UNIVERSITY OF SOUTHAMPTON

The kinetics and mechanisms of destabilisation and aggregation of microcolloidal iron and associated phosphate during simulated estuarine mixing.

By

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of the degree of Doctor of Philosophy.

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Abstract

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The removal of iron from the <0.45μm fraction of Tamar River water on addition of both calcium chloride solution and sea water was studied using a continuous autoanalytical system. The addition of increasing concentrations of either calcium ions or sea water caused increased iron removal, but at all of the concentrations studied a fraction of iron was found to remain within the <0.45μm fraction (termed the residual or unreactive fraction). Storage time was shown to have a marked effect on the residual concentration. Kinetic analysis of the experimental results showed that when a residual fraction was taken into account, the data could be described by either a first or second order kinetic model. The first order model gave an approximately linear increase in rate constant with increasing concentrations of calcium ions or sea water, ranging from 1.02 $x10^{-3}$ to 6.14 $x10^{-3}$ s^{-1} for the addition of calcium ions and from 3.97 $x10^{-3}$ to 6.95 $x10^{-3}$ s^{-1} for the addition of sea water. The second order rate constant also showed an increase with increasing calcium concentration, from 3.95 $x10^{-5}$ to 3.02 $x10^{-4}$ l mol^{-1} s^{-1}. When the first and second order profiles were studied and the fit of the model to the experimental residual values was considered, the first order was shown to be a better descriptor of the observed removal of microcolloidal iron.

A comparative study was made of iron removal under different conditions of simulated estuarine mixing, following the procedures of Fox & Wofsy (*Geochim. Cosmochim. Acta*, 1983, vol 47 p211), Mayer (*Geochim. Cosmochim. Acta*, 1982, vol 46 p2527), Hunter & Leonard *(Geochim. Cosmochim. Acta*, 1988, vol 52 p1123) - all using 'discrete sampling during mixing and Duffy (PhD Thesis, University of Southampton) - using continuous sampling with more rapid mixing. Variations among the 'discrete' methods are small relative to those between them and the method of Duffy (1985) e.g. 65 % for the 'continuous' method as compared with 36%, at a salinity of 5, and the first order rate constant was seen to be about an order of magnitude greater for the 'continuous' method e.g. 3.97 $x10^{-3}$ s^{-1} as compared with 1.97 $x10^{-4}$ s^{-1}, at a salinity of 5. Further experiments looking specifically at the effect of stirring rate on a 'discrete' sampling method concurred with these observations. In experiments carried out at a salinity of 8, the iron removal increased from 44% to 55% and the first order rate constant increased from 2.96 $x10^{-3}$ to $3.58x10^{-3}$ s^{-1} as a result of a relative increase in stirring rate from 1 to 5. The fact that the first order rate constant for iron removal varied with the energy of the system, even in the least energetic system studied, and that under all conditions the first order model provided the best descriptor of the observed process, showed that the mechanism of microcolloidal aggregation under all these conditions could not be accounted for by Brownian Motion. Shear must therefore be a significant factor and it was concluded that none of the systems studied could afford a test of kinetic order under conditions where Brownian Motion dominantly accounts for particle collisions. The experiments, however, are still of relevance to environmental conditions, since estuarine mixing is greatly influenced by turbulence due to tidal energy and wind stress.

Phosphate behaviour was studied concurrently with that of iron and both the percentage removal and kinetic rate constants showed comparable dependence on calcium ion / sea water concentration, although the percentage phosphate removal was consistently lower than that observed for iron. Kinetic rate constants ranged from 0.0019 to 0.0179 s^{-1} for the first order model and 0.29 $x10^{-4}$ to 5.3 $x10^{-4}$ l mol^{-1} s^{-1} for second order. When the removal profiles were studied and the fit of the first and second order models to the experimental residual values was considered, the first order model was again shown to be a better descriptor of the observed removal. Phosphate behaviour remained essentially unaffected by changes in experimental methodologies or stirring rate. The factor which most affected iron (stirring) had no major systematic effect on phosphate and therefore it must be concluded that the results indicate a co-removal of phosphate during iron colloid aggregation rather than removal of a common colloidal population containing both constituents.

This work is dedicated to all of the long lost hours and days, alone at a desk while outside the sun shone and the rest of the world played. To all of the infinitely more pleasurable things that time could have been spent doing, that were passed over in the endless pursuit of scientific endeavour.

But most of all this work is dedicated to Penelope Louise Raymond, without whom I could never have persevered and spent all of those long hard hours finishing this thesis, but without whom those hours would have been wasted anyway.

To my darling Pens with all of my love..........

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Chapter One

Introduction and Literature Review

1.1. General Introduction

Estuaries represent a dynamic zone of mixing between river water and coastal sea water; consequently the estuarine environment is of fundamental importance to our understanding of the geochemical cycle of weathering, transport and sedimentation. Fairbridge (1980) defined an estuary as :

> " an inlet of the sea, reaching into a river valley as far as the upper limit of the tidal rise, usually being divisible into three sections :
>
> a) a marine, or lower, estuary in free connection with the open sea.
> b) a middle estuary subject to strong salt and fresh water mixing.
> c) an upper, or fluvial, estuary - characterised by fresh water, but subject to daily tidal action. "

This definition covers the majority of brackish water regions, including coastal plain estuaries, fjords, some gulfs, sounds and inlets. It is important to note that estuaries may both influence and be influenced by fluctuations a considerable distance from the defined estuarine region, in plumes extending beyond the topographic limits.

There are a number of variables controlling the composition and physico-chemical characteristics of riverine input into estuaries. The major factors include: drainage basin lithology, land use, amount and composition of rain in catchment area, surface and ground water run off, climate, anthropogenic inputs and ongoing terrestrial and riverine processes (Dyer, 1973; Burton, 1976).

The estuarine reactivity of components is largely governed by the physical and chemical relationships between trace metals, organic material, hydrous iron oxides and major sea water cations (Burton, 1976; Liss, 1976; Olausson & Cato, 1980). The mixing of fresh and saline waters, occurring in estuaries, induces a variety of chemical interactions. Accordingly there are zones in which there are major changes in physicochemical properties and in composition (Dyer, 1972; Phillips, 1972; Burton, 1976). Since the major transport of continentally derived material occurs through estuaries, the estuarine environment may influence the flux of continentally derived riverine material to the open ocean. Many estuaries are effective in retaining sediments from both riverine and marine sources. The marked changes in physicochemical properties within estuaries together with unusually high concentrations of suspended particulate material (SPM) give rise to the transfer of elements between dissolved and particulate phases (Pomeroy *et al.,* 1965; Subramanian & D'Anglejan, 1973; Aston & Chester, 1973; Sholkovitz, 1978; Sholkovitz & Copland, 1981). Such transfers are believed to act as a major control on the composition of estuarine waters and play an important role in the determination of source and sink functions within estuaries. Reactions that take place within estuaries are predominantly between dissolved and mineral phases, though biogenic particles can also play important roles, primarily involving elements and compounds located at particle surfaces. It is important to emphasise the heterogeneous nature of estuarine particles. Particulate matter is present in all estuaries from the limits of material in true solution, through the colloidal state, to readily filterable particles. There are spatial, temporal and intra estuarine variations in particle populations and their size distribution. The shape and density of particles is dependent to some degree on their composition and origin - which can be from one of three sources: lithogenous - inorganic and derived ultimately from erosive weathering of continental material; authigenous or hydrogenous - material generated in the aquatic phase or biogenous - generated by biological processes. All estuarine particles, regardless of composition, possess a net negative charge - due to the presence of a ubiquitous coating of organic material, the composition of the which varies between estuaries (Hunter & Liss 1979). The stability of colloids and small particles transported through estuaries is controlled by surface electrical properties, the nature of this organic coating governs the stability of the particles throughout the estuarine region. There is a general trend of decreasing stability with distance down the estuary, as salinity increases. It is also essential to characterise surface properties of particles to gain an understanding of the interaction of trace metals and organic compounds between dissolved and particulate phases. Specific surface area, heat of immersion and cation exchange capacity are surface properties that can only be calculated for a particle population, rather than individual particles. It is very difficult to get data on individual particles; one of the few properties that can be individually determined is the electrophoretic mobility - which gives the surface charge and an indication of stability. More accurate characterisation of particle surfaces awaits further developments in our understanding of surface chemistry.

Although there are no unique chemical, physical or biological processes operating within individual estuaries, the extent to which they occur reflects the environmental parameters applicable to the specific system. Wide behavioural differences are noted between elements in a given estuary and considerable variation is also noted in the behaviour of individual species between estuaries and in some cases in a particular estuary at different times. This estuarine variability is caused by differences in distribution of reactants and their rates of reactivity between estuaries or temporally in a single system. These factors are themselves controlled by fluctuations in environmental factors such as hydrodynamic residence times, the nature of inputs and internal mixing, as well as transport processes. Temporal and spatial variation in distribution and chemical forms of elements within estuaries arise from continuous fluctuations in inputs and on the efficiency of internal processes such as vertical mixing, biological productivity.

Aston (1978) summarised some of the major controls on estuarine behaviour thus :

- Tidal mixing on a semidiurnal / diurnal timescale, producing temporal changes in the contribution of species from sea water and fresh water *e.g.* estuaries enriched in nutrients with respect to oceans.

- Circulation and / or stratification leading to vertical / horizontal variations of species within estuaries.

- Estuarine topography which can lead to restricted circulation *e.g.* fjords - where mixing is greatly reduced thus altering the chemical environment.

- The current regime which affects the deposition and resuspension of sediments within estuaries.

- Chemical reactions occurring during mixing which can cause addition or removal of species.

- Biological production and metabolism which affect especially the distribution of nutrients and some gases *e.g.* CO_2 and O_2.

Many studies have been carried out since the 1970s and in an effort to collate this wealth of material, several authors have reviewed the chemistry of estuarine processes : Church (1975), Burton & Liss (1976), Aston (1978), Olausson & Cato (1980), Morris (1983), Head (1985) and Burton (1988). Two distinct approaches to studies of flux changes throughout estuaries can be recognised :

> **1) Field Observations** - this approach involves a comprehensive study of the chemical species within the estuary and their distribution in order to identify the existence of sources and sinks for the different species. In order to gain the quality and quantity of information required for such a study, in depth field surveys must be undertaken. Morris (1983) and Head (1985) provide thorough guides to estuarine study.

The simplest way of analysing the data from a field study is by way of property / salinity plots, usually referred to as mixing diagrams. From these plots changes in the concentration of a species from fresh water to coastal sea water can be observed. If a linear relationship is observed between the concentration of the constituent and the salinity throughout the estuary the component is said to show conservative behaviour. Boyle *et al.*, (1974) pointed out that curvature in the mixing diagram was indicative of non-conservative behaviour during estuarine mixing. Non-conservative behaviour can encompass addition or removal of the component, or a combination of both throughout the estuary. Further information can be gained on the repeatability and seasonal variation of the behaviour of species by carrying out rapidly repeated transects in the same region. Another refinement, though one less commonly employed is to sample simultaneously at a number of sites - giving exact conditions over a wide area at a specific time. A different approach involves the use of a Lagrangian method of following a body of water throughout the estuary and observing the changes it undergoes (Uncles *et al.,* 1983).

> **2) Laboratory Simulation** - the laboratory based approach involves the simulation of the estuarine environment under controlled conditions. This enables specific processes to be isolated and individually studied, to give information on rates of reactions and mechanisms.

There are a number of approaches to estuarine simulation that can be employed, the most simple being batch mixing. Samples of river and sea water endmembers are mixed together in suitable proportions to create the desired salinity and analysis is carried out on the mixture (Sholkovitz, 1976; Eckert & Sholkovitz, 1976; Boyle *et al.,* 1977; Sholkovitz *et al.,* 1978; Fox & Wofsy, 1983). A refinement on this process is to study the changes in concentration of the species through time, following a batch mixing experiment, via either continuous autoanalytical techniques or by analysis of discrete samples taken at known time intervals. Such studies can be used to examine kinetics of the processes of removal or addition occurring during the mixing (Mayer 1982b; Duffy 1985; Hunter & Leonard 1988).

Batch mixing experiments represent an oversimplification of the situation occurring in real estuaries as the direct addition of sea water to river water may bring some of the constituents into a salt induced regime they would not normally experience. In real estuaries mixing occurs in a continuous manner, there is seldom direct mixing of fresh and saline endmembers, with the exception of fresh water seep into saline waters. A more accurate approximation of estuarine mixing is provided by a continuous mixing experiment.

Two different experimental approaches to continuous mixing have been used :

- That introduced by Smith & Longmore (1980) who utilised a beaker, with a sidearm overflow to maintain constant volume, filled with river water and continuously stirred. Sea water was continually added to the beaker, causing a gradual increase in the salinity of the mixture, simulating the salinity gradient over the estuarine region. Analysis can be carried out on the water removed from the system via the overflow arm.

- That of Bale & Morris (1981) who described a more advanced system consisting of five adjacent constant volume reaction tanks. Gradual mixing occurs throughout the tanks with one side being supplied with river water endmember and the opposite side having sea water pumped into it. This system provides an adaptable laboratory analogue of a one dimensional estuarine mixing profile.

Such laboratory experiments detailed above are of great value as they allow particular processes to be isolated, for detailed studies of the effects of various parameters on them. They do, however, provide only a small scale simulation of the estuarine system. It is also desirable to create a more holistic analogue of the large scale natural ecosystem, allowing the biological processes and sediment interactions to be studied more thoroughly, under controlled conditions. Such simulations are known as micro- or mesocosms, depending upon the size of the simulation. A microcosm is a collection of sediments, organisms belonging to various trophic levels and chemical species, composed in such a way that their mutual relationships are similar to those found in nature. Within such a system, the physical and biotic variables: light input, benthic surface area to water volume ratio, flushing time, composition and density of flora and fauna and turbulence values, can all be adjusted to approximate the field conditions. Microcosms can be used to study the effects of environmental parameters on the fate, movement, potential bioaccumulation and interaction of chemical constituents under controlled experimental conditions. The size of the microcosm can vary considerably - ideally being large enough to incorporate as much, or as many of the ecosystem components as possible without sacrificing the ease of replication, manipulation and response measurements. The Rhode Island mesocosm uses a number of 150 litre water tanks (Perez *et al.*, 1977; Oviatt *et al.*, 1977) whereas the Texel aquarium houses a number of experimental halls, ranging in size from ~10 - 450m^3 (De Blok, 1975).

For the study of the effect of flow characteristics (and other physical parameters) on the ecosystem, it is necessary to create a more accurate approximation of the sediments and currents acting in the region studied. Flumes can be used to simulate flow conditions, either in the laboratory (Nowell & Jumars, 1987) or *in situ* (Amos *et al.*, 1992). Laboratory simulations do not provide an exact picture of the estuarine environment, but assist formulation of theories of constituent behaviour. Basic information on behaviour of a chemical species can be acquired by an estuarine field study *e.g.* whether the species behaves conservatively or non-conservatively during estuarine mixing. Once the general processes have been established, mixing experiments can be carried out under controlled conditions *e.g.* variables such as temperature, Eh, pH, concentration of associated species and salinity can all be individually controlled and isolated, to gain insight into those which affect the process under investigation. Using the observations from the laboratory experiments, a hypothetical model of the behaviour of species can be formed and applied to the real estuary. The model can then be further refined, if necessary, and used to gain information on the rates of processes and used as a basis for a mechanistic explanation of the observed behaviour. A combination of estuarine study and laboratory experiments can be used to maximum effect to achieve a clearer insight into behaviour in the estuarine environment.

Trace metals are an important group of constituents, representing a wide range of reactivities and behaviours. The chemical form in which the trace metals occur, along with the physical properties and the chemical, physical and biological constraints of the system, influence the behaviour to a large extent.

Trace metals can occur :-

i) in solution - as inorganic ions or organic / inorganic complexes.
ii) adsorbed onto particulate surfaces.
iii) in solid organic particles.
iv) coating detrital particles - co-precipitation / sorption with Fe/Mn oxides.
v) in lattice positions of crystalline material.
vi) precipitated pure phases.

These species can then interact by flocculation, precipitation, chelation, complexation, sorption or biological processes.

The importance of the transfer of elements between particulate and dissolved phases must also be taken into consideration as a control on the composition of estuarine waters, including transfers with bottom sediments. The differences in behaviour of various trace metals in their transfers with bottom sediments is believed to be related to differing degrees of mobilisation.

The definition of the 'dissolved' fraction is usually based on an arbitrarily defined cut off between particulate and non particulate phases - conventionally defined as that fraction which can be separated from larger particles by filtration through a 0.4-0.5μm pore size filter. This operational definition of dissolved material is well recognised and widely used throughout most facets of water quality analysis, though the nature of filters used to separate the fractions may vary between studies.

During estuarine mixing, a net removal has been observed for dissolved iron, nickel, cobalt, copper and manganese in a number of estuaries. The degree of removal varies markedly between the elements and it is thought that a number of independent processes may be responsible for these observations.

In the laboratory mixing experiments of Sholkovitz (1978) the following observations of behaviour of the dissolved trace metals, iron, nickel, cobalt, copper and manganese was observed:

Element	% Removal During Estuarine Mixing
Iron	95%
Manganese	25-45%
Copper	40%
Nickel	40%
Zinc	20%
Cobalt	10%
Cadmium	5%

Table 1.1 - Dissolved trace metal removal (Whatman GF/F) during estuarine mixing in the Waters of Luce, Scotland. Sholkovitz (1978).

Though this removal is widely observed in a number of estuaries, there is a definite variability in behaviour of each specific element between estuaries, as explained previously. This invariably leads to interpretation and modelling of estuarine behaviour being complex and requiring some degree of simplification *i.e.* laboratory experiments, to elucidate the mechanisms of these processes.

Iron is abundant in river water, and exhibits changes in its oxidation state in response to redox conditions, this has major consequences for its geochemical cycling - see section 1.3, on the speciation of iron. In a number of studies of estuarine behaviour, (Coonley *et al.,* 1970; Holliday & Liss, 1976; Sholkovitz., 1976; Boyle *et al.*, 1977; Fox, 1984; Duffy, 1985 and many others) 'dissolved' iron (i.e. the fraction passing a conventional filter with a nominal cut off in the region of 0.4μm filter) has been seen to exhibit the most markedly non conservative behaviour of all of the trace metals during estuarine mixing (see example in Fig 1.1). This behaviour is thought to be due to the rapid coagulation of microcolloidal iron by both electrostatic and chemical destabilisation of iron-humic colloids (Eckert & Sholkovitz, 1976). This process is of environmental significance as it is ubiquitous in estuaries receiving river water rich in iron and dissolved organic carbon (DOC) and because a large number of trace metals, nutrients and also pollutants are believed to co-precipitate with or adsorb onto the hydrous iron oxide phase.

One such species thought to interact with this iron rich material is orthophosphate, which is the major form of dissolved phosphorus in river waters. The behaviour of dissolved phosphorus in estuaries is of importance due to its presence in fertilisers and domestic waste, its importance as a major nutrient and also because of its links with eutrophication. Due to the environmental significance of both iron and phosphate, and their proposed relationship during estuarine mixing - one aim of this study is to attempt to elucidate the kinetics of destabilisation and the mechanisms of removal of the two species and subsequently to quantify any links between the species.

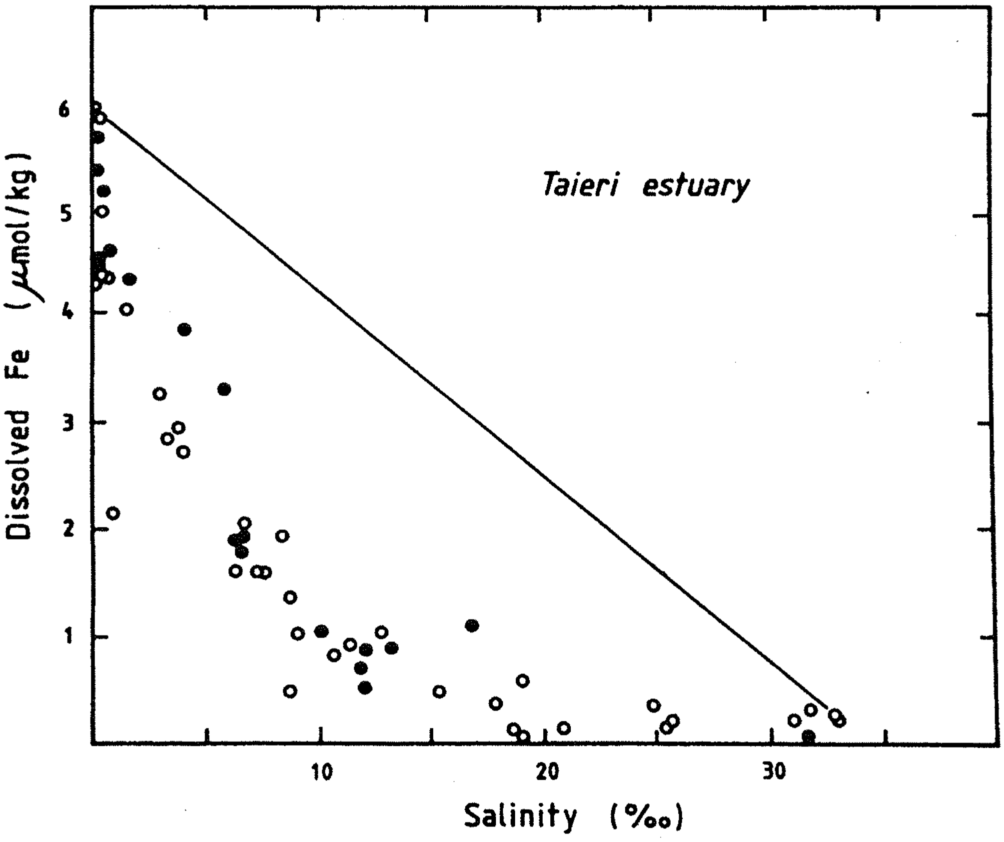

Fig 1.1 : The behaviour of dissolved iron (Whatman 0.8μm GF/F filters) during mixing in the Taieri River estuarine system. (Hunter & Leonard, 1988)

1.2. Iron in the Natural Environment

Iron is the fourth most abundant element in the earth's lithosphere - accounting for ~ 6 % of the earth's crust, but is generally present at relatively low concentrations in natural waters. The iron in the crust is mobilised by the weathering of iron silicates and carbonates, producing a range of iron oxides, hydroxides, colloidal species, complexes and free ions. The geochemical mobility of iron under oxidising conditions is controlled by the susceptibility of iron (III) to hydrolysation and by the very low solubility of the hydroxide phase for which $K_{sp} = 2.0*10^{-39}$ mol^4 l^{-4} at 298 K (Stark & Wallace, 1988). Under reducing conditions *i.e.* suboxic and anoxic environments, iron (II) is the prevalent ion, which is potentially more mobile than the ferric ion. In such conditions however, there is the tendency for formation of the iron (II) sulphide.

The chemical properties of iron make it important in a variety of environmental processes. Iron plays a unique role in a number of biological systems (in the form of the porphyrin molecule), as well as being essential to the growth of marine plants (along with Mn, Cu, Zn, Co, Mo) and occurring in the non-haem protein complex ferrodoxin, which plays a vital role in photosynthesis.

Recent work of Martin & Fitzwater (1988) and Martin *et al.* (1994) has indicated that iron is a limiting factor in primary production in some areas of the ocean. Iron, present predominantly in the colloidal form, is apparently unavailable for uptake by phytoplankton (Martin *et al.,* 1989; Rich & Morel, 1990, Wells *et al.,* 1991). Mechanisms by which this colloidal iron could be converted into more labile forms include thermal dissolution (Wells *et al.,* 1983), photochemical reactions (Waite & Morel, 1984; Wells & Mayer, 1991) ligand complexation (Wells *et al.,* 1995) and digestion of colloidal iron in acid vacuoles of protozoan grazers (Barbeau *et al.*, 1996).

A further major geochemical significance of iron in natural waters is its influence on the behaviour and distribution of trace metals and nutrients by its actions as a scavenger or carrier phase. Estuaries are environments where the behaviour of iron may be of especial importance because of the potential for transport of material between reducing and oxidising zones and for phase transfer involving colloidal fractions.

Though the boundary between dissolved and particulate material is usually operational, fundamental compositional differences between the particulate and the colliodal fractions have been observed (Sigleo *et al.,* 1981). In samples from the Patuxent River from the summer of 1979, the particulate phase was found to consist of mineral particles and planktonic organisms, whereas the colloidal phase was mainly biogenic in nature, with a minor mineral component. Samples of winter colloidal material were found to consist of poorly sorted clay minerals (illite and kaolinite). The trace metal concentration varied proportionally with the mineral component of the colloids, leading to the hypothesis that the two are in some way associated. Summer colloidal material behaved conservatively under increasing salinity conditions, whereas the winter colloidal fraction exhibited marked non-conservative removal. This difference could be related to the different origin of the colloids - winter material was proposed to be derived mainly from continental weathering and summer material mainly from biological processes. Analysis of the organic fraction of colloids (Sigleo *et al.* in press), revealed the major source of colloidal organic material in river water to be aquatic micro-organisms, rather than terrestrial plants.

During the processes of estuarine mixing, the dissolved iron fraction in the river waters undergoes a marked non conservative removal, in the low salinity region. The removal of dissolved iron could occur by one of the following mechanisms :

- The oxidation of iron (II) to iron (III), and subsequent precipitation of iron (III) hydroxide.
- Scavenging of iron by natural sedimentary particles, which could act as nuclei for iron bearing colloid aggregation.
- The coagulation of iron bearing colloids during estuarine mixing.

The dissolved iron fraction in Beaulieu river water has been shown, by ultrafiltration experiments (Moore *et al.,* 1979), to be comprised of forms almost wholly in the $>10^5$ molecular weight range. This observation is consistent with the view that the dissolved iron fraction consists of colloidal iron (III) oxides stabilised in suspension to some degree by the presence of high molecular weight humic acids (Shapiro, 1964; Boyle *et al.*, 1977; Moore *et al.,* 1979). Thus the non-conservative removal of dissolved riverine iron during

estuarine mixing is readily explicable in terms of destabilisation of the colloid population by increasing electrolyte concentrations. - see section 1.5.2 on colloid stability.
The geochemical cycle of iron is, in its nature, interlinked with those of phosphorus, sulphur, heavy metals, oxygen and carbon. Although the total mass of particles in the colloidal size spectrum is comparatively very small, they do contribute a significant proportion of the surface area. Hence colloidal material has a high potential for the adsorption of trace metals from solution. The iron containing colloids in fresh water act as important support phases for many dissolved chemical forms, and are able to sequester surface active organic pollutants such as chlorinated pesticides, solvents, poly-nuclear aromatic hydrocarbon plasticisers and detergents, as well as scavenging trace metals and nutrients from the water column.

There have been numerous estimates of an average value for dissolved iron concentration in rivers - some on a global scale and others in more localised areas. As techniques of sampling and analysis improve through time, errors in determinations are minimised and more realistic values are likely to be obtained :

Livingstone 1963 (global average) 12μmol l^{-1}
Durum & Haffy 1963 (N.America) 5.4μmol l^{-1}
Martin & Meybeck 1979 (5 largest rivers) 0.7μmol^{-1}
Meybeck 1988 (10 rivers worldwide) 0.9 +/-0.5 μmol l^{-1}

The global average derived by Livingstone (1963) is perhaps too much of an oversimplification to be of any real value - as the data are treated as a straight average, with any effects of local and / or regional variation on concentrations in individual rivers *e.g.* catchment area, bedrock, soil, run off; temporal variability and anthropogenic influences unaccounted for by weighting. Martin & Meybeck (1979) however attempted to address this problem in his estimate based on the 5 largest rivers - thus achieving a potentially more realistic value. It should be noted that the two most recent estimates of average dissolved iron in river water, Martin & Meybeck (1979) and Meybeck (1988), are one order of magnitude smaller than the original Livingstone (1963) estimate. The comparability of results in such reviews of global iron concentrations is greatly dependent upon the compatibility of sampling, filtering and analytical techniques used in individual river studies. Table 1.2 shows dissolved iron concentrations from a number or rivers throughout the world along with the analytical techniques used for the determination.

The concentration of iron in the Mullica river was found to be the highest of all the rivers studied (23.4μ mol l^{-1} compared to 0-10μ mol l^{-1} for the other rivers studied). This anomalous concentration is thought to be a direct result of the acidic peat land nature of the drainage basin. Due to the chemistry of the drainage area, the Mullica has an enhanced concentration of dissolved organic matter and the iron is stabilised by its presence. - see section 1.4 on the association between iron and OM. The available information on the pH and DOC of the systems listed in Table 1.2 concurs with the findings that lower iron concentrations occur in those river waters which have a higher alkalinity and are lower in DOC. The Beaulieu has a pH of 7.2-7.6, a DOC concentration of 3.0-8.2 mg l^{-1} (Moore *et al.*, 1979) and a dissolved iron concentration of 7-8 μmol l^{-1}. High iron concentrations are also found in both the Ogeechee, Florida: 2.6-8.9 μmol l^{-1} iron (Windom, 1975), DOC 55 mg l^{-1} (Waslenchuck *et al.*, 1978) and the Taieri, New Zealand: 6 μmol l^{-1} iron, pH 6.5-6.8. This is in contrast to the Test and Itchen river systems which show low iron concentrations (0.17-0.23 and 0.27 μmol l^{-1} respectively - Fang, 1995) but have a significantly lower DOC content of 1.7-3.4 μg l^{-1} (Moore *et al.*, 1979). The Bank Pakong system, Thailand also displays similar features, despite having a pH of 5.9-6.3, it has an iron concentration of only 0.23-0.46 μmol l^{-1} due to a low DOC content of 200-300 μg l^{-1} (Windom *et al.*, 1988). The Tamar river system, under study in the present work, has a reported DOC content of 310 μmol l^{-1}. and a pH of either 7.3 (Morris *et al.*, 1978) or 6.9 (Morris *et al.*, 1982).

Significantly higher values of dissolved iron concentration, upwards of 69,000 μmol l^{-1}, have been found in low pH river systems draining metlliferous areas with mining waste such as the Afon Goch, N. Wales (Foster *et al.* 1978). Such unusual systems are not included here as the low pH means that the colloidal role of iron will be reduced.

Some of the more recent data sets of dissolved iron in sea water are presented in the Table 1.3. It can be clearly seen that dissolved iron occurs only in very minor quantities in surface oceanic waters, between 0-1 nmol l^{-1}, but increases in most instances to a maximum at the oxygen minimum zone - up to 6.1 nmol l^{-1}. There appears to be wide variation in the dissolved iron concentrations in the Antarctic, Martin *et al.* (1990), with values ranging from 0.14 in Drake Passage to 7.40 in the Gerlache Strait.

River	Location	Author	Filter size (μm)	Dissolved iron conc. μmol l^{-1}	Method of iron analysis
Ogeechee	Georgia	Windom (1975)	0.45	2.6-8.9	Colorimetric (ferrozine)
Beaulieu	S.W England	Holliday & Liss (1978)	0.45	7-8	Colorimetric (TPTZ)
Mullica	Southern USA	Boyle *et al.* (1977)	0.45	23.4	Colorimetric (ferrozine)
Amazon	S. America	Sholkovitz *et al.*(1978)	0.45	8-9	Colorimetric (ferrozine)
Waters of Luce	Scotland	Sholkovitz (1978)	0.45	3.0	Colorimetric (ferrozine)
Potomac	Chesapeake Bay USA	Eaton (1979)	0.45	0.5	Colorimetric (ferrozine)
Sheepscott	Gulf of Maine	Mayer (1982b)	0.45	5-6	Colorimetric (ferrozine)
Tarieri	New Zealand	Hunter (1983)	0.45	6	AAS
Broadkill	Southern USA	Fox (1984)	0.45	10.8	Colorimetric (ferrozine)
Mispillion	Southern USA	Fox (1984)	0.45	6.2	Colorimetric (ferrozine)
Bank Pakong	Thailand	Windom *et al.* (1988)	0.45	0.23-0.46	Solvent Extraction + AAS
Leith	New Zealand	Hunter (1990)	0.45	3-4	Colorimetric (ferrozine)
Ochlockonee	Florida	Powell *et al.* (1996)	0.45	6.98	Direct Injection AAS
Garonne	France	Krapiel *et al.* (1997)	0.45	0.27	Solvent Extraction + AAS
Dordogne	France	Krapiel *et al.* (1997)	0.45	0.06-0.08	Solvent Extraction + AAS
Itchen	SW England	Fang (1995)	0.45	0.27	Solvent Extraction + AAS
Test	SW England	Fang (1995)	0.45	0.17-0.23	Solvent Extraction + AAS

Table 1.2. Concentrations of Dissolved Iron in a Number of River Systems.

Author	Filter Size (μm)	Area of Study	Iron Conc. (nmol l^{-1})
Landing & Bruland (1987).	0.4	**Pacific**	
		Surface	0.1-0.7
		Oxygen minimum zone	2-6
Martin & Gordon (1988)	0.4	**N.E. Pacific**	
		Surface	<0.1
		between 0.5 and 1km depth	1.0-1.3
Saager et al. (1989)	0.4	**Indian Ocean**	
		Surface	0.3
		Oxygen minimum zone	5.1
Martin et al. (1990)	0.4	**Antarctic**	
		Drake Passage	0.14
		Gerlache Strait	7.40
De Baar *et al.* (1990)	0.4	**Southern Ocean**	0.1-1.0
Martin *et al.* (1994)	0.2	**Equatorial Pacific**	0.06
Measures *et al.* (1995)	0.2	**Arctic Ocean** (0 to 80 m)	1-3
Powell *et al.* (1996)	0.2	**Southeastern + Eastern Atlantic**	
		Surface waters	<0.5-10
Johnson *et al.*(1997)	0.2	**30 stations N + S Pacific, Southern Ocean, N Atlantic.**	
		Surface	0.07 (Average)
		Below 500m	0.76 (Average)

Table 1.3 : Concentration of dissolved iron in sea water.

1.3. Iron Speciation in Natural Systems

The tendency of iron to form colloidal and particulate material in the estuarine environment provides us with a mechanism for sorption / co-precipitation of dissolved trace metals and other constituents from natural fresh waters. This diverse range of chemical processes make it important for us to establish a reliable understanding of iron's behaviour in these waters.

1.3.1 Oxidation States

The cycling of iron throughout the atmosphere, oceans, soils and sediment depends upon the various physical, chemical and biological processes. Ferrous iron is much more soluble than ferric, and therefore has a greatly increased mobility in solution. The iron cycle can be shown to illustrate some of the redox processes observed at oxic - anoxic boundaries (see Fig 1.2).

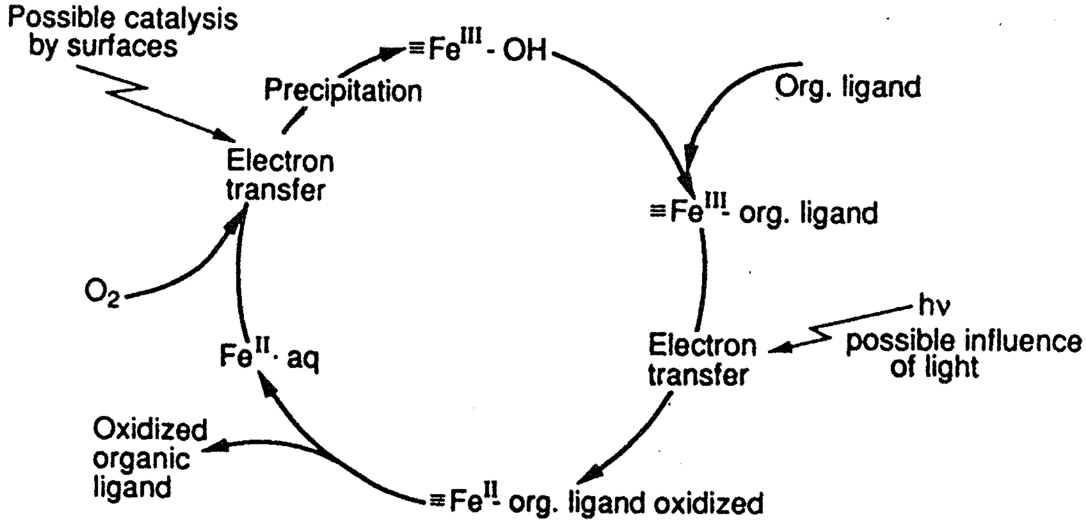

Fig. 1.2 - Schematic diagram of the cycling of iron between its oxidation states at the oxic - anoxic boundary (Stumm & Sulzberger, 1991).

N.B. The oxidation of iron (II) to iron (III) (hydr)oxides is accompanied by the binding of reactive compounds (*e.g.* organic material, heavy metals and phosphates). Similarly the reduction of iron (III) leads to the release of these compounds from carrier phases.

Ferrous iron occurs in anoxic fresh waters, marine basins and in interstitial waters in anoxic environments. In such environments, iron oxides / hydroxides are used as terminal electron acceptors in the oxidation of organic material. They fit into the order of redox potential after oxygen and manganese oxide but before sulphates. In such environments, the reduction of iron (III) to iron (II) will occur, with the fate of the Fe^{2+} dependent upon the oxygen demand. If the oxidation process continues as far as sulphate reduction, the result will be the formation of iron sulphide - the solubility of which determines the concentration of Fe^{2+} and S^{2-} ions in the water column. Fe^{2+} ions can also be produced by the oxidation of iron sulphide species in zones near to the sediment / water interface.

In fresh waters of pH ~ 8, the oxidation of iron (II) to iron (III) is believed to be almost instantaneous, thus making it almost impossible to measure any ferrous iron by conventional techniques. Any iron (II) found is thought to be present due to either analytical error or stabilisation by organic material.Liang & Kester (1977) measured the rate of oxidation of iron (II) to iron (III) to be ~ 100 times slower than expected in sea water, due to the increased ionic strength causing an increase in the amount of organic complexation. This argument was corroborated by the fact that the addition of sodium salts to a fresh water sample in the laboratory induced the same effect as seen in the sea water.

The redox system is unlikely to be in a state of total equilibrium, due to the fluctuating nature of riverine inputs and oxidation conditions, but we can assume that at least a partial equilibrium will be set up - in which a number of reactions tend towards the same equilibrium. These equilibria can be represented in a pH-Eh plot (Fig 1.3), which illustrates the stable iron species in given thermodynamic conditions, and changes that will occur with influxes of protons or electrons.

In natural waters, redox conditions vary considerably throughout the length and depth of the estuarine system. There is, however, a general trend of reduction predominating in the sediments, giving way to oxidation towards the surface, with superimposed fluctuations on a local scale.

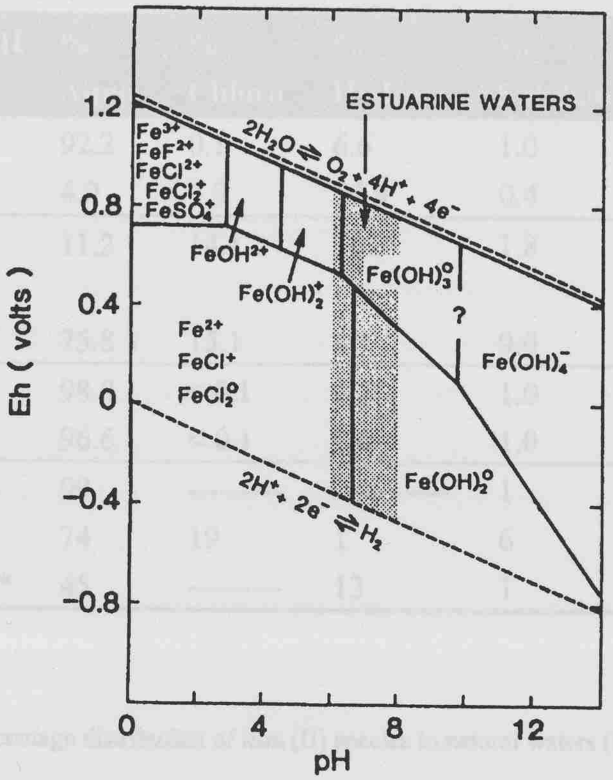

Fig. 1.3 - Redox speciation of iron in sea water at various conditions of Eh & pH (Morris, 1983).

1.3.2 Ionic Ligand Associations with Iron

In natural waters iron (III) is strongly hydrolysed, forming hydroxides / oxy hydroxides of very limited solubility *e.g.* $Fe(OH)_3$ - $K_{sp} = 2.0*10^{-39}$ $mol^4\ l^{-4}$ - Stark & Wallace (1988). Because of this we shall confine the review of the ligand associations of iron in natural waters to the ferrous ion.

Various thermodynamic models including various complexing ligands, have been used to predict the speciation of iron (II) - using data on stability constants of proposed complexes in the environment (Hem & Cropper, 1959; Morel & Morgan, 1972; Davison, 1979; Kester *et al.*, 1975; Whitfield *et al.*, 1980).

It was predicted by Davison (1979), that $Fe(H_2O)^{2+}$ is the dominant species in both fresh and sea water.

Author	pH	% Aquo	% Chloro	% Hydroxy	% Sulphato	% $FeSO_4/Fe^{2+}$
Kester *et al.* (1975)	7	92.2	0.1	6.6	1.0	0.011
	8	4.0	7.9	87.9	0.4	0.1
Morel & Morgan (1975)	8	11.2	14.1	70.7	1.8	0.16
	7	75.8	15.1	0.1	9.0	0.12
Davison (1979)	7	98.8	< 0.1	0.2	1.0	0.010
	8	96.6	< 0.1	2.4	1.0	0.010
Whitfield *et al.* (1980)	6	99	---------	-----------	1	---------------
	8	74	19	1	6	---------------
	9*	45	---------	13	1	---------------

Table 1.4 : Percentage distribution of iron (II) species in natural waters (Davison (1979)).

* Whitfield *et al.*, (1980) predicted that at pH 9, some iron (II) would be complexed with carbonate ligands. The proportion complexed with carbonate ligands accounts for the 41% of the iron (II) not referred to in the table.

It has been proposed, by Windom *et al.* (1988), that, in tropical climates, the concentration of iron in fresh waters is controlled by iron (III) hydroxide equilibria, due to the formation of solid phase iron forms produced under tropical weathering conditions. The decrease in dissolved iron with increasing salinity in the Bank Pakong Estuary appears to be explicable by the oxidation of iron (II) to $Fe(OH)_3$ and / or the decrease of solubility of $Fe(OH)_3$ at increased pH.

1.4. Organic Material and its Association with Dissolved Iron

On estuarine mixing, iron is largely removed, mostly in the low salinity region, whereas bulk DOC shows conservative behaviour. Some fractions of the organic material have been shown to be removed during estuarine mixing and it has been noticed that there is a marked similarity between the behaviour of some fractions of organic material, in particular humic acids and that of dissolved iron (Sholkovitz *et al.,* 1978; Fox, 1983, 1984). This has lead to postulation that there is some association between the two species within estuarine systems. Indeed, work of Stumm & Morgan (1981) predicted that in normal, highly oxygenated river water, pH 4-8, there would only be expected to be nanomolar concentrations of iron. In practice 'dissolved' iron concentrations are significantly higher ($\sim$1-30μm l^{-1}), this is believed to be due to an intrinsic connection between iron and organic material (OM). Two feasible mechanisms have been proposed by which a stabilisation of iron could take place :

1) Formation of a complex between iron and organic matter.

2) Organic stabilisation of microcolloidal particles in solution.

Perdue *et al.,* (1976) presented evidence for the former, finding a strong positive correlation for a range of river waters between the sum of dissolved iron and aluminium versus the total dissolved organic carbon. Plots for iron and or aluminium alone against dissolved organic carbon (DOC), showed wide scatter, which was interpreted as evidence of the competition between the iron and aluminium to form organic complexes with the OM.

It has become widely accepted, however that the majority of dissolved iron in natural waters is present in a colloidal state, with individual microcolloids being stabilised by the presence of OM (Shapiro, 1964; Stumm & Morgan, 1981 etc.). Cameron & Liss (1984) found, through laboratory experiments, that dissolved iron could be stabilised by humic acids, tannic acids, surfactants, silicate and phosphate ions, indicating that iron was retained in solution by colloid stabilisation rather than by specific complexation. Work done by Krom & Sholkovitz, (1978), on pore waters, showed that between 74 & 84% of the dissolved iron fraction was retained by ultrafiltration with a molecular weight cut off

of 10^3. In similar experiments by Boyle *et al.,* (1977) it was found that almost three quarters of the dissolved iron (73%), was removed by filtration at 0.1μm and 80% at 0.05μm. This led to the assumption that most of the iron in the 0.45μm filtered fraction of natural waters consists of colloidal particles between 0.05-0.45μm in diameter.
It was noted, by Moore *et al.*, (1979), that a relatively high dissolved iron concentration (136-314 $\mu g l^{-1}$) occurred in acidic streams, specifically in the Beaulieu river in association with an enhanced concentration of dissolved organic material (DOM). A small, but significant, fraction of the DOM (18%), was found to lie in the $>10^5$ molecular weight fraction, with 70% in the 10^3-10^5 range (77-84% of DOM passed through a 10^5 molecular weight filter). This contrasts with dissolved iron, of which only 2-10% passes through a 10^5 molecular weight filter. This leads to the conclusion that only the larger size humic material was capable of stabilising dissolved iron. Experiments by Rashid, (1971), and Mantoura & Riley, (1975), have shown that this is not the case, and that humic material over the whole size range possesses the metal binding properties to stabilise the iron. The stabilising ability of $<10^5$ molecular weight humic material was shown in laboratory experiments of Moore *et al.*, (1979), using Beaulieu river water (initial concentration 136-314μg Fe l^{-1}). Two aliquots were removed from a single sample and in one the OM was destroyed by photo-oxidation. Both had 400μg l^{-1} of iron added to them and were stirred for ~ 48hr then analysed for iron. The sample with the OM destroyed was found to have a dissolved iron concentration of <10μg Fe l^{-1}, whereas the non oxidised sample had 260μg Fe l^{-1} remaining. It is possible that by its association with the dissolved iron, the dissolved humic material increases its apparent weight from the 10^3-10^5 fraction to the $>10^5$ fraction. The experiments also highlight the fact that only a small amount of humic material (~ 30 μg l^{-1}) is required to stabilise 100μg l^{-1} of iron.

During the estuarine mixing process, it has been observed that bulk DOC behaves in an approximately conservative manner, (Duursma, 1961; Mantoura & Woodward, 1983; Fox, 1984), whilst dissolved humic acids undergo a significantly non conservative removal. When looked at quantitatively, only a small amount of DOM is rapidly and preferentially removed during estuarine mixing (Sholkovitz *et al.,* 1978). This portion represents the high molecular weight riverborne organic material, and includes within it 60-80% of the high weight fraction humic acids. In the Amazon estuary, 80% of the humic acids were removed, in a manner almost identical to the dissolved iron fraction, leading to a conclusion of a common removal mechanism. Laboratory experiments using river water from the Waters of Luce were carried out to follow up these ideas. The water was filtered at 0.45μm, 0.1μm, 0.05μm, 0.01μm, 0.005μm and 0.001μm[1] then used in a series of batch mixing experiments. Extensive removal was observed in the 0.45μm to 0.1μm fractions - 65% of total humic acids were removed. In the <0.01μm fraction there was very little removal of humic acids by rapid aggregation, implying that the removal reaction involves almost exclusively on the high molecular weight humic acids. DOC was fairly evenly distributed throughout the size fractions observed.

The theory of iron / humic acid association was challenged by both Eastman & Church, (1984) and Fox, (1984). Eastman & Church, (1984) claimed conservative dilution of humic acids concurrently with a non conservative dissolved iron removal. The analytical precision of the C-H-N analyser used for the determinations was quoted at +/- 25% precision thus leaving the claim somewhat open to scepticism. Fox, (1984), however, claimed that the similarities between the aggregation profiles for dissolved iron and humic acids, with increasing salinity were a mere coincidence. As previously observed, the estuarine profiles of the dissolved iron and humic acids showed a definite similarity for the rivers in the Delaware Bay estuary. Laboratory experiments were carried out using filtered river and sea water endmembers, and the mixing process was studied over a 3 hr period. The experiments showed that the removal of humic acids (defined here as the acid insoluble fraction of DOM) and dissolved iron had differing kinetic rate constants and also that the extent of removal of humic acid showed no consistent trend with respect to dissolved iron. Using Mullica river water, humic acid was removed in greater abundance than dissolved iron for salinities 0-13, whereas in the St Jones and Broadkill rivers there appeared to be only minor removal of humic acids - even at high salinities (this variation between rivers is thought to be due to differences in the nature of humic acids between rivers - specifically the organic carbon content). Further experiments were carried out on humic acids removed from river water by acid precipitation. The humic acids were redissolved and added to a colloidal iron hydroxide - to investigate the stabilisation of iron by humic material. The humic acid had no noticeable effect on the stability of the iron hydroxide - leading to the assumption, by Fox, (1984), that humic acids were not involved in the stabilisation of microcolloidal iron. These findings are contrary to those of Moore *et al.,* (1979) - in which iron was found to be stabilised by the low weight humic acid fraction. One possible rationalisation of the results is that there is only a certain fraction of the dissolved iron that is susceptible to stabilisation by humic material. This

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[1] 0.001μm - 0.05μm samples were collected by ultrafiltration techniques.

fraction of the iron is already stabilised, as there is an excess of humic material already available in natural waters hence a further addition of humic acid to the water will serve only to increase the amount in excess - rather than affect the dissolved iron concentration. Colloids with the greatest abundance of iron are the least stable, therefore if iron and humic acids were associated in colloidal form, the ratio of humic carbon : dissolved iron would be expected to increase, in the dissolved fraction, due to aggregation of material at the lowest ionic strengths. However, it was observed by Fox (1984) that the ratio of humic carbon : soluble iron decreased as a function of increasing salinity in three of the seven estuaries studied.

The aggregation of dissolved iron / humic acids during mixing experiments is found to be consistent with the Schulze-Hardy rule for colloid coagulation - explainable in terms of the DVLO theory (see section 1.5.2 on colloid stability). Maximum amounts of humate and inorganic elements precipitating from natural waters show a dependence on the valence and ionic size of the ion causing aggregation. This indicates that both chemical and electrostatic interactions are involved in aggregation processes.

A number of studies were carried out to investigate the nature of the association between dissolved iron and organic material. Fiella & Buffle, (1993) and Buffle & Leppard, (1995) used transmission electron microscopy (TEM) studies of natural colloidal material to illustrate the interaction of colloidal and organic material. Using TEM studies it was possible to distinguish between two types of natural organic material : soil derived fulvic acids, which are very small particles (nanometer) that can aggregate together or adsorb at the surface of larger colloids forming a comparatively thin coating layer at their surface; and comparatively larger organic structures which can be observed bridging between inorganic structures. Both types of organic material affect the aggregation and stabilisation of colloidal material.

Loder & Liss, (1985) demonstrated that positively charged iron oxide particles (and all other estuarine particles) acquire a negative surface charge on immersion into water containing natural organic material - due to the formation of a ubiquitous coating of organic material, as observed in TEM studies of Fiella & Bufle, (1993) and Buffle & Leppard, (1995). Further work revealed that widely different surfaces, when exposed to a natural water environment, became covered with a tenacious film of surface active organic material which dominated their subsequent surface chemistry. Two characteristic types of behaviour with respect to particles in estuaries were noted by Hunter & Liss, (1979) :

- Estuaries receiving river waters with a low concentration of dissolved cations (Ca^{2+} in particular) had negative electrophoretic mobilities at all salinities. There was a slight increase in the high salinity to 5-10 region and a marked increase in the gradient in the 5-10 to fresh water region. (*e.g.* River Conwy and River Beaulieu).

- In estuaries receiving river waters with a high Ca^{2+} concentration, only a slight increase in electrophoretic mobility is observed from sea water to fresh water. No gradient change was seen in the range studied (*e.g.* Rivers Alde and Orwell).

This indicates that although the particles are all ubiquitously coated in organic material, the chemistry of the water they are in appears to be a major factor in controlling the electrophoretic mobility / salinity relationship. In waters with high levels of dissolved cations, in particular polyvalent cations such as Ca^{2+}, some of the natural electrokinetic charge will already have been neutralised, in the fresh water region, by the incorporation of the cations into the fixed part of the double layer; in more acidic rivers this change will not occur until such cations are encountered in the low salinity region of the estuary. The increased stability effect provided by the presence of this organic coating was illustrated by Tipping & Ohnstad, (1984), using colloidal iron oxide from Esthwaite Water, Lake District. The particulate material used was 30-40% iron by weight and ~ 30% organic material - of which one third was humics. Mixing experiments were carried out, with addition of Ca^{2+} ions, to compare their behaviour with that of hematite (synthesised in the laboratory and equilibrated in Esthwaite water for ~ 48hr to achieve a humic coating). The estuarine particles were found to be stabilised to a greater degree than the hematite, which was due most probably, to a bridging flocculation mechanism by high molecular organics, algal / bacterial exudates or organic fibrils. The importance of the organic coating was demonstrated by Gibbs, (1983). Mixing experiments were carried out using both natural iron containing particles and the same particles with their organic coating removed by oxidation with sodium hypochlorite. The particles with coatings removed were found to aggregate much more quickly than the untreated particles. With the Yukon river particles the half time, ($T_{1/2}$) for aggregation was 55 minutes for natural particles and only 11 minutes for the treated particles; the collision efficiencies[2] (α) were 0.28 and 0.77 respectively. For the Amazon the effect was less pronounced, with α being 0.69, natural, compared with 0.82. The effect was largest at low salinities. These findings show that the differences in the stability of riverine microcolloids under the two conditions are due, most likely, to the differing OM contents of the samples. One viable explanation for this observation is that stability of riverine microcolloids under estuarine conditions is subject to steric stabilisation effects. A fuller description of the chemistry underlying the steric stabilisation of organic coated colloids is given in section 1.5.4 - steric stabilisation.

The effects of steric stability varies considerably between rivers. In the Tamar and Beaulieu river estuaries a small increase in salinity will induce a large destabilisation (Duffy, 1985), whereas in the Broadkill and St Jones estuaries stabilisation is significantly stronger and therefore destabilisation occurs at a slower rate (Fox & Wofsy, 1983). This results in a smaller percentage of the colloid population being destabilised for a given increase in salinity in the Broadkill and St Jones estuaries in comparison with the Tamar and Beaulieu river estuaries. Contrasts between the rivers are due to differences in the drainage area of the river, which affects the chemistry of the river and thus the surface state of the iron bearing colloid particle population prior to estuarine mixing.
Although steric effects and their interactions with electrostatic and van der Waals forces in controlling stability of naturally occurring colloids await further developments in our understanding, the fundamental concepts can be used to explain, at least qualitatively, the effects of the association between dissolved iron colloids and organic material.

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[2] Collision efficiency is an empirical dimensionless parameter, equivalent to the fraction of interparticle collisions that result in aggregation. Determination takes into account chemical factors influencing the kinetics, as well as kinetics of particle transport.

1.5. Colloids and Colloid Stability

1.5.1 The Colloidal State

Colloidal particles are classified as those having at least one dimension in the nm to μm size range. Colloids in natural waters are composed of inorganic or organic molecular constituents, a mixture of both or micro-organisms. They include silica, weathered mineral products (such as clays), large molecular weight organic material and cellular debris and also occasionally calcium carbonate.

In aquatic systems colloids form inherently unstable suspensions due to their propensity to undergo conformational changes, aggregate and then sediment. Colloidal dispersions have a large surface area to volume ratio and are thus able to sorb significant quantities of dissolved constituents It is well known that large proportions of vital or toxic compounds in aquatic systems are associated with particulate and colloidal material (Salomans & Forstner, 1984; Santschi, 1984; Sigg, 1987; Brooke & Moore, 1988; Moulin & Ouzounian 1992 and Honeyman & Santschi, 1992). Thus the circulation of these compounds and consequently their impact on the biosphere are strongly dependent upon the nature and behaviour of carrier colloids.

Characterising the nature and behaviour of natural colloids is a fully interdisciplinary problem. The processes of coagulation and sedimentation depend not only on the physical properties of the colloidal material (size, density, compactness and rigidity) but also on the chemical properties of the surfaces, which determine the binding strength between colloidal particles (Liang & Morgan, 1990) and microbial activity.

The individual negatively charged colloidal particles are initially stabilised by forces of electrostatic repulsion acting between them; these forces can be reduced readily by the addition of cations to the system. A small increase in the ambient ionic strength of the supporting medium would be sufficient to severely diminish the electrostatic repulsion. It has in fact been shown that an increase in salinity to 3 would be enough to cause full destabilisation of a colloid population, as there is a reduction in the double layer thickness to ~ 1nm (Hunter, 1983).

In a polar medium, *e.g.* water, a colloidal dispersion has a net surface electrical charge due to the imbalance of its component positive and negative charges. These charges influence the distribution of the polar molecules in the water: attracting the counter ions (oppositely charged) and repelling the co-ions (like charged) leading to the formation of an electrical double layer stabilising the colloid with a net surface charge of zero. The electrical double layer can be regarded as consisting of two regions: an inner region including adsorbed ions and a diffuse outer region in which ions are distributed according to the influence of electrostatic forces and thermal motion. The theory of the diffuse double layer was independently proposed by Gouy, (1910) and Chapman, (1913) and subsequently refined by Stern, (1924). The inner, or 'Stern' layer consists of counter ions which are strongly associated with the particle, and maintain their integrity as the particle moves through the medium. The outer, more diffuse layer - the 'Gouy' layer - contains both positive and negative charges to neutralise any remaining surface charges. The Gouy layer is in a state of dynamic equilibrium, being continually altered as the particle moves through the medium. Somewhere between the Stern and Gouy layers lies an interface known as the 'shear boundary', with the potential between this and the homogeneous bulk medium being known as the electrokinetic or zeta potential. The zeta potential cannot be measured directly, but is related to particle charge, as determined by electrophoresis, and as such is a measure of the stability of a dispersion. The calculation of zeta potential requires an estimate of the Stern layer thickness.

1.5.2 Colloid Stability

The stability of colloidal dispersions is determined by particulate interactions. Aggregation of colloids is primarily caused by van der Waals forces, so to maintain stability there must be forces counteracting them - such as electrostatic and polymeric stabilisation.

The coagulation of colloids in natural waters on addition of relatively small amounts of electrolyte is due primarily to a compression of the diffuse layer around the particle, though ion adsorption may also effect the Stern layer. Coagulation occurs when the electrolyte concentration compresses the double layer thickness sufficiently to allow van der Waals forces to dominate. Deryagin & Landau, (1941) and Verwey & Overbeek, (1948) independently developed a theory of colloid stability which treats the problem in terms of the energy changes that occur when particles approach one another - known as the DLVO theory. According to the theory, colloid stability is determined by the balance between potential forces of attraction and repulsion as the interparticle radius decreases. The forces acting are those of long range repulsion - due to the coulombic repulsion of overlapping electrical double layers; and short ranging attractive van der Waals forces. The forces are considered in terms of inter particle distance and summed graphically to give an interaction energy against distance curve (see fig. 1.4). The nature of the overall interaction curve determines the stability of the dispersion with respect to coagulation. At short range, van der Waals forces dominate strongly and at very long distance (>10nm), they also dominate, but less strongly. In the intermediate region double layer repulsion may be sufficient to dominate and form a potential energy maximum. For a colloid to be stable there must be a significantly large, repulsive potential energy maximum. Colloids aggregate when the kinetic energy is sufficient to overcome this maximum.

The theory can be used to calculate the relative stability of a colloid but not the absolute stability. This is due to the uncertainty over the absolute values of some properties of natural colloids *i.e.* size, shape and surface characteristics.

Theories of colloid stability indicate that the effect of electrolyte concentration on colloid aggregation may be divided into two concentration regimes. At low concentrations, the diffuse layer shrinks closer to the particle surface, until the barrier to close particle encounters disappears. Although electrostatic repulsion is important, efficiency of interparticle collisions is much less than 100% - and is a sensitive function of the electrolyte concentration. At high electrolyte concentration most collisions result in aggregation and the kinetics become independent of electrolyte concentration.

1.5.3 Aggregation of Colloids

A reduction in the stability of a colloid can result in the aggregation of a colloidal system. There are three main methods of destabilisation of colloids :

1. Addition of an electrolyte, compressing the double layer, decreasing ν_{max} - the net repulsive potential energy maximum., thus the colloid becomes more susceptible to aggregation[1].

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[1] The effects of electrolytes added to a colloid are summarised in the Schulze Hardy rule - derived from experiments on colloids. The destabilisation of colloids is caused by ions of opposite charge to the colloid, the amount of destabilisation caused being dependent upon the valency, size and

2. Adsorption of specific ions : net reduction in the surface charge of molecule, thus repulsive forces are decreased.

3. Formation of molecular bridges between molecules.

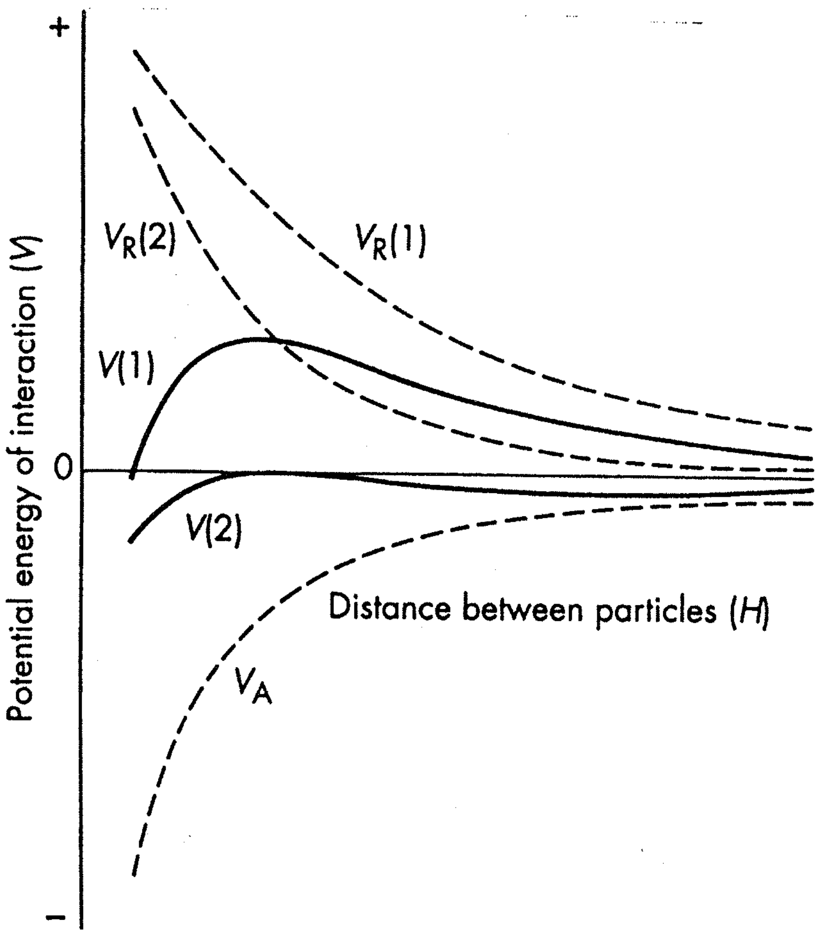

Fig 1.4 : Schematic Total Interaction Energy Curves, V(1) &V(2), obtained by summation of an attractive curve, V_A, with different repulsion curves, $V_R(1)$ and $V_R(2)$ (Shaw (1992)).

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concentration of the ion. Destabilisation power is increased by increasing charge and radius, hence the destabilisation power of cations increases $Na^+ < Mg^{2+} < Ca^{2+}$.

Once the colloids have become destabilised, there are two major processes of aggregation to be considered :

a) Coagulation - defined as the aggregation of colloids resulting from reduction of potential energy of interaction between electrical double layers of two similar particles (La Mer, 1964).

b) Flocculation - aggregation of colloidal particles into a 3D network linked by chemical bridges.

The rate of coagulation depends upon both the frequency of particle / particle encounters and also on the probability that the collision will have sufficient energy to overcome the repulsive potential energy barrier to coagulation.

Assuming perikinesis, the rate of particle aggregation can be described by a second order rate equation :

$$\frac{-dn}{dt} = k_2 n^2 \qquad \text{equation 1}$$

where n = No. of particles and k_2 = second order rate constant.

During coagulation, the rate of the reaction usually decreases to an equilibrium state - in which the sol may or may not be fully coagulated. This is due to an increase in the repulsive energy barrier due to an increase in particle size. Rapid coagulation was studied by von Smoluchowski, (1917) who proposed, for monodisperse spherical sols, the rate constant for rapid coagulation :

$$k_2{}^o = \frac{4KT}{3\eta} \qquad \text{equation 2}$$

$k_2{}^o$ = rate constant.

η = viscosity of medium.
K = Boltzmann constant.
T = absolute temperature.

In practice the theoretical reaction rate is increased by attraction due to van der Waals forces, but slowed down by liquid between particles blocking gaps, making it difficult for particles to flow away - this results in the rates being approximately half of their expected value. With a repulsive energy barrier, only a fraction of collisions give rise to coagulation ($1/\omega$), where ω is the stability ratio : $\omega = k_2^o/k_2$

The frequency of collisions between particles is dependent upon the means by which particle - particle encounters occur. There are two conditions, excluding differential settling, under which collisions can be brought about :

- Perikinetic conditions - interparticle collisions occur wholly as a result of Brownian motion. The implications of such conditions are that the removal of dissolved iron should show a second order dependency with respect to the concentration of iron, as shown in equation 1.
- Orthokinetic conditions - interparticle collisions occur as a direct result of agitation. Shear velocity increases the particle flux, hence the particle collisions, proportionally to the third power of their collision diameter.

Classic colloid theory (von Smoluchowski, 1917), predicts that for particles of a diameter up to 1 μm, perikinetic aggregation will dominate, whilst for the larger end of the particle size spectrum, orthokinetic behaviour dominates. Fiella & Buffle, (1993) set up a model of colloidal coagulation combining basic coagulation theory and Stoke's Law for gravitational settling - giving a dynamic equation describing the behaviour of hydrophobic particles in an aqueous system. Particle transport, Brownian motion, fluid shear and differential settling are all taken into consideration.

From the model three coagulation regimes were identified :

1. initially small particles coagulate rapidly to form more stable aggregates (> 100nm).
2. intermediate sized particles (100-700nm), slowly coagulate forming aggregates hardly larger than the initial particle size.
3. initially larger particles (>700nm), are subject to sedimentation.

The observations of a stable region between 100 - 700 nm in size are consistent with the observations on the natural environment that a significant proportion of 'dissolved' species are actually colloidal in nature *e.g.* Moore *et al.,* (1979) determined that over 90% of the dissolved iron present in the Beaulieu river was in the 100-450nm nominal size range. This high concentration of particles contains within it the dissolved iron species under study. Fiella & Buffle, (1993) observed links between the colloidal particles and organic material thought to be exerting a stabilising effect, using transmission electron microscopy (TEM). Two types of natural organic material were observed in this way, soil derived fulvic acids which form a thin coating on the colloid and comparatively larger organic structures, of a filamentous nature, both of which can affect coagulation processes (Buffle & Leppard, 1995). The association appears to be one of chemical bridging (La Mer & Healy, 1963) of iron and organic material; see section 1.4 for a more detailed discussion.

The phenomenon of flocculation of dissolved iron should not be regarded as a large scale removal of iron from the estuarine environment, but rather as an increase in the size of the smaller estuarine particles. The newly formed aggregates will not necessarily be removed from the water parcel, but will more likely remain conservative within it (Mayer, 1982a). This is backed up by literature documenting the presence of iron rich particles filterable but non-settleable, within the turbid regime of the estuary. The larger, more dense particles are likely to settle out in the estuary, or become scavenged. The majority of the iron rich colloids will become flushed out into the shelf waters, where either gravity settling over the greater settling time, or plankton biodepositional mechanisms will result in eventual removal from the water column.

1.5.4 Steric Stabilisation

In river waters with zero salt addition, the high kinetic stability of colloids can be accounted for by strong mutual repulsion between electrical double layers. As previously stated, a small increase in the ambient ionic strength would compress these layers significantly and cause a full destabilisation by a salinity of ~ 3. As a proportion of the colloid population is still stable at and above this salinity, there must be some means of stabilisation occurring - the most likely being steric stabilisation caused by the presence of adsorbed organics on the surface of natural colloids (Napper, 1977; Ottewill, 1977; Overbeek, 1977).

Possible mechanisms for steric stabilisation are :

- Particle collisions could result in desorption of stabilisation agent at point of contact. The positive free energy of this process[2] corresponds to particle - particle repulsion and enhanced stability.

- During interparticle collision it is possible that the adsorbed layers of particles may become compressed rather than penetrating one another. This would lead to a reduction in the available configurations of polymer molecules, giving an entropy decrease, a free energy increase and increased stability.

- Possible interpenetration of adsorbed layers could give a localised increase in the concentration of polymer segments. This can lead to osmotic repulsion or attraction depending upon the balance between polymer-polymer and polymer-dispersion medium interactions.

Shaw, (1992)

The close approach of organically coated particles is opposed by a free energy increase due to a restriction of potential conformations of adsorbed molecules (volume effect) and also by an increase in concentration of adsorbed molecules (osmotic effect). The power and range of these effects depend upon the adsorption density, the molecular size and the chemical structure of the molecule. A sufficient density of adsorbed molecules can maintain particle separation beyond the range of van der Waals attractive forces (Ottewill, 1977). To destabilise sterically stabilised colloids, chemical interactions must take place which alter either the adsorption density or the conformation of the attached molecules. It is thought that changes in the conformation of the adsorbed humic molecules are the most important (Tipping & Cooke, 1983), although the adsorption density is sensitive to the chemistry of the ambient medium. (Tipping, 1981 and Davis, 1982).

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[2] ΔG_{ads} is positive, whereas ΔG_{des} is negative.

Complexation of the ionised functional groups in waters of increasing salinity reduces the coulombic repulsion within and between adsorbed humic acids thus allowing them to contract in size to an extent at which van der Waals can act to cause aggregation. De Haan *et al.* (1987) showed a significant decrease in the size of aquatic humic substances with increasing salinity.

A more precise description of steric stabilisation and its associated effects awaits an increased knowledge in the behaviour of the surfaces of organically coated naturally occurring colloids.

1.6. Kinetics of Iron Aggregation in the Estuarine Environment

During the mixing of river water and sea water, riverine iron colloids are destabilised by the increase in the concentration of sea water cations which cause them to undergo aggregation via interparticle collisions. This aggregation leads to an increase in particle size and therefore to a decrease in the fraction of iron in the operationally defined dissolved fraction (Boyle *et al.,* 1977; Sholkovitz *et al.,* 1978; Fox, 1983; Fox & Wofsy 1984; Mayer, 1982b; Duffy, 1985; Hunter & Leonard, 1988; Hunter, 1990). Though this effect has been well documented in the majority of estuaries studied, only a limited number of studies on the kinetics of this process have been carried out.

According to the classical colloid theory developed by von Smoluchowski, (1917), the rate of aggregation for particles less than 1μm in diameter is insensitive to shear and is controlled mainly by the frequency of collisions, which is itself controlled by Brownian motion.. The rate of decrease in the number of particles, N, in a suspension of uniform particles follows a second order rate law :

$$\frac{-dN}{dt} = \alpha \cdot k_{\max} N^2$$

$k_{\max}$ = rate constant for a fully destabilised colloidal particle population.
α = collision efficiency.

This equation can be applied to dissolved iron concentrations if :

i) the microcolloids fall into a small size range.
ii) there is a uniform distribution of dissolved iron.

This is probably somewhat of an oversimplification of the real situation, but it has generally been argued that removal of 'dissolved' iron under conditions simulating estuarine mixing is a second order rate process.

Mayer, (1982b), with a combination of laboratory experiments and field data from the Saco River Estuary, Southern Maine USA, presented evidence for the second order kinetic model of dissolved iron aggregation. Through a series of batch mixing experiments with filtered river and sea water, the aggregation was found to consist of a rapid initial reaction, over the first ~2 minutes, followed by a distinctly slower second reaction. The kinetics of the second reaction were found to be dependent upon the presence of the aggregates formed in the initial reaction. Due to its rapidity, kinetic analysis of the first reaction was not carried out, the second reaction was found to show a second order kinetic dependence using the integrated rate expression *i.e.* the results approximate linearity for a plot of 1/[Fe] vs. time. Daily variations were noted for the second order rate constants. Mayer, (1982b) predicted that the overall kinetics of the reaction were pseudo second order - being a 2nd order reaction with 1st order dependency on the aggregates formed in the first reaction. The work of Fox & Wofsy, (1983), studying the rivers in the Delaware Bay area, also concurred with the predicted second order kinetic model. Batch mixing experiments were carried out over 3 hours and again plots of 1/[Fe] vs. time approached linearity. There was, however, significant curvature in the plots, especially in the higher salinity regions for all of the rivers studied - casting some doubt on the applicability of the second order model (Duffy, 1985).

The second order model was challenged independently by Duffy, (1985) and also by Hunter & Leonard (1988). Studies were carried out using water collected respectively from the Tamar and Beaulieu estuaries in Southern England and from the Leith and Dunedin Estuaries by these authors. It was found that although the plots of 1/[Fe] vs. time did approach linearity in some regions of the plots, the data were certainly not linear enough to confirm a second order model for destabilisation, even worse fits were obtained for zero and first order plots. Duffy also tested the data by a number of kinetic methods[1] other than the integrated rate expression and still the order could not be determined.

In the kinetic analysis of the data until this point, it had been assumed that all of the iron present was susceptible to destabilisation - despite the observations of Boyle *et al.,* (1977) that the dissolved iron concentration decreases to an apparent equilibrium level rather than to zero. Taking this fraction into consideration, the integrated rate expression becomes :

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[1] Methods used were : Fractional life method, Powell plot, Van't Hoff method and the Guggenheim approach.

$$kt(n-1)=\left[\frac{1}{(C_o-C_f)^{n-1}}\right]-\left[\frac{1}{(C_o-C_t)^{n-1}}\right]$$

C_o = original iron concentration.
C_t = concentration of iron at time, t.
C_f = unreactive iron concentration.
k = rate constant.

This simplifies to :

$$k_2t=\frac{(C_o-C_t)}{(C_t-C_f)(C_o-C_f)}$$

for 2nd order kinetics.

where : k_2 = second order rate constant.

Duffy (1985) calculated the unreactive fraction of dissolved iron by extrapolation of the kinetic curves[2]. Using this method, both first and second order models were found to give correlation coefficients of 0.990 or greater (however, no fits of the modelled data to the removal profile were provided). Greater amounts of cation added were found to decrease the amount of iron in the unreactive fraction. (the first order model predicted greater iron destabilisation than the second order). Rate constants for the first order kinetic model were : $7.1\text{-}12.1*10^{-3}s^{-1}$ for the Tamar and $7.3\text{-}13.9*10^{-3}s^{-1}$ for the Beaulieu. Second order rate constants showed significant variability, between different samples collections for a river and also between rivers.

Earlier studies were re-evaluated in the light of the occurrence of an unreactive fraction and it was found that though the actual amounts of unreactive dissolved iron varied markedly from river to river, the results of previous studies could also be fitted to either first or second order kinetic models.

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[2] The loss of dissolved iron could be expressed by an exponential term, and the asymptotic value of dissolved iron represents the unreactive fraction. Values obtained in this way were close to the concentrations of residual dissolved iron measured after 24 hours.

These findings put the second order behaviour of microcolloidal aggregation into question. Second order kinetic behaviour of iron was possibly so readily accepted because it was seen to agree with the understood mechanism of colloid aggregation. If the first order model is to have any credence, then it must be backed up with a rational mechanistic explanation.

- One possible mechanism is that of shear, as orthokinetic aggregation occurs via first order kinetics. For particles of the size that are being dealt with (<0.45μm) however a velocity gradient of $100s^{-1}$ would be required for orthokinetic aggregation to exceed perikinetic aggregation. This value is significantly higher than the shear rates liable to be experienced as a result of stirring in any of the experiments carried out (~ $10s^{-1}$) - thus Duffy, (1985) argued that shear is unlikely to be the cause of first order kinetics.

- Another possible explanation for the reaction occurring by first order kinetics is dependent upon the distribution of dissolved iron throughout the microcolloidal particle population (Morris pers. comm.). It is unlikely that every particle in river water contains iron, therefore we can assume that within a microcolloidal particle population there are a number of particles, n, that do contain iron (type a) and a number, N, of those which do not (type b). During the aggregation of such a population there will be three possible types of collision : a-a collisions, a-b collisions and b-b collisions. The latter type need not be considered as it does not result in loss of iron. Thus we are considering the loss of iron by collisions of two iron bearing particles and by the collision of an iron bearing particle with an iron free particle. Obviously there is twice as much iron removed in the first reaction type. The rate of loss of iron can be considered as :

$$\frac{-d[Fe]}{dt} = k_{\max}\left(\alpha \cdot n^2 + \beta \cdot nN\right)$$

If we consider the situation where n >> N *[3], then collisions between a-type particles will dominate aggregation[4]. The equation in this case approximates a second order rate expression. In the converse situation, with N >> n, iron is held within a small fraction of

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*[3] approximately a uniform distribution of iron throughout the particle size spectrum.

[4] apart from the unlikely scenario where $\alpha >> \beta$.

particle population, a-b collisions will dominate the aggregation process[5], and the equation approximates to :

$$\frac{-d[Fe]}{dt} = k_{\max}\beta \cdot nN$$

which is a first order expression for the loss of dissolved iron - provided N remains effectively constant.

It has been shown by particulate analysis of suspended material from the Ems river estuary that iron is non uniformly distributed throughout the particle population in the 1-6 μm size range (Bernard *et al.,* 1986). There is no reason to suggest that there should be any difference in the sub-micron region. This illustrates that the removal of dissolved iron is of a first or possibly a non integral rate order.

Hunter & Leonard, (1988) also suggested that the use of the second order model had been somewhat overstated in previous kinetic interpretations. According to these authors, experimental artefacts are present in much of the work published (pre-1988), as unstable colloids in river water aggregate considerably before salt addition. It is important to appreciate that kinetic analysis based upon likely collision models is rendered invalid if the efficiency of collisional encounter is not constant (*i.e.* if the stabilities of the colloid particles are not uniform). In natural systems such as river water, it is very likely that surface chemistry and electrostatic properties determining stability are variable. Theoretical work suggests that stability also depends upon particle size and is affected by variations in particle size and surface charge in polydisperse suspensions (Prieve & Lin, 1982). This means that a kinetic interpretation of aggregation experiments in terms of a simple colloidal aggregation model is likely to be ruled out by the changing stability ratios of particles.

The initial rapid aggregation suggests the occurrence of a fraction of dissolved iron very unstable with respect to salt induced aggregation, due to complete or near complete electrolyte destabilisation of colloids by sea water cations. The increase in the amount of dissolved iron aggregated with increasing salinity leads to the assumption of a spectrum of inherent colloid stabilities in the particle population- an increase in salinity bringing a new fraction of iron into an unstable region. These fractions of stabilised iron may be regulated by particle size, shape, surface properties or by differing degrees of stabilisation

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[5] apart from the unlikely scenario where $\beta >> \alpha$.

by association with humic acids and / or specifically adsorbed ions. Concurrent with this rapid aggregation it is possible that more stable colloids are progressively aggregated at lower rates over several hours.

Hunter et al. (unpublished) found that the kinetics of aggregation could be described by a fairly simple kinetic law, when looking at an increase in aggregation with increasing salinity. From the results of experiments using a single stirred tank to which sea water is continually added, a heterogeneous kinetic model for aggregation was presented. The model adequately describes the observed behaviour and the dissolved iron / salinity profiles seen both in the laboratory and in the field. The model considers the aggregation in terms of a Gaussian distribution of activation energies, equivalent to a log - normal distribution of rate constants. Kinetic data is parameterised by a mean rate constant (the reciprocal of an exponential decay constant - the e-folding time) and the standard deviation of the distribution. The model predicts that almost all reactions are independent of shear - implying perkinetic nature of particle aggregation which agrees with original hypotheses.

The mean rate constant for aggregation is approximately linearly dependent on the rate constant for salinity increase. The dissolved iron / salinity profile which results is almost independent of the rate of salinity increase in an estuary, which opposes the Fox (1984) model. The principal factor controlling the shape of the profile is the standard deviation of the rate constant distribution - probably related to the heterogeneity of colloids with respect to particle size and surface chemistry.

1.7 Objectives of present study.

The initial objectives of the present work were :

- To investigate the extent and rate of removal of dissolved iron during laboratory simulated estuarine mixing, using the methodology of Duffy (1985) in a fuller set of experiments with fewer variables than in her work, and to examine the validity of both first and second order kinetic models as descriptors of the removal process. The aim was to obtain a basis for a more critical evaluation of the rate order and potentially to throw light on the mechanism of iron removal.

- To investigate, in the same experiments and using the same approach to kinetic analysis of the data, the extent and rate of removal of dissolved phosphate, with the aim of obtaining a better understanding of the relationships between removal of iron rich colloids and the behaviour of phosphate, potentially at the mechanistic level

- To examine the effects of sample storage on the subsequent behaviour of iron during simulated estuarine mixing experiments, as raised by the findings of Hunter & Leonard (1988), and to extend the work to include phosphate.

In the course of these studies, a further objective emerged, namely :

- To examine critically the effects of experimental variables on findings on the iron removal processes, covering the range of these variables in the methodologies used by previous investigators. Again the objective was extended to include the effects of variables on the behaviour of phosphate.

Chapter Two

Experimental Methods

There have previously been a number of different experimental approaches to the simulation of estuarine mixing, ranging from simple batch mixing to more complex multi-tank dual flow simulations. Studies of the reactions of dissolved iron using such approaches have been, for the most part, limited to simple batch mixing experiments, with only the experiments of Bale & Morris, (1981), Smith & Longmore, (1981), and Hunter *et al.*, (1990) attempting to simulate a gradual salinity increase. 'Dissolved' iron is operationally defined as that fraction of iron passing through a 0.45μm nominal pore size filter, which includes microcolloidal material as well as truly dissolved species. A comparison of the key methodologies of batch mixing used in these studies shows that the experimental conditions employed have differed considerably. The main factors that vary among the different experimental methodologies are : water sampling strategy; pre-filtering of river and/or sea water; initial mixing and subsequent stirring regime; procedure for sampling at intervals during the experiments and analytical technique. Four of the previous methods were compared in the present work, as described in Chapter 5, in order to investigate the extent to which differences in findings might reflect differences in methodology. Previous kinetic studies have not included an examination of the behaviour of both iron and phosphate; the latter was investigated in all of the present investigations Further experiments were carried out to isolate and study the effects of stirring rate on the removal of iron and phosphate, in batch mixing experiments. Details of the different methods investigated, together with other procedures used in the present work are given below.

Among the methods used in the studies, only that of Duffy, (1985) employs continuous sampling, which enables the time course of the reactions to be investigated more intensively. This method was used in the detailed examination of the behaviour of iron and phosphate in filtered river water on addition of calcium ions as described in Chapters 3 and 4.

2.1 Sample Collection.

River water samples were collected in acid cleaned 25 litre polypropylene carboys, from the zero salinity region of the Tamar river - 4 miles up river of the Gunnislake weir at Latchley. The samples were transported back to the laboratory for analysis, with each individual carboy being used for a single batch of individual experimental runs. Any treatment processes of filtering or temperature equilibration were carried out just prior to each individual experimental run. In the investigation into the effects of storage time, the samples were left undisturbed in a carboy, and aliquots removed after set time periods. Again no treatment processes were carried out until just before the experimental run. Samples for the comparison of batch mixing methodologies were collected in containers analogous to those used by the original authors, and were treated in the same manner as in the original publications - see Section 2.5 for batch mixing methodologies.

Sea water was collected from the frequently refilled reservoir in the Plymouth Marine Laboratory seawater hall. The water in the reservoir is collected weekly from Plymouth Sound beyond the breakwater, by the Eddystone Lighthouse. Sea water was used unfiltered or was filtered according to the procedures specified by the authors, to conform to the approach adopted in the original study.

2.2 Colorimetric Determinations

It is well documented in the literature, that the major changes in the concentration of dissolved iron and phosphate during estuarine mixing simulations occur within the first 2-3 minutes following mixing (Boyle *et al.,* 1977; Smith & Longmore, 1980; Bale & Morris, 1981; Tyler, 1989; see fuller discussion in section 3.5). Therefore a method of continuous autoanalysis offers substantial advantages over a discrete sampling method. For this purpose, the Technicon Auto Analyser II system was used as it provides a method of closed flow analysis, with techniques for the colorimetric determination of both dissolved iron and inorganic phosphate. In the majority of the previous studies, excluding that of Duffy (1985), who used 2,4,6-tri-pyridyl-s-triazine (TPTZ), the colorimetric determinations were carried out using ferrozine as the colorimetric reagent. A comparison between the ferrozine and TPTZ methods was carried out to establish whether or not this was a potential source of methodological differences.

2.2.1 The colorimetric determination of dissolved iron, using ferrozine.

The colorimetric determination of dissolved iron, using ferrozine is based on the method of Stookey, (1970), as adapted and updated for autoanalysis by Gibbs, (1979).

The sample was supplied to the reaction manifold (Fig 2.1), from the filtration block, at a rate of 0.4 ml min^{-1}. An acid reductant consisting of acidified hydroxylammonium hydrochloride was added, which reduced all of the iron present to the Fe(II) state, and kept it in solution. After mixing, a buffered colour forming reagent of sodium acetate tri-hydrate and ferrozine was introduced to the sample to adjust the pH to an optimum level for the colour forming reaction to take place. The tridentate Ferrozine ligand attaches to the Fe(II) ions, forming a magenta coloured planar compound. Absorbance was measured at 540nm, using a 50mm flow cell.

The colorimeter was calibrated with standard solutions of ferrous ammonium sulphate. The detection limit of the technique (3 x std dev. of blank) was ~ 0.2 μmol l^{-1}, and linearity is observed over the concentration ranges found in the environment studied.

Prior to the preparation of reagents, all glassware was rinsed thoroughly with concentrated hydrochloric acid, followed by MilliQ water.

Reagents

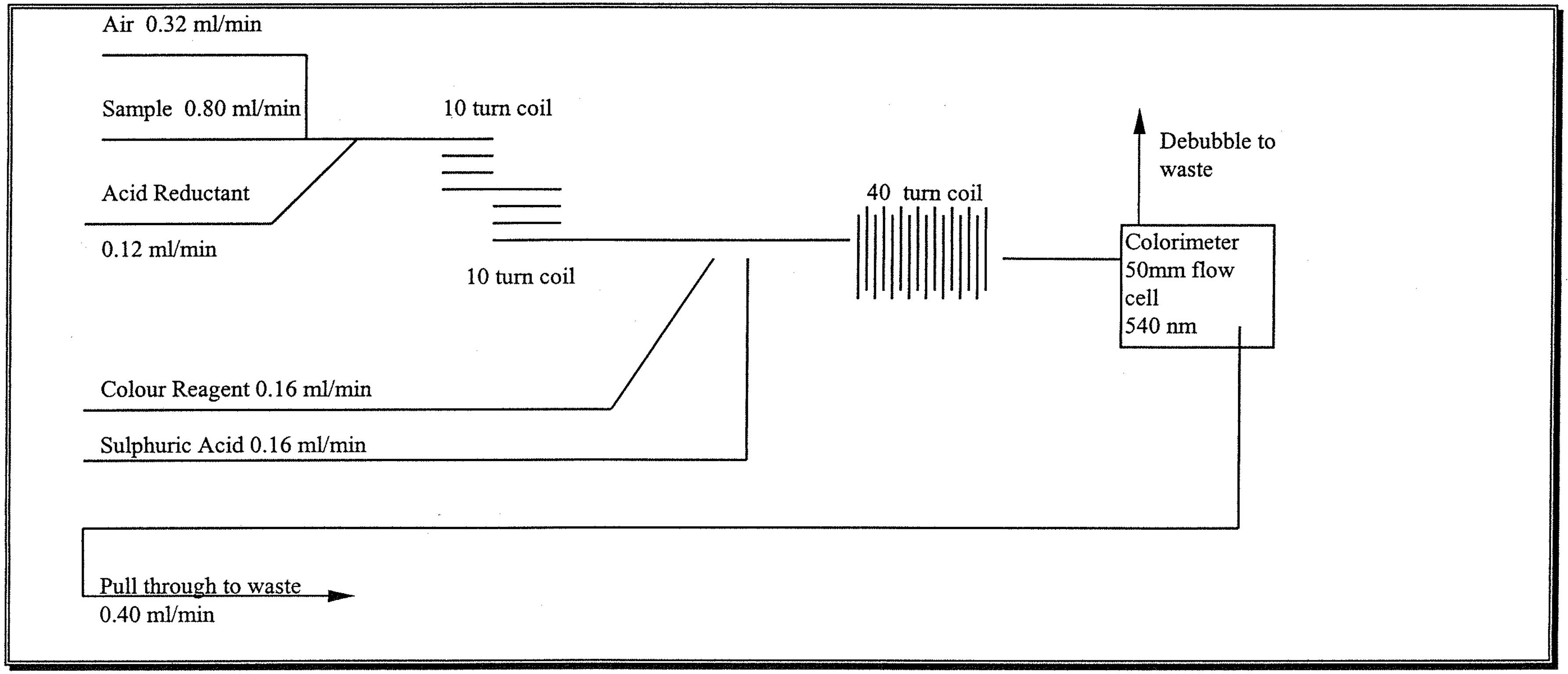
Acid Reductant

In a 100 ml volumetric flask 10.0g of hydroxylammonium hydrochloride was dissolved in 50 ml MilliQ water. To this 30 ml of 5.0 N hydrochloric acid was added and the solution was subsequently diluted to 100 ml with MilliQ water. The reagent was stable for three weeks.

Colour-forming reagent

The colour-forming reagent consisted of a combination of a buffer solution and a ferrozine solution which were mixed in the ratio five to two. It was stable for one day.

Figure 2.1 Reaction manifold for the colorimetric determination of iron using ferrozine.



Buffer :

In a one litre volumetric flask, 473g of sodium acetate trihydrate was dissolved in 500 ml MilliQ water with warming. To this 115 ml of glacial acetic acid was added and the resultant solution was diluted to 1 litre with MilliQ water. The reagent was stable for at least one month.

Ferrozine Solution :

In a 100ml volumetric flask 0.075g ferrozine was dissolved in 50 ml of MilliQ water. To this 2.0 ml 5.0 N hydrochloric acid was added and the solution was subsequently diluted to 100 ml. The reagent was stable for one month.

Standards :

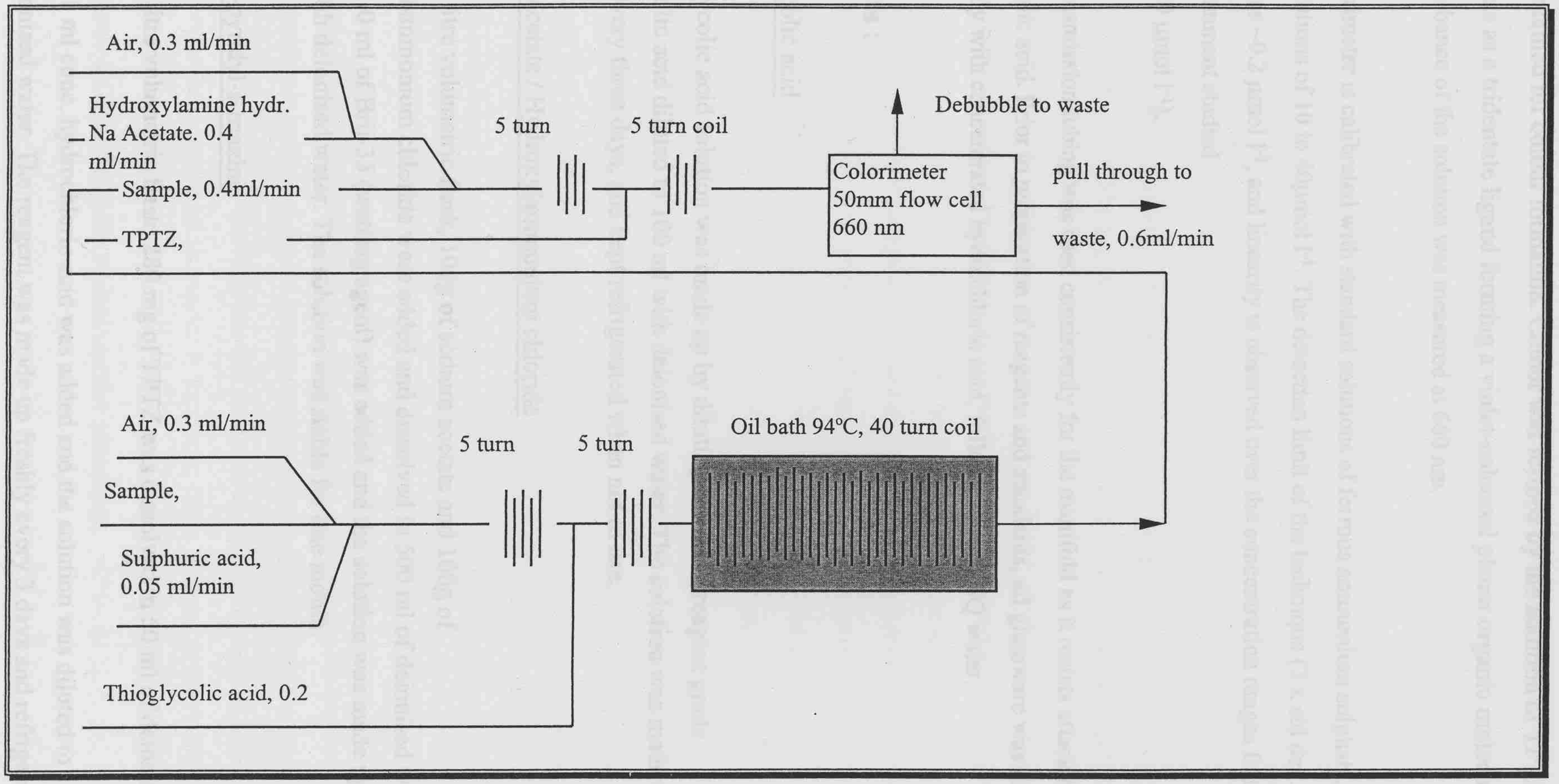
A 10mmol l^{-1} solution was prepared by dissolving 0.559g of ferrous ammonium sulphate in 0.1N sulphuric acid, dilute to 1 litre with the same. An intermediate solution of 1mmol l^{-1} was prepared by dilution of 10.0 ml of the 10mmol l^{-1} stock standard to 100 ml with 0.1N sulphuric acid in a 100 ml volumetric flask. From this solution, working iron standards were prepared of 10, 20, 30 and 40 μmol l^{-1}, by dilution of 1.0, 2.0, 3.0 and 4.0 ml respectively of the intermediate standard to 100 ml with 0.1N sulphuric acid in a 100 ml volumetric flask.

2.2.2 The colorimetric determination of dissolved iron, using TPTZ.

The method of colorimetric determination of dissolved iron, using TPTZ was based on the method of Collins & Diehl, (1960), updated for autoanalysis by Howland *et al.*, (1988).

The sample was supplied to the reaction manifold (see Fig 2.2), from the filtration block at a rate of 0.4 ml min^{-1}. To the sample, 1N sulphuric acid was added to the sample to maintain the iron species in solution. Thioglycolic acid was added to the sample stream, which was then heated to 95 ^{o}C for approximately 8 minutes, to convert the soluble colloidal iron complexes and precipitated iron to an ionic form. Hydroxylammonium chloride / sodium acetate buffer was then introduced to ensure that all of the free iron in the solution was reduced to the ferrous state, and that the optimum pH range (3.4 - 5.8),

Figure 2.2 : Reaction manifold for the colorimetric determination of iron using TPTZ.



was maintained for colour formation. Colour was formed by the addition of TPTZ, which acts as a tridentate ligand forming a violet-coloured planar organic molecule. The absorbance of the solution was measured at 660 nm.

The colorimeter is calibrated with standard solutions of ferrous ammonium sulphate, using solutions of 10 to 40μmol l^{-1}. The detection limit of the technique (3 x std dev. of blank) was ~0.2 μmol l^{-1}, and linearity is observed over the concentration ranges found in the environment studied
(up to 100 μmol l^{-1}).

Glass transmission tubing was used consistently for the manifold as it resists attack by the thioglycolic acid. Prior to preparation of reagents and standards, all glassware was rinsed thoroughly with concentrated hydrochloric acid, followed by MilliQ water.

Reagents :

Thioglycolic acid

A thioglycolic acid solution was made up by diluting 5.4 ml of reagent grade thioglycolic acid diluted to 100 ml with deionised water. The solution was made up freshly every three days, and kept refrigerated when not in use.

Sodium acetate / Hydroxylammonium chloride

In a one litre volumetric flask, 100g of sodium acetate and 100g of hydroxylammonium chloride were added and dissolved in 500 ml of deionised water. To this 1.0 ml of Brij-35 (wetting agent) was added and the solution was made up to 1 litre with deionised water. The solution was stable for one month.

2,4,6-tri-pyridyl-s-triazine

In a one litre volumetric flask, 280 mg of TPTZ was dissolved in 50 ml of deionised water.
To this 1 ml conc. hydrochloric acid was added and the solution was diluted to 1 litre with deionised water. The reagent was made up freshly every 3 days and refrigerated when not in use.

Standards :

Standards were prepared as for the ferrozine method (section 2.3.1)

2.3.3 The colorimetric determination of inorganic phosphate, using molybdenum blue.

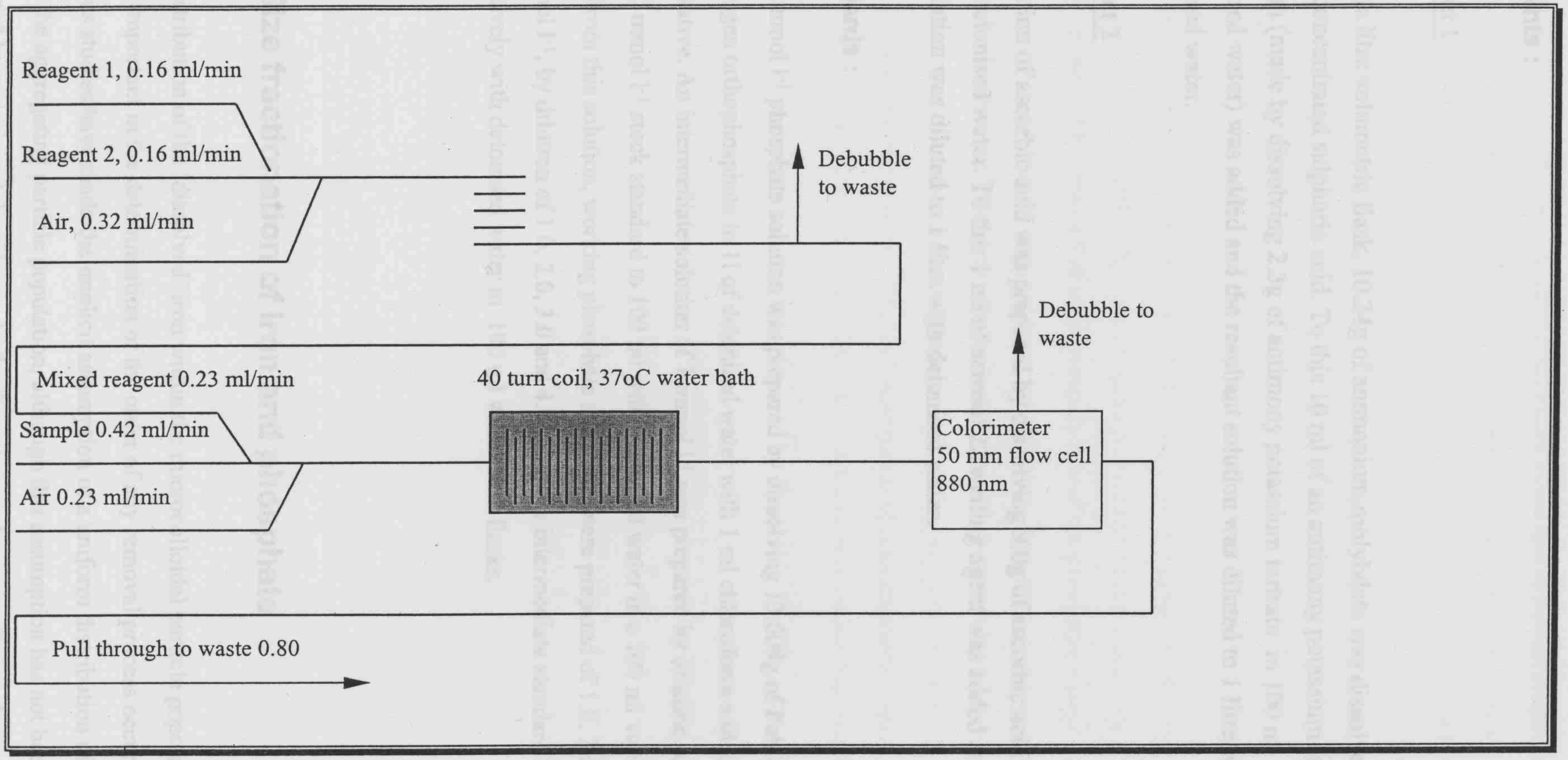
The colorimetric determination of inorganic phosphate, using molybdenum blue is based on the technique of Murphy & Riley, (1962), as updated by Kirkwood, (1989).

Under acid conditions, phosphate and molybdate react to form a dodecahedral poly acid. The presence of trivalent antimony ions increases the molecular extinction coefficient of the complex formed. Ascorbic acid reduces the heteropoly acid to an intensely coloured phospho-molybdenum blue compound, the absorbance of which was measured at 880nm. The ammonium molybdate and ascorbic acid were added as separate reagents, as they become unstable if they are mixed prior to addition to the sample. The colorimeter is calibrated with standard solutions of potassium dihydrogen phosphate.

Detection is possible down as far as 15nmol l^{-1}, under optimum conditions. Interference is possible with both arsenate and silicate however the arsenate reaction forming the molybdenum blue complex is significantly slower than for phosphate and causes no significant problems with the relative concentrations usually present in natural waters. Silicate has been found to cause interference only when at concentrations in excess of 150 μmol l^{-1}.

The method of phosphate determination can considerably overestimate the true soluble orthophosphate concentration, due to acid hydrolysis of polyphosphates and organic phosphorus compounds and the dissolution of phosphorus-containing colloids under the analytical conditions employed (Kuenzler & Ketchum, 1962; Downes & Paerl, 1978; Peters, 1978). In recognition of these analytical uncertainties, results obtained by this method alone are conventionally termed reactive phosphate.

Figure 2.3 : Reaction manifold for the colorimetric determination of inorganic phosphate using molybdenum blue and colour forming reaction.



$$PO_4^{3-} + 12\ MoO_4^{2-} + 27H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12\ H_2 0$$

$$H_3PO_4(MoO_3)_{12} \xrightarrow[\text{reductant}]{} \text{Phosphomolybdenum blue.}$$

Reagents :

Reagent 1

In a one litre volumetric flask, 10.24g of ammonium molybdate was dissolved in 115 ml of concentrated sulphuric acid. To this 10 ml of an antimony potassium tartrate solution (made by dissolving 2.3g of antimony potassium tartrate in 100 ml deionised water) was added and the resultant solution was diluted to 1 litre with deionised water.

Reagent 2

A solution of ascorbic acid was prepared by dissolving 9.0g of ascorbic acid in 500 ml of deionised water. To this 1 ml of aerosol 22 wetting agent was added and then the solution was diluted to 1 litre with deionised water.

Standards :

A 100 mmol l^{-1} phosphate solution was prepared by dissolving 13.609g of Potassium dihydrogen orthophosphate in 1l of deionised water with 1 ml chloroform added as a preservative. An intermediate solution of 1 mmol l^{-1} was prepared by dilution of 1.0 ml of the 100 mmol l^{-1} stock standard to 100 ml with deionised water in a 100 ml volumetric flask. From this solution, working phosphate standards were prepared of 1.0, 2.0, 3.0 and 4.0 μmol l^{-1}, by dilution of 1.0, 2.0, 3.0 and 4.0 ml of the intermediate standard to 100 ml respectively with deionised water in 100 ml volumetric flasks.

2.3 Size fractionation of iron and phosphate

The distribution of the 'dissolved' iron within the microcolloidal particle population is highly important in the determination of the order of any removal process occurring. Previous studies have made the implicit assumption of a uniform distribution of iron within the aggregating particle population, although this assumption has not been supported by experimental evidence. In the Ems river and estuary, Bernard *et al.,* (1986) demonstrated that iron was not uniformly distributed amongst riverine colloidal material, showing instead a highly non-uniform distribution in the one to six µm range. Hence there is no evidence to suggest that a uniform distribution should be observed when a study of a smaller size fraction is carried out. Theoretical work also suggests that stability within a colloidal system is dependent to some extent on particle size (Overbeek, 1977) as well as surface chemical and electrical properties - see section 1.5. For this reason a study of the size distribution of iron within the 0.1 to 8.0 µm size fractions of Tamar river water was carried out.

It is unclear at present the extent to which phosphate present in the smaller size fractions of river water is associated with microcolloidal particles or within a truly dissolved form, Bale & Morris, (1981) found that approximately half of the phosphate passing through a 5.0 µm filter also passed through a 0.1 µm cut off filter. The nature of the relationship between iron and phosphate as evidenced in the removal observed during simulated estuarine mixing is believed to be influenced to some degree by the relative size distributions of the two species. The size fractionation of microcolloidal iron and dissolved inorganic phosphate was studied, in an attempt to elucidate any links between their distribution throughout the size range of river water and behaviour.

A sample of river water was collected, and sub-samples were filtered through a range of differently sized polycarbonate Nuclepore filters : 8.0, 5.0, 3.0, 2.0, 1.0, 0.8, 0.45, 0.4, 0.2 and 0.1 µm. The filtrate in each case was then analysed for both iron and phosphate to determine their relative proportions in the nominal size ranges 8-5, 5-1, 1-.45, .45-0.1 and <0.1µm.

2.4 Procedures used in mixing experiments

A number of different methodologies which have been used in estuarine mixing simulations, as applied to the study of dissolved iron removal, were investigated in order to identify the effect of experimental differences on the various observations of iron behaviour. Investigations of the behaviour of phosphate were incorporated into the experimental sphere.

In this study the methodologies of Mayer, (1982); Fox & Wofsy, (1983); Duffy, (1985) and Hunter & Leonard, (1988) were considered. The experimental methodologies can be categorised with regard to the type of solution used to initiate destabilisation. All four workers used sea water, however Duffy, (1985), also used individual ions (sodium, calcium and magnesium. The experimental methodologies can also be categorised in terms of the sampling method used in the experiments (see chapters three and four for iron behaviour and comparable phosphate behaviour in continuous sampling methods, and chapter five for the comparison with discrete sampling methods). Mayer, (1982); Fox & Wofsy, (1983) and Hunter & Leonard, (1988) analysed discrete samples, which were removed from the mixing tank at set times throughout the course of the mixing simulation whereas Duffy, (1985) employed a continuous sampling method which enabled the time course of the reactions to be investigated more intensively.

2.4.1 Method of Mayer (1982)

- River water samples were collected in acid cleaned polyproplyene bottles, as described in section 2.2.

- River and sea water samples were filtered with a Gelman A/E glass fibre filter underlain by a Millipore 8.0μm filter, giving a nominal pore size of 0.5μm, and mixed together in a 4 litre glass container to make solutions of intermediate salinities.

- Solutions were placed on a reciprocating shaker at room temperature (~24^{0}C).

- 50 ml aliquots were periodically removed with an acid washed syringe and filtered through a Swinnex in-line filter holder with a Gelman A/E glass fibre filter underlain by a Millipore 8.0 μm filter prior to colorimetric analysis for iron and phosphate.

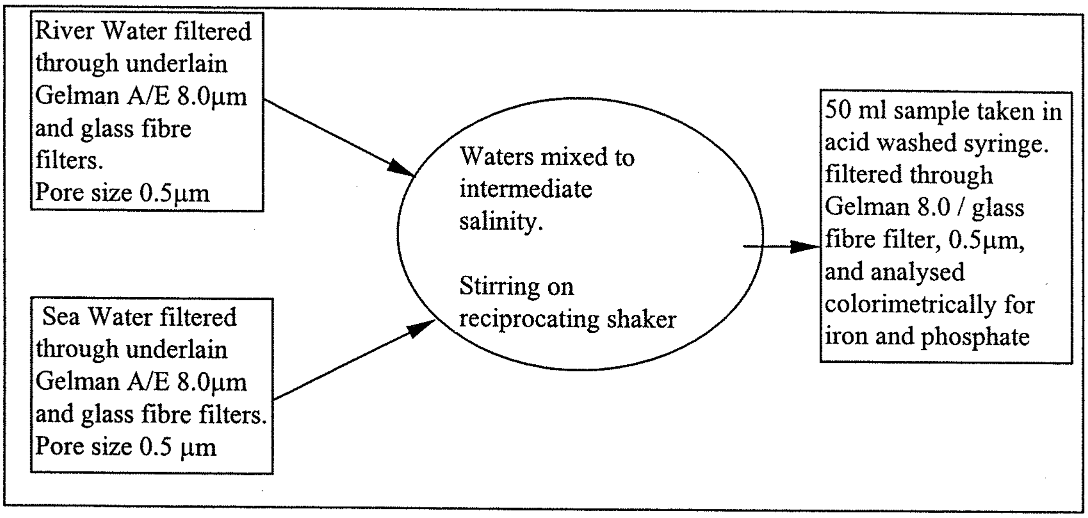


Figure 2.4. Schematic diagram of Mayer, (1982) mixing methodology.

2.4.2 Method of Fox & Wofsy, (1983).

- Samples of river water were collected in acid cleaned polypropylene bottles, as described in section 2.2.

- Unfiltered river water (of a salinity of <0.5) and GF/C filtered sea water (salinity of 33.5) were mixed together in 4 litre glass containers to make solutions of intermediate salinities.

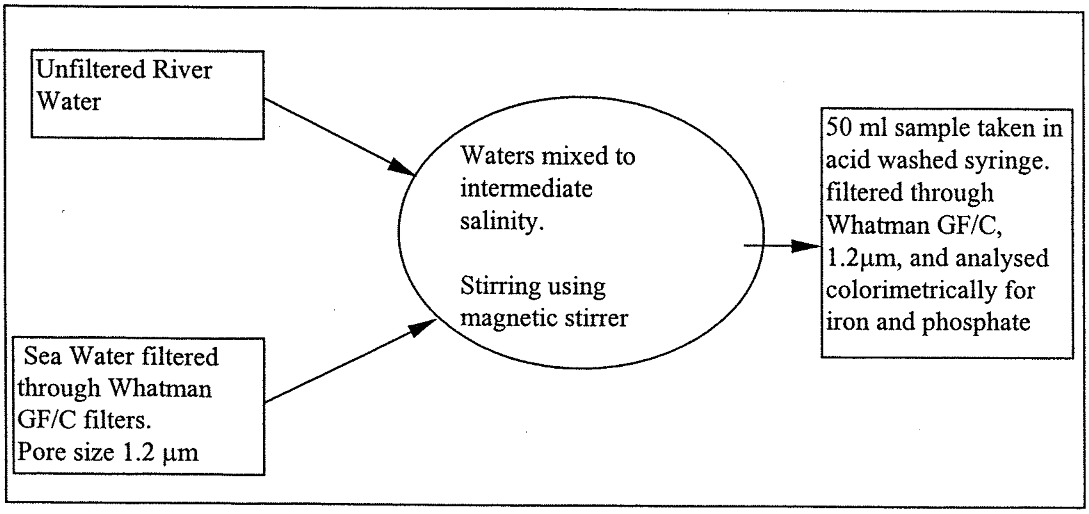


Figure 2.5. Schematic diagram of Fox & Wofsy, (1983) mixing methodology.

- Solutions were maintained at room temperature (~24^{0}C) and stirred with a magnetic stirrer.

- 50 ml aliquots were removed periodically and filtered through Whatman GF/C filters, nominal pore size 1.2μm, prior to colorimetric analysis for both iron and phosphate.

2.5.3 Method of Duffy, 1985.

The Duffy methodology (i) was extensively used in the course of the kinetic experiments, as it provides a continuous record of the removal process, as opposed to the discrete sampling, method of the other authors. The method (ii) was used in the comparison study with the other authors.

i) Kinetic experiments

- A sample of river water (4 litres), from the fresh water region of the Tamar river, as described in section 2.2, was placed into a 10 litre polyethylene mixing tank.

- Water in the mixing tank was circulated by use of a centrifugal immersion pump, connected to an on line perspex tangential filter block - housing an acid washed 0.45μm membrane filter. The system has been described by Morris *et al.,* (1978).

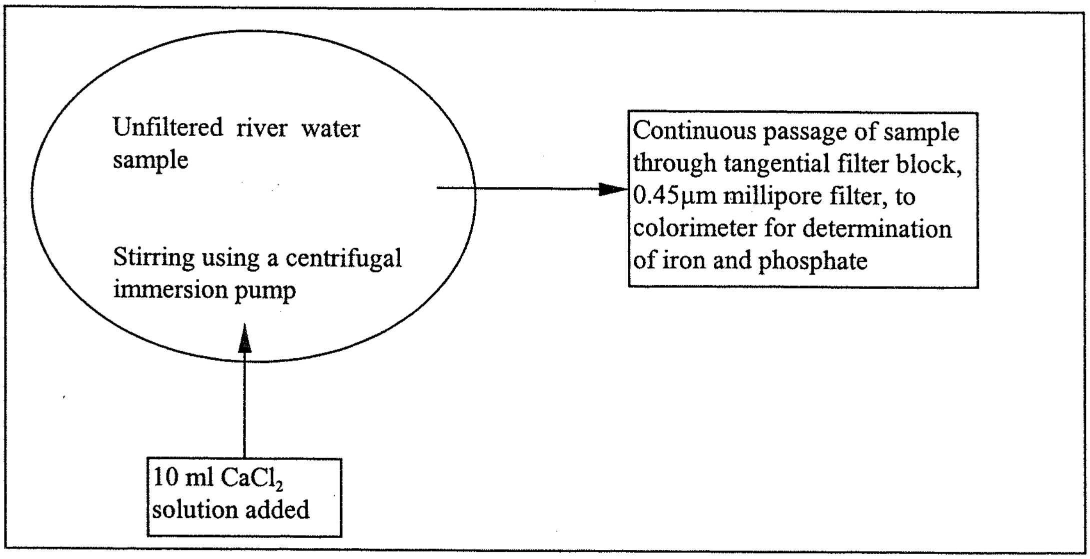


Figure 2.6. Schematic diagram of Duffy, (1985) mixing methodology (i).

- Water was pumped, at a rate of 0.4 ml min^{-1}, through two separate channels, from the filter block to the autoanalyser for colorimetric determination of dissolved iron and inorganic phosphate to get a fresh water baseline for dissolved iron and inorganic phosphate.

- A solution containing Ca^{2+} ions was added to the mixing chamber, in a 10 ml aliquot to control the salinity of the experiment . The concentrations used in different experiments were calculated to cover those corresponding to the full range of salinities experienced during estuarine mixing, from the fresh water end to the open sea at a salinity of approximately 35.

- In the comparison of methodologies, sea water was added to the filtered fresh water, as described below, to create samples of intermediate salinity

ii) Methodological Comparison

- Between two and four litres of river water (depending on the overall salinity of the experiment) was placed into a polyethylene mixing tank.

- Water was circulated by means of a centrifugal immersion pump, connected to an on line perspex tangential filter block - housing an acid washed 0.45μm membrane filter (Morris *et al.,* 1978).

- Water was pumped, at a rate of 0.4 ml min^{-1}, through two separate channels, from the filter block to the autoanalyser, to get a fresh water baseline for dissolved iron and inorganic phosphate.

- Sea water added to the tank to produce the required salinity in a total water volume of four litres, and mixed using the centrifugal immersion pump to give a continuous record of dissolved iron and inorganic phosphate during the removal process.

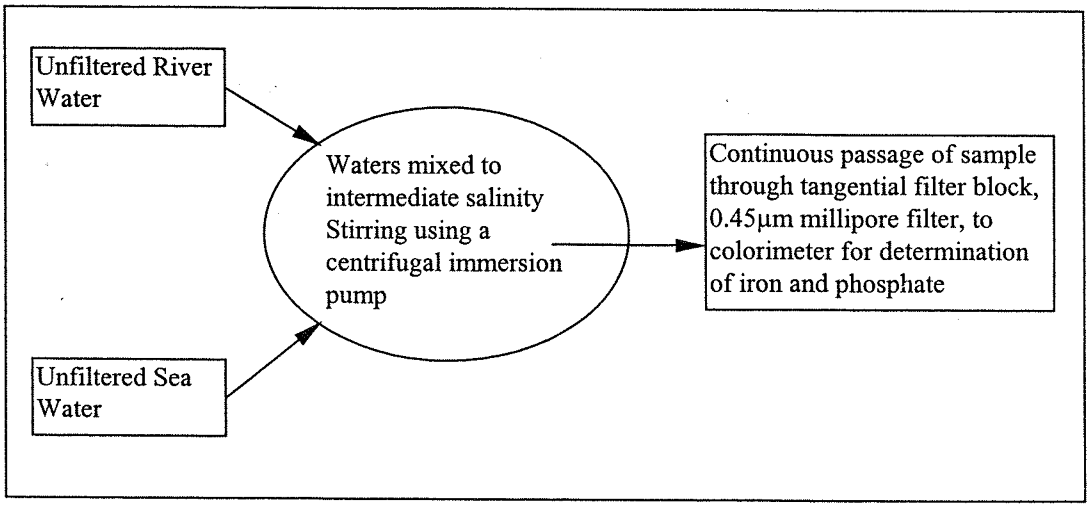


Figure 2.7. Schematic diagram of Duffy, (1985) mixing methodology (ii).

2.5.4 Method of Hunter & Leonard, (1988).

- River water samples were collected in acid cleaned polyethylene containers, upstream of the salt intrusion as detailed in section 2.2.

- Solutions of river and sea water were equilibrated to 25^{0}C.

- Unfiltered river water and sea water were mixed together in a 4 litre glass container to make solutions of intermediate salinities and stirred using a glass paddle.

- 50 ml aliquots were withdrawn via an acid cleaned syringe and filtered through an acid cleaned Whatman glass fibre filter in a Swinnex in-line filter holder, nominal pore size of 1.2µm, and analysed colorimetrically for iron and phosphate.

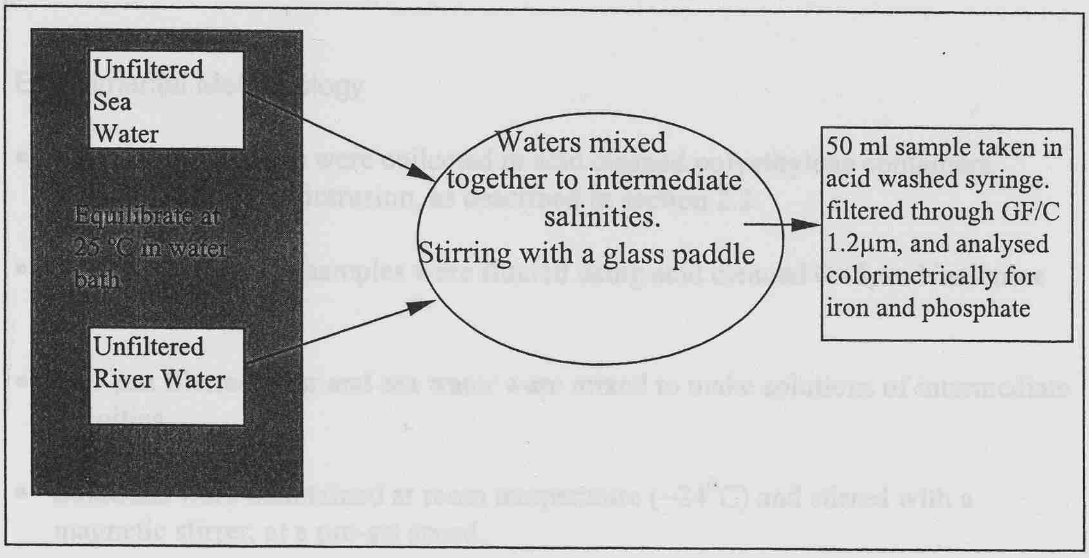


Figure 2.8. Schematic diagram of Hunter & Leonard, (1988) mixing methodology.

Prior to the addition of either sea water or Ca^{2+} ions, each fresh water sample was analysed for 2-3 minutes in order to achieve a reference for the initial concentrations of dissolved iron and inorganic phosphate. A baseline reading was established with distilled water between experimental runs and the linearity of response of the methods was tested both before and after experimental runs with a set of standards:

Phosphate - 0, 1, 2, 3, 4 µmol l^{-1} standards, were prepared by dilution from 100 mmol l^{-1} potassium dihydrogen orthophosphate stock standard.

Iron - 0, 10, 20, 30, 40 μmol l^{-1} standards, were prepared by dilution from 10 mmol l^{-1} ferrous ammonium sulphate stock standard.

The data from the experiments was logged onto a JJ Lloyds CR452 chart recorder and taken from these traces, via a digitiser tablet, to a spreadsheet for data handling.

2.6 Stirring Rate Experiments

Since stirring rates vary along with other experimental conditions among the different procedures given in section 2.5. An experiment was set up to look at the effects of stirring rate on the behaviour of microcolloidal iron and phosphate. Three sets of experiments were carried out, at different salinities in which all experimental parameters apart from the stirring rate were kept constant.

Experimental Methodology

- River water samples were collected in acid cleaned polyethylene containers, upstream of the salt intrusion, as described in section 2.2.
- River and sea water samples were filtered using acid cleaned 0.45μm Nuclepore filters.
- 0.45 μm filtered river and sea water were mixed to make solutions of intermediate salinities.
- Solutions were maintained at room temperature (~24^0C) and stirred with a magnetic stirrer, at a pre-set speed.
- 50 ml aliquots were removed periodically and filtered through 0.45um Nuclepore filters, prior to colorimetric analysis.

Experiments were carried out using the methodology outlined above at three separate stirring rates.

Chapter Three

Kinetics of Iron Removal

3.1 Introduction

Studies of iron within the estuarine environment have focused primarily on the operationally defined dissolved iron fraction (Coonley *et al.*, 1971; Windom *et al.*, 1971; Bewers *et al.*, 1974; Holliday & Liss, 1976; Boyle *et al.*, 1977; Sholkovitz *et al.*, 1978; Mayer, 1982b; Fox & Wofsy, 1983; Hunter, 1983; Hunter & Leonard, 1988; Kraepiel *et al.* 1997). Riverine dissolved iron, conventionally defined by its ability to pass through a membrane filter with a nominal pore size of 0.4 - 0.5 μm diameter exists mainly in the form of colloidal iron (III) oxides stabilised by association with humic substances (Shapiro, 1964; Perdue *et al.*, 1976; Sholkovitz, 1976; Sugimura *et al.*, 1978; Krom & Sholkovitz, 1978; Moore *et al.*, 1979; Tipping, 1981; Fox, 1984; Cameron & Liss, 1984; Powell *et al.*1996). Kraepiel *et al.* (1997) demonstrated that approximately 70 % of dissolved iron in the Garonne river was actually in the colloidal phase . The behaviour of these iron containing colloids is of great relevance in environmental processes, as various chemical components with chemistries which favour their presence in truly dissolved forms may become associated with them. They are able to adsorb or bind inorganic species, as well as with compounds such as chlorinated pesticides, solvents, detergents, polynuclear aromatic hydrocarbons and plasticisers.

Iron-containing colloids in river water come into contact with gradually more saline waters as they undergo estuarine mixing, and a rapid large scale removal is observed. This non conservative behaviour is an almost universal phenomena, observed to a greater or lesser degree wherever iron is found in relatively high concentrations in river water (Coonley *et al.*, 1971; Windom *et al.*, 1971; Bewers *et al.*,1974; Holliday & Liss, 1976; Boyle *et al.*, 1977; Sholkovitz *et al.*, 1978; Mayer, 1982b; Fox & Wofsy, 1983; Hunter, 1983; Hunter & Leonard, 1988). Destabilisation of the negatively charged iron-containing colloids by sea water cations allows an aggregation of these colloids on subsequent collision. This aggregation of colloids, though not directly representing a total removal of iron from river water but rather an increase in particle size could provide a mechanism for transfer of material initially dispersed in the water column

The iron removal process is the most ubiquitously observed phenomenon modifying riverine input in the estuarine environment. It has a potential to influence the estuarine behaviour and fluxes of other constituents, including pollutants. The transfer of pollutants to suspended particulate matter or deposited sediments will influence pathways through food chains. Because the removal of iron appears to be a consistent feature in iron rich waters, the inclusion of the non-conservative behaviour of iron in estuarine transport models potentially has a more coherent basis than is the case for other constituents which often show a wide range of estuarine behaviours involving processes and factors which are less well defined. This has led to a significant body of work which has addressed questions of both the rates and mechanisms of the removal process. It should again be emphasised that it is the dominance of colloidal aggregation in the estuarine chemistry of iron, as against the less well defined particle / solution interactions which dominate the behaviour of other non-conservative constituents, that has facilitated progress in these directions. The capability to analyse iron in many estuaries over most of the concentration range encountered, without the need for pre-concentration and separation, has also facilitated kinetic studies.

It was shown in experiments by Sholkovitz *et al.,* (1978) and latterly by Duffy, (1985) that the fraction of iron destabilised in a given experiment increased with increasing ionic strength of the cation used. At a given ionic strength of cation the percentage destabilisation caused increased in the order :

$$Na^{+} < Mg^{2+} < Ca^{2+}$$

The destabilisation per unit increase in ionic strength was also significantly greater for calcium in comparison with either sodium or magnesium ions.

These results were in accordance with the Schulze - Hardy rules ; increased destabilisation being caused by ions of larger ionic charge :

$$Ca^{2+} / Mg^{2+} > Na^{+}$$

and by ions of larger ionic radius :

$$Ca^{2+} > Mg^{2+}$$

It is important that we gain an understanding of the processes involved, and attempt to quantify the reactions and mechanisms involved to further our understanding of anthropogenic influences on estuarine environments.

Since the non conservative behaviour of iron was first observed (Coonley *et al.*, 1971; Windom *et al.,* 1971; Bewers *et al.,* 1974; Holliday & Liss, 1976; Boyle *et al.,* 1977) there have been a number of attempts to elucidate the kinetics of the removal reaction. Though initial work consisted of field surveys in estuaries themselves, a number of laboratory simulations have since been undertaken, in which comparable behaviour has been observed (Sholkovitz, 1976; Boyle *et al.,* 1977; Sholkovitz 1978; Mayer 1982b; Fox & Wofsy, 1983; Gardiner 1983; Fox, 1984; Hunter & Leonard, 1988). Laboratory simulations have the advantage that individual parameters can be isolated and controlled, simplifying the study of the factors influencing the removal process. Findings from controlled environment simulations can thus potentially improve our understanding of the mechanisms of the removal process under investigation.

It was predicted, from the theoretical work of von Smoluchowski (1917), that the rate of decrease in particle numbers would show a second order dependency on the number of particles present (equivalent to the concentration for a monodisperse colloid population) provided that all particles were completely destabilised and particles were sufficiently small that collisions result from Brownian motion only (perikinetic coagulation). However, under the influence of a velocity gradient, the rate of decrease in particle numbers can be described by first order kinetics, with the first order rate constant dependant upon the velocity gradient, the volume of total mass suspended per volume of medium and the collision efficiency (orthokinetic coagulation). As summarised in Stumm & Morgan (1970), a velocity gradient of 5 s^{-1} would be sufficient to significantly increase rate of decrease in particles numbers for particles greater than 1 μm in size. The overall rate of decrease in concentrations of particles of all size ranges is assumed to be a sum of both mechanisms outlined above, with perikinetic coagulation shown to be of negligible importance for particles $\geq$ 1 μm under the influence of a velocity gradient > 5 s^{-1}, and orthokinetic coagulation shown to be of negligible effect for particles << 1 μm. This led to the expectation that the removal of microcolloidal particles would conform to a second order kinetic model.

Initial work of Boyle *et al.,*(1977); Mayer, (1982b) and Fox & Wofsy, (1983) sought to fit the observed removal to a simple integral first or second order rate equation. Mayer, (1982) and Fox & Wofsy, (1983) presented their data as verifying the expected observations of a second order reaction. Re-examination of their data, by Duffy (1985) (and also Duffy, pers comm.) showed that the fit of their experimental observations to a second order model is inconclusive. The second order rate equation plots of 1/[Fe] vs time for the work of both Mayer and Fox & Wofsy showed significant deviation from linearity at higher salinities. The observation that the removal of iron did not fit to the expected second order model, meant that further work was necessary to describe quantitatively the removal phenomena.

It was was recognised (Boyle *et al.* 1977; Sholkovitz 1978; Duffy 1985) that although the iron level throughout the estuary decreased to a level close to the detection limits at the saline end, in most experimental removal profiles at intermediate salinities the dissolved iron concentration decreased to an apparent equilibrium level determined by the salinity of the simulation, rather than to zero. Despite this observation, it was apparently not until the work of Duffy (1985) that the implications for the kinetic interpretations were recognised. The iron that remained in the <0.45um fraction at the end of these laboratory experiments was termed the resistant, or unreactive iron fraction. This unreactive fraction was found to be inversely proportional to the salinity of the solution. Duffy (1985) carried out kinetic analysis of her experimental data, using a methodology similar to that described in section 3.4 - taking the unreactive fraction into account, using modified versions of the first and second order rate equation. In initial kinetic analyses, the unreactive fraction was presumed to be equivalent to the concentration of iron remaining at the end of the experiments (approx. 15 minutes), but the fits using this value were found to be poor ($r^2 < 0.85$). When studied more closely, it became apparent that the iron concentration continued to decrease beyond this time in an asymptotic fashion, and a computer model was used to predict the concentration after an infinite time. Using this value for the unreactive iron concentration, very high correlation coefficients were obtained for the first order kinetic model ($r^2 > 0.980$ in all cases). Subsequent examination of the data (Duffy, pers comm.) indicated that high correlation coefficients were also obtained for the second order model when an unreactive fraction was taken into account. It has subsequently been shown in this work, section 3.4, that high correlation coefficients do not necessarily represent good fits to the removal profile observed.

The experimental findings of Hunter & Leonard, (1988) led those workers to conclude that the removal of dissolved iron could not be fitted to a simple kinetic order. Although they noted the presence of a residual fraction, during the kinetic analysis its presence was not taken into account. Hunter & Leonard, (1988) postulated that the microcolloidal iron species within river water exhibit a range of inherent stabilities. This behaviour was reflected in the mixing experiments; at low salinity only the most unstable colloids became destabilised and subsequently aggregated; as the salinity in the experiments is increased, more stable colloidal species were brought into an unstable regime and were themselves aggregated. No experiments carried out to date have examined the effects of recreating a salinity equivalent to that in the open ocean, where following this assumption almost all colloidal iron would be removed. This theory of inherent stabilities would give rise to the phenomena observed in actual estuaries - that of a decrease in the iron concentration as the salinity of the water increases, up to a point in the estuarine mouth or coastal waters, where the iron concentration is close to the limits of detection for the methods employed in these studies It was also observed by Hunter & Leonard, (1988) that storage effects could cause significant changes in the observed behaviour of dissolved iron during simulated estuarine mixing, a factor which could compromise the comparability of the results of previous authors.

The work to date, while increasing our understanding of the factors influencing the removal of dissolved iron during estuarine mixing, has failed to resolve the kinetics sufficiently to allow a definitive mechanistic explanation to be put forward. Conclusions of Duffy, (1985), and also material of Duffy, (pers. comm.) in relation to the second order model, were based on a relatively small number of kinetic runs in which the effects of various single cations (Na^+, Mg^{++}, Ca^{++}) as well as sea water were examined. The present experiments were undertaken to obtain a fuller data set which might provide a better statistical basis to enable identification of differences between the extent to which data fit a given kinetic model. Although the ions cause destabilisation to different extents, it can reasonably be assumed that there is a common basic process of aggregation. In examining the kinetics in order to throw light on the mechanism of aggregation a single cation was chosen for the experiments, simplifying interpretation by eliminating any variability due to the cation type. Calcium ions were used in the experiments in preference to either sodium or magnesium ions due to their greater effectiveness in colloid aggregation. Concentrations of calcium ions were chosen for the experiments which approximated to those observed over the full range of estuarine mixing, from river water to coastal waters.

In this section of the thesis it was attempted to :

- Carry out a fuller set of experiments with fewer variables (all experiments were carried out using Ca^{2+} ions) to examine further the validity of the various kinetic models in describing the results and potentially achieve a more unequivocal interpretation of the rate order.

- Consider the implications of the kinetic interpretations in terms of a mechanism of removal of microcolloidal iron within estuaries.

- Investigate further the question raised by the work of Hunter & Leonard, (1988) of storage effects on the simulated estuarine behaviour.

3.2 : Experimental Methods

It is well documented that the important changes in the concentration of dissolved iron during estuarine mixing simulations can often occur within the first 2-3 minutes following mixing (Boyle *et al.,* 1977; Smith & Longmore, 1980; Bale & Morris, 1981; Mayer, 1982b; Tyler, 1989). The experimental design of previous laboratory studies, other than those of Duffy, (1985) has, however, not provided sufficiently frequent observations to enable the course of the reaction, particularly in the early stages, to be analysed in detail. The application of continuous autoanalysis was shown by Duffy, (1985) to offer substantial advantages over discrete sampling methods. The Technicon Auto Analyser II system provided a method of closed flow analysis, with techniques for the colorimetric determination of both dissolved iron (Gibbs, 1979) and inorganic phosphate (Kirkwood, 1989). Further detail on experimental methods are given in chapter 2. The results of phosphate analysis and comparison of them with those for iron are given in chapter 4.

3.2.1 Sample Collection

Samples of water were collected from the zero salinity region of the Tamar river, at Latchley - 4 miles up river of the weir at Gunnislake. The samples were collected in 25 litre carboys, previously acid washed and thoroughly rinsed with MilliQ water, and transported back to the laboratory for immediate analysis (see section 3.3.3 for a discussion of the effects of storage on the water samples.).

3.2.2 Mixing Experiments

The mixing experiments were carried out using the basic method outlined by Duffy, (1985). A 4l sample of river water, from the zero salinity fresh water region of the Tamar river, was placed into a polyethylene mixing tank. The water was circulated by use of a centrifugal immersion pump. Connected to this pump was an on-line perspex tangential filter block, housing an acid washed 0.45μm membrane filter (Morris *et al.,* 1978), through which water was pumped to two separate channels for the colorimetric determination of dissolved iron and inorganic phosphate. The use of an autoanalyser system coupled with an on-line tangential filter block (Morris *et al.,* 1978) allowed for a continuous measurement of the changes in the concentrations of the riverine constituents over the whole timescale of the experiments, including the early stages. It was only in the work of Duffy, (1985), prior to this study, that such a system was used for the kind of detailed kinetic studies discussed in this work. The iron was determined using 2,4,6- tri-pyridyl triazine, and the phosphate as phosphomolybdenum blue. A baseline reading was established with distilled water and linearity of response was tested both before and after experimental runs with a set of standards (0-4μmol l^{-1} for phosphate, 0-40μmol l^{-1} for iron). The river water was analysed for 2-3 minutes in order to achieve a reference for the initial concentrations of dissolved iron and inorganic phosphate

The destabilisation process was initiated, in these experiments, by the addition of Ca^{2+} ions in the form of calcium chloride. The concentration of the calcium ions in a 10 ml aliquot was calculated to give an overall calcium ion concentration in the mixing chamber of between 0.0014 to 0.0112 mol l^{-1} (corresponding to concentrations found in salinities 5 to 35), thus giving an overall concentration within the mixing tank approximate to those concentrations found over the full range of salinities experienced in the zone of estuarine mixing. The concentrations of both iron and phosphate were measured continuously for 900 s, after which time the reaction was considered as essentially complete. Sub- samples from each of the mixing experiments were filtered at 0.45μm after 24 hours, and analysed.

3.3 : Results

Changes in the concentration of 'dissolved' iron were initiated by addition of varying concentrations of calcium chloride solution to water from the Tamar river system, to approximate concentrations observed within the zone of estuarine mixing.
The results of the experiments are summarised in Tables 3.1-3.4, and typical examples of the dissolved iron profiles observed over the duration of the experiments (~15 minutes following mixing), are shown in Figure 3.1.

The waters used in the suite of experiments were all collected from a single source on the Tamar river, at Latchley. As the experiments were carried out over a period of months, seasonal and temporal variations in the initial concentrations of iron in the <0.45 μm fraction were observed. The initial iron concentration varied from 10.6 to 21.5 μmoles l^{-1} iron, and 0.84 to 1.60 μmol^{-1} phosphate during the months October 1993 and May 1994. Highest values were recorded in January and lowest in May. A correlation between the highest concentrations of iron and phosphate was observed throughout the duration of the experiments.

To facilitate graphical comparison of the data from all of the individual experimental runs, the results were analysed in the form of the percentage of the initial concentration in the <0.45μm fraction. The treatment of the data in percentage terms also allowed the data collected on the behaviour of iron to be more readily correlated with that of phosphate. (see Chapter 4)

3.3.1 Behaviour of Dissolved Iron during Simulated Estuarine Mixing

On addition of the aliquot of calcium chloride, a lag of 20 - 30 seconds was followed by a pronounced rapid decrease in the concentration of 'dissolved' iron within the simulated mixing tank *e.g.* in run 1a. 60% of dissolved iron was removed within 150 seconds. Within a few minutes following mixing, the decrease in concentration of dissolved iron had slowed considerably, concentrations approaching a plateau level after 300 to 400 seconds. After this time only minor decreases in dissolved iron concentration were observed until the end of the mixing experiments, after 900 seconds (t = 0.25 hours). When the sub-samples from the mixing experiments were analysed after 24 hours there had been a subsequent

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (μmol l^{-1})	Final Iron Conc. (μmol l^{-1})	Iron μmol l^{-1}	Removal %	Correlation Coefficient	1st Order Rate Constant (*10-3) s^{-1}	Storage Time (hr)
0.0112	18.2	0.5	17.7	97.3	0.971	5.7	3.75
0.0112	18.5	0.1	18.4	99.5	0.975	4.97	6.17
0.0112	18.4	1.0	17.4	94.6	0.994	5.63	7.00
0.0112	17.2	0.0	17.2	100.0	0.992	5.73	13.33
0.0112	18.4	0.2	18.2	99.1	0.979	5.92	16.33
0.0112	18.0	1.1	16.9	94.0	0.992	4.9	18.17
0.0112	17.2	0.4	16.8	97.6	0.984	5.03	24.67
0.0112	17.0	0.5	16.5	97.2	0.994	5.11	28.67
0.0112	17.6	0.2	17.4	98.7	0.988	6.14	33.67
0.0112	16.9	0.4	16.5	97.5	0.986	5.04	44.83
0.0056	18.1	2.8	15.3	84.3	0.994	1.98	5.50
0.0056	16.9	3.3	13.6	80.5	0.986	2.47	8.58
0.0056	17.9	3.6	14.3	79.8	0.992	2.53	14.17
0.0056	18.1	4.6	13.5	74.6	0.991	2.98	16.67
0.0056	17.5	4.6	13.0	74.0	0.993	2.98	19.67
0.0056	17.4	4.7	12.7	72.9	0.998	3.26	21.67
0.0056	17.2	5.1	12.1	70.3	0.994	3.5	30.50
0.0056	17.0	5.5	11.6	67.9	0.971	3.92	35.83
0.0056	17.6	6.7	10.9	61.9	0.992	3.99	47.50
0.0028	17.1	8.3	8.8	51.5	0.984	1.14	8.83
0.0028	17.7	8.9	8.8	49.7	0.991	1.27	12.00
0.0028	17.0	9.1	7.9	46.5	0.989	1.68	15.00
0.0028	19.2	10.1	9.1	47.4	0.994	1.7	23.67
0.0028	18.0	9.8	8.2	45.6	0.986	1.76	26.67
0.0028	16.9	9.5	7.4	43.8	0.976	2	40.50
0.0028	17.0	10.5	6.5	38.2	0.989	2.55	50.33

Table 3.1 Influence of the addition of calcium chloride on the first order rate constant and extent of removal of iron from Tamar River water - Batch one.

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (μmol l^{-1})	Final Iron Conc. (μmol l^{-1})	Iron μmol l^{-1}	Removal %	Correlation Coefficient	1st Order Rate Constant (*10-3) s^{-1}	Storage Time (hr)
0.0056	14.1	1.2	12.9	91.3	0.994	2.21	3.00
0.0056	12.7	1.1	11.6	91.1	0.986	2.7	4.00
0.0056	14.0	1.4	12.6	90.1	0.989	2.62	6.00
0.0056	12.8	1.2	11.6	90.7	0.991	2.98	7.17
0.0056	13.2	1.5	11.7	88.4	0.990	3.04	10.00
0.0056	13.3	1.7	11.6	87.0	0.993	3.21	13.67
0.0056	13.6	1.9	11.7	85.8	0.986	3.57	15.67
0.0056	11.7	1.9	9.8	83.6	0.989	3.95	17.00
0.0056	10.6	1.7	8.9	84.0	0.993	3.88	21.33
0.0056	12.4	2.1	10.3	83.5	0.972	4.02	23.33
0.0056	13.2	2.3	10.9	82.3	0.979	4.29	25.83
0.0056	13.0	2.5	10.5	80.8	0.992	4.32	26.83
0.0056	11.0	2.3	8.7	79.1	0.994	4.86	35.50
0.0056	11.4	2.8	8.6	75.6	0.986	5.08	40.08
0.0056	12.5	3.3	9.2	73.8	0.984	5.25	46.92
0.0056	12.8	3.5	9.3	72.4	0.980	5.33	48.17
0.0056	13.5	3.8	9.7	71.8	0.992	5.81	48.58
0.0056	12.2	3.6	8.6	70.3	0.979	5.99	51.50
0.0056	12.3	3.9	8.5	68.7	0.994	6.45	53.00

Table 3.2 : Influence of the addition of calcium chloride on the first order rate constant and extent of removal of iron from Tamar River water - Batch two.

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (μmol l^{-1})	Final Iron Conc. (μmol l^{-1})	Iron	Removal	Correlation Coefficient	1st Order Rate Constant (*10-3) s^{-1}	Storage Time (hr)
			μmol l^{-1}	%			
0.0056	14.8	1.9	12.9	87.4	0.993	4	1.50
0.0056	13.5	2.1	11.3	84.1	0.989	4.92	2.08
0.0056	13.4	2.1	11.3	84.6	0.991	4.64	2.50
0.0056	14.1	2.3	11.8	83.8	0.994	3.98	3.00
0.0056	14.1	2.2	11.9	84.4	0.992	5.22	3.50
0.0056	13.0	2.2	10.8	83.0	0.986	4.38	4.25
0.0028	12.4	3.5	8.9	71.6	0.988	2.55	4.67
0.0028	14.0	4.2	9.8	69.8	0.971	2.74	5.17
0.0028	13.1	3.9	9.2	70.0	0.98	2.65	5.67
0.0028	12.7	4.0	8.7	68.5	0.981	2.2	6.33
0.0028	12.7	3.9	8.8	69.3	0.983	2.84	6.83
0.0028	12.6	4.2	8.5	67.1	0.987	3.02	7.50
0.0028	13.4	4.0	9.4	69.9	0.993	2.36	7.92
0.0028	13.5	4.4	9.1	67.4	0.992	2.48	8.42
0.0028	13.6	4.2	9.4	69.3	0.993	2.96	9.33
0.0014	14.0	8.2	5.8	41.1	0.994	1.27	9.83
0.0014	14.3	8.2	6.0	42.2	0.989	1.77	10.17
0.0014	12.8	7.2	5.6	43.7	0.995	1.02	10.58
0.0028	13.6	5.4	8.2	60.4	0.993	3.25	11.08
0.0056	12.6	1.8	10.8	85.8	0.997	5.66	11.50

Table 3.3 : Influence of the addition of calcium chloride on the first order rate constant and extent of removal of iron from Tamar River water - Batch three.

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (µmol l^{-1})	Final Iron Conc. (µmol l^{-1})	Iron µmol l^{-1}	Removal %	Correlation Coefficient	1st Order Rate Constant (*10-3) s^{-1}	Storage Time (hr)
0.0014	19.8	8.4	11.4	57.6	0.984	2.21	1.50
0.0014	21.5	9.8	11.7	54.4	0.990	2.7	2.08
0.0014	20.7	8.5	12.2	59.0	0.994	2.62	2.50
0.0014	19.9	9.3	10.6	53.4	0.991	2.68	3.00
0.0014	19.0	9.2	9.8	51.7	0.981	2.04	3.50
0.0028	18.7	5.7	12.9	69.4	0.987	3.21	4.25
0.0028	20.7	6.3	14.4	69.4	0.990	3.57	4.67
0.0028	18.7	5.5	13.2	70.7	0.983	3.95	5.17
0.0028	19.2	5.4	13.9	72.2	0.989	3.88	5.67
0.0028	19.3	7.0	12.3	63.8	0.991	4.02	6.33
0.0028	19.0	5.0	14.0	73.5	0.990	4.29	6.83
0.0028	19.7	6.2	13.5	68.5	0.992	4.32	7.50
0.0056	19.3	4.4	14.8	77.1	0.987	4.86	7.92
0.0056	20.3	3.7	16.7	82.0	0.984	5.08	8.42
0.0056	19.0	3.7	15.3	80.7	0.986	5.32	9.33
0.0056	19.5	4.2	15.2	78.4	0.992	5.25	9.83
0.0056	19.9	3.6	16.3	81.7	0.978	5.33	10.17
0.0056	19.4	3.7	15.6	80.7	0.990	5.81	10.58
0.0056	18.6	4.2	14.5	77.6	0.989	5.99	11.08
0.0056	19.2	4.5	14.8	76.7	0.986	6.45	11.50

Table 3.4 : Influence of the addition of calcium chloride on the first order rate constant and extent of removal of iron from Tamar River water - Batch four.

small further decrease in the fraction of dissolved iron remaining. The magnitude of the decrease between the end of the normal experiments (t=0.25hours) and the reanalysis of the samples (t = 24 hours) was small in comparison with that observed over the course of the experiments (typically 1 to 10% of that occurring between t = 0 to t = 0.25 hours) but consistently showed that removal was still occurring after the reaching of an apparent plateau level with typically between one and ten percent of the initial iron concentration being lost. The observations are in contrast to those of control experiments in which no cation was added and no discernible change in the dissolved iron concentration was observed, over either 900 seconds or twenty four hours.

In the majority of experiments, a substantial proportion of the initial dissolved iron was still measurable at the end of the experiments - even after 24 hours. The proportion of iron remaining at this time is thought to represent the fraction of iron resistant to destabilisation at the chosen salinity. In some of the experiments with the highest experimental calcium ion concentration the fraction of iron remaining approached the detection limits for the colorimetric technique used.

The observations of dissolved iron behaviour show these basic features at all of the experimental salinities studied (Figure 3.1) with the steepness of curve and the overall concentration of iron resisting destabilisation determined by the concentration of calcium irons added in the experiment. The fraction of dissolved iron resistant to destabilisation was inversely proportional to the concentration of calcium ions added, showing an almost linear trend of decreasing iron fraction with increasing calcium ion concentration (Figure 3.2). These findings concur with the hypothesis of Hunter & Leonard, (1988) of a range of inherent iron stabilities within the river water, with increasingly more iron becoming susceptible to destabilisation and therefore removal from the <0.45μm fraction as the overall concentration of cations is increased.

The results of this set of experiments are comparable with those of other authors (Eckert & Sholkovitz, 1976; Sholkovitz & Copland, 1981; Duffy, 1985; Hunter & Leonard, 1988; Hunter *et al.,* 1990), who also noted a decrease in the concentration of iron remaining in the dissolved fraction in response to an increase in cation concentration.

When the results of experiments carried out at the same calcium ion concentration were compared, although the removal profiles all show the same basic features (as described

Fig. 3.1 - Changes in the concentration of dissolved iron, with time, following the addition of calcium chloride to Tamar River Water.

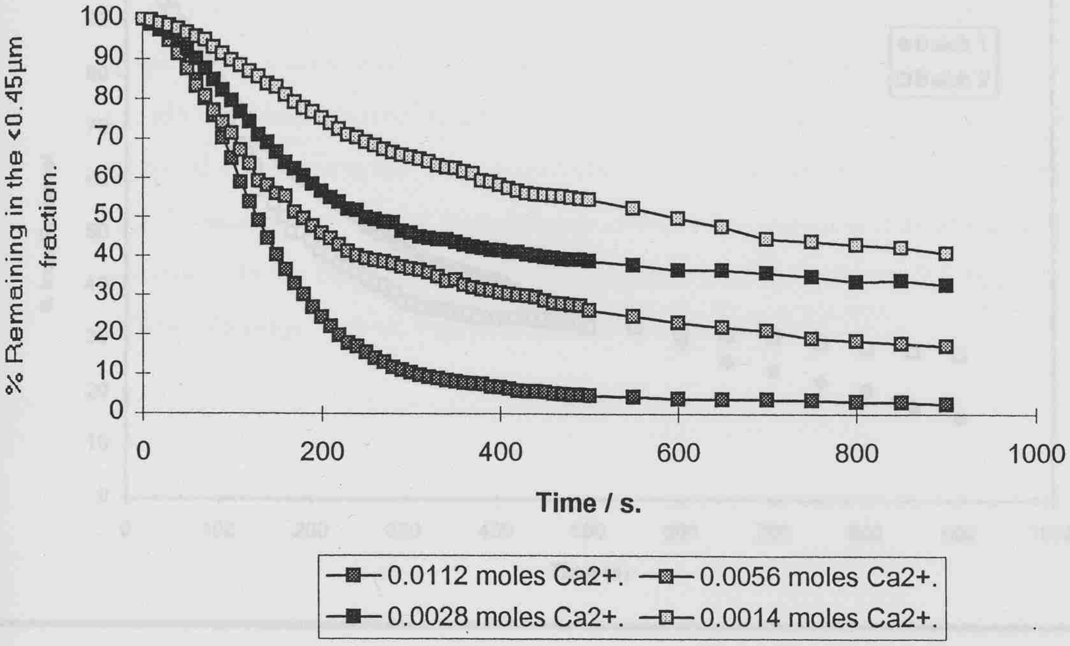


Fig. 3.2 - The influence of calcium ion concentration on the % of dissolved iron and phosphate remaining 900 seconds after addition of calcium chloride to Tamar River Water.

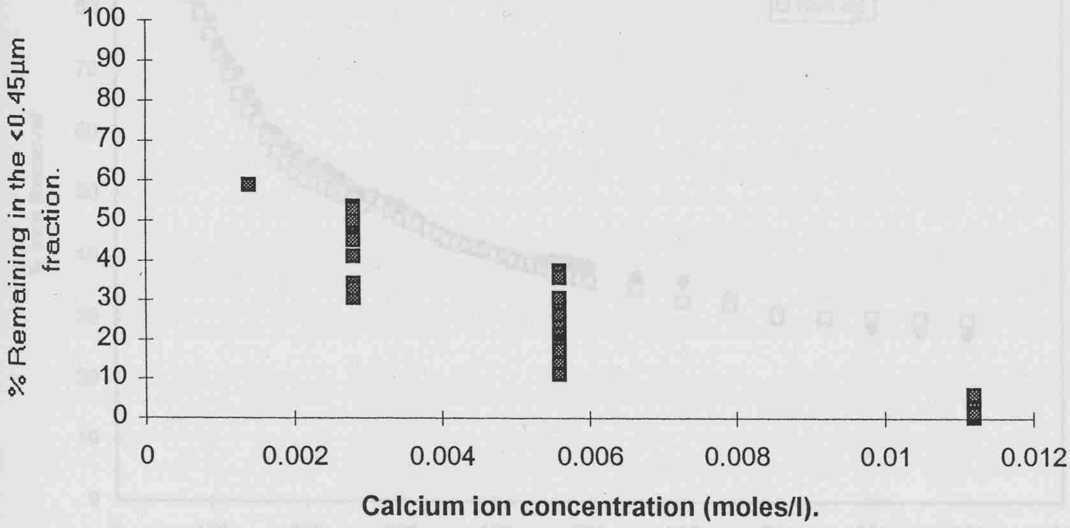


Fig. 3.3 (a) Variability in observed iron removal between river water batches (calcium ion concentration 0.0056 mol l-1)

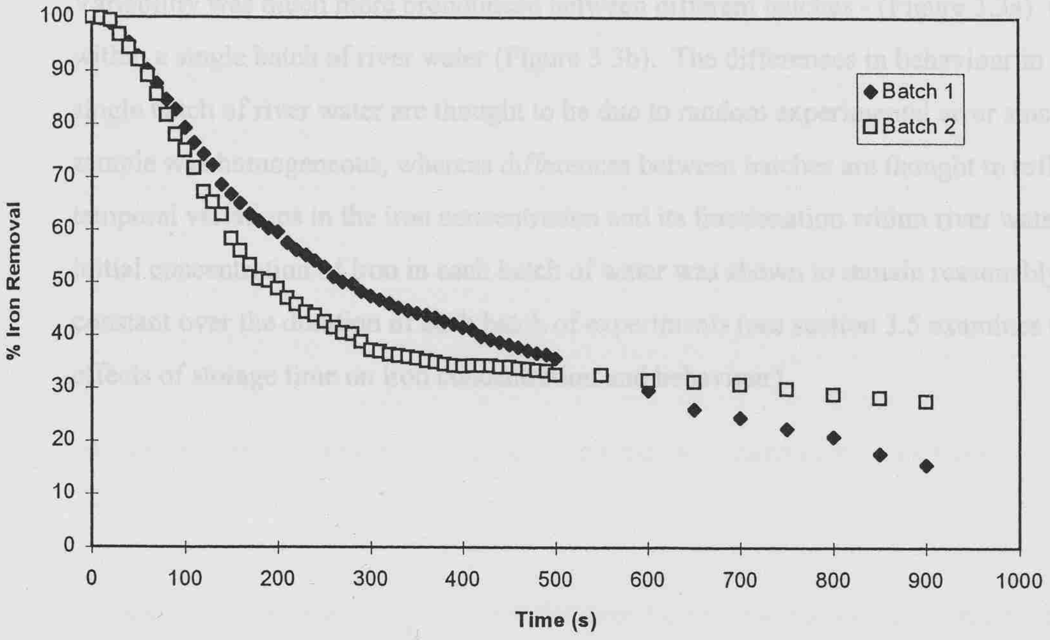
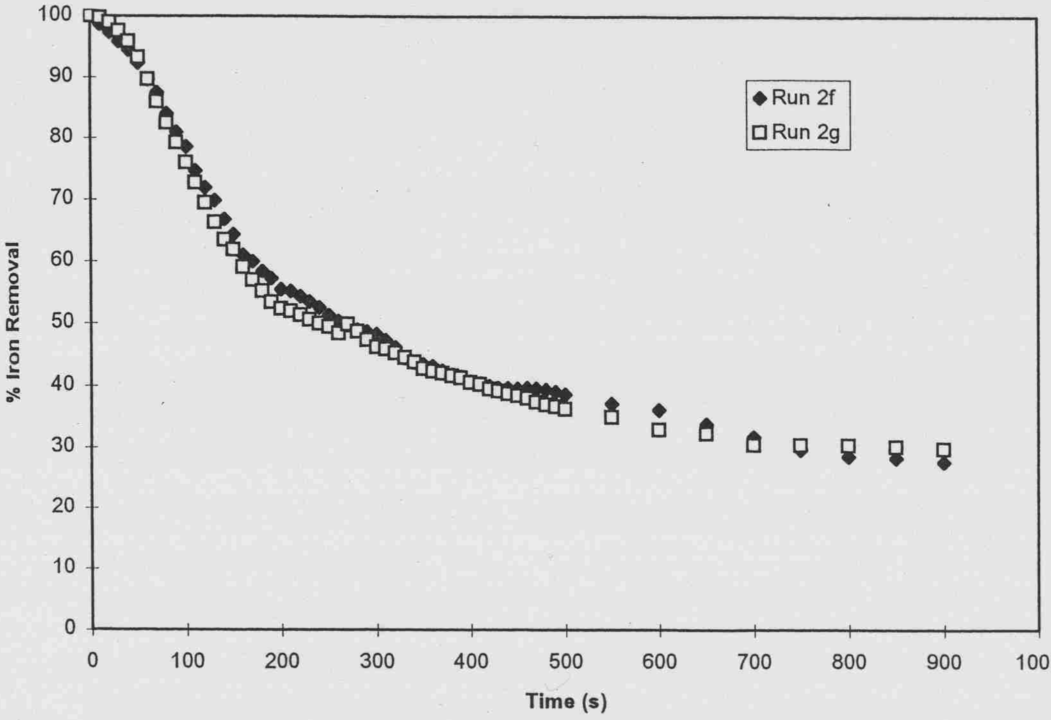


Fig. 3.3 (b) Variability in observed iron removal using a single river water batch (calcium ion concentration 0.0056 mol l-1)



above), some variability was noted both between runs using the same river water batch, and more markedly with waters from different batches.

Variability was much more pronounced between different batches - (Figure 3.3a) than within a single batch of river water (Figure 3.3b). The differences in behaviour in a single batch of river water are thought to be due to random experimental error since the sample was homogeneous, whereas differences between batches are thought to reflect temporal variations in the iron concentration and its fractionation within river water. The initial concentration of iron in each batch of water was shown to remain reasonably constant over the duration of each batch of experiments (see section 3.5 examines the effects of storage time on iron concentration and behaviour)

3.4 Kinetic Interpretation of the Iron Data

Duffy (1985) and Hunter & Leonard (1988) showed that a second order kinetic model as used in previous work to interpret the aggregation of dissolved iron did not accurately describe the observed phenomenon in their experiments. It was suggested by Duffy (1985), that there was a fraction of the dissolved iron that remained resistant, or unreactive, to destabilisation. The resistant fraction of iron was considered to be equivalent to the asymptotic value of the iron concentration in concentration versus time plots. The value of the unreactive fraction is estimated by an extrapolation of the kinetic curve data. When this fraction was taken into account, during kinetic interpretation of the data it was found that excellent fits could be obtained for both first order (Duffy, 1985) and second order kinetic models (Duffy, pers comm.) - section 3.4.4 looks at the effect of the unreactive fraction in kinetic interpretation of the data.

Taking the resistant fraction into consideration the first and second order rate equations become :

$$k_1 t = \ln\left(\frac{C_o - C_f}{C_t - C_f}\right) \text{................................equation 3.1}$$

for first order,

and

$$k_2 t = \frac{(C_o - C_t)}{(C_t - C_f)(C_o - C_f)} \text{...........equation 3.2}$$

for second order.

k_1 = first order rate constant.

k_2 = second order rate constant.

C_o = initial dissolved iron concentration.

C_t = dissolved iron concentration at time, t.

C_f = unreactive iron concentration.

The data was analysed via a non-linear regression model on the statistics package SYSTAT (version 5.03, for windows). The data sets were modelled in the form :

$$\text{1st order} \quad C_t = C_f + e^{-k_1 t}\left(Co - C_f\right) \text{................equation 3.3}$$

$$\text{2nd order} \quad C_t = \frac{k_2 t\left(C_o.C_f - C_f^{\,2}\right) + C_o}{1 + k_2 t.\left(C_o - C_f\right)} \text{..................equation 3.4}$$

The non-linear model was used in preference to an analogous linear model, as it allowed an optimisation of the C_f value, by the least squares criterion, to give the best fit to the kinetic rate expression used. Kinetic rate constants and residual iron fractions were calculated for both the first and second order models using the modified forms of the integrated rate equation (equations 3.3 and 3.4).

Tables 3.1 to 3.4 summarise the data from the first order kinetic model, with a breakdown of the range and mean first order rate constant for each batch and calcium ion concentration studied given in table 3.5. Tables 3.6 to 3.9 compare the observed resistant fractions remaining in the experiments after both 15 minutes and 24 hours with the predicted residual fractions for both the first and second order models. Data from the second order model is presented in tables 3.10. to 3.13. with a summary of the mean and range of second order rate constants given in table 3.14.

The first and second order kinetic models both gave good fits to the experimental data when an unreactive fraction was taken into account, with high correlation coefficients. Data fitted to the first order kinetic model gave correlation coefficients ranging from 0.971 to 0.998, with a mean of 0.987 and a relative standard deviation (RSD) of 0.43%. Data fitted to the modified second order kinetic model gave correlation coefficients ranging from 0.956 to 0.992, with a mean of 0.979 and a relative standard deviation of 1.02%. More detailed considerations of the kinetic models, as discussed in section 3.4.3, including a comparison of curves (experimental vs. modelled) and agreement with the residual fraction observed, indicated that the first order model is a better descriptor.

As was previously observed for the measured iron remaining, the predicted unreactive fraction was seen to decrease with an increasing concentration of calcium ions. At the highest experimental calcium ion concentrations large scale removal occurred, with the unreactive iron fraction approaching the limits of detection in some experiments.

3.4.1 First Order Model

The values for the calculated first order rate constant ranged from $4.70*10^{-4}$ to $6.45*10^{-3}$ s^{-1} over the range of calcium ion concentrations used in the current estuarine simulations. The variability in first order rate constant at each given calcium ion concentration both within and between experimental batches is illustrated in Table 3.5. The variations in first order rate constants are reflected by the relative standard deviations shown. There was some variation observed between runs but standard deviations were significantly greater over the course of the experimental batches one and two, in which storage time was a major variable. At a calcium ion concentration of 0.0056 mol l^{-1}, the relative standard deviations for the experiments in batches one and two were 21.9 percent and 29.6 percent respectively, in comparison with 13.5 percent and 8.75 percent for batches three and four.(The effects of storage time on simulated estuarine behaviour, and more specifically on rate constants are discussed in section 3.5.)

Figures 3.4.-3.6 show plots of the first order rate constants against calcium ion concentration for individual experimental batches one, three and four. The plots all show linear trends of an increasing first order rate constant in proportion to the increase in calcium ion concentration, with r^2 values ranging from 0.988 to 0.998.
The mean values for the first order rate constant at a given calcium ion concentration, illustrated in figure 3.7, show marked variation between experimental runs, e.g. at a calcium ion concentration of 0.0056 mol l^{-1}, the mean first order rate constant varied between $3.07*10^{-3}$ s^{-1} for batch one and $4.18*10^{-3}$ s^{-1} to $4.68*10^{-3}$ s^{-1} and $5.60*10^{-3}$ for batch two to four respectively. Within each experimental batch an increase in the calcium ion concentration caused an approximately linear increase in the mean first order rate constant. The increase in rate constant for a given increase in salinity is similar between

Fig 3.4 Effect of calcium ion concentration on first Order rate constant (batch 1)

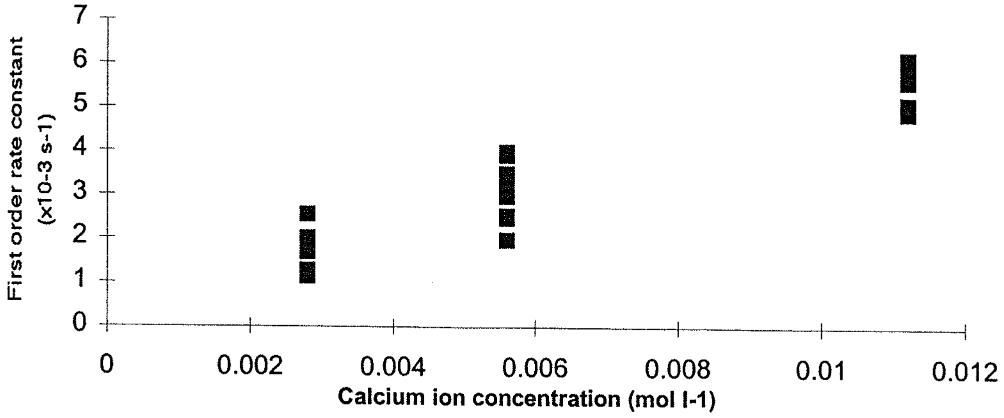


Fig 3.5 Effect of calcium ion concentration on first order rate constant (batch 3)

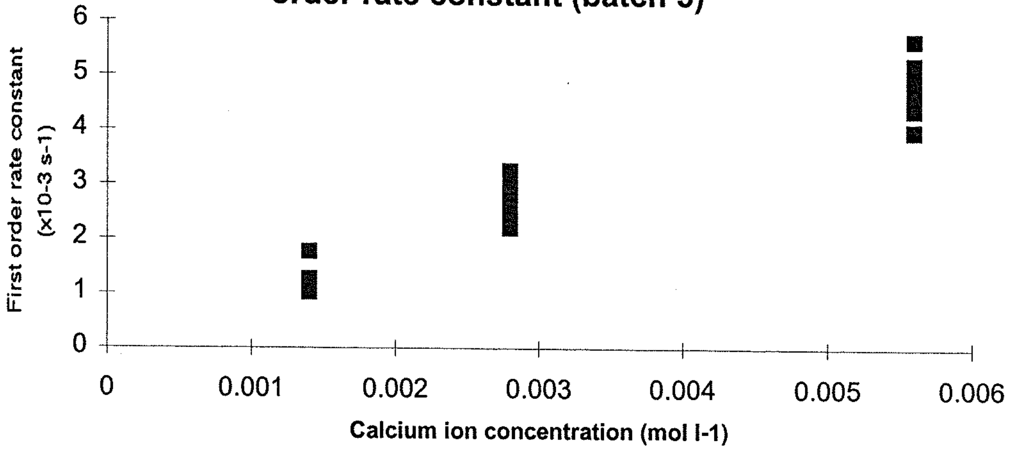
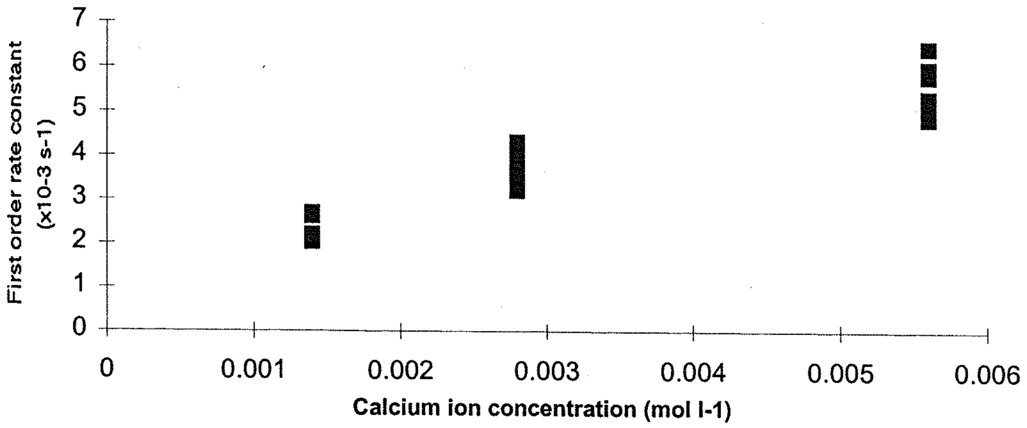


Fig 3.6 Effect of calcium ion concentration on first order rate constant (batch 4)



	Calcium Ion Concentration	First Order Rate Constant (s^{-1})		Standard Deviation	n
		Range	Mean		
Batch ONE	0.0112	4.9 to 6.14 $*10^{-3}$	5.41 $*10^{-3}$	0.454 $*10^{-3}$	10
	0.0056	1.98 to 3.99 $*10^{-3}$	3.07 $*10^{-3}$	0.675 $*10^{-3}$	9
	0.0028	1.14 to 2.55 $*10^{-3}$	1.73 $*10^{-3}$	0.467 $*10^{-3}$	7
Batch TWO	0.0056	2.21 to 6.45 $*10^{-3}$	4.18 $*10^{-3}$	1.24 $*10^{-3}$	19
Batch THREE	0.0056	3.98 to 5.66 $*10^{-3}$	4.68 $*10^{-3}$	0.630 $*10^{-3}$	7
	0.0028	2.20 to 3.25 $*10^{-3}$	2.71 $*10^{-3}$	0.322 $*10^{-3}$	10
	0.0014	1.02 to 1.77 $*10^{-3}$	1.35 $*10^{-3}$	0.381 $*10^{-3}$	3
	0.0056	5.08 to 6.45 $*10^{-3}$	5.60 $*10^{-3}$	0.490 $*10^{-3}$	8
Batch FOUR	0.0028	3.21 to 4.32 $*10^{-3}$	3.89 $*10^{-3}$	0.394 $*10^{-3}$	7
	0.0014	2.04 to 2.70 $*10^{-3}$	2.45 $*10^{-3}$	0.304 $*10^{-3}$	5

Table 3.5 : Variation in first order rate constant for iron removal with calcium ion concentration both within and between experimental batches.

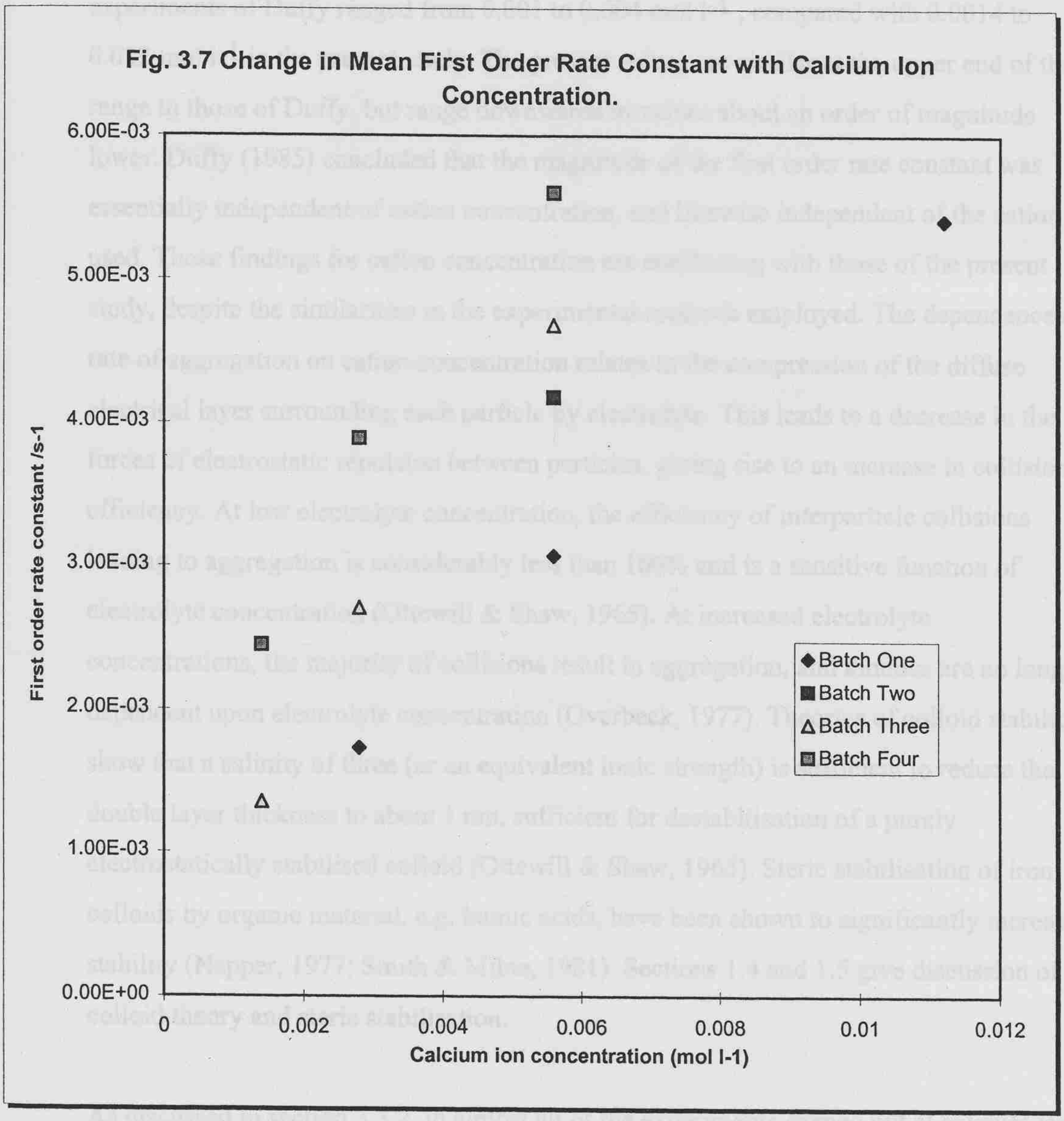


Fig. 3.7 Change in Mean First Order Rate Constant with Calcium Ion Concentration.

experimental batches *e.g.* the gradient of the best fit line varies from 0.435 for batch one to 0.780 and 0.734 for batches three and four respectively. The values derived for the first order rate constant are directly comparable with those of Duffy (1985) from experiments on Tamar river water with calcium ions used to initiate aggregation under equivalent experimental conditions. The values derived from the data of Duffy (1985) ranged from $7.18*10^{-3}$ s^{-1} at a calcium ion concentration of 0.0025 mol l^{-1} to 0.012 s^{-1} at a concentration of 0.004 mol l^{-1}. The full range of calcium ion concentrations used in the experiments of Duffy ranged from 0.001 to 0.004 mol l^{-1}, compared with 0.0014 to 0.012 mol l^{-1} in the present study. The present values are similar at the upper end of the range to those of Duffy, but range downwards to values about an order of magnitude lower. Duffy (1985) concluded that the magnitude of the first order rate constant was essentially independent of cation concentration, and likewise independent of the cation used. Those findings for cation concentration are conflicting with those of the present study, despite the similarities in the experimental methods employed. The dependence of rate of aggregation on cation concentration relates to the compression of the diffuse electrical layer surrounding each particle by electrolyte. This leads to a decrease in the forces of electrostatic repulsion between particles, giving rise to an increase in collision efficiency. At low electrolyte concentration, the efficiency of interparticle collisions leading to aggregation is considerably less than 100% and is a sensitive function of electrolyte concentration (Ottewill & Shaw, 1965). At increased electrolyte concentrations, the majority of collisions result in aggregation, and kinetics are no longer dependent upon electrolyte concentration (Overbeek, 1977). Theories of colloid stability show that a salinity of three (or an equivalent ionic strength) is sufficient to reduce the double layer thickness to about 1 nm, sufficient for destabilisation of a purely electrostatically stabilised colloid (Ottewill & Shaw, 1965). Steric stabilisation of iron colloids by organic material, e.g. humic acids, have been shown to significantly increase stability (Napper, 1977; Smith & Milne, 1981). Sections 1.4 and 1.5 give discussion of colloid theory and steric stabilisation.

As discussed in section 3.3.2, in almost all of the experiments carried out at calcium ion concentrations of 0.0014, 0.0028 and 0.0056 mol l^{-1}, there was found to be a fraction of iron resisting destabilisation at both t=0.25hr and t=24 hr. The concentration resisting destabilisation was consistently lower after 24 hours than after fifteen minutes. The first order kinetic model predicted values for the resistant iron concentration (C_f) to be greater than zero for all of these experimental data sets and in almost all cases the value was seen

Calcium Ion Concentration	Measured Iron Concentration µmol l^{-1}		Predicted Iron Concentration µmol l^{-1}	
(mol l^{-1})	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0112 moles	0.5	0.4	0.0	0.0
0.0112 moles	0.1	0.0	0.0	0.0
0.0112 moles	1.0	0.8	0.8	0.0
0.0112 moles	0.0	0.0	0.0	0.0
0.0112 moles	0.2	0.0	0.0	0.0
0.0112 moles	1.1	0.9	0.9	0.0
0.0112 moles	0.4	0.3	0.2	0.0
0.0112 moles	0.5	0.4	0.2	0.0
0.0112 moles	0.2	0.1	0.0	0.0
0.0112 moles	0.4	0.2	0.2	0.0
0.0056 moles	2.8	2.0	1.4	0.0
0.0056 moles	3.3	2.6	1.8	0.0
0.0056 moles	3.6	3.0	2.4	0.0
0.0056 moles	4.6	4.2	3.2	0.2
0.0056 moles	4.6	4.2	1.7	0.0
0.0056 moles	4.7	4.5	3.8	0.4
0.0056 moles	5.1	4.2	3.7	0.0
0.0056 moles	5.5	4.9	5.8	1.8
0.0056 moles	6.7	6.0	5.0	0.0
0.0028 moles	8.3	7.7	6.9	0.0
0.0028 moles	8.9	8.0	6.4	2.3
0.0028 moles	9.1	8.2	6.6	1.0
0.0028 moles	10.1	9.0	7.2	0.5
0.0028 moles	9.8	9.4	7.1	1.0
0.0028 moles	9.5	9.0	7.4	2.3
0.0028 moles	10.5	9.6	8.8	6.6

Table 3.6 : Comparison of the measured iron removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch one.

Calcium Ion Concentration (mol l^{-1})	Measured Iron Concentration µmol l^{-1}		Predicted Iron Concentration µmol l^{-1}	
	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0056 moles	1.2	1.0	0.8	0.0
0.0056 moles	1.1	1.0	0.9	0.0
0.0056 moles	1.4	1.2	0.8	0.0
0.0056 moles	1.2	1.0	1.0	0.5
0.0056 moles	1.5	1.3	0.3	0.0
0.0056 moles	1.7	1.6	0.9	0.9
0.0056 moles	1.9	1.7	1.3	0.0
0.0056 moles	1.9	1.5	1.0	1.5
0.0056 moles	1.7	1.2	0.9	0.2
0.0056 moles	2.1	1.4	0.7	0.0
0.0056 moles	2.3	1.1	0.8	0.0
0.0056 moles	2.5	2.1	2.1	1.6
0.0056 moles	2.3	2.0	0.0	0.0
0.0056 moles	2.8	2.6	2.3	1.0
0.0056 moles	3.3	2.7	2.5	1.2
0.0056 moles	3.5	3.1	3.1	1.0
0.0056 moles	3.8	3.2	2.7	2.6
0.0056 moles	3.6	3.2	3.0	0.0
0.0056 moles	3.9	3.1	2.9	2.5

Table 3.7 : Comparison of the measured iron removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch two.

Calcium Ion Concentration	Measured Iron Concentration µmol l^{-1}		Predicted Iron Concentration µmol l^{-1}	
(mol l^{-1})	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0056 moles	1.9	1.7	1.5	0.0
0.0056 moles	2.1	2.1	1.9	0.0
0.0056 moles	2.1	1.8	1.8	0.3
0.0056 moles	2.3	1.9	1.4	0.4
0.0056 moles	2.2	1.9	1.7	0.0
0.0056 moles	2.2	2.0	1.8	0.0
0.0028 moles	3.5	2.7	2.4	0.1
0.0028 moles	4.2	4.0	3.2	0.7
0.0028 moles	3.9	3.2	3.4	2.6
0.0028 moles	4.0	3.6	2.9	0.7
0.0028 moles	3.9	3.4	3.0	0.0
0.0028 moles	4.2	3.8	3.5	3.1
0.0028 moles	4.0	3.7	3.6	0.0
0.0028 moles	4.4	4.0	4.0	2.5
0.0028 moles	4.2	3.8	3.7	1.2
0.0014 moles	8.2	7.4	7.0	1.0
0.0014 moles	8.2	7.3	7.2	6.2
0.0014 moles	7.2	5.2	4.3	2.6
0.0028 moles	5.4	5.1	4.7	3.0
0.0056 moles	1.8	1.5	1.3	0.0

Table 3.8 : Comparison of the measured iron removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch three.

Calcium Ion Concentration (mol l^{-1})	Measured Iron Concentration µmol l^{-1}		Predicted Iron Concentration µmol l^{-1}	
	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0014 moles	8.4	7.7	6.9	2.3
0.0014 moles	9.8	8.2	7.2	2.2
0.0014 moles	8.5	8.0	7.6	1.5
0.0014 moles	9.3	8.4	7.8	3.5
0.0014 moles	9.2	8.3	7.5	1.2
0.0028 moles	5.7	5.2	4.1	0.6
0.0028 moles	6.3	5.5	4.6	0.0
0.0028 moles	5.5	4.9	4.1	1.0
0.0028 moles	5.4	4.9	4.1	1.1
0.0028 moles	7.0	6.6	5.0	1.4
0.0028 moles	5.0	4.0	0.1	0.0
0.0028 moles	6.2	5.5	5.3	1.3
0.0056 moles	4.4	4.1	4.0	0.2
0.0056 moles	3.7	3.2	2.8	0.0
0.0056 moles	3.7	2.7	2.0	0.0
0.0056 moles	4.2	2.9	2.7	0.0
0.0056 moles	3.6	2.6	2.2	0.0
0.0056 moles	3.7	0.0	0.0	0.0
0.0056 moles	4.2	3.8	3.0	0.0
0.0056 moles	4.5	3.2	2.6	0.2

Table 3.9 : Comparison of the measured iron removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch four.

to be similar to although less than the residual dissolved iron concentration observed at t=24hr. The predicted value of C_f decreased as the calcium ion concentration increased, in a manner comparable to that of the observed resistant iron fraction at both t=0.25 and 24 hr.

In the experiments carried out at the highest calcium concentration, 0.0112 moles, the value of the residual dissolved iron fraction was found to be significantly lower than in the other experiments, approaching the limits of detection at both t=0.25hr and t=24 hr in some experiments (Tables 3.6 - 3.9). The first order kinetic interpretation of the experimental data sets at this calcium ion concentration also predicted C_f to be close to or below the limits of detection.

Kinetic modelling of the simulated mixing experiment data predicted a fraction of iron resistant to removal (by destabilisation and aggregation) which is seen to vary in inverse proportion to the total experimental calcium ion concentration. A significantly larger resistant iron fraction is predicted for the first order model when compared to the second order model.

3.4.2 Second Order Model

The values calculated for the second order rate constant ranged from $5.40*10^{-5}$ $mol^{-1}ls^{-1}$ at a calcium ion concentration of 0.0014 mol l^{-1} to $5.14*10^{-4}$ $mol^{-1}ls^{-1}$ at a calcium ion concentration of 0.0056mol l^{-1}. The changes in second order rate constant with calcium ion concentration are shown in Figures 3.8. to 3.10. The mean second order rate constants are shown in Figure 3.11.

A general increase in the second order rate constant was observed with increasing calcium ion concentration in all of the experimental batches, barring batch two which was carried out at a single calcium ion concentration. The spread of results however was significantly greater than was observed for the first order rate constants. The variations in second order rate constants at each of the calcium ion concentrations studied, for each of the experimental batches are given in table 3.14. As was observed for the first order rate constants the standard deviation was significantly greater over the course of the two experimental batches in which storage time was a major variable. At a calcium ion concentration of 0.0056 mol l^{-1} the relative standard deviation ranged from 53.4 and 37.5

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (μmol l^{-1})	Final Iron Conc. (μmol l^{-1})	Iron μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) $lmol^{-1}s^{-1}$	Storage Time (hr)
0.0112	18.2	0.5	17.7	97.3	0.969	2.68	3.75
0.0112	18.5	0.1	18.4	99.5	0.974	1.72	6.17
0.0112	18.4	1.0	17.4	94.6	0.994	1.76	7.00
0.0112	17.2	0.0	17.2	100.0	0.989	3.02	13.33
0.0112	18.4	0.2	18.2	99.1	0.981	1.77	16.33
0.0112	18.0	1.1	16.9	94.0	0.990	2	18.17
0.0112	17.2	0.4	16.8	97.6	0.985	1.52	24.67
0.0112	17.0	0.5	16.5	97.2	0.981	2.6	28.67
0.0112	17.6	0.2	17.4	98.7	0.986	1.53	33.67
0.0112	16.9	0.4	16.5	97.5	0.979	2.75	44.83
0.0056	18.1	2.8	15.3	84.3	0.988	0.57	5.50
0.0056	16.9	3.3	13.6	80.5	0.982	0.49	8.58
0.0056	17.9	3.6	14.3	79.8	0.976	0.92	14.17
0.0056	18.1	4.6	13.5	74.6	0.977	1.39	16.67
0.0056	17.5	4.6	13.0	74.0	0.980	1.16	19.67
0.0056	17.4	4.7	12.7	72.9	0.982	1.59	21.67
0.0056	17.2	5.1	12.1	70.3	0.988	1.77	30.50
0.0056	17.0	5.5	11.6	67.9	0.976	2.6	35.83
0.0056	17.6	6.7	10.9	61.9	0.984	2.62	47.50
0.0028	17.1	8.3	8.8	51.5	0.980	0.32	8.83
0.0028	17.7	8.9	8.8	49.7	0.988	0.48	12.00
0.0028	17.0	9.1	7.9	46.5	0.988	0.7	15.00
0.0028	19.2	10.1	9.1	47.4	0.991	0.59	23.67
0.0028	18.0	9.8	8.2	45.6	0.980	0.8	26.67
0.0028	16.9	9.5	7.4	43.8	0.970	0.77	40.50
0.0028	17.0	10.5	6.5	38.2	0.981	1.45	50.33

Table 3.10 : Influence of the addition of calcium chloride on the second order rate constant and extent of removal of iron from Tamar River water - Batch one.

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (μmol l^{-1})	Final Iron Conc. (μmol l^{-1})	Iron μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) lmol^{-1}s^{-1}	Storage Time (hr)
0.0056	14.1	1.2	12.9	91.3	0.979	0.6	3.00
0.0056	12.7	1.1	11.6	91.1	0.989	1.05	4.00
0.0056	14.0	1.4	12.6	90.1	0.984	1.68	6.00
0.0056	12.8	1.2	11.6	90.7	0.980	2.56	7.17
0.0056	13.2	1.5	11.7	88.4	0.983	3.02	10.00
0.0056	13.3	1.7	11.6	87.0	0.977	2.71	13.67
0.0056	13.6	1.9	11.7	85.8	0.982	2.76	15.67
0.0056	11.7	1.9	9.8	83.6	0.985	3.02	17.00
0.0056	10.6	1.7	8.9	84.0	0.990	3.28	21.33
0.0056	12.4	2.1	10.3	83.5	0.977	3.47	23.33
0.0056	13.2	2.3	10.9	82.3	0.974	2.76	25.83
0.0056	13.0	2.5	10.5	80.8	0.992	3.4	26.83
0.0056	11.0	2.3	8.7	79.1	0.986	4.65	35.50
0.0056	11.4	2.8	8.6	75.6	0.983	3.59	40.08
0.0056	12.5	3.3	9.2	73.8	0.981	3.99	46.92
0.0056	12.8	3.5	9.3	72.4	0.973	4.65	48.17
0.0056	13.5	3.8	9.7	71.8	0.989	2.57	48.58
0.0056	12.2	3.6	8.6	70.3	0.970	3.98	51.50
0.0056	12.3	3.9	8.5	68.7	0.986	5.14	53.00

Table 3.11 : Influence of the addition of calcium chloride on the second order rate constant and extent of removal of iron from Tamar River water - Batch two

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (μmol l^{-1})	Final Iron Conc. (μmol l^{-1})	Iron μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) $lmol^{-1}s^{-1}$	Storage Time (hr)
0.0056	14.8	1.9	12.9	87.4	0.988	3.04	1.50
0.0056	13.5	2.1	11.3	84.1	0.982	3.58	2.08
0.0056	13.4	2.1	11.3	84.6	0.986	2.84	2.50
0.0056	14.1	2.3	11.8	83.8	0.979	2.29	3.00
0.0056	14.1	2.2	11.9	84.4	0.985	1.98	3.50
0.0056	13.0	2.2	10.8	83.0	0.990	2.67	4.25
0.0028	12.4	3.5	8.9	71.6	0.986	1.6	4.67
0.0028	14.0	4.2	9.8	69.8	0.972	1.35	5.17
0.0028	13.1	3.9	9.2	70.0	0.976	1.31	5.67
0.0028	12.7	4.0	8.7	68.5	0.981	0.5	6.33
0.0028	12.7	3.9	8.8	69.3	0.984	0.67	6.83
0.0028	12.6	4.2	8.5	67.1	0.982	1.98	7.50
0.0028	13.4	4.0	9.4	69.9	0.978	2.64	7.92
0.0028	13.5	4.4	9.1	67.4	0.987	1.38	8.42
0.0028	13.6	4.2	9.4	69.3	0.985	1.32	9.33
0.0014	14.0	8.2	5.8	41.1	0.972	0.39	9.83
0.0014	14.3	8.2	6.0	42.2	0.991	0.44	10.17
0.0014	12.8	7.2	5.6	43.7	0.986	1.4	10.58
0.0028	13.6	5.4	8.2	60.4	0.989	2.55	11.08
0.0056	12.6	1.8	10.8	85.8	0.991	3.86	11.50

Table 3.12 : Influence of the addition of calcium chloride on the second order rate constant and extent of removal of iron from Tamar River water - Batch three.

Calcium Ion Conc. (mol l^{-1})	Initial Iron Conc. (µmol l^{-1})	Final Iron Conc. (µmol l^{-1})	Iron µmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) lmol^{-1}s^{-1}	Storage Time (hr)
0.0014	19.8	8.4	11.4	57.6	0.975	0.95	1.50
0.0014	21.5	9.8	11.7	54.4	0.989	0.44	2.08
0.0014	20.7	8.5	12.2	59.0	0.988	0.54	2.50
0.0014	19.9	9.3	10.6	53.4	0.990	1.29	3.00
0.0014	19.0	9.2	9.8	51.7	0.986	1.05	3.50
0.0028	18.7	5.7	12.9	69.4	0.982	1.28	4.25
0.0028	20.7	6.3	14.4	69.4	0.989	1.32	4.67
0.0028	18.7	5.5	13.2	70.7	0.990	1.59	5.17
0.0028	19.2	5.4	13.9	72.2	0.972	1.83	5.67
0.0028	19.3	7.0	12.3	63.8	0.984	1.82	6.33
0.0028	19.0	5.0	14.0	73.5	0.990	2.01	6.83
0.0028	19.7	6.2	13.5	68.5	0.987	2.01	7.50
0.0056	19.3	4.4	14.8	77.1	0.979	2.56	7.92
0.0056	20.3	3.7	16.7	82.0	0.984	2.46	8.42
0.0056	19.0	3.7	15.3	80.7	0.982	2.06	9.33
0.0056	19.5	4.2	15.2	78.4	0.983	1.86	9.83
0.0056	19.9	3.6	16.3	81.7	0.977	2.32	10.17
0.0056	19.4	3.7	15.6	80.7	0.975	2.88	10.58
0.0056	18.6	4.2	14.5	77.6	0.989	2.11	11.08
0.0056	19.2	4.5	14.8	76.7	0.987	1.89	11.50

Table 3.13 : Influence of the addition of calcium chloride on the second order rate constant and extent of removal of iron from Tamar River water - Batch four.

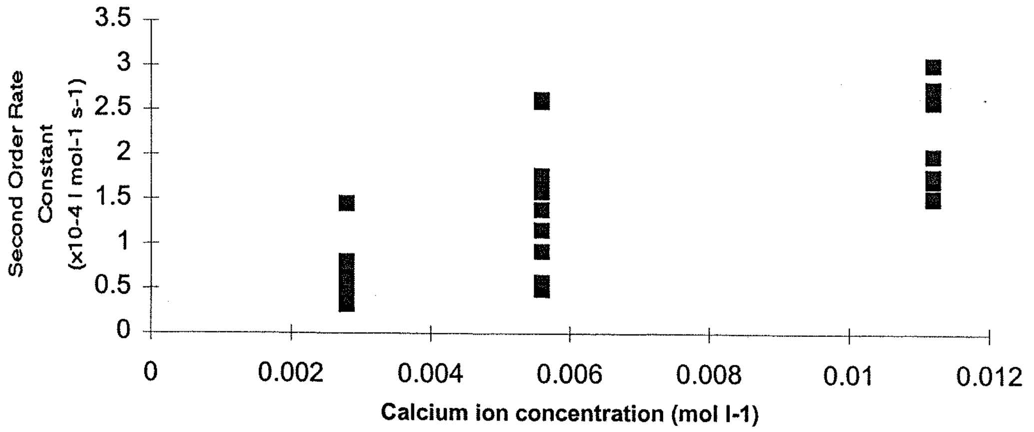


Fig 3.8 Effect of calcium ion concentration on second order rate constant (batch 1)

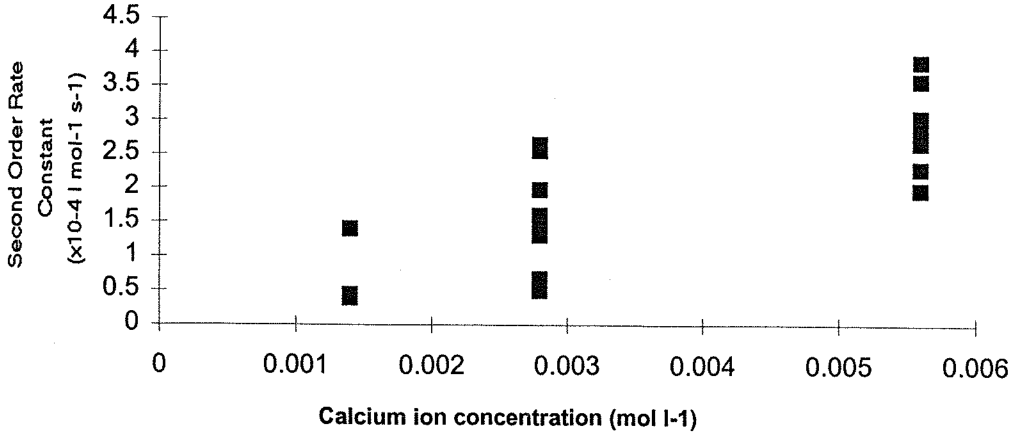


Fig 3.9 Effect of calcium ion concentration on second order rate constant (batch 3)

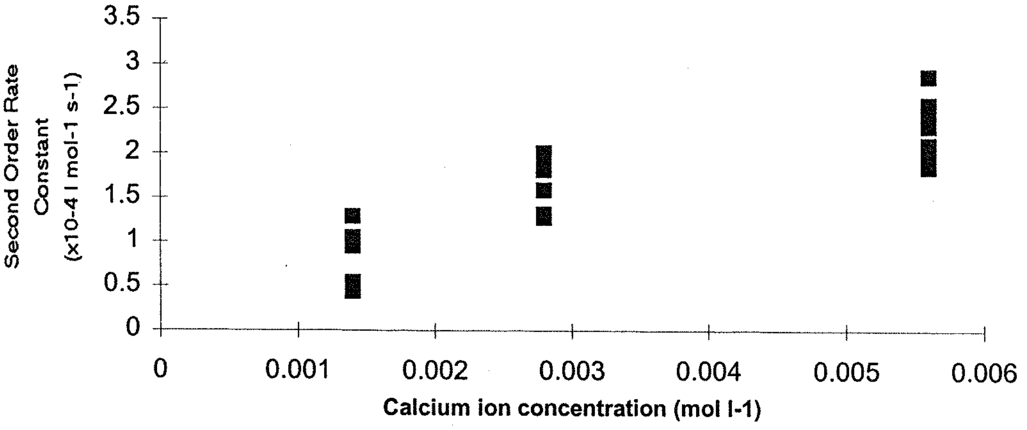


Fig 3.10 Effect of calcium ion concentration on second order rate constant (batch 4)

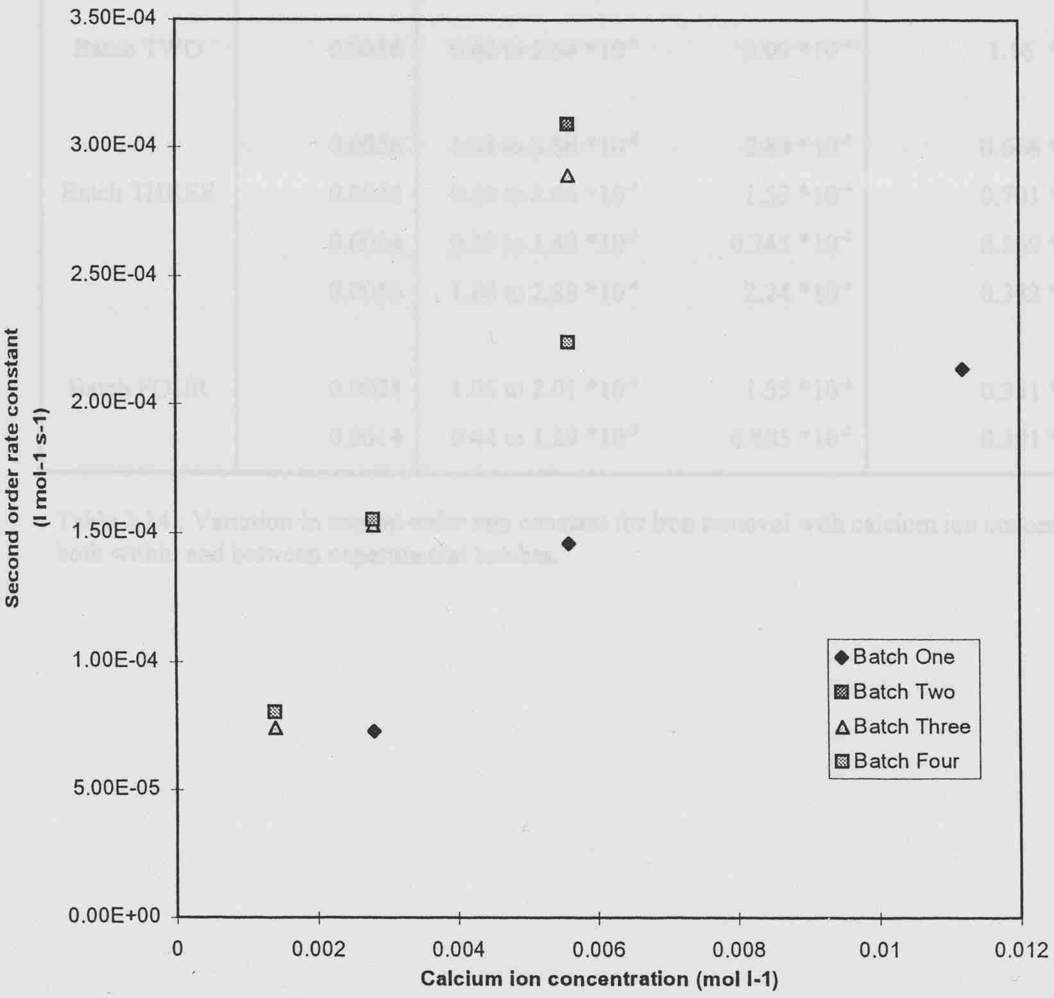


Fig. 3.11 Change in Mean Second Order Rate Constant with Calcium Ion Concentration.

	Calcium Ion Concentration	Second Order Rate Constant $(l\ mol^{-1}s^{-1})$		Standard Deviation	n
		Range	Mean		
Batch ONE	0.0112	1.52 to 3.02 $*10^{-4}$	2.14 $*10^{-4}$	0.566 $*10^{-4}$	10
	0.0056	0.490 to 2.62 $*10^{-4}$	1.46 $*10^{-4}$	0.780 $*10^{-4}$	9
	0.0028	0.32 to 1.45 $*10^{-4}$	0.73 $*10^{-4}$	0.360 $*10^{-4}$	7
Batch TWO	0.0056	0.60 to 2.64 $*10^{-4}$	3.09 $*10^{-4}$	1.16 $*10^{-4}$	19
Batch THREE	0.0056	1.98 to 3.86 $*10^{-4}$	2.89 $*10^{-4}$	0.668 $*10^{-4}$	7
	0.0028	0.50 to 2.64 $*10^{-4}$	1.53 $*10^{-4}$	0.701 $*10^{-4}$	10
	0.0014	0.39 to 1.40 $*10^{-4}$	0.743 $*10^{-4}$	0.569 $*10^{-4}$	3
Batch FOUR	0.0056	1.86 to 2.88 $*10^{-4}$	2.24 $*10^{-4}$	0.342 $*10^{-4}$	8
	0.0028	1.05 to 2.01 $*10^{-4}$	1.55 $*10^{-4}$	0.351 $*10^{-4}$	7
	0.0014	0.44 to 1.29 $*10^{-4}$	0.805 $*10^{-4}$	0.391 $*10^{-4}$	5

Table 3.14 : Variation in second order rate constant for iron removal with calcium ion concentration both within and between experimental batches.

percent for batches one and two respectively in comparison with 23.1 and 15.3 percent for batches three and four. The relative standard deviations of the second order rate constants were significantly greater than those observed for the first order model, e.g batch one at a calcium ion concentration of 0.0056 mol l^{-1} the relative standard deviation of the first order model was 21.9 percent compared with 53.4 percent for the second order model.

The pattern of changes in second order rate constant with calcium ion concentration was less obvious than for the first order model. The same general observation of a decrease in the unreactive fraction with an increase in the calcium ion concentration was observed. The mean second order rate constants showed a reasonable fit to linearity with a comparable increase per unit increase in calcium ion concentration observed between experimental batches, correlation coefficients ranging from 0.956 to 0.999. Gradients for increase ranged from $1.61*10^{-2}$ $mol^{-1}ls^{-1}$ (batch 1) to $5.08*10^{-2}$ $mol^{-1}ls^{-1}$ (batch 3). Values of mean second order rate constant showed less deviation at a calcium ion concentration than the analogous first order model e.g. at 0.0014 mol l^{-1} of calcium, the second order rate constant was $0.743*10^{-4}$ $mol^{-1}ls^{-1}$ for batch three and $0.805*10^{-3}$ $mol^{-1}ls^{-1}$ for batch four. The values of the second order rate constants showed a much greater spread, as expressed by the RSD at a given calcium ion concentration, (Table 3.14).

The second order rate constants derived by Duffy (pers comm.) for experiments using calcium ions to initiate aggregation in Tamar river water ranged from $1.20*10^{-3}$ to $2.87*10^{-2}$ $mol^{-1}ls^{-1}$. The wide disparity between the two sets of calculated second order rate constants can be partially explained by the dependence of the rate constant on the initial iron concentration, which showed significant variation between the two sets of results.

3.4.3 Comparison of the first and second order kinetic models

The prediction of the unreactive fraction in the second order kinetic interpretation of the data gave considerably different results to those of the first order model. The majority of calculations predicted a total removal of dissolved iron and only a small number predicted any iron resistant to destabilisation. For the cases in which the second order model actually predicted a residual iron concentration, the calculated value was significantly lower than the experimental residual value. There appeared to be some correlation between the first order model, high resistant iron concentrations and those for the second order model where C_f was predicted to be greater than zero. In these cases the second order model predicted significantly lower unreactive fractions than the first order. These results are consistent with the less extensive observations of Duffy (pers. comm.).

Typical examples of the modelled first and second order removal profiles, as compared with the experimentally observed removal profile, are shown in figures 3.12 a) and b) for experiment 1n (0.0056 mol l^{-1} calcium ions), and figures 3.13 a) and b) for experiment 1b (0.0112 mol l^{-1} calcium ions). The predicted profiles using the first order model both follow a path visibly close to the observed experimental removal for the duration of the experiments. Predicted values for the unreactive iron fraction using the first order model show a good agreement with the actual concentration of iron remaining after twenty four hours, in contrast to the second order model. The value of the first order rate constant shows a linear increase with increasing calcium ion concentration in comparison with the second order model which shows only a general trend of increase with increasing calcium ion concentration. For the modelled second order removal profile, the resistant iron fraction was predicted to be significantly lower than the value observed after 24 hours, and also therefore lower than that predicted by the first order model. The point that the second order removal profiles predicted consistently lower values than those observed is well illustrated in figure 3.13 b), for the experiment (1b) carried out at a calcium ion concentration of 0.0112 moles. The fit, as illustrated in both figures 3.12 and 3.13 b) was more discrepant in the earlier stages of the removal, showing a closer fit from approximately 300-400 seconds onwards.

It is clear that the second order model still gives a reasonable fit to the experimental removal profile for those experiments in which total removal of iron from the <0.45μm fraction was not observed (i.e. Figure 3.12 b). In such cases it would not be misleading to consider the second order model in a predictive mode. Figure 3.13 b) illustrates that data from those experiments in which total removal of iron from the <0.45μm fraction was observed appear to fit much less well to the second order rate model (Figure 3.13 b). The observed experimental removal appeared to give a closer fit to the first order modelled profile, in preference to the second order model, in all of the experimental batches, however

Fig 3.12 a) Comparison of removal profile and 1st order modelled fit of the data for removal of iron, run 1n

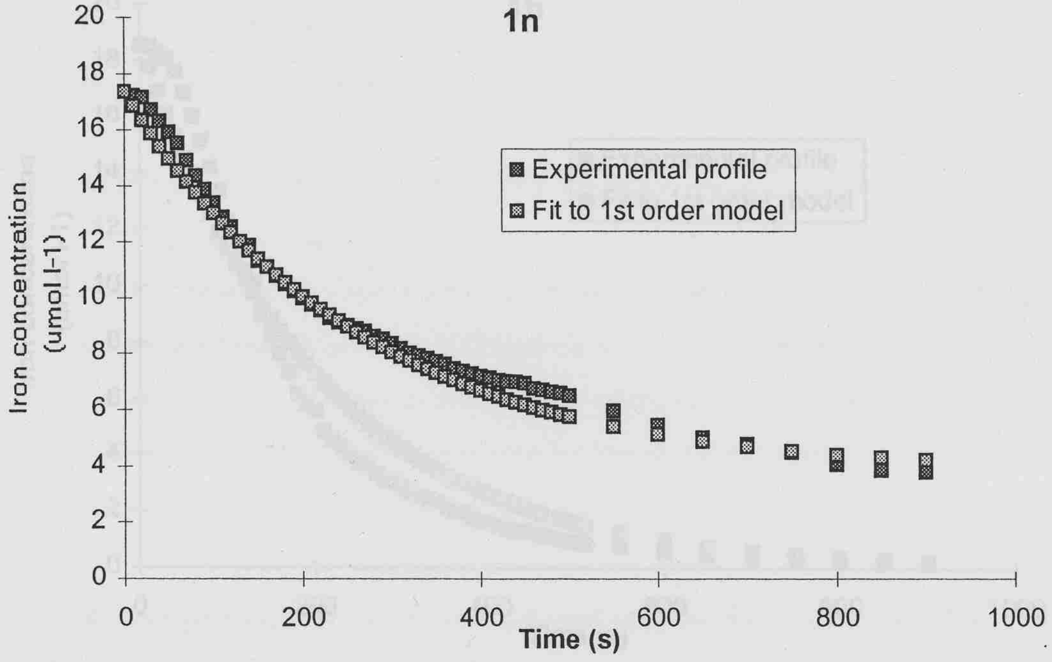
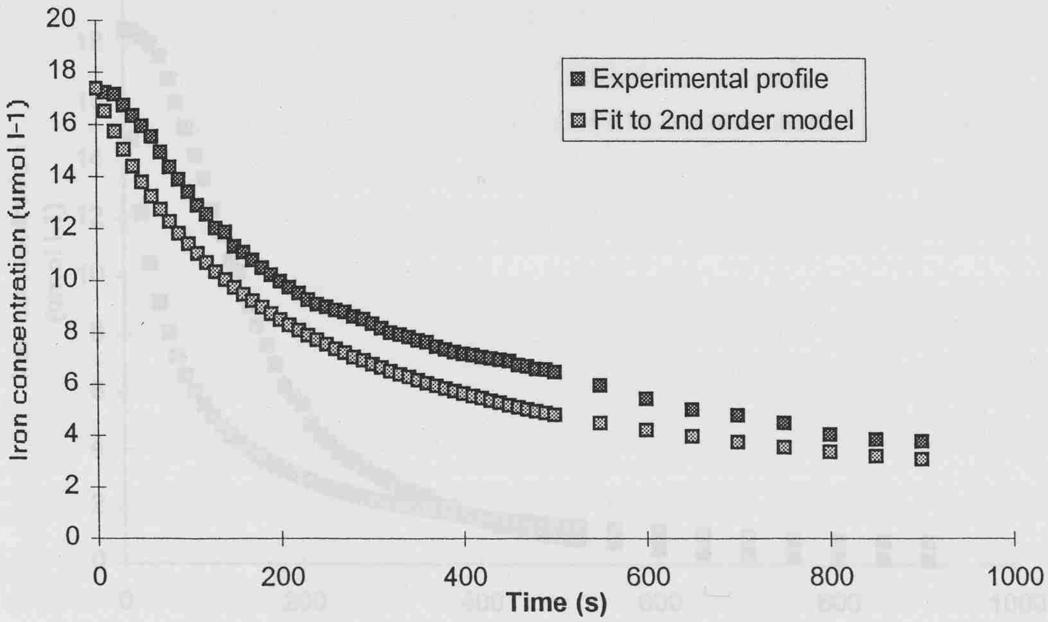


Fig 3.12 b) Comparison of removal profile and 2nd order modelled fit of the data for removal of iron, run 1n



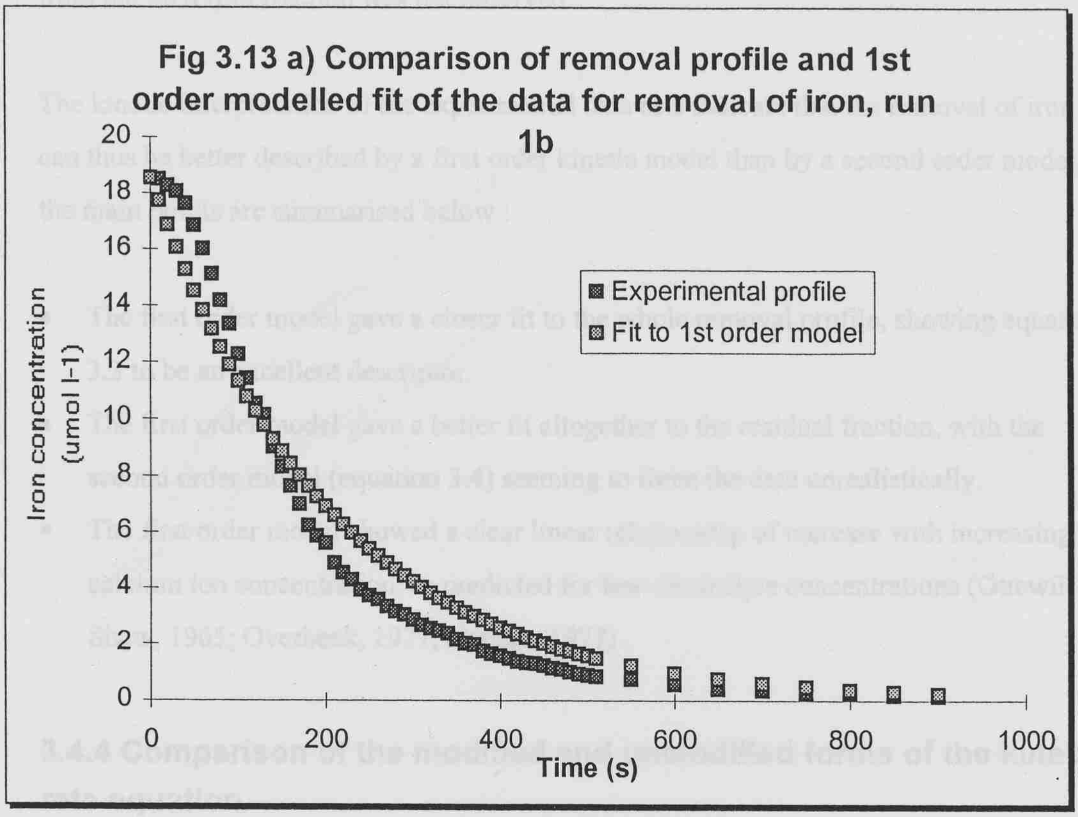


Fig 3.13 a) Comparison of removal profile and 1st order modelled fit of the data for removal of iron, run 1b

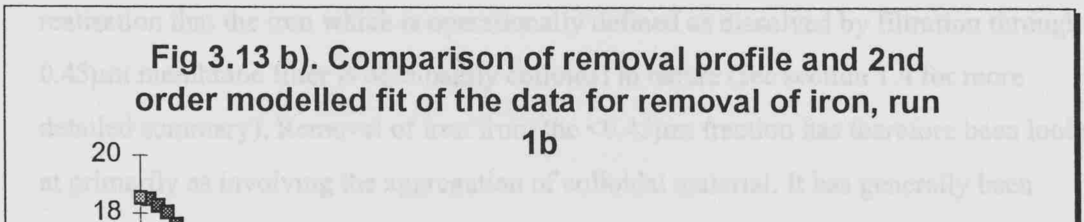


Fig 3.13 b). Comparison of removal profile and 2nd order modelled fit of the data for removal of iron, run 1b

the differences were less obvious in those experiments in which total removal of iron from the <0.45μm fraction was not observed.

The kinetic interpretation of the experimental data sets indicate that the removal of iron can thus be better described by a first order kinetic model than by a second order model, the main points are summarised below :

- The first order model gave a closer fit to the whole removal profile, showing equation 3.3 to be an excellent descriptor.
- The first order model gave a better fit altogether to the residual fraction, with the second order model (equation 3.4) seeming to force the data unrealistically.
- The first order model showed a clear linear relationship of increase with increasing calcium ion concentration, as predicted for low electrolyte concentrations (Ottewill & Shaw, 1965; Overbeek, 1977; Napper, 1977)

3.4.4 Comparison of the modified and unmodified forms of the kinetic rate equation.

The main body of work looking at the removal of iron from natural waters is based on the realisation that the iron which is operationally defined as dissolved by filtration through a 0.45μm membrane filter is dominantly colloidal in nature (see section 1.4 for more detailed summary). Removal of iron from the <0.45μm fraction has therefore been looked at primarily as involving the aggregation of colloidal material. It has generally been assumed that, by analogy with the perikinetic behaviour of a uniform, monodisperse suspension of particles, the removal of dissolved iron during estuarine mixing could be described by a second order rate law. It was also shown theoretically by Mayer (1982b) that the assumption of a monodisperse suspension need not apply provided that iron distribution fulfilled certain conditions.

Kinetic treatments of experimental data in the literature (Mayer (1982b), Fox & Wofsy (1983), Gardiner (1983) and Fox (1984)) were based on this premise with plots of 1/C vs. t, from the integrated rate, expected to show linearity with the slope of the line equivalent to the second order rate constant. Mayer (1982b) and Fox and Wofsy (1983) presented their data in this form to confirm the expected second order hypothesis. However the data

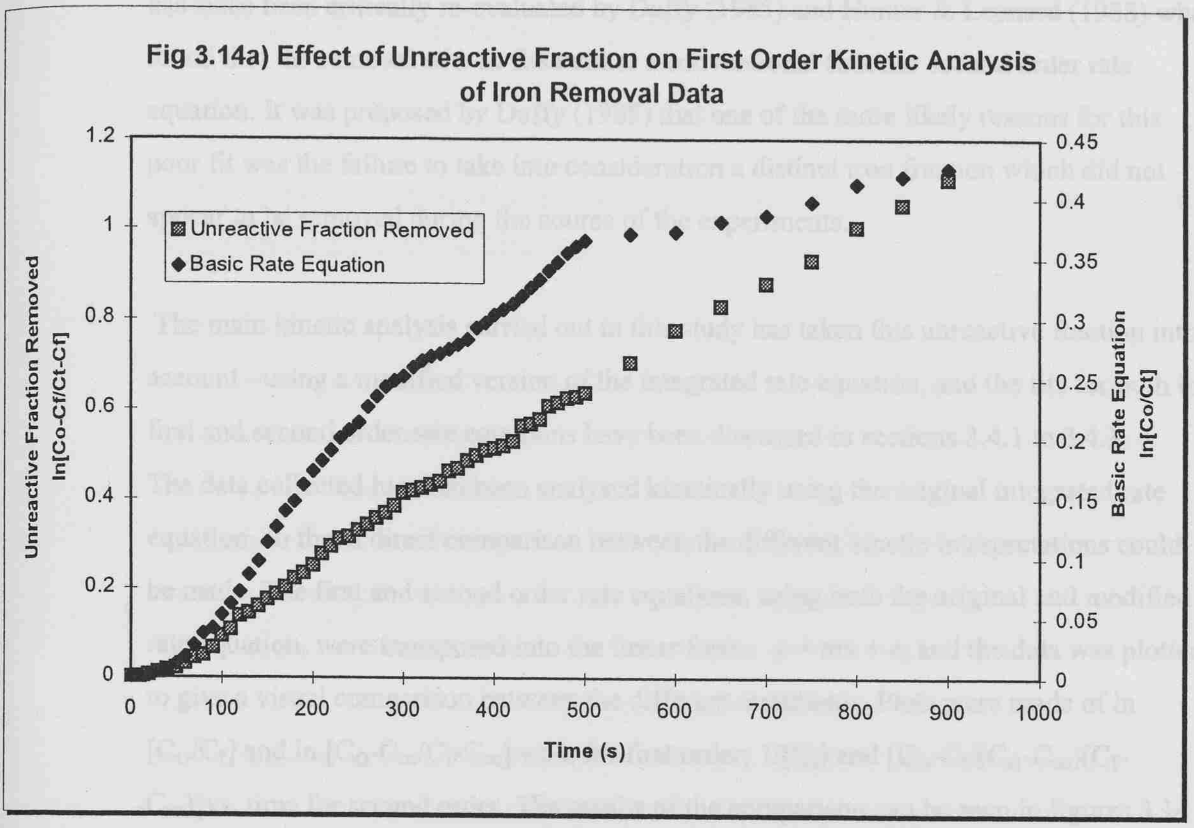


Fig 3.14a) Effect of Unreactive Fraction on First Order Kinetic Analysis of Iron Removal Data

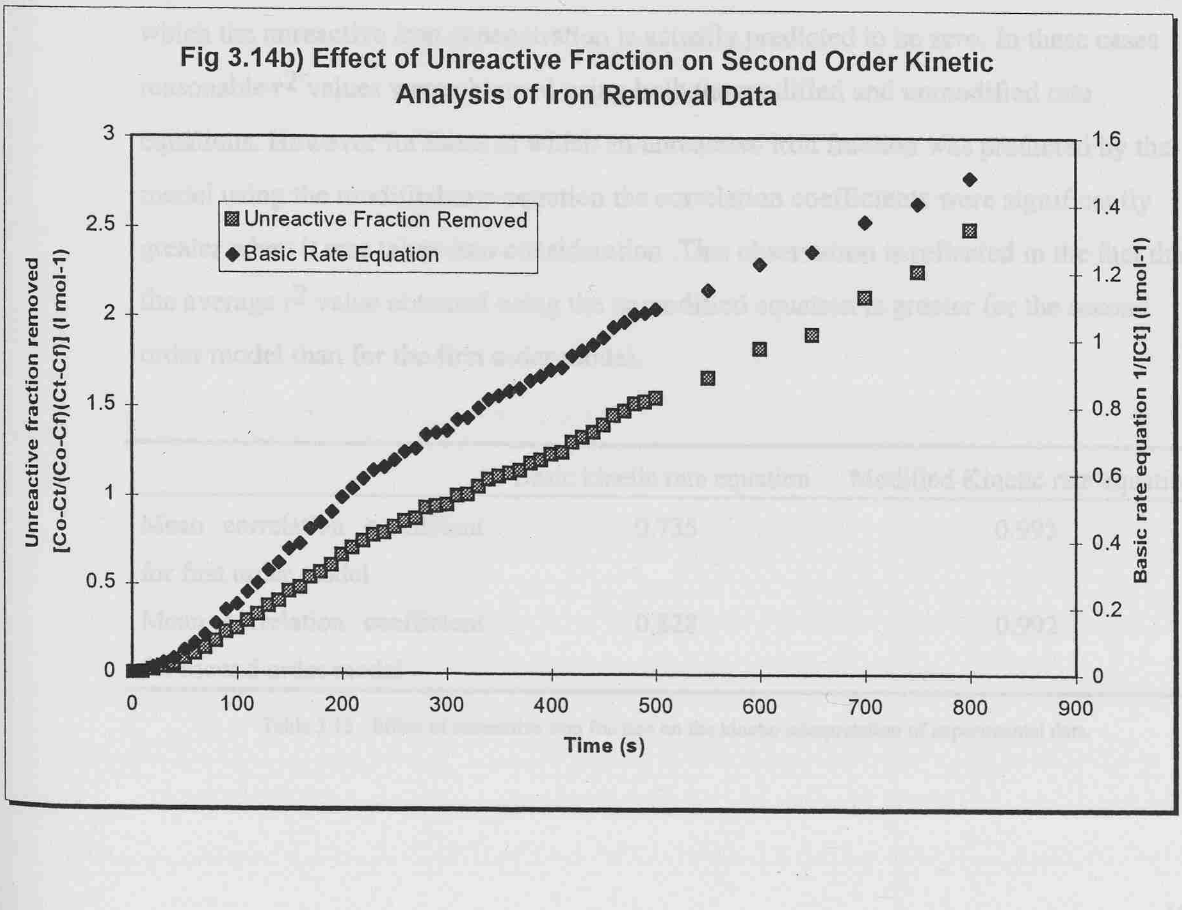


Fig 3.14b) Effect of Unreactive Fraction on Second Order Kinetic Analysis of Iron Removal Data

has since been critically re-evaluated by Duffy (1985) and Hunter & Leonard (1988) who found that the removal of iron fits neither a conventional first nor second order rate equation. It was proposed by Duffy (1985) that one of the more likely reasons for this poor fit was the failure to take into consideration a distinct iron fraction which did not appear to be removed during the course of the experiments.

The main kinetic analysis carried out in this study has taken this unreactive fraction into account - using a modified version of the integrated rate equation, and the fits for both the first and second order rate equations have been discussed in sections 3.4.1 to 3.4.3. The data collected has also been analysed kinetically using the original integrated rate equation, so that a direct comparison between the different kinetic interpretations could be made. The first and second order rate equations, using both the original and modified rate equation, were transposed into the linear form : $y = mx + c$, and the data was plotted to give a visual comparison between the different treatments. Plots were made of ln $[C_o/C_t]$ and ln $[C_o\text{-}C_\infty/C_t\text{-}C_\infty]$ vs. t, for first order; $1/[C_t]$ and $[C_o\text{-}C_t/(C_o\text{-}C_\infty)(C_t\text{-}C_\infty)]$vs. time for second order. The results of the comparison can be seen in figures 3.14 a and b. Table 3.15 displays the effects of the unreactive fraction on the model fit to the experimental data. Significant curvature is evident in the basic first order kinetic plots, in comparison with those using the modified integrated rate equation, which shows a good linear fit. For the case of the second order rate equations there are a number of cases in which the unreactive iron concentration is actually predicted to be zero. In these cases reasonable r^2 values were obtained using both the modified and unmodified rate equations. However for those in which an unreactive iron fraction was predicted by the model using the modified rate equation the correlation coefficients were significantly greater when it was taken into consideration .This observation is reflected in the fact that the average r^2 value obtained using the unmodified equation is greater for the second order model than for the first order model.

	Basic kinetic rate equation	Modified Kinetic rate equation
Mean correlation coefficient for first order model	0.735	0.993
Mean correlation coefficient for second order model	0.828	0.992

Table 3.15 : Effect of unreactive iron fraction on the kinetic interpretation of experimental data.

3.5 The Influence of Storage Effects on the Behaviour of 'Dissolved' Iron During Simulated Estuarine Mixing.

3.5.1 Effect of Storage on the Removal of 'Dissolved' Iron during Simulated Estuarine Mixing.

Hunter and Leonard (1988) proposed on the basis of experimental observations that due to the presence of highly unstable colloids in river water, significant aggregation may occur in the river water samples in the period of time prior to carrying out the mixing experiments. This phenomenon was investigated in the present work by comparing the changes in removal of both iron and phosphate in a series of experiments carried out under similar experimental conditions. Data from batches one and two were analysed with respect to storage time. Run one was carried out over a period of 50 hours using a single batch of river water. Mixing experiments were carried out using three calcium ion concentrations, 0.0028, 0.0056 and 0.0112 mol l^{-1}. Run two was carried out over a period of 53 hours. Twenty six experiments were carried out on a separate batch of river water, with addition of calcium ions to give an overall concentration in the mixing experiment of 0.0056 mol l^{-1} in each, leaving storage time as the only variable parameter.

The batches of water used for the experimental batches one and two upon which studies of storage time effects were carried out had initial concentrations of dissolved iron of 18.2 μmol l^{-1} and 14.1 μmol l^{-1} respectively. During the course of the study into storage time effects, from t=0 to t=54 hours, the initial dissolved iron concentrations, prior to addition of calcium chloride , varied from 16.9 - 19.2 μmol l^{-1} (mean = 17.6μmol l^{-1}; RSD = 3.56 percent)for batch one and for 10.6 μmol l^{-1} to 14.1 μmol l^{-1} (mean =12.6μmol l^{-1} ; RSD = 7.53 percent) for batch two. Over the period of the study, the fluctuations observed represented random variation about a mean value, rather than a systematic trend with increased storage. This concurs with the work of Hunter & Leonard (1988) who found that storage time had no effect on the overall concentration of dissolved iron found in the <0.45μm fraction of river water.

Fig. 3.15 Change in % iron removal with storage time (0.0056 mol l-1 calcium, run 1)

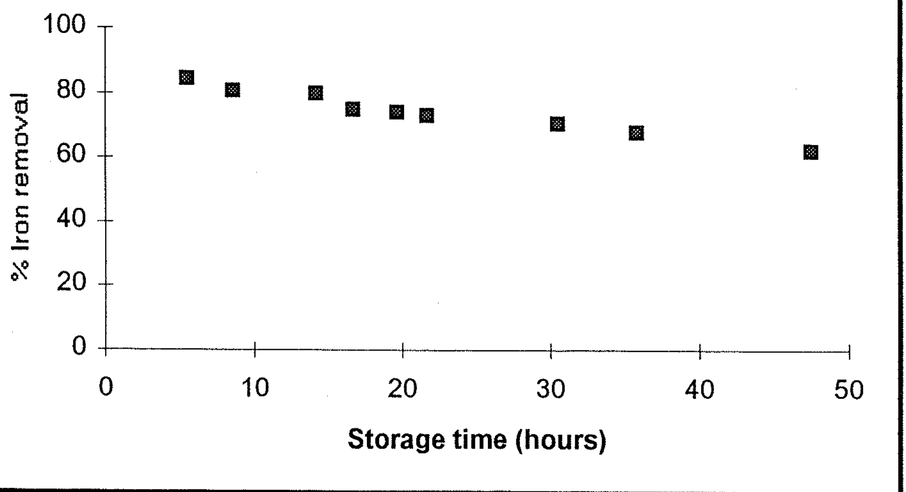


Fig 3.16 Change in % iron removal with storagetime (0.0056 mol l-1 Calcium, batch 2)

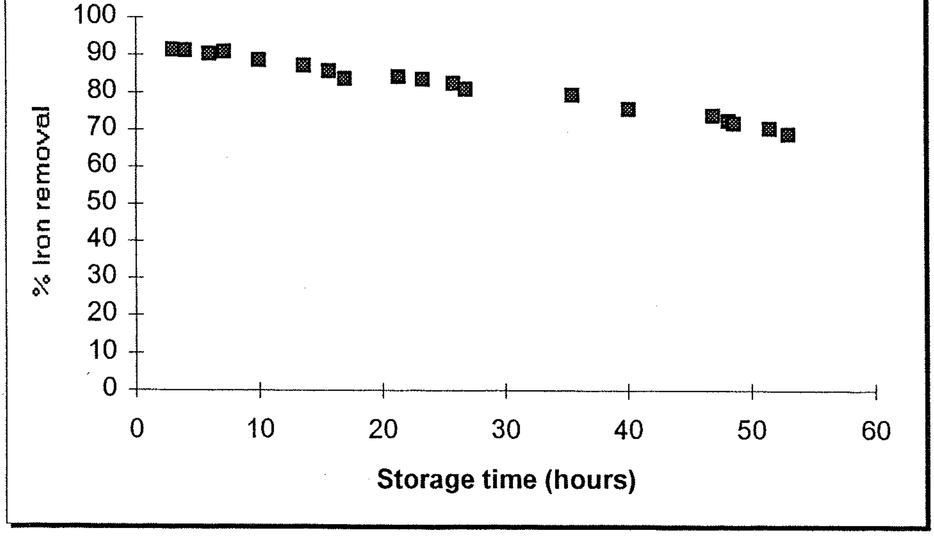


Fig 3.17 Change in % iron removal with storage time (0.0028 mol l-1 calcium, batch 1)

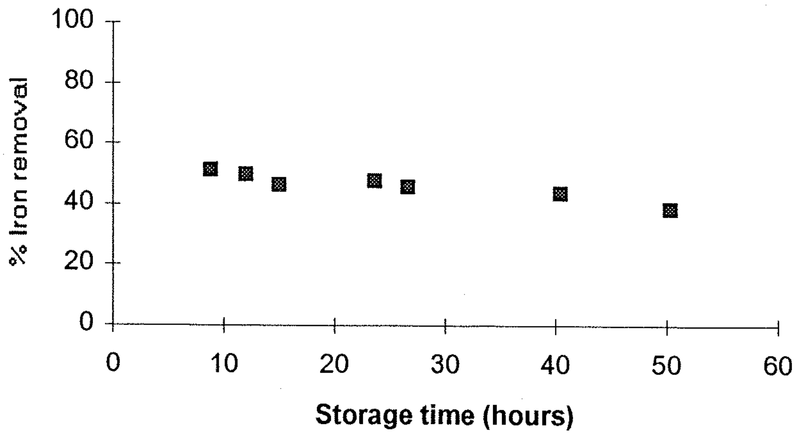
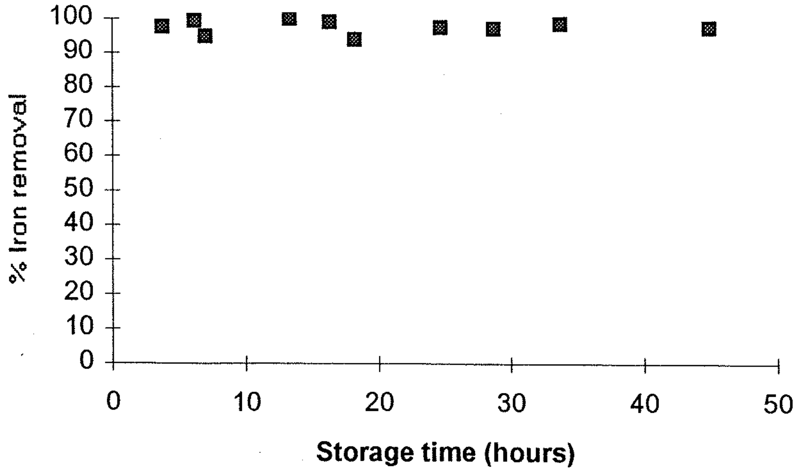


Fig 3.18 Change in % iron removal with storagetime (0.0112 mol l-1 calcium, batch 1)



The effects of storage time, prior to cation addition, on the final concentration of dissolved iron resisting destabilisation in the experiments are shown in Figures 3.15 to 3.18. In the suites of experiments the zero point for storage time (T_S = 0 hr) was taken as the time of sampling.

The effects of storage time on the percentage of dissolved iron destabilised in experiments with an overall calcium ion concentration of 0.0056 mol l^{-1} (equivalent to salinity of 18) are illustrated in Figures 3.15. and 3.16. for batches one and two respectively. Figures 3.17. and 3.18. show the comparative changes in experiments carried out with overall calcium ion concentrations of 0.0028 and 0.0112 mol l^{-1}. The data from batch one, as illustrated in Figure 3.15. shows a discernible decrease in the percentage of iron removal with increasing storage time prior to the beginning of the experiments. The percentage of iron removal decreased from 84.3 percent after 5.5 hours to 61.9 percent after 47.5 hours. Figure 3.16., showing data from batch two, illustrates that in the experiment carried out at T_s= 3 hr the percentage removal of dissolved iron was 91.3 percent fifteen minutes after the addition of calcium ions and 92.2 percent after twenty four hours had elapsed. The percentage removal of dissolved iron removal stayed around this value of 90 percent with only small fluctuations about the mean value for experiments carried out up to a storage time (Ts) of six hours. A slow but regular decrease in the percentage removal of dissolved iron was observed after this time, reaching 83.5 percent at Ts = 23 hr, 75.6 percent at Ts = 40 hr and 68.7 percent at Ts = 53 hours. There was a good degree of comparability in the observed effects of storage time on the behaviour of dissolved iron in experiments carried out at a calcium ion concentration of 0.0056 mol l^{-1} between batches one and two.

A smaller suite of experiments were carried out during the course of batch one, between T_s = 9 and T_s = 50, at an initial calcium ion concentration of 0.0028 mol l^{-1} as illustrated in Figure 3.17. The results exhibited an increase in the resistant fraction of iron with increasing storage time : at T_s = 9 hr the fraction of iron removed was 61.5 % at T_s = 15 hr 46.5 % and at T_s = 50 hr the resistant fraction had decreased to 38.2%.

This clear trend of a decreasing fraction of iron susceptible to destabilisation with storage time was not reflected in the experiments carried out in batch one, with a calcium concentration of 0.0112 mol l^{-1}. As illustrated in Figure 3.18., in the initial experiment carried out at t = 1hr the fraction of iron removed was 97.4 percent (after 15 minutes, and 97.6 percent 24 hours after addition of calcium ions). Over the suite of experiments carried out up to $T_s = 45$ hr the resistant fraction varied from 94 percent removed to 100 percent within analytical error without a discernible pattern.

The findings of the experiments with overall calcium concentration of 0.0056 mol l^{-1} (and those at 0.0028 mol l^{-1}) lead to the same conclusions as those of Hunter & Leonard (1988), storage time having affected the behaviour of the dissolved iron fraction during simulated estuarine mixing, and also decreased the overall iron removal observed. This suggests that during the storage period changes occurred within the colloidal fraction, possibly due to aggregation processes, which increased the stability of the iron with respect to the subsequent mixing process. The experiments carried out at a calcium concentration of 0.0112 mol l^{-1} showed an almost total removal of the dissolved iron fraction apparently regardless of storage time prior to mixing. The experimental calcium concentration is far in excess of the equivalent salinities in the experiments of Hunter & Leonard (1988) and it possibly due to the high concentration forcing the destabilisation of most of the colloids present, irrespective of the possible differences in their resistance to destabilisation thus masking the demonstrated storage effects.

3.5.2 Effects of Storage Time on Rate Constants

Using the methods outlined in section 3.4.1 the first and second order rate constants were calculated, equations 3.3 and 3.4 respectively, from the data obtained in the investigation into the storage time effects. Variability in the first and second order rate constants was examined in relation to the amount of time water had been stored prior to addition of calcium ions in the simulated mixing experiments.

Figures 3.19 to 3.22. illustrate the effects of storage time on the calculated first order rate constants, while Figures 3.23. and 3.24. show the corresponding changes in calculated second order rate constant. The data from the kinetic interpretations is summarised in Tables 3.1. - 3.4. for evaluations by the first order model and Tables 3.5. to 3.8. for second order.

Fig. 3.19 Change in first order rate constant with storagetime (0.0056 mol l-1 calcium, batch 1)

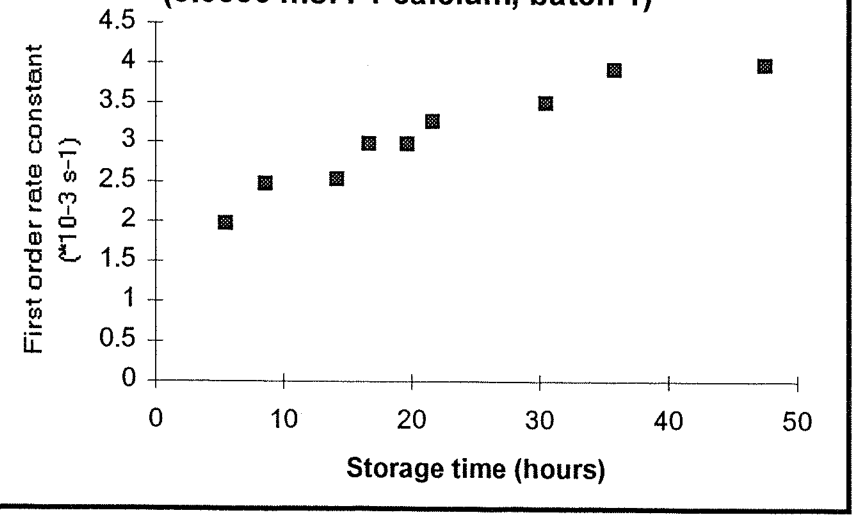
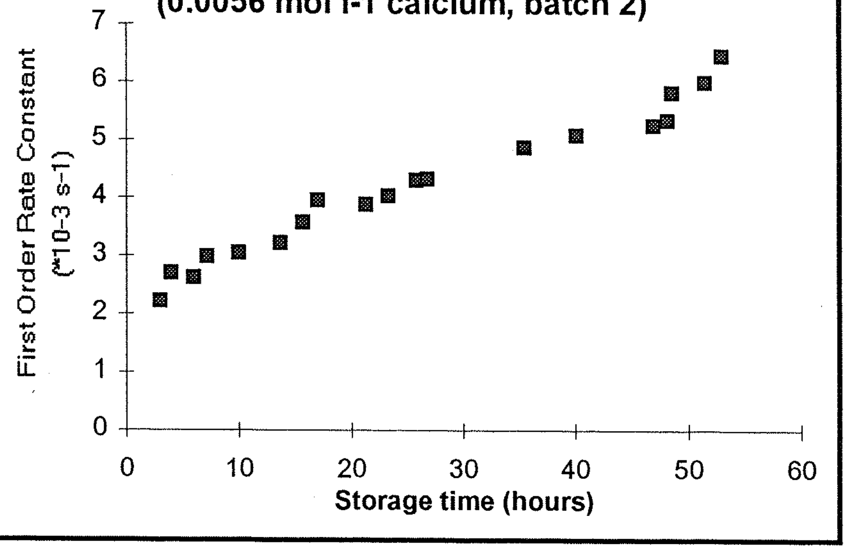


Fig. 3.20 Change in first order rate constant with storage time (0.0056 mol l-1 calcium, batch 2)



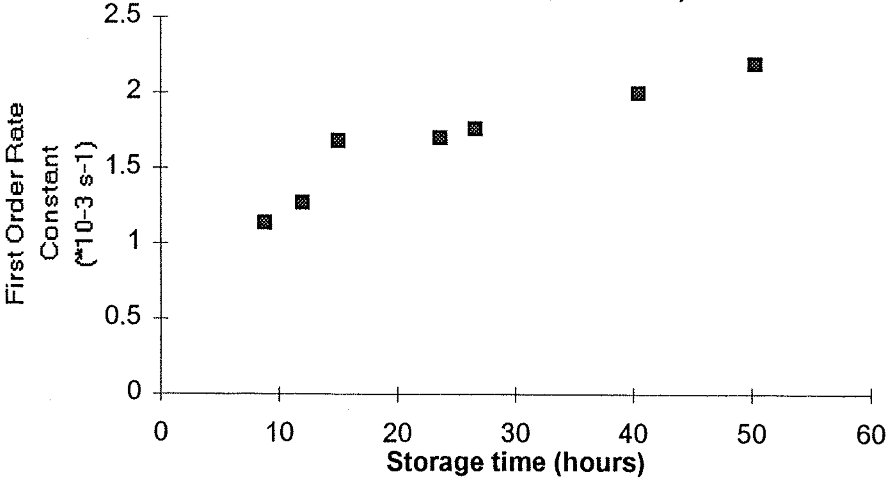


Fig. 3.21 Change in First Order Rate Constant with StorageTime (0.0028 mol l-1 Calcium, batch 1)

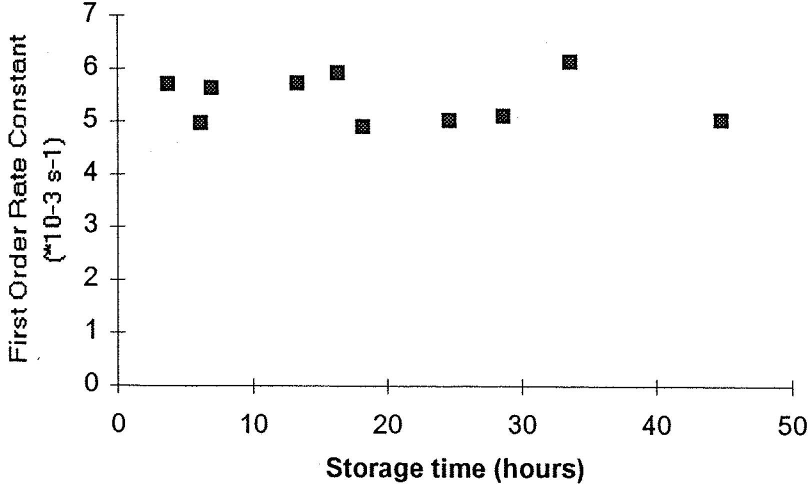


Fig. 3.22 Change in first order rate constant with storage time (0.0112 mol l-1 calcium, batch 1)

i) First Order Model

For both batches one and two, at a calcium ion concentration of 0.0056 mol l^{-1} there was a positive approximately linear relationship between the first order rate constant and storage time (Figure 3.19. for batch one and Figure 3.20 for batch two). The first order rate constant increased gradually from 2.21*10^{-3} s^{-1} at T_s =1hr through to 4.32 *10^{-3} s^{-1} at T_s = 27 hr and finally up to 6.45*10^{-3} s^{-1} at Ts = 53 hours for batch two. For batch one an increase in rate constant was also observed from 1.98*10^{-3} s^{-1} at T_s = 5.5 hr to 2.98 *10^{-3} s^{-1} at T_s = 20 hr and finally to 3.99*10^{-3} s^{-1} at T_s = 47.5 hr. At a calcium ion concentration of 0.0028 mol l^{-1}, Figure 3.21 illustrates a gradual increase in rate constant with increasing storage time from 1.14*10^{-3} s^{-1} at T_s = 8.8 hr to 2.55*10^{-3} s^{-1} at T_s = 50.33 hr.

At a calcium ion concentration of 0.0112 mol l^{-1} there appeared to be only very slight fluctuations in the first order rate constants with increased storage. The rate constant varied between 5.04*10^{-3} and 6.14*10^{-3} s^{-1} in a random manner.(Figure 3.22.)

These findings correlate with those observed in Section 3.5.1 showing that storage time had a significant effect on the behaviour of the dissolved iron fraction at lower salinities (Calcium ion concentrations of 0.0028 and 0.0056 mol l^{-1})whilst at the highest experimental calcium ion concentration there appeared to be little or no effect upon either the first order rate constant or the experimental removal profile. The effects of storage time on the first order rate constant diminished with increasing cation concentration in the simulated mixing experiments

ii) Second Order Model

The effects of storage time on the calculated second order rate constant for a calcium ion concentration of 0.0056 mol l^{-1} in batch two are shown in Fig 3.23. The second order rate constant showed a definite increase with increasing storage time, but the results appear much more widely scattered than those obtained using the first order model and do not show a distinct linear pattern. A general increase in second order rate constant with increasing storage time is also observed for the experiments carried out at calcium ion concentrations of 0.0056 and 0.0028 moles for batch one, Figures 3.24 and 3.25 respectively.

Fig 3.23 Change in second order rate constant with storage time (0.0056 mol l-1 Calcium, batch one)

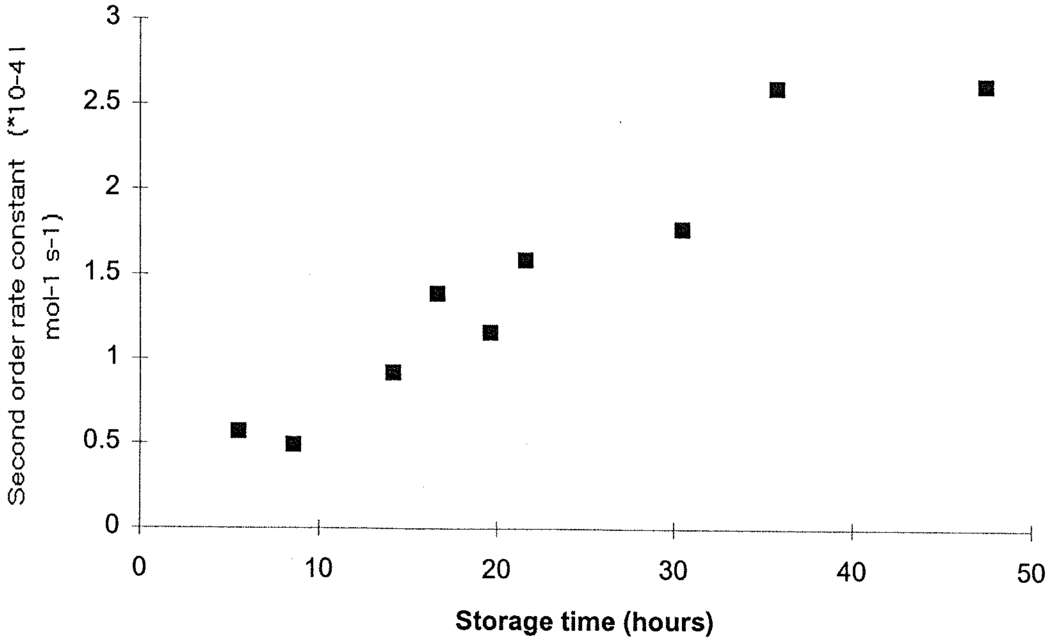
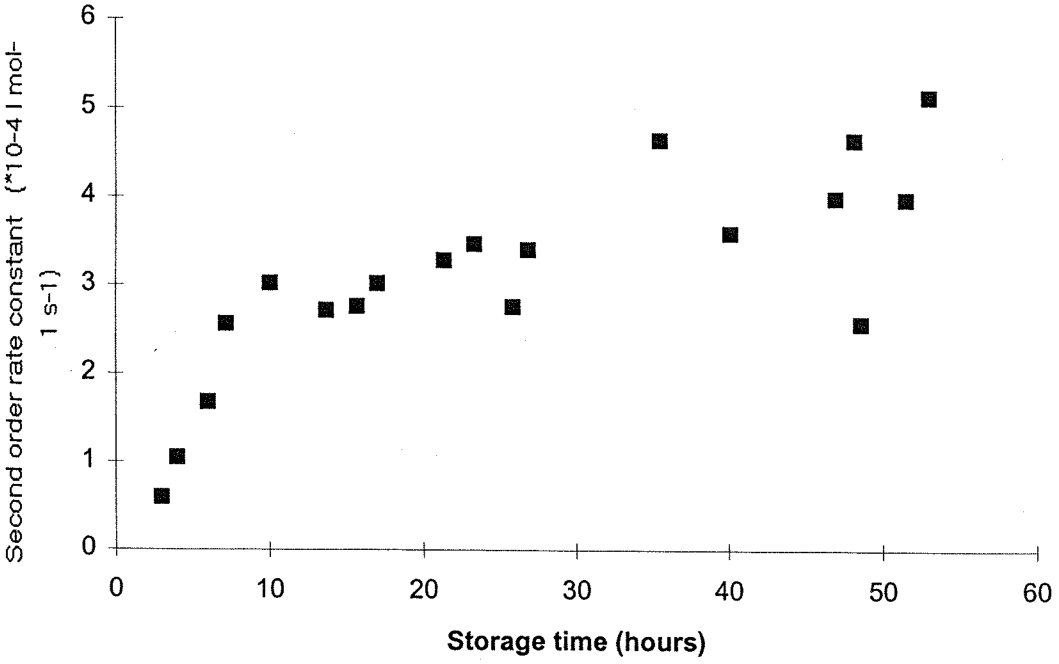


Fig 3.24 Change in second order rate constant with storage time (0.0056 mol l-1 Calcium, batch two)



As with the first order rate constant, at a concentration of 0.0112 mol l^{-1} of calcium the second order rate constant did not show a definite trend with changing concentrations, instead fluctuating between 0.000152 and 0.000268 $mol^{-1}ls^{-1}$ in a random manner (Figure 3.26).

The interpretation of the data using the second order model to derive rate constants thus shows similar patterns to those found using the first order model, but systematic features in the variability with storage time are not as well defined

Fig 3.25 Change in second order rate constant with storage time (0.0028 mol l-1 Calcium, batch one)

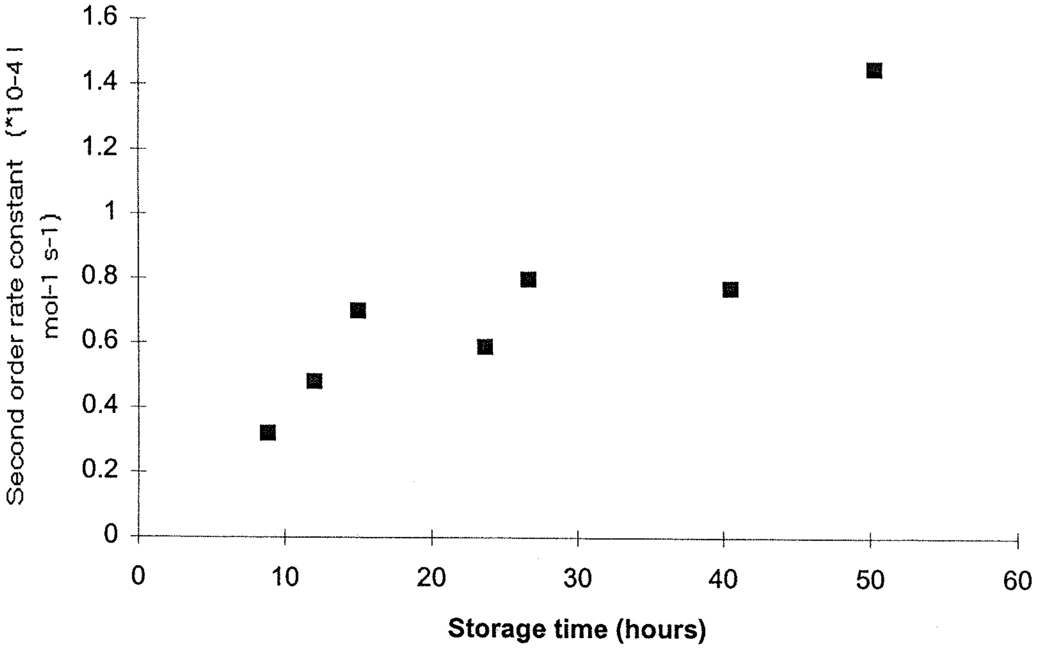
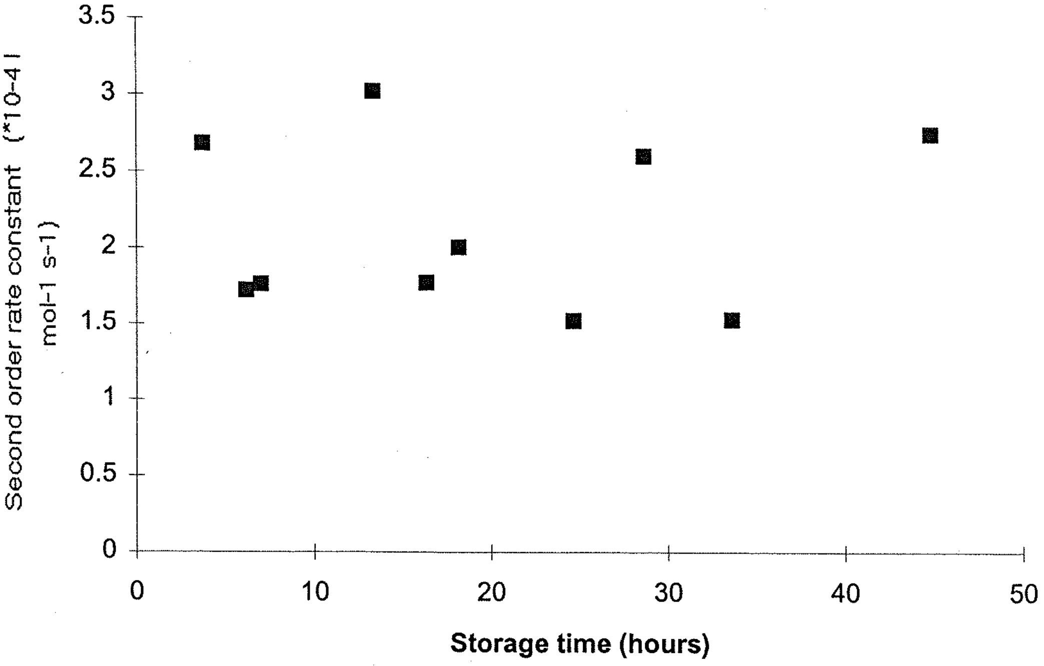


Fig 3.26 Change in second order rate constant with storage time (0.0112 mol l-1 Calcium, batch one)



3.6 : Discussion

3.6.1 Interpretation of kinetics of iron removal

Initial experimental investigations into the behaviour of the dissolved iron fraction during simulated estuarine mixing reported a rapid loss of dissolved iron in the early stages. The rate of loss of iron decreased noticeably within minutes continuing for several hours until the dissolved iron concentration had decreased to an apparent equilibrium level. Despite these observations, many of the earlier investigations of this phenomena did not closely examine the initial time period (0-200 s) measurement of discrete samples not commencing until several minutes after addition of the destabilising agent (Mayer, 1982b; Fox & Wofsy, 1983; Hunter & Leonard, 1988).

Mayer (1982b) proposed that the aggregation of dissolved iron occurred by two separate reactions : a rapid initial reaction, taking place over a few minutes, and a second, mechanistically different reaction, occurring at a slower rate over the following hours. Such observations of the aggregation reaction taking place over the course of several hours are borne out by the results of Eckert & Sholkovitz (1976), Boyle *et al.* (1977), Fox & Wofsy (1983), and Hunter & Leonard (1988). The time scale of the aggregation reactions observed in the experiments carried out in the present study are contrary to such findings, as they show a rapid removal within the first few minutes after which the dissolved iron concentration approaches a residual level (within approximately five to six minutes). These results are, however, analogous with the findings of Duffy (1985) whose experimental methods were employed here. It must be noted that in the bulk of the work of Duffy (1985) and that of the current study, the aggregation reaction was initiated by the addition of a major cation component of sea water, rather than by the addition of sea water. Duffy (1985) however, carried out experiments with addition of sea water and the reaction proceeded similarly as with single cations.

The observed differences in the timescale of removal of dissolved iron during simulated estuarine mixing between the experiments of Boyle *et al.* (1977), Mayer (1982b) and Fox & Wofsy (1983) and those in this study and that of Duffy (1985) are further illustrated by a comparison of the calculated rate constants. Kinetic interpretations of data from this study and that of Duffy (1985) used a modified version of the integrated rate equation, taking into account an unreactive fraction of dissolved iron. This kinetic model was used by Duffy (1985) to re-evaluate the experimental data of Boyle *et al.* (1977), Mayer (1982b) and Fox & Wofsy (1983). The first order rate constants in the present study ranged from 0.90 to $6.45*10^{-3}$ s^{-1},for the Tamar river system, compared with 7.10 to 12.1 10^{-3} s^{-1}, calculated by Duffy for the same river system. The present values are similar at the upper end of the range to those of Duffy, but range downwards to values about an order of magnitude lower. Duffy (1985) concluded that the magnitude of the first order rate constant was essentially independent of cation concentration, and likewise independent of the cation used. Such findings are conflicting with those of the present study, despite the similarities in the experimental methods employed. The rate constants calculated by Duffy (1985) using Boyle's (1977) data on the Mullica river ranged from 1.5 to 3.4 10^{-3} s^{-1}, thus overlapping with the lower end of the range for the present study. Those calculated for the Saco estuary, using the data of Mayer (1982b), were an order of magnitude lower, ranging from 1.0 to 1.6 10^{-4} s^{-1} and for the experiments using waters from the Mullica, St Jones and Broadkill estuaries, using data of Fox & Wofsy (1983), the values calculated were between one and two orders of magnitude lower, ranging from $5.2*10^{-5}$ to $4.7*10^{-4}$ s^{-1}.

Significant differences in the nature of the 'dissolved' iron fraction between different river waters have been observed with respect to their behaviour during simulated estuarine mixing (Fox & Wofsy, 1983). In the light of kinetic re-evaluation of the data by Duffy (1985) from the experiments of Boyle *et al.* (1977), Mayer (1982b) and Fox & Wofsy (1983), significant differences appear in the calculated first order rate constants, not only between the different river systems studied but also between independent studies of the same river system. The differences in reaction time scale could be caused by either an inherent difference in the nature of samples, or a difference in experimental procedure. The rate of the reaction studied is a function of : a rate constant, k_{max}, which describes the aggregation of a fully destabilised colloid population, the collision efficiency, α, and the initial number of aggregating particles - which is itself dependent on sample origin. k_{max} is unlikely to vary sufficiently between samples to cause the orders of magnitude differences seen in the rate constants - as it is dependent on Boltzman's constant, temperature, viscosity and a size distribution function, all of which remain reasonably uniform between samples. This leads to the conclusion that either the collision efficiency and / or the initial number of aggregating particles must be the principal factors responsible for the wide divergence in reaction rates observed. The initial iron concentration varies considerably between the rivers in each study from 1.5 μmol l^{-1} for the Saco Estuary to 58μmol l^{-1} for the Mullica Estuary. This wide variation in initial dissolved iron concentration between rivers is likely to be accompanied by differences in colloidal characteristics such as size distribution, stabilisation by organic material etc.

There were several major differences between the experimental approaches in previous studies. Pre-filtration of initial river and / or sea water samples was carried out in some experiments, and the size of the filter used for the separation of the aggregated iron fraction during the course of the experiment varied greatly. Different colorimetric reagents have been used for the iron determination, at a variety of temperatures, which further complicates the comparison - Boyle *et al.* (1977) found that temperature affects the amount of colloidal iron available for determination. The effects of storage time of samples prior to mixing must be taken into consideration as this has also been shown to have an effect on the behaviour of the colloidal fraction (Hunter & Leonard (1988)). Work in this study found that the storage effects had a pronounced effect on the behaviour of the colloidal iron fraction, during simulated estuarine mixing, while not greatly afecting the initial concentration in a river water sample - see Section 3.5 and 3.6.2 for a full consideration of the implications of storage effects.

The Mullica Estuary was studied by Boyle *et al.* in 1977) and was one of the estuaries studied by Fox & Wofsy in 1983. A similar overall percentage removal of iron was removed at comparable salinities; Boyle *et al.* (1977) found 81 % removed at salinity 9 and 93 % removed at a salinity of 14; while Fox and Wofsy (1983) found 84 % removed at a salinity of 8 and 88 % removed at a salinity of 13. In contrast to this, the calculated first order rate constants were an order of magnitude greater as derived from the work of Boyle *et al.* (1977) (1.5 to $3.4*10^{-3}$ s^{-1}) than those calculated from the data of Fox & Wofsy (1983) (2.4 to $4.7*10^{-4}$ s^{-1}). The derived second order rate constants differed to a similar extent ranging from $1.4*10^{-4}$ mol l^{-1} s^{-1} to $1.78*10^{-2}$ mol l^{-1} s^{-1},as derived from the data of Boyle and from $6.76*10^{-2}$ mol l^{-1} s^{-1} to $7.53*10^{-1}$ mol l^{-1} s^{-1} as derived from the data of Fox & Wofsy (1983) The large discrepancy between rate constants raises questions as to whether the reaction studied in the different experiments is identical. It is obvious that the reaction observed in the present study does not conform with Mayer's (1982b) observation of a two stage reaction. It is possible that the reaction observed could correspond to the first stage in his hypothesis, with a lesser degree of steric stabilisation of colloids in the Tamar as compared with the Saco giving rise to a larger proportion of the microcolloidal iron being removed within the first reaction. The removal of the remainder of the destabilised iron in a second stage, if present, may be occurring at a slower rate due again to differences in the nature of the microcolloidal population. The reaction observed in this study, and also in that of Duffy (1985) took place very rapidly, relative to those observed by Boyle *et al.* (1977), Mayer (1982b) Fox & Wofsy (1983), and Hunter & Leonard (1988), occurring in minutes rather than hours, however the overall fractions removed under comparable destabilising conditions are of a similar magnitude. As the overall removal observed is analogous with the experimental data of the other authors it is reasonable to propose that the same fundamental reaction is being observed.

Although there was a large time period between the two sets of experiments, it does not appear likely that the variability in first order rate constant between the two sets of experiments can be solely attributed to a change in the characteristics of the Mullica river water itself, given the close similarity in the magnitude of the unreactive fraction. The present study has shown that temporal variability in the magnitude of the unreactive iron fraction and in the rate constant for removal tend to be related. A variation in methodology may conceivably lead to a difference in the estimation of the colloidal size range, the initial particle number and the speciation of the dissolved iron fraction. In the experiments of Boyle *et al.*(1977) water was filtered through Mead and Whatman glass fibre filters and subsequently through a Millipore 0.45µm membrane filter. Fox & Wofsy carried out experiments using unfiltered river water and sea water passed through an unknown filter size. The work of Duffy (1985) found there to be no significant effects of the presence of particles on the removal rate of 'dissolved' iron solution, in contrast to the findings of Mayer (1982) and Hunter & Leonard (1988) who argued that larger particles played a vital role in any aggregation reaction. The concentration of unaggregated iron measured after mixing was defined by Boyle *et al.*(1977) as that passing through a 0.45µm membrane filter in comparison with a 1.2µm glass fibre filter used by Fox & Wofsy (1983). This difference in filter pore size may help to understand the discrepancies observed in the rate constants: on addition of cations a fraction of the initial aggregates formed would be retained by the filter in the work of Boyle *et al.*(1977), but would pass through the GF/C filters used by Fox & Wofsy (1983), leading to the observation of an apparently slower reaction being observed by Fox & Wofsy (1983).

Due to our inability to accurately quantify the effects of these experimental differences, it is impossible to tell precisely how much of the difference in dissolved iron concentration is due to the fundamentally different nature of samples. The work carried out in chapter five attempts to address these problems and offer an insight into the controls on the behaviour of iron during removal.

3.6.2 Mechanism of Iron Removal

The results derived from the present experiments using mixing conditions closely similar to those used by Duffy (1985) indicate that the modified first order rate expression, taking account of the residual fraction, is a good descriptor of the reaction taking place. The kinetic evaluation of data from previous authors in the literature also gave a good fit to the first order kinetic model (Duffy, pers comm.). While the modified second order rate expression can also be an adequate descriptor in some cases it is less satisfactory for the reasons given in section 3.4.3.

Observations of a first order kinetic rate for the aggregation is in contradiction to the previously accepted mechanistic explanation of the removal of iron during estuarine mixing, which assumes second order kinetics based on classic colloid theory which predicts perikinetic aggregation for colloids of the size range concerned.

A first order reaction could be induced by shear effects generated within the mixing tank, as orthokinetic aggregation of colloids can be described by pseudo first order kinetics if particle volume is conserved (Stumm & Morgan, 1981). This mechanism was considered by Duffy, (1985) to be unlikely for particles <0.45μm in diameter as a velocity gradient in excess of $100s^{-1}$ would be required for orthokinetic aggregation to dominate over perikinetic. In the present experimental system the velocity gradient is estimated to be of the magnitude of $10s^{-1}$. The existence of zones of higher shear within the solution might, however, make the argument over simplistic. With rapid mixing, the frequency with which the solution encounters higher shear conditions would be increased. The influence of stirring rates on the kinetics is addressed further by the experiments described in Chapter 5.

The distribution of 'dissolved' iron within the microcolloidal particle population is potentially crucial in determining the reaction rate, as discussed in Section 1.6. If iron is sufficiently non uniform in its distribution in the 'dissolved' fraction (which it is in 1-6μm fraction; Bernard *et al.,* 1986) the loss of iron can be explained by a first order removal expression. It was intended originally to do fractionation within the <0.45μm material, however the difficulty arises that most of the colloid lies in a relatively narrow 'size' band and the size fractions containing low concentrations present problems because of analytical detection limits for continuous measurement. Data on size fractionation, confirming a non uniform distribution within the larger size fractions is given in Section 4.2.2.

3.6.3. Effects of Storage time on Estuarine Constituents

The effects investigated provide evidence that the microcolloidal population is not static but is subject to reorganisation and is relevant as a factor potentially influencing comparability of results among different experimental studies and within these studies. The total concentration of iron within the <0.45μm fraction of a river water sample did not appear to be influenced by storage time, fluctuations observed were non systematic and within the limits of experimental error.

The behaviour of the dissolved iron fraction during simulated estuarine mixing experiments was shown to be affected by storage time, with an increase in storage time leading to an increase in the fraction of iron resistant to destabilisation. This concurred with the findings of Hunter & Leonard (1988) who observed that the initial concentration of iron within a sample did not alter significantly with storage, but differences became apparent during the simulated mixing behaviour. A positive linear correlation between the increased storage time and the observed changes in the first order rate constant was observed. The changes in second order rate constant with storage whilst displaying an increase showed a much less distinct pattern. The effects of storage time were most evident in experiments with lower experimental calcium concentrations.

The observations indicate a re-ordering of iron within the <0.45μm fraction, possibly due to an aggregation and disaggregation within the colloidal population during prolonged storage. The effects of this re-ordering were seen in the increase in the resistant iron fraction and also in the increased rate constants with increased storage.

Observed differences in behaviour found in the work of previous authors could, as discussed in Section 3.5, be in part as a result of different storage conditions and time. The magnitude of these observed effects must reflect the characteristics of the river water itself, in respect to the composition and stabilisation of colloidal material. These indications that changes in the stability of the colloid population occur as a result of storage, with stabilisation of the colloidal fraction, have serious implications for the results from estuarine simulation work. If the collection and storage of water samples changes the inherent properties of the sample, as appears to be the case, the validity of findings is diminished in terms of truly simulating estuarine behaviour. In the light of these findings, subsequent experiments were carried out as soon possible after mixing to negate possible storage artefacts.

Further work is required to investigate the mechanisms of the re-ordering of the colloidal fraction and why the original concentration is not significantly affected. A study of the changes in microcolloidal iron concentration within different size fractions with storage could provide some information. Changes in the nature of the colloids could be probed by examining quantifiable properties, such as metal complexation capacity. While such approaches are empirical, they could provide complementary evidence for changes which are, at present, poorly defined.

Section 3.7 : Conclusions

- As previously observed, the kinetic order of iron removal does not fit to the formerly accepted second order model when the total concentration of dissolved iron is considered as available to react. The data gives a significantly better fit when the unreactive iron concentration is taken into account during kinetic analysis.
- Storage time has been shown to affect both the amount and rate of aggregation, but not the concentration of iron within the <0.45μm fraction. Indicating a re-ordering of the microcolloidal iron population during prolonged storage.

While the first order model is superior as a descriptor, the capacity of the second order model to provide an adequate, though generally less satisfactory descriptor in some cases means that there is not an unequivocal basis to argue that the mechanism is definitely orthokinetic under the conditions used. The results, however, do give some provisional support to this. Overall the findings emphasise that experimental conditions have an important influence on the conclusions from different studies (e.g. stirring conditions, sample storage etc.) and the work described in Chapter 5 was undertaken in this light.

Chapter Four

The Behaviour of Phosphate and its Relationship with Iron during Simulated Estuarine Mixing.

The total phosphorus content of natural waters consists of both particulate and dissolved forms, the latter being operationally defined as that fraction which passes through a 0.45μm nominal pore size filter. Due to the operational nature of this definition, the 'dissolved' phosphate fraction can contain significant amounts of high relative molecular mass colloidal organic phosphorus species as well as truly dissolved species. The dissolved inorganic phosphorus fraction is essentially comprised of orthophosphate, which is found to be partially associated with the colloidal fraction in some rivers (Sholkovitz, 1976; Wollast, 1982; Ormaza-Gonzalez, & Statham 1992; Zwolsman, 1994; Mayer & Jarrell, 1995) and some condensed phosphates. The dissolved organic fraction can consist of nucleic acids, phosphamides, phospholipids, phosphoproteins aminophosphanic acids pesticides and organic condensed phosphates.

In this study we are primarily concerned with the 'dissolved' inorganic phosphorus (DIP) fraction, basically comprised of orthophosphate. Orthophosphate can occur in river and sea waters as H_3PO_4, HPO_4^{2-}, or PO_4^{3-}, the exact chemical species being dependent upon the pH of the water. In sea waters the natural pH is close to 8 and the predominant species found is HPO_4^{2-}. In general discussion we will refer to the phosphate ion - PO_4^{3-}.

Levels of DIP in river water have increased over recent years with the main source being direct discharges from sewage works, the majority in the phosphate fraction, derived from washing powders and detergents. DIP is one of the major nutrients utilised by phytoplankton and seasonal biological removal of dissolved phosphate, related to phytoplankton dynamics, has been reported in some estuaries (e.g. Sharp *et al.*, 1982). It is an essential nutrient for the growth of both macroalgae and phytoplankton, and greatly increased levels can contribute to eutrophication. Phytoplankton biomass accumulates, resulting in high sedimentation rates of organic material and subsequent oxygen depletion during decomposition, with eutrophication of the water column occurring as a result (Malone *et al.,* 1986; Lebo & Sharp, 1993). Phytoplankton usually satisfy their phosphorus requirements by direct assimilation of orthophosphate, and its subsequent conversion to organic phosphorus compounds proceeds at all times. At phosphate concentrations above 10μg P l^{-1}, the rate of growth of many species is independent of the concentration, however as the concentration drops below the critical level cell division becomes increasingly inhibited and photosynthesis ceases. It is clear that nitrogen is not always the limiting nutrient in the marine environment with a great deal of controversy still existing over which nutrients limit primary production on a temporal and spatial scale. The Redfield ratio, indicating the rate of nutrient uptake from an aquatic system by organisms, is of tremendous use in helping to predict the limiting nutrient in a system. The average uptake of Carbon : Nitrogen : Phosphorus, as determined by Redfield (1958), is 106 : 16 : 1. This indicates the overall required nutrient ratio for the occurrence of primary production in open ocean waters, any move away from this ratio indicates the potential limiting nutrient. In a real system the situation is complicated by, amongst other things, short term local regeneration and the use of organic nutrients by phytoplankton. A more detailed discussion of growth limiting nutrients is given in Williams (1996).

The proportion of phosphate passing through an estuary to the open ocean is dependent on the phosphate reactivity within the estuary. Phosphate has been shown to have a complex chemistry within the estuarine environment (Liss, 1976; Aston, 1980; Smith & Longmore, 1980; Fox *et.al.,* 1986; Fox, 1990), and the processes which govern DIP levels in natural waters have not been clearly elucidated - despite the importance of phosphorus in the global biosphere. Measurements of dissolved phosphate within estuaries have shown wide variations in behaviour, exhibiting conservative behaviour, non-conservative behaviour, both addition and removal and also constant phosphate concentration over the whole estuary.

Where phosphate concentrations at intermediate salinities are those expected from dilution of river waters phosphate is exhibiting conservative behaviour. Deviations from the theoretical dilution line are indicative of non-conservative behaviour, showing either addition or removal. Conservative behaviour of dissolved phosphate was observed in the Dee and Don estuaries, Scotland (Balls, 1994). In rapidly flushed estuaries, e.g. the Dee and Don estuaries, in which the effects of particle / water interactions are minimal simple mixing behaviour will dominate.

Ormaza-Gonzalez & Statham (1991) studied the various fractions of phosphorus in the Beaulieu and Itchen estuaries and at tidal stations in the Thames and Humber. Significant variation was observed between the estuaries, the Itchen had very high DIP concentrations (up to 55μmol l^{-1}) in the upper estuary (salinity of 0 to 10) due to sewage inputs and a gradual decrease from a salinity of 10 to coastal waters. In contrast the Beaulieu estuary had a low initial DIP concentration (~0.1μmol l^{-1}) which remained relatively constant throughout the estuary. The Thames and the Humber were found to be comparable with the Itchen and the Beaulieu respectively. The comparison of the behaviour of phosphate between estuaries is complicated by anthropogenic inputs into the estuary, e.g. from sewage treatment plants, and also from input from tributaries.

Removal of phosphate has been shown in field observations on a number of estuaries including the Tamar (Morris *et al.,* 1982), the Delaware (Lebo & Sharp, 1993), the Sepik (Fox, 1990), the Amazon (Fox, 1986) and Glen Burn and The Waters of Luce (Sholkovitz, 1976). In a number of these cases, Tamar, Sepik, Glen Burn and the Waters of Luce, the removal was observed in the low salinity region, where steep ionic strength gradients and changes in the pH and of the water, can exert a dramatic influence on the constituents of the river waters. The removal of phosphate at low salinity has also been reported in several laboratory studies (Liss, 1976); by precipitation with humics, (Sholkovitz, 1976), or by aggregation with iron-rich colloids (Bale & Morris, 1981). In the Tamar estuary, Bale & Morris, (1981) and Morris *et al.,* (1982) observed non-conservative behaviour of phosphate, concurrent with the extensive removal of dissolved iron. Sholkovitz (1976) showed in laboratory experiments using river waters from Glen Burn and the Waters of Luce that the salinity functionalities of iron, manganese, aluminium, phosphorus and humates were similar, with a particularly close association between those of iron and phosphate.

Addition of phosphate has also been observed some estuarine systems. Eastman & Church (1984) in a Delaware salt marsh creek, and Simpson *et al* ., (1975) in the Hudson observed significant increase in phosphate in the low salinity region whereas Smith & Longmore (1980) observed a significant increase in the dissolved phosphate concentration in the Yarra estuary at a the coastal end of the estuary in February and a slow gradual increase over the whole zone of mixing in June.

Other studies have highlighted estuaries in which the phosphate concentration has been shown to remain essentially constant throughout the whole of the estuarine region. Levels of phosphate, in the experiments of Fox (1989) using water from the Amazon, Delaware and Sepik river estuaries were seen to remain constant when suspensions of river / estuary sediments were diluted with distilled water or sea water. There appears in some systems to be a buffering process controlling concentrations of phosphate within estuarine waters involving reversible solid phase sorption of phosphate onto mineral particles (Steffansson & Richards, 1963; Butler & Tibbits, 1972; Liss, 1976). Phosphates have been shown to be desorbed from estuarine sediments when mixed with waters of a lower phosphate concentration, including de-ionised water, (Pomeroy *et al.,* 1965; Butler & Tibbits, 1972; Upchurch *et al.,* 1974). Upchurch *et al.* 1974 suggested that phosphate is held in suspended sediments by the formation of an iron-phosphorus complex of limited stability. It was also shown that dissolved (colloidal) iron, can be stabilised by addition of phosphate by Cameron & Liss (1984). Jones *et al.* (1993) and Shaw (in press) showed that dissolved iron and phosphate in epilimnetic lake waters moved to fractions of a greater apparent molecular size in the presence of dissolved humic substances whilst no transformation occurred in clear waters. Jones *et al.* (1993) also showed that when phosphate was added to suspensions of varying compositions, the fraction of phosphate retained by a 0.2μm nominal pore size filter was dependent on pH, salinity and the concentrations of iron oxyhydroxide and dissolved humic substances.

Phosphate is chemically associated with iron and aluminium hydroxides in sediments (Williams *et al.,* 1967; 1970; 1976; Shukla *et al.,* 1971; Kuo & Lotse 1974 and Ku *et al.* 1978). Uptake by soils and iron minerals is well documented and generally characterised by adsorption isotherms (Parfitt *et al.,* 1975; Yates & Healey, 1975; Lijkema, 1980; Crosby *et al.,* 1983; 1984). Although these isotherms are purely empirical, they can emphasise the influence of suspended particles on the concentration of dissolved phosphate.

Work has been carried out on the inter-relationship between dissolved iron and phosphate, looking at the capacity for phosphate to bind to iron (Lijklema, 1980; Crosby *et al.,* 1984; Hawke , 1989) and the effects of estuarine constituents on observed behaviour (Carpenter & Smith, 1984). Bale & Morris, (1981) found that a significant proportion of the phosphate in Tamar river was found to be in a colloidal state, with 20.6 % of the phosphate passing through a 5.0μm filter retained by a 0.45μm filter and 46.3 % by a 0.1μm filter. Removal of these phosphate-containing colloids would be expected to proceed in a manner analogous with that observed for iron, explaining the observed losses in the low salinity region. The removal of phosphate within an estuarine simulation was shown to be temperature dependent however, which suggests that chemisorption of phosphate was also involved in the observed estuarine removal. The possibility of chemisorption of phosphate by estuarine particles has previously been reported by Carrit & Goodgal (1954), Burns & Salomon (1969) and Chen *et al.* (1973). These studies, whilst providing possible mechanisms for the interaction of phosphate and iron, have not looked specifically at their relative behaviour during estuarine mixing.

In some of the studies discussed removal of phosphate has been observed concurrently with extensive removal of microcolloidal iron. As emphasised by Bale & Morris (1981) it is difficult, because of the highly variable and dynamic nature of the estuarine system, to come to detailed conclusions on the processes affecting phosphate from field data.

Buffle *et al.* (1989) characterised physical and chemical properties of iron oxyhydroxide colloidal particles from the redox transition boundary layer in a eutrophic lake (Lake Bret, Switzerland). The particles were found to lie within the size range 0.04 to 0.4 μm, with the lower limit determined by experimental conditions. Larger particles were observed, but were found to consist of loose aggregates of smaller iron rich particles. Iron in the particles was equally divided between the Fe(II) and Fe(III) and the phosphorus in the particles was present as phosphate. It was found that a well defined chemical entity was formed at the redox interface in the water column composed predominantly of iron(II), iron(III), phosphate and calcium, as well as hydroxide ions. A ratio of phosphate to total iron, of 0.22 was observed consistently between August 1986 and October 1987, with no noticeable seasonal changes. In the oxic epilimnetic layer of lake waters there was some variation in the ratio, believed to be related to phosphate assimilation by organisms.

In estuarine systems with iron rich river inputs, most of the iron is microcolloidal. However it is expected that, while some phosphate may be associated with microcolloids (Buffle *et al.*, 1989), a significant part will be in true solution. Mayer & Jarrell (1995) found that in waters from the Tualatin River Basin, that between 0 and 48% of the total phosphorus was within the colloidal fraction, with the remainder in the truly dissolved phase and evidence from this work, section 4.2.2, demonstrated that for the Tamar River, a significant proportion of the phosphate (20-30%) is within the particulate / colloidal fraction. Further work on the characterisation of colloidal and particulate phosphorus was carried out by Persson (1984). The microcolloidal fraction can potentially be destabilised and aggregated, the truly dissolved fraction can only be removed on addition of salt to a filtered sample if the phosphate is adsorbed onto the products of aggregation.

The laboratory experiments undertaken to study the kinetics of aggregation of microcolloidal iron under conditions simulating estuarine mixing, as described in chapter 3, afforded an opportunity to examine the behaviour of phosphate in relation to that of iron in 0.45μm filtered river water. Moreover the experiments simulated mixing in the Tamar system in which field studies of the behaviour of both iron and phosphate have been made. Thus during the course of these experiments continuous measurements of the concentration of phosphate were carried out, in parallel with the determination of dissolved iron. The kinetics of the observed removal of phosphate have been examined using the modified first and second order models applied to the iron data as described in section 3.4. An examination of the size fractionation of iron and phosphate within Tamar river water was also carried out.

The overall objective of this part of the work was to obtain quantitative information on the extent and removal of phosphate on addition of calcium to river water at concentrations representative of those encountered within the range of salinities in estuaries. This information was utilised with the objective of obtaining a better understanding of the relationships between removal of iron rich colloids and the behaviour of phosphate, potentially at the mechanistic level.

4.1 Experimental Methods

4.1.1 Experimental methodology

The mixing experiments were carried out using the basic method outlined by Duffy (1985). A 4l sample of river water, from the zero salinity fresh water region of the Tamar river, was placed into a polyethylene mixing tank. The water was circulated by use of a centrifugal immersion pump. Connected to this pump was an on line perspex tangential filter block - housing an acid washed 0.45μm membrane filter (Morris *et al.,* 1978), through which water was pumped to two separate channels for the colorimetric determination of dissolved iron and inorganic phosphate. The destabilisation process was initiated, in these experiments, by the addition of calcium ions in the form of calcium chloride. The concentrations of calcium ions added to the mixing chamber, in a 10 ml aliquot, were calculated to give an overall concentration within the mixing tank approximate to those concentrations found over the full range of salinities experienced during estuarine mixing, from zero salt addition at fresh water end to a salinity approximately 35 at the open sea. The concentrations of both iron and phosphate were measured continuously for 900 s, after which time the reaction was considered as be essentially complete. Sub- samples from each of the mixing experiments were collected after 24 hours, filtered at 0.45μm and analysed.

To facilitate comparison between the individual experiments, the results were analysed in the form of a percentage of their initial concentration in the <0.45μm fraction. This treatment of the data in terms of a percent also allows the data on dissolved iron removal to be more readily correlated with that for phosphate.

The distribution of iron and phosphate within Tamar River water, in the < 0.1 to 8.0μm size range, was also investigated. A series of acid washed polycarbonate Nuclepore filters, pore size 8.0, 5.0, 3.0, 2.0, 1.0, 0.8, 0.45, 0.4, 0.2 and 0.1μm, were used to filter sub samples of Tamar River water, with the resulting filtrate being analysed for iron and phosphate

4.1.2 Sample collection

The water samples were all collected from a single site - 4 miles upstream of the Gunnislake Weir at Latchley. The sampling conditions are more fully described in section 2.1

4.1.3 Determination of phosphate

Phosphate was determined using the phosphomolybdenum blue method as described by Chan & Riley (1966) for a continuous flow method. A baseline reading was established with distilled water and linearity of response was tested both before and after experimental batches with a set of standards in the range 0-4μmol l^{-1}, for phosphate. The river water was analysed for 2-3 minutes in order to achieve a stable reference for the initial concentration of dissolved inorganic phosphate. The analysis was carried out concurrently with that of iron, using automated colorimetric systems for the determination of the two species in parallel.

4.1.4 Kinetic analysis

The data collected from the experimental runs for phosphate was examined in terms of fit to the following equations which describe the modified first and second order kinetic models, as described in fuller detail in section 3.4.

$$C_t = C_f + e^{-k_1{}'t}\left(Co - C_f\right)$$

for first order, and

$$C_t = \frac{k_2 t\left(C_o . C_f - C_f^{\,2}\right) + C_o}{1 + k_2 t.\left(C_o - C_f\right)}$$

for second order.

k_1 = first order rate constant.
k_2 = second order rate constant.
C_o = initial dissolved phosphate concentration.
C_t = dissolved phosphate concentration at time, t.
C_f= unreactive iron concentration.

Section 4.2 : Behaviour of Phosphate During Simulated Estuarine Mixing, Using Calcium Ions.

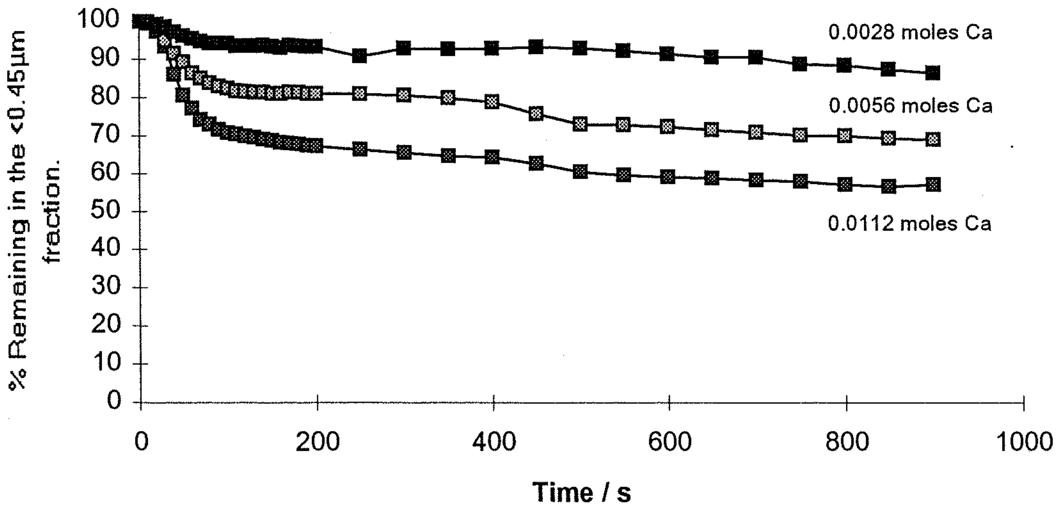
Changes in the concentration of phosphate were initiated simultaneously with those of iron by the addition of varying amounts of calcium chloride to water from the Tamar river. The concentration of the calcium chloride was varied, from 0.0014 to 0.0112 mol l^{-1} of Ca^{2+}, to represent those corresponding to salinities within the range in the zone of estuarine mixing. The waters used in the suite of experiments were all collected from a single source on the Tamar river, at Latchley. The experiments were carried out over a period of months and temporal variations in the initial concentrations of dissolved phosphate were observed. Variation in the initial concentrations of iron and phosphate was observed with iron concentrations ranging from 10.6 to 21.5 μ mol l^{-1}, and those for phosphate ranging from 0.84 to 1.60 μmol l^{-1} during the months October 1993 and May 1994. The highest values were recorded in January and lowest in May. The highest initial concentrations of iron and phosphate were observed to coincide over the course of the experiments. Treatment of the data in terms of a percentage of the initial concentration in the 0.45μm fraction allowed for an easy graphical comparison of the data from the individual experimental runs. The treatment of the data in percentage terms also allowed the data on phosphate behaviour to be more readily correlated with that obtained for iron - see Chapter 3 for full description of the behaviour of iron in the 0.45μm fraction.

4.2.1 Basic Phosphate Behaviour

The removal of phosphate commences essentially instantaneously on addition of the calcium cations with an initial rapid rate of decrease in the dissolved phosphate concentration. The rate of removal of phosphate from the <0.45μm fraction decreases with time after the initial rapid removal, and a gradual levelling out of the dissolved phosphate fraction is evident over the course of the experiments. The reaction is essentially complete within approximately ten minutes following the addition of the cation, after which time the phosphate concentration remains reasonably constant with only minor changes. In all of the experiments, it was evident that there remained a fraction of phosphate which was not susceptible to removal from the <0.45 μm fraction after fifteen minutes. Analysis of sub-samples from the experiments after 24 hours showed a further small decrease in the phosphate concentration from the value at the end of the experiments (t=0.25 hours). In the majority of cases the value at t=24 hours was smaller than that measured at t=0.25 hours, though the decrease was small in comparison to the decrease observed during the normal course of the experiments. In all of the experiments final phosphate concentration was observed to reach a plateau at a level significantly above zero. In control experiments, in which no cation was added to the mixing chamber, the decrease in the phosphate concentration over the experimental period was found to be negligible.

The behaviour of phosphate during the simulated estuarine mixing is illustrated in Figure 4.1, showing the effect of the addition calcium ions at three experimental concentrations. The three removal profiles all show the same basic characteristics, with initial rate of decrease of phosphate, and the overall concentration of phosphate removal at the end of the experiment varying with the calcium ion concentration. In a small number of the experiments an increase in the phosphate concentration was observed after the initial decrease in phosphate concentration during the simulated estuarine mixing. The results of the experiments are summarised in the tables 4.1 to 4.4.

Fig. 4.1 - Changes in the concentration of inorganic phosphate, with time, following the addition of calcium chloride to Tamar river water.



Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	r2	1st Order Rate Constant (*10-2) s^{-1}	Storage Time (hr)
0.0112	0.96	0.45	0.51	53.49	0.979	1.32	3.75
0.0112	1.02	0.44	0.57	56.39	0.964	1.43	6.17
0.0112	1.02	0.53	0.49	47.84	0.972	1.36	7.00
0.0112	1.06	0.57	0.49	46.36	0.976	1.36	13.33
0.0112	0.97	0.54	0.43	44.42	0.958	1.44	16.33
0.0112	0.96	0.52	0.44	45.75	0.979	1.46	18.17
0.0112	1.01	0.56	0.45	44.30	0.955	1.48	24.67
0.0112	0.93	0.53	0.40	42.75	0.940	1.58	28.67
0.0112	1.03	0.68	0.36	34.53	0.951	1.79	33.67
0.0112	0.97	0.60	0.38	38.79	0.947	1.55	44.83
0.0056	0.98	0.56	0.42	42.93	0.913	0.65	5.50
0.0056	0.99	0.58	0.41	41.05	0.917	0.66	8.58
0.0056	0.98	0.61	0.37	37.40	0.933	0.73	14.17
0.0056	0.93	0.59	0.34	36.63	0.982	0.82	16.67
0.0056	1.14	0.70	0.44	38.48	0.959	0.88	19.67
0.0056	1.07	0.70	0.37	34.64	0.959	0.84	21.67
0.0056	1.10	0.78	0.31	28.56	0.938	0.82	30.50
0.0056	0.99	0.76	0.23	23.26	0.932	0.94	35.83
0.0056	0.90	0.68	0.23	25.14	0.993	0.99	47.50
0.0028	1.07	0.77	0.31	28.50	0.957	0.41	8.83
0.0028	0.99	0.72	0.27	27.49	0.940	0.48	12.00
0.0028	1.03	0.87	0.16	15.73	0.941	0.43	15.00
0.0028	1.02	0.92	0.11	10.29	0.987	0.48	23.67
0.0028	0.87	0.78	0.10	11.23	0.934	0.51	26.67
0.0028	0.90	0.84	0.07	7.43	0.989	0.53	40.50
0.0028	0.95	0.87	0.08	8.11	0.949	0.58	50.33

Table 4.1 Influence of the addition of calcium chloride on the first order rate constant and extent of removal of phosphate from Tamar River water - Batch one.

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	r2	1st Order Rate Constant (*10-2) s^{-1}	Storage Time (hr)
0.0056	1.41	0.71	0.70	49.50	0.959	0.58	3.00
0.0056	1.50	0.78	0.72	47.80	0.966	0.57	4.00
0.0056	1.45	0.76	0.69	47.76	0.981	0.64	6.00
0.0056	1.60	0.87	0.73	45.71	0.952	0.62	7.17
0.0056	1.47	0.83	0.63	43.28	0.997	0.59	10.00
0.0056	1.42	0.87	0.56	39.03	0.995	0.63	13.67
0.0056	1.20	0.77	0.43	35.79	0.906	0.67	15.67
0.0056	1.12	0.79	0.34	29.80	0.899	0.66	17.00
0.0056	1.05	0.74	0.31	29.53	0.986	0.71	21.33
0.0056	1.09	0.80	0.29	26.77	0.983	0.74	23.33
0.0056	1.10	0.84	0.26	23.41	0.942	0.73	25.83
0.0056	0.97	0.74	0.23	23.46	0.985	0.76	26.83
0.0056	1.01	0.86	0.15	14.82	0.989	0.85	35.50
0.0056	0.97	0.87	0.10	10.71	0.903	0.88	40.08
0.0056	0.92	0.81	0.11	11.71	0.988	0.92	46.92
0.0056	0.84	0.76	0.08	9.38	0.966	0.89	48.17
0.0056	0.90	0.80	0.10	11.17	0.968	0.96	48.58
0.0056	0.84	0.78	0.06	7.36	0.976	0.95	51.50
0.0056	0.91	0.87	0.04	4.06	0.909	0.97	53.00

Table 4.2 Influence of the addition of calcium chloride on the first order rate constant and extent of removal of phosphate from Tamar River water - Batch two.

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	r2	1st Order Rate Constant (*10-2) s^{-1}	Storage Time (hr)
0.0056	1.06	0.64	0.42	39.75	0.919	0.97	1.50
0.0056	1.13	0.66	0.47	41.74	0.873	0.96	2.08
0.0056	1.00	0.66	0.35	34.50	0.980	0.89	2.50
0.0056	1.14	0.68	0.46	40.28	0.891	0.94	3.00
0.0056	1.04	0.62	0.41	39.71	0.942	0.96	3.50
0.0056	1.14	0.70	0.44	38.46	0.882	0.92	4.25
0.0028	1.03	0.80	0.23	22.44	0.945	0.57	4.67
0.0028	0.96	0.75	0.21	21.63	0.963	0.54	5.17
0.0028	1.02	0.78	0.24	23.21	0.972	0.52	5.67
0.0028	0.95	0.76	0.20	20.61	0.977	0.54	6.33
0.0028	1.03	0.80	0.23	21.87	0.935	0.49	6.83
0.0028	1.12	0.90	0.22	19.71	0.966	0.48	7.50
0.0028	1.02	0.82	0.20	19.53	0.946	0.54	7.92
0.0028	0.98	0.78	0.20	20.47	0.954	0.58	8.42
0.0028	0.96	0.78	0.18	18.72	0.983	0.56	9.33
0.0014	0.99	0.97	0.02	2.23	0.985	0.21	9.83
0.0014	0.90	0.85	0.04	4.79	0.954	0.25	10.17
0.0014	0.95	0.89	0.06	6.74	0.96	0.19	10.58
0.0028	1.25	1.07	0.18	14.39	0.963	0.58	11.08
0.0056	1.21	0.74	0.47	38.74	0.987	0.86	11.50

Table 4.3 Influence of the addition of calcium chloride on the first order rate constant and extent of removal of phosphate from Tamar River water - Batch three.

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	r2	1st Order Rate Constant (*10-2) s^{-1}	Storage Time (hr)
0.0014	1.16	1.06	0.10	8.72	0.919	0.26	1.50
0.0014	1.14	0.97	0.16	14.35	0.950	0.27	2.08
0.0014	0.96	0.84	0.12	12.54	0.942	0.33	2.50
0.0014	1.03	0.95	0.08	8.07	0.932	0.28	3.00
0.0014	1.05	0.97	0.08	7.98	0.882	0.3	3.50
0.0028	0.99	0.77	0.22	22.37	0.939	0.89	4.25
0.0028	1.00	0.78	0.22	21.76	0.924	0.84	4.67
0.0028	1.15	0.93	0.23	19.67	0.976	0.86	5.17
0.0028	1.02	0.77	0.25	24.61	0.935	0.88	5.67
0.0028	0.97	0.77	0.20	20.79	0.974	0.83	6.33
0.0028	1.02	0.76	0.26	25.73	0.972	0.9	6.83
0.0028	0.98	0.77	0.21	21.36	0.953	0.87	7.50
0.0056	1.10	0.74	0.37	33.21	0.884	1.36	7.92
0.0056	0.97	0.61	0.36	37.45	0.936	1.42	8.42
0.0056	1.03	0.65	0.37	36.38	0.977	1.53	9.33
0.0056	1.11	0.71	0.40	35.79	0.956	1.35	9.83
0.0056	0.99	0.68	0.32	31.79	0.978	1.48	10.17
0.0056	0.98	0.67	0.31	31.47	0.901	1.39	10.58
0.0056	1.04	0.71	0.33	31.85	0.953	1.52	11.08
0.0056	1.09	0.71	0.38	34.83	0.924	1.55	11.50

Table 4.4 Influence of the addition of calcium chloride on the first order rate constant and extent of removal of phosphate from Tamar River water - Batch four.

The amount of phosphate resisting destabilisation was seen to decrease with increasing calcium ion concentration, as was observed for iron in chapter three. The amount of dissolved iron removed during the simulated estuarine mixing experiments, both as a percentage of the original concentration and as an actual concentration, was much greater than the corresponding removal of dissolved phosphate (see Figures 4.2 and 4.3); the difference between the percentages of iron and phosphate resisting removal remained reasonably constant at the calcium ion concentrations studied. The decrease in percentage removal per unit increase in calcium molarity was similar for both iron and phosphate, as illustrated in Figure 4.2, with a gradient of $8.83*10^3$ for phosphate compared with $8.72*10^3$ for iron. Over the range of calcium ion concentrations studied, the percentage of iron removed at the end of the experiments was consistently 40-50 % greater than that observed for phosphate. Thus at any given calcium ion concentration there is a significantly larger proportion of dissolved iron susceptible to removal. This comparability between the removal profiles of iron and phosphate implies a constant ratio of removal of iron and phosphate from the <0.45μm fraction during the simulated estuarine mixing experiments. This could have wide ranging implications with respect to the relationship between the two species, and their subsequent behaviour during estuarine mixing.

When experiments carried out at an equivalent calcium ion concentration were looked at comparatively, although the removal profiles all show the same basis features (as described above), some variability was noted both between runs using the same river water batch, and more markedly with waters from different batches.

Figures 4.4 a) and b) show the differences in observed phosphate removal at a given calcium ion concentration between batches and within a batch respectively. It is evident that greater variability was observed in Fig. 4.4 a), showing the removal profiles 1k and 2f at a calcium ion concentration of 0.0056 mol l^{-1}, than was observed between two profiles from within a single batch of river water, Fig. 4.4 b) showing profiles 2f and 2g. The differences in behaviour in a single batch of river water are thought to be due to random experimental variations occurring

Fig.4.2 - The influence of ionic strength on the % of dissolved iron and phosphate remaining 900 seconds after addition of calcium chloride to Tamar river water.

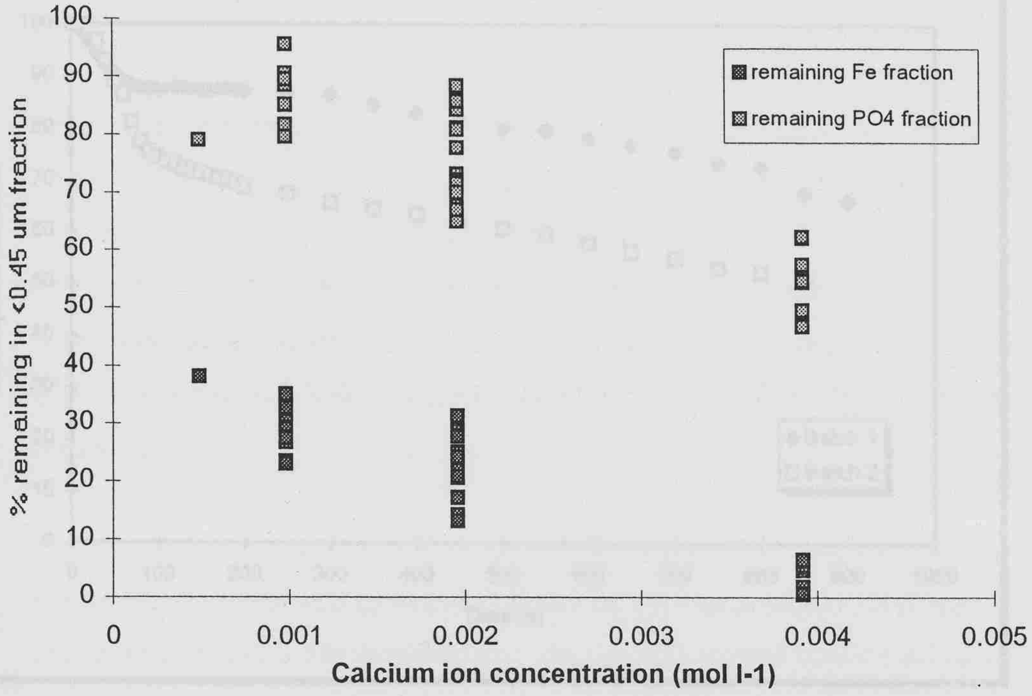


Fig. 4.3 - Changes in the concentration of dissolved iron and phosphate, with time, following addition of calcium chloride to Tamar River water. (0.0056 mol l-1 calcium)

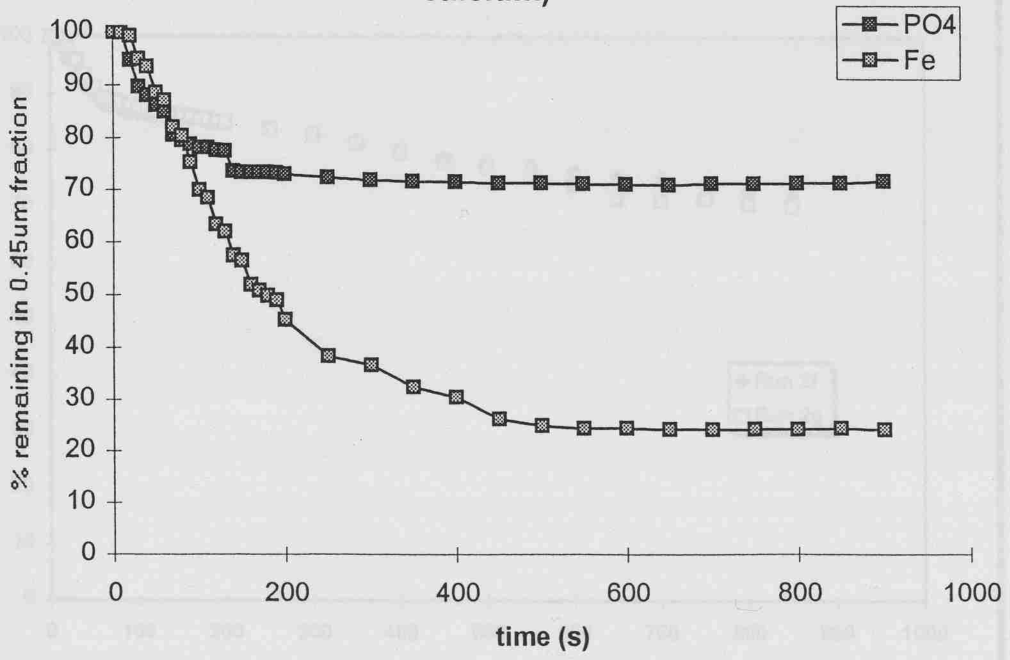


Fig. 4.4 (a) Variability in observed removal between river water batches (calcium ion concentration 0.0056 mol l-1)

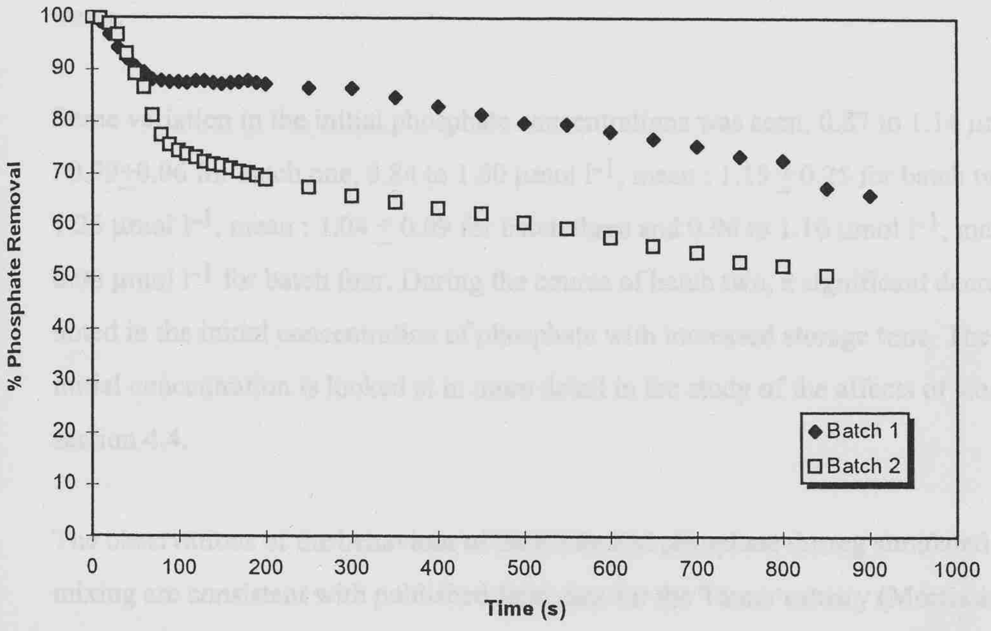
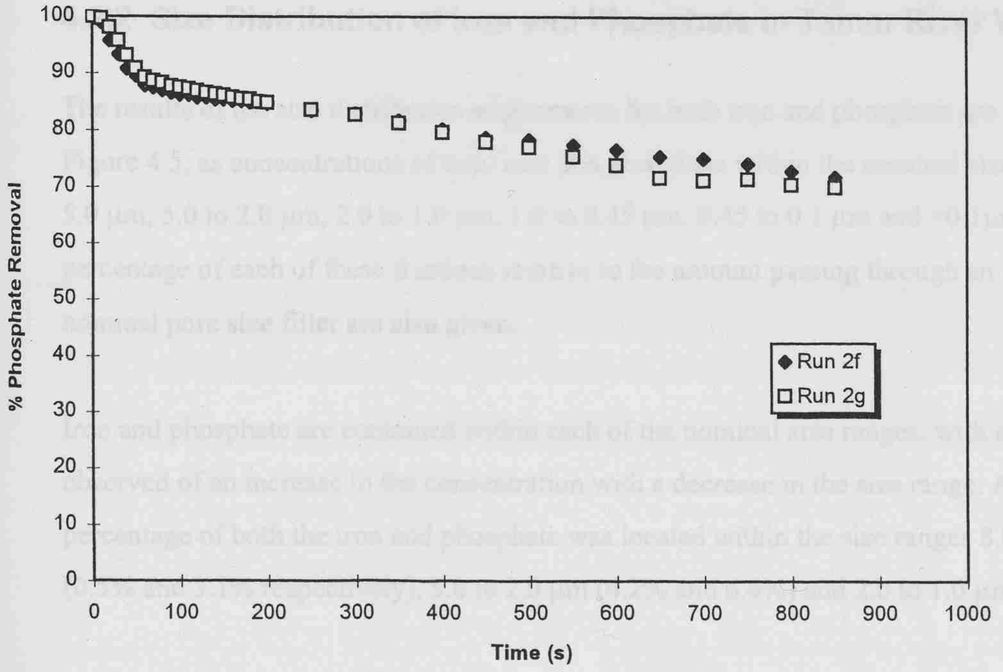


Fig. 4.4 (b) Variability in observed removal between experimental runs using a single river water batch (calcium ion concentration 0.0056 mol l-1)



with a given homogeneous sample, whereas differences between batches are thought to represent temporal variations in the phosphate concentration and its fractionation within river water.

Some variation in the initial phosphate concentrations was seen; 0.87 to 1.14 μmol l^{-1}, mean : 0.99±0.06 for batch one, 0.84 to 1.60 μmol l^{-1}, mean : 1.15 ± 0.25 for batch two, 0.90 to 1.25 μmol l^{-1}, mean : 1.04 ± 0.09 for batch three and 0.96 to 1.16 μmol l^{-1}, mean : 1.04 ± 0.06 μmol l^{-1} for batch four. During the course of batch two, a significant decrease was noted in the initial concentration of phosphate with increased storage time. The variation in initial concentration is looked at in more detail in the study of the affects of storage time, section 4.4.

The observations of the behaviour of both iron and phosphate during simulated estuarine mixing are consistent with published field data for the Tamar estuary (Morris *et al.*, 1982; Bale & Morris, 1981). The dissolved iron concentration showed strong non-conservative behaviour, decreasing from approximately 20 μmol l^{-1} in river water to below the limits of detection at the seaward end of the estuarine zone and a smaller decrease in the phosphate concentration occurring in the low salinity region of the estuary, with measurable concentrations still persisting at the seaward end.

4.2.2 Size Distribution of Iron and Phosphate in Tamar River Water

The results of the size distribution experiments for both iron and phosphate are presented in Figure 4.5, as concentrations of total iron and phosphate within the nominal size ranges 8.0 to 5.0 μm, 5.0 to 2.0 μm, 2.0 to 1.0 μm, 1.0 to 0.45 μm, 0.45 to 0.1 μm and <0.1μm. The percentage of each of these fractions relative to the amount passing through an 8.0 μm nominal pore size filter are also given.

Iron and phosphate are contained within each of the nominal size ranges, with a general trend observed of an increase in the concentration with a decrease in the size range. A small percentage of both the iron and phosphate was located within the size ranges 8.0 to 5.0 μm - (0.5% and 3.1% respectively), 5.0 to 2.0 μm (4.2% and 6.4%) and 2.0 to 1.0 μm (2.5% and

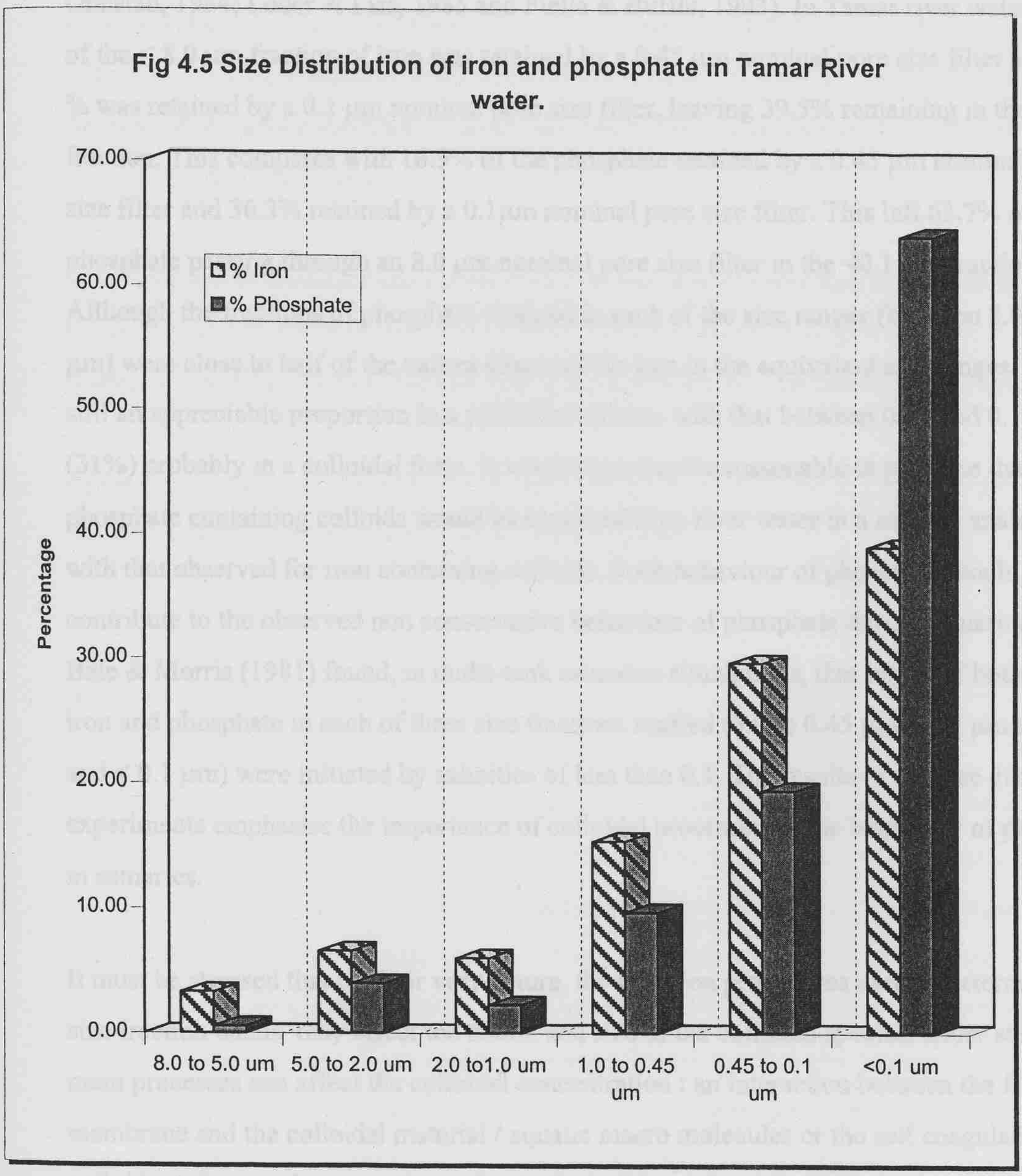


Fig 4.5 Size Distribution of iron and phosphate in Tamar River water.

5.9%), with the majority within the <1.0 μm fraction of Tamar river water. Iron in the 'dissolved' fraction is known to be consist of iron containing colloids, stabilised by its association with organic material (Hunter & Liss, 1979; Moore *et al.,* 1979; Tipping & Ohnstad, 1984; Loder & Liss, 1985 and Fiella & Buffle, 1993). In Tamar river water, 30.7% of the < 8.0 μm fraction of iron was retained by a 0.45 μm nominal pore size filter and 60.5 % was retained by a 0.1 μm nominal pore size filter, leaving 39.5% remaining in the < 0.1μm fraction. This compares with 16.9% of the phosphate retained by a 0.45 μm nominal pore size filter and 36.3% retained by a 0.1μm nominal pore size filter. This left 63.7% of the phosphate passing through an 8.0 μm nominal pore size filter in the <0.1 μm fraction. Although the fractions of phosphate retained in each of the size ranges (between 8.0 and 0.1 μm) were close to half of the values observed for iron in the equivalent size ranges, there was still an appreciable proportion in a particulate phase, with that between 0.45 and 0.1μm (31%) probably in a colloidal form. It would therefore be reasonable to presume that the phosphate containing colloids would be removed from river water in a manner analogous with that observed for iron containing colloids. Such behaviour of phosphate would contribute to the observed non conservative behaviour of phosphate during estuarine mixing. Bale & Morris (1981) found, in multi-tank estuarine simulations, that losses of both dissolved iron and phosphate in each of three size fractions studied (5.0 to 0.45 μm, 0.45 μm to 0.1 μm and < 0.1 μm) were initiated by salinities of less than 0.1. The results of the size distribution experiments emphasise the importance of colloidal processes on the behaviour of phosphate in estuaries.

It must be stressed that by their very nature, the filtration procedures used to determine the size fraction bands may affect the nature and size of the colloidal species, under study. Two main processes can affect the colloidal concentration : an interaction between the filter membrane and the colloidal material / aquatic macro molecules or the self coagulation of colloids at the membrane surface - due to the build up of an increased concentration of colloidal material at the surface leading in turn to increased aggregation (Buffle & Leppard, 1995).

Section 4.3 : Kinetic Interpretation of the Phosphate Data

It has been shown (Duffy, 1985; this work Chapter 3) that for a meaningful kinetic analysis of the aggregation of microcolloidal iron it is necessary to take account of the fraction of the potentially available reactant which does not react under the experimental conditions. The fraction of phosphate resisting removal was greater than in the case of iron and a similar approach to the kinetic analysis was tested.

A comparison of modified and unmodified first and second order kinetic modelling of the experimental data for phosphate conclusively showed that the data gave a better fit to both models when the unreactive fraction was taken into account. The modified first and second order kinetic models both gave good fits to the experimental data for the majority of experimental batch. Correlation coefficients ranged between 0.884 to 0.997 for the first order model and 0.853 to 0.998 for the second order model.

4.3.1 First Order Kinetic Analysis

As shown above, data for phosphate removal gave a good fit to the modified first order kinetic rate equation. The values calculated for the first order rate constant ranged from 0.0021 to 0.0242 s^{-1} over the range of calcium ion concentrations used in the experiments. Figures 4.6 to 4.9 show the effects of calcium ion concentration on the calculated first order rate constant, over the course of all of the experiments. The first order rate constants exhibited a wide degree of variability at each of the calcium ion concentrations studied, both within experimental batches and also between them. The largest variability was observed between experiments carried out with different batches of river water e.g. the first order rate constant varied from 0.0037 to 0.0101 s^{-1} at a calcium ion concentration of 0.0028 mol l^{-1}.

For each of the experimental batches a distinct linear trend of an increase in first order rate constant corresponding to an increase in the calcium ion concentration was observed. The results are summarised in tables 4.1.to 4.4, which show the effects on calculated first order

Fig 4.6 Effect of calcium ion concentration on first order rate constant for phosphate removal (batch 1)

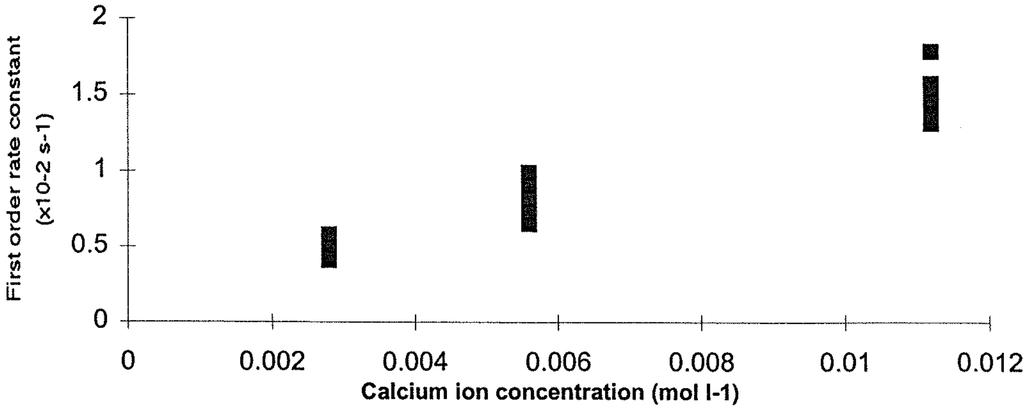


Fig 4.7 Effect of calcium ion concentration on first order rate constant for phosphate removal (batch 3)

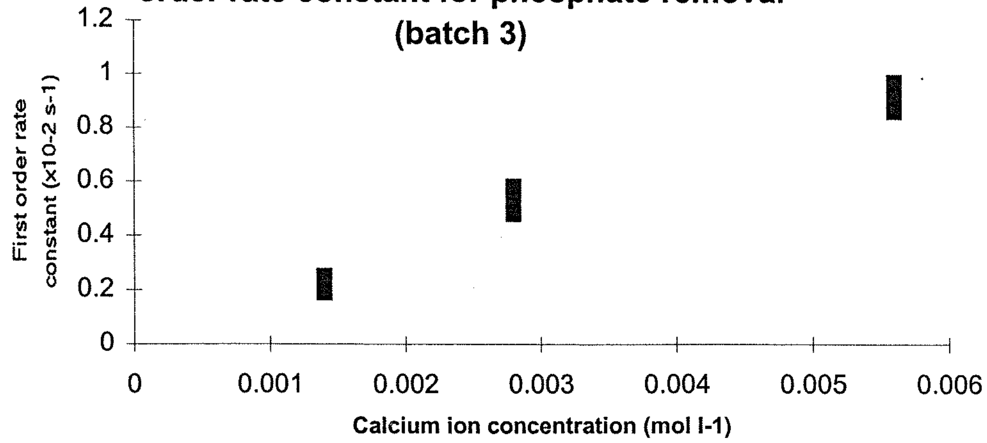
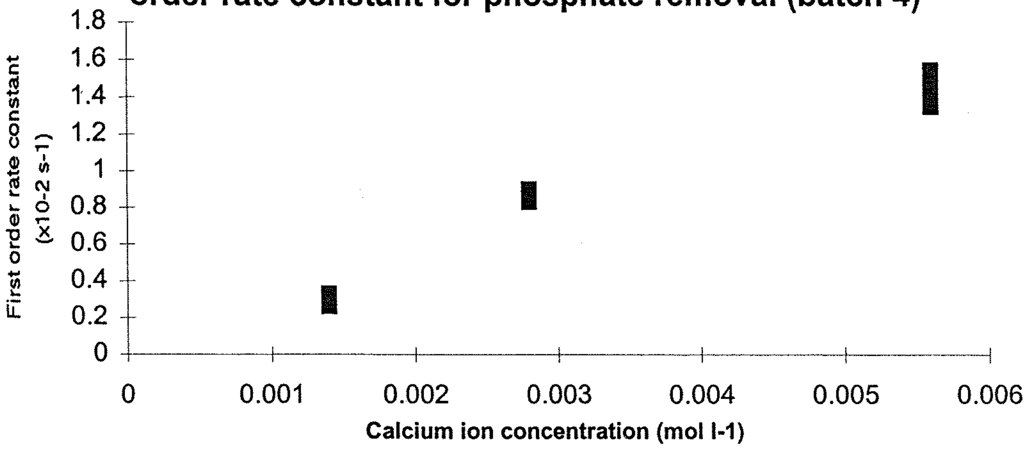


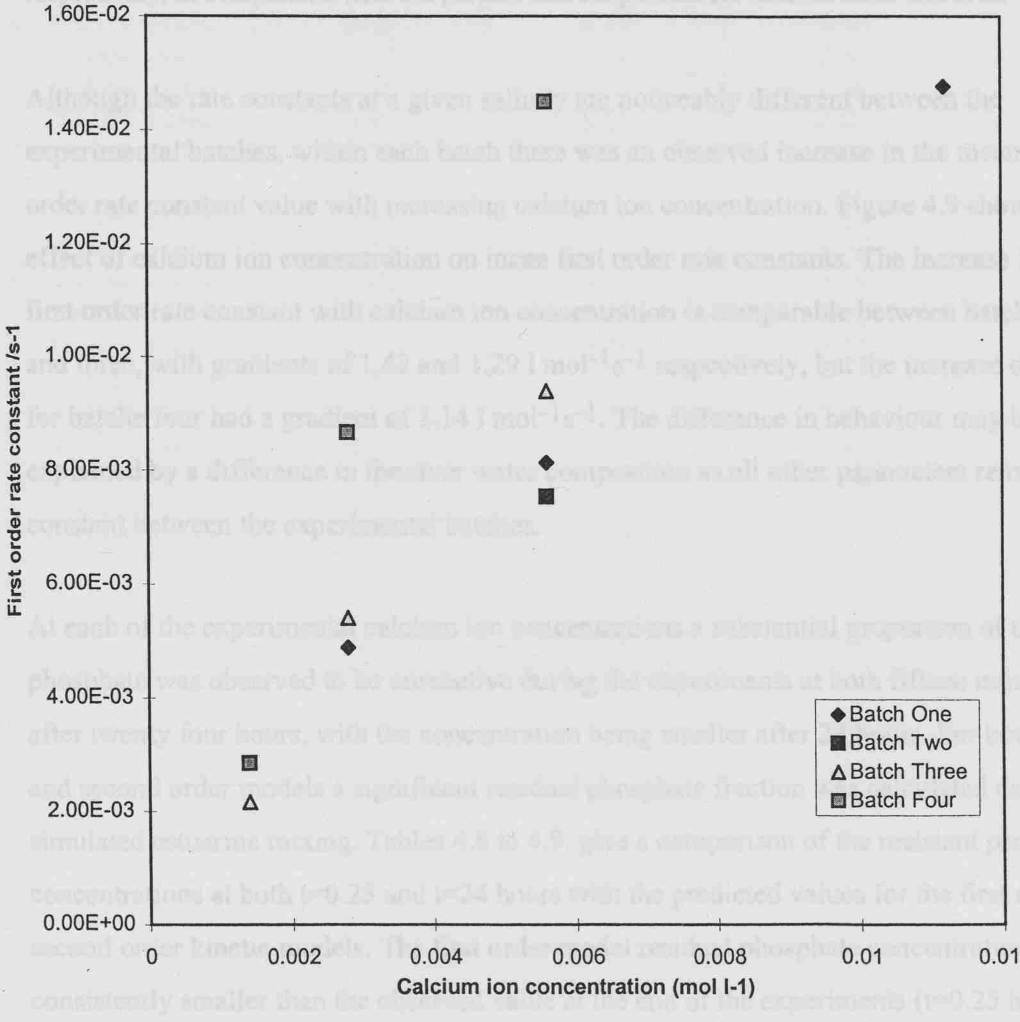
Fig 4.8 Effect of calcium ion concentration on first order rate constant for phosphate removal (batch 4)



	Calcium Ion Concentration	**First Order Rate Constant (s^{-1})**		**Standard Deviation**	**n**
		Range	Mean		
Batch ONE	0.0112	1.32 to 1.79 $*10^{-2}$	1.477 $*10^{-2}$	0.137 $*10^{-2}$	10
	0.0056	0.65 to 0.99 $*10^{-2}$	0.814 $*10^{-2}$	0.117 $*10^{-2}$	9
	0.0028	0.41 to 0.58 $*10^{-2}$	0.488 $*10^{-2}$	0.058 $*10^{-2}$	7
Batch TWO	0.0056	0.57 to 0.97 $*10^{-2}$	0.754 $*10^{-2}$	0.140 $*10^{-2}$	19
Batch THREE	0.0056	0.89 to 0.97 $*10^{-2}$	0.94 $*10^{-2}$	0.030 $*10^{-2}$	7
	0.0028	0.48 to 0.58 $*10^{-2}$	0.54 $*10^{-2}$	0.0349 $*10^{-2}$	10
	0.0014	0.19 to 0.25 $*10^{-2}$	0.216 $*10^{-2}$	0.035 $*10^{-2}$	3
	0.0056	1.35 to 1.55 $*10^{-2}$	1.45 $*10^{-2}$	0.080 $*10^{-2}$	8
Batch FOUR	0.0028	0.83 to 0.90 $*10^{-2}$	0.867 $*10^{-2}$	0.0256 $*10^{-2}$	7
	0.0014	0.26 to 0.33 $*10^{-2}$	0.285 $*10^{-2}$	0.031 $*10^{-2}$	5

Table 4.5 : Variation in first order rate constant for phosphate removal with calcium ion concentration both within and between experimental batches one to four.

Fig. 4.9 Change in mean first order rate constant for phosphate removal with calcium Ion concentration.



rate constant of changes in calcium ion concentration and storage time for each of the individual experimental runs. There was also significant variability between experimental runs using the same batch of river water. Table 4.5 illustrates the variability in first order rate constant at a given salinity, for each of the runs made. The highest relative standard deviations (RSD's) were observed for batches one and two, where storage time has previously been shown to exert an influence on the process of phosphate removal observed (see section 4.3.2). At a calcium ion concentration of 0.0056 mol l^{-1} the relative standard deviations for the experiments in batches one and two were 14.4 percent and 18.6 percent respectively, in comparison with 3.2 percent and 5.5 percent for batches three and four.

Although the rate constants at a given salinity are noticeably different between the experimental batches, within each batch there was an observed increase in the mean first order rate constant value with increasing calcium ion concentration. Figure 4.9 shows the effect of calcium ion concentration on mean first order rate constants. The increase in mean first order rate constant with calcium ion concentration is comparable between batches one and three, with gradients of 1.42 and 1.29 l $mol^{-1}s^{-1}$ respectively, but the increase observed for batche four had a gradient of 3.14 l $mol^{-1}s^{-1}$. The difference in behaviour may be explained by a difference in the river water composition as all other parameters remained constant between the experimental batches.

At each of the experimental calcium ion concentrations a substantial proportion of the phosphate was observed to be unreactive during the experiments at both fifteen minutes and after twenty four hours, with the concentration being smaller after 24 hours. For both the first and second order models a significant residual phosphate fraction was calculated during the simulated estuarine mixing. Tables 4.6 to 4.9. give a comparison of the resistant phosphate concentrations at both t=0.25 and t=24 hours with the predicted values for the first and second order kinetic models. The first order model residual phosphate concentrations were consistently smaller than the observed value at the end of the experiments (t=0.25 hours) and of a very similar magnitude to the values observed after twenty four hours.

Thus a first order mechanism for phosphate removal from the 0.45 μm fraction is consistent with the experimental results when an unreactive fraction is taken into account.

Calcium Ion Concentration	Measured Phosphate Concentration (μmol l^{-1})		Predicted phosphate Concentration (μmol l^{-1})	
(mol l^{-1})	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0112 moles	0.45	0.40	0.38	0.33
0.0112 moles	0.44	0.40	0.39	0.30
0.0112 moles	0.53	0.53	0.54	0.47
0.0112 moles	0.57	0.56	0.57	0.52
0.0112 moles	0.54	0.54	0.50	0.49
0.0112 moles	0.52	0.52	0.50	0.50
0.0112 moles	0.56	0.50	0.53	0.31
0.0112 moles	0.53	0.50	0.53	0.51
0.0112 moles	0.68	0.65	0.64	0.53
0.0112 moles	0.60	0.62	0.58	0.52
0.0056 moles	0.56	0.54	0.52	0.39
0.0056 moles	0.58	0.57	0.56	0.50
0.0056 moles	0.61	0.61	0.61	0.59
0.0056 moles	0.59	0.60	0.55	0.48
0.0056 moles	0.70	0.69	0.69	0.65
0.0056 moles	0.70	0.66	0.62	0.54
0.0056 moles	0.78	0.78	0.79	0.71
0.0056 moles	0.76	0.70	0.69	0.65
0.0056 moles	0.68	0.66	0.61	0.42
0.0028 moles	0.77	0.75	0.77	0.68
0.0028 moles	0.72	0.71	0.70	0.64
0.0028 moles	0.87	0.84	0.69	0.35
0.0028 moles	0.92	0.89	0.90	0.84
0.0028 moles	0.78	0.76	0.75	0.72
0.0028 moles	0.84	0.83	0.82	0.72
0.0028 moles	0.87	0.82	0.77	0.86

Table 4.6 : Comparison of the measured phosphate removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch one.

Calcium Ion Concentration (mol l^{-1})	Measured Phosphate Concentration (μmol l^{-1})		Predicted phosphate Concentration (μmol l^{-1})	
	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0056 moles	0.71	0.70	0.68	0.62
0.0056 moles	0.78	0.70	0.67	0.67
0.0056 moles	0.76	0.74	0.70	0.55
0.0056 moles	0.87	0.75	0.71	0.59
0.0056 moles	0.83	0.80	0.72	0.63
0.0056 moles	0.87	0.83	0.85	0.77
0.0056 moles	0.77	0.76	0.74	0.68
0.0056 moles	0.79	0.77	0.74	0.70
0.0056 moles	0.74	0.74	0.73	0.67
0.0056 moles	0.80	0.75	0.78	0.69
0.0056 moles	0.84	0.80	0.83	0.79
0.0056 moles	0.74	0.71	0.71	0.65
0.0056 moles	0.86	0.82	0.81	0.77
0.0056 moles	0.87	0.86	0.84	0.83
0.0056 moles	0.81	0.80	0.81	0.67
0.0056 moles	0.76	0.77	0.76	0.62
0.0056 moles	0.80	0.77	0.75	0.45
0.0056 moles	0.78	0.76	0.75	0.62
0.0056 moles	0.87	0.86	0.84	0.80

Table 4.7 : Comparison of the measured phosphate removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch two.

Calcium Ion Concentration	Measured Phosphate Concentration (μmol l^{-1})		Predicted phosphate Concentration (μmol l^{-1})	
(mol l^{-1})	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0056 moles	0.64	0.63	0.62	0.65
0.0056 moles	0.66	0.62	0.64	0.60
0.0056 moles	0.66	0.64	0.64	0.59
0.0056 moles	0.68	0.64	0.66	0.51
0.0056 moles	0.62	0.58	0.60	0.46
0.0056 moles	0.70	0.69	0.70	0.67
0.0028 moles	0.80	0.74	0.76	0.72
0.0028 moles	0.75	0.73	0.72	0.71
0.0028 moles	0.78	0.78	0.77	0.65
0.0028 moles	0.76	0.72	0.72	0.68
0.0028 moles	0.80	0.80	0.79	0.67
0.0028 moles	0.90	0.87	0.85	0.78
0.0028 moles	0.82	0.79	0.78	0.72
0.0028 moles	0.78	0.77	0.75	0.70
0.0028 moles	0.78	0.76	0.75	0.70
0.0014 moles	0.97	0.94	0.90	0.89
0.0014 moles	0.85	0.80	0.80	0.69
0.0014 moles	0.89	0.88	0.87	0.75
0.0028 moles	1.07	1.00	1.03	1.01
0.0056 moles	0.74	0.72	0.73	0.70

Table 4.8 : Comparison of the measured phosphate removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch three.

Calcium Ion Concentration	Measured Phosphate Concentration (μmol l^{-1})		Predicted phosphate Concentration (μmol l^{-1})	
(mol l^{-1})	t=0.25 hours	t=24 hours	First Order Model	Second Order Model
0.0014 moles	1.06	0.98	0.97	0.92
0.0014 moles	0.97	0.96	0.95	0.92
0.0014 moles	0.84	0.81	0.81	0.80
0.0014 moles	0.95	0.93	0.92	0.90
0.0014 moles	0.97	0.89	0.95	0.92
0.0028 moles	0.77	0.74	0.76	0.70
0.0028 moles	0.78	0.72	0.75	0.74
0.0028 moles	0.93	0.89	0.90	0.87
0.0028 moles	0.77	0.76	0.76	0.68
0.0028 moles	0.77	0.75	0.75	0.69
0.0028 moles	0.76	0.76	0.76	0.65
0.0028 moles	0.77	0.74	0.75	0.70
0.0056 moles	0.74	0.72	0.73	0.71
0.0056 moles	0.61	0.60	0.60	0.44
0.0056 moles	0.65	0.62	0.63	0.56
0.0056 moles	0.71	0.70	0.70	0.66
0.0056 moles	0.68	0.66	0.67	0.63
0.0056 moles	0.67	0.66	0.67	0.64
0.0056 moles	0.71	0.69	0.71	0.70
0.0056 moles	0.71	0.70	0.71	0.63

Table 4.9 : Comparison of the measured phosphate removal in simulated estuarine mixing experiments, fifteen minutes and twenty four hours after addition of calcium chloride, with the predicted first and second order model residual values - Batch four.

As was observed for the first order treatment of the iron removal data, the values for the first order rate constant at 0.0056 mol l^{-1} of Ca^{2+} increased in the order : batch 1 < batch 2 < batch 3 < batch 4.

4.3.2 Second Order Kinetic Analysis

The second order rate constants showed a wide variation, from 0.0032 to 0.0542 $mol^{-1} l\ s^{-1}$ over the range of calcium ion concentrations used in the estuarine simulations. Figures 4.10 to 4.12 show the effect of calcium ion concentration on the calculated second order rate constant. It is evident that the values for the second order rate constants showed a much greater spread at a given calcium ion concentration than those calculated using the modified first order model.

The results of the second order modelling of the phosphate removal data are summarised in tables 4.10 to 4.13. The effects of calcium ion concentration on the values calculated for the second order rate constant, as illustrated in Figures 4.10 to 4.12, showed the same general features as the first order model, i.e. an increase in the second order rate constant corresponding to an increase in the calcium ion concentration, although the increase did not show as clear a linear trend.

Table 4.14 shows the variation of the second order rate constant data in terms of the mean value and the standard deviation at each calcium ion concentration for each experimental batch. The relative standard deviations (RSD's) observed for all of the experimental runs were significantly greater than those seen for the first order model. At a calcium ion concentration of 0.0056 mol l^{-1} the relative standard deviations for the experiments in batches one and two were both 25 percent , in comparison with 7.6 percent and 22 percent for batches three and four. Thus the effects of storage time on the standard deviations were less pronounced for the second order model in comparison with the first order.

Although the mean second order rate constants showed a reasonable linear fit for each experimental batch, the standard deviations were significantly greater than those observed for the first order model (Table 4.6)

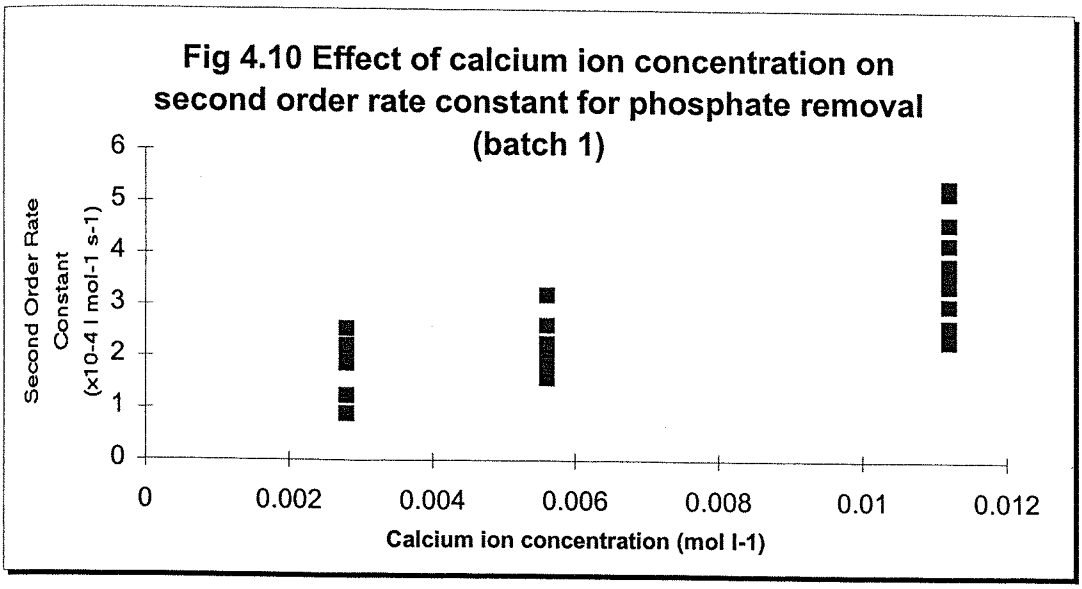


Fig 4.10 Effect of calcium ion concentration on second order rate constant for phosphate removal (batch 1)

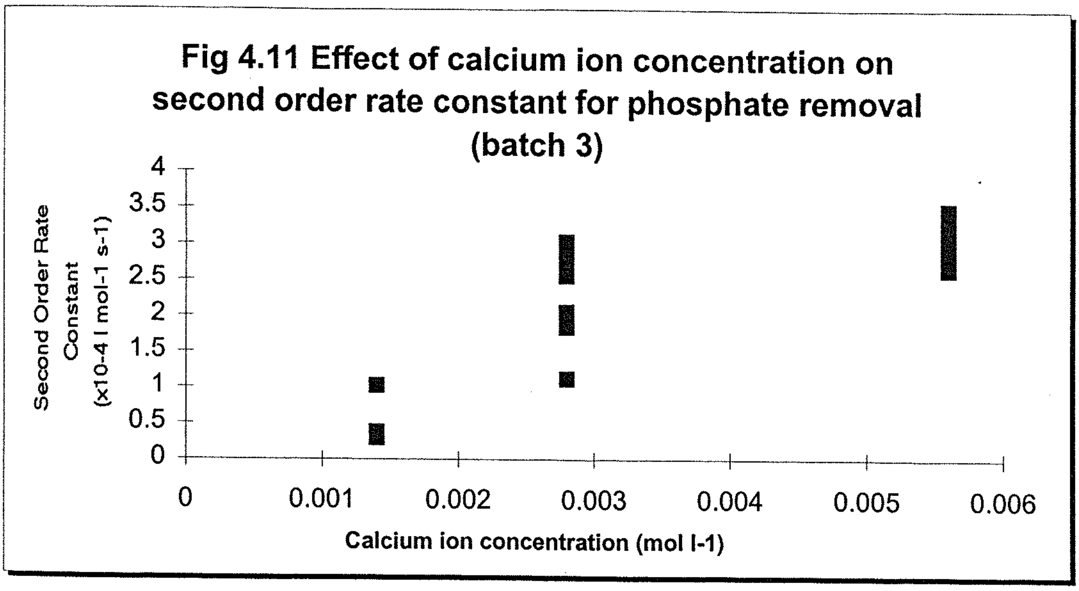


Fig 4.11 Effect of calcium ion concentration on second order rate constant for phosphate removal (batch 3)

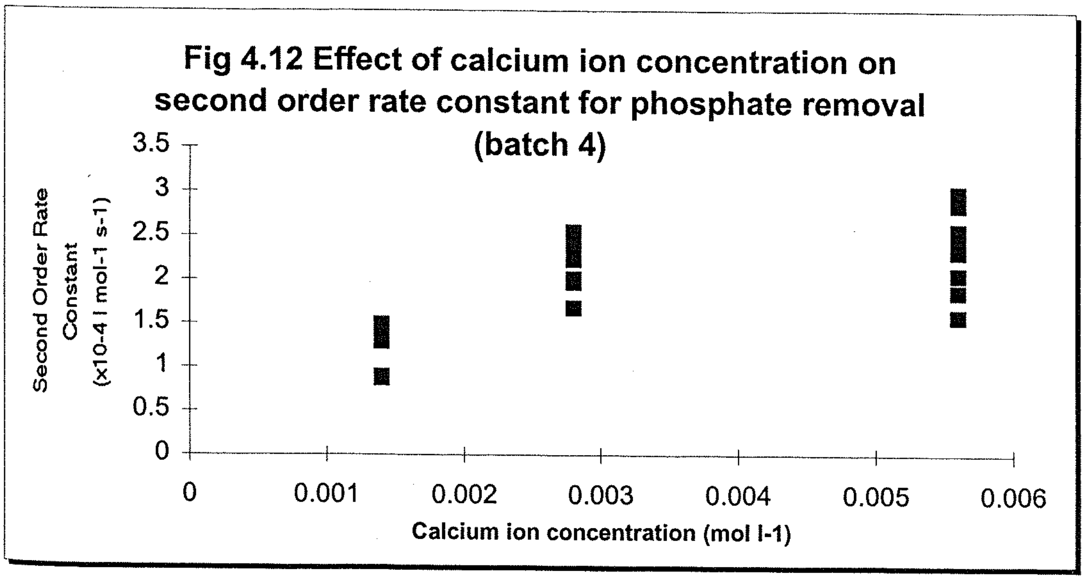


Fig 4.12 Effect of calcium ion concentration on second order rate constant for phosphate removal (batch 4)

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) $lmol^{-1}s^{-1}$	Storage Time (hr)
0.0112	0.96	0.45	0.51	53.49	0.950	2.32	3.75
0.0112	1.02	0.44	0.57	56.39	0.921	3.4	6.17
0.0112	1.02	0.53	0.49	47.84	0.934	2.6	7.00
0.0112	1.06	0.57	0.49	46.36	0.947	3.02	13.33
0.0112	0.97	0.54	0.43	44.42	0.956	3.8	16.33
0.0112	0.96	0.52	0.44	45.75	0.954	4.2	18.17
0.0112	1.01	0.56	0.45	44.30	0.946	3.6	24.67
0.0112	0.93	0.53	0.40	42.75	0.960	5.2	28.67
0.0112	1.03	0.68	0.36	34.53	0.975	5.3	33.67
0.0112	0.97	0.60	0.38	38.79	0.914	4.6	44.83
0.0056	0.98	0.56	0.42	42.93	0.876	2.26	5.50
0.0056	0.99	0.58	0.41	41.05	0.884	2.02	8.58
0.0056	0.98	0.61	0.37	37.40	0.905	2.24	14.17
0.0056	0.93	0.59	0.34	36.63	0.945	2.15	16.67
0.0056	1.14	0.70	0.44	38.48	0.903	2.24	19.67
0.0056	1.07	0.70	0.37	34.64	0.920	1.59	21.67
0.0056	1.10	0.78	0.31	28.56	0.930	1.77	30.50
0.0056	0.99	0.76	0.23	23.26	0.952	3.21	35.83
0.0056	0.90	0.68	0.23	25.14	0.984	2.62	47.50
0.0028	1.07	0.77	0.31	28.50	0.941	2.54	8.83
0.0028	0.99	0.72	0.27	27.49	0.946	1.86	12.00
0.0028	1.03	0.87	0.16	15.73	0.937	1.24	15.00
0.0028	1.02	0.92	0.11	10.29	0.984	0.89	23.67
0.0028	0.87	0.78	0.10	11.23	0.984	1.99	26.67
0.0028	0.90	0.84	0.07	7.43	0.973	1.86	40.50
0.0028	0.95	0.87	0.08	8.11	0.965	2.21	50.33

Table 4.10 : Influence of the addition of calcium chloride on the second order rate constant and the extent of removal of phosphate from Tamar River water - Batch one.

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) $lmol^{-1}s^{-1}$	Storage Time (hr)
0.0056	1.41	0.71	0.70	49.50	0.934	2.21	3.00
0.0056	1.50	0.78	0.72	47.80	0.954	1.98	4.00
0.0056	1.45	0.76	0.69	47.76	0.984	1.98	6.00
0.0056	1.60	0.87	0.73	45.71	0.935	2.67	7.17
0.0056	1.47	0.83	0.63	43.28	0.973	2.59	10.00
0.0056	1.42	0.87	0.56	39.03	0.986	2.4	13.67
0.0056	1.20	0.77	0.43	35.79	0.884	4.01	15.67
0.0056	1.12	0.79	0.34	29.80	0.889	2.75	17.00
0.0056	1.05	0.74	0.31	29.53	0.978	3.28	21.33
0.0056	1.09	0.80	0.29	26.77	0.948	3.47	23.33
0.0056	1.10	0.84	0.26	23.41	0.937	2.76	25.83
0.0056	0.97	0.74	0.23	23.46	0.935	3.46	26.83
0.0056	1.01	0.86	0.15	14.82	0.974	2.26	35.50
0.0056	0.97	0.87	0.10	10.71	0.936	2.98	40.08
0.0056	0.92	0.81	0.11	11.71	0.979	3.54	46.92
0.0056	0.84	0.76	0.08	9.38	0.906	3.54	48.17
0.0056	0.90	0.80	0.10	11.17	0.964	4.02	48.58
0.0056	0.84	0.78	0.06	7.36	0.935	3.79	51.50
0.0056	0.91	0.87	0.04	4.06	0.874	4.68	53.00

Table 4.11 : Influence of the addition of calcium chloride on the second order rate constant and the extent of removal of phosphate from Tamar River water - Batch two.

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) lmol^{-1}s^{-1}	Storage Time (hr)
0.0056	1.06	0.64	0.42	39.75	0.931	3.46	1.50
0.0056	1.13	0.66	0.47	41.74	0.885	3.02	2.08
0.0056	1.00	0.66	0.35	34.50	0.965	2.87	2.50
0.0056	1.14	0.68	0.46	40.28	0.885	2.65	3.00
0.0056	1.04	0.62	0.41	39.71	0.940	3.25	3.50
0.0056	1.14	0.70	0.44	38.46	0.899	2.67	4.25
0.0028	1.03	0.80	0.23	22.44	0.942	1.86	4.67
0.0028	0.96	0.75	0.21	21.63	0.952	2.05	5.17
0.0028	1.02	0.78	0.24	23.21	0.955	3.02	5.67
0.0028	0.95	0.76	0.20	20.61	0.974	2.84	6.33
0.0028	1.03	0.80	0.23	21.87	0.905	2.67	6.83
0.0028	1.12	0.90	0.22	19.71	0.948	1.98	7.50
0.0028	1.02	0.82	0.20	19.53	0.942	2.64	7.92
0.0028	0.98	0.78	0.20	20.47	0.926	1.84	8.42
0.0028	0.96	0.78	0.18	18.72	0.973	1.12	9.33
0.0014	0.99	0.97	0.02	2.23	0.969	0.37	9.83
0.0014	0.90	0.85	0.04	4.79	0.950	0.29	10.17
0.0014	0.95	0.89	0.06	6.74	0.953	1.02	10.58
0.0028	1.25	1.07	0.18	14.39	0.973	2.55	11.08
0.0056	1.21	0.74	0.47	38.74	0.925	3.05	11.50

Table 4.12 : Influence of the addition of calcium chloride on the second order rate constant and the extent of removal of phosphate from Tamar River water - Batch three.

Calcium Ion Conc. (mol l^{-1})	Initial Phosphate Conc. (μmol l^{-1})	Final Phosphate Conc. (μmol l^{-1})	Phosphate μmol l^{-1}	Removal %	Correlation Coefficient	2nd Order Rate Constant (*10-4) $lmol^{-1}s^{-1}$	Storage Time (hr)
0.0014	1.16	1.06	0.10	8.72	0.898	1.32	1.50
0.0014	1.14	0.97	0.16	14.35	0.976	0.87	2.08
0.0014	0.96	0.84	0.12	12.54	0.963	0.89	2.50
0.0014	1.03	0.95	0.08	8.07	0.932	1.29	3.00
0.0014	1.05	0.97	0.08	7.98	0.880	1.49	3.50
0.0028	0.99	0.77	0.22	22.37	0.953	1.97	4.25
0.0028	1.00	0.78	0.22	21.76	0.916	2.54	4.67
0.0028	1.15	0.93	0.23	19.67	0.979	1.68	5.17
0.0028	1.02	0.77	0.25	24.61	0.932	2.23	5.67
0.0028	0.97	0.77	0.20	20.79	0.956	1.98	6.33
0.0028	1.02	0.76	0.26	25.73	0.931	2.41	6.83
0.0028	0.98	0.77	0.21	21.36	0.973	2.01	7.50
0.0056	1.10	0.74	0.37	33.21	0.903	2.56	7.92
0.0056	0.97	0.61	0.36	37.45	0.933	2.46	8.42
0.0056	1.03	0.65	0.37	36.38	0.916	2.06	9.33
0.0056	1.11	0.71	0.40	35.79	0.963	1.86	9.83
0.0056	0.99	0.68	0.32	31.79	0.923	2.32	10.17
0.0056	0.98	0.67	0.31	31.47	0.894	1.58	10.58
0.0056	1.04	0.71	0.33	31.85	0.963	2.98	11.08
0.0056	1.09	0.71	0.38	34.83	0.972	2.85	11.50

Table 4.13 : Influence of the addition of calcium chloride on the second order rate constant and extent of removal of phosphate from Tamar River water - Batch four.

	Calcium Ion Concentration	Second Order Rate Constant ($l\ mol^{-1}s^{-1}$)		Standard Deviation	n
		Range	Mean		
Batch ONE	0.0112	2.32 to 5.8 $*10^{-1}$	3.98 $*10^{-1}$	1.14 $*10^{-1}$	10
	0.0056	1.51 to 3.21 $*10^{-1}$	2.23 $*10^{-1}$	0.563 $*10^{-1}$	9
	0.0028	0.89 to 2.54 $*10^{-1}$	1.79 $*10^{-1}$	0.472 $*10^{-1}$	7
Batch TWO	0.0056	1.98 to 4.68 $*10^{-1}$	3.09 $*10^{-1}$	0.76 $*10^{-1}$	19
Batch THREE	0.0056	2.46 to 3.05 $*10^{-1}$	2.78 $*10^{-1}$	0.212 $*10^{-1}$	7
	0.0028	1.85 to 2.84 $*10^{-1}$	2.24 $*10^{-1}$	0.380 $*10^{-1}$	10
	0.0014	0.29 to 0.81 $*10^{-1}$	0.643 $*10^{-1}$	0.311 $*10^{-1}$	3
Batch FOUR	0.0056	1.86 to 2.98 $*10^{-1}$	2.34 $*10^{-1}$	0.512 $*10^{-1}$	8
	0.0028	1.68 to 2.54 $*10^{-1}$	1.98 $*10^{-1}$	0.637$*10^{-1}$	7
	0.0014	0.87 to 1.49 $*10^{-1}$	0.805 $*10^{-1}$	0.201 $*10^{-1}$	5

Table 4.14 : Variation in second order rate constant for phosphate removal with calcium ion concentration both within and between experimental batches.

4.3.3 Comparison of First and Second Order Kinetic Analysis

Plots of the modelled first and second order removal profiles, as compared with the experimentally observed removal at calcium ion concentrations of 0.0112 and 0.0056 mol l^{-1} are shown in Figures 4.13 a) and b) and 4.14 a) and b) respectively. It is apparent that both the first and second order models give a reasonable approximation to the observed experimental removal profile at each of the calcium ion concentrations studied. The fit of the first order model removal appears to be somewhat closer to the experimental profile than that of the second order model as shown in the Figures 4.13 and 4.14. This better fit to the first order model is also witnessed in the correlation coefficients, shown in tables 4.1 to 4.4 for the first order model as compared with those in tables 4.10 to 4.13 for those of the second order model, although as discussed in section 3.4.3, these coefficients have been shown to be a somewhat misleading basis for comparison. Both kinetic model profiles, however, decrease to a level below that of the experimental residual value and predict a residual phosphate concentration that is significantly lower than the experimentally observed value. The first order profile considered to be a better descriptor of the process as there is generally observed a better agreement with the residual phosphate concentration and a tighter relationship is observed between the kinetic rate constant and salinity, as expected (see section 3.4.1 for discussion of expected salinity dependence of rate constants).

The kinetic modelling of phosphate removal, showed the same features observed for the kinetic modelling of the iron removal from the same experiments, however the observed superiority of the first order model as opposed to the second order model was much better defined in the case of the iron study. The experimental data for the iron removal gave a better fit to both the first and second order models than that of the comparative phosphate removal data.

The second order kinetic model predicted resistant phosphate concentrations that were consistently lower than both the values observed at t=24 hours and also the values predicted for the first order model. The predicted resistant concentrations for both the first and second

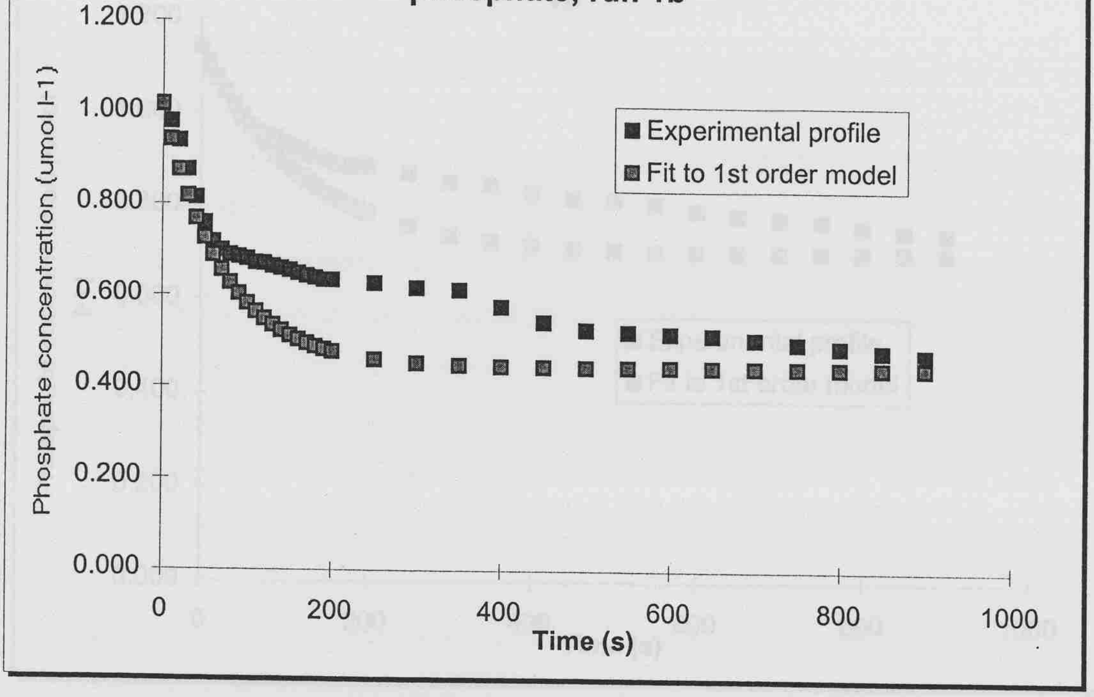


Fig 4.13 a) Comparison of removal profile and 1st order modelled fit of the data for removal of phosphate, run 1b

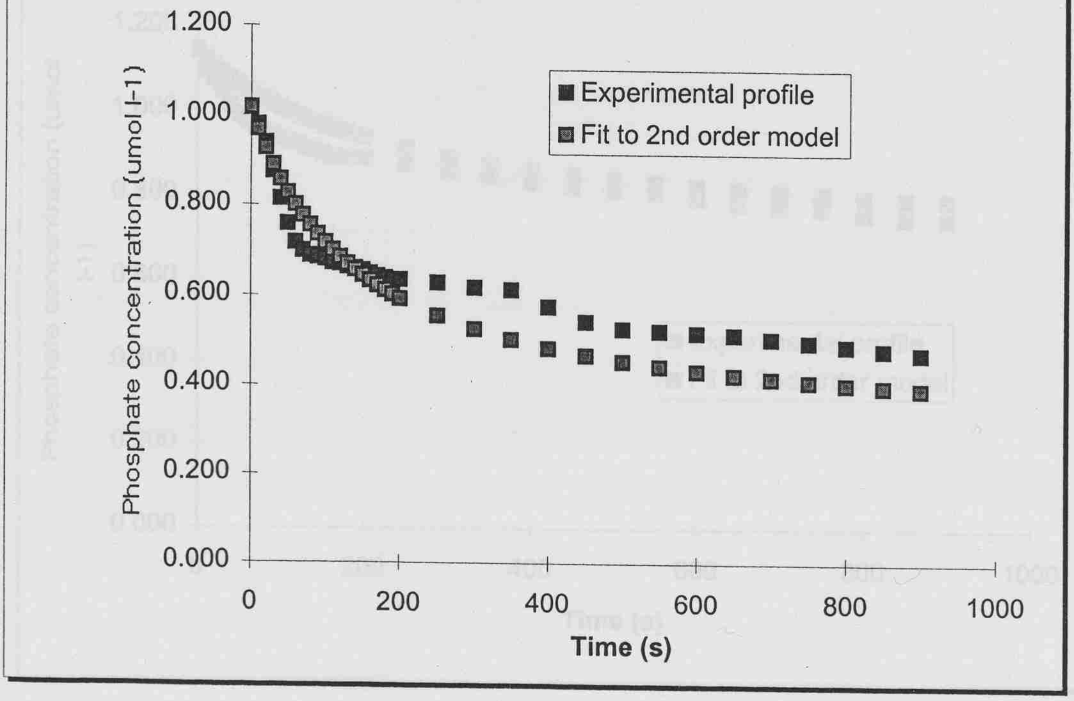


Fig 4.13 b). Comparison of removal profile and 2nd order modelled fit of the data for removal of phosphate, run 1b

Fig 4.14 a) Comparison of removal profile and 1st order modelled fit of the data for removal of phosphate, run 1n

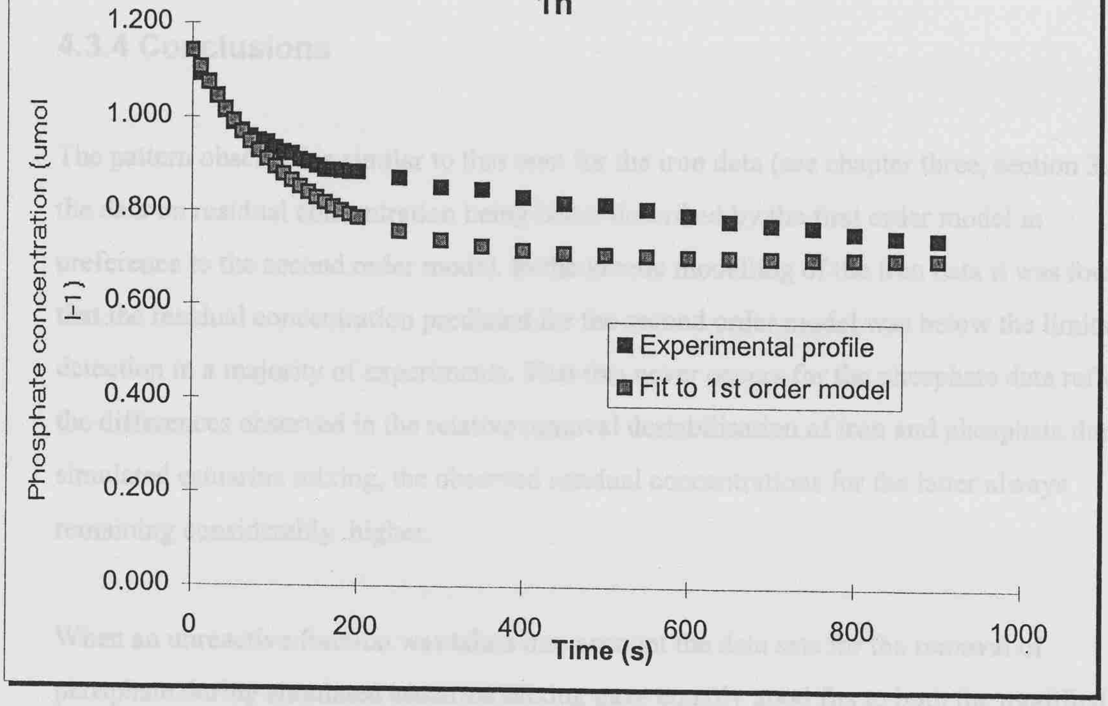
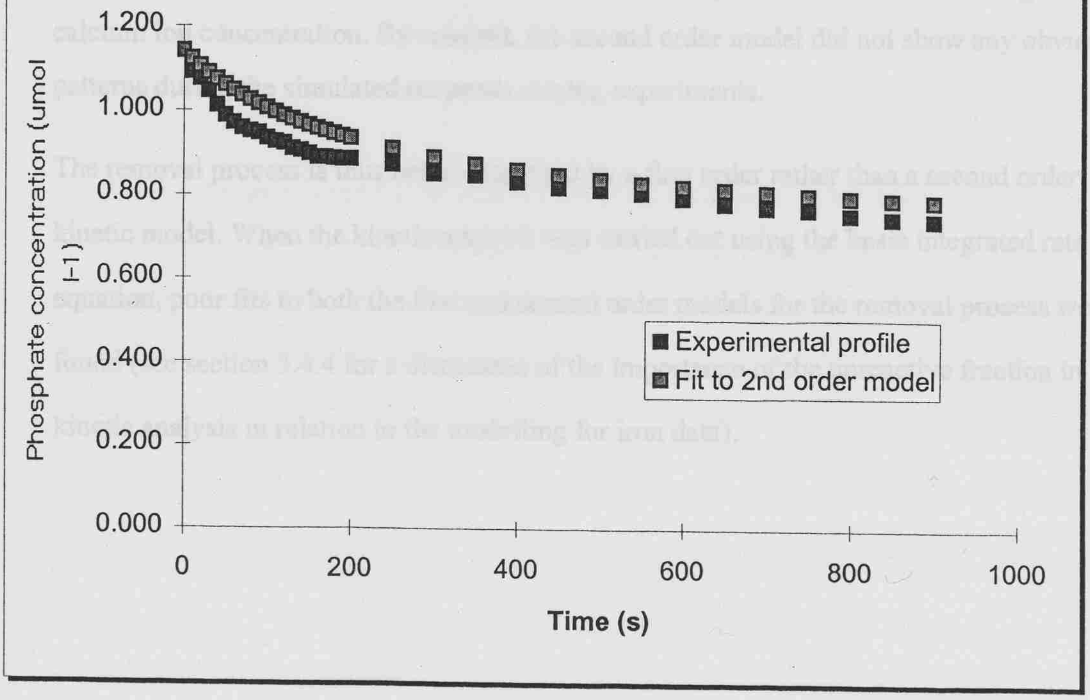


Fig 4.14 b). Comparison of removal profile and 2nd order modelled fit of the data for removal of phosphate, run 1n



order models followed the pattern observed for the experimental data of decreasing with an increase in the calcium ion concentration.

4.3.4 Conclusions

The pattern observed is similar to that seen for the iron data (see chapter three, section 3.4.2) the data on residual concentration being better described by the first order model in preference to the second order model. In the kinetic modelling of the iron data it was found that the residual concentration predicted for the second order model was below the limits of detection in a majority of experiments. That this never occurs for the phosphate data reflects the differences observed in the relative removal destabilisation of iron and phosphate during simulated estuarine mixing, the observed residual concentrations for the latter always remaining considerably higher.

When an unreactive fraction was taken into account the data sets for the removal of phosphate during simulated estuarine mixing gave equally good fits to both the modified first and second order kinetic models, using equations 3 and 4. A closer fit of the residual phosphate fraction to the actual value measured after 24 hour was obtained from the first order model in preference to the second order model for almost all of the data sets. The first order model also showed a clear linear trend of an increase in the rate constant with increasing calcium ion concentration, and less variability in the rate constant at a given calcium ion concentration. By contrast, the second order model did not show any obvious patterns during the simulated estuarine mixing experiments.

The removal process is thus better described by a first order rather than a second order kinetic model. When the kinetic analysis was carried out using the basic integrated rate equation, poor fits to both the first and second order models for the removal process were found (see section 3.4.4 for a discussion of the importance of the unreactive fraction in the kinetic analysis in relation to the modelling for iron data).

4.4 The Influence of Storage Effects on the Behaviour of 'Dissolved' Phosphate During Simulated Estuarine Mixing.

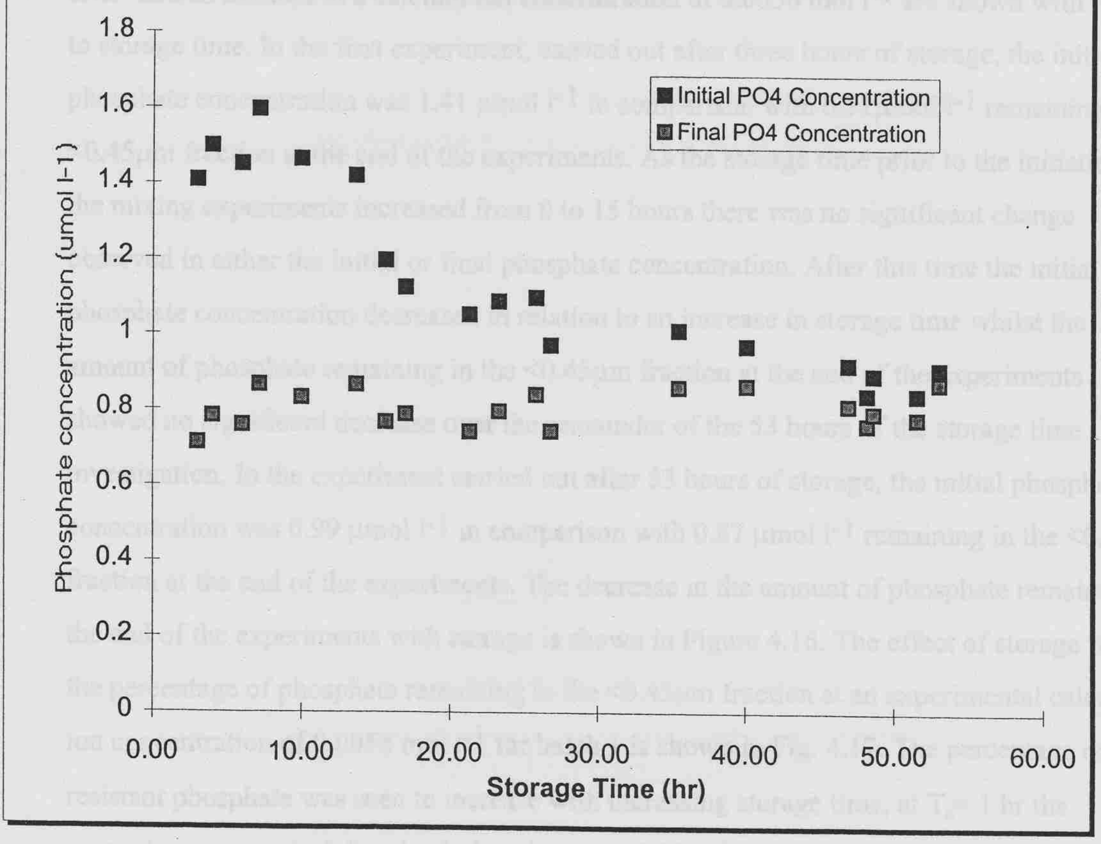
4.4.1 Effect of Storage on the Removal of 'Dissolved' Phosphate during Simulated Estuarine Mixing.

Significant aggregation may occur in river water samples in the period of time prior to carrying out the mixing experiments, due to the unstable nature of the colloids in river water (Hunter & Leonard 1988). This phenomenon was investigated by comparing the changes in removal of both iron and phosphate in a series of experiments carried out under similar experimental conditions. Data from batches one and two were analysed with respect to storage time. Batch one was carried out over a period of 50 hours on a single batch of river water. Mixing experiments were carried out using three calcium ion concentrations, 0.0028, 0.0056 and 0.0112 mol l^{-1}. Batch two was carried out over a period of 53 hours. Twenty six experiments were carried out on a single batch of river water, with addition of the same calcium ion concentration, 0.0056 mol l^{-1} in each, leaving storage time as the only variable parameter.

It was concluded, in section 3.5, that whilst the initial concentration 'dissolved' iron was largely unaffected by storage, the behaviour of the 'dissolved' iron fraction was significantly altered during the period of storage prior to carrying out the simulated estuarine mixing experiments. Increases over time in the percentage of the 'dissolved' iron resisting aggregation and in the calculated first and second order rate constants were observed.

The batches of water used for the experimental batches one and two during which studies of storage time effects were carried out had initial concentrations of dissolved phosphate of 0.95 μmoll^{-1} and 1.41 μmol l^{-1} respectively. During the course of the study into storage time effects, from t=0 to t=54 hours, the initial dissolved iron concentrations, prior to addition of calcium chloride , varied from 0.87 to 1.14 μmol l^{-1} (mean : 0.993 ± 0.06) for batch one and

Fig 4.15 Effect of storage on the behaviour of phosphate during simulated estuarine mixing.



0.84 to 1.59 μmol l^{-1} (mean : 1.14 ± 0.25) for batch two. The data from batch one showed no significant effects of storage on the initial concentrations of phosphate in the <0.45μm fraction, concurring with the work in Section 3.5 on the behaviour of dissolved iron found in the <0.45μm fraction of river water. However the data from batch two showed clear indications of a decrease in the initial phosphate concentration with an increase in storage time. The data on the effects of storage time on the initial and final phosphate concentrations is summarised in tables 4.1 and 4.2 for batches one and two respectively.

In Figure 4.15 the decrease in the initial concentration of phosphate for the experiments carried out in batch two and the final concentration of phosphate remaining in the filtrate after fifteen minutes at a calcium ion concentration of 0.0056 mol l^{-1} are shown with respect to storage time. In the first experiment, carried out after three hours of storage, the initial phosphate concentration was 1.41 μmol l^{-1} in comparison with 0.71μmol l^{-1} remaining in the <0.45μm fraction at the end of the experiments. As the storage time prior to the initiation of the mixing experiments increased from 0 to 15 hours there was no significant change observed in either the initial or final phosphate concentration. After this time the initial phosphate concentration decreased in relation to an increase in storage time whilst the amount of phosphate remaining in the <0.45μm fraction at the end of the experiments showed no significant decrease over the remainder of the 53 hours of the storage time investigation. In the experiment carried out after 53 hours of storage, the initial phosphate concentration was 0.99 μmol l^{-1} in comparison with 0.87 μmol l^{-1} remaining in the <0.45μm fraction at the end of the experiments. The decrease in the amount of phosphate remaining at the end of the experiments with storage is shown in Figure 4.16. The effect of storage time on the percentage of phosphate remaining in the <0.45μm fraction at an experimental calcium ion concentration of 0.0056 mol l^{-1} for batch 1 is shown in Fig. 4.17. The percentage of the resistant phosphate was seen to increase with increasing storage time, at T_s= 1 hr the percentage removal of dissolved phosphate was 34 %, the % removal of phosphate decreased to 25% removal at T_s= 16 hr and had fallen to 6% by T_s= 52 hours. Figure 4.18 shows the effect of the storage time on the removal of dissolved phosphate at a calcium ion concentration of 0.0112 mol l^{-1}. The effects are less pronounced at the higher calcium ion

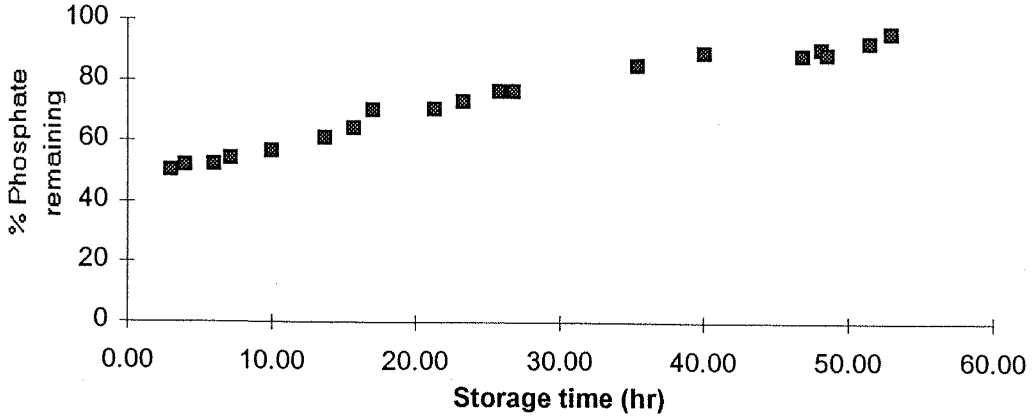


Fig 4.16 Effect of storage on phosphate removal (0.0056 mol l-1 calcium, batch 2)

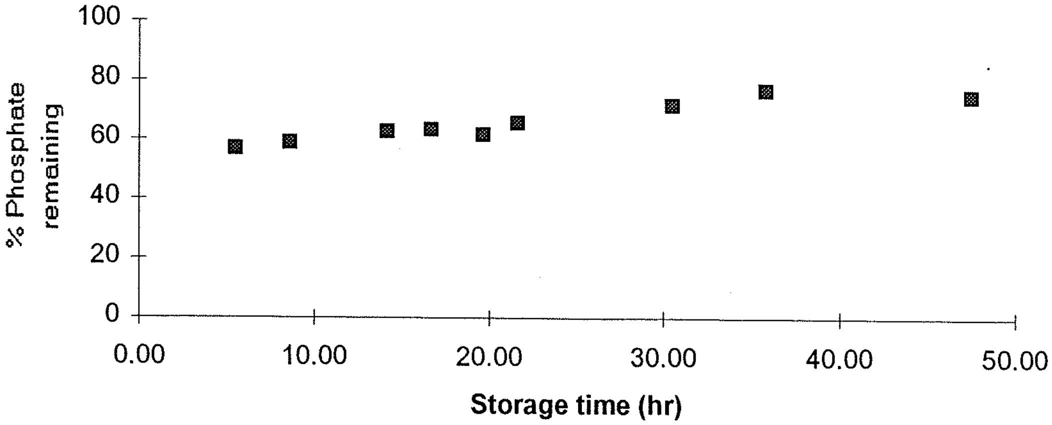


Fig 4.17 Effect of storage time on phosphate removal (0.0056 mol l-1 calcium, batch 1)

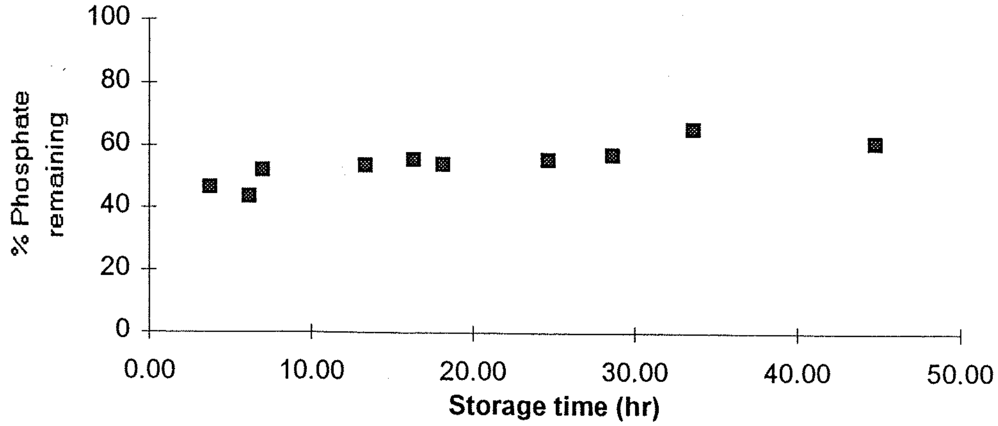


Fig 4.18 Effect of storage time on phosphate removal (0.0112 mol l-1 calcium, batch 1)

concentration, at T_s= 1 hr the 54 % removal of dissolved phosphate was observed, the % removal of phosphate decreased to 45% at T_s= 26 hr and fell to 40% by T_s= 52 hours. The observed decrease in the resistant phosphate fraction during these experiments is taken to reflect a reordering of the size fractionation of phosphate over the period of storage which lead to a decrease in the available phosphate in the <0.45μm fraction. Storage time did not affect the overall concentration of iron that remained in the <0.45 μm size fraction, however the phosphate available for removal appeared to be so unstable that it was as easily removed during prolonged storage as by the addition of calcium ions.

4.4.2 Effects of Storage Time on Rate Constants

First and second order rate constants were calculated for the data from the investigation into the storage time effects. Changes in the first and second order rate constants were looked at in relation to the amount of time water had stored prior to addition of calcium ions in the simulated mixing experiments.

Figures 4.19 to 4.21 illustrate the effects of storage time on the calculated first order rate constants, while Figures 4.22 and 4.24 show the comparative changes in calculated second order rate constant. The data from the kinetic interpretations is summarised in tables 4.1 - 4.4 for first order and 4.10 to 4.13 for second order.

First Order Model

Figures 4.19 to 4.21 show the effect of storage time on the 1st order rate constant at calcium ion concentrations of 0.0028, 0.0056 and 0.0112 mol l^{-1} respectively. At all calcium ion concentrations, there is an observation of increasing 1st order rate constant with increasing storage. The effects are most marked in Figure 4.20, which shows data from batch two, (0.0056 mol l^{-1} calcium). The behaviour of phosphate is similar to that of iron at the lower calcium ion concentrations, but at 0.0112 mol l^{-1} of calcium, Figure 4.21 no change in the rate constant was observed for iron.

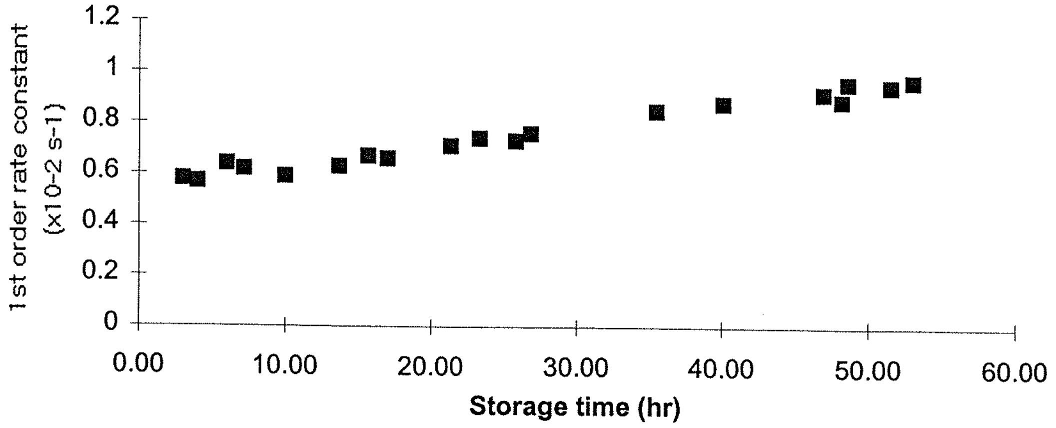


Fig 4.19 Effect of storage time on 1st order rate Constant (0.0056 mol l-1 calcium, batch 2)

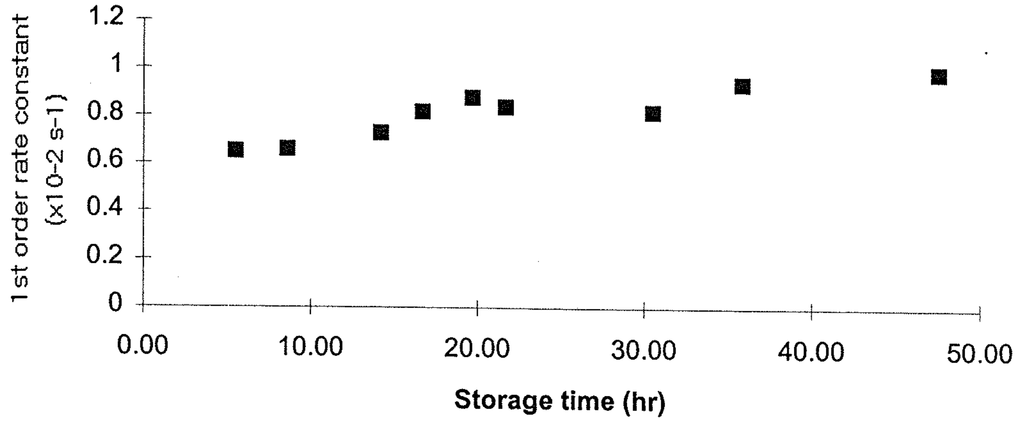


Fig 4.20 Effect of storage time on 1st order rate Constant (0.0056 mol l-1 calcium, batch 1)

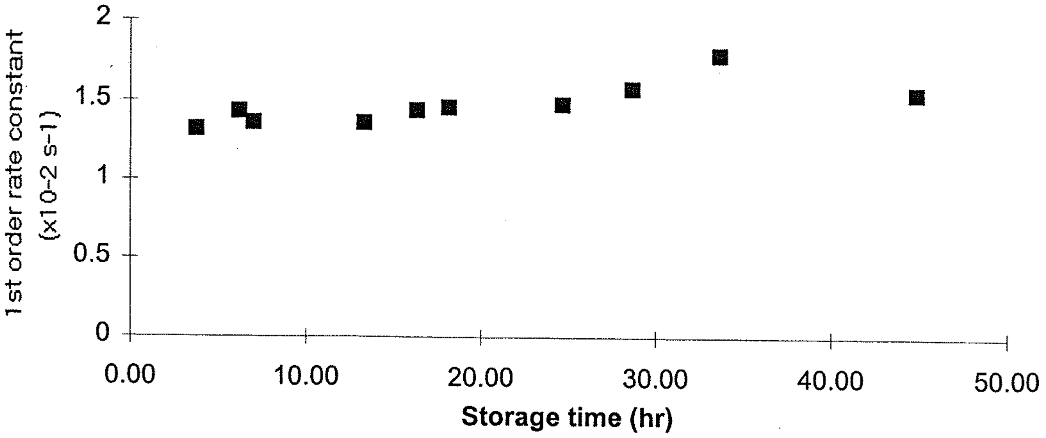


Fig 4.21 Effect of storage on 1st order rate constant (0.0112 mol l-1 calcium, batch 1).

The findings correlate with the observations from the removal profiles, in that the most marked effects of storage time are observed for the data from batch two.

Second Order Model

The second order model showed a similar pattern to that of the first order, with an increase in the rate constant with increasing storage, however the patterns observed were not so well defined. Figure 4.22 shows the variation of second order rate constant with storage at a calcium ion concentration of 0.0056 mol l^{-1}, for batch two (cf. Fig. 4.1 for batch two, first order rate constants) the results show a wide distribution with no distinct linear pattern. A similar pattern was observed for the data from batch one carried out at a calcium ion concentration of 0.0056 mol l^{-1}, as illustrated in fig. 4.23. The changes in the resistant phosphate fraction at a calcium ion concentration of 0.0112 mol l^{-1} show no clear trend with increasing storage, as illustrated in Figure 4.24.

Storage time has a greater effect on the behaviour of phosphate than was observed for the behaviour of dissolved iron. It has some effect on the initial concentration of phosphate measured in the experiments and also has an effect on the behaviour during simulated estuarine mixing at all of the calcium ion concentrations studied.

Fig 4.22 Effect of storage time on 2nd order rate constant (0.0056 mol l-1calcium, batch 2).

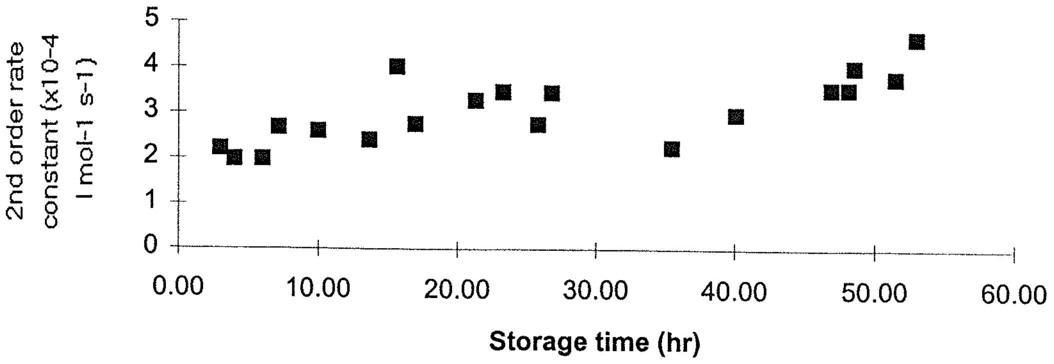


Fig 4.23 Effect of storage time on 2nd order rate constant (0.0056 mol l-1calcium, batch 1).

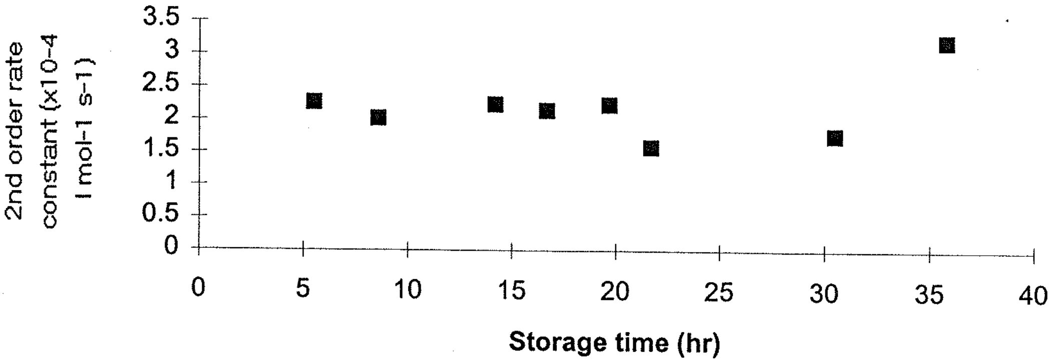
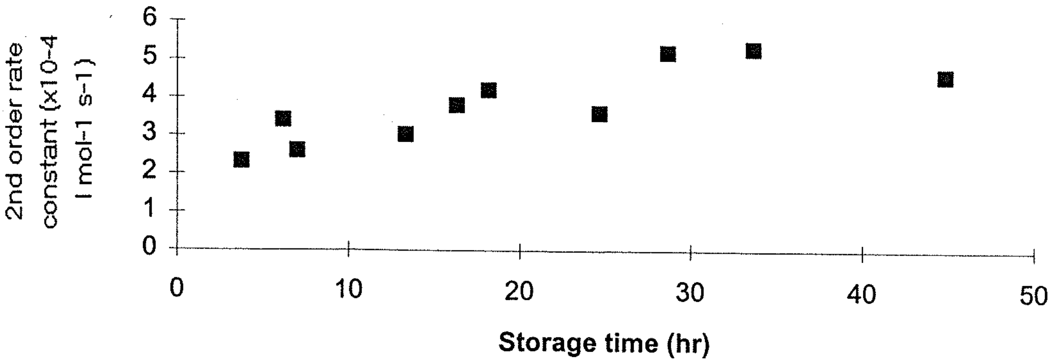


Fig 4.24 Effect of storage time on 2nd order rate constant (0.0112 mol l-1calcium, batch 1).



4.5 Discussion

There are various lines of argument, and some more direct evidence, indicating a relationship between the processes which influence the behaviour of dissolved iron and phosphate during mixing of iron rich river water with sea water.

It is known that the majority of the operationally defined "dissolved iron" is actually in the form of colloidal iron (III) oxides (Moore *et al.* 1979, Section 1.4 this work), and it was shown in a study of size distributions (section 4.2.2, Bale & Morris (1981)) that approximately a third of the phosphate within the <0.45μm fraction of Tamar river water was carried by the river as phosphate bearing colloids. The precise nature of these phosphate bearing colloids are not fully known, but it is likely that it is this colloidally associated fraction which demonstrates the rapid loss during the course of the experiments in a manner analogous with that observed for iron (section 3.3). Scavenging of dissolved phosphate by the larger particles formed during this removal of colloidal material represents a further possible mechanism of removal of phosphate during simulated estuarine mixing. The remaining phosphate fraction in river waters is thought to be in a truly dissolved form (Burton & Liss 1976; Aston 1980; Froelich 1985).

Iron oxyhydroxides provide active surfaces for the adsorption of phosphate and other riverine constituents (Boyle *et al.*, 1977; Sholkovitz *et al.* 1978; Bale & Morris, 1981; and Millward & Moore, 1982). During the formation of microcolloidal particles, phosphate has a tendency to become adsorbed onto the colloidal iron. The amount and nature of the phosphate adsorbed will depend to a large degree on the physical, chemical and biological characteristics of the river water (Liss & Burton, 1976). Upchurch (1973) proposed that there were iron-inorganic phosphate complexes holding phosphate to suspended sediments and it is reasonable to assume that such complexes would also be formed between inorganic phosphate and colloidal material. The initial gross removal of colloidal iron was proposed to take a proportion of this associated phosphate with it and a strong interdependence between rate constants. However there are a number of factors that are thought to have an effect only on the phosphate removal, these include initial phosphate concentration and particle size (Pomeroy *et al.*, 1965, Mortimer, 1971; Butler & Tibbits, 1972; Patrick & Khalid, 1974; Liss

& Burton 1976; Stirling & Wormald, 1977 and Bale & Morris (1981)), pH, biological activity and temperature (Chen *et al.*, 1973; Bale & Morris, 1981). Some of these parameters, e.g. biological activity, are not relevant to the proposed process of colloidal removal observed during estuarine mixing, and several of the other parameters will remain constant within a given estuarine system. The dependence of phosphate behaviour on initial phosphate concentrations is consistent with the belief that phosphate levels are buffered by larger particles (Mortimer, 1971; Butler & Tibbits, 1972; Patrick & Khalid, 1974; Liss & Burton, 1976; Stirling & Wormald, 1977 and Bale & Morris, 1981). Mixing history and the presence and concentration of other constituents also have a pronounced effect on phosphate removal. It was shown, in laboratory studies with goethite particles, that humic acids can become adsorbed onto the surface of iron particles. It is thought that the humic material competes with phosphate for the available sites on the iron particles in the river water. Adsorption of humic acids is most effective at medium pH levels (Hawke *et al.,* 1989). Hawke *et al.,* (1989) also showed that the presence of magnesium, sulphate and fluoride ions can affect the uptake of phosphate onto goethite particles. Laboratory studies on goethite are believed to simulate the behaviour of iron colloids seen in the estuarine environment.

4.5.1 Interpretation of kinetics of phosphate removal

In the experiments carried out in this study, both dissolved iron and phosphate were initially lost at a rapid rate from the $< 0.45\mu m$ fraction. This observation of concurrent iron and phosphate removal could be explained either by an aggregation of colloidal material containing both iron and phosphate or possibly by the scavenging of dissolved phosphate by the large newly formed iron-containing colloidal aggregates. It must be emphasised, however, that the formation of these particles does not present any new surfaces for adsorption. After 50-150 seconds, the removal of phosphate was essentially complete, whereas the removal of dissolved iron continues on until 300-400 seconds after mixing. The deviation in the behaviour of the dissolved iron and phosphate observed during the mixing experiments could be caused by a difference in their size distributions within the $0.45\mu m$ fraction. Results of a study of the size distributions of phosphate and iron in Tamar River water concluded that a significant portion of the iron in the $<0.45\ \mu m$ fraction was microcolloidal in nature, whereas only a small percentage of the phosphate in the same fraction was colloidal in nature (33% of the phosphate fraction compared with 48% of the iron was found to be colloidal in nature in the study of Morris & Bale, 1981) with the remainder believed to be to be in a truly dissolved form. A significantly larger proportion of the phosphate was seen to pass through the smallest filter with approximately 80 % of the phosphate in the <0.45 μm fraction passing through a 0.1μm nominal pore size filter in comparison to approximately to 50% with that for iron.

Due to the nature of the size fractions studied in the present work it is not possible to categorically state the percentage of iron and phosphate within the colloidal and truly dissolved states, as the smallest size cut off (0.1μm) is not sufficient to remove the finest colloidal material. The conclusions would, however, indicate that there is a sizeable fraction of the phosphate which is not removable by the processes of destabilisation / aggregation because it is in solution. When the percentages of iron and phosphate removed during the simulated estuarine mixing experiments were considered, the removal of both species showed a linear relationship proportional to the increasing calcium ion concentration. As illustrated in Figure 4.2, the decrease in resistance to destabilisation per unit increase in calcium ion concentration was equivalent for iron and phosphate with the percentage of iron removed at the end of the experiments consistently 40-50 % greater than that observed for phosphate. This percentage difference corresponds to the differences observed in the relative colloidal fractions of iron and phosphate, as stated above. Thus at any given calcium ion concentration, there is a significantly larger proportion of dissolved iron than phosphate susceptible to destabilisation. These findings fit with the rationale of a colloidal aggregation mechanism for phosphate removal from the <0.45μm fraction of river water, in preference to scavenging by aggregated iron colloids.

Results from the experiments indicated that the initial level of phosphate in the <0.45μm fraction decreased over long periods of storage prior to simulated estuarine mixing. This decrease in phosphate concentration, illustrated in Figure 4.14, is thought to be due to adsorption of 'dissolved' phosphate onto either the larger particles present in the river water, or onto the walls of the mixing chamber. Addition of phosphate was observed in a few of the experimental batches, during the period after major removal. This could be due to the break up of the iron-inorganic phosphate complexes, which occurs as salinity increases, releasing the phosphate back into solution, and may represent the release of the phosphate lost during prolonged storage. A fuller examination of the effects of storage is presented in section 4.4. It is also possible that the phosphate is released from larger particles, which are thought to act as a buffer on phosphate concentration levels (Smith & Longmore, 1980). This feature is not universally observed in the experiments, though it does concur with previous observations of phosphate behaviour (Bale & Morris, 1981), and the mechanism is not fully understood.

4.5.2 Effects of Storage time on Estuarine Constituents

The initial concentrations of dissolved iron were not significantly affected by storage time prior to the simulated estuarine mixing experiments, whereas a decrease in the initial phosphate concentration was observed, as seen most clearly in Figure 4.14 which shows the change in initial phosphate concentration with storage time during batch two. At the highest calcium ion concentration used in the experiments no significant change was observed in the behaviour of iron (Figure 3.17) while an increase in the phosphate fraction resistant to aggregation was observed as storage time was increased, as shown in Figure 4.15. The effect of storage time on the behaviour of both of the constituents was greater in experiments carried out at a lower calcium ion concentration as illustrated in Figures 3.15 and 4.16 for iron and phosphate respectively in experiments carried out with 0.0056 mol l^{-1} of calcium. The percentage of iron resistant to aggregation is seen to increase from 9 to 32 % over the 54 hour period of storage, while the residual phosphate fraction increased from 50 to 95 % over the same time period. The effect of storage time on the residual fraction was consistently shown to be greater for phosphate in relation to that observed for dissolved iron.

The kinetic interpretation of the experimental data showed a similar pattern for the calculated first rate constants, and to a lesser degree the second order rate constants. Increase in the first order rate constant was observed with storage, which was more pronounced at lower calcium ion concentrations. In experiments with an overall calcium concentration of 0.0112 mol l^{-1} the first order rate constant for removal of iron remained unaffected. The effects of storage on first order rate constant at calcium concentrations of 0.0056 and 0.0112 mol l^{-1} are shown in Figures 3.19 and 3.22 for iron and in Figures 4.19 and 4.20 for phosphate.

It is evident that the behaviour of both iron and phosphate is affected to some degree by storage time, with the effects shown to be more pronounced for phosphate. This implies a change in the distribution of iron and phosphate within the riverine sample during storage, most likely due to processes of either aggregation or adsorption.

4.6 Conclusions

The removal of both iron and phosphate from the <0.45μm fraction of river water during simulated estuarine mixing was shown (in sections 3.4 and 4.3 respectively) to be more accurately described by a first order rather than a second order kinetic model. Both models yield rate constants which show a dependency upon the increase in the calcium ion concentration but the observed relationship is tighter for the first order rate constants. The observed relationship between the two species within river water extends to their simultaneous removal from the <0.45μm fraction by a common mechanism. Different rate constants were predicted for the removal of iron and phosphate however, implying that they are not solely dependent upon one another.

Although it seems evident that there are links between the behaviour of iron and phosphate, in the later stages of the mixing experiments they behave in a very different manner -as illustrated in Figure 4.3, the overall percentage removal of phosphate is both consistently and considerably less than that of iron, *e.g.* at a calcium ion concentration 0.0112 mol l^{-1}, 95% iron removal, c.f. 53% phosphate removal.

As phosphate has been shown to be present within the colloidal as well as the truly dissolved fraction, it is possible that it could be associated with the iron rich colloids. The removal observed could therefore represent a co-removal of the iron and phosphate by a common mechanism, of destabilisation / aggregation. The removal of phosphate is, however, complete earlier than that observed for iron so the colloids involved can not be entirely a common carrier for both. Since we know that some of the phosphate is colloidal, the most obvious mechanism for phosphate removal is destabilisation / aggregation, but with the phosphate bearing colloids not identical to the iron bearing colloids, as the removal rates observed are markedly different for the two species. If the phosphate removal was occurring by co-precipitation, this would imply that the colloidal phosphate fraction (which has been shown to be present within Tamar water) is not removed during the experiments. Such behaviour would be analogous with that observed by Kraepiel *et. al.,* (1997) who observed that, unlike iron, colloidal copper, cadmium, lead, nickel, zinc and possibly manganese fractions were not removed during estuarine mixing. It was found in the study of Kraepiel *et al.,* (1997) that colloidal fraction of river water could be further split into two distinct subfractions, iron and non-iron fractions, each exhibiting significantly different behaviour. Finely dispersed iron oxides which can coagulate and become part of the particulate load made up the majority of the former fraction (which may include some manganese) and organic macromolecules, which bind to most other metals and behave approximately conservatively formed the latter fraction. Phosphate may be bound to the organic molecules in the same manner as the majority of metals, thus providing a possible explanation for the observed differences in behaviour for iron and phosphate.

Chapter Five

Behaviour of Iron and Phosphate in Laboratory Simulations of Estuarine Mixing : A Comparative Investigation of Procedures and of Effects of Variables on Removal.

As discussed in chapter 1, the removal of a large fraction of operationally defined 'dissolved' iron during the early stages of estuarine mixing is a widely observed feature in and the primary process responsible has been shown to be the destabilisation and aggregation of microcolloidal forms of iron present in river water. In addition to field observations in some twenty five estuaries, various laboratory experimental studies of the process have been undertaken. These studies have led to some significantly different interpretations concerning the kinetics of the reaction and in some cases these interpretations are equivocal (see section 3.4). The work of Mayer (1982b) and Fox & Wofsy (1983) presented iron removal data as fitting the second order model predicted by classical colloid theory, however plots of 1/[Fe] showed significant deviation from linearity to raise doubts about the applicability of the second order model. In those studies above, neither was a first order model considered, or an unreactive fraction taken into account. The conclusion of the current work (Chapter 3) was that the removal of iron from the <0.45µm fraction was better described by a first order kinetic model rather than a second order model.

Although the phenomenon of estuarine removal is general wherever river water with relatively high concentrations of 'dissolved' iron mixes with sea water, and a common general mechanism of microcolloidal destabilisation and aggregation probably explains the observations, differences in rate and perhaps in the order of the reaction may be expected because of inherent differences in the nature of the river water. The stability of constituents within river waters is dependent upon the composition of the river water, for example differences in the stability of microcolloids and as argued by Morris (pers comm.), differences in the distribution of the iron within the various components of the total microcolloidal particle population may affect the reaction order. Microcolloids are believed to be stabilised primarily by the presence of organic material although Cameron & Liss (1984) demonstrated that microcolloidal iron could be stabilised to some degree by the presence of surfactants, silicate and phosphate ions as well as both humic acids and tannic acids,. Therefore the distribution and concentration of such species in the original river water, as well as the initial iron and phosphate concentrations, will potentially affect the stability of the colloidal iron and alter its susceptibility to destabilisation on addition of electrolyte solution.

It is possible that some reported differences may reflect differences in the experimental approaches employed. Although the precise mechanism of the removal is not fully understood, it may in some part be a result of shear effects associated with the high stirring rate observed in this set of experiments. Indeed Mayer (1982b) showed that agitation of the solution caused an increase in the fraction of iron aggregated, with a small but measurable increase at a filter cut off of 0.2μm, and a more pronounced effect at a higher filter cut off size of 1.0μm. Other factors which could influence the observed behaviour include sample storage and filtration procedures, which have already been shown by Hunter & Leonard (1988) to be important in affecting microcolloidal behaviour; time at which measurements begin following mixing; frequency and overall timescale of observations; mixing procedures; and possibly the analytical methods used. The experiments of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) all used a Ferrozine colorimetric method, whereas Duffy (1985) used a TPTZ colorimetric method. While these methods are essentially similar in principle involving reduction of all the iron present to the Fe(II) state, followed by reaction with one of the bi-dentate colour forming compounds, Ferrozine or TPTZ, to give a coloured complex, the absorbence of which is measured colorimetrically, the question as to whether they differ significantly in their capacity to measure "dissolved" iron is clearly basic to a comparison of the two techniques. It is also a limitation for a critical evaluation of the different findings in previous studies that in some cases the fits of data to different orders of reaction have not been specifically compared.

Accordingly the present work has been undertaken to clarify the extent to which differences in previous finding and interpretations may reflect effects related to the experimental methodologies used and to attempt to ascertain whether the various methods employed by previous workers give consistent results when a common kinetic modelling approach is applied. The work in chapters three and four was based on experiments carried out using only a single cation which plays a major role in the destabilisation process under observation. As discussed there, this approach offers some advantages with respect to simplification of variables when attempting to evaluate potentially small differences in the fits of experimental data to different kinetic models. In most previous work, however, sea water has been used as the destabilising agent and therefore for the comparative study this approach has been adopted. Experiments were carried out using river and sea water from a single system, thus eliminating effects on rate constants due to compositional differences, in particular in the river water, and employing the conditions used in the three main previous investigations (Mayer, 1982b; Fox & Wofsy, 1983 and Hunter & Leonard, 1988). As one objective of the present work overall was to investigate the behaviour of phosphate in the context of the removal of iron, measurements of phosphate were included in this comparative study of methods.

5.1 : Experimental Methods

Four major methodologies, used to simulate estuarine mixing and the associated behaviour of 'dissolved' iron were investigated, namely those of Mayer (1982b) Fox and Wofsy (1983), Duffy (1985) and Hunter & Leonard (1988). Each of the methods used different conditions of pre-experiment treatment, mechanics of mixing, sampling as the reaction proceeds and pre-analysis treatment.

The use of a single source for the river water meant that the effects of river water composition could be regarded as minor. A constant source of sea water was also used. After an initial comparison of analytical procedures all analyses were performed by the same technique. Thus any differences found in the reaction of 'dissolved' iron can be attributed to differences in experimental methodology. The key difference involved are : initial treatment of river and sea water with regard to filtration; temperature of reaction; procedure for sampling during the reaction and filtration to remove aggregated material. Mayer (1982b) Fox & Wofsy (1983) and Hunter & Leonard (1988) all used basically similar procedures, with mixing of river water and sea water, in appropriate proportions to give the desired salinity. Samples were collected in 50 ml aliquots and passed via an acid washed syringe, through a Swinnex in-line filter holder prior to analysis. The principal differences between methodologies stemmed from the initial treatment of the river and sea water and the mixing methods. Section 2.3 gives a full description of each of the experimental methods.

The basic differences are summarised below :

Pre-experimental filtering.

> Hunter & Leonard (1988) carried out experiments using unfiltered river and sea water; Fox & Wofsy (1983) used unfiltered river water and filtered sea water; Mayer (1982b) filtered both the river and sea water samples.

Stirring mechanism.

In the experiments of Mayer (1982b) stirring was carried out using a shaking Table, those of Fox & Wofsy (1983) used a magnetic stirrer and Hunter & Leonard (1988) employed a glass paddle for this purpose.

Pre-analysis filtering.

Both Fox & Wofsy (1983) Hunter & Leonard (1988) utilised GF/C filters (nominal pore size 1.2μm) as the cut off prior to analysis; Mayer (1982b) combined Gelman A/E and glass fibre filters, (giving an equivalent pore size of 0.5μm).

The method used in the experiments carried out by Duffy (1985) differs markedly in both the method of mixing and sample collection. Though the addition of river water and sea water is analogous, the water is stirred by use of a centrifugal immersion pump, which also feeds the sample, via a tangential flow filter block, housing an acid washed 0.45μm membrane filter, to a continuous flow manifold for colorimetric determination of iron (TPTZ method). The Duffy type experiments had a duration of ten minutes during which detailed time-course measurements were taken and the extent of further removal after 24 hours was monitored In comparison to this, the experiments of Fox & Wofsy (1983) and Hunter & Leonard (1988), had a duration of 180 minutes, and those of Mayer (1982b) had a duration of 360 minutes.

The experiments were carried out using water freshly collected from the zero salinity end of the Tamar river. As soon as possible after collection (30-60 minutes) an experiment using an experimental system basically as described by Duffy (1985) was carried out, with unfiltered river and sea water mixed together to the desired salinity. Subsequent to this an experiment was carried out using one of the discrete methodologies, at the same salinity and using the same batches of river and sea water as in the basic method of Duffy. A series of such experimental couplets was undertaken, at a range of salinities corresponding to various stages of estuarine mixing, with the three discrete methodologies employing discrete sampling being compared with that using continuous sampling. A second series of experiments were then undertaken, again comparing the continuous and discrete methods, but using initial filtration in both cases - to investigate the effect of filtration and also the increased stirring rate between the two methods on the <0.45um iron fraction.

Kinetic modelling of the data obtained from the experiments was carried out using the approaches described in section 3.4

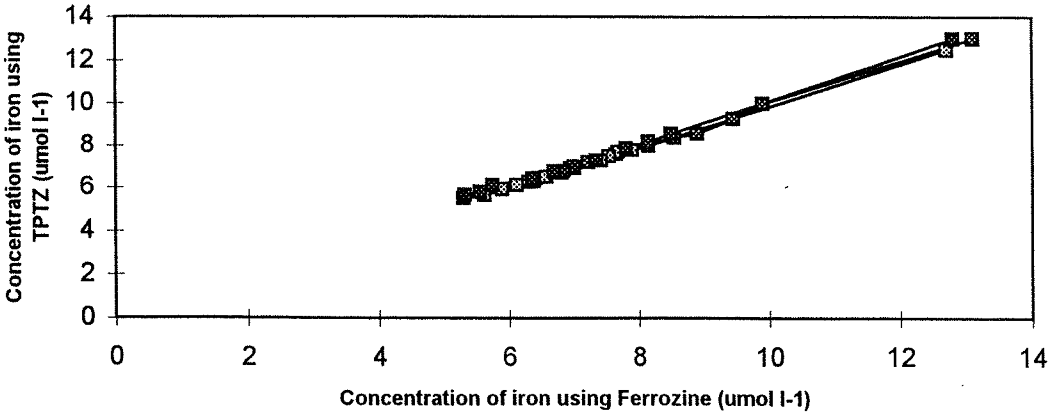
5.2 : Comparison of the Colorimetric Determination of Iron Using Ferrozine and TPTZ

A series of discrete samples of Tamar river water were analysed using both ferrozine and TPTZ, and several simulated estuarine mixing runs were carried out with the manifolds for the two reagents run in parallel. The data collected from the two channels and the iron concentrations recorded is summarised in Table 5.1. Replicate samples showed a high level of consistency between the two analytical techniques, with good precision for each method RSD's of 6% and 7% for the ferrozine and TPTZ methods respectively.

Figure 5.1 shows the 'dissolved' iron concentration measured using the two colorimetric methods and a good 1:1 linear correlation is observed between the values determined by the two separate techniques, correlation coefficient of 0.997 with an intercept of 0.002 on the y axis. This demonstrates that the two methods are measuring the same iron fraction, although this may not necessarily be the total iron fraction.

These results show that there is no analytical factor that would lead to a significant difference between iron concentrations measured in the experiments of Duffy (1985) using TPTZ, in comparison with those measured in the experiments of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) all of whom used ferrozine.

Fig 5.1 Comparison of TPTZ and Ferrozine, for determination of iron.



	Iron Concentration (umol l-1) TPTZ	Iron Concentration (umol l-1) FERROZINE
Run One	12.8	13.0
	8.5	8.6
	8.2	8.2
	7.8	7.9
	7.4	7.3
	7.0	7.0
	6.8	6.8
	6.7	6.8
	6.4	6.4
	5.8	6.1
	5.3	5.6
Run Two	12.7	12.5
	7.9	7.8
	7.7	7.7
	7.5	7.5
	7.4	7.3
	7.0	6.9
	6.6	6.5
	6.3	6.3
	6.1	6.1
	5.9	5.9
	5.3	5.5
Run Three	13.1	13.0
	9.9	10.0
	9.5	9.3
	8.9	8.6
	8.6	8.4
	8.2	8.0
	7.7	7.6
	7.2	7.2
	7.0	6.9
	6.8	6.7
	6.4	6.5
	6.4	6.3

Table 5.1 Comparison of TPTZ and Ferrozine for iron determination.

5.3 : Effect of Batch Mixing Methodology on Removal

In simulated estuarine mixing studies involving the addition of calcium ions, see section 3.3, the calcium ions were of sufficiently high a concentration that on addition the ionic strength was increased without significantly altering the concentration of any of the river water constituents. In experiments using sea water to initiate the destabilisation, however, the volumes used were such that there was significant dilution of the iron and phosphate along with the other river water constituents. This dilution of the concentrations of both iron and phosphate was taken into account before analysis of the data.

5.3.1 Basic Behaviour of Dissolved Iron

Laboratory studies investigating the removal of iron from the <0.45μm fraction during batch mixing estuarine simulations have consistently observed a removal comparable with, and believed to correspond to, that observed in estuaries with a relatively high iron concentration (Boyle 1977, Bale & Morris 1981, Mayer 1982b, Fox and Wofsy 1983, Duffy 1985, Hunter & Leonard 1988).

In all of the experiments carried out in this study, using water from the Tamar river system, the removal of iron from the <0.45 μm fraction begins almost instantaneously on addition of sea water to river water with an initial rapid rate of decrease of the iron in the <0.45um fraction. Differences observed in the behaviour of iron between experiments are considered with respect to the differences in the experimental methodologies employed.

a) Procedure following that of Mayer (1982b).

Simulated estuarine mixing experiments were carried out on Tamar river water using the experimental methodology as outlined by Mayer (1982b), at a salinities of 8.3 and 12, as in the original work using Saco river water.

An initial rapid decrease in the dissolved iron fraction was observed, 14% of the iron was removed after one minute at S = 8, in comparison with 21% removal at S=12. The apparent rate of decrease in iron concentration fell with time as the fraction removed began to level off. The removal reached a plateau level at approximately 36% and 55 % after approximately 100 minutes for salinities of eight and twelve respectively. The fraction removed remained reasonably constant after this time, showing only minor increases until the end of the experiments, with final removal values observed after 360 minutes of 43% at a salinity of 8 and 61% at a salinity of 12.

An increase in the salinity of the solution resulted in a greater initial increase in the removed fraction and a higher final fraction removed at the end of the experiment (six hours). This observation corresponds well with the findings of the experiments using calcium ions in place of sea water.

The data in Table 5.2 give a comparison of the data from the current set of experiments using waters from the Tamar estuary system with the original findings of Mayer (1982b) for the Saco estuary.

	Saco Estuary, Mayer 1982b		**Tamar Estuary, this study**	
Salinity	8.3	12	8	12
Initial Iron Concentration (μmol l^{-1})	70.3	84	13.7	12.2
Final iron Concentration (μmol l^{-1})	18.3	22	7.81	3.2
Initial % Removal	6 (t=13.5min)	30 (t=2min)	14 (t=1min)	21 (t=1min)
% Removal (t=60 min)	40	50	24	40
% Removal (t=180 min)	53	62	36	55
% Removal (t=240 min)	63	69	39	58
% Removal (t=300 min)	62	69	40	61
% Removal (t=360 min)	75	73	43	61

Table 5.2 : Comparison of data from simulated estuarine mixing experiments on Tamar River water following the procedure of Mayer (1982b) with data on the Saco Estuary from the original paper (Mayer, 1982b).

A comparison of the results of this study with those of Mayer's original study are given in Figures 5.2 and 5.3 for experiments carried out at a salinity of 8.3 and 12 respectively.

Figure 5.2 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study) and the Saco (Mayer, 1982) rivers,following the procedure of Mayer (1982), salinity = 8.3

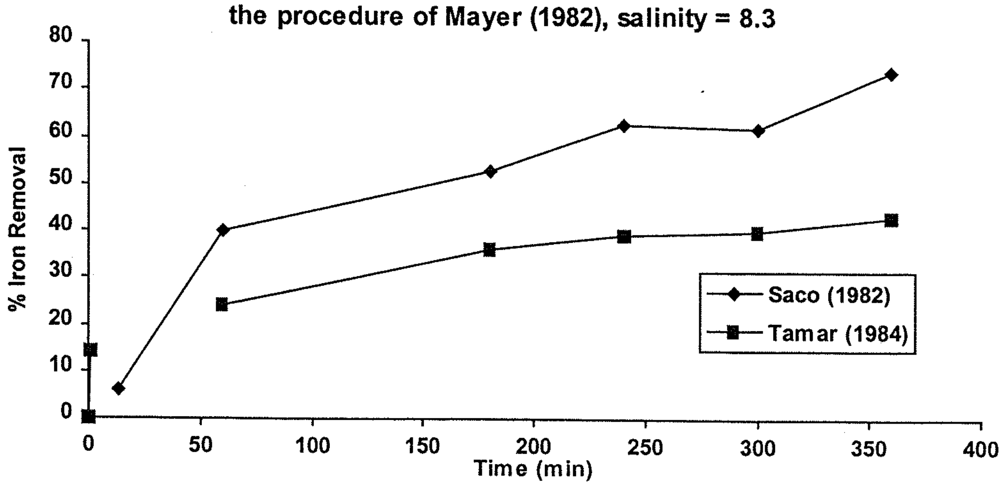
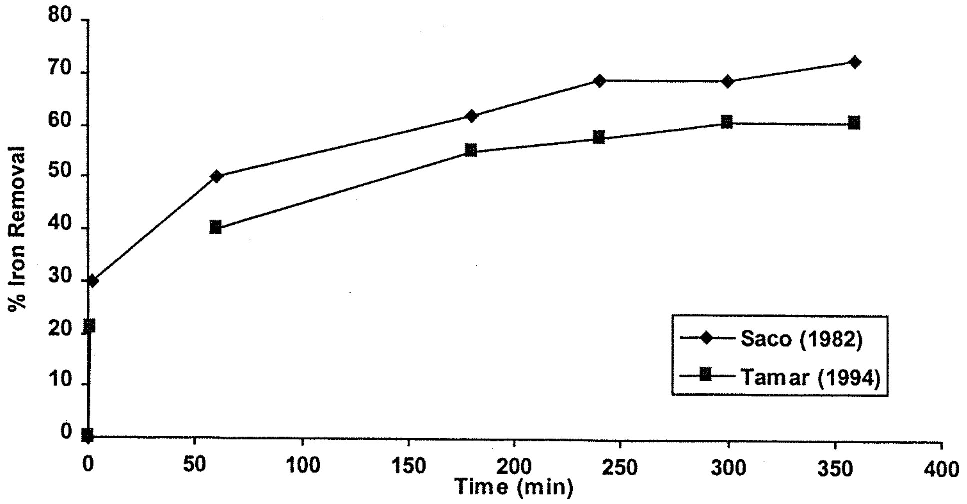


Figure 5.3 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study) and the Saco (Mayer, 1982) rivers, following the procedure of Mayer (1982), salinity = 12.



In the experiments carried out using water from the Tamar system there was an immediate removal of iron on addition of sea water, 14% removal at a salinity of 8 after 1 minute compared with 6% removal after 13.5 minutes for the Saco estuary at a salinity of 8.3. After the rapid initial removal observed for Tamar river water, subsequent removal occurred at a slower rate reaching 30 % after 100 minutes and showing only minor removal after this time. In the experiments carried out by Mayer on the Saco river water, the slow initial removal continued, reaching 40% after the first hour. The percentage removal between one and five hours was greater in experiments using water from the Saco river system than in those using Tamar river water, as the percentage removal began to level off for both sets of experiments. A further significant increase was observed in the experiments using water from the Saco between five and six hours. The experiments carried out at a salinity of 12 showed the same trend, with an immediate increase in iron removal observed for waters from both the Tamar and Saco river systems. After four hours the overall percentage removal was again greater for the Saco river than for the Tamar, with subsequent changes being small in each case. For the Tamar water there was only a small removal after three hours

b) Procedure following that of Fox & Wofsy (1983).

Simulated estuarine mixing experiments were carried out on Tamar river water using the experimental methodology as outlined by Fox and Wofsy (1983), at salinities of 8, 12 and 18, as in the original work on waters from the Broadkill.

On addition of sea water to the river water in the mixing tank a rapid removal of iron from the <0.45μm fraction was observed. The magnitude of this removal was controlled, to some degree, by the overall salinity in the mixing tank, and was seen to increase with increasing salinity; at a salinity of eight, 4% was removed after one minute compared with 9% and 18% respectively for salinities of 12 and 18 after comparable time. The rate of removal decreased with time and at a salinity of 8 or 12 had basically levelled out after 100 minutes with only minor losses observed after this time. In experiments carried out at a salinity of 18 significant removal was still occurring after one hundred minutes. The overall removal of iron at the end of the experiments increased with increasing salinity, in line with observations of section 3.3 and 5.3.1 (a) and those reported in the literature (Boyle (1977), Mayer (1982b), Duffy (1985), Hunter & Leonard (1988)), from 44% at a salinity of 8 to 61% at a salinity of 12 and 72% at a salinity of 18.

The results of the experiments are summarised in Table 5.3 alongside data taken from the original paper of Fox & Wofsy (1983) for the Broadkill, the Mullica and the St Jones estuaries.

As discussed in chapter 1, differences in the extent of removal of iron at intermediate salinities are seen between different estuaries. Estuarine mixing simulations using waters from different estuarine systems have also supported this observation (Boyle (1977), Fox & Wofsy (1983), Duffy (1985), Hunter & Leonard (1988)). The data from the original experiments of Fox & Wofsy(1983) in Table 5.3 show significant differences in behaviour between the Broadkill and St Jones on the one hand and the Mullica estuary on the other, but the experimental removal observed in all three cases showed a similar trend of a slower, more gradual removal persisting throughout the course of the experiment. It is evident from the Table that in the experiments carried out in this study, using water from the Tamar estuary, the early removal is significantly higher, with a substantial fraction removed essentially instantaneously; at a salinity of 8, 4 % of iron in Tamar river water is removed within one minute of mixing and 26% removal was observed after 15 minutes in comparison with only 9% and 12% were removed for the Broadkill and St Jones respectively, by 15 minutes which was the earliest sampling interval from mixing. The Tamar river water showed a comparable fraction of the iron removed to that observed for water from the Broadkill and the St Jones at any comparable time at for experiments with overall salinities of 8 and 12. At a salinity of 18 a greater final removal was observed for the Broadkill waters, 80% removal, than was observed for the Tamar, 72% removal. The data from the experiments using Mullica river water showed a large initial increase when compared with the other experiments of Fox & Wofsy at a salinity of 17, the removal observed being greater than that found using Tamar water at a salinity of 18 with 75% removed after 15 minutes for the Mullica compared with 42% for the Tamar and a final fraction removed (t=180 minutes) of 93% compared with 72% for the Tamar. At a salinity of eight, the initial removal was greater in the Tamar than that observed for the Broadkill, with 26% and 12% removal observed respectively after 15 minutes, but the final removal of iron corresponds with that from experiments at a salinity of 18, with greater removal observed in the Mullica, 73 % as compared with 44% for the Tamar. In the experiments using water from the Mullica estuary system the overall behaviour was similar to that observed in the Broadkill, in that the removal continued over the whole duration of the experiments, before reaching a plateau level. At a salinity of 17 the Mullica data show the removal process to be nearly complete by 90 minutes, the pattern being very similar to the Tamar at a salinity of 18, but with somewhat greater removal at all times that could be compared.

A comparison of the results of this study with those of Fox & Wofsy's original study are given in Figures 5.4, 5.5 and 5.6 for experiments carried out at a salinity of 8, 12 and 18 respectively.

c) Procedure following that of Hunter & Leonard (1988).

Simulated estuarine mixing experiments were carried out on Tamar river water using the experimental methodology as outlined by Hunter & Leonard (1988), at salinities of five and ten and fifteen, as in the original work on waters from the Leith and Taieri rivers. The data from these experiments is summarised in Table 5.4.

Within one minute of the addition of sea water to the mixing tank, a significant proportion of the iron was removed from the <0.45μm fraction, the fraction removed being determined by the overall salinity in the mixing tank; 10% at a salinity of five, 21% at a salinity of ten and 37% removal at a salinity of 15. At a salinity of 5, the rate of iron removal decreased rapidly after the first minute and the removal gradually increased over the following minutes, to 20% after ten minutes, 25% after 30 minutes and 31% after 90 minutes. The subsequent removal was small after this point, with only a further 5% increase observed over the remaining 90 minutes of the experiment. In the experiments carried out at salinities of 10 and 15, the removal of iron that occurred after the first minute was smaller than that occurring within the first minute, the removal rate reached a plateau after approximately ninety minutes, and following this only minor losses were observed for the remainder of the experiments.

	TAMAR (1994)			BROADKILL (1983)			MULLICA (1983)		St. JONES (1983)
Salinity	8	12	18	8	12	18	8	17	12
Initial Iron Concentration (μmol l^{-1})	13.2	11.7	8.8	4.3	3.4	2.9	15.3	?	8.44
Final Iron Concentration (μmol l^{-1})	7.4	4.6	2.46	2.4	1.3	0.6	4.1	?	3.03
% Removal @ t=1 min	4	9	18	------	------	------	------	------	------
% Removal @ t=2.5 min	12	19	20	------	------	------	------	------	------
% Removal @ t=5 min	19	24	22	------	------	------	------	------	------
% Removal @ t=10 min	23	25	30	------	------	------	------	------	------
% Removal @ t=15 min	26	35	42	9	10	40	12	75	16
% Removal @ t=30 min	35	40	48	25	23	52	36	84	23
% Removal @ t=60 min	36	52	50	24	39	64	46	86	43
% Removal @ t=90 min	39	55	54	31	47	72	58	90	51
% Removal @ t=120 min	43	57	60	36	51	71	65	91	59
% Removal @ t= 150min	44	59	68	40	53	78	67	92	62
% Removal @ t=180 min	44	61	72	43	63	80	73	93	64

Table 5.3 : Comparison of data from simulated estuarine mixing experiments on Tamar River water following the procedure of Fox & Wofsy (1983) with data on the Broadkill, Mullica and St Jones Estuaries from the original paper (Fox & Wofsy, 1983).

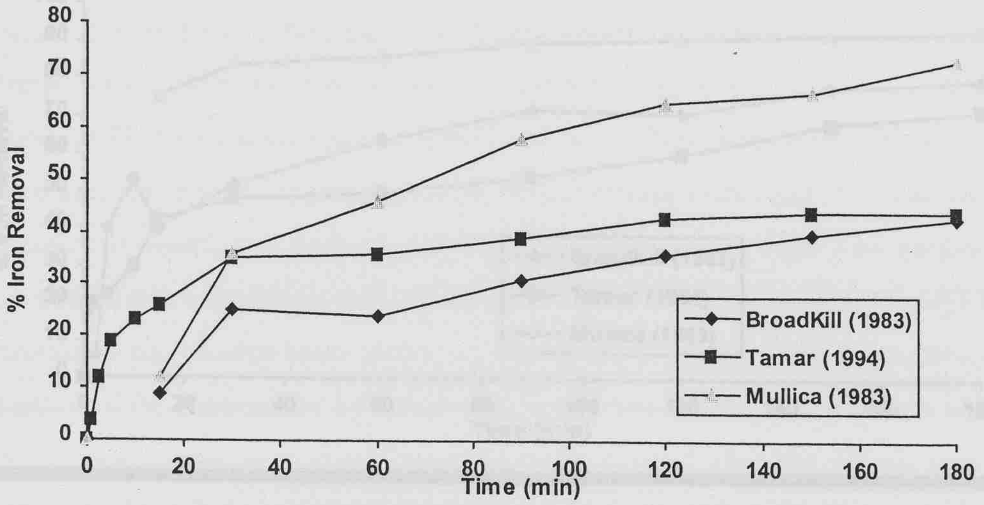


Figure 5.4 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study), Broadkill and the Mullica rivers, following the procedure of Fox & Wofsy (1983), salinity = 8.

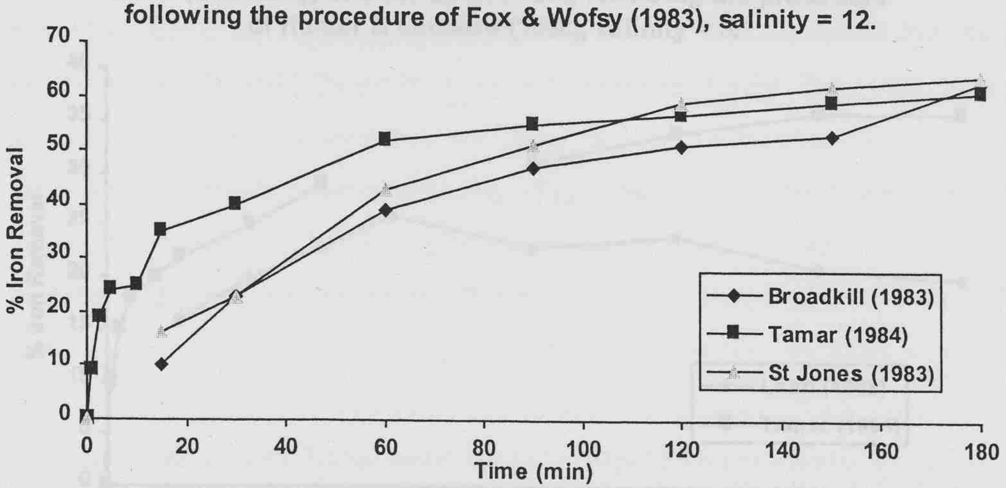


Figure 5.5 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study) the Broadkill, and the St Jones rivers, following the procedure of Fox & Wofsy (1983), salinity = 12.

Figure 5.6: Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study), the Mullica and the Broadkill rivers, following the procedure of Fox & Wofsy (1983), salinity =18.

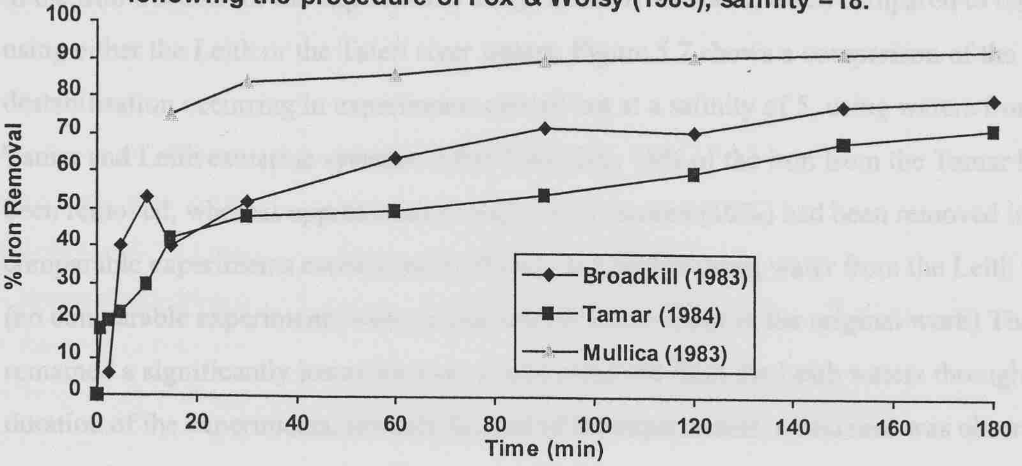
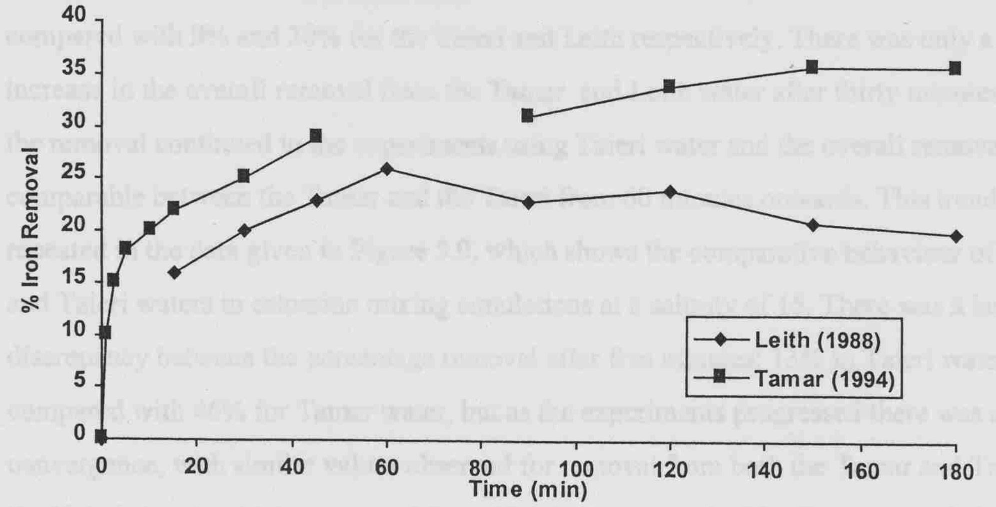


Figure 5.7 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study) and the Leith rivers, following the procedure of Hunter & Leonard (1988), salinity = 5.



In Figures 5.7 to 5.9 the data from the experiments carried out using the experimental methodology of Hunter & Leonard (1988) is compared with the findings from their original paper, on the Leith and Taieri estuaries. In all three of the plots there is a rapid initial decrease in the iron fraction for the experiments using Tamar river water, when compared to those using either the Leith or the Taieri river waters. Figure 5.7 shows a comparison of the destabilisation occurring in experiments carried out at a salinity of 5, using waters from the Tamar and Leith estuarine systems. After 5 minutes, 18% of the iron from the Tamar had been removed, whereas approximately half of that amount (10%) had been removed in comparable experiments carried out by Hunter & Leonard using water from the Leith river (no comparable experiments were carried out on Taieri water in the original work) There remained a significantly lower fraction of iron removed from the Leith waters throughout the duration of the experiments, towards the end of the experiments, a decrease was observed in the iron fraction removed, after 120 minutes 24 % removed, after 180 minutes only 20 % was removed, although this could represent experimental variability rather than a real feature.

Figure 5.8 compares the behaviour of the dissolved iron fraction from the Tamar, the Leith and the Taieri rivers in estuarine mixing simulations carried out with an overall salinity of 10. It is clear that the removal from the Tamar water occurs with a greater initial rate than from either the Leith or the Taieri waters; after five minutes, 45% was removed from the Tamar, compared with 9% and 20% for the Taieri and Leith respectively. There was only a small increase in the overall removal from the Tamar and Leith water after thirty minutes, however the removal continued in the experiments using Taieri water and the overall removal was comparable between the Tamar and the Taieri from 60 minutes onwards. This trend was repeated in the data given in Figure 5.9, which shows the comparative behaviour of Tamar and Taieri waters in estuarine mixing simulations at a salinity of 15. There was a large discrepancy between the percentage removal after five minutes; 13% in Taieri water compared with 46% for Tamar water, but as the experiments progressed there was a convergence, with similar values observed for removal from both the Tamar and Taieri, with the Taieri showing higher removal from 90 minutes onwards. The final removal observed was 71% for the Tamar in comparison with 76% for the Taieri river system.

	TAMAR (1994)			LEITH (1988)		TAIERI (1988)	
Salinity	5	10	15	5	10	10	15
Initial Iron Concentration (μmol l^{-1})	14.7	12.3	9.7	??	??	??	??
Final Iron Concentration	9.4	3.8	2.8	??	??	??	??
% Removal @ t=1 min	10	38	37	------	------	------	------
% Removal @ t=2.5 min	15	43	43	------	------	------	------
% Removal @ t=5 min	18	45	46	10	20	9	13
% Removal @ t=10 min	20	------	48	------	------	------	------
% Removal @ t=15 min	22	51	51	16	27	47	37
% Removal @ t=30 min	25	59	55	20	36	53	50
% Removal @ t=45 min	29	------	------	------	------	------	------
% Removal @ t=60 min	------	61	58	26	40	64	63
% Removal @ t=90 min	31	64	67	23	43	65	65
% Removal @ t=120 min	34	65	69	24	42	66	72
% Removal @ t=150 min	36	68	69	21	48	70	76
% Removal @ t=180 min	36	69	71	20	45	71	76

Table 5.4 : Comparison of data from simulated estuarine mixing experiments on Tamar River water following the procedure of Hunter & Leonard (1983) with data on the Leith and Taieri Estuaries from the original paper (Hunter & Leonard, 1988).

Figure 5.8 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study), Leith and the Taieri rivers, following the procedure of Hunter & Leonard (1988), salinity =10.

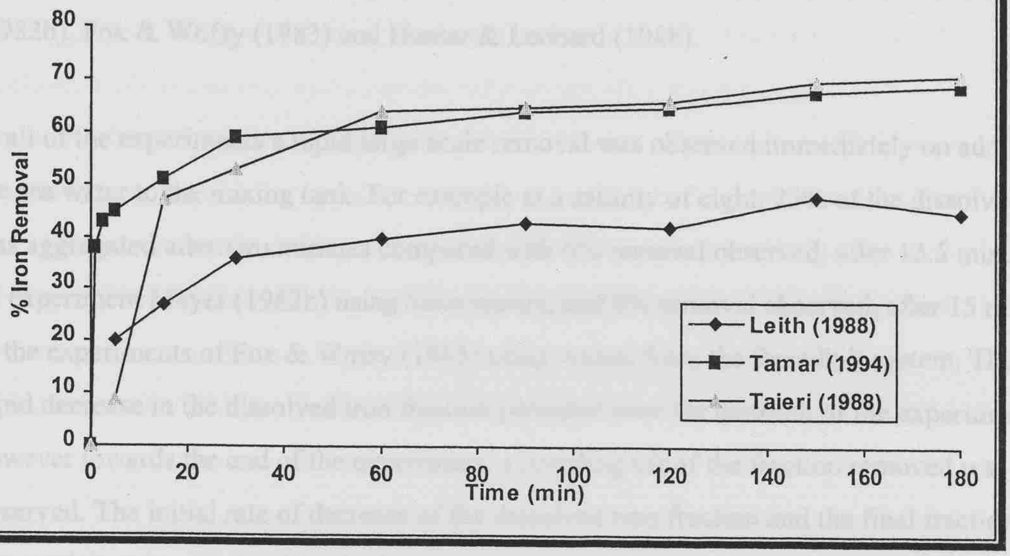
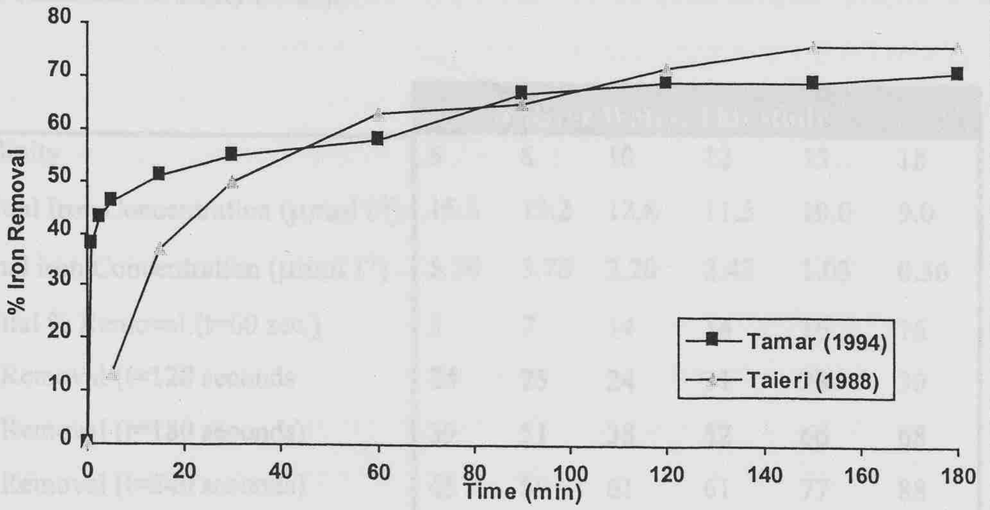


Figure 5.9 : Comparison of the fraction of iron removed during simulated estuarine mixing experiments using water from the Tamar (this study), and the Taieri rivers, following the procedure of Hunter & Leonard (1988), salinity =15.



d) Procedure following that of Duffy (1985).

Simulated estuarine mixing experiments were carried out on Tamar river water using the experimental methodology as outlined by Duffy (1985) and used in section three of this study, at salinities of 5, 8, 10, 12, 15, and 18 covering the salinities used in the work of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988).

In all of the experiments a rapid large scale removal was observed immediately on addition of the sea water to the mixing tank. For example at a salinity of eight, 25% of the dissolved iron was aggregated after two minutes compared with 6% removal observed, after 13.5 minutes, in an experiment Mayer (1982b) using Saco waters, and 9% removal observed, after 15 minutes, in the experiments of Fox & Wofsy (1983) using waters from the Broadkill system. This rapid decrease in the dissolved iron fraction persisted over the duration of the experiments, however towards the end of the experiment, a levelling off of the fraction removed was observed. The initial rate of decrease of the dissolved iron fraction and the final fraction removed were seen to be directly dependant upon the salinity of the mixing experiment. In experiments carried out at salinities of five, ten and fifteen the fraction of iron remaining at the end of the experiments, after ten minutes, was observed to be 35%, 25% and 11% respectively. Table 5.5 shows the data from the complete set of experiments carried out using the conditions of Duffy (1985).

	Tamar River Water, This study					
Salinity	5	8	10	12	15	18
Initial Iron Concentration (μmol l^{-1})	15.3	13.2	12.8	11.5	10.0	9.0
Final iron Concentration (μmol l^{-1})	5.36	3.78	3.20	2.42	1.03	0.36
Initial % Removal (t=60 sec.)	5	7	14	14	16	16
% Removal (t=120 seconds	24	25	24	31	28	30
% Removal (t=180 seconds)	39	51	38	52	66	68
% Removal (t=240 seconds)	45	59	61	61	77	88
% Removal (t=300 seconds)	60	67	65	67	83	92
Final % Removal (t=600 seconds)	65	72	75	79	89	96

Table 5.5 : Data from simulated mixing experimeriments on Tamar River water, following the procedure of Duffy (1985).

e) Comparison of the experimental procedures.

A discussed in section 2.4 and 5.1, the experimental procedures group into 'discrete' and 'continuous' sampling, however the important difference is in the mechanics of mixing and sampling. The procedure of Duffy (1985) was designed to enable the progress of the reaction to be examined with much greater resolution and therefore to obtain a more detailed evaluation of the kinetics, including the early period after mixing.
For each of the experimental methodologies, the amount of iron removal decreased with time, and the concentration after approximately 10 minutes under the conditions of Duffy (1985), and after approximately 100 minutes in the experiments carried out using the methodologies of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) the fraction of iron remaining had reached a residual level. In all of the experiments, the concentration of iron remaining in the <0.45um fraction after the duration of the experiments was found to be inversely proportional to the overall salinity of the solution.

It is apparent that the experiments using the three procedures that employ discrete sampling procedures, Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988), whilst not showing identical behaviour, do show comparable rates of iron removal and also a similar fraction aggregated in experiments at the same salinity, in contrast to the experiments using the continuous sampling method of Duffy (1985). Of the three 'discrete' methods it appears that using Mayer's procedure experiments show the least removal at a given salinity. The results in Figure 5.10, for a salinity of eight show that after 180 minutes the fraction of iron aggregated under the conditions of used by Fox & Wofsy was 44% compared with 36% when Mayer's conditions were used. The data in Figure 5.11 for a salinity of 12 show once more that the smallest fraction aggregated is found under the conditions used by Mayer, with 55% aggregated after 180 minutes compared with 61% when the conditions of Fox & Wofsy were used. The data from the experiments using the conditions of Hunter & Leonard, in the same Figure, showed that a greater fraction, 69% was aggregated at a salinity of 10 than for experiments carried out using the conditions of either Fox & Wofsy or Mayer. In Figure 5.12 this trend is again illustrated as experiments carried out at a salinity of 15 under the conditions of Hunter & Leonard showed an almost identical removal profile to those carried out using the conditions of Fox & Wofsy at a salinity of 18, with a removal after 180 minutes of 71% and 72% respectively. A comparison at a constant salinity gives an order of increasing aggregation for the three methods using discrete sampling as follows:

Mayer < Fox & Wofsy < Hunter & Leonard

It was immediately apparent using the conditions of Duffy (1985), that the overall removal observed at a given salinity takes place on a significantly faster timescale by comparison with those observed for the methodologies of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) and the final fraction aggregated was of a greater magnitude. The overall fraction removed at a given salinity is greater in the experiments using the method of Duffy (1985) at all of the salinities as illustrated in Table 5.6

	Tamar River Water, This study					
Salinity	5	8	10	12	15	18
Final % Removal, Duffy (1985) Methodology	65	72	75	79	89	96
Final % Removal, Mayer (1982b) Methodology	N/A	36	N/A	55	N/A	N/A
Final % Removal, Fox & Wofsy (1983)Methodology	N/A	44	N/A	61	N/A	72
Final % Removal, Hunter & Leonard (1988) Methodology	36	N/A	69	N/A	71	N/A

Table 5.6 : Influence of salinity on the removal of iron from Tamar River water during simulated estuarine mixing, for each of the methodologies studied : Mayer (1982b); Fox & Wofsy (1983); Duffy (1985) and Humter & Leonard (1988).

5.3.2 Basic Behaviour of Phosphate

In the works of the original authors from which the experimental methodologies were taken phosphate behaviour was not studied and all the data to be considered come from the present study. Table 5.7 gives a summary of the behaviour of phosphate in the series of estuarine mixing simulations using sea water.

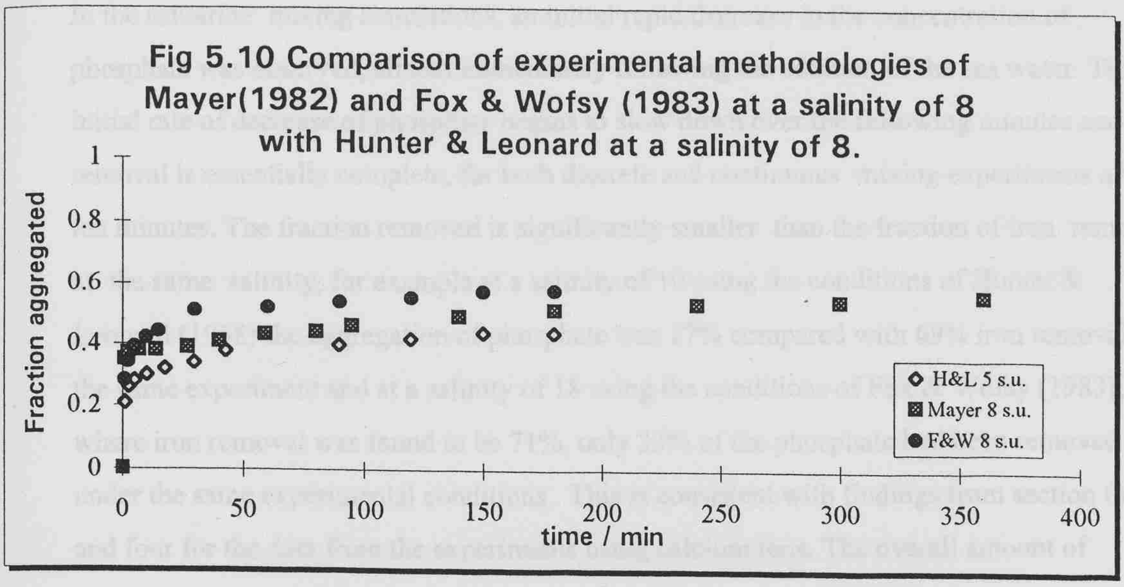


Fig 5.10 Comparison of experimental methodologies of Mayer(1982) and Fox & Wofsy (1983) at a salinity of 8 with Hunter & Leonard at a salinity of 8.

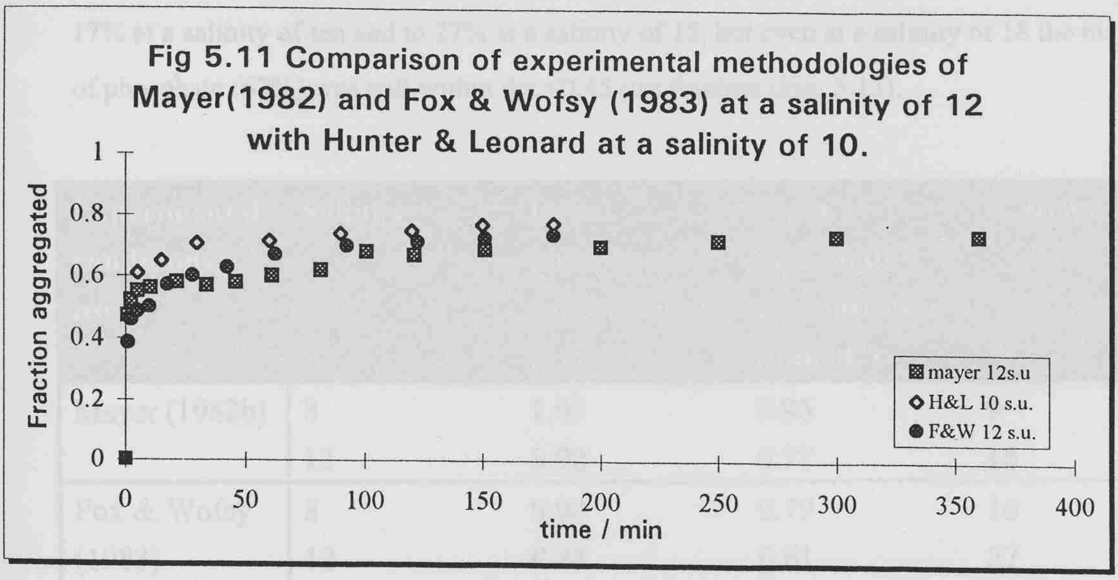


Fig 5.11 Comparison of experimental methodologies of Mayer(1982) and Fox & Wofsy (1983) at a salinity of 12 with Hunter & Leonard at a salinity of 10.

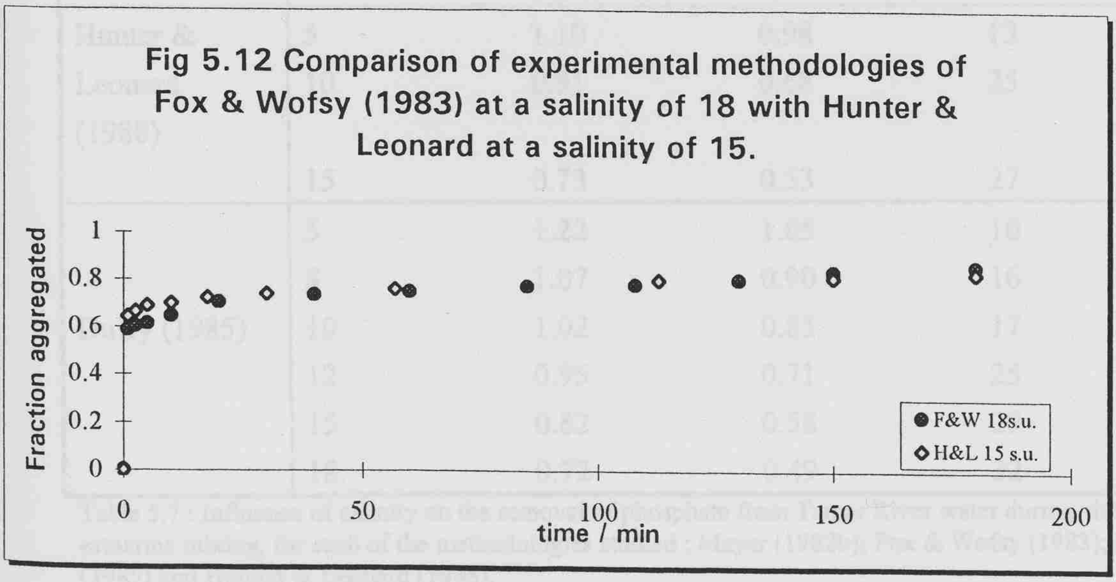


Fig 5.12 Comparison of experimental methodologies of Fox & Wofsy (1983) at a salinity of 18 with Hunter & Leonard at a salinity of 15.

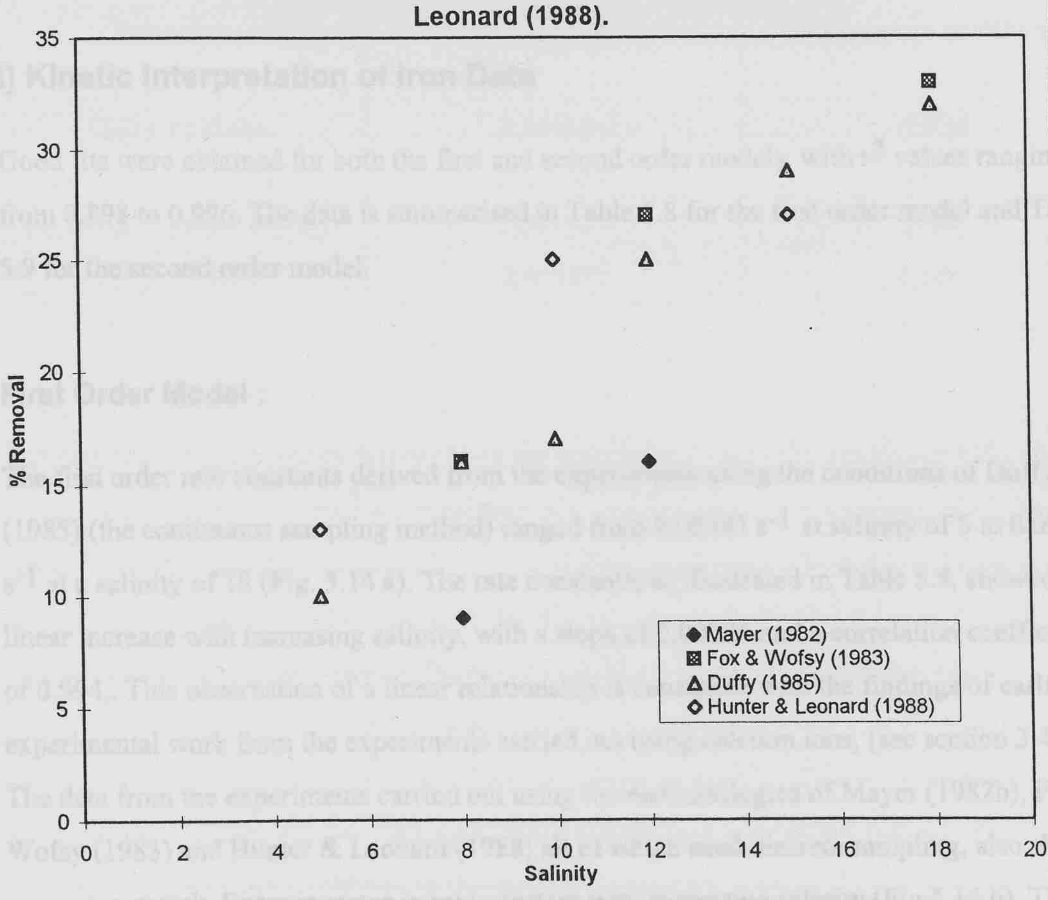
In the estuarine mixing simulations, an initial rapid decrease in the concentration of phosphate was observed, almost immediately following the addition of the sea water. This initial rate of decrease of phosphate begins to slow down over the following minutes and the removal is essentially complete, for both discrete and continuous mixing experiments after ten minutes. The fraction removed is significantly smaller than the fraction of iron removed at the same salinity, for example at a salinity of 10 using the conditions of Hunter & Leonard (1988) the aggregation of phosphate was 17% compared with 69% iron removal in the same experiment and at a salinity of 18 using the conditions of Fox & Wofsy (1983), where iron removal was found to be 71%, only 33% of the phosphate had been removed under the same experimental conditions. This is consistent with findings from section three and four for the data from the experiments using calcium ions. The overall amount of phosphate aggregated increases with increasing salinity, from 13% at a salinity of five, to 17% at a salinity of ten and to 27% at a salinity of 15, but even at a salinity of 18 the majority of phosphate (67%) was still within the <0.45 µm fraction (Fig. 5.13).

Experimental conditions used	**Salinity**	**Initial phosphate concentration (µmol l^{-1})**	**Final phosphate concentration (µmol l^{-1})**	**% Removal**
Mayer (1982b)	8	1.05	0.96	9
	12	0.92	0.77	16
Fox & Wofsy (1983)	8	0.94	0.79	16
	12	0.83	0.61	27
	18	0.63	0.42	33
Hunter & Leonard (1988)	5	1.10	0.98	13
	10	0.91	0.68	25
	15	0.73	0.53	27
Duffy (1985)	5	1.22	1.05	10
	8	1.07	0.90	16
	10	1.02	0.85	17
	12	0.95	0.71	25
	15	0.82	0.58	29
	18	0.72	0.49	32

Table 5.7 : Influence of salinity on the removal of phosphate from Tamar River water during simulated estuarine mixing, for each of the methodologies studied : Mayer (1982b); Fox & Wofsy (1983); Duffy (1985) and Humter & Leonard (1988).

It was evident from the data that, contrary to the findings for the iron fraction, a comparison of the behaviour of phosphate between the discrete and the continuous mixing experiments showed similar findings for the two methods. It is therefore possible that the removal of the iron during the 'discrete' procedures corresponds only to a removal of that fraction of iron which is associated with the phosphate. Whatever process causes the increased rate and extent of removal of iron in the continuous experiments, has no obvious effect on the behaviour of phosphate.

Fig. 5.13 Final % removal of phosphate from Tamar River Water during simulated estuarine mixing following the procedures of Mayer (1982), Fox & Wofsy (1983), Duffy (1985) and Hunter & Leonard (1988).



5.3.3 Kinetic Interpretation of the Iron and Phosphate Data from Mixing Experiments

The results of the experiments described in sections 5.3.1 and 5.3.2 have been examined for their fit to both the first and second order kinetic models, taking into account the unreactive iron or phosphate fractions. This treatment used equations (3) and (4) and a fuller discussion of the approach has been given in section 3.4. This analysis of the kinetics has been carried out on the data obtained in the present comparative experiments using the different procedures and on data extracted from the original papers.

i) Kinetic Interpretation of Iron Data

Good fits were obtained for both the first and second order models, with r^2 values ranging from 0.898 to 0.996. The data is summarised in Table 5.8 for the first order model and Table 5.9 for the second order model.

First Order Model :

The first order rate constants derived from the experiments using the conditions of Duffy (1985) (the continuous sampling method) ranged from 0.00397 s^{-1} at salinity of 5 to 0.00695 s^{-1} at a salinity of 18 (Fig. 5.14 a). The rate constants, as illustrated in Table 5.8, showed a linear increase with increasing salinity, with a slope of 0.00026 and a correlation coefficient of 0.994,. This observation of a linear relationship is consistent with the findings of earlier experimental work from the experiments carried out using calcium ions, (see section 3.4.) The data from the experiments carried out using the methodologies of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) all of which used discrete sampling, also showed an approximately linear increase in rate constant with increasing salinity (Fig 5.14 b). The experiments using the conditions of Mayer (1982b) showed an increase in first order rate constant from $1.97*10^{-4}$ s^{-1} at a salinity of eight to $3.4*10^{-4}$ s^{-1} at a salinity of 12, with a gradient of $2.7*10^{-5}$, and a correlation coefficient 0.934. The experiments using the conditions of Fox & Wofsy (1983) showed an increase in first order rate constant from $1.92*10^{-4}$ s^{-1} at a salinity of 8 to $4.54*10^{-4}$ s^{-1} at a salinity of 18, with a correlation coefficient of 0.89 and a gradient of $2.54*10^{-5}$ s^{-1}. The experiments using the conditions of Hunter & Leonard (1988) showed an increase in first order rate constant from $1.97*10^{-4}$ s^{-1} at a salinity of five to $4.01*10^{-4}$ s^{-1} at a salinity of 15, with a correlation coefficient of 0.84

and a gradient of 0.204. Figures 5.14 a) and b) illustrates these changes in first order rate constant with increasing salinity. The values calculated for the data from the experiments using the conditions of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) all gave very similar values. The values for the first order rate constant were an order of magnitude lower than those derived from the experiments using the method of Duffy (1985). The values predicted by the model for the residual iron concentration were lower than those observed at the end of the experiments, but were similar in magnitude. The gradient of best fit lines for the four data sets illustrated in Figures 5.14 a) and b) were :

Procedure	Gradient	Correlation coefficient
Mayer (1982b)	$2.70*10^{-5}$	0.934
Fox & Wofsy (1983)	$2.54*10^{-5}$	0.890
Hunter & Leonard (1988)	$2.04*10^{-5}$	0.843
Duffy (1985)	$2.6*10^{-4}$	0.994

The first order rate constants derived from the experiments using the conditions of Duffy (1985) ranged from $3.97*10^{-3}$ s-1 at salinity of 5 to $6.95*10^{-3}$ s-1 at a salinity of 18. The results compare with the calculated first order rate constant ranged from experiments using calcium ions (Chapter 3) which gave results of $4.70*10^{-4}$ to $6.45*10^{-3}$ s^{-1} over the range of calcium ion concentrations used in the current estuarine simulations. Calcium ion concentrations equivalent to those found at salinities of approximately 5 to 35 were used in the experiments carried out in chapter three, in comparison with salinities ranging from 5 to 18 in the current experiments. This wider range of salinities is reflected in the wider range of first order rate constants observed in the earlier experiments. Values of the first order rate constants were greater for the experiments using sea water than for experiments carried out at a concentration of calcium ions, 6.95 $*10^{-3}$ s^{-1} a salinity of 18 compared with 1.95 to 6.45 $*10^{-3}$ s^{-1} at a calcium ion concentration of 0.0056 mol l^{-1}.

Experimental conditions used	Salinity	Initial iron concentration µmol l^{-1}	Final iron concentration µmol l^{-1}	Residual iron concentration µmol l^{-1}	1st order rate constant s^{-1}	Correlation coefficient
Mayer (1982b)	8	13.7	7.8	7.10	$1.97*10^{-4}$	0.952
	12	12.2	4.8	4.62	$3.4*10^{-4}$	0.963
Fox & Wofsy (1983)	8	13.2	7.37	6.98	$1.92*10^{-4}$	0.990
	12	11.7	4.56	3.32	$3.57*10^{-4}$	0.966
	18	8.8	2.46	2.32	$4.54*10^{-4}$	0.986
Hunter & Leonard (1988)	5	14.7	9.38	8.86	$1.97*10^{-4}$	0.983
	10	12.3	3.82	3.31	$3.67*10^{-4}$	0.976
	15	9.7	2.81	2.65	$4.01*10^{-4}$	0.998
Duffy (1985)	5	15.3	5.36	5.08	$3.97*10^{-3}$	0.968
	8	13.2	3.73	3.56	$4.53*10^{-3}$	0.995
	10	12.8	3.22	2.87	$5.05*10^{-3}$	0.983
	12	11.5	2.42	2.21	$5.59*10^{-3}$	0.978
	15	10.0	1.03	0	$6.36*10^{-3}$	0.993
	18	9.0	0.36	0	$6.95*10^{-3}$	0.992

Table 5.8 : First order modelling of simulated estuarine iron behaviour, showing influence of salinity on iron removal, predicted residual iron concentration and first order rate constant following the procedures of Mayer (1982b); Fox & Wofsy (1983); Duffy (1985) and Humter & Leonard (1988).

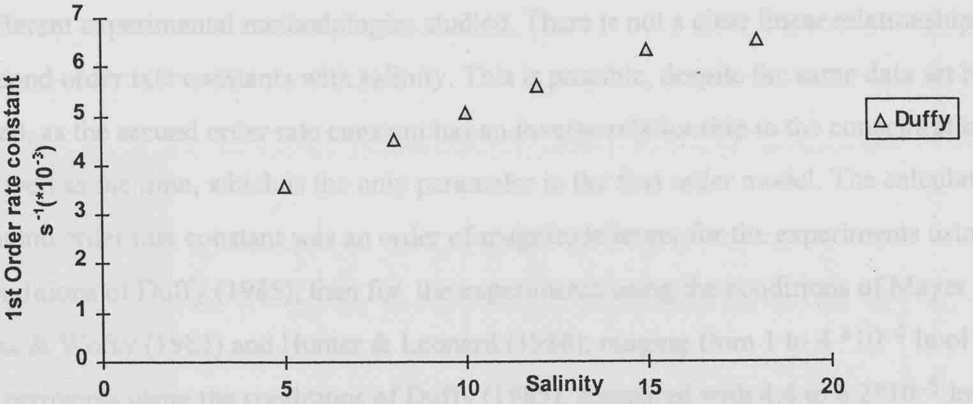


Figure 5.14 a) : Effect of salinity on first order rate constant for iron removal, following procedure of Duffy (1985).

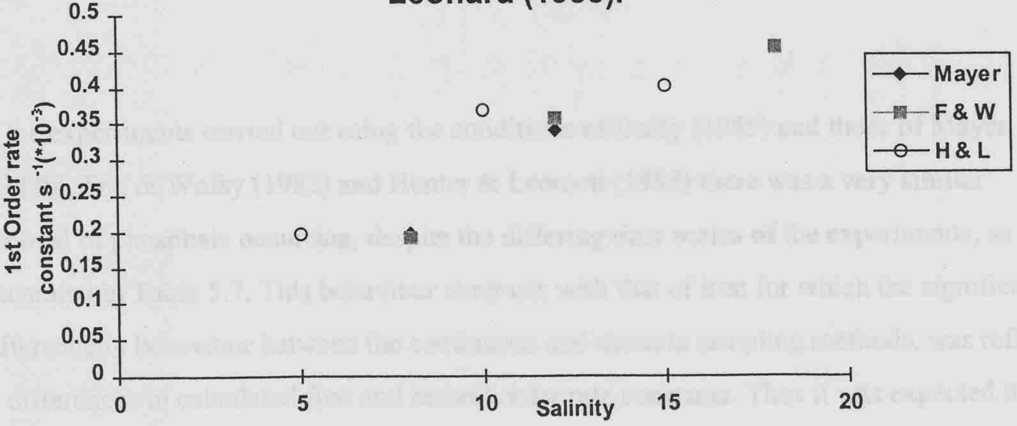


Figure 5.14 b) : Effect of salinity on first order rate constant for iron removal, following procedures of Mayer (1982), Fox & Wofsy (1983) and Hunter & Leonard (1988).

Second Order Model :

Table 5.9 shows the variation in second order rate constants with increasing salinity for the different experimental methodologies studied. There is not a clear linear relationship of second order rate constants with salinity. This is possible, despite the same data set being used, as the second order rate constant has an inverse relationship to the concentration of iron as well as the time, which is the only parameter in the first order model. The calculated second order rate constant was an order of magnitude larger for the experiments using the conditions of Duffy (1985), than for the experiments using the conditions of Mayer (1982b); Fox & Wofsy (1983) and Hunter & Leonard (1988); ranging from 1 to 4 $*10^{-4}$ $lmol^{-1}$ s^{-1} for experiments using the conditions of Duffy (1985), compared with 4.4 to $6.2*10^{-5}$ $lmol^{-1}$ s^{-1} for conditions of Mayer (1982b); 4.5 to $10.4*10^{-5}$ $lmol^{-1}$ s^{-1} for experiments using conditions of Fox & Wofsy (1983) and 1.4 to $20.0*10^{-5}$ $lmol^{-1}$ s^{-1} for the experiments using the conditions of Hunter & Leonard (1988).

The residual concentration of iron predicted for the experiments was found to be zero for a number of the experimental runs, and was consistently lower than the value predicted by the first order model and that actually observed.

ii) Kinetic Interpretation of Phosphate data

In the experiments carried out using the conditions of Duffy (1985) and those of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) there was a very similar removal of phosphate occurring, despite the differing time scales of the experiments, as illustrated in Table 5.7. This behaviour contrasts with that of iron for which the significant difference in behaviour between the continuous and discrete sampling methods, was reflected in differences in calculated first and second order rate constants. Thus it was expected that the kinetic rate constants from the two methods would be comparable between the different experimental methods employed. The data sets gave a reasonably good fit the first order kinetic model, r^2 values ranging from 0.906 to 0.980, and also to a lesser degree for the second order model with r^2 values ranging from 0.796 to 0.970.

Experimental conditions used	Salinity	Initial iron concentration	Final iron concentration (μmol l^{-1})	Residual iron concentration (μmol l^{-1})	2nd order rate constant $lmol^{-1}$ s^{-1}	Correlation coefficient
Mayer (1982b)	8	13.7	7.8	5.9	$6.2*10^{-5}$	0.988
	12	12.2	4.8	3.2	$4.4*10^{-5}$	0.962
Fox & Wofsy (1983)	8	13.2	7.37	5.5	$4.54*10^{-5}$	0.962
	12	11.7	4.56	3.04	$10.4*10^{-5}$	0.954
	18	8.8	2.46	0	$5.4*10^{-5}$	0.898
Hunter & Leonard (1988)	5	14.7	9.38	8.20	$4.9*10^{-5}$	0.906
	10	12.3	3.82	2.77	$1.4*10^{-5}$	0.991
	15	9.7	2.81	0	$19.9*10^{-5}$	0.941
Duffy (1985)	5	15.3	5.36	4.59	$1.1*10^{-4}$	0.984
	8	13.2	3.73	2.78	$3.5*10^{-4}$	0.978
	10	12.8	3.22	0	$3.9*10^{-4}$	0.932
	12	11.5	2.42	0	$4.3*10^{-4}$	0.911
	15	10.0	1.03	0	$2.0*10^{-4}$	0.965
	18	9.0	0.36	0	$1.2*10^{-4}$	0.971

Table 5.9 : Second order modelling of simulated estuarine iron behaviour, showing influence of salinity on iron removal, predicted residual iron concentration and second order rate constant following the procedures of Mayer (1982b); Fox & Wofsy (1983); Duffy (1985) and Humter & Leonard (1988).

First Order Model :

The first order rate constants for both continuous (Duffy 1985) and discrete sampling methods (Mayer, 1982b; Fox & Wofsy, 1983 and Hunter & Leonard, 1988) showed a similar linear incremental increase in rate constant with increasing salinity (Fig. 5.15). The data in Table 5.10 shows both the similarities between the rate constants and also the increase in rate constant shown with increasing salinity for all four experimental methodologies under examination. Values ranged from 0.0084 to 0.035 s^{-1} using the conditions of Duffy (1985) at salinities of 5 and 18 respectively, as compared to values ranging from 0.0076 s^{-1} at a salinity of eight to 0.0173 s^{-1} at a salinity of twelve using the conditions of Mayer (1982b); 0.0080 s^{-1} at a salinity of eight to 0.0361 s^{-1} at a salinity eighteen using the conditions of Fox and Wofsy (1983) and from 0.0082 s^{-1} at a salinity of five to 0.035 s^{-1} at a salinity of fifteen, using the conditions of Hunter & Leonard (1988).

The gradient of best fit lines, as illustrated in Figure 5.15, for the four data sets were : Mayer (1982b) method gradient 0.0025 s^{-1}, correlation coefficient 1, Fox & Wofsy (1983) method, gradient 0.0027 s^{-1}, correlation coefficient 0.867; Duffy (1985) method, gradient 0.0022 s^{-1}, correlation coefficient 0.967; and Hunter & Leonard (1988) method, gradient 0.0027 s^{-1}, correlation coefficient 0.979. This confirms the observations witnessed in the phosphate removal profiles, that removal of phosphate appears to be independent of the differences in experimental methodologies. The process takes place in the same manner, and with both the same rate of decrease and the same overall destabilisation and aggregation occurring for a given experimental salinity. This behaviour is in marked contrast to that of iron, which exhibited major behavioural differences between procedures in the two categories.

This leads to the theory that there are two distinct fractions within the <0.45 μm iron, as discussed in Kraepiel (1997), a dispersed iron oxide and an organic macromolecule containing fraction. It is possible that in some rivers, there may be some truly dissolved iron associated with the organic macromolecules as well as the majority in the iron oxide form. The observations show that the majority of phosphate removed may be associated only with that fraction of iron removed during the discrete experiments.

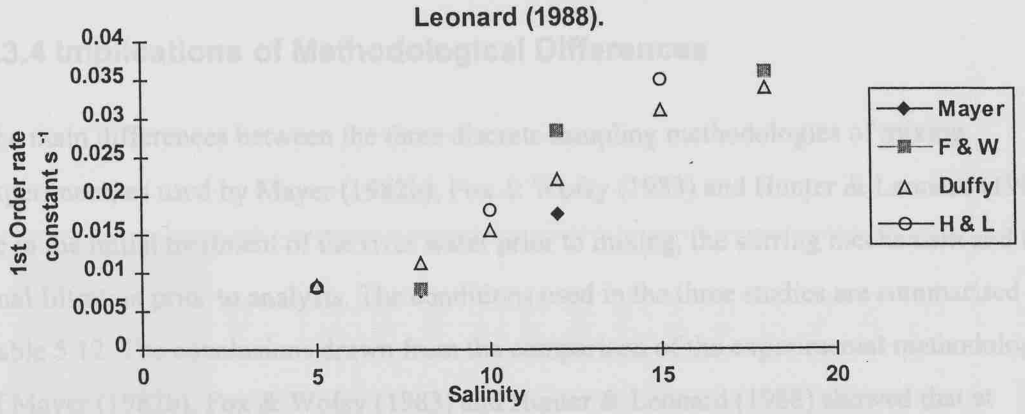


Figure 5.15 : Effect of salinity on first order rate constant for phosphate removal, following procedure of Mayer (1982), Fox & Wofsy (1983), Duffy (1985) and Hunter & Leonard (1988).

The first order rate constants in this set of experiments using sea water ranged from 0.76 to $3.4*10^{-2}$ s^{-1} between salinities of 5 and 18. The experiments carried out using calcium ions to initiate removal in the Duffy method, chapter 4, gave a range of first order rate constants between 0.26 to $1.79*10^{-2}$ s^{-1} .The value of the first order rate constants were greater for the experiments using sea water than for experiments carried out at a comparable ionic strength of calcium ions, $3.4 *10^{-2}$ s^{-1} for the Duffy methodology and $3.61 *10^{-2}$ s^{-1} for the method of Fox & Wofsy, at a salinity of 18 compared with the range of 0.58 to $1.55 *10^{-2}$ s^{-1} at a calcium ion concentration of 0.0056 mol l^{-1}.

Second Order Model :

Table 5.11 shows the data of calculated second order rate constant with increasing salinity for the four different experimental methods. The second order rate constants do not show a well defined pattern as was exhibited by the first order rate constants. There is again a trend of increasing rate constant with an increase in salinity, with the values obtained using the continuous sampling method ranging from 0.0036 at a salinity of 5 to 0.0737 lmol l^{-1} s^{-1} at a salinity of 15 and those obtained using the discrete sampling method changed from 0.0014 to 0.385 lmol l^{-1} s^{-1} over the same range of salinities. The second order rate constants for the discrete sampling method show a less clear variation with salinity than for the continuous method samples which approximate a linear increase. ($r^2 = 0.634$, slope = 0.000434). The second order rate constants for phosphate are two orders of magnitude greater than those for iron - due to the effects of different concentrations of the two constituents in the river water, (as K2 is inversely dependent upon the concentration).

5.3.4 Implications of Methodological Differences

The main differences between the three discrete sampling methodologies of mixing experiment, as used by Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) lie in the initial treatment of the river water prior to mixing, the stirring mechanism and the final filtration prior to analysis. The conditions used in the three studies are summarised in Table 5.12. The conclusions drawn from the comparison of the experimental methodologies of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) showed that at comparable salinities, the fraction of iron removed from the <0.45 μm fraction increased in the order :

Mayer < Fox & Wofsy < Hunter & Leonard

In the light of the differences in experimental methodology presented in Table 5.12, it is possible to examine possible reasons for the differing extents of removal observed.

Experimental methodology	Pre-experimental filtering	Stirring mechanism	Pre-analysis filtration
Mayer (1982b)	Filtered river and sea water	Reciprocating shaker	Gelman A/E 8.0μm filters underlain by Whatman GF/F, equivalent pore size 0.5μm
Fox & Wofsy (1983)	Unfiltered river water, filtered sea water	Magnetic stirrer	Whatman GF/C filters nominal pore size 1.2μm
Hunter & Leonard (1988)	Unfiltered river and sea water	Glass paddle	Whatman GF/C filters nominal pore size 1.2μm

Table 5.12 : Comparison of the experimental conditions of the procedures of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988).

Experimental conditions used	Salinity	Initial phosphate concentration (μmol l^{-1})	Final phosphate concentration (μmol l^{-1})	Residual phosphate concentration (μmol l^{-1})	1st order rate constant s^{-1}	Correlation coefficient
Mayer (1982b)	8	1.05	0.96	0.95	0.0076	0.906
	12	0.92	0.77	0.72	0.0177	0.949
Fox & Wofsy (1983)	8	0.94	0.79	0.80	0.0080	0.978
	12	0.83	0.61	0.51	0.0285	0.965
	18	0.63	0.42	0.37	0.0361	0.965
Hunter & Leonard (1988)	5	1.10	0.98	0.96	0.0082	0.953
	10	0.91	0.68	0.64	0.0182	0.942
	15	0.73	0.53	0.44	0.035	0.948
Duffy (1985)	5	1.22	1.05	0.93	0.0084	0.969
	8	1.07	0.90	0.81	0.0115	0.980
	10	1.02	0.85	0.84	0.0154	0.935
	12	0.95	0.71	0.66	0.0221	0.962
	15	0.82	0.58	0.57	0.031	0.955
	18	0.72	0.49	0.46	0.034	0.919

Table 5.10 : First order modelling of simulated estuarine phosphate behaviour, showing influence of salinity on phosphate removal, predicted residual phosphate concentration and first order rate constant following the procedures of Mayer (1982b); Fox & Wofsy (1983); Duffy (1985) and Humter & Leonard (1988).

Experimental conditions used	Salinity	Initial phosphate concentration (μmol l^{-1})	Final phosphate concentration (μmol l^{-1})	Residual phosphate concentration (μmol l^{-1})	2nd order rate constant $lmol^{-1}s^{-1}$	Correlation coefficient
Mayer (1982b)	8	1.05	0.96	0.95	0.385	0.946
	12	0.92	0.77	0.72	0.188	0.907
Fox & Wofsy (1983)	8	0.94	0.79	0.80	0.231	0.912
	12	0.83	0.61	0.51	0.202	0.796
	18	0.63	0.42	0.37	0.149	0.904
Hunter & Leonard (1988)	5	1.10	0.98	0.96	0.0167	0.892
	10	0.91	0.68	0.64	0.00036	0.918
	15	0.73	0.53	0.44	0.051	0.944
Duffy (1985)	5	1.22	1.05	0.93	0.037	0.943
	8	1.07	0.90	0.81	0.074	0.939
	10	1.02	0.85	0.84	0.035	0.928
	12	0.95	0.71	0.66	0.113	0.968
	15	0.82	0.58	0.57	0.0049	0.952
	18	0.72	0.49	0.46	0.135	0.970

Table 5.11 : Second order modelling of simulated estuarine phosphate behaviour, showing influence of salinity on phosphate removal, predicted residual iron concentration and second order rate constant following the procedures of Mayer (1982b); Fox & Wofsy (1983); Duffy (1985) and Humter & Leonard (1988).

When the differences are considered in terms of the stirring rate the major feature is that the experiments of Mayer (1982b), used a shaking Table inducing a gentle shaking regime whereas those carried out by Fox and Wofsy (1983), utilising a magnetic stirrer and by Hunter & Leonard (1988) using a glass paddle employed relatively vigorous mixing. Thus, as observed in the work of Mayer, the removal of a comparably larger iron fraction in the experiments of Fox & Wofsy and Hunter & Leonard than that observed in the experiments of Mayer can be possibly explained as a result of this more vigorous mixing.

All three methodologies used different degrees of pre-experimental filtering. Mayer (1982b) used Gelman A/E 8.0μm filters underlain by Whatman GF/F filters to filter both river and sea water; Fox & Wofsy (1983) used unfiltered river water and Whatman GF/C filtered sea water; Hunter & Leonard (1988) used unfiltered river and sea water. Both Mayer (1982b) and Hunter & Leonard (1988), in their original papers, showed the dependence of the removal of iron from the 'dissolved' fraction of river water on the presence of larger particles within the river water. Removal of larger particles prior to mixing, by filtration, was shown to result in a decrease in the extent of removal observed in the simulated estuarine mixing. The overall number of large particles present decreased from the conditions of Hunter & Leonard, with no pre-filtration to those of Fox & Wofsy in which the sea water was filtered and finally to those of Mayer in which both the river and sea water were filtered. This would suggest that the removal observed would be greatest in the experiments of Hunter & Leonard (1988) followed by those of Fox & Wofsy (1983) and finally those of Mayer (1982b). This pattern was reflected in the experimental findings, but the effect was not as pronounced as expected, due to the effect of pre-analysis filtering. Both Hunter & Leonard and Fox & Wofsy used Whatman GF/C filters (nominal pore size 1.2μm) prior to analysis whereas Mayer utilised a combination of Gelman A/E and glass fibre filters, (equivalent pore size 0.5μm). Therefore the experiments of Mayer had the smallest cut-off for the dissolved fraction prior to analysis, with particles nominally larger than 0.5μm being removed in comparison to the removal of particles at a nominal size of 1.2μm in the experiments of Hunter & Leonard and Fox & Wofsy. However as previously stated the experiments of Mayer used the slowest stirring rate, as well as having no larger particles. Hunter & Leonard and Fox & Wofsy used the same final filter size and had comparable stirring rates, however Hunter & Leonard carried out no pre-filtering of the estuarine end members (cf. Fox & Wofsy who used pre-filtered sea water) which increased the number of larger particles in the water, and thus the likelihood of particle aggregation resulting in a particle size increase to above the final filter size.

The differences between these three methodologies were however, small in comparison with the difference observed between them and the continuously sampled method of Duffy (1985). For the remainder of this section they will be referred to collectively as 'discretely sampled methods (or discrete method) in comparison with the continuously sampled (or continuous) method.

Direct comparisons between these methods are possible using data taken from the experimental pairs where pre-filtering of river water and sea water and the sample filtration methods were the same for both the continuous and discrete methods. This eliminates all variables other than the sampling method and the mixing rate. When this direct comparison is made between the two methods, in terms of a plot of % iron remaining in <0.45um fraction, the differences in removal rate and also in total removal become obvious as shown in Figures. 5.16 and 5.17.

The plots clearly highlight the differences between the methodologies. In the first three to five minutes the removal of iron from the <0.45 μm fraction follows a similar course, decreasing to approx. 60-70% of its original value. After this time, however, iron removal is essentially levelling off to a residual value in the discrete methods with only minor subsequent decreases observed. Using the continuous method, iron removal continues after this time for the majority of the experiment, before levelling off to a residual level. Despite the large difference in the duration of the removal process in the two types of experiment, the continuous method exhibited a greater total aggregation than the discrete method with 79% aggregated after 10 minutes compared with 61% aggregated over 180 minutes at a salinity of 18.

The most obvious reason for the difference between the two types of method is that the increased rate and extent of aggregation is a function of the increased shear in the continuous mixing experiments through the use of the centrifugal pump.

Whilst distinct differences were observed in the behaviour of iron between the discrete and continuous methodologies, the different velocity gradients in the experiments had no discernible effect on the behaviour of phosphate. Both the removal profiles and the total aggregation occurring over the course of the experiments were very similar for both experimental types. The calculated first order rate constants for the two methodological types corroborate this similarity, with both exhibiting an almost identical linear increase with increasing salinity.

Further laboratory experiments were therefore carried out to look into the effects of stirring rate on simulated estuarine mixing behaviour of microcolloidal iron and associated phosphate.

Fig 5.16 Comparison of experimental methods of Duffy (1985) and Hunter & Leonard (1988) using filtered Tamar river water, salinity = 10.

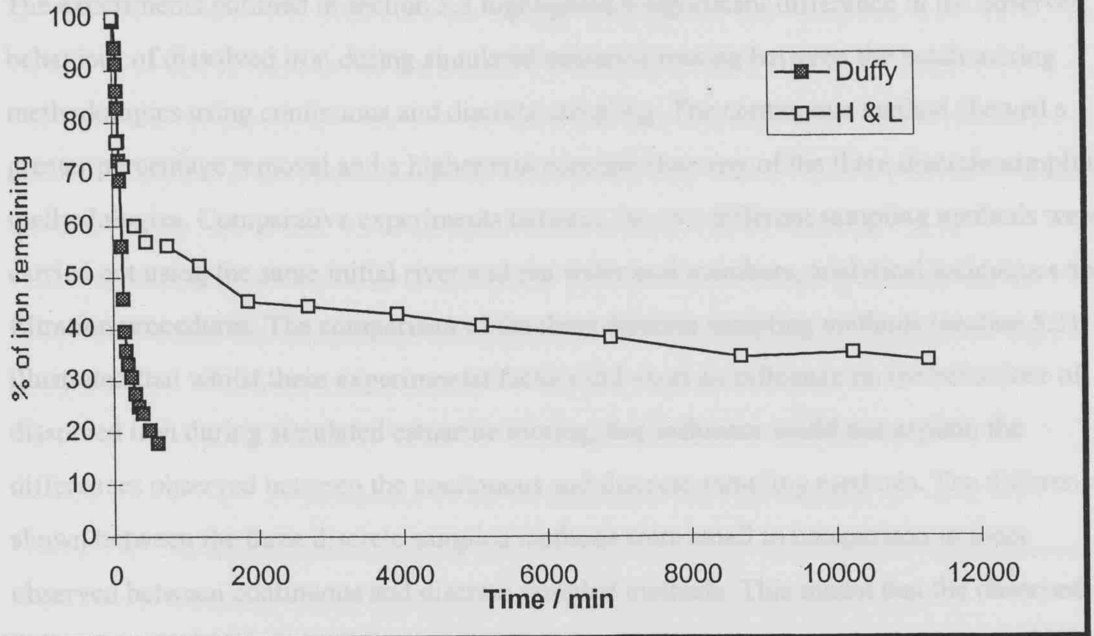
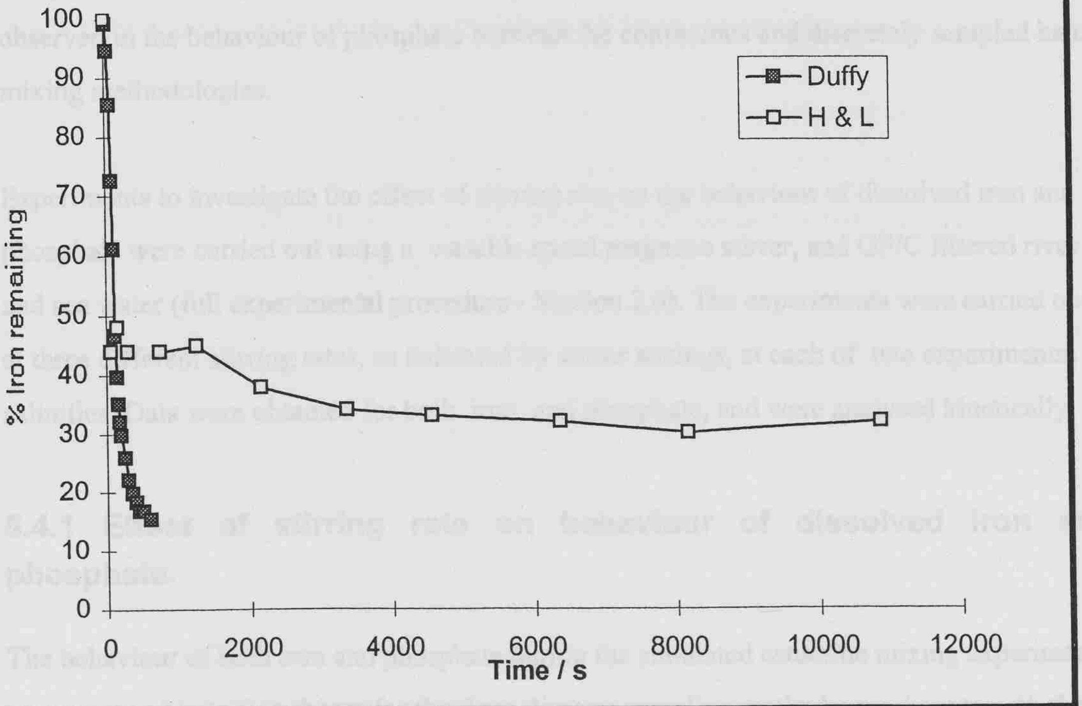


Fig 5.17 Comparison of experimental methods of Duffy (1985) and Hunter & Leonard (1988) using filtered Tamar river water, salinity = 15.



5.4 The Effects of Stirring Rate on the Behaviour of Iron and Phosphate during Simulated Estuarine Mixing Experiments

The experiments outlined in section 5.3 highlighted a significant difference in the observed behaviour of dissolved iron during simulated estuarine mixing between the batch mixing methodologies using continuous and discrete sampling. The continuous method showed a greater percentage removal and a higher rate constant than any of the three discrete sampling methodologies. Comparative experiments between the two different sampling methods were carried out using the same initial river and sea water end members, analytical techniques and filtration procedures. The comparison of the three discrete sampling methods (section 5.3) illustrated that whilst these experimental factors did exert an influence on the behaviour of dissolved iron during simulated estuarine mixing, this influence could not explain the differences observed between the continuous and discrete sampling methods. The differences shown between the three discrete sampled methods were small in comparison to those observed between continuous and discrete sampled methods. This meant that the observed differences could be explained only by differences in the sampling method or by the different mixing rates induced in the mixing tank during the course of the experiments. The continuous sampling method had a significantly higher mixing rate using the centrifugal immersion pump in comparison with either the magnetic stirrer, glass paddle or reciprocating shaker. The differences in sampling in terms of the filtration are not large and therefore it appears more likely that the mixing conditions are the important factor. No significant difference was observed in the behaviour of phosphate between the continuous and discretely sampled batch mixing methodologies.

Experiments to investigate the effect of stirring rate on the behaviour of dissolved iron and phosphate were carried out using a variable speed magnetic stirrer, and GF/C filtered river and sea water (full experimental procedure - Section 2.6). The experiments were carried out at three different stirring rates, as indicated by stirrer settings, at each of two experimental salinities. Data were obtained for both iron and phosphate, and were analysed kinetically.

5.4.1 Effect of stirring rate on behaviour of dissolved iron and phosphate.

The behaviour of both iron and phosphate during the simulated estuarine mixing experiments was comparable to that shown for the three discrete sampling method experiments with the percentage removal of iron and phosphate dependent upon the salinity of the solutions. The changes in removal profiles with increasing stirring rate observed for iron and phosphate at a salinity of eight are shown in Figures 5.18 and 5.19 respectively, whilst the overall fraction removed at the end of the experiments are presented in Figure 5.20 for iron and Figure 5.21 for phosphate. Table 5.13 illustrates the changes in both iron and phosphate with stirring rate. As was observed in Section 5.3, the percentage removal of iron was significantly greater than that observed for phosphate with 44% of iron removed compared with 19% of phosphate at a salinity of eight and 69% compared with 26% at a salinity of twelve for experiments carried out at a stirring rate of one. The fraction of dissolved iron removed at each of the experimental salinities shows an almost linear increase with increasing stirring rate the gradient of which was comparable between the two salinities at 6.25 at a salinity of eight compared to 6.75 at a salinity of twelve.

At a salinity of eight no noticeable increase in the removal was observed for phosphate, however at a salinity of twelve a small increase was observed, with the removal increasing from 26% at a stirring rate of one to removal of 29% at a stirring rate of five.

The data set for iron and phosphate behaviour during the simulated estuarine mixing experiments were analysed kinetically using the modified integrated rate equations 3 and 4 as outlined in section 3.4.

5.4.2 Effect of stirring rate on kinetics of iron removal.

The data sets gave good fits to both the first and second order models with correlation coefficients ranging from 0.965 to 0.984 for the first order and 0.949 to 0.982 for the second order model. Table 5.14 presents the data calculated from the iron removal profiles and the changes in first and second order rate constants with stirring rate are shown in Figures 5.22 and 5.23. As was observed in section 5.4, the first order rate constant, at a stirring rate of one, was greater at the highest salinity, $4.13*10^{-4}$ s^{-1} at a salinity of twelve compared with $2.96*10^{-4}$ s^{-1} at a salinity of eight. As illustrated in Figure 5.22 there was an increase observed in the rate constant as the stirring rate was increased.

The second order rate constants did not show any consistent pattern as illustrated in Figure 5.23.

Fig 5.18 Effect of stirring rate on removal of iron, during simulated estuarine mixing, salinity = 8.

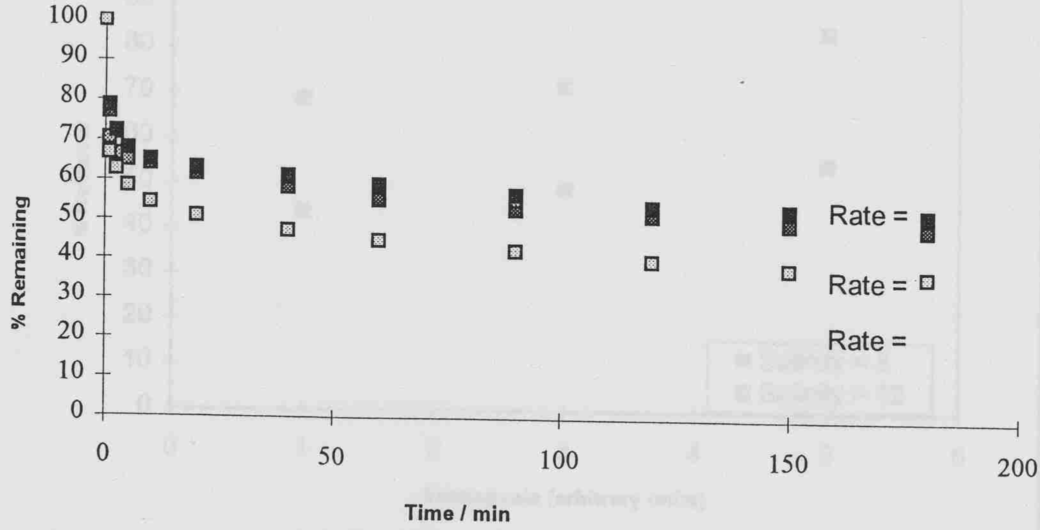


Fig 5.19 Effect of stirring rate on removal of phosphate during simulated estuarine mixing, salinity = 8.

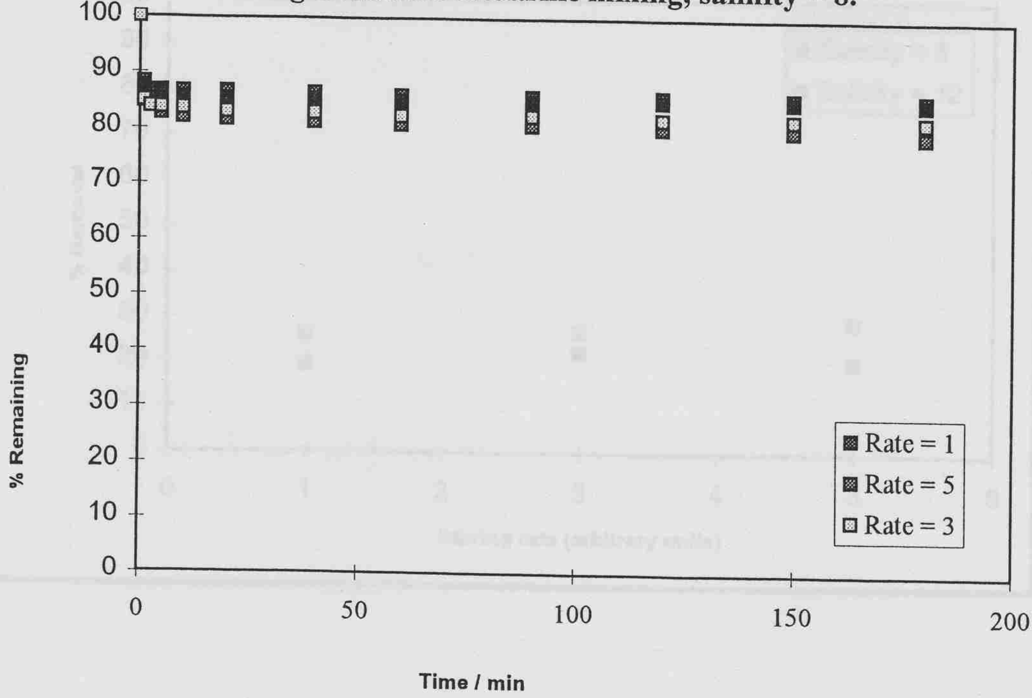


Fig. 5.20 Effect of stirring rate on total iron removal during simulated estuarine mixing at a salinity of 8 and 12.

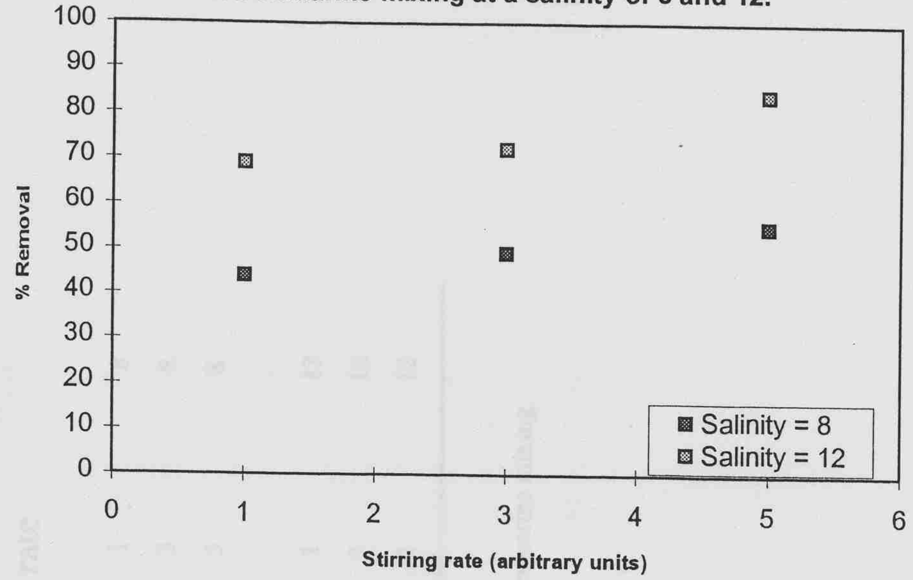
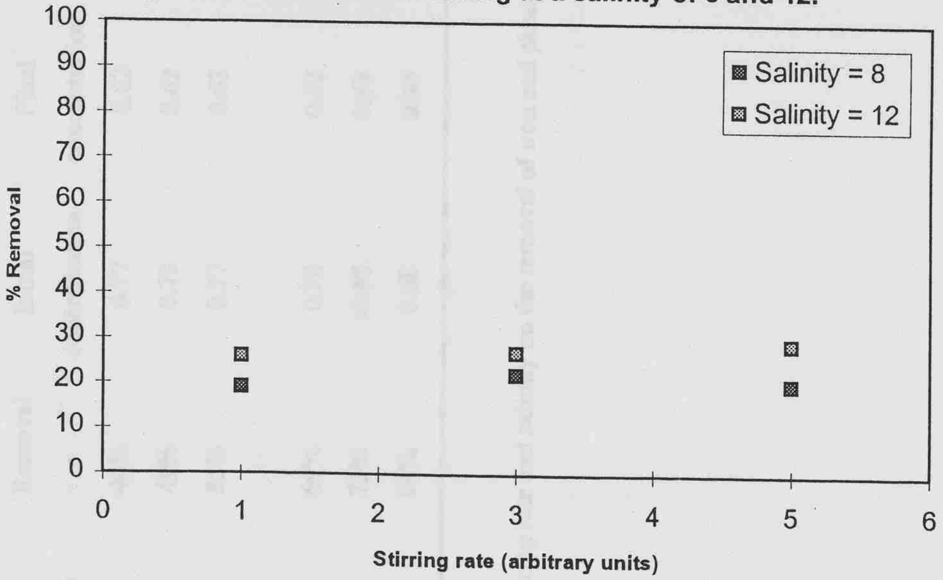


Fig. 5.21 Effect of stirring rate on total phosphate removal during simulated estuarine mixing at a salinity of 8 and 12.



Iron			Phosphate			Stirring	Salinity
Initial concentration	Final concentration	Removal	Initial concentration	Final concentration	Removal	rate	
14.6	8.2	44%	0.77	0.62	19%	1	8
14.0	7.1	49%	0.79	0.62	22%	3	8
14.3	6.4	55%	0.77	0.62	20%	5	8
12.5	3.9	69%	0.70	0.52	26%	1	12
12.4	3.5	72%	0.68	0.49	27%	3	12
12.6	2.0	84%	0.68	0.48	29%	5	12

Table 5.13 : The influence of stirring rate and salinity on the removal of iron and phosphate during simulated estuarine mixing.

First order			Second order			Stirring rate	Salinity
Rate constant s^{-1}	correlation coefficient	Residual iron fraction	Rate constant $lmol^{-1}s^{-1}$	correlation coefficient	residual iron fraction		
$2.96*10^{-4}$	0.972	7.24	0.0000434	0.968	3.68	1	8
$3.28*10^{-4}$	0.983	4.66	0.0000193	0.981	3.11	3	8
$3.58*10^{-4}$	0.984	3.29	0.0000193	0.974	0.25	5	8
$4.13*10^{-4}$	0.982	5.13	0.0000229	0.976	0.269	1	12
$4.21*10^{-4}$	0.981	3.02	0.0000396	0.965	1.35	3	12
$4.26*10^{-4}$	0.965	1.67	0.0000267	0.949	0	5	12

Table 5.14 : The influence of stirring rate and salinity on the first and second order kinetic analysis of iron removal during simulated estuarine mixing.

First order			Second order			Stirring rate	Salinity
Rate constant s^{-1}	Correlation coefficient	Residual phosphate fraction	Rate constant $l mol^{-1} s^{-1}$	Correlation coefficient	Residual phosphate fraction		
0.0324	0.943	0.628	0.449	0.909	0.476	1	8
0.0247	0.976	0.602	0.174	0.935	0.507	3	8
0.0344	0.972	0.585	0.350	0.973	0.424	5	8
0.023	0.981	0.514	0.188	0.983	0.341	1	12
0.028	0.957	0.486	0.0134	0.974	0.265	3	12
0.017	0.968	0.417	0.0661	0.944	0.225	5	12

Table 5.15 : The influence of stirring rate and salinity on the first and second order kinetic analysis of phosphate removal during simulated estuarine mixing.

5.4.3 Effect of stirring rate on kinetics of phosphate removal data

The data sets gave reasonable fits to both the first and second order models with correlation coefficients ranging from 0.943 to 0.981 for the first order and 0.909 to 0.983 for the second order model. Table 5.15 presents the kinetic data calculated from the removal profiles of phosphate, and the changes in first and second order rate constants with increasing stirring rate are illustrated in Figures 5.24 and 5.25. No obvious systematic trend was observed for the first order rate constant with changes in stirring rate, in contrast to that observed for iron. Significant scatter was observed in the second order rate constants which bore no relationship to changes in stirring rate. The second order fits are so forced that the values obtained are of doubtful significance.

5.5 Conclusions

From the study of the discrete and continuously sampled batch mixing estuarine simulations, marked differences were observed between the behaviour of iron and phosphate in the two basic experimental systems (discrete and continuous sampled methods) :

1. The experimental methodology of the estuarine simulation carried out has a distinct effect on the removal of iron observed within the simulation. Two distinct types of experiment have been applied, the discrete sampled method (Mayer, 1982b; Fox & Wofsy, 1983; and Hunter & Leonard, 1988) and the continuous sampled method (Duffy, 1985; and this study). The major difference between the two types is the relative mixing speeds experienced within the simulations. The experiments with the greater mixing speed (continuous) showed a greater extent and rate of removal of iron, though in both cases the removal of iron increased with increasing salinity.

Fig 5.22 Effect of stirring rate on 1st order rate constants for removal of iron during simulated estuarine mixing at a salinity of 8 and 12.

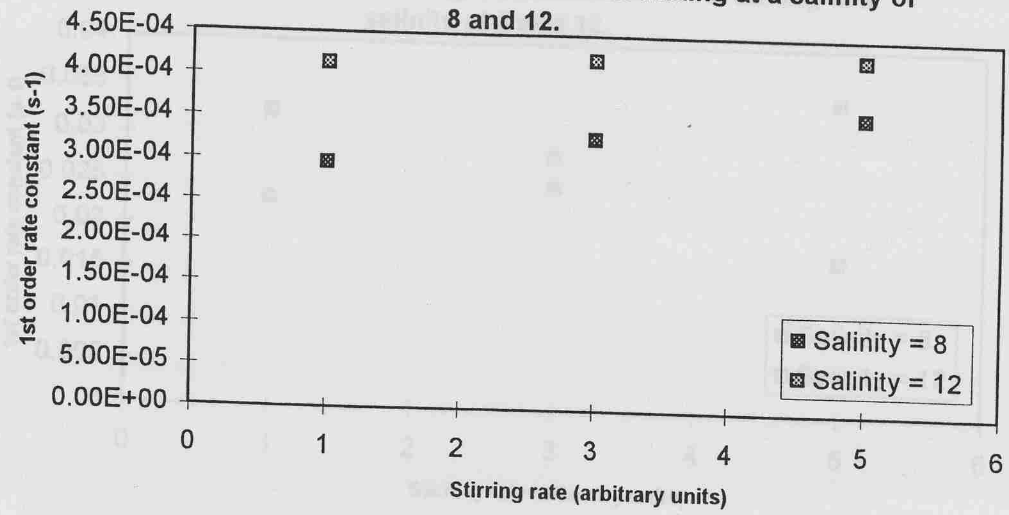
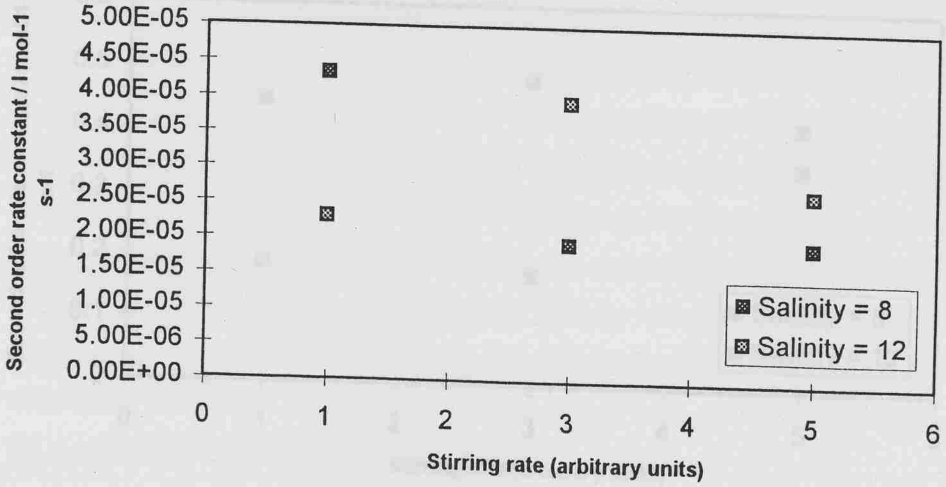


Fig 5.23 Effect of stirring rate on the second order rate constants for removal of iron, during simulated estuarine mixing at a salinity of 8 and 12.



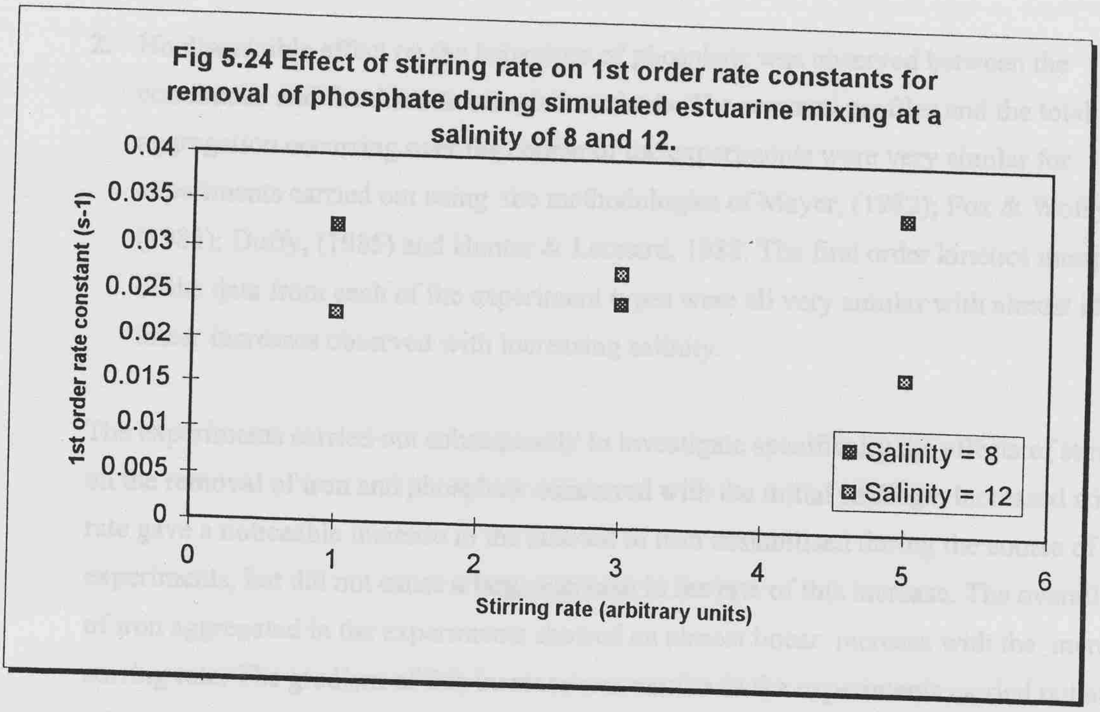


Fig 5.24 Effect of stirring rate on 1st order rate constants for removal of phosphate during simulated estuarine mixing at a salinity of 8 and 12.

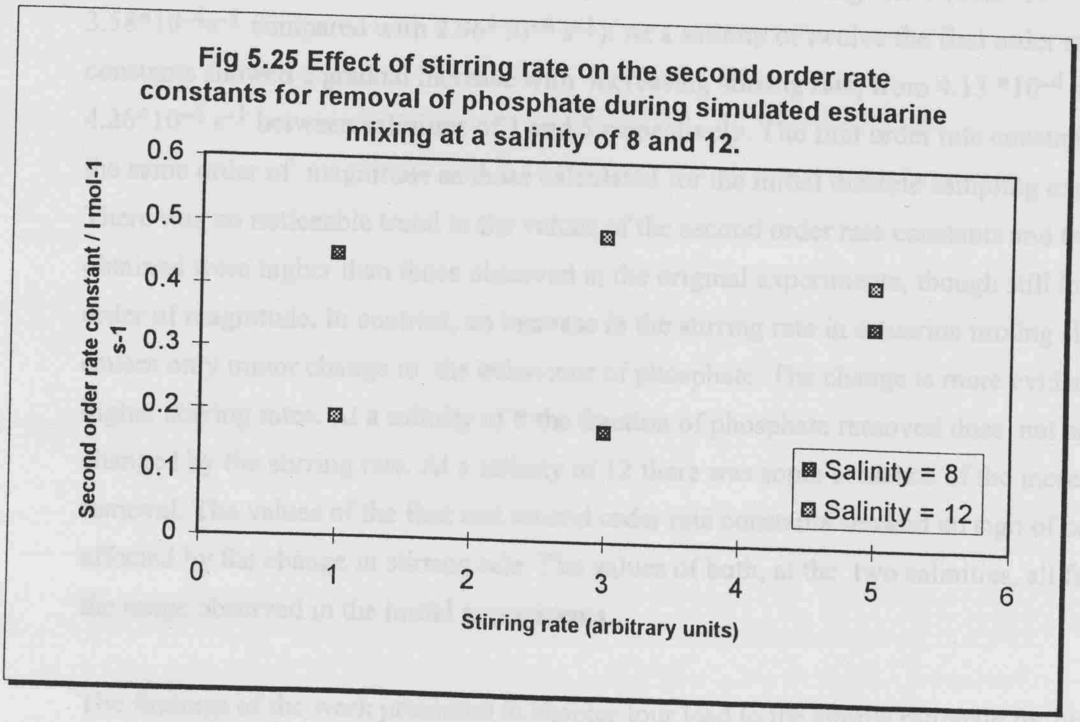


Fig 5.25 Effect of stirring rate on the second order rate constants for removal of phosphate during simulated estuarine mixing at a salinity of 8 and 12.

2. No discernible effect on the behaviour of phosphate was observed between the continuous and the discrete sampled methods. The removal profiles and the total aggregation occurring over the course of the experiments were very similar for experiments carried out using the methodologies of Mayer, (1982); Fox & Wofsy, (1983); Duffy, (1985) and Hunter & Leonard, 1988. The first order kinetics interpretation of the data from each of the experiment types were all very similar with almost identical linear increases observed with increasing salinity.

The experiments carried out subsequently to investigate specifically the effects of stirring rate on the removal of iron and phosphate concurred with the initial findings. Increased stirring rate gave a noticeable increase in the amount of iron destabilised during the course of the experiments, but did not cause a large increase in the rate of this increase. The overall fraction of iron aggregated in the experiments showed an almost linear increase with the increase in stirring rate. The gradient of this increase was similar in the experiments carried out at salinities of 8 and 12 (6.25 cf. 6.75). At a salinity of eight the first order rate constants at stirring rate of 3 and 5 were significantly greater than at a stirring rate 1 ($3.28*10^{-4}$ s^{-1} and $3.58*10^{-4}s^{-1}$ compared with $2.96*10^{-4}$ s^{-1}). At a salinity of twelve the first order rate constants showed a gradual increase with increasing stirring rate, from 4.13 $*10^{-4}$ s^{-1} to $4.26*10^{-4}$ s^{-1} between salinities of 1 and 5 respectively. The first order rate constants were of the same order of magnitude as those calculated for the initial discrete sampling experiments. There was no noticeable trend in the values of the second order rate constants and the values obtained were higher than those observed in the original experiments, though still in the same order of magnitude. In contrast, an increase in the stirring rate in estuarine mixing simulations causes only minor change in the behaviour of phosphate. The change is more evident at higher stirring rates. At a salinity of 8 the fraction of phosphate removed does not appear changed by the stirring rate. At a salinity of 12 there was some evidence of the increased removal. The values of the first and second order rate constants showed no sign of being affected by the change in stirring rate. The values of both, at the two salinities, all fall within the range observed in the initial experiments.

The findings of the work presented in chapter four lead to the simple rationale for phosphate behaviour reflecting co-removal of a colloidal fraction of phosphate by the same basic process as that put forward for iron. The colloidal phosphate fraction, however, did not correspond to the colloidal iron fraction in behaviour, suggesting that the colloidal phosphate was not identical with the iron colloid. However, given the present findings, results may favouring a scavenging mechanism, in that they indicate that the factor which most affects iron (stirring) has no major systematic effect on phosphate - most striking when the method of Duffy is compared with the other methodologies. For the argument above, therefore, we would have to further qualify our statement that the colloids with phosphate associated behave differently from the iron colloids in response to shear. Thus we would have to postulate a difference in the phosphate and iron colloids not only in stability but also in the mechanism of aggregation, as the role of shear would not be applicable to the removal of phosphate. The similarity of behaviour of phosphate within a range of behaviours of iron could be relatively simply explained as due to a scavenging on the aggregated iron colloid. If this were the case, the phosphate colloid which we have observed to be present, would then have to be essentially unaffected by the addition of salt. This theory would fit with the observations, as detailed in the introduction to chapter four, that phosphate behaviour in actual systems does not indicate a ubiquitous response to iron removal.

The fact that the iron removal rate constant varies with the energy of the system, even down as far as the least energetic system studied shows that the mechanism under all these conditions cannot be accounted for by Brownian Motion. Shear must therefore be a significant factor and while the distribution of iron within the colloid can be postulated as an explanation for the kinetics being best described in terms of a first order reaction, as discussed in section 1.6, the importance of shear, as demonstrated, means that it cannot be considered as a major factor determining the kinetic order. As pointed out earlier (section 3.6.2) the use of velocity gradient as an indicator of shear appears simplistic in the context of these results; the important factor is the frequency with which the bulk solution encounters the zone of maximum shear within the system. It must be concluded that none of the systems studied can afford a test of kinetic order under conditions where Brownian Motion accounts for particle collisions. This does not mean, however, that the experiments are without relevance to environmental conditions, since estuarine mixing is influenced by turbulence in the near bottom zone and the wind mixed layer.

Chapter Six

Behaviour of Iron and Phosphate in Laboratory Simulations of Estuarine Mixing : Conclusions and Further Work.

6.1 The destabilisation of iron in natural waters

The present work (chapter 5), indicates that differences in stability of microcolloidal iron and its resistance to destabilisation and aggregation on the addition of cations (as indicated by residual fractions), can arise from experimental factors in simulated estuarine mixing, but there is nevertheless clear evidence of real differences among various systems. Experiments were carried out on Tamar River water following the experimental procedures of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988) at salinities comparable to those of the original authors. The initial removal of iron was seen to be significantly greater in the Tamar than in any of the rivers studied in the original papers, with the exception of the Mullica and Saco rivers at a salinity of 12, (see tables 5.2 to 5.4). Following the procedure of Mayer (1982b) at a salinity of 8, an initial removal of 6 % was observed after 13.5 minutes for Saco water in comparison with 14 % removal after one minute for Tamar water. Similarly following the procedure of Fox & Wofsy (1983) at a salinity of 8, a removal of 26 % was observed for Tamar water in comparison with 9 % for the Broadkill and 12 % for the Mullica waters in the original papers. For the experiments following the procedure of Hunter & Leonard (1988) at a salinity of 10, 45 % removal was observed in Tamar waters compared with 20 % in the Leith and 9 % in the Taieri. Thus the steric stabilisation of colloids carried within the Tamar appears to be relatively weak , with a small increase in salinity being sufficient to destabilise a relatively large proportion of the colloid population. However when the total iron removal for the same rivers is studied, a different pattern was observed. At a salinity of 8, a final removal of 75% was observed for Saco water in comparison with 43 % removal for Tamar water; similarly at a salinity of 8, a removal of 44 % was observed for Tamar water in comparison with 43 % for the Broadkill and 73 % for the Mullica waters and at a salinity of 10, 69 % removal was observed in Tamar waters compared with 45 % in the Leith and 71 % in the Taieri. From these experiments it would appear that residual steric stabilisation of colloids in the Saco and Mullica rivers is weak relative to the Tamar River, where the subsequent colloid aggregation rate is markedly influenced. The removal from the Broadkill and the Taieri river water showed a comparable behaviour to the Tamar whilst that of the Leith indicated relatively strong steric stabilisation. A smaller fraction of the colloid population was destabilised by an equivalent addition of salinity and the fraction aggregated at a slower rate. It appears that after the initial destabilisation in the Tamar and Leith river water, residual steric stabilisation is much less readily counteracted, leading to low collision efficiencies and slower aggregation. These contrasts in estuarine behaviour must arise from differences between their influent rivers in the surface states of iron bearing colloid particle populations generated by differing origins and histories prior to discharge into each individual estuary (Morris, pers comm.)

The dependence of rate of aggregation on cation concentration relates to the compression of the diffuse electrical layer surrounding each particle by electrolyte. This leads to a decrease in the forces of electrostatic repulsion between particles, giving rise to an increase in collision efficiency. At low electrolyte concentration, the efficiency of interparticle collisions leading to aggregation is considerably less than 100% and is a sensitive function of electrolyte concentration (Ottewill & Shaw, 1965). At increased electrolyte concentrations, the majority of collisions result in aggregation, and kinetics are no longer dependent upon electrolyte concentration (Overbeek, 1977). Theories of colloid stability show that a salinity of three (or an equivalent ionic strength) is sufficient to reduce the double layer thickness to about 1 nm, sufficient to for a purely electrostatically stabilised colloid (Ottewill & Shaw, 1965). However steric stabilisation of iron colloids by organic material, has been shown to significantly increase stability (Napper, 1977; Smith & Milne, 1981) by opposing the effect of electrolyte concentration on collision efficiency. Therefore even at higher electrolyte concentrations, the destabilisation of stabilised colloids is still a sensitive function of electrolyte concentration.

Differences observed in reaction time scale could be caused by either an inherent difference in the nature of samples, or a difference in experimental procedure. The rate of the reaction studied is a function of : a rate constant, k_{max}, which describes the aggregation of a fully destabilised colloid population, the collision efficiency, α, and the initial number of aggregating particles - which is itself dependent on sample origin. k_{max} is unlikely to vary sufficiently between samples to cause the differences seen - as it is dependent on Boltzman's constant, temperature, viscosity and a size distribution function, all of which remain reasonably uniform between samples. This leads to the conclusion that either the collision efficiency and / or the initial number of aggregating particles must be the principal factors responsible for the wide divergence in behaviour observed. As discussed above, the presence of organic material can cause steric stabilisation which will affect the collision efficiency.

In a field survey of US east coast estuaries, Boyle *et al.*, (1977) found that the initial iron concentration varies considerably between the rivers in each study from 3 μmol l^{-1} for the Conneticut Estuary to 24 μmol l^{-1} for the Mullica Estuary. When the salinity profiles of the estuaries were studied, although removal was observed in each estuary, the rate and extent of removal was shown to vary significantly both between estuaries, (54 to 96 % removal in the Merrimac and Mullica) and also temporally within those estuaries (54 to 71 % removal in the Merrimac). The rivers of higher iron concentration showed a greater total removal in their estuaries. The wide variation in initial dissolved iron concentration between rivers is likely to be accompanied by differences in colloidal characteristics such as size distribution, stabilisation by organic material etc. which could account for the differences in behaviour observed .

An investigation into the effects of storage time provided further evidence that the microcolloidal population is not static but is subject to reorganisation and storage effects are relevant as a factor potentially influencing comparability of results among different experimental studies and within these studies. The total concentration of iron within the <0.45μm fraction of a river water sample did not appear to be influenced by storage time, fluctuations observed were non systematic and within the limits of experimental error. The present study has shown that temporal variability in the magnitude of the unreactive iron fraction and in the rate constant for removal tend to be related. The behaviour of the dissolved iron fraction during simulated estuarine mixing experiments was shown to be affected by storage time, with an increase in storage time leading to an increase in the fraction of iron resistant to destabilisation concurring with the findings of Hunter & Leonard (1988). It was also shown by both Mayer (1982b) and Hunter & Leonard (1988) that the presence of larger particles will have a distinct influence on the observed removal.

6.2 The kinetics of iron removal

The iron removal process is the most ubiquitously observed phenomenon modifying riverine input in the estuarine environment. As such, it has a potential to influence the estuarine behaviour and fluxes of other constituents, including pollutants. Kinetic evaluations of the experimental data are therefore of great importance offering both the potential to throw light on the mechanism of iron removal and also the ability for modelling, including predictive modelling, of behaviour.

The two basic conditions under which particle collisions and therefore potential destabilisation can be brought about are :

1) Perikinetic conditions - interparticle collisions occur wholly as a result of Brownian motion. The implications of such conditions are that the removal of dissolved iron should show a second order dependency with respect to the concentration of iron.

2) Orthokinetic conditions - interparticle collisions occur as a direct result of agitation. Shear velocity increases the particle flux, hence the particle collisions, proportionally to the third power of their collision diameter.

Classic colloid theory (von Smoluchowski, 1917), predicts that for particles of a diameter up to $1\mu m$, perikinetic aggregation will dominate, whilst for the larger end of the particle size spectrum, orthokinetic behaviour dominates. This led to the expectation that the removal of microcolloidal particles would conform to a second order kinetic model as presented by Mayer (1982b) and Fox & Wofsy (1983). Mayer (1982b) showed that the equation for second order destabilisation was equally applicable to a polydisperse microcolloid population, provided the rates of aggregation were equal within the different size ranges. Duffy (1985) found that when the unreactive fraction of dissolved iron was taken into account, the first order model was found to give correlation coefficients of 0.990 or greater (however, no fits of the modelled data to the removal profile were provided and it has subsequently been shown in this work, section 3.4, that high correlation coefficients do not necessarily represent good fits to the removal profile observed). This fit to the first order model could occur as a result of shear, as orthokinetic aggregation occurs via first order kinetics. A further possible explanation for the reaction occurring by first order kinetics is dependent upon the distribution of dissolved iron throughout the microcolloidal particle population (Morris pers. comm.), as described in section 1.6 in further detail. Thus both the first and second order models can be backed up by rational mechanistic explanations.

The present set of experiments was carried out with fewer variables (all experiments were carried out using Ca^{2+} ions) to examine further the validity of the various kinetic models in describing the results and potentially achieve a more unequivocal interpretation of the rate order. The kinetic interpretation of the all of the experimental data sets in this study, chapters 3 & 5, indicated that the removal of iron can be better described by a first order kinetic model than by a second order model, with the key points summarised below :

- The first order model gave a closer fit to the whole removal profile, showing equation 3.3 to be an excellent descriptor.
- The first order model gave a better fit altogether to the residual fraction, with the second order model (equation 3.4) seeming to force the data unrealistically.
- The first order model showed a clear linear relationship of increase with increasing calcium ion concentration, as predicted for low electrolyte concentrations (Ottewill & Shaw, 1965; Overbeek, 1977; Napper, 1977)

The work carried out in chapter 5 led to the conclusion that experimental methodology of the estuarine simulation carried out has a distinct effect on the removal of iron observed within the simulation. Two distinct types of experiment have been applied, the discrete sampled method (Mayer, 1982b; Fox & Wofsy, 1983; and Hunter & Leonard, 1988) and the continuous sampled method (Duffy, 1985; and this study). The major difference between the two types is the relative mixing speeds experienced within the simulations. The experiments with the greater mixing speed (continuous) showed a greater extent and rate of removal of iron, though in both cases the removal of iron increased with increasing salinity. Furthermore the experiments carried out specifically to investigate the effects of stirring rate on the removal of iron and phosphate concurred with the initial findings. Increased stirring rate gave a noticeable increase in the amount of iron destabilised during the course of the experiments, but did not cause a large increase in the rate of this increase. The overall fraction of iron aggregated in the experiments showed an almost linear increase with the increase in stirring rate. The gradient of this increase was similar in the experiments carried out at salinities of 8 and 12 (6.25 cf. 6.75). At a salinity of eight the first order rate constants at stirring rate of 3 and 5 were greater than at a stirring rate 1 although the differences observed were small ($3.28*10^{-4}$ s^{-1} and $3.58*10^{-4}$ s^{-1} compared with $2.96*10^{-4}$ s^{-1}). The first order rate constants were of the same order of magnitude as those calculated for the initial discrete sampling experiments.

The present work suggests that in addition to other factors, the mechanics of mixing affect the fraction of iron resisting destabilisation and the rate of aggregation at a given concentration of destabilising cations. The fact that the iron removal rate constant varies with the energy of the system, even down as far as the least energetic system studied shows that the mechanism under all these conditions cannot be accounted for by Brownian Motion. This raises questions about the process of aggregation, implying that shear must therefore be a significant factor. While a non uniform distribution of iron within the colloid can be postulated as an explanation for the kinetics being best described in terms of a first order reaction, Morris, (pers. comm.) as discussed in section 1.6, the importance of shear, as demonstrated, means that it cannot be considered as a major factor determining the kinetic order in the experimental studies. As pointed out earlier (section 3.6.2) the use of velocity gradient as an indicator of shear appears simplistic in the context of these results; the important factor is the frequency with which the bulk solution encounters the zone of maximum shear within the system. It must be concluded that none of the systems studied can afford a test of kinetic order under conditions where Brownian Motion accounts for particle collisions.

From the stirring meter ratings it was possible to calculate the Watts input to the beaker volume, where values of (dissipation in $m^2\ s^{-3}$), $Wm^{-3}/10^3$ (water density in kg m^{-1}) are equivalent to dissipation in cm^2s^{-3}. Calculated values for the current experimental system (discrete mixing) yielded values of 0.005 cm^2s^{-3} which correspond to values observed in near surface turbulence measurements in a lake by Dillon *et al.* (1981) of 10^{-2} to 10^{-3} cm^2s^{-3} for depths of 0 to 6 meters with an average wind speed of 4.8 ms^{-1}. Estuarine systems are also subject to another important factor in mixing due to the tidal energy, which may exert a considerable influence. This suggests that the kinetics observed in the estuarine simulations are applicable to the estuarine environment in terms of the energy dissipation of the system. The energy dissipation in the system is proportional to the cube of the mean wind speed, therefore even the experiments carried out using the continuous sampled methodology, which has a significantly higher energy dissipation may have some relevance in more regions of higher turbulence.

We can therefore conclude that the kinetic interpretations are consistent with shear being an important factor. The kinetic interpretations of estuarine simulations do not provide an unequivocal basis for evaluating mechanism. For modelling purposes, they may suggest that the first order models of 'removal' provide a better description of the process but the second order models may also provide a satisfactory basis for parameterising in practice. Second order kinetics will still apply in the environment in any zone where molecular diffusion dominates over turbulent diffusion.

The greater attention given to the higher energy system in the present work reflects the evolution of the project, which was designed to examine further the findings of Duffy (1985). The conclusions from all the experiments are coherent, in that the results can all be best described by the first order model when the residual fraction is taken into account. In this context, the data set derived by the Duffy (1985) methodology remains particularly valuable for its comprehensive demonstration of the superiority of the first order model as a descriptor of the kinetics of the reaction.

6.3 The behaviour of iron and phosphate in simulated estuarine mixing.

Observations of the behaviour of both iron and phosphate during simulated estuarine mixing are consistent with published field data for the Tamar estuary (Morris *et al.*, 1981; Bale and Morris, 1981), with the dissolved iron concentration showing strong non-conservative behaviour, decreasing from approximately 20μmol l^{-1} in river water to below the limits of detection at the seaward end of the estuarine zone and a smaller decrease in the phosphate concentration occurring in the low salinity region of the estuary, with measurable concentrations still persisting at the seaward end.

In the original set of experiments, discussed in chapter four, the amount of phosphate resisting destabilisation was seen to decrease with increasing calcium ion concentration, as was observed for iron in chapter three. The amount of dissolved iron removed during the simulated estuarine mixing experiments, both as a percentage of the original concentration and as an actual concentration, was much greater than the corresponding removal of dissolved phosphate. The difference between the percentages of iron and phosphate resisting removal remained reasonably constant at the calcium ion concentrations studied. The decrease in percentage removal per unit increase in calcium molarity was similar for both iron and phosphate, with a gradient of $8.83*10^3$ for phosphate compared with $8.72*10^3$ for iron. Over the range of calcium ion concentrations studied, the percentage of iron removed at the end of the experiments was consistently 40-50 % greater than that observed for phosphate. Thus at any given calcium ion concentration there is a significantly larger proportion of dissolved iron susceptible to removal.

When an unreactive fraction was taken into account the data sets for the removal of phosphate during simulated estuarine mixing gave equally good fits to both the modified first and second order kinetic models, using equations 3 and 4. A closer fit of the residual phosphate fraction to the actual value measured after 24 hour was obtained from the first order model in preference to the second order model for almost all of the data sets. The first order model also showed a clear linear trend of an increase in the rate constant with increasing calcium ion concentration, and less variability in the rate constant at a given calcium ion concentration. By contrast, the second order model did not show any obvious patterns during the simulated estuarine mixing experiments. The removal process is thus better described by a first order rather than a second order kinetic model. When the kinetic analysis was carried out using the basic integrated rate equation, poor fits to both the first and second order models for the removal process were found

In contrast to the behaviour of iron, an increase in the stirring rate in estuarine mixing simulations causes only minor change in the behaviour of phosphate. The change is more evident at higher stirring rates. At a salinity of 8 the fraction of phosphate removed does not appear changed by the stirring rate. At a salinity of 12 there was some evidence of the increased removal. The values of the first and second order rate constants showed no sign of being affected by the change in stirring rate. The values of both, at the two salinities, all fall within the range observed in the initial experiments.

It was initially thought that the most simple rationale for phosphate behaviour was that of co-removal of a colloidal fraction of phosphate by the same basic process as that put forward for iron. The colloidal phosphate fraction, however, did not correspond to the colloidal iron fraction in behaviour, suggesting that the colloidal phosphate was not identical with the iron colloid. However, given the present findings, results may favouring a scavenging mechanism, in that they indicate that the factor which most affects iron (stirring) has no major systematic effect on phosphate. This observation was most striking when the method of Duffy (1985) representing the highest energy system, was compared with the other, considerably lower energy methodologies of Mayer (1982b), Fox & Wofsy (1983) and Hunter & Leonard (1988). For the co-removal of a colloidal fraction to be a viable explanation, therefore, we would have to further qualify our statement that the colloids with phosphate associated behave differently from the iron colloids in response to shear. Thus we would have to postulate a difference in the phosphate and iron colloids not only in stability but also in the mechanism of aggregation, as the role of shear would not be applicable to the removal of phosphate. The similarity of behaviour of phosphate within a range of behaviours of iron could, however, be relatively simply explained as due to a scavenging on the aggregated iron colloid. If this were the case, the phosphate colloid which we have observed to be present, would then have to be essentially unaffected by the addition of salt. The evidence concerning phosphate behaviour in actual systems where iron is extensively removed does not indicate a ubiquitous response to iron removal. This has also been shown to apply equally to arsenate (Marsh, 1984), which resemble phosphate in being scavenged by newly formed iron oxyhydroxide (i.e. formed in situ from Fe^{3+}). It was shown by Crosby *et al.*(1981) that the uptake of phosphate onto fresh Fe (III) derived precipitates reached an equilibrium in less than 5 minutes, which represents a similar timescale to the phosphate removal observed in the current experiments. The adsorption profile of phosphate onto iron oxyhydroxides showed marked similarities with the removal observed in the simulated estuarine mixing studies. Crosby *et al.*(1984) showed that the uptake of phosphate by adsorption onto iron oxyhydroxides could be described by either first or second order kinetics, as concluded from the experimental work in this study and also showed a strong temperature and pH dependency (also observed by Likjema, 1980) which has been observed to exert an influence on phosphate removal in estuarine mixing simulations (Bale & Morris, 1981; Carpenter & Smith, 1984; Fox, 1989).

It is not clear, however, whether the aggregated iron colloids represent a newly available surface sorption of phosphate, therefore it must be concluded that the experiments show a co-removal of phosphate with iron colloid aggregation, consistent with what is seen in the Tamar (Bale & Morris, 1981; Morris *et al.*, 1982). The question as to the nature of the process underlying the co-removal must remain open.

6.4 Further Work

There are a number of potential areas for complimentary work to be carried out to enhance our understanding of the behaviour of iron and phosphate within the estuarine environment.

We have demonstrated that the current methodologies of estuarine mixing are all subject to some degree of shear, thus making them less applicable to the estuarine environment as a whole. It would therefore be highly informative to look at a mixing experiments using a method similar to that of Bale & Morris (1981), who utilised gradual mixing in a series of reactor tanks, as this may represent a more close approximation of conditions found within the estuarine environment.

A more in depth look at the size fractionation, using ultra filtration techniques in conjunction with conventional filtration, could be used to obtain more information with regard to the truly dissolved / colloidal nature of the iron and phosphate within riverine waters. More sensitive analytical techniques would be required, due to the small concentrations likely to be encountered at the lower end of the size spectrum. The use of sub fractions of the river water in mixing experiments could provide more detailed information on the nature and behaviour of the species present in these sub fractions and in the water as a whole.

Parameters obtained for the removal processes by laboratory simulations could be used to predict the estuarine removal as a function of salinity using a hydrodynamic model with geochemical reaction terms (i.e. ECOS) and then compared with field observations. This would provide direct evidence of the extent to which data obtained from laboratory experiments represent the environmental situation.

Field studies carried out on a range of estuaries with differing physico-chemical characteristics and residence times would provide detailed information on the range of behaviour of estuarine constituents. It would also be of interest to isolate and study the estuarine components at various points within the system to see if the constituents, in particular the microcolloids, are in equilibrium, with respect to their stability, at a given point within the estuary. Both the stability over time of the iron and phosphate within estuarine waters at a given salinity and also their response to the addition of further cations could be easily monitored in simple tank experiments.

Further work on the nature of estuarine particles, in particular with respect to the association of iron and phosphate using electron microscopy methods similar to those of Buffle *et al.* (1989) and Fiella & Buffle (1993) would also be of great importance to this study. Experiments to investigate the potential for adsorption of phosphate onto the microcolloidal aggregates formed during estuarine mixing would help to increase knowledge of the co-removal of iron and phosphate observed.

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