. Confirmation of this was obtained by the use of an adsorption/desorption model conducted on natural water from the River Carnon. This indicated that while Fe and As were removed from solution upon precipitation of the Fe, both Mn and As were desorbed from particulates collected from the same source. Taking

the non-detrital metal data of Mn and As for this particulate, and assuming a suspended solids content at the F.B.I. of 100 mg/L, gives a maximum potential contribution to the water column from desorption of 0.02 mg/L Mn and 51 µg/L As. The value for Mn is similar to the average resuspension value for the River Tamar of 0.05 mg/L Mn and high for As, with only some 0.5-3.0 µg/L As being resuspended on average. This figure would, however, be reasonable if Mn were releasing the As, for only a proportion of the available As is likely to be remobilised. It must be borne in mind, though, that these figures are only a very rough guide, as the values are taken from the River Carnon, which has much greater levels of dissolved and sedimentary Fe, Mn and As compared to the River Tamar, and an apparently very different estuarine chemistry for these metals.

This behaviour is in agreement with the sedimentary composition of Mn, which is present largely (80-100%) in the non-detrital form. This is probably derived from the weathering of FeAsS, which is known to contain large amounts of Mn (Fleischer, 1955), and is confirmed by significant correlations for Mn, with Fe and As in the total sediment fraction. Further confirmation of a redox couple between Mn and As comes from an As speciation study carried out on the River Tamar. It showed that dissolved As is present in the estuary predominantly as As (V), with a constant, small, background level of As (III). The resuspension peaks of As observed were due entirely to As (V). A semi-quantitative estimate of the contribution of As to the water column from pore water injection in the River Tamar was calculated in Chapter 3, based on the data of Langston (1983, personal communication). This gave a range of 0.12-0.26 µg/L As, which is low compared to the average 0.5-3.0 µg/L As observed. These estimates contrast, however, with the average 3.0 µg/L As calculated by Langston (1983, personal communication) himself.

5.1.3   The Effect of Physicochemical Factors on the Timescale of Estuarine Processes

Physicochemical factors such as pH and the speciation of the dissolved metal inputs into an estuary can affect the timescales over which the individual processes previously discussed operate. This can alter the overall behaviour of individual elements within a particular estuary. The dissolved metal surveys carried out on the River Carnon indicated that in this estuary, the behaviour of Fe, Mn and As in the water column was significantly different to that exhibited in the River Tamar. These results, however, do not conflict with the conclusions proposed on the basis of the River Tamar data. Rather, they indicate the variability that exists between individual estuaries and the effect that different environments can impose on the magnitude and timescales of the processes involved.

The profiles of dissolved Fe in the River Carnon indicated a conservative mixing behaviour on two occasions. This was thought to be due to colloidal Fe passing through the 0.45 μm filter, although subsequent analysis could not establish this. The remaining surveys indicated removal of Fe within the estuary. No resuspension was observed. A similar profile was followed by As, with resuspension occurring at low salinities on several occasions. This was thought to be associated with run-off from the extensive mudbanks found in the middle region of this estuary. No resuspension was observed in the higher salinity regions, analogous to that found in the River Tamar. The speciation studies conducted showed that As was present predominantly as As (III), in contrast to the River Tamar, with As (V) appearing only in the higher salinity regions, presumably as a result of in situ oxidation. Manganese

exhibited a conservative or removal profile in the estuary, with no evidence of resuspension occurring.

These profiles contrast sharply with those obtained in the River Tamar, and reflect the different conditions pertaining in the River Carnon. This river is subject to continuous inputs of Fe/As waste from active mine workings, and the river upstream of the estuary has a pH of ~3.5. This results in a large dissolved metal burden in the river and levels of Fe, Mn and As in the estuary are generally an order of magnitude higher than those of the River Tamar. The effect of this low pH is to maintain a high dissolved metal component in the water column by greatly reducing the rates of oxidation and hydrolysis of the Fe present. The adsorption experiments conducted on water from the Carnon showed that an increase in pH was all that was required to initiate precipitation. The timescales of the short-term adsorption processes described in section 5.1.1 are therefore extended so that the majority of As adsorption now takes place within the main body of the estuary.

Klumpp & Peterson (1979) have indicated that As is input into the River Carnon as As (III), and the low pH of the river retards the oxidation process to As (V) within the water column. The lack of a Mn remobilisation cycle within this estuary prevents the resuspension of Mn oxidised As (V) into the water column. Why Mn is not reduced in the sediments in this case is difficult to explain. It is possible, because of the relatively high dissolved metal levels present, that the remobilisation, if it were occurring on the same scale as that in the River Tamar, is simply not seen in this estuary, because of the high total metal content.

5.1.4   The Physical and Chemical Timescales of Arsenic Cycling within the Estuarine Environment

It is now possible, in the light of the conclusions drawn in the previous sections regarding the timescales of physical and chemical processes occurring within the estuary, to summarise these processes in diagrammatic form. This is done in fig. 5.2. This diagram is based on the data pertaining to the River Tamar. The timescales for the individual chemical processes illustrated are based on those given in table 5.1. The conclusions of section 5.1.3 must be borne in mind, however, for the exact magnitude of these processes will vary between estuaries, depending on a number of factors. These include the pH and temperature of the riverine and estuarine regions, the levels of dissolved metal inputs, the topography and hydrography of the estuary and its flushing time.

5.2   Recommendations for Further Work

It has become apparent from the discussion in this work that certain areas of investigation require further attention and also that certain new areas of research need to be initiated, on the basis of the conclusions drawn from this study. Briefly the recommendations for further work are as follows:

1.   A larger database of water column and sediment metal levels is required, collected on specifically designed surveys, to elucidate the seasonal influence on Fe, Mn and As cycling within the Tamar estuary. These extended surveys should include an investigation of pore water metal levels and of metal speciation. A study of the sediments in the
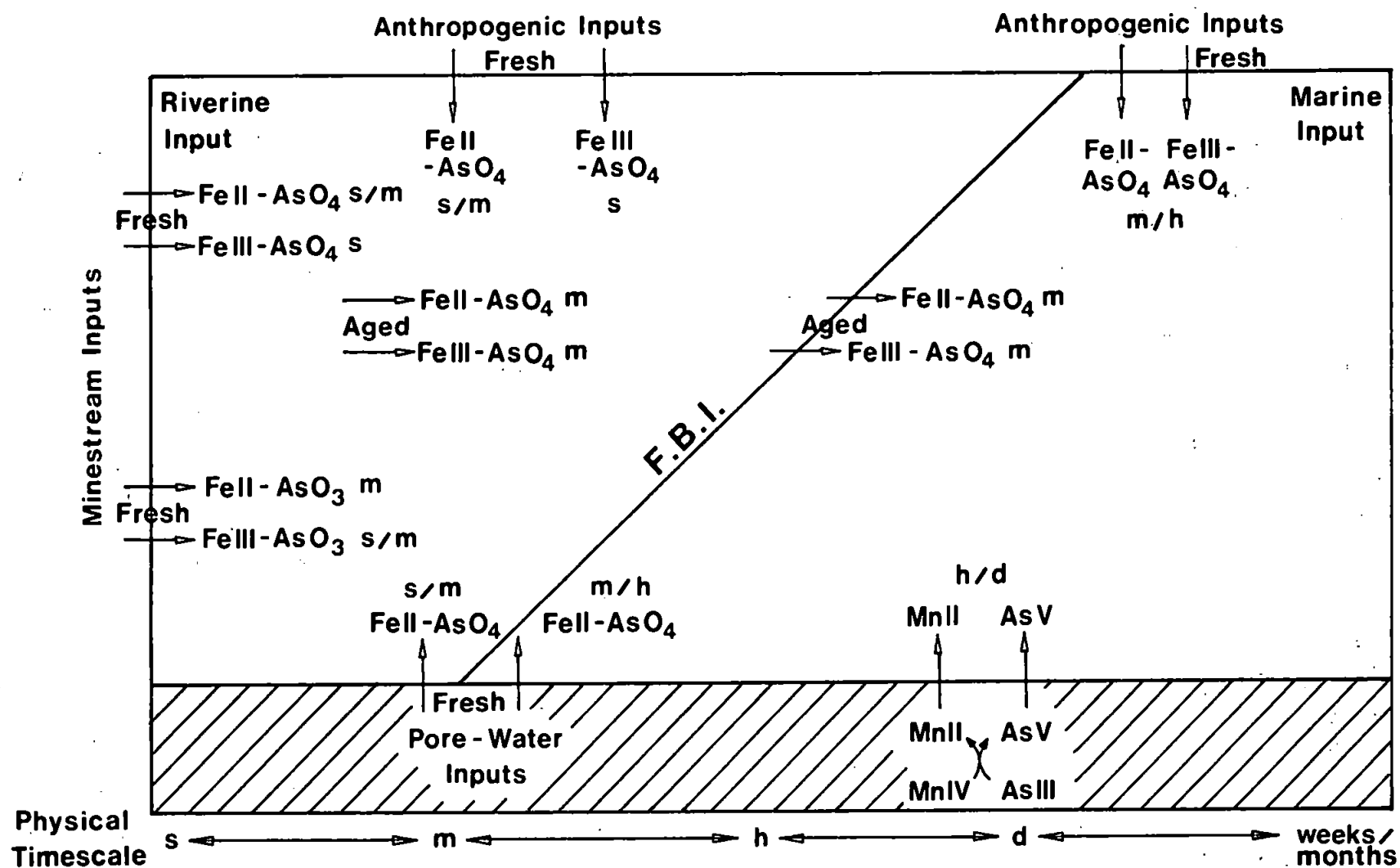
Figure 5.2 The physical and chemical timescales involved in the estuarine cycling of As within the River Tamar. For quantitative values of chemical processes, see table 5.1.

River Carnon estuary is also required, in order to complete an under-standing of the processes operating in this possibly unique environment. The proposed model for As cycling can then be further refined.

2.   Further investigation of the characterisation of natural Fe precipitates is required, in order to elucidate the factors influencing the complex nature of these oxyhydroxides, when compared to those precipitated in the laboratory. This work must be complemented with further modelling studies of aged Fe precipitates from natural waters, so that the kinetic basis of these reactions can be explained.

3.   An important factor in the cycling of As in aquatic systems that has been revealed in this study is the existence of a redox couple between Mn and As in the environment. This should be followed up by laboratory modelling studies, on both synthetic and natural media. This would help to elucidate the exact extent of such a reaction, and in combination with further environmental studies of the River Carnon, should help to explain the contrasting behaviours observed between this estuary and that of the River Tamar. These studies should also help to determine the relative roles of desorption from suspended particulates at the F.B.I. and pore water injection into the water column, with regard to the resuspension of As.

4.   Extensions to the present work would include the addition of further components to the laboratory modelling system. A priority in this area would be the investigation of organic complexation in aquatic media. This would be a complicated procedure because of the complexity of organic matter. However, the initial steps would involve the use

of totally organic-free media, followed by the introduction of fully characterised humic acids. Alternatively, simpler organic acids, such as citric acid, might be studied. These have a known complexing capacity for metals and are present in the natural aquatic environment. Other modifications which could be made to the modelling system include the study of Eh variation and dissolved O_2 concentration.

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APPENDIX I

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
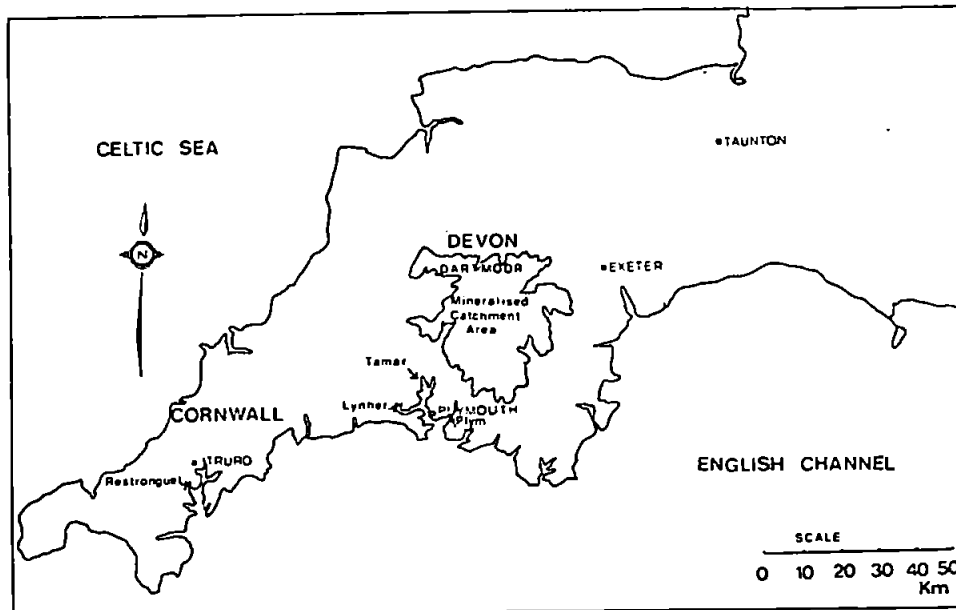

Fig. 1. The south-west peninsula of England showing the location of the Tamar and Lnyher Estuaries and the mineralised catchment area of Dartmoor. Restronguet Creek, Cornwall, also receives acid mine waste.

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)

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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 Tamar[a] (range)	274 545—154	317 605—221	150 239—19	— —	289 1500—105	23,120 49,000—21,000	50.7 25—236	2.1 1.5—0.2	10.5 2.3—16.5	This work Ackroyd & Marsh (1981)
Plym	—	256	—	9.3	171	12,100	41	0.35	4.1	Langston (1980) Millward & Herbert (1981) Bryan & Hummer-stone (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.

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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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