UNIVERSITY OF SOUTHAMPTON

THE BEHAVIOUR OF DISSOLVED PHOSPHATE DURING MIXING IN THE BEAULIEU ESTUARY AND ITS RELATION TO THAT OF IRON AND OTHER ELEMENTS

by

Gullaya Umnuay

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Department of Oceanography,
University Road,
Southampton,
SO9 5NH

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ABSTRACT

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THE BEHAVIOUR OF DISSOLVED PHOSPHATE DURING MIXING IN THE BEAULIEU ESTUARY AND ITS RELATION TO THAT OF IRON AND OTHER ELEMENTS

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Ultrafiltration of River Beaulieu water indicated that 50 to 85% of the reactive dissolved phosphate occurred, in association with, on average, more than 93% of the dissolved iron, in the colloidal fraction of molecular weight $> 10^5$. Dissolved organic carbon mostly occurred ($\sim 65\%$) in the molecular weight range $< 10^3$, with $< 5\%$ associated with iron colloids in the high molecular weight range ($> 10^5$). Dissolved silicon was almost wholly in true solution.

During mixing in the Beaulieu Estuary, extensive removal of dissolved iron was observed with 90-95% removal in the salinity range 0 - 15°/oo and almost complete removal as the salinity approached about 20°/oo. The extent of removal of iron appeared to be influenced by the amount of DOC in the river water. In contrast, the DOC behaved essentially conservatively except for one survey in which there was an apparent removal of 20% relative to the river water concentration.

Dissolved silicon showed conservative behaviour in one survey but on other occasions there was evidence of removal, generally in the range 10 - 25% but up to an apparent 70% in another survey It is suggested that this large-scale apparent removal may reflect uncertainties in interpretation.

The behaviour of phosphate in the Beaulieu Estuary was complex. An initial increase in concentration with increasing salinity, which commonly occurred, may be due to desorption from river-borne suspended solids. After this stage, some removal was usually observed, probably associated with the process of iron removal. The pattern of behaviour of phosphate was irregular, however, and it is possible that mobilization from bottom sediments led to changes not directly related to the mixing of the river and sea water end-members.

Laboratory experimental studies were carried out on the interaction of dissolved phosphate with estuarine sedimentary material. Maximum adsorption of phosphate in river water occurred between pH 3-6; adsorption was decreased in more saline water, supporting the view that desorption may occur in the early stages of estuarine mixing. There was a marked reduction in the capacity of suspended solids to adsorb phosphate when iron coatings were removed from the particles. Removal of organic matter also tended to decrease the adsorption capacity of the sediment.

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CHAPTER I

INTRODUCTION

1.1 River Inputs to the Ocean

The transport of continentally derived material to the ocean is by four major pathways: by streams and river systems following weathering processes, by wave erosion, by wind and by glaciers. Apart from these natural sources, man also contributes material through waste discharges.

Of these several sources, the input from streams and rivers is greater than any other. Garrels and Mackenzie (1971) estimated that 90% of the total terrestrial material inputs is supplied by rivers to the oceans; the total input of riverborne is around 2 x 10^{13} kg yr^{-1} (Livingstone, 1963; Holeman, 1968; Meybeck, 1976).

The composition of river water is made up of suspended particulate material, which comprises inorganic material such as oxides, carbonate, silicates and aluminosilicates (Carroll,1958; Hahn and Stumm, 1970), and organic particulate matter from biological activity, and dissolved forms. The amount of suspended material averages about 80% of the riverborne material, the estimated value of the annual input of the world rivers into the oceans being about 3.9 x 10^{12} kg of dissolved material (Livingstone, 1963), and 1.8 x 10^{13} kg of suspended solids (Holeman, 1968).

Because of the importance of river inputs for the geochemical mass balance of material in the ocean, increasing effort has been devoted to the study of river composition. Much of the reliable information obtained has been for rivers which are relatively minor in terms of the global inputs but recently major tropical rivers have been investigated, for example the Amazon River (Gibbs, 1967; Moore, 1967; Williams, 1968; Gibbs, 1970, 1972; Marlier, 1973; Milliman and Boyle, 1975; Milliman *et al.*, 1975; Gibbs, 1977; Sholkovitz and Price, 1980), and the Zaire River (see issue of Neth. J Sea Res., 1978, Vol.12, Nos 3/4). It has also become recognised that the inputs of material to the coastal seas and oceans may be substantially altered by geochemical processes occurring in estuaries. This is one of the factors which have given rise to more systematic studies of estuarine chemical processes, which have been summarized recently by Burton and Liss (1976) and Aston (1978).

A proper understanding of the interactions in estuaries requires a detailed knowledge of the chemical forms of the material introduced by rivers. Despite the increased information now available, estimates of river inputs for minor constituents are at best very approximate and much remains to be learned about both the total element concentrations and the chemical forms in the river supply as well as their fates in estuaries.

1.1.1 Dissolved material in river waters

Estimates of the input of dissolved constituents by rivers and streams into the ocean (Alekin and Brazhnikova, 1961; Livingstone, 1963; Gibbs, 1967) show differences both in the total discharge and dissolved materials values, even though the same basic sources of information are used. Of these estimates Livingstone's (1963) values are based on the most comprehensive data. The estimated value of the discharge of dissolved material by rivers of the world to the ocean is 3.9×10^{12} kg yr^{-1} which corresponds to an average content of 120 mg l^{-1} of total dissolved solids (Livingstone, 1963) or 117 mg l^{-1} according to Gibbs (1972). Of this only 10 mg l^{-1} is dissolved organic matter (Garrels and Mackenzie, 1971), with a corresponding annual input of $3.0 - 3.2 \times 10^{13}$ gC to the ocean (Handa, 1977).

A. Composition of major constituents

The average concentrations of the dissolved major elements of world rivers are shown in Table 1-1. The composition of the major constituents of the dissolved material in river water is quite variable, this variability resulting from the various

Table 1-1. Estimated average concentrations of some of the major dissolved constituents in the world river waters.

Constituents	Concentration mg l^{-1}		
	Livingstone (1963)	Meybeck (1977)	Meybeck (1979)
Silicon (SiO_2)	13.1	11.6	10.4
Calcium	15.0	14.6	13.4
Magnesium	4.1	3.8	3.35
Sodium	6.3	5.1	5.15
Potassium	2.3	1.35	1.30
Chloride	7.8	5.3	5.75
Sulphate	4.2	8.5	8.25
Bicarbonate	58.4	57.7	52.0

origins of these elements, and the environmental parameters which control these sources, such as climate, relief, geology and major types of river waters (Meybeck, 1976, 1977, 1978). The ratio of elemental dissolved load/elemental total load (soluble transport index) and the variation of this index value from the average values may be used to compare the geochemical behaviour of each dissolved element in rivers under various environmental factors (Meybeck, 1977; Martin and Meybeck, 1978). The importance of relief in relation to the major elements in river reflects the significance of mountainous areas in weathering (Gibbs, 1970).

The elemental transport in rivers is even more variable than the total dissolved transport. For example the dissolved silicon content in rivers varies depending on temperature - increased temperature results in higher dissolved silica (Meyer and Gloss, 1980) - on geographical characteristics of the basin - on discharge (Kennedy, 1971; Gibbs, 1972; Depetris, 1976; Holland, 1978) and the nature of silicon containing minerals. The silicon concentrations vary less widely, however, than the other major constituents and this has been suggested to reflect control by sorption reactions (Edwards and Liss, 1973).

B. Composition of minor constituents

The minor components differ significantly from the major components, in that their concentrations in rivers are in many important cases higher than in seawater (Turekian, 1969, 1971). The concentration of the trace element in the dissolved form in the streams and rivers does not correspond with the trace element concentration in the suspended particulate matter or the suspended matter content in the rivers (Turekian and Scott, 1967; Kharkar *et al.*, 1968). Also there is no general correlation between the major element concentrations and those of the trace elements in the lower part of the river (Turekian *et al.*, 1967).

Trace elements are supplied to the ocean by streams and rivers in several forms, dissolved both in inorganic and organically associated forms, as well as adsorbed on riverborne suspended solids, bound in the lattices of suspended particles or associated with organic matter or metal oxide coatings on suspended solids. The results of Gibbs (1973, 1977) indicated that for some important elements such as Fe, Mn, Cu, Co, and Ni, the fractions transported in solution are relatively small (0.6 to 17%).

The average concentrations of the dissolved minor elements of world rivers are shown in Table 1-2. Recent work on trace metals in sea water has led to downward revision of accepted concentrations in many instances and it is likely that similar revisions will be needed for river waters. This is supported by the much lower estimate by Boyle et al. (1977b) of Cu in the global average river supply. For some trace elements, a significant portion may be transported in colloidal form, so the fractionation between the 'dissolved' and the particulate form by a conventionally defined filtration method by membranes with 0.45 µm nominal pore size is not a sharp distinction. Among these are Fe and Al which occur as colloidal hydrous oxides in rivers; the concentration of these element in 'dissolved' fractions varies with the pore size of the membranes used for filtration (Stumm and Bilinski, 1972; Kennedy et al., 1974; Wageman and Brunskill, 1975; Liss, 1976; Meadows et al., 1978; Burton, 1978b; Figuères et al., 1978).

1.1.2 Suspended particulates in river waters

The amount of suspended particulate matter transported in river waters is about 80% of the total material or 1.8 x 10^{10} ton/annum (Livingstone, 1963; Holeman, 1968; Meybeck, 1976). It has been calculated that the amount of suspended load discharged with the total river runoff to the ocean is equivalent to 8.3 x 10^{9} ton/annum (Mackenzie and Garrels, 1966), 3.0 x 10^{10} ton/annum (Turekian, 1968) or 3.25 x 10^{10} ton/annum (Kuenen, 1950), assuming that the annual world-wide river runoff average is 3.3 x 10^{16} l (Livingstone, 1963). Thus the ratio of dissolved material to suspended material for the total world river water ranges from 0.5 to 0.1 according to these estimates.

Table 1-2. Estimated average concentrations of some of the minor dissolved constituents in the world river waters

Elements	Concentration $\mu g\ l^{-1}$			
	Turekian (1969)	Turekian (1971)	Martin and Meybeck (1979)	Livingstone (1963)
Al	400	-	50	-
B	-	10	18	-
Ba	-	10	60	-
Cu	1.2*	7	10	-
Fe	-	-	40	670 (All forms)
Mn	-	7	8.2	-

* Boyle _et_ _al_. (1977b)

The suspended material content of each stream and river fluctuates with the discharge, but from the estimates of suspended load for the major rivers a value can be derived as the average for world rivers. Holeman (1968) estimated the world average suspended load as 560 mg l^{-1} and Turekian (1971) estimated a value of 330 mg l^{-1}. These high average values reflect the influence of large rivers in South East Asia, which carry some of the largest amount of suspended solids, caused by intensive physical erosion. For the Zaire River, the second largest river in the world, a low suspended load is reported of 50 mg l^{-1} (NEDECO, 1959), or 32 mg l^{-1} according to Eisma, Kalf and van der Gaast (1978) because of the predominance of chemical erosion.

The main componentsof suspended matter in streams and rivers are aluminosilicate minerals and quartz with lesser amounts of organic matter (Mackenzie and Garrels, 1966; Turekian, 1971). There is relatively little knowledge of the detailed chemistry of this suspension in rivers and its behaviour when it is transported to the ocean. Sayles and Mangelsdorf (1979) suggested that the primary reaction of suspended material from rivers on contact with sea water is an ion exchange reaction, whereas Gibbs (1967, 1972) estimated this influence less than 10%.

The importance of the suspended particles on the transport of trace elements by rivers is shown by Gibbs' (1973, 1977) investigations. The major transport of the transition metals Cr, Mn, Fe, Co, Ni and Cu on the solid particles is in association with hydroxide coatings and crystalline material, ranging between 65% to 92% of the total transported, with 5% to 19% as solid organic material, and 0.02% to 8% as sorbed material. These properties of particles and associationsof elements with specific components may influence the behaviour of elemental species during estuarine mixing, as they influence particle reactivity, i.e. the capacity to take up dissolved constituents or to release material into solution under changing chemical condition in the estuary.

1.1.3 The behaviour of dissolved and suspended materials in estuaries

As the dissolved and suspended load of rivers enters the marine environment changes occur by mixing of water bodies. Such interactions may either reduce or amplify the flux of dissolved elements to the ocean and knowledge of them is therefore important in understanding the chemical mass balance of rivers and oceans (Krauskopf, 1956a; Mackenzie and Garrels, 1966).

An estuary is a transition zone in which there is mixing of water of very different chemical composition, concentration (Table 1-3) and properties, each of which also carries particulate material of differing character as discussed by Burton (1978b). Due to the rapid changes in the physicochemical properties such as ionic strength and pH coupled with the presence of riverborne and estuarine suspended material which may serve as a reaction site for dissolved trace elements, there are diverse reactions and processes occurring during the estuarine mixing.

Suspended particles in the estuarine and marine environments originate from several sources. Within the estuaries they may arise from terrestrial and riverborne suspended matter, by flocculation processes in estuaries or by resuspension of estuarine sediments in addition to *in situ* production by biological activity.

In practice it is difficult to distinguish the components in suspended particulates other than by selective chemical leaching methods as illustrated by the works of Gibbs (1973, 1977) discussed above. The variations in the composition of suspended matter with particle size are relevant to the geochemistry of the deposited sediments in estuaries rather than to the chemical processes during estuarine mixing, according to Sholkovitz (1979). He found no general relation between the size and trace element composition of suspended matter; the small and fine particles with higher cation-exchange capacity do not generally contain more trace elements than the coarser particles as was suggested by Turekian and Scott (1967).

Because of the difficulty of trying to characterize processes occurring during estuarine mixing through changes in the

Table 1-3. Estimated average concentrations of some dissolved constituents in the global river water and in sea water.

Elements	Concentration mg l^{-1}	
	River water (Meybeck, 1979)	Sea water (Burton and Liss, 1976)
SiO_2	10.4	6
Ca^{++}	13.4	412
Mg^{++}	3.35	1,294
Na^{+}	5.15	10,770
K^{+}	1.30	399
Cl^{-}	5.75	19,340
$SO_4^{=}$	8.25	2,712
HCO_3^{-}	52.0	140

Elements	Concentration µg l^{-1}	
	River water	Sea water
Al	50 (1)	1 (2)
Fe	40 (1) 670 (4)	< 0.01 (4)
Mn	8.2 (1)	0.4 (2)
Ni	0.3 (2)	6.6 (2)
Cr	1.0 (2)	0.2 (2)
Zn	20 (2)	5 (2)
Cu	10 (1)	0.9 (2)
Ba	60 (1)	21 (2)
B	18 (1)	4,450 (2)

(1) Martin and Meybeck (1979)
(2) Turekian (1969)
(3) Turekian (1971)
(4) Livingstone (1963)

composition of particulates, many investigators have focussed on the dissolved components which are easier to observe and interpret in terms of the changes in their concentrations in estuaries. Considering the dissolved material entering the estuaries, some constituents or elements will undergo changes by physicochemical reactions or biological activity before they finally reach the sea. These changes may alter both the flux and the chemical form of dissolved material reaching the ocean.

The role of suspended particles in the estuarine cycles of many elements has nevertheless begun to receive more attention. In previous studies of the role of suspended particles in transporting of river trace elements, Kharkar et al. (1968) suggested that when trace elements are transported with the riverborne suspended particles, on entering the estuary some material may be released to the saline water as a result of displacement by the Mg^{2+}, Na^{+} ions and other major cations in sea water.

In the analysis of natural water, 0.5 μm membrane filters are conventionally used to separate the dissolved fraction from the suspended fraction. In fact, this filtrate still contains particles smaller than the specified pore size, as colloidal material and organic macromolecules with heterogeneous phases of various size ranges above the cut-off for truly dissolved material between 1 and 10 nm (Stumm and Brauner, 1975; Burton, 1978a; 1979). Thus processes which affect the stability of the colloid also affect the dissolved concentration as conventionally defined. It is important to note that several investigators suggested that some elements, particularly Fe, in the river dissolved material are dominantly in a colloidal suspension, in which their stability is controlled by the electrical properties at the surface (Black, 1960; Stumm and O'Melia, 1968; Stumm and Morgan, 1970; Liss et al., 1975; Boyle et al., 1977a). In river waters with low ionic strength, the colloidal suspensions are relatively stable and maintained in suspension by the repulsive forces (Hahn and Stumm, 1970; Edzwald et al., 1974). The stability of colloids is dependent upon the salinity, increasing salinity causing coagulation very rapidly. This is because the interparticle forces become dominant and result in particle collision and association to form 'flocs' (Edzwald *et al.*, 1974). Eckert and Sholkovitz (1976) have observed the interrelation between the three major salts in sea water and the flocculation of Fe, Al and humates as it occurred by chemical and electrostatic interactions. They found that the flocculation of iron and aluminium humate colloids is controlled by the role of Ca^{2+} ion in destabilizing the more hydrophilic of the humic colloids in the river water (see also Sholkovitz, 1976; Sholkovitz *et al.*, 1978).

1.2 General aspects of estuarine processes

1.2.1. Conservative and non-conservative behaviour

It has been pointed out above that, because of the complexity of the processes affecting particulates, which are transported in the estuary uncoupled from net water transport, attempts to study behaviour of elements have mainly concentrated on dissolved fractions (with the complication that these will include some colloidal material) and particularly on the question as to whether the dissolved fractions behave conservatively or non-conservatively during estuarine mixing.

If a constituent behaves conservatively, i.e. changes in concentration only by physical mixing of different water bodies without chemical interactions, then a plot of its concentration against salinity, or other index of mixing, will give a linear relationship, conforming to the theoretical dilution line for mixing of the river and sea water end members. Deviation from the theoretical dilution line (Liss, 1976) indicates non-conservative behaviour. Figure 1 shows the distribution patterns of non-conservative behaviour when the sea water content is more than that in river water (Fig. 1a) and when the river water content is more than that in sea water (Fig. 1b).

More quantitative approaches to the assessment of conservative and non-conservative constituents have been developed by several workers. Boyle et al. (1974) derived a mathematical relationship for the variation of the flux of a given dissolved constituent constituent (Q_c) with salinity. They showed that for conservative behaviour (i.e. no accumulation or loss of the constituent during mixing)

$$\frac{dQ_c}{dS} = 0 = \frac{d^2C}{dS^2}$$

where C = Concentration of the dissolved constituent at a iso-haline surface of salinity S.

If behaviour is non-conservative

$$\frac{d^2C}{dS^2} \neq 0$$

and the graph of concentration of the constituent against salinity should be curved. This indicates that where the apparent removal is described by several straight-line segments, evidence for non-conservative behaviour has not been obtained. Officer (1979) has also emphasized this last point in his examination of the procedures used to estimate quantitatively the extent of removal in cases of non-conservative behaviour. Li and Chan (1979) also discussed mass-balance models for mixing and for adsorption-desorption processes in estuaries. The equations derived in the former model are essentially similar to those given by Boyle et al. (1974).

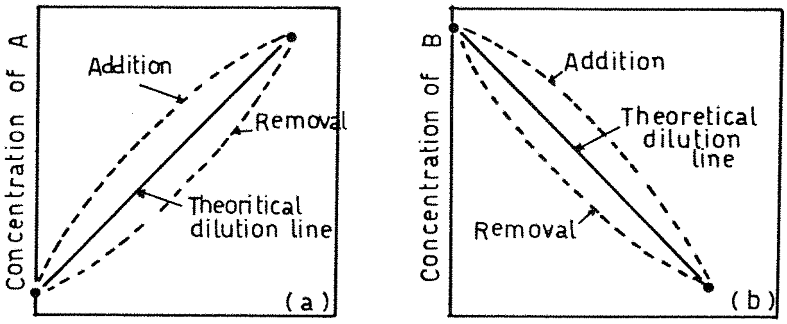


Figure 1. Idealized representation of the relationship between concentration of a dissolved component and a conservative index of mixing, for an estuary in which there are single sources of river and seawater: (a) for a component (A) whose concentration is greater in seawater than in river water and (b) for a component (B) whose concentration is greater in river water than in seawater (Liss, 1976).

1.2.2 Approaches

In previous studies of estuarine chemistry most investigators have concentrated on the phenomena in the real environment in estuarine mixing, by in situ investigation, sampling the whole salinity range in the estuary and analysing the relationship between the concentrations of individual constituents and salinity. This 'survey' approach has certain limitations. Burton (1978a) has summarized the main limitations of the survey approach:

A. With a constituent which is higher in concentration in sea water than in river water, the marine source dominates its concentration even at low salinities. It is then difficult to detect removal relative to the river input.

B. The subsidiary input sources of different composition and concentration of water from the primary source will contribute varying amounts.

C. The presence of various water masses in the estuary and the variation in the concentration of input, and the time they remain in the estuaries, will all contribute to variation in the mixture.

D. It is often difficult to interpret the results unequivocally if the amounts removed are small.

The 'product' approach was developed for the study of the estuarine mixing by Sholkovitz (1976, 1978, 1979) and Sholkovitz et al. (1978). They mixed filtered end-members under experimental condition and analysed the flocculants or precipitates. This avoids the uncertainties of the survey approach but it is important to note that the product approach may not closely simulate the real phenomena of estuarine mixing in which the original suspended matter and its hydrous metal oxide coating may change the extent of the removal of the elements by acting as a site for reactions such as adsorption, desorption and scavenging process (Goldberg, 1954; Kharkar et al., 1968;

Aston and Chester, 1973). Also the mixing experiments in which filtered river water is mixed with sea water of salinity about 35°/oo do not represent the real situation of estuarine mixing in which mixing is continuous along salinity gradients.

There is often considerable disagreement in published work on the behaviour of dissolved constituents in estuaries. This arises from both real variability between estuaries and problems of interpretation as discussed above. Information on a wide range of elements has been summarized by Liss (1976) and an account is given later in the present work of recent investigations on elements of relevance to this study.

1.2.3 Exchange processes

A. Processes of removal of dissolved constituents from estuarine water

The removal of elements can occur by several processes as a result of changes in physicochemical conditions along an estuarine mixing gradient.

A.1 Flocculation and aggregation of colloids

Much of the dissolved iron in river water may occur in colloidal suspension as iron hydroxide or oxide colloidal sols associated with organic matter (Lamar, 1968; Stumm and Morgan, 1970; Schnitzer, 1971; Langmuir and Whittemore, 1971; Holliday and Liss, 1976; Boyle et al., 1977a; Hem, 1978), and this material will, as already discussed, be partly included in the filtrate for filters of pore sizes of about 0.45 μm (Greenland, 1971; Boyle et al., 1977a).

Organic matter appears to play an important role in controlling the non-conservative behaviour of iron. The main component of river organic matter is humic material, comprising a range of fulvic and humic acids of varying molecular weight (Gjessing, 1965, 1970, 1971, 1973, 1976; Gjessing and Lee, 1967; Rashid, 1971; Mantoura and Riley, 1975; Mantoura, 1976; Allen, 1976; Smith, 1976; Buffle et al., 1978). Beck et al. (1974) showed that there is a correlation between the concentration of Fe, Al and dissolved organic matter. It has been suggested that this reflects transport as complexes. The transport of greater amounts of iron in organic rich waters may, however, reflect the colloidal nature of the iron, as suggested for example by Shapiro (1964). The flocculation of organic matter, especially humic substances, has been observed in sea water by Swanson and Palacas (1965) and Sieburth and Jensen (1968); this may result from the neutralization of negatively-charged humic colloids (Sholkovitz, 1976; Eckert and Sholkovitz, 1976; Boyle et al., 1977a), from polymerization of lower molecular weight to higher molecular weight (Swanson et al., 1972), from the decrease of microcolloid stability by excluding the outermost hydrophilic functional groups from the particles (Beck et al., 1974), from the destabilizing of organic associated colloids (Moore et al., 1979).

A.2 Precipitation of metal oxides and their scavenging effect

Iron in the river supply is derived from rock weathering with oxidation of ferrous iron to ferric iron in the water as iron oxides became associated on the surface of clay mineral particles (Carroll, 1958). The stability of ferric oxide is controlled by the pH and Eh of the water; with increasingly aerobic conditions ferric oxide becomes dominant. Comparing the pH range for precipitation of iron and manganese, ferrous iron is oxidized to ferric iron at a lower pH values than manganese (Hem, 1978). The organic matter in the water may influence the oxidation of ferrous iron, retarding the process (Hem, 1960; Theis and Singer, 1973, 1974). When the ferric hydroxide colloid is transported into the estuarine environment, the precipitated hydrous iron oxides, often coating pre-existing suspended particles (Aston and Chester, 1973), can incorporate other trace elements on their surfaces by the process of coprecipitation or scavenging due to the highly active sites for adsorption, especially with a fresh, disordered precipitate (Krauskopf, 1956a; Kharkar et al., 1968; Morgan and Stumm, 1965; Murray, 1975; Plumb and Lee, 1975; Hem, 1977; Murray and Gill, 1978). It should be noted, however, that riverborne colloids already carry incorporated metals, and their surface area is reduced on coagulation.

A.3 Adsorption on suspended particles

As noted above, the amount of suspended particulate matter in the river supply is more than the amount of dissolved trace material and furthermore the suspended solids, including any contribution from resuspended bottom sediments may provide sufficient adsorption sites for dissolved trace elements. The adsorption may arise from unsatisfied chemical bonds or electric charges at surfaces in which the ions of different charge will be adsorbed (Martin *et al*., 1971; Hem, 1978). Jitts (1959) and Pomeroy *et al*. (1965) suggested that the adsorption of phosphate on suspended solids is the main removal process of phosphate in estuaries, and that the sorption reaction is compensated by release from the sediment, these processes effectively 'buffering' phosphate in the water.

Silica has been observed to be removed by adsorption on suspended solids of the kind found in estuaries (Bien *et al*., 1958; Liss and Spencer, 1970).

A.4 Coupled adsorption-catalysed oxidation reactions

Since the pH dependence of the precipitation of iron and manganese is different, the iron hydroxide which precipitates first will provide substrates for the manganese oxides which precipitate later in higher pH estuarine water by coating on the particles. The autocatalysed oxidation at the surface of pre-existing manganese oxide solids in aerated water will result in continued uptake of dissolved manganese from the water (Hem, 1964; Morgan, 1967; Crerar and Barnes, 1974; Van der Weijden, 1975; Hem, 1977, 1978; Morris and Bale, 1979).

A.5 Biological activity

The importance of biological processes in the removal of dissolved materials varies from a small to a large extent in estuaries. Direct uptake of dissolved elements for metabolic processes may occur and organisms, especially micro-organisms, attach on the surface of suspended solids, including organic matter coating suspended solids, and organic particulates can also remove dissolved elements from estuarine water. Jeffries (1962), Johannes (1968), Pomeroy *et al*. (1969, 1972), Pomeroy (1970), and Kuenzler (1971) all observed that the turnover and annual cycles of phosphate in estuaries are related to the cycle of primary productivity and metabolic processes seem to be the main factor in controlling the phosphate cycle. Wollast and de Broeu (1971) found markedly non-conservative behaviour of silicon in the eutrophified Scheldt Estuary as a result of diatoms taking up the element. Milliman and Boyle (1975) also found that dissolved silica in the Amazon Estuary is removed by diatom uptake to the extent of about 25%. In addition to the estuarine system, the uptake of silica by diatoms also occurred with the high diatom population of the freshwater section of the Amazon (Livingstone, 1963).

B. Processes of release of dissolved elements into estuarine waters

B.1 Desorption of adsorbed elements from suspended solids

The trace elements adsorbed on the surface of suspended solids in one environment may desorb into water when they are transported into another environment (Kharkar *et al*., 1968; Rohatgi and Chen, 1975). The riverborne suspended particles with adsorbed trace elements will release some fraction of the adsorbed trace elements on contact with sea water(Kharkar *et al*., 1968; Turekian, 1970). The process of desorption or release is complex and depends upon the element concerned and its mode of association. For example, at a given salinity, some elements may be released from particulates while others remain associated with the solid phase (Kharkar *et al*., 1968; de Groot *et al*., 1969; Martin *et al*., 1971).

The mechanisms involved in the desorption of trace elements from suspended solids have not yet been unequivocally established in real estuarine systems because of their complexity (Turekian, 1971), but this process probably arises from the displacement of ions held on suspended solids, by the mass action effect of abundant sea water ions on passing from freshwater to saline water. The observed desorption of cobalt, silver and selenium from stream-borne particles results from the displacement by Mg^{2+} and Na^+ ions in sea water, according to Kharkar *et al*. (1968). The desorption of trace elements from riverborne particles in estuaries as a function of salinity has been observed (Clanton, 1963; de Groot, 1966; de Groot *et al*., 1969).

B.2 Diffusion and remobilization of elements from sediments

Under the physicochemical conditions in deposited bottom sediments, considerable changes can occur in the chemical forms of elements in both the solid phases and the interstitial waters, and in the distribution of material between solution and the solid phases. These phenomena are largely related to the oxidation of organic matter by bacterial activity, resulting in an anoxic condition in the sediment. Sulphate will be used as an electron acceptor by sulphate-reducing bacteria to oxidize organic matter, and the reducing environment and sulphide formed will change the oxidation state of the sediment and destabilize the oxide coatings, with their associated trace elements, on the sediment particles. Thus, iron, manganese and trace elements enter the interstitial water and will eventually be controlled in concentration by new solid phases stable under the reducing conditions, such as ferrous sulphide (pyrite).

The higher concentration of Mn and Fe in the pore water may lead to an input to the overlying water either by the resuspension of material resulting from the scouring effect of tides or by diffusion, as Morris and Bale (1979) observed in the Tamar estuary. Evans et al. (1977) suggested that in the Newport River estuary, the gain of manganese resulted from a recycling mechanism. Tidal transport occurred of particulate matter with manganese from the lower part of the estuary into the upper part of the estuary where it was deposited; biological activity subsequently caused the reduction and solubilization of manganese and then transport into the overlying water.

B.3 Biological activity and metabolic processes

The process of release of dissolved constituents by organisms seems to have most effect on the growth limiting element such as phosphorus. The amounts and forms of phosphorus components in estuarine environments are influenced directly or indirectly by biological activity. The turnover of phosphorus between water and organism may be a primary control on phosphate in the estuarine system. Phosphate is consumed by phytoplankton and returned to the water as organic phosphorus compounds. If the phosphate content of the water is reduced to less than about 1 μg-at l^{-1} phosphate will be released from sediments which act as a reservoir of phosphate in the estuarine environment (Johannes, 1968; Pomeroy et al., 1969; 1972; Pomeroy, 1970; Kuenzler, 1971). Biological processes also will increase the concentration of dissolved organic matter in the water with consequent high oxygen consumption caused by the mortality of organisms and cell autolysis (Morris et al., 1978).

1.2.4 Recent work on the estuarine behaviour of iron, manganese, dissolved organic carbon, phosphate and silicon

A. Iron, manganese and dissolved organic carbon

There are extensive data from many estuaries showing the removal of iron in the estuarine mixing of iron-rich river water (Coonley et al., 1971; Windom et al., 1971; Bewers et al., 1974; Boyle et al., 1974, 1977a; Eisma, 1975; Windom, 1975; Holliday and Liss, 1976; Sholkovitz, 1976; Subramanian and D'Anglejan, 1976; Yeat and Bewers, 1976; Duinker and Nolting, 1976; Sholkovitz et al., 1977, 1978; Murray and Gill, 1978; Figuères et al., 1978; Moore et al., 1979). Several of the recent studies have provided substantial evidence that this removal is due to flocculation of colloidal material. Dissolved organic matter has been recognised to play an important role in maintaining dissolved iron in solution, but there has been uncertainty as to the relative importance of complexation and colloid formation in this process (Shapiro, 1964; Christman, and Ghassemin, 1966; Piper, 1971; Perdue et al. 1976).

From the molecular weight fractionation of dissolved organic carbon (DOC) and dissolved iron in River Beaulieu water, by Diaflomembrane ultrafiltration, Moore et al. (1979) found a marked difference in the percentage distribution of these two components, especially in the high molecular weight range ($> 10^5$)

of material passing a 0.45 μm filter. The retentivity of dissolved iron in this fraction was $>$90% while that for DOC was about 20%. It was concluded that a small amount of the DOC may be removed together with iron in estuarine mixing. This agrees with the results of Sholkovitz <u>et al</u>. (1978) from mixing experiments; they observed about 5-10% removal of dissolved organic matter, this fraction consisting of high molecular weight humic acid. Removal to this extent would probably not be distinguished from the essentially conservative behaviour of DOC observed in surveys of the Beaulieu Estuary.

Previous studies (Swanson and Palacas, 1965; Sieburth and Jensen, 1968; Hair and Bassett, 1973; Brown, 1975, 1977) had also led to suggestions that the high molecular weight fraction of dissolved humic acid in river water flocculates during estuarine mixing.

Moore <u>et al</u>. (1979) examined the stability of iron added to river water from which the DOC of molecular weight $>10^5$ had been removed. Some 250 μg l^{-1} could be maintained in 'solution' by the lower molecular weight organics, suggesting that they can stabilize iron colloids. They suggested that the apparent high molecular weight DOC may consist of smaller molecules associated with colloidal ferric hydroxide.

The behaviour of manganese is independent of that of iron and during estuarine mixing shows great differences between various estuaries probably due to significant differences in physicochemical parameters and estuarine characteristics. One important difference between iron and manganese is that the oxidation of Mn^{2+} is slower than that of Fe^{2+}. Extensive transfer of dissolved manganese from the lower part of the estuary into the mixing zone or from interstitial water into the overlying water can occur giving rise to an excess of manganese in the estuary relative to predicted values from a linear mixing model; this has been observed in the Tamar Estuary (Morris and Bale, 1979). Furthermore ferric hydroxide which has been formed at lower pH can subsequently precipitate manganese oxide. . This phenomenon will lead to manganese removal in estuarine mixing due to the catalytic effect of uptake of dissolved manganese on the manganese oxides surface (Crerar and Barnes, 1974; Hem, 1977, 1978; Sholkovitz, 1978; Morris and Bale, 1979).

In the Beaulieu Estuary, however, manganese has been shown to behave essentially conservatively while iron undergoes large scale removal (Holliday and Liss, 1976; Moore et al., 1979). The molecular weight fractionation of dissolved manganese also contrasts here with dissolved iron, as iron in the river water is mostly in the size fraction $>10^5$, whereas manganese occurs to the extent of only about 5% in this fraction and is dominantly present in true solution (Moore et al., 1979).

B. Dissolved silicon and orthophosphate

B.1 Dissolved silicon

Silicon is the most investigated of elements with respect to estuarine mixing. The findings have been extensively reviewed and discussed (Burton and Liss, 1973; Boyle et al., 1974; Liss, 1976; Aston, 1978); a summary is given in Table 1-4. Most recent work has indicated a generally conservative behaviour of dissolved silicon in estuaries which have not undergone eutrophication; there is little evidence for significant removal when river input concentration are $\leqslant 14$ mg Si l^{-1} (Liss, 1976, Aston, 1978).

In these circumstances measurements of silicon can often assist interpretation by indicating the validity or otherwise of the assumption of a two end-member mixing model with constancy of input over the period relevant to the survey.

B.2 Dissolved orthophosphate

Estuarine surveys of dissolved phosphate (Table 1-5) have frequently failed to provide clear indications of behaviour which could be interpreted in terms of a two end-member mixing model, in contrast with the situation for dissolved silicon.

Table 1-4. Previous studies on the behaviour of dissolved silicon in estuaries

Estuary	Finding	Reference	River Concentration (mg l^{-1})
Various Japanese	Conservative	Maeda (1952, 1953)	-
		Makimoto et al.(1955)	-
		Maeda and Tsukamoto (1959)	-
		Maeda and Takesue (1961)	-
Kiso and Nagara, Japan	Conservative	Kobayashi (1967)	-
Southampton Water, U.K.	Conservative	Burton et al. (1970a)	10
Columbia, U.S.A.	No significant removal	Park et al. (1970)	-
Various New England, U.S.A.	Conservative	Dengler (1973)	-
Merrimac, U.S.A.	Conservative	Boyle et al. (1974)	5
Columbia, U.S.A.	Conservative in winter, minor biological removal in summer	Stefánsson and Richards (1963)	12
Various, Scotland	No significant removal	Sholkovitz (1976)	0.3-1.3
Magdalena, Colombia	Completely conservative	Fanning and Maynard (1978)	13
Zaire (Congo)	Linearity to 30°/oo (1976)	Bennekom, Berger, Helder and de Vries (1978)	10
	Linearity to 25°/oo (1978)		10
Mississippi, U.S.A.	10-20% removal	Bien et al. (1958)	6
Jiu Long, China	20-30% removal	Fa-Si et al. (1964)	16

Cont'd

Table 1-4 (Continued)

Estuary	Finding	Reference	River Concentration (mg l^{-1})
Vellar, India	At least 10% removal	Burton (1970)	39
Hamble, U.K.	10% removal	Burton *et al*. (1970b)	12
Conway, U.K.	10-20% removal	Liss and Spencer (1970)	3
Chikugogawa, Japan	20-30% removal	Hosokawa *et al*. (1970)	30
St Marks, U.S.A.	Considerable removal	Stephens and Oppenheimer (1972)	12
Alde, U.K.	25-30% removal, unspecified mechanisms	Liss and Pointon (1973)	7
Savanah, U.S.A.	Conservative	Fanning and Pilson (1973)	9
Mississippi, U.S.A.	7% removal	Fanning and Pilson (1973)	6
Orinoco, Venezuela	No significant removal, no fresh water value	Fanning and Pilson (1973)	-
Scheldt, Belgium	80-90% removal by diatoms (eutrophicated estuary)	Wollast and de Broeu (1971)	14
Amazon, U.S.A.	25% removal by diatoms - between 0-5^{o}/oo S	Milliman and Boyle (1975)	-
Scheldt, Belgium	Linear relation (Feb 1973) Intense removal by diatoms (Sep 1973)	Wollast (1978)	15 15

Adapted from interpretation of Burton and Liss (1973), Boyle *et al*. (1974) and Aston (1978)

Table 1-5. Previous studies of the behaviour of dissolved orthophosphate in estuaries.

Estuary	Finding	Reference
Port Hacking, Australia	Buffering mechanism of sediment to about 31 $\mu g\ l^{-1}$	Rochford (1951)
Various, E, USA	Seasonal cycle, metabolic processes - controlling	Jeffries (1962)
Colombia, USA	Constancy of concentration over a wide salinity range (about 37 $\mu g\ l^{-1}$)	Stefánsson and Richards (1963)
Charlotte Harbor, USA	Apparent linearity, neither biological - nor chemical processes	Alberts *et al.* (1970)
Pamlico River, USA	Linear relationship	Hobbie (1970)
Ythan, Scotland	Seasonal variations depend on river - supply, retention by biological uptake and sediment adsorption	Leach (1971)
Tamar, UK	'Buffering' control 21-29 $\mu g\ l^{-1}$	Butler and Tibbitts (1972)
Various, Georgia Coast, USA	Maximum in the mid of estuaries, 1-2 orders of magnitude\than river water and sea water	Pomeroy et al.(1972) \ different
Hudson, USA	The supply dominates the distribution, little biological activity	Simpson *et al.* (1975)
Clyde, Scotland	Rare occasions of removal	Mackay and Leatherland (1976)
Southampton Water, UK	Substantially constant level (about 1 $mg\ l^{-1}$)	Collins (1978)
Zaire (Congo)	Maximum (45-80%) at salinity 10°/oo, decrease from 25°/oo S	Bennekom, Berger, Helder and de Vries (1978)
Magdalena, Colombia	Scatter, tendency to decrease to 25°/oo S	Fanning and Meynard (1978)

Several studies have been interpreted as indicative of a 'buffering' control of phosphate. Pomeroy et al. (1965) suggested that concentrations were controlled at about 1 μg-at P l^{-1}(*) in the Doboy Sound. Stefánsson and Richards (1963) showed that concentrations over a range of salinities in the plume of the Columbia River were also maintained around 1 μg-at P l^{-1}. Further environmental evidence of a control on phosphate concentration was obtained by Butler and Tibbits (1972) on the Tamar Estuary. They found that the variation in the concentration of phosphate between samples of different salinity and between different surveys were relatively small in the range 21-29 μg l^{-1}.

Pomeroy et al. (1965, 1972) and Johannes (1968) found that the equilibrium between water and suspended solids tends to stabilize at a concentration at about 1 μg-at P l^{-1}, suggesting that sediments could act as a trap or reservoir for phosphate, depending on the concentration in the water.

At certain times in the Ythan (Scotland) and Hudson (U.S.A) estuaries, concentrations of phosphate in river water were found to be lower than in the sea water, and this has been considered to reflect the seasonal variation in the river composition (Leach, 1971; Simpson et al., 1975) and possibly the fact that some internal process in the estuaries maintains the levels there.

The sorption properties of suspended material, that may provide the main mechanisms for controlling the concentration of phosphate in estuaries, have been investigated in several aspects. It has been demonstrated that the adsorption of phosphate will not occur at pH more than 6 or less than 4 in freshwater (Carritt and Goodgal, 1954; MacPherson et al., 1958; Jitts, 1959) and release of dissolved phosphate following sorption on bottom sediment is likely when the pH is increased (Carritt and Goodgal, 1954).

High correlations between the concentrations of phosphorus and iron in sediments in certain estuaries (Upchurch et al., 1974; Edzwald, 1977) have led to the view that iron oxide hydrates in the estuaries may play an important role in phosphate

(*) $\cong$ 31 μg P l^{-1}

coprecipitation. Previous studies have indicated that phosphorus is bound in colloids with iron (Fe^{3+}) by ligand exchange in natural water (Morgan and Stumm, 1965; Levesque and Schnitzer, 1967); this complex will be precipitated at slightly acid pH, and a pH increase from about 5.5 to alkaline will cause the solubilization of the ferric phosphate precipitate (Morgan and Stumm, 1965). These findings support the results for pH effects of Carritt and Goodgal (1954). Furthermore an increase in salinity results in the reduction of the adsorption ability of suspended solids. This may arise from the competition for adsorption sites by other anions in sea water.

Also from the study of the correlation between the amounts of inorganic phosphate and oxalate extractable iron in the Pamlico River estuary, Edzwald (1977) found that the correlation between those two components in the sediment from the region of salinity of 1°/oo agreed well when compared to sediments from the zone of salinity $>$1-15°/oo, in which increasing salinity seems to increase the desorption of phosphorus from the iron-phosphorus complex.

In addition to the release of phosphate from bottom sediments under oxic conditions, changes in the redox potential at the sediment/water interface, after $FePO_4$ precipitates have been deposited, to reducing conditions, will lead to reduction of ferric iron to ferrous iron and release of phosphate into the overlying water (Mortimer, 1971). Apart from the chemical processes involved, micro-organisms, especially bacteria, in bottom sediments, can assimilate and solubilize dissolved phosphate from precipitated forms (Wood, 1965, 1967) leading to liberation into the water.

1.3 Objective of the present work

The Beaulieu Estuary has previously been shown to exhibit interesting geochemical interactions during estuarine mixing (Holliday and Liss, 1976; Moore *et al.*, 1979). The behaviour of iron in particular has been studied in detail, demonstrating the value of measuring fractions, defined operationally in terms of molecular weight, in understanding the environmental processes.

The present work was intended to provide fuller evidence concerning the behaviour of DOC in the Beaulieu system and to extend the approaches of Moore *et al.* (1979) to include dissolved phosphate, an ion which might be expected to be considerably influenced by association with iron in both the chemical form in which it is transported in river water and in its estuarine chemistry.

The role of hydrous iron oxides in coprecipitating phosphate can be expected to be considerably influenced by the presence of organic material and the removal of phosphate in the mixing of river and sea water will be affected by any existing association of phosphate with the colloidal complex containing iron and organic material.

In the environmental surveys, the behaviour of iron and silicon has also been examined in order to give additional information to assist interpretation. In considering the reactions of organic matter and phosphate it is clearly useful to have direct information on the behaviour of iron from the same surveys even though its removal pattern is already well known in general terms for this system and other estuaries. Data on silicon are useful in assessing the validity of the two end-member model. It was also thought of interest to examine how silica behaves in the Beaulieu Estuary, there being no published information on this question.

CHAPTER II

BEAULIEU ESTUARY

2.1 Background Information

2.1.1 The physical background

The Beaulieu estuary is situated in the southeast of the New Forest (Figure 2-1) within limits of 50° 50' N. to 50° 46' N., and 1° 22' W. to 1° 29' W. The estuary is supplied by the Beaulieu river system which has arisen from a large number of river captures resulting in a gradually evolving pattern, forming an extensive valley-bog (Tremlett, 1965). The Beaulieu River drains a complex of leached, peaty and fertile alluvial soils including particularly the bogs and wet heath in valleys and basins. The most extensive heathland occurs in the southern half of the New Forest, where a gently contoured slope, with a wide and shallow drainage, holds up the percolated water. A rusty red deposition of iron and other minerals can be detected, colouring most of the gravels in the stream (Tubbs, 1968).

2.1.2 Geology and Geography

There is a generalized geological structure of the catchment area of the Beaulieu River, the area that is now the centre of the downfold of the chalk known as the Hampshire Basin of the geological record of the Tertiary Era. The area of surface rocks of Eocene and Oligocene age is overlain by Pleistocene gravels, sands and clays and is surrounded by low chalk downlands, in which the surface water drainage is particularly held up by the clay beds.

The climate of the Beaulieu River system is generally mild with mean temperature of 7°C or maximum temperature of 18°C and minimum temperature of 0.8°C.

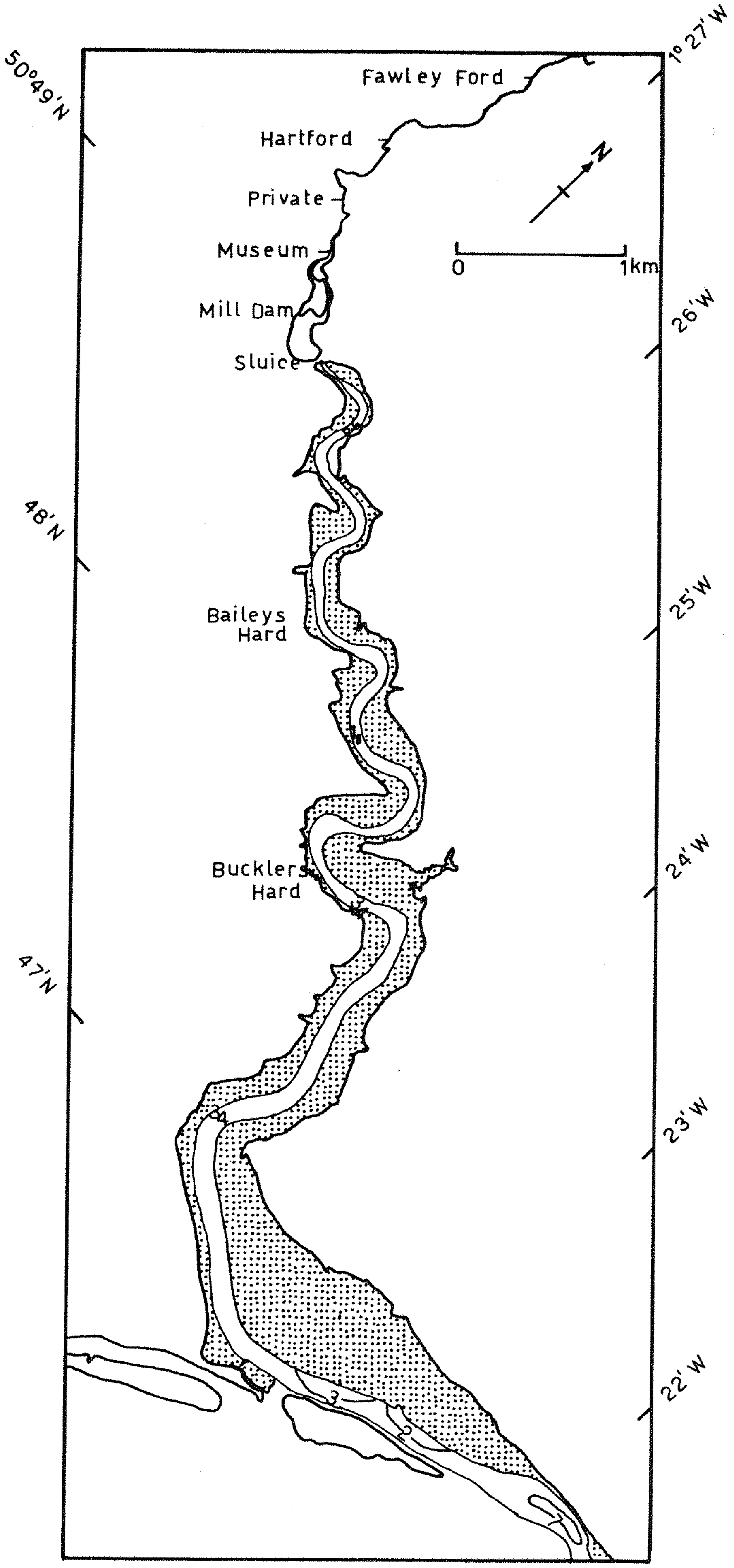


Figure 2-1 Beaulieu River Estuary, showing the marsh and depth, (m).

The mean annual precipitation is 951 mm. The heathland area of Hants is mild, even during the wet winter, and reflects the 'Mediterranean' and 'oceanic' elements in its vegetation, related to the climate (Tubbs, 1968).

2.1.3 Hydrography of the Beaulieu Estuary

The Baeulieu estuary is about 8 km long, connected to the Solent area, with a 3 km width at the mouth of the estuary; the upper estuary varies in width from about 30 m to 80 m and its bathymetry is depicted in Figure 2-1 . The estuary is relatively shallow, the depth in the channel ranging from about 1 m to 8 m. Much of the estuary is nearly homogeneous vertically but at the upstream limits of salt intrusion, which can reach into the pond at Beaulieu at high tide, there is stratification. In this region, a 1‰ salinity was observed at the surface and 19‰ salinity was found at 0.5 m below surface water. The fresh water flow in the Beaulieu River was found to be higher during the winter at about 1 m^3 sec^{-1} than during the summer and autumn of 1977, when it fell as low as 0.03 m^3 sec^{-1} (Southern Water Authority data, A. J. Phillips, personal communication).

2.2 Survey methods

The Beaulieu estuarine study was undertaken during five different periods: 10th April, 4th June, 16th August, 26th September and 9th November 1979. The sampling was conducted from the boat 'Labrax' during the flood tide, by longitudinal sampling transect from the sea water end up to Bailey's Hard. The water samples were collected in 10 litre acid-washed plastic bottles by using a pump or loading a plastic bottle. The sampling positions are shown in Figure 2-2 to 2-4.

Samples of estuarine water from Bailey's Hard up to the sluice were also collected from a dinghy, in order to obtain the very low salinity water. The surface water samples were collected directly into 5 litre pre-cleaned plastic bottles by holding the mouth below the surface of the water.

The sampling positions were chosen to give the largest possible range of salinity over a tidal period; this was ensured by measuring the salinity and temperature by using a probe. The river samples were collected at several points from a bridge; the plastic bottles were lowered from the bridge in order to obtain the water from the central part of the river flow.

The samples were filtered as soon as possible using a vacuum filtration. A 250 ml aliquot, withdrawn for the DOC analyses, was filtered immediately after collection using a precombusted (500°C) Whatman GF/F glass fibre filter (47 mm, 0.7 µm pore size) after discarding the first 50 ml of sample filtrate; the remaining 200 ml was filtered, transferred to a 150 ml precombusted glass bottle, and placed in a refrigerator storage at 5°C.

Another 1.5 litre aliquot was filtered through a Sartorius membrane filter (47 mm, 0.45 µm pore size). The filters had been previously soaked in 1 N nitric acid overnight and rinsed several times in distilled water in order to decontaminate the trace metal content of these filters (Wallace <u>et al</u>., 1977).

The filtration was carried out until the filter clogged, when a plastic holder was used to change the filter. The filtration was continued until a 1 litre volume of the filtrate was obtained. The filtrates for iron determination were collected directly in nitric acid-washed 500 ml polyethylene bottles and acidified with 0.5 ml redistilled nitric acid, and were frozen until time for analysis.

A 250 ml filtrate for phosphorus and silicon analysis was transferred to a 50% sulphuric acid-washed 250 ml polyethylene bottle and stored at 5°C. The analyses were performed as soon as possible.

The salinities of waters were remeasured with an Autolab inductively coupled salinometer.

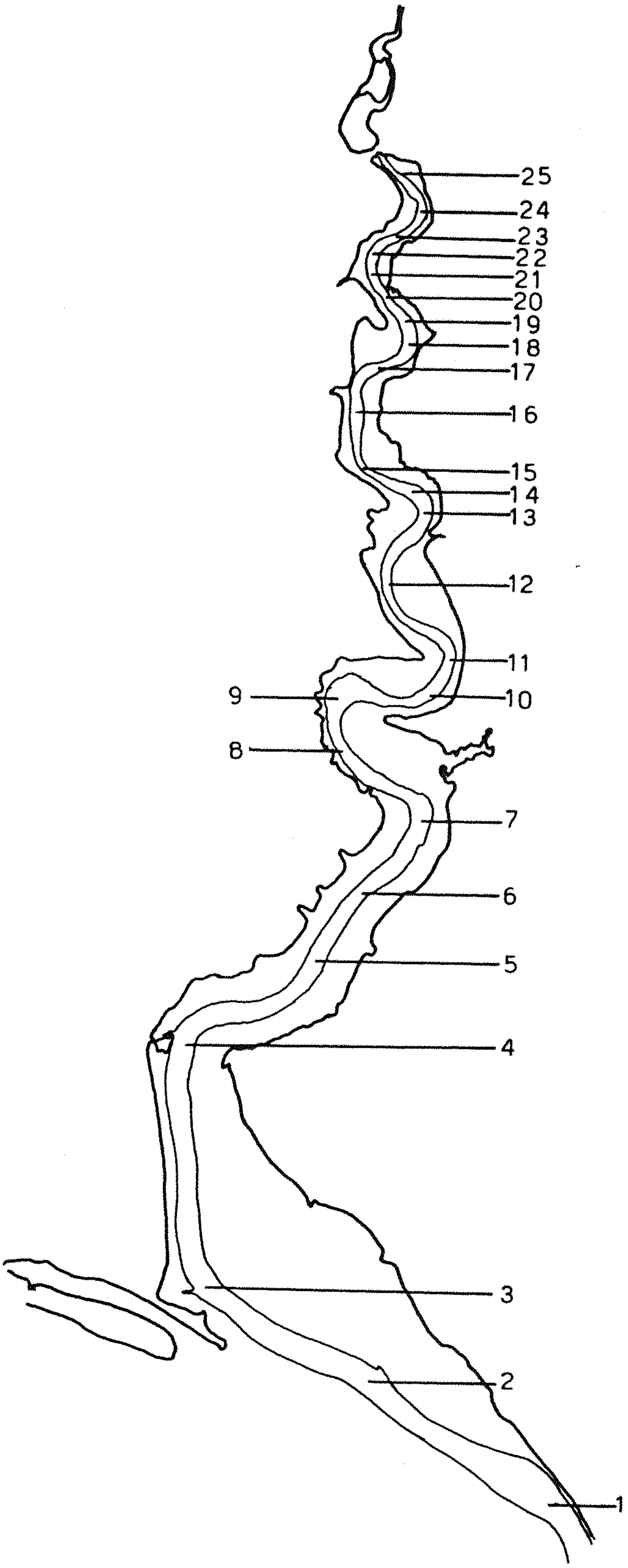


Figure 2-2. Beaulieu River Estuary with station locations; survey of 10 April,1979.

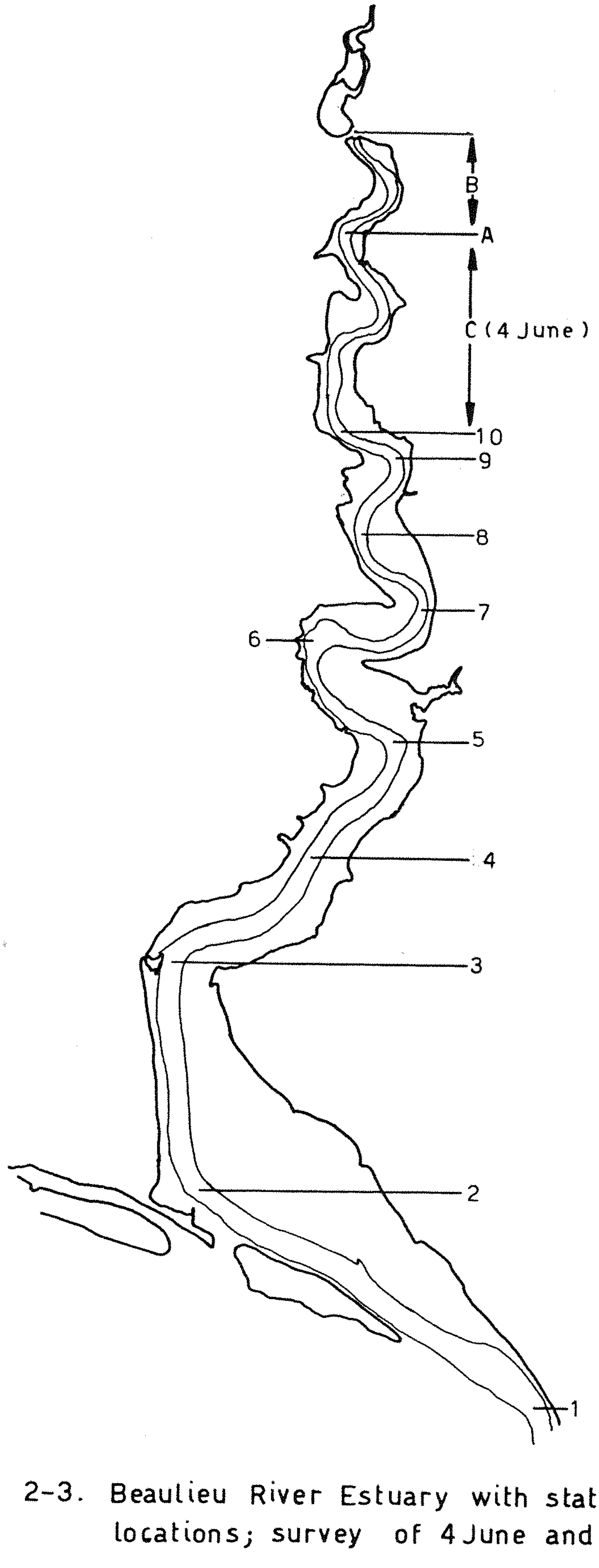


Figure 2-3. Beaulieu River Estuary with station locations; survey of 4 June and 16 August, 1979.

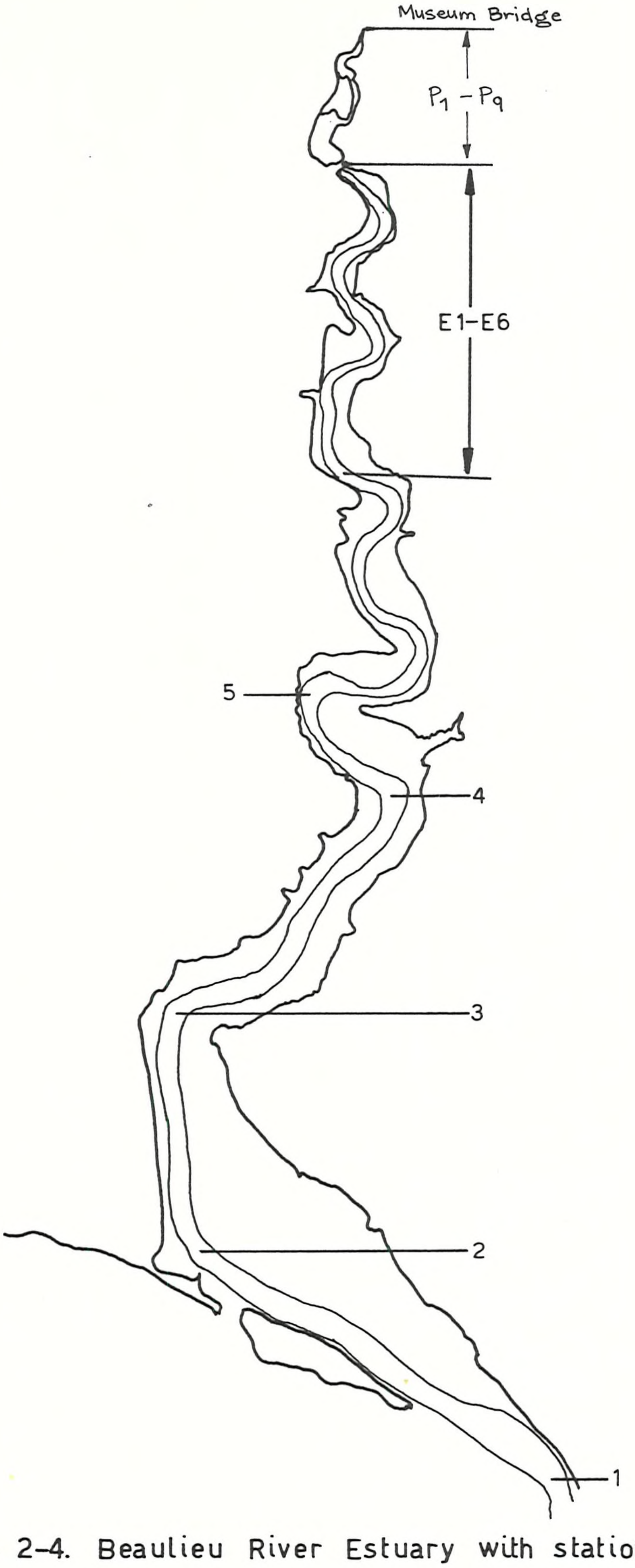


Figure 2-4. Beaulieu River Estuary with station locations; survey of 26 September and 9 November, 1979.

CHAPTER III

ANALYTICAL METHODS

3.1 Methods for the determination of iron

3.1.1 Introduction

There are several methods used in the determination of iron in fresh water and sea water. Amongst these the spectrophotometric method, and atomic absorption spectrophotometry combined with solvent extraction for sea water, are most commonly used.

Of the many spectrophotometric methods for determining iron, complex formation with either bathophenanthroline (4,7-diphenyl - 1,10-phenanthroline), 1-10 - phenanthroline, 2-2′ - bipyridyl, mercaptoacetic acid, 2,4,6-tripyridyl-s-triazine (TPTZ), 3-(2-pyridyl) - 5,6-diphenyl - 1,2,4-triazine (PDT) coated on Amberite XAD-2 (Lundren and Schilt, 1978) or Ferrozine [3-(2-pyridyl) 5-6-diphenyl - 1,2,4-triazine - 4,4′ - disulphonic acid, disodium salt] (Stookey, 1970), are the most commonly employed.

The ferrozine method, however, uses a new iron reagent which is preferable due to the low cost, the high sensitivity (high molar absorptivity) and water solubility, which facilitate analyses.

In the analysis of estuarine waters comprising a wide range of iron concentrations, the ferrozine method was found to be reasonably sensitive over the whole range of concentrations (Lewin and Chen, 1973; Boyle *et al.*, 1977; Sholkovitz *et al.*, 1978; Murray and Gill, 1978). Boyle *et al.* (1977) suggested that in determining dissolved iron by the ferrozine method, the most accurate result can be obtained by the reduction of ferric iron by boiling in the presence of hydroxylamine hydrochloride for 30 minutes. The ratio of total iron/colorimetric iron obtained by this method is nearly constant for each estuary.

The flameless atomic absorption spectrophotometric method gives a better sensitivity and lower detection limit for iron. With the preconcentration technique, i.e. solvent extraction, ion-exchange reaction, the very low concentration of iron in sea water below the sensitivity limit of atomic absorption spectrophotometric can be determined.

The solvent extraction of iron from sea water matrix elements in order to eliminate the interfering elements, is preferable and is an ideal technique, as quantitative extraction is possible over a wide range of concentration.

The solvent extraction of metal pyrrolidine dithiocarbamate (APDC) into methyl isobutyl ketone (MIBK) is most commonly used (Brooks et al., 1967; Brewer et al., 1969). The extraction procedure for analyzing iron in 1 ml samples of sea water by APDC-MIBK and subsequent determination by flameless AAS, was developed by Kremling and Petersen (1974). The extraction from sea water into MIBK is pH dependent (Stolzberg, 1975).

The difficulty of direct injection of organic solvent into the graphite tube arises from the tendency of the solvent to wet the surface of the carbon rod. The back extraction of metals from organic phase into an aqueous solution by using a small amount of nitric acid is found to be a fully satisfactory technique. The detection limit of iron has been found to be 2 ng l^{-1} (Segar, 1973).

The mixture of chelating agents, APDC and DDDC (diethylammonium diethyldithiocarbamate) was applied in the solvent extraction of metals into MIBK by Kinrade and Van Loon (1974) showing a good sensitivity. Furthermore, Danielson et al. (1978) found an enhancement in the extraction with 90-100% extraction efficiency by using the mixture of APDC and DDDC extraction into Freon.

3.1.2 Ferrozine spectrophotometric method

A. Preparation of reagents

The reagents are prepared after Stookey (1970) but, due to the precipitation which occurs rapidly (Gibbs, 1976), the reducing agent (hydroxylamine hydrochloride solution), and the ferrozine solution, are kept separately in acid clean glass bottles. The concentration of iron in the reagent blank was found to reduce by repeated extractions of the reagents with 0.001 M bathophenanthroline in isoamyl alcohol in a separating funnel.

B. Standard iron solution

The standard iron solution is prepared by dissolving 0.1727 g ammonium iron (III) sulphate $[NH_4 Fe (SO_4)_2.12 H_2O]$ in 20 ml distilled water, containing 1 ml of 18 M sulphuric acid, and diluting to 1000 ml in a volumetric flask.

Concentration = 20 μg Fe ml^{-1}

The series of dilute iron standards are prepared and analysed as in the procedure for sample. The standard curve is shown in Figure 3-1, and the absorbance values are compiled in Table 3-1.

C. Reagent blank reduction

The absorbance of the reagent blank before, and after, the cleaning by extraction, was determined, the values were found to reduce from 0.055 (equivalent to ~10 μg Fe l^{-1}) to 0.005 (equivalent to ~1 μg Fe l^{-1}) on average in the 10 cm cell.

D. Recovery of iron

Filtered sea water samples from Beaulieu River, Buckler's Hard and the Solent area were determined for the recovery experiment. Two 40 ml aliquots were spiked with standard iron and analysed for the iron concentration (Table 3-2). Recoveries of 96-98 % were obtained.

E. Reproducibility

The precision of the method was determined by running

Table 3-1. The absorbance of the standard iron solution by the spectrophotometric ferrozine method

Iron $\mu g\ l^{-1}$ 40 ml sample	Absorbance (at 562 nm)		
	10 cm cell	4 cm cell	1 cm cell
5	0.019	0.007	-
10	0.041	0.016	0.005
25	0.115	0.045	0.012
50	0.225	0.087	0.023
100	0.461	0.175	0.044
150	0.710	0.268	0.066
200	0.957	0.353	0.086
250	-	0.461	0.114
500	-	0.998	0.225
750	-	-	0.334
1,000	-	-	0.442
2,000	-	-	0.880*

*The Beer-Lambert law is obeyed to approximately 2 mg Fe l^{-1}.

Table 3-2. Recovery of iron added

Sample	Iron $\mu g\ l^{-1}$			
	Initial	Added	Recovered	% Recovery
River water	375	100	471	96
Estuarine water	15.5	5.0	19.8	96
Sea water	5.5	5.0	10.4	98

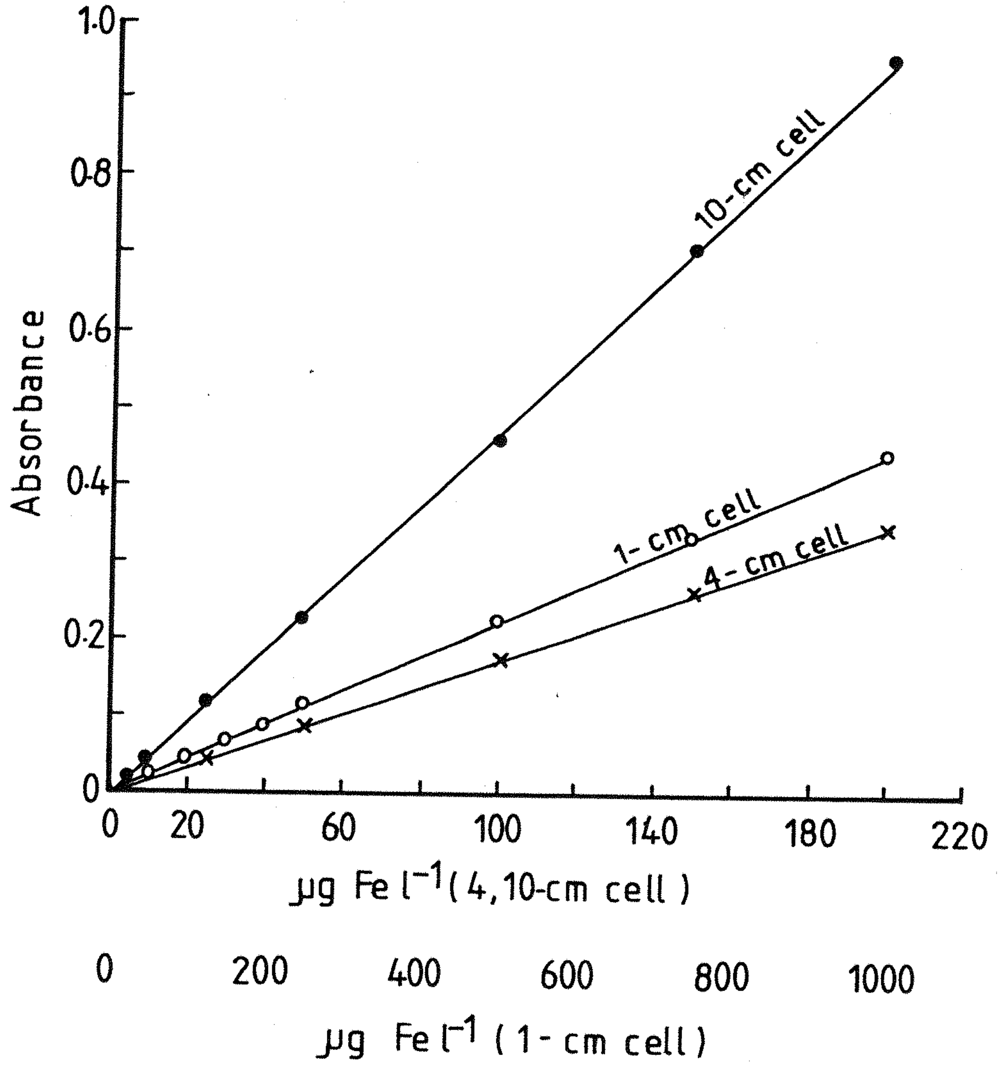


Figure 3-1. Standard iron curve by ferrozine spectrophotometric method.

analyses of ten replicates of standard iron of various concentrations against the blank. The results of corrected absorbance are shown in Table 3-3. The coeffecient of variation was about 1%.

F. Effect of boiling time

The effect of the period of the boiling time on the reduction of ferric iron to ferrous iron by hydroxylamine hydrochloride solution was investigated by using the same concentration of standard iron solution and boiling it in the water bath. The time period of 30 minutes gave a sufficiently complete reduction.

	$80\ \mu g\ l^{-1}$ Iron
Time (hour)	Absorbance (10 cm cell)
0.25	0.356
0.5	0.374
1.0	0.374
1.5	0.373
2.0	0.374
3.5	0.365

3.1.3 Atomic absorption spectrophotometry

A. Determination of iron and manganese in river water by flameless AAS

The dissolved iron and manganese in the river water, and in the ultramembrane filtrates, were measured by flameless AAS, applying the standard addition method. A series of dilute standards was prepared from the BDH standard solution of 1 mg ml^{-1}. A constant volume of standard solution was added to each of the samples, which were acidified to pH 2 using redistilled nitric acid.

Table 3-3. Reproducibility of the ferrozine method for dissolved iron determination

Trial	Optical Density (10 cm Cell)				
	Reagent Blank	10 µg Fe l^{-1}	20 µg Fe l^{-1}	50 µg Fe l^{-1}	85 µg Fe l^{-1}
1	0.006	0.046	0.096	0.225	0.381
2	0.005	0.046	0.094	0.227	0.382
3	0.006	0.046	0.094	0.228	0.386
4	0.006	0.044	0.094	0.227	0.386
5	0.005	0.046	0.095	0.229	0.384
6	0.006	0.045	0.094	0.232	0.386
7	0.005	0.045	0.096	0.224	0.381
8	0.006	0.045	0.094	0.222	0.384
9	0.006	0.045	0.094	0.224	0.378
10	0.006	0.046	0.095	0.227	0.387
Average	0.005	0.045	0.095	0.226	0.385
Standard deviation			0.001	0.003	0.005
% Coefficient of variation	8.5	1.5	0.9	1.3	1.3

B. Determination of iron

A linear working range for the determination of dissolved iron by flameless AAS is 0.5-5.0 ng, using a 5 mm diameter graphite tube and a 10 µl volume of sample injection, with the sensitivity of 37 pg.

A Perkin-Elmer HGA-72 graphite furnace at the 248.3 nm absorption line, 5 mA lamp current, was used:

Settings	Dry	Ash	Atomize	Burn-off
Time (sec.)	30	30	3	2
Digital Setting	17	120	800	990

C. Determination of manganese

A linear working range for the determination of dissolved manganese by flameless AAS is 5-20 ng Mn ml^{-1}, using the 5 mm diameter graphite tube and a 10 µl volume of sample injection, with the sensitivity of 1.2 pg.

Measurements were made at the 279.48 nm absorption line, with a 5 mA lamp current.

Settings	Dry	Ash	Atomize	Burn-off
Time (sec.)	30	30	3	2
Digital Setting	17	100	862	990

D. The precipitation of iron in the UV-photooxidation

In order to observe any loss of dissolved iron in the river water in the determination of total iron by applying to a UV-irradiation (Hanovia 1000 W medium pressure mercury vapour lamp), four silica tubes of river water were irradiated for 2 hours. Two tubes were then decanted for the solution and the other two tubes had a few drops of hydrochloric acid added to dissolve the precipitates which deposited on the wall, and at the bottom of the silica tube. These samples were analysed for iron by flameless AAS and compared with the original concentration. significant losses occurred with samples which were not acidified.

	Iron ($\mu g\ l^{-1}$)	
	6th Dec. 1978	14th Nov. 1978
Original	400	387
uv-irradiated - acid added	437	422
uv-irradiated - without acid added	305	335

3.1.4 Solvent extraction and atomic absorption spectrophotometric method in the determination of iron

A comprehensive study of the formation of metal chelates with dithiocarbamates showed that several metals formed potentially-extractable chelates with APDC. Of these, the APDC technique is applicable to concentrate the low concentration of metals in sea water which are below the detection limits of the AAS.

Kinrade and Van Loon (1974) suggested using two chelating agents APDC and DDDC in the solvent extraction into MIBK to improve the sensitivity and the precision. The solvent extraction of iron with APDC-DDDC in MIBK was studied to observe the pH dependence and the extraction efficiency.

A. pH dependence in the extraction of iron with APDC-DDDC

The reagents were prepared following the method described by Kinrade and Van Loon (1974). Using filtered sea water from the Solent area, with the concentration of 20 $\mu g\ l^{-1}$ of standard iron, the pH effect in the extraction was observed using diluted ammonia solution and nitric acid to adjust the pH of the solution and exact pH measurement with pH meter. The pH of best extraction was found to range between 3-7 with the extraction efficiency of 95-98% and the maximum efficiency at pH 5.5 (Figure 3-2).

B. Sensitivity and linearity

Linearity was observed to 400 $\mu g\ l^{-1}$, and

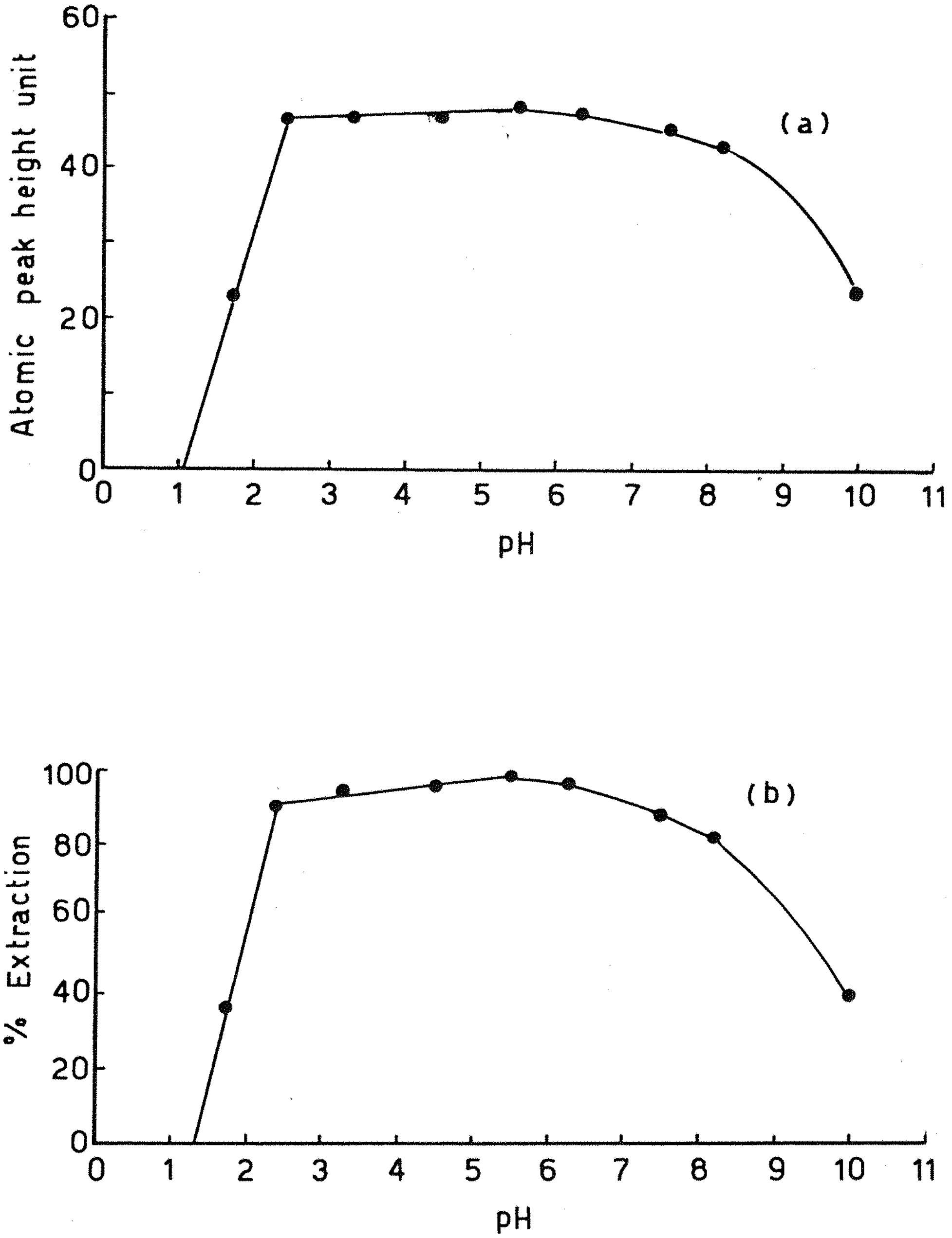


Figure 3-2. pH dependence in the extraction of iron with APDC - DDDC, (a) atomic peak height (b) percentage of extraction.

the detection limit can be enhanced by concentration from the larger initial volume of sample to the small volume of the extracting solution.

C. APDC-DDDC extraction of iron in the estuarine water

For the determination of iron in estuarine waters, the method of Kinrade and Van Loon (1974) using flameless AAS was compared with the ferrozine spectrophotometric method (see Section 3.1.5).

Because of the variable concentrations of matrix elements, interfering ions, and iron itself in estuarine waters, it is difficult to prepare standards sufficiently similar to the waters. To overcome this difficulty, the method of standard additions was used. In this method four identical samples were prepared with varying amounts of standard added to three of them.

The four sample volumes of 100 ml were pipetted into a 250 ml separating funnel and the standard was added at varying concentration into three of them. The pH was adjusted to 5.5 using dilute ammonia solution or nitric acid, with 2 ml of 10% Ammonium acetate-acetic acid buffer added, 2 ml of 1% APDC-DDDC solution was added and shaken for 30 seconds, 10 ml of MIBK was added and shaken for 1 minute. The layer was allowed to separate and the aqueous layer was drained off. The back-extraction was performed using 2 ml of 8 N nitric acid and was shaken for 30 seconds. After 1 hour, 10 ml of distilled water was added and the separating funnel was reshaken. The aqueous solution was drained into an acid cleaned 50 ml conical flask, any organic solvent present was evaporated, the extracting solution was made up to 10 ml volume in the volumetric flask. The solution was determined for iron using the Perkin-Elmer HGA-72 graphite furnace AAS at the 348.3 nm absorption line with settings as in determining iron in river water.

3.1.5 Comparison of the ferrozine method and the AAS method

The results for samples of various salinities determined by the two procedures (ferrozine spectrophotometric method and the atomic absorption spectrophotometry method with both direct injection for river waters and solvent extraction for saline waters) are compared in Table 3-4. The ferrozine method gave very similar results to those obtained by AAS and was used for the estuarine survey of dissolved iron.

Table 3-4. Iron concentrations in Beaulieu Estuary by ferrozine spectrophotometric method and atomic absorption spectrophotometric method

	Iron ($\mu g\ l^{-1}$)			Iron ($\mu g\ l^{-1}$)	
Salinity ($^{o}/oo$)	Ferrozine method	AAS method*	Salinity ($^{o}/oo$)	Ferrozine method	AAS method*
0	475	479	8.3	132	127
0	407	437	11.2	62.0	62.0
0	447	457	17.0	33.0	33.7
0	475	490	17.1	19.5	19.5
0	575	591	17.4	29.0	30.5
0	425	447	18.51	25.0	25.8
0.3	450	458	18.54	19.0	20.2
0.3	402	428	30.5	11.0	10.6
0.5	385	391	33.2	6.0	6.0
2.3	350	363	33.6	5.0	5.3
4.4	302	323	34.05	6.0	5.3
6.1	220	226	34.06	5.0	4.7
8.0	175	177			

* Direct injection for river water
Solvent extraction for saline water

3.2 Dissolved organic carbon determination

3.2.1 Introduction

Dissolved organic carbon in fresh water and sea water can be determined by three principal methods: dry combustion which was recently suggested by MacKinnon (1978) to be a referee method; wet chemical oxidation using potassium persulfate as an oxidant; photochemical oxidation as applied to sea water analysis by Armstrong and Tibbitts (1968) and subsequently by a continuous photo-oxidation procedure (Ehrhardt, 1969; Collins and Williams, 1977).

Schreurs (1978) has developed an automated colorimetric-UV photooxidation method for the DOC range in sea water. Gershy, *et al*. (1979) compared the results of the DOC determination among three methods and found consistent results with $< 5\%$ difference between the high-temperature oxidation and the photooxidation methods.

The method used in this work was that described by Collins and Williams (1977) with a modification of Moore (1978). This is an automated photooxidation procedure; the carbon dioxide produced is determined by an infra-red analyser.

3.2.2 Preparation of organic-free distilled water

Organic-free distilled water is required for the preparation of standard solutions, and as a blank. The concentration of DOC in distilled water was observed to be about 0.3 $mgC\,l^{-1}$. The UV-irradiation of fresh distilled water with an addition of a few drops of 40% analytical grade hydrogen peroxide in a clean silica tube for a period of 4-5 hours was found to reduce the DOC content down to less than 0.05 $mgC\,l^{-1}$ which is similar to the value which has been given by Moore (1978).

3.2.3 Preparation of samples for DOC determination

To determine the DOC content of the sample, in order to reduce the contamination in the filtration, the Whatman GF/F glass filters are combusted at 550°C for 2 hours and the filtration was carried out using a clean filtering unit which had been washed several times with the low organic content distilled water. The filtered sample was kept in a combusted glass bottle and preserved in the refrigerator at 5°C until the time of analysis.

3.3 Nutrient determination

3.3.1 Determination of phosphate

Phosphate was determined in the water samples by the method of Murphy and Riley (1962), but the reducing agent (ascorbic acid) was freshly prepared before every analysis. Due to the severe contamination in the analysis, all the glassware for phosphate analysis was first thoroughly cleaned and soaked in concentrated sulphuric acid for one week, and always stored in dilute sulphuric acid. This glassware was kept for phosphate determination, alone.

3.3.2 Determination of silicon

The concentration of dissolved silicon was determined by the method of Mullin and Riley (1955), with correction for the salt effect, on the same set of samples used in the phosphate determination.

3.4 Salinity measurement

The salinity of samples was measured by the 'Autolab' inductively coupled salinometer and calibrated with the IOS standard sea water.

3.5 pH measurement

The pH of the samples was measured by the EIL pH meter with a combined glass electrode and standardized with the BDH buffers in the pH-range of the sample.

3.6 Ultrafiltration

3.6.1 Introduction

In order to obtain information about the molecular weight fractionation and the characteristic of the complex composition of the dissolved organic matter in natural water, Gjessing (1970) and Wilander (1972) found ultramembrane filtration more useful, and more practical, than the gel filtration method which has been used by several workers (Gjessing 1965; Gjessing and Lee, 1967; Plumb and Lee, 1973; Betz, 1979). Gjessing (1973) suggested the usefulness of ultramembrane filtration by comparing the results of the two methods in the fractionation of aquatic humus. The results of molecular size distribution from both methods correspond poorly, due to the interaction and adsorption of humus on the gel. Also considering the processes of separation and concentration in the gel filtration, the ultramembrane filtration process is preferable, more advantageous, and more practical, than the gel filtration.

Ultramembrane filtration techniques have been applied to the study of natural water, especially in the approach to the study of the role of organic matter in chelation of trace metal and influence on the availability of trace metals in the natural water system.

Allen (1976) observed a strong chelation-complexation of dissolved organic matter and iron in the M.W. $>10^5$ which is predominantly colloidal material. Ogura (1974) found 8-23% of the total organic carbon in the coastal sea water is retained in the molecular weight fraction $>10^5$ and about 24-42% in the molecular weight fraction <500. Smith (1976) also observed a significant amount of DOC at salinity $0^o/oo$ in the M.W. size $>10^5$, and suggested the coprecipitation of organic matter with ferric hydroxide explains the lower carbon content of the high salinity sea water.

In the ultrafiltration of natural water, especially in the fractionation of dissolved organic matter, the contamination of organic matter from a new ultrafiltration membrane, was observed to affect the fractionation; this may arise from the glycerine and ethanol which has been used during packing (Smith, 1976). Wilander (1972) suggested a cleaning technique in order to reduce the organic contamination by filtering a certain amount of distilled water prior to use. Schindler and Alberts (1974) suggested leaching out the organic packing material by eluting with UV-irradiated 2 N sodium chloride solution overnight, and subsequently filtering with 50 ml of 2 N sodium chloride solution before filtering the sample. The carbon will be leached from the non-cellulosic filter polymer in the high ionic strength solution. Also the sodium chloride solution was found to reduce the selective retention of the UM-series by blocking the available ionic sites in the filter (Schindler and Alberts, 1974). Amicon Pub. 1-101G recommended the preparation of a new filter by rinsing with distilled water or by flushing in the cell and as the cleaning technique to reuse the membrane by rinsing with either dilute sodium hydroxide, ammonia solution or 1-2 M sodium chloride.

3.6.2 Diaflo ultrafiltration membranes characteristics

Diaflo ultrafiltration membranes are made of non-cellulosic polymer. Individual Diaflo membranes are characterized by their 'cut-off'. The cut-off refers to the molecular weight (M.W.) of a globular solute at which the solute is 90% rejected. They retain larger molecules than those of stated size and pass smaller species and water (Amicon Pub. NV 400).

3.6.3 General retention characteristics

Type	Nominal M.W. cut-off	Filter characteristics
XM 100A	100,000	Nonionic, negligible charge
PM 30	30,000	Inert, nonionic polymer
PM 10	10,000	
UM 10	10,000	Net neutral charge, ionic sites available
UM 2	1,000	
UM 05	500	Anionic charge

3.6.4 Preparation of ultrafilters

The new ultrafilters were soaked overnight with distilled water in a clean, glass, Petri dish and rinsed with changes of distilled water several times before fitting in the filtration cell; before filtering the sample, especially for DOC determination, washing was done with 200 ml of UV-irradiated distilled water. The last 50 ml volume of UV-irradiated distilled water was kept for the reagent blank correction of the DOC determination. For other analyses, the fresh distilled water was used instead of UV-irradiated distilled water, and using the same process in preparing the ultrafilter.

The used ultrafilters were cleaned by rinsing well with distilled water to remove the film which deposited on the surface of the menbrane. The ultrafilters were soaked in 0.1 N sodium hydroxide overnight and rinsed several times with distilled water prior to re-use.

3.6.5 Ultramembrane filtration technique

The model 402 ultrafiltration cell was used with a 76 mm diameter membrane. The ultrafiltration cell was soaked in 5% nitric acid overnight in order to reduce the contamination of metals, especially for fractionation of iron. For other parts of the ultrafiltration cell, the cleaning technique is recommended in the Amicon Pub. No. 465. The cell, with the filter which has been previously washed, is then ready to use for fractionating the sample. The sample was first filtered through a 0.45 µm membrane filter. The first 50 ml aliquot of sample is filtered and discarded. Subsequently, the rest of the sample is added into the cell and filtered. The pressure of nitrogen gas and the speed of the stirrer are adjusted to the recommended values for each type of membrane. The last 50 ml aliquot of sample was left in the cell after collecting the ultrafiltrate.

3.6.6 The effect of ultrafiltrate volume on the phosphate fractionation

To determine the concentration dependence of the phosphate in the ultrafiltrate of molecular weight $<10^5$ as the ultrafiltrate volume changes, four aliquots of 400 ml river water (5th April 1979) (which were first filtered through a 0.45 µ Sartorius membrane filter) were ultrafiltered using XM-100 ultrafilter. The filtered volumes of 100 ml (25% fractionation), 200 ml (50% fractionation), 300 ml (75% fractionation) and 380 ml (95% fraction) were collected. The ultrafiltrate and retentate at each fractionation were analysed for dissolved phosphate, and the retentivity relative to the original concentration was calculated and shown in Table 3-5. The results showed that the percentage filtration was slightly reduced as the volume of the ultrafiltrate increased; this may be due to some clogging of the macromolecules on the surface of the membrane.

3.6.7 Iron in ultrafiltrate and retentate

In order to observe any adsorption of dissolved iron which may occur in the deposit at the surface of the ultrafilter during the fractionation, the concentrations of iron in the ultrafiltrate and the retentate of the membrane XM-100 (M.W. cut-off 10^5) were determined compared with the initial concentration.

The Beaulieu River sample was collected on 22nd Nov. 1978 and was first filtered through a 0.45 µm Sartorius membrane filter. The initial volume of 300 ml river water was filtered through a XM-100 ultramembrane, and 150 ml volume of ultrafiltrate was collected. The ultrafiltrate and the retentate were determined for iron by flameless atomic absorption spectrophotometric method.

	Iron (µg l^{-1})
Initial	410
Retentate	393
Ultrafiltrate	12

The results showed that there was a separation by fractionation between the ultrafiltrate and the retentate and that the change in concentration was not an effect attributable to absorption of iron on the surface of the ultrafiltration membrane.

Table 3-5. The percentage filtered of the phosphate on the XM-100 membrane as a function of the ultrafiltrate volume

% Volume of ultrafiltrate	Concentration ($\mu g\ l^{-1}$)		% Filtered
	Filtrate	Retentate	
25	5.0	14.6	65.7
50	5.2	14.6	64.4
75	5.6	14.4	61.6
95	5.6	-	61.6

Original concentration 14.6 $\mu g\ P\ l^{-1}$

The ultrafilter is rinsed between each filtration

3.7 Conclusions

The determination of dissolved iron by the spectrophotometric ferrozine method was found to give a reasonable sensitivity covering the whole range of iron concentration in the Beaulieu estuarine waters compared to the atomic absorption spectrophotometric method, with good reproducibility and recovery. The analysis is not time-consuming; thus a long period in preserving samples can be avoided.

The concentration of total iron in the photoxidized river waters was observed to reduce due to the forming of precipitates, but this was recovered by adding acid.

From the result of the similar concentration of iron in the retentate of M.W. cut-off 10^5 and the 0.45 µm fraction compared to the lesser amount of that in the ultrafiltrate, it was concluded that a large amount of iron (~90%) in the water of Beaulieu river is in the M.W. size $> 10^5$ and can be fractionated from that of smaller M.W. by a XM-100 filter without the effect of absorption on the membrane.

The percentage of filtered dissolved phosphate by XM-100 ultrafilter was reduced by about 4% as the volume of the rententate reduced from 75% to 5%; this may arise due to the clogging effect.

CHAPTER IV

RESULTS AND DISCUSSION (ENVIRONMENTAL OBSERVATIONS)

4.1 River Water Chemical Characteristics

4.1.1 Introduction

There is considerable evidence, as previously discussed, that some dissolved constituents exist as colloids in river waters, the stability of such colloids being dependent on several factors, for example chemical factors such as ionic strength, pH, the content of iron and dissolved organic matter, and also physicochemical factors such as the electrical charge at the surface of colloid particles (Hahn and Stumm, 1970; Edzwald *et al*., 1974; Hall and Lee, 1974; Boyle *et al*., 1977a). For iron, the dominant role of organic matter in stabilizing colloidal iron $[Fe(OH)_3]$ in a dispersed state is by an association reaction (Shapiro, 1964; Hem, 1978); the interaction of ferric iron with organic matter and inorganic bases such as orthophosphate will also enhance the stability of colloids (Morgan and Stumm, 1965; Levesque and Schnitzer, 1967).

Preliminary studies of the characteristics of dissolved and colloidal form of elements have been made by applying membrane filtration or gel filtration to separate the 'dissolved' material into a series of molecular weight fractions after 0.45 µm membrane filtration. First, Sephadex gel filtration was used (Gjessing, 1965; Gjessing and Lee, 1967; Plumb and Lee, 1973) and later ultramembrane filtration (Gjessing, 1970), especially to study the relation between iron and dissolved organic matter in natural waters.

The results of Gjessing (1973), Schindler and Alberts (1974) and Moore *et al*. (1979), showed that much of the colloidal iron in natural surface water, to the extent of 50 to 100%, is retained in the molecular weight fraction $>10^5$. This compares with the dissolved organic matter of which less than 30% is retained by membrane with a molecular weight cut-off of 3×10^4 (Moore et al., 1979). This can be explained on the basis that a small quantity of dissolved organic matter, possibly of molecular weight $<10^5$, is in association with iron in the colloid, This amount may be removed during iron removal in estuarine mixing (Sholkovitz _et al_., 1978; Moore _et al_., 1979).

On the molecular weight fractionation of phosphate and silicate in river water, little work has been done. Schindler and Alberts (1974) found that both phosphate and silicon in Georgia fresh water systems are in 'true' solution, and there were no apparent high molecular weight fractions. Gjessing (1973) observed that about 38% of the phosphate in the natural humus water was retained on a membrane with molecular weight cut-off of 1000 and Wilander (1972) found a corresponding value of about 77% for natural water from the Swedish Waters Quality Network. Silicon was retained to only about 2.5% at this level of cut-off in the natural humus water (Gjessing, 1973).

The relationship to colloidal material, as shown by molecular weight distributions, of dissolved constituents such as iron, dissolved organic matter, phosphate and silicon can help explain the dominant processes which may influence these elements as they are transported into the estuarine mixing zone, either to be removed by flocculation, adsorption or coprecipitation with iron oxides or diluted by simple physical mixing.

4.1.2 Ultramembrane fractionation of iron

Samples of Beaulieu river water, taken on 28th June 1979, 12th February and 31st March 1980, were filtered to obtain the dissolved fraction passing 0.45 μm Sartorius membrane filters and were then fractionated on the basis of molecular weight ranges, using ultrafilters with cut-offs ranging from molecular weight 10^5 to 500. The filtrates were analysed for iron by direct injection, flameless atomic absorption spectrophotometry, using the standard addition method. The results are summarized in Table 4-1, in which the concentration of iron in filtrates and the percentage retained on each molecular weight are shown. The results clearly show that the largest amounts of "dissolved"

Table 4-1. Dissolved iron and manganese in River Beaulieu waters and their fractionation by ultra-filtration.

Sample/Date	Total dissolved (μg l^{-1})	Concentration (μg l^{-1}) in solution passing Diaflo ultra-filters of type and nominal molecular weight cut-off as shown.					
		XM-100 (10^5)	PM-30 (3×10^4)	PM-10 (10^4)	UM-10 (10^4)	UM-2 (10^3)	UM-05 (500)
IRON							
Fawley Ford Bridge							
28th Jun 1979	1,810	127(93)	68(96)	-	12(99)	-	-
12th Feb 1980	360	95(73)	24(93)	-	24(93)	-	-
31st Mar 1980	780	67(91)	67(91)	38(95)	32(96)	7.5(99)	2.0(99)
MANGANESE							
Fawley Ford Bridge							
31st Mar 1980	158	153(3)	153(3)	153(3)	153(3)	103(35)	-

Values in parentheses are percentage retained iron are in the fraction of molecular weight $>10^5$, the percentage retained ranging from 73 to 93%. This reflects the presence of dissolved iron in Beaulieu river water in colloidal suspension, which is consistent with earlier investigations of this river (Moore *et al.*, 1979).

4.1.3 Ultramembrane fractionation of DOC

The same set of water samples that were fractionated for iron were analysed for DOC by the method of Collins and Williams (1977), together with another river sample from Ashurst in the heathland of the New Forest. The results are shown in Table 4-2. They show that the DOC in the main stream river water mostly occurred in the lower molecular weight fractions with up to 75% below 10^4. Only small fractions of about 2.5 to 5% were retained by the membrane with a cut-off of 10^5. For the sample from upstream at Ashurst, the DOC concentration was about 20 mg l^{-1}, about twice that in the main stream of the Beaulieu river. The distribution of the molecular weight size of DOC in this sample differed from the other three river samples with less retention of DOC on the XM-100 to PM-30 filters and a sudden increase in retention on the smaller size UM-10 filter (cut-off 10^4). This suggests that the water from the headstream contains a high concentration of DOC mostly (up to $\sim$99%) of low molecular weight ($< 3 \times 10^4$) with about 63% in the fraction $< 10^4$.

The molecular weight distribution given here differs in detail from that given by Moore *et al.* (1979), with greater amounts appearing in the fractions of lower molecular weight (Table 4-3). The mean values of total DOC concentration are similar, but there is a marked difference in the distributions of the DOC between the different molecular weight fractions. The sampling position used in this work for Beaulieu river water was sited further inland than that used by Moore *et al.* (1979) in order to avoid the effects of a greater intrusion of salt water found in the course of the present work, but this is unlikely to account for the difference. The difference in composition between the Ashurst sample and the main stream samples suggests that differences in the flow pattern in the

Table 4-2 Dissolved organic carbon (DOC) in River Beaulieu waters and its fractionation by ultra-filtration

Sample/Date	Total DOC ($mgC\ l^{-1}$)	Concentration DOC ($mg\ l^{-1}$) in solution passing Diaflo ultra-filters of type and nominal molecular weight cut-off as shown XM-100 (10^5)	PM-30 (3×10^4)	UM-10 (10^4)
<u>Fawley Ford Bridge</u>				
28th June 1979	10.7	10.2(4.7)	9.4(12.2)	7.8(27)
12th Feb. 1980	8.3	8.1(2.4)	6.6(20.5)	6.2(25)
31st March 1980	4.1	4.0(2.4)	3.8(7.2)	1.4(66)
<u>Ashurst</u>				
5th July 1979	20.2	20.0 (1)	20.0 (1)	12.7(37)

Values in parenthesis are percentage retained

Table 4-3 Comparison of results[(a)] of ultrafiltration of DOC in Beaulieu river water as found in this work and by Moore *et al*. (1979)

	Total DOC ($mg\ C\ l^{-1}$)	No. of samples	Percentage retained by Diaflo ultra-filters XM-100	PM-30	UM-10
This work	7.7	3	3.2	13.3	39.5
Moore *et al*. (1979)	7.7	6	18	23	78

(a) Values shown are means of measurements on samples collected on various occasions drainage basin might significantly alter the detailed characteristics of DOC in the river water end-member in the estuary.

This study of iron and DOC molecular weight fractionation showed that the large amount of dissolved iron in the molecular weight fraction $>10^5$ was accompanied by only 2 to 5% of the DOC, which thus has a low association with the iron in colloid.

4.1.4 Ultramembrane fractionation of phosphate

River water samples from the Beaulieu system were taken at various times during 1978 and 1979. These samples were first filtered through 0.45 µm Sartorius membrane filter and were then fractionated with a series of Ultrafiltration membranes ranging from XM-100 (molecular weight cut-off 10^5) to UM-10 (molecular weight cut-off of 10^4). The first and the last 50 ml volume of filtrates in each fraction was discarded. The filtrate was analysed for dissolved orthophosphate by the method of Murphy and Riley (1962). The results are shown in Table 4-4 and clearly show the retention of considerable amounts of 'dissolved' phosphate by the XM-100 membrane especially for samples from Fawley Ford bridge, which represent the fresh water entering the Beaulieu Estuary.

The percentage retained on the XM-100 membrane ranged between 50 to 82%, with the exceptions of the sample collected on 5th April for which retention was 36% and samples from small streams from Ashurst Lodge and Dibden in the New Forest. The results of molecular weight distributions of these latter samples showed that the molecular weight distribution shifted with greater proportions in the range lower than 3×10^4 (PM-30). The sample from Ashurst contained 495 $\mu g\ l^{-1}$ of iron and 20 $mg\ l^{-1}$ of dissolved organic carbon; these concentrations being higher than in the samples from downstream (Fawley Ford bridge). The higher amount of dissolved organic matter may have controlled the capacity of phosphate binding of colloidal iron oxide.

The average values of the molecular weight distribution of phosphate in Beaulieu River are 63% $>10^5$, 70% $>3 \times 10^4$ and 74% $>10^4$.

Table 4-4 Dissolved phosphate in River Beaulieu Waters and their fractionation by ultra-filtration

Sample/Date		Total concentration (μg P l^{-1})	Concentration (μg l^{-1}) in solution passing Diaflo ultra-filters of type and nominal molecular weight cut-off as shown		
			XM-100 (10^5)	PM-30 ($3x10^4$)	UM-10 (10^4)
Fawley Ford Bridge					
25 July 1978		32.5	5.8(82)	5.8(82)	5.4(83)
24 Nov. 1978		10.6	4.3(59)	1.8(83)	1.5(86)
17 May 1979		13.5	6.7(50)	6.3(53)	6.3(53)
5 July 1979		9.5	3.2(66)	2.5(74)	2.5(74)
26 Sep 1979		12.3	4.3(65)	3.3(73)	1.3(89)
5 Apr 1979		14.6	5.2(36)	-	-
Fawley Ford Bridge	Mean Values	15.5	4.9(59)	3.9(73)	3.4(77)
Ashurst					
5 July 1979		15.2	10.6(30)	8.3(45)	2.2(85)
Dibden Purlieu					
25 July 1978		12.8	12.6(1.6)	3.9(69)	3.9(69)
Museum Bridge					
22 Jan 1979	10.30	10.2	5.0(51)	4.5(56)	3.3(68)
	13.30	12.0	5.1(58)	4.1(66)	4.1(66)
	15.30	11.0	1.8(84)	1.8(84)	1.5(86)
Weir					
22 Jan 1979	11.00	10.2	3.8(63)	3.5(66)	2.5(75)
	14.00	12.8	6.6(48)	4.7(63)	4.7(63)
	16.00	15.3	6.7(56)	5.6(63)	5.2(66)

Values in parenthesis are percentage retained

The distribution of phosphate between molecular weight fractions was also examined (Table 4-5) after photo-oxidation of organic material by ultra-violet irradiation using a 1 kW medium-pressure mercury arc lamp. An increase in reactive phosphate was observed which was reflected in all molecular weight fractions with the proportion in the lower molecular weight fraction increasing. In a filtered water sample containing a considerable amount of colloidal material it is possible that some inorganic phosphorus is not included in the analysis of reactive phosphorus. The nature of the fraction made available by photo-oxidation is thus uncertain. This normally unreactive fraction could contain both phosphorus bound in colloids and organic phosphorus compounds in solution.

The phosphorus incorporated with the colloid of hydrous iron oxide in river waters, as it is transported into the estuary, where changes in the physicochemical properties lead to the flocculation of the iron colloid in early mixing and result in iron removal, may be expected to undergo removal through its prior association with the colloid rather than by adsorption or scavenging from solution.

4.1.5 Ultramembrane fractionation of dissolved silicon

The results in Table 4-6, for three samples from Fawley Ford bridge and one sample from Ashurst in the New Forest, show that silicon did not occur to any significant extent other than in true solution. Only for one sample (on 5th April) the silicon retained on the UM-2 membrane amounted to about 8%. These results imply that the silicon in Beaulieu River occurs as monosilicic acid or low polymer forms and not in the colloidal suspension as with phosphate. This is supported by Krauskopf (1956b), who suggested that the silica in most stream waters is in 'true' solution, in solubility equilibrium with amorphous silica, and by the absence of polymeric silicon in river water or sea water as shown by Alexander (1953) and Burton et al. (1970a). The changes in concentration during estuarine mixing may then be caused by simple dilution as

Table 4-5. Comparison of the ultramembrane fractionation of dissolved orthophosphate and total phosphorus

Analyses	Total concentration (μg l^{-})	Concentration (μg l^{-1}) in solution passing Diaflow ultra-filters of type and nominal molecular weight cut-off as shown.		
		XM-100 (10^5)	PM-30 (3×10^4)	UM-10 (10^4)
Dissolved phosphate	10.6	4.3(59)	1.8(83)	1.5(86)
Total dissolved phosphorus	18.7	9.8(47)	9.8(47)	9.0(52)

Values in parentheses are percentage retained.

Table 4-6. Dissolved silicon in River Beaulieu waters and their fractionation by ultra-filtration.

Sample/Date	Total concentration (mg l^{-1})	Concentration (mg l^{-1}) in solution passing Diaflo ultra-filters of type and nominal molecular weight cut-off as shown.			
		XM-100 (10^5)	PM-30 (3×10^4)	UM-10 (10^4)	UM-2 (10^3)
Fawley Ford Bridge					
5th Apr 1979	2.63	2.59(1.5)	2.59(1.5)	2.59(1.5)	2.41(8)
17th May 1979	4.20	4.20(0)	4.20(0)	4.20(0)	-
5th July 1979	4.52	4.48(~1)	4.46(1.3)	4.46(1.3)	-
Mean	3.78	3.76(~1)	3.75(1.4)	3.75(1.4)	2.41(8)
Ashurst - 5th July 1979	4.88	4.74(2.9)	4.74(2.9)	4.68(4.1)	-

Values in parentheses are percentage retained.

Maéda (1952; 1953), Makimoto et al. (1955), Maéda and Tsukamoto (1959), Kobayashi (1967) and Boyle et al. (1974) suggested, or by inorganic process involving adsorption onto the surface of particulates as demonstrated experimentally by Bien et al. (1958) and Liss and Spencer (1970) or by diatom uptake (Wollast and de Broeu, 1971; Milliman and Boyle, 1975), rather than by direct coagulation of dissolved silicon. Thus the process of removal of dissolved silicon and phosphate and their behaviour during estuarine mixing are expected to be different in the Beaulieu Estuary.

4.2 Behaviour of constituents during estuarine mixing

4.2.1 Introduction

The Beaulieu Estuary is a relatively simple system with one main input of fresh water, formed by drainage from the heathland and bogs of the New Forest. A dominant characteristic of the water is the yellowish-brown colour with a high concentration of dissolved organic matter stabilizing inorganic colloidal forms of iron; it has an unusually high concentration of manganese. Earlier studies (Holliday and Liss, 1976) and more recent work (Moore, et al., 1979) have shown the markedly non-conservative behaviour of dissolved iron in mixing in the Beaulieu Estuary with extensive removal in early mixing and almost complete removal of the river input concentration as the salinity approaches 15‰. In contrast, the DOC tends to behave conservatively within the limits which can be established by the survey approach, which is consistent with the conservative behaviour of DOC in the Amazon Estuary (Sholkovitz et al., 1978). The lack of clearly apparent DOC removal may reflect the small amount of DOC in colloidal association which would be removed with the iron, relative to the total amount of DOC in the water (Moore et al., 1979). From several investigations on the correlation of DOC and POC (particulate organic carbon), it has been suggested that DOC is transformed into POC (Sutcliffe et al., 1963; Riley, 1963), either by aggregation on inorganic matter nuclei (Riley, 1970) or by direct flocculation as has been suggested to occur for humic material (Shapiro, 1964; Ong and Bisque, 1968; Bondarenko, 1971). DOC removal by flocculation in mixing experiments has been found to the extent of 3-11% between salinities of 15-20‰ (Sholkovitz, 1976).

Another significant finding on the behaviour of iron in the Beaulieu Estuary, is that the non-lattice held fraction of iron in suspended particulate matter decreases in a non-linear manner with increasing salinity along the estuary, similarly to the pattern of dissolved iron. This may reflect both the precipitates formed very rapidly from iron removal during early stages of mixing and the gradient mixing of riverborne suspended solids with marine particulates (Moore et al., 1979)

4.2.2 Estuarine surveys

A. Dissolved iron

The results for iron during surveys in 1979 in the Beaulieu Estuary are summarized in Figure 4-1, which shows the relationship between the concentration of dissolved iron and salinity. The expected extensive removal of dissolved iron during estuarine mixing was observed.

Samples were obtained on 10th April under conditions of low tidal amplitude, which can be seen from the distribution of salinity (Figure 4-2). The highest point that the salt wedge reached was above Bailey's Hard. Because of the rapid changes in salinity between samples only a few metres apart, no water samples were obtained with salinities between 4 and 17°/oo. The distribution of dissolved iron with salinity is shown in Figure 4-1a. Iron concentrations decreased rapidly from the concentration of 320 µg l^{-1} in river water to concentrations of less than 10 µg l^{-1} at salinity 32°/oo. A substantial degree of removal occurred between salinities of 0 to 5°/oo.

For the second survey on 4th June, the variation of dissolved iron with salinity is shown in Figure 4-1b. Maximum removal of dissolved iron was observed to occur between salinity 0 to 10°/oo; the concentration of iron in river water of 435 µg l^{-1} was reduced to less than 10 µg l^{-1} at salinity 30°/oo. The magnitude of removal was estimated to be > 90% by salinity 10°/oo and is almost complete by 15°/oo with a greater than 95% removal.

In the third survey, on 16th August (Figure 4-1c) removal was almost complete around a salinity value of 13°/oo. Samples between 2 and 13°/oo were not obtained but the extent of dissolved iron removal was more than 95% at the latter salinity.

Figure 4-1d, giving the results for the survey on 26th September, shows large removal of iron between salinity 0 and

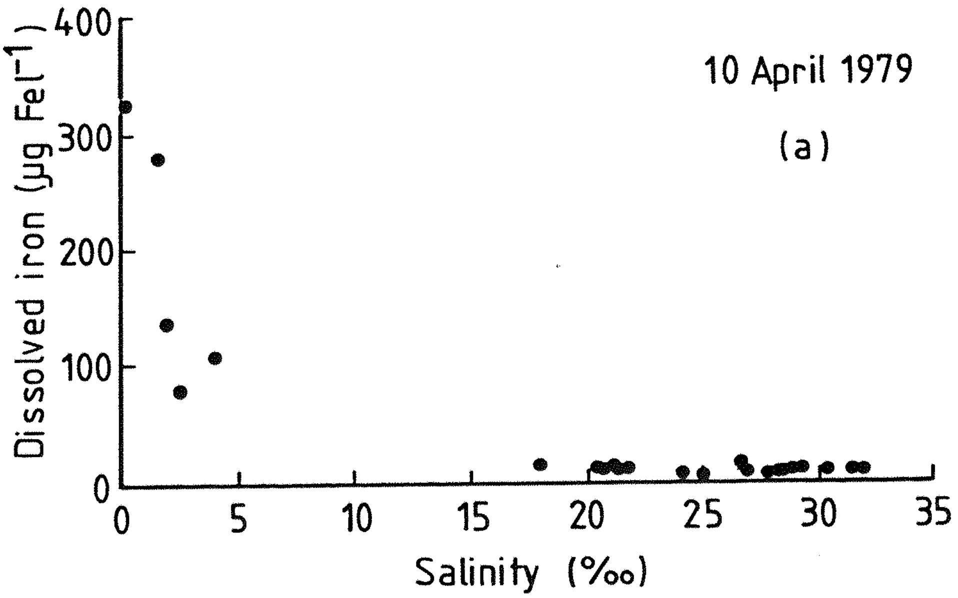


Figure 4-1. Relationship between concentrations of dissolved iron and salinity in the Beaulieu Estuary; survey of (a) 10 April, 1979.

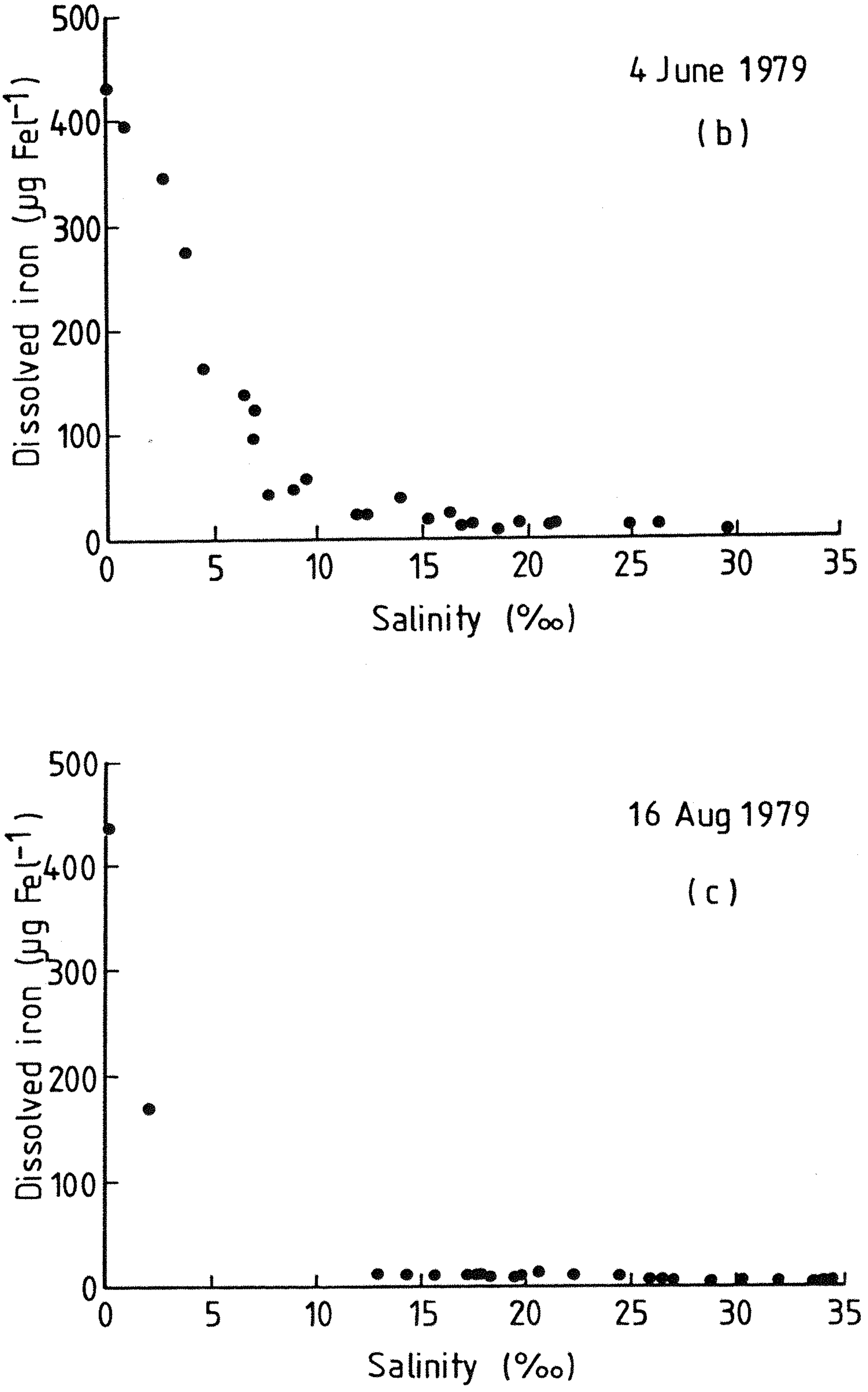


Figure 4-1. (b) 4 June, (c) 16 August, 1979.

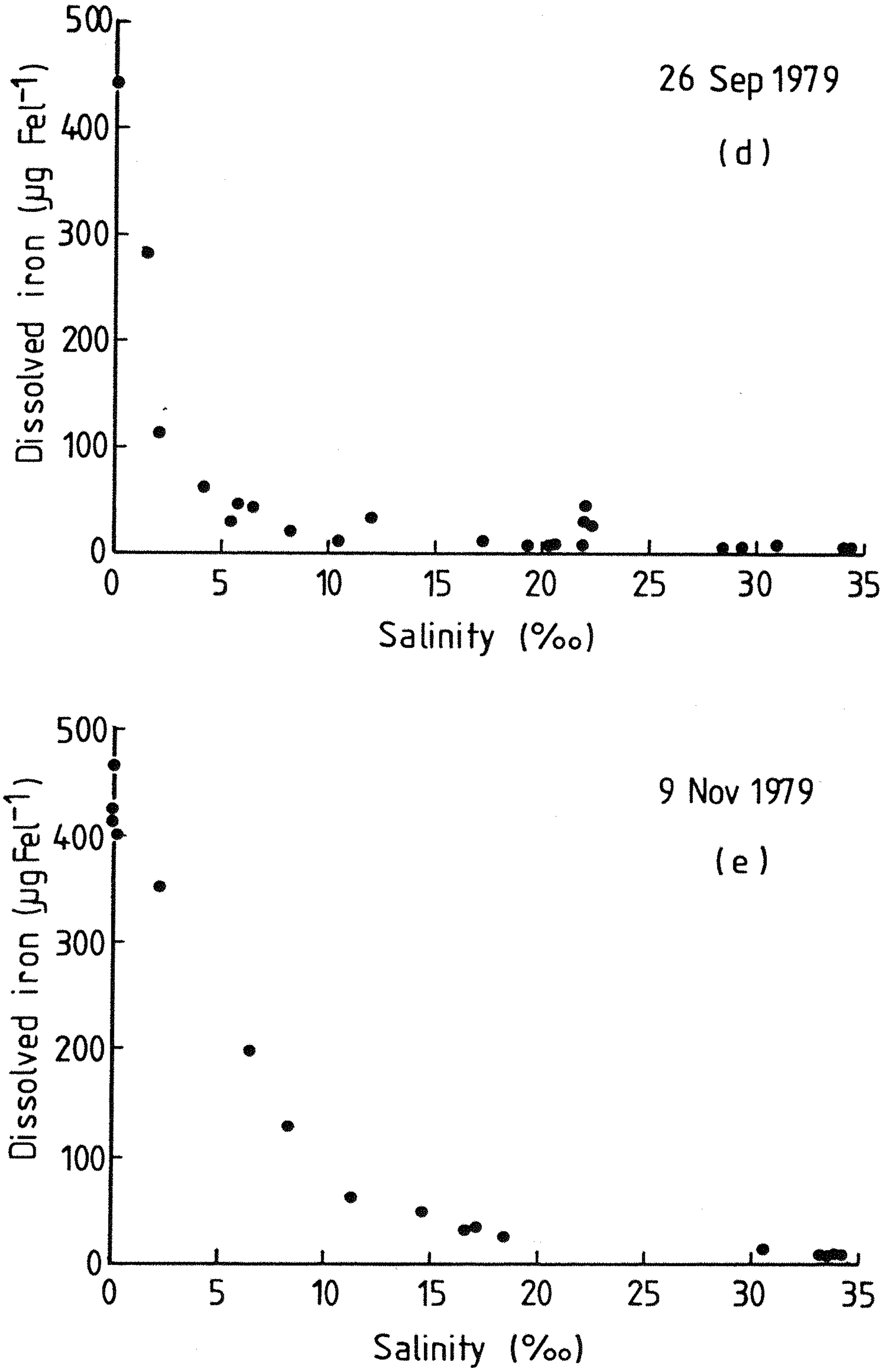
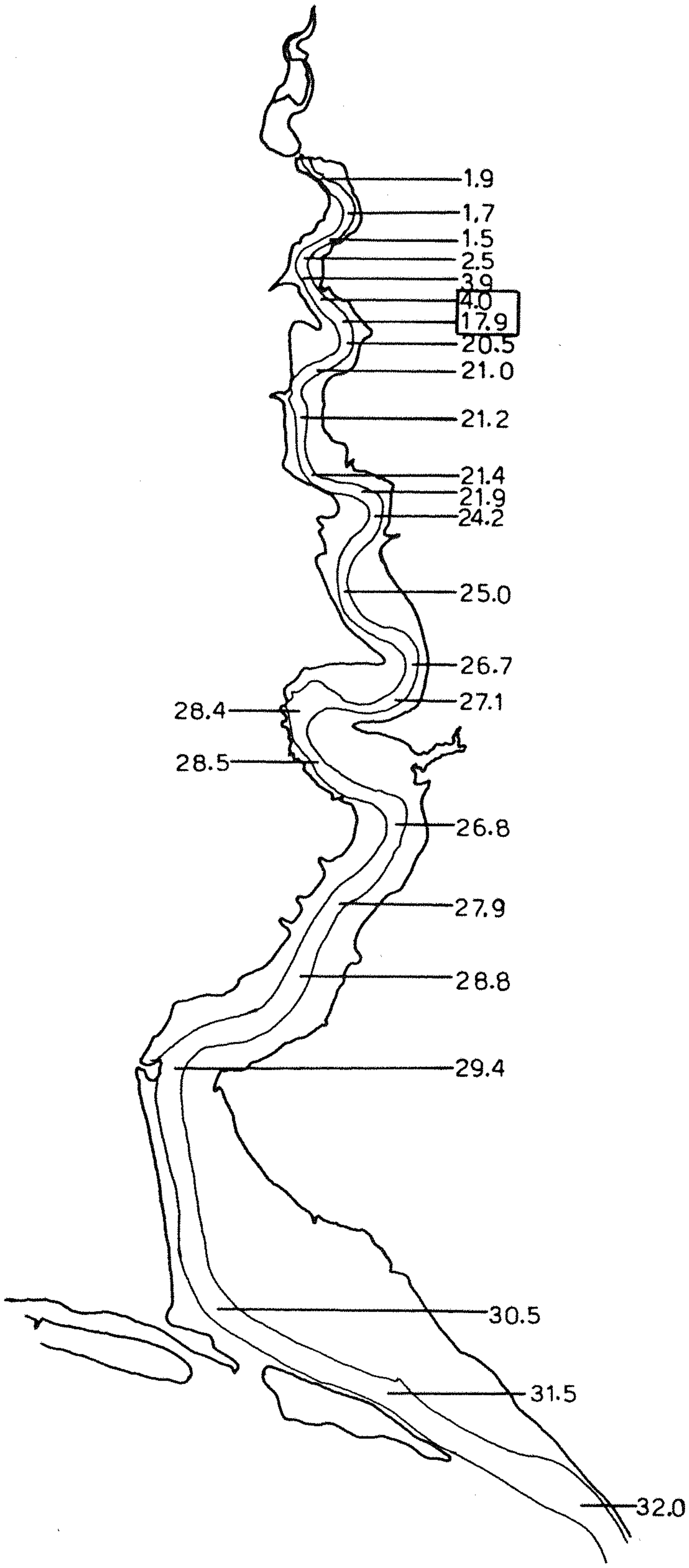


Figure 4-1. (d) and (e).



gure 4-2. Salinity distribution in the Beaulieu Estuary; survey of 10 April, 1979.

oo with an estimated 90% of the input removal, and almost mplete removal ($>$95%) by salinity 10°/oo.

Removal of iron was more complete at lower salinities in the survey of 26th September than in that of 4th June. The concentrations of iron in the river water were similar in these surveys but the concentration of DOC was considerably lower in the time of later survey (3.6 mg C l^{-1} as compared with 9.2 mg l^{-1}). It is possible that the higher organic content has some stabilizing effect so that the flocculation process is retarded and is not complete until a high salinity is reached.

In the last survey on 9th November the salinity dependence of removal of iron is similar to that of the June survey. The lesser extent of iron removal with increase in salinity was pronounced, as shown in Figure 4-1e. The concentration of iron in river water was high at 470 µg l^{-1}, with 10.3 mg DOC l^{-1}. The maximum iron removal seems to occur over a higher salinity range between 0-15°/oo and removal was almost complete around 20°/oo S. This supports the view that of removal may be influenced by the amounts of dissolved organic material.

B. Dissolved organic carbon

The results for DOC, examined in relation to the mixing index, salinity, are shown in Figure 4-3. For the survey of 4th June, the concentration of DOC in river water was about 9 mg l^{-1}. The conservative behaviour of DOC during estuarine mixing was apparent (Figure 4-3a), changes in concentration being close to the theoretical dilution line.

During the survey on 16th August (Figure 4-3b) the DOC content of river water was about 6.5 mg l^{-1}. Although samples were not obtained between salinities 2-15°/oo, the relationship between DOC concentration and salinity is evidently linear up to a salinity of 32°/oo. The sudden decrease in the amount of DOC in sea water samples to about 1 mg l^{-1} at salinities of 32-34°/oo is unlikely to reflect removal at such high salinities but probably reflects the presence of a sea water end-member with a different mixing history, possibly one influenced by biological activity.

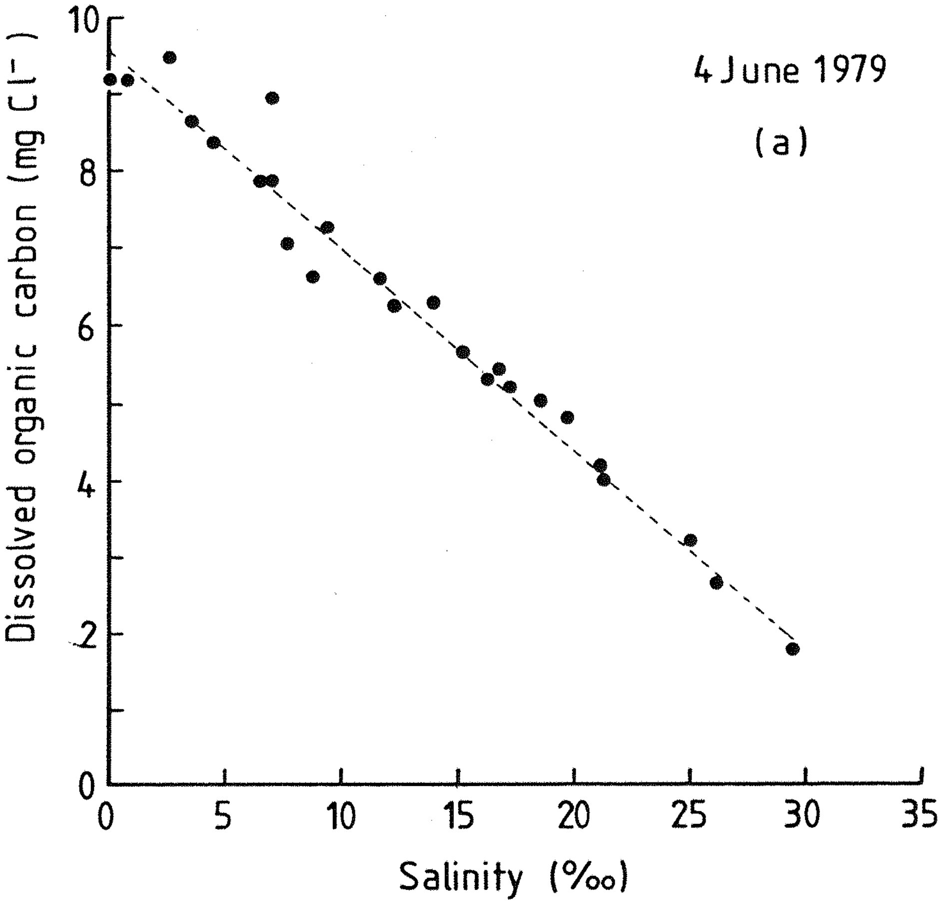


Figure 4-3. Relationship between concentrations of DOC and salinity in the Beaulieu Estuary; survey of (a) 4 June,1979.

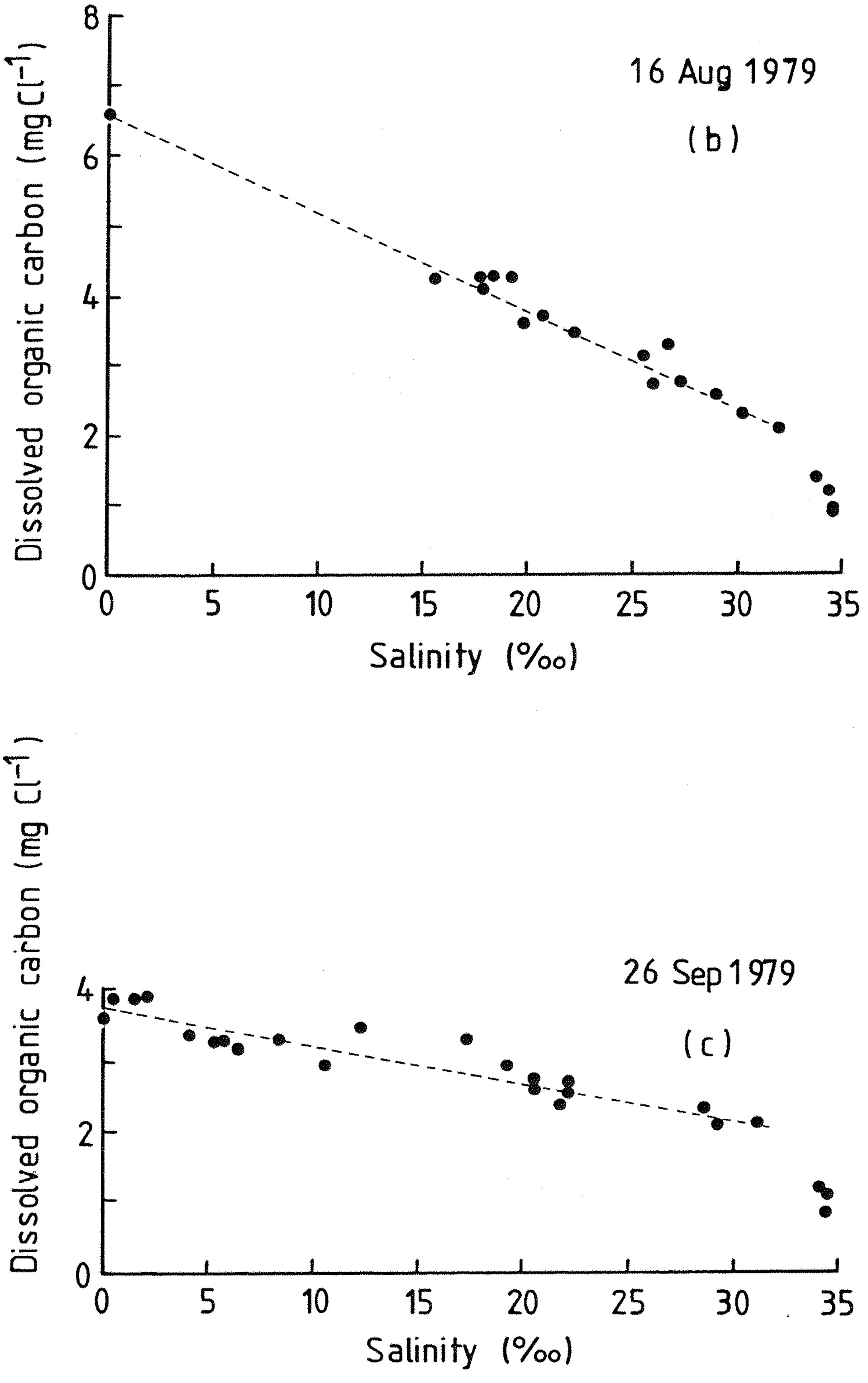


Figure 4-3. (b) 16 August, 1979, (c) 26 September, 1979.

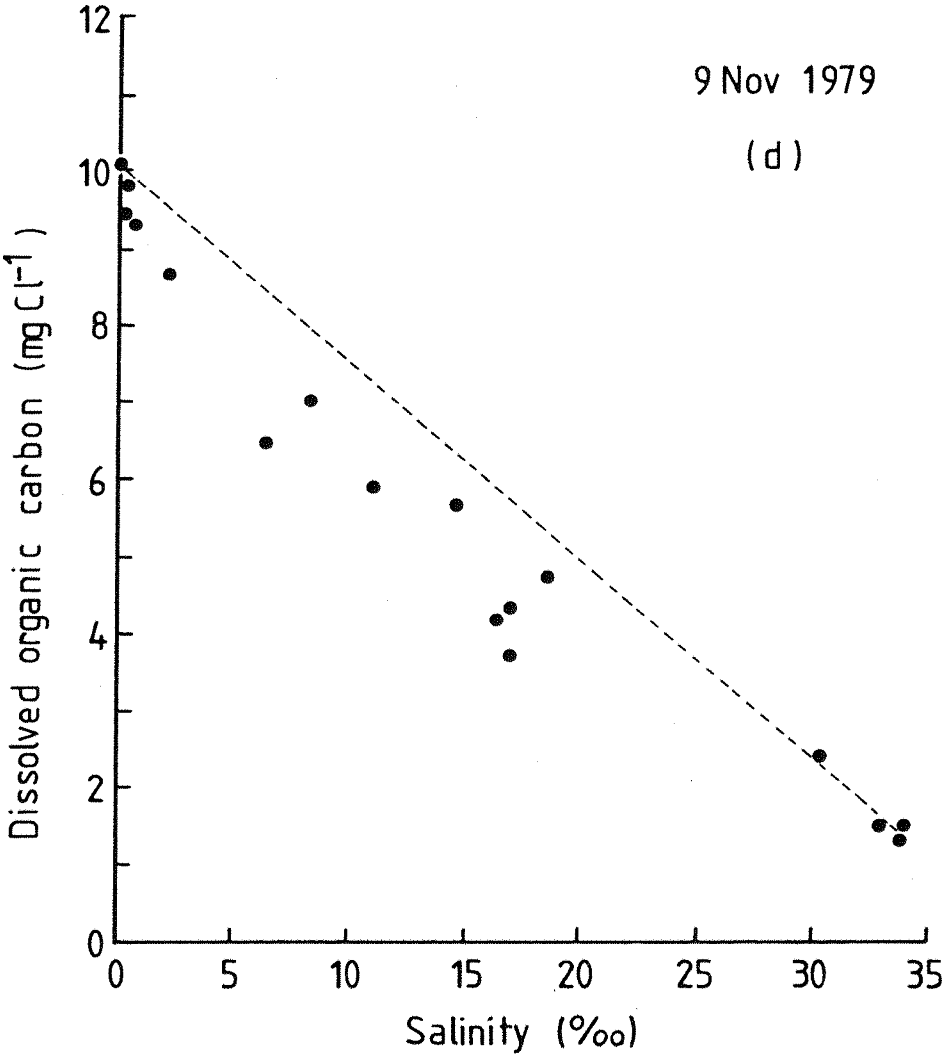


Figure 4-3. (d) 9 November, 1979.

During the survey on 26th September, the river water content of DOC was about 3.5 mg l^{-1}, considerably less than those in other surveys. The results in Figure 4-3c indicate a linear relationship between salinity 0-31°/oo. It therefore seems reasonable to conclude that during this survey, DOC behaved conservatively despite the deviation from the theoretical dilution line of samples at 34°/oo S.

For the last survey on 9th November (Figure 4-3d), nearly all points lie below the theoretical dilution line between salinity 0-18°/oo. The river water end-member contained about 10 mg DOC l^{-1}. Despite the lack of samples in the salinity range between 19-30°/oo, the theoretical dilution line between the two end-members enables the same conclusions to be drawn concerning the non-conservative behaviour of DOC at the time of this survey. Removal of DOC is estimated to account for some 20% of the river input of dissolved organic carbon. In this survey it was also observed (see above) that removal of iron was less complete at lower salinities than was the case in other surveys. The retarded flocculation reaction of iron may influence the behaviour of DOC itself by providing, through its precipitation, sites for the aggregation of DOC (Baylor and Sutcliffe, 1963) to form POC.

C. Silicon

During the period of this study, variability in the concentration of dissolved silicon in Beaulieu river waters was observed (Table 4-7), the concentration ranging from 2.6 mg Si l^{-1} during spring to 6.0 mg Si l^{-1} during autumn, with a yearly average of 4.5 mg Si l^{-1}.

The concentration of dissolved silicon in the Beaulieu Estuary during the 1979 surveys and its relationship to salinity is shown in Figure 4-4.

The results of the survey on 10th April (Figure 4-4a) indicate apparent removal of silicon; the magnitude of removal was estimated to be 70%.

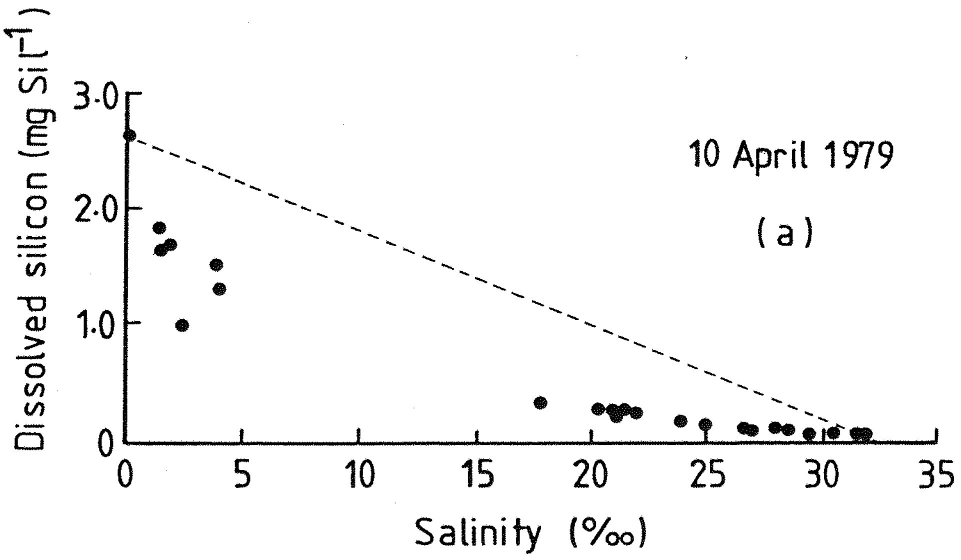
Table 4-7 The variations in concentration of dissolved phosphate, silicon, iron and DOC in river water and sea water in the Beaulieu Estuary during 1979.

Date 1979	River Water				Sea Water				
	Phosphate (µg l^{-1})	Silicon (µg l^{-1})	Iron (µg l^{-1})	DOC (mg l^{-1})	Phosphate (µg l^{-1})	Silicon (µg l^{-1})	Iron (µg l^{-1})	DOC (mg l^{-1})	Salinity (°/oo)
22nd Jan	10.2	4,200	202	-	-	-	-	-	-
29th Mar	-	-	-	-	24.7	42.0	-	-	32.8
5th Apr	14.6	-	-	-	-	-	-	-	-
10th Apr	20.5	2,625	320	-	3.8	48.5	10.2	-	32.0
17th May	13.5	4,200	390	6.9	-	-	-	-	-
4th Jun	13.0	4,087	435	9.2	5.9	270	12.0	1.8	29.5
5th Jul	9.5	4,520	-	-	-	-	-	-	-
16th Aug	15.8	5,725	437	6.5	11.2	150	5.5	0.9	34.5
26th Sep	16.5	5,900	437	3.6	17.5	117	6.0	0.9	34.3
9th Nov	14.5	4,450	470	10.3	23.2	227	5.0	1.4	34.1
Mean	14.2	4,463	384	7.3	14.4	142	7.7	1.25	32.9

Subsequently, on 4th June, the plot of silicon against salinity (Figure 4-4b) shows a linear relationship. No systematic deviation from the theoretical dilution line was observed, but extrapolation of the concentration of silicon at zero salinity from the graph gives a value about 9% lower than that actually determined in the river water. This possibly arose from a change in the distribution between the dissolved silicon and the silicate minerals of the suspended solids (Miller, 1967) or from the time variation in the concentration of silicon in river water. Apart from this difference, the linear relationship, reflecting simple mixing of two end-members, is pronounced in this survey.

The results for the survey of 16th August suggest an apparent removal of silicon to the extent of 15% as indicated by deviation from the theoretical dilution line (Figure 4-4c). The river concentration of silicon was increased to about 5.7 mg l^{-1} compared with the previous survey. Due to the lack of samples at lower salinity values, the interpretation of this data has uncertainties, but if the few points for the river water and the lower salinity samples are adopted as most reasonable for the beginning of the dilution line, almost all the observed values lie below the theoretical dilution line, suggesting that a small removal of silicon occurred.

For the survey on 26th September (Figure 4-4d), some silicon removal was also apparent from the deviation of the data from the theoretical mixing line. The magnitude of removal was estimated to be about 25% of the silicon in the river water mixing in the estuary. Almost all the mixing points lie below the theoretical dilution line. The removal observed during estuarine mixing (between 10-25%) in the surveys of 16th August and 26th September may be related to the presence of appreciable amounts of suspended solids during flood tide mixing, as a result of the scouring effect on the bottom sediment as the flood tide came into the estuary, resulting in a high level of resuspended sediment. On 26th September, when a high tidal amplitude was observed, affecting the uppermost point in the river system, this tidal energy was probably more effective in resuspending the sediment than on 16th August.



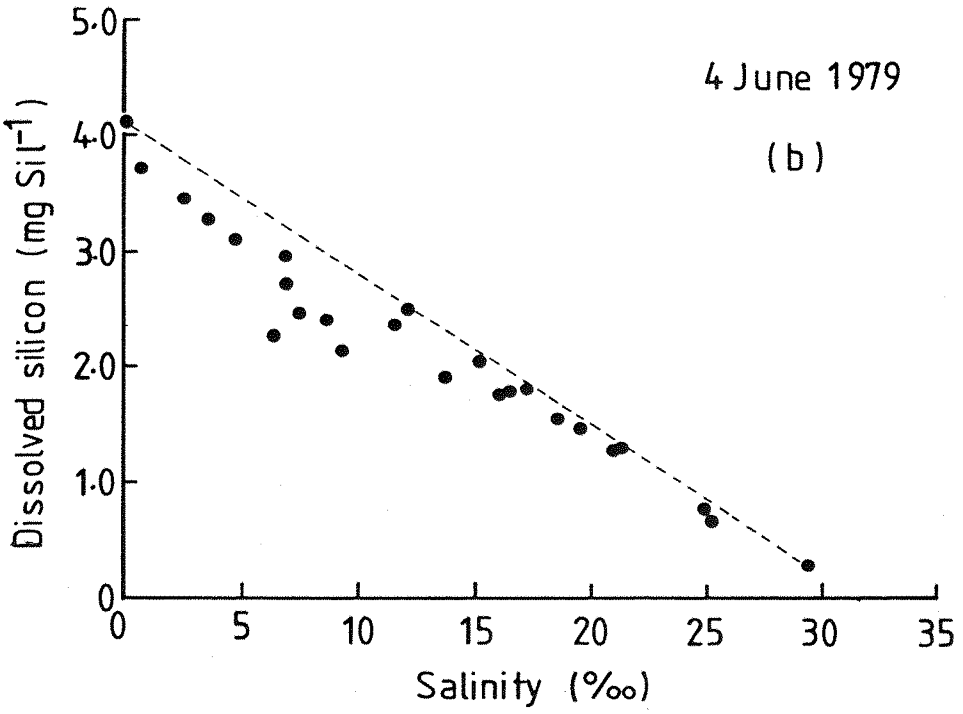


Figure 4-4. Relationship between concentrations of dissolved silicon and salinity in the Beaulieu Estuary; survey of (a) 10 April, (b) 4 June, 1979.

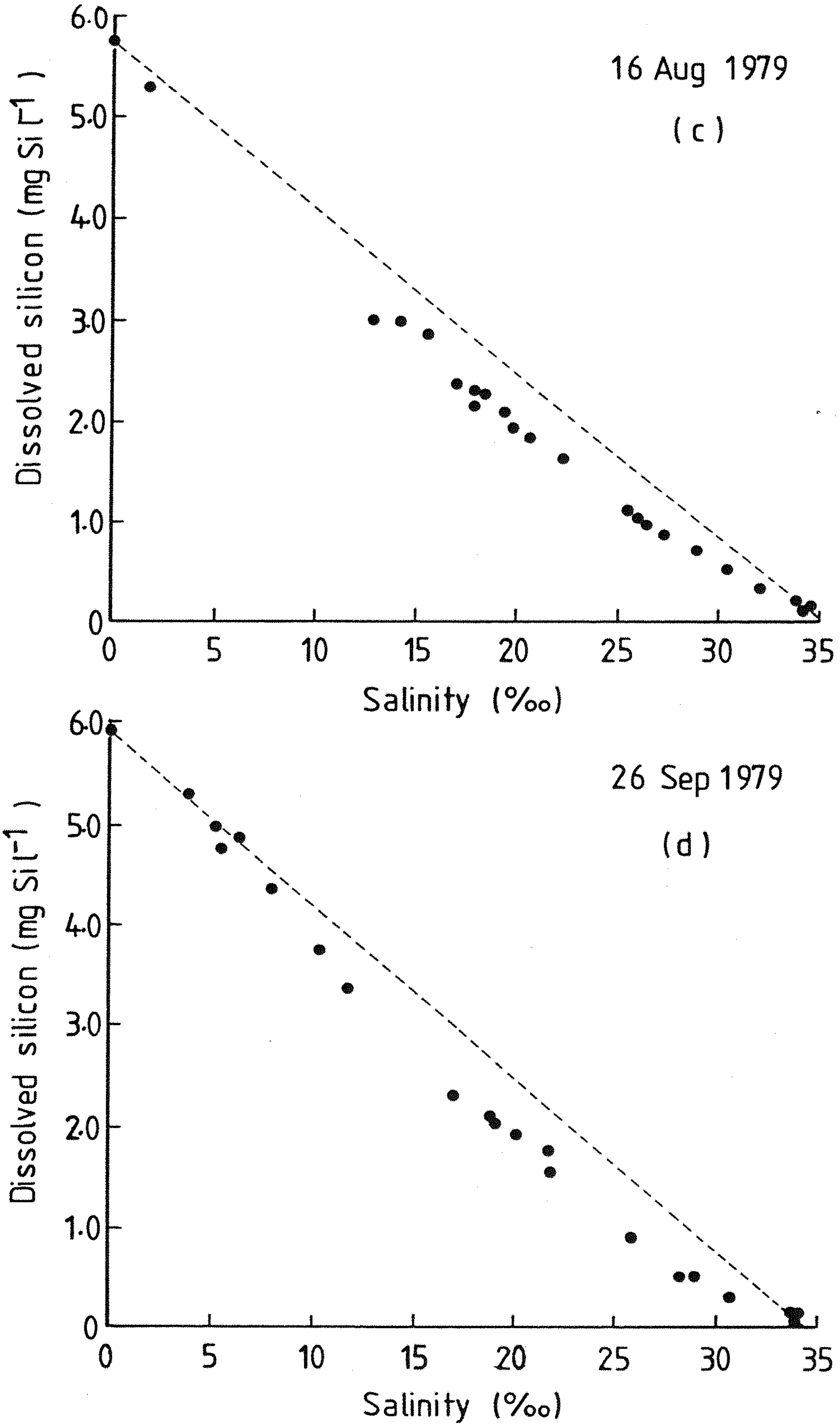


Figure 4-4. (c) 16 August and (d) 26 September, 1979.

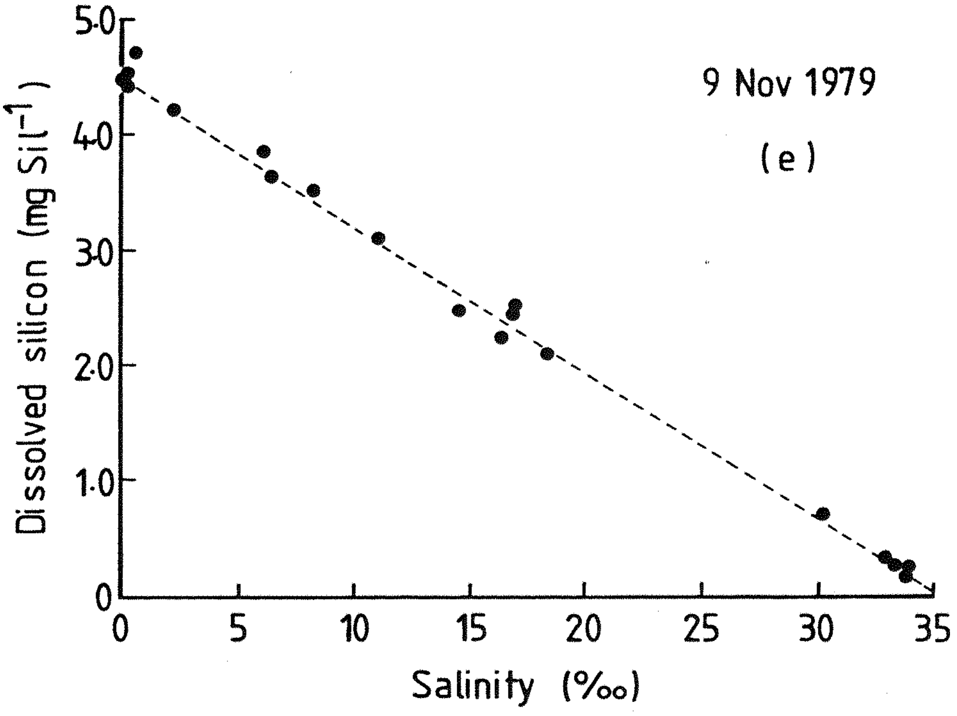


Figure 4-4. (e) 9 November, 1979.

In the last survey on 9th November (Figure 4-4e), silicon seems to behave conservatively with no systematic deviation from the theoretical dilution line. All the points in Figure 4-4e lie close to the theoretical dilution line.

The behaviour of dissolved silicon thus shows considerable variability insofar as it can be deduced from the survey approach. The conservative behaviour of DOC suggests that the assumptions made in this approach may be justified and on this basis the differences in behaviour may be considered real and the explanation of removal sought in interactions with suspended particulates, as indicated by the work of, for example, Liss and Spencer (1970). The river water concentrations of dissolved silicon vary independently of those of DOC, however, and it is possible that the deviation from linearity reflects short-term changes in the input concentration of dissolved silicon, so that samples taken in the estuary at different salinities had different mixing histories. In this case, it would not be expected, however, that all deviations would correspond to apparent removal.

D. Phosphate

The results for phosphate behaviour in the Beaulieu Estuary during 1979 are summarized in Figure 4-5. The relationships of phosphate concentration to salinity are scattered and apparently reflect complex factors. The pattern in each survey differs more from the simplified general model than with the other dissolved constituents examined. A marked difference in phosphate behaviour between seasons is also observed. This may reflect factors such as the variability in the concentration of phosphate in the river supply (Table 4-7), which in turn is influenced by the inputs from several small streams which are different in chemical composition.

An uncertainty arises in the interpretation of these data because of the ponding of river waters at Beaulieu, inputs being non-continuous. During this work it was observed that mixed saline water from the lower part of the estuary can intrude and penetrate into the pond through sluice gates during high tides. The aged saline water which has been accumulated in the pond may influence directly the phosphate behaviour in the estuary by supplying water which has interacted with the saline bottom sediments in the pond for a period of time. This effect was not, however, observed to influence other dissolved constituents (Si, DOC, Fe).

The total range of phosphate* concentration during this study in the river water inputs was 9.5 to 20.5 μg l^{-1}, with an average of 14 μg l^{-1}.

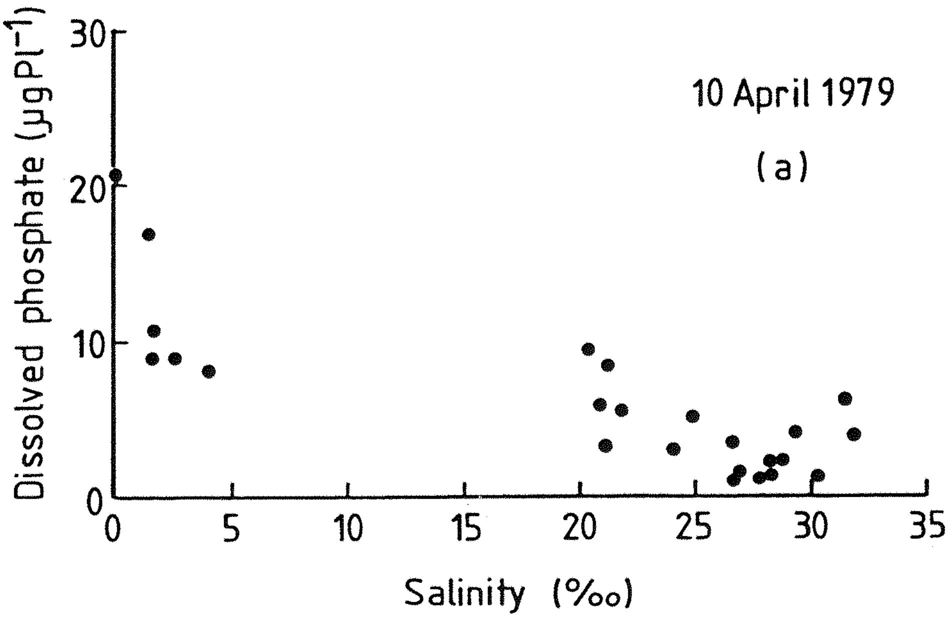
The variation of phosphate concentration with salinity for the survey of 10th April (Figure 4-5a), shows a general trend for phosphate concentrations to decrease non-linearly as salinity increases, but shows also more scatter than either silicon or DOC. The phosphate concentration in river water was about 20 μg l^{-1} more than that in sea water which contained about 3.8 μg l^{-1}. The salinity of maximum phosphate removal was around 2°/oo, with apparent removal of phosphate to the extent of about 65%. At this time the mixing plume reached the highest point above Bailey's Hard, with a rapid change from a salinity of 18°/oo, within only a few metres along the estuary, to 4°/oo. As pointed out previously, this meant that samples were not obtained uniformly over the salinity range.

On 4th June, the scatter in the relationships of phosphate with salinity was very great. The river water contained a lower phosphate content of 13 μg l^{-1}, while the sea water contained about 6 μg l^{-1}. At low salinities an increase in the concentration of phosphate was observed; at a salinity of 2.5°/oo, the concentration of phosphate increased to 27 μg l^{-1}. This effect may have resulted from the desorption of phosphate from river-borne suspended solids upon contact with sea water with increase in the ionic strength; the difference in pH is not sufficient to have a large effect in this respect.

In the mid salinity range between 5 and 30°/oo, phosphate tended to decrease as salinity increased (Figure 4-5b). Due to the great scatter, interpretation is difficult, but some of the phosphate input appears to have been removed. A plot of phosphate against silicate (Figure 4-6) also showed considerable scatter.

The relationships between dissolved silicon, DOC and salinity for this survey fit closely to the simple mixing of two

* All concentrations are given as phosphate-phophorus (μg P l^{-1})



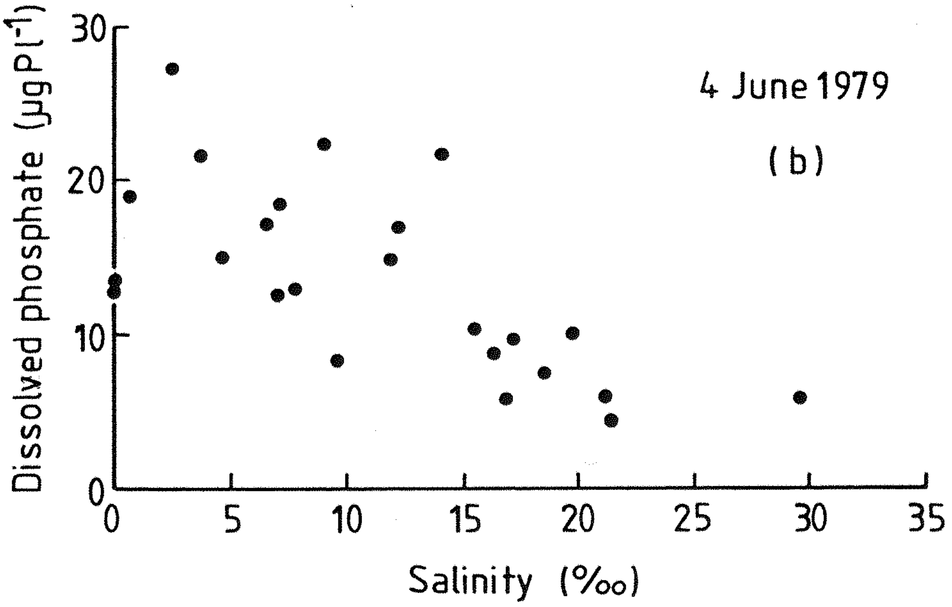


Figure 4-5. Relationship between concentrations of dissolved phosphate and salinity; survey of (a) 10 April (b) 4 June, 1979.

end-members, suggesting that the variations found with phosphate are attributable to interactions and not to hydrographic factors.

The same feature of an increase in phosphate at low salinity, possibly reflecting desorption of phosphate from suspended solids during early estuarine mixing, was also indicated by the results of the survey on 16th August (Figure 4-5c). The concentration increased from 15 $\mu g\ l^{-1}$ in river water to 30 $\mu g\ l^{-1}$ at salinity around 2°/oo. The maximum concentration of phosphate (53 $\mu g\ l^{-1}$) occurred at a salinity of 16°/oo. A marked but fairly regular drop occurred in the concentration at salinities above the maximum in phosphate, the concentration decreasing to 2.5 $\mu g\ l^{-1}$ at salinity 32°/oo. This decrease in phosphate occurred in the clearer estuarine water with lower amounts of suspended particulate matter; it conforms quite closely to a simple mixing effect but some variations may reflect shifting of the sorption equilibrium between water and sediment toward sediments as the concentration of the phosphate in the water is more than 30 μg P l^{-1} (Pomeroy et al., 1965). A decrease in the concentration of phosphate at salinities above 25°/oo was observed in the Zaire River estuary by Bennekom et al. (1978) and in the Magdalena plume by Fanning and Meynard (1978).

The increase in the concentration of phosphate at the highest salinities, after a large decrease in phosphate, is notable. The increase in the concentration of phosphate was from 2.5 $\mu g\ l^{-1}$ to 11 $\mu g\ l^{-1}$ between salinities 32 to 34.5°/oo. This increase in the concentration of phosphate corresponds with a drop in DOC concentration (Figure 4-3b), and may be similarly related to a different history of the high salinity waters, perhaps influenced by biological processes.

The phosphate/salinity relationships for 26th September and 16th August were similar; in particular the alternating stages of release and removal with changes in salinity. On 26th September the most pronounced features were the low concentrations, below the river input concentration, at low salinities, the rise to a maximum at intermediate salinities, subsequent decrease and, as in the previous survey, an increase at the sea water end of the estuary. The maximum concentration of phosphate reached was

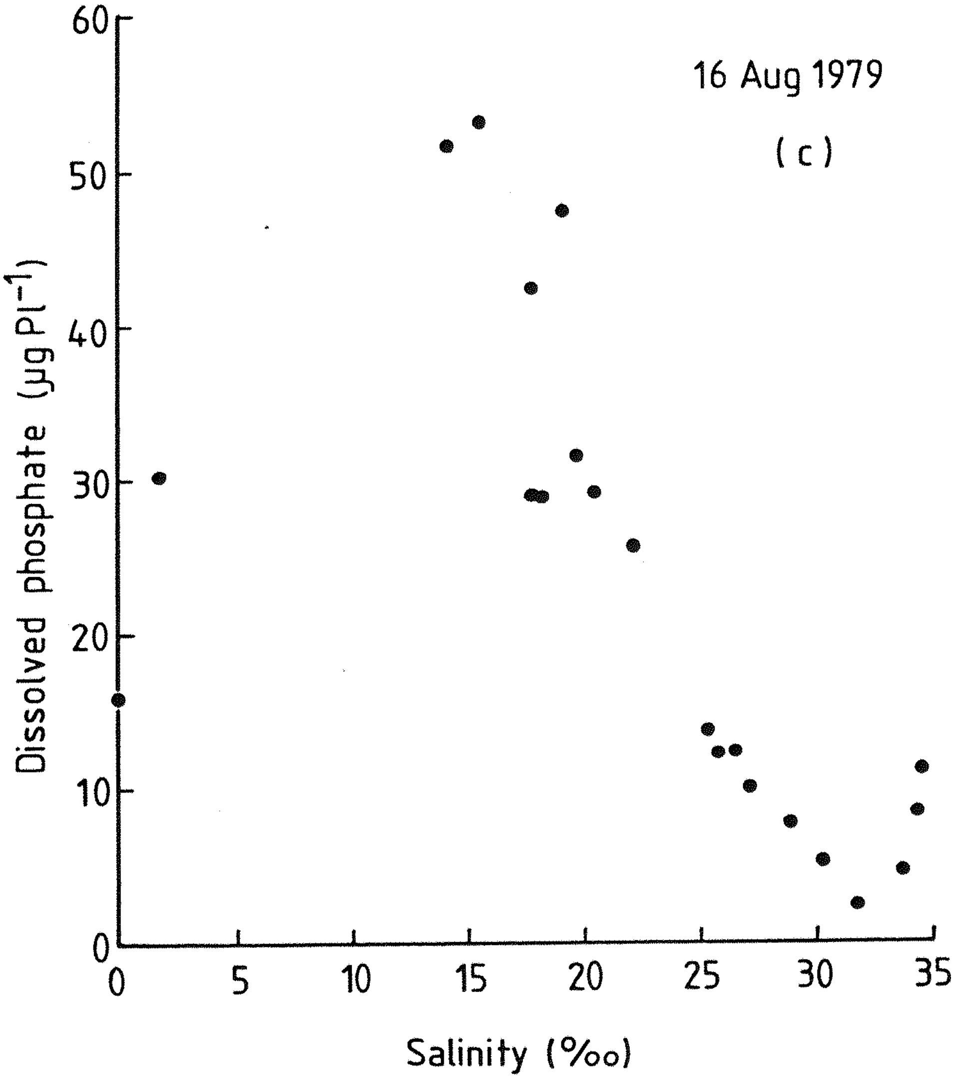


Figure 4-5. (c) 16 August, 1979.

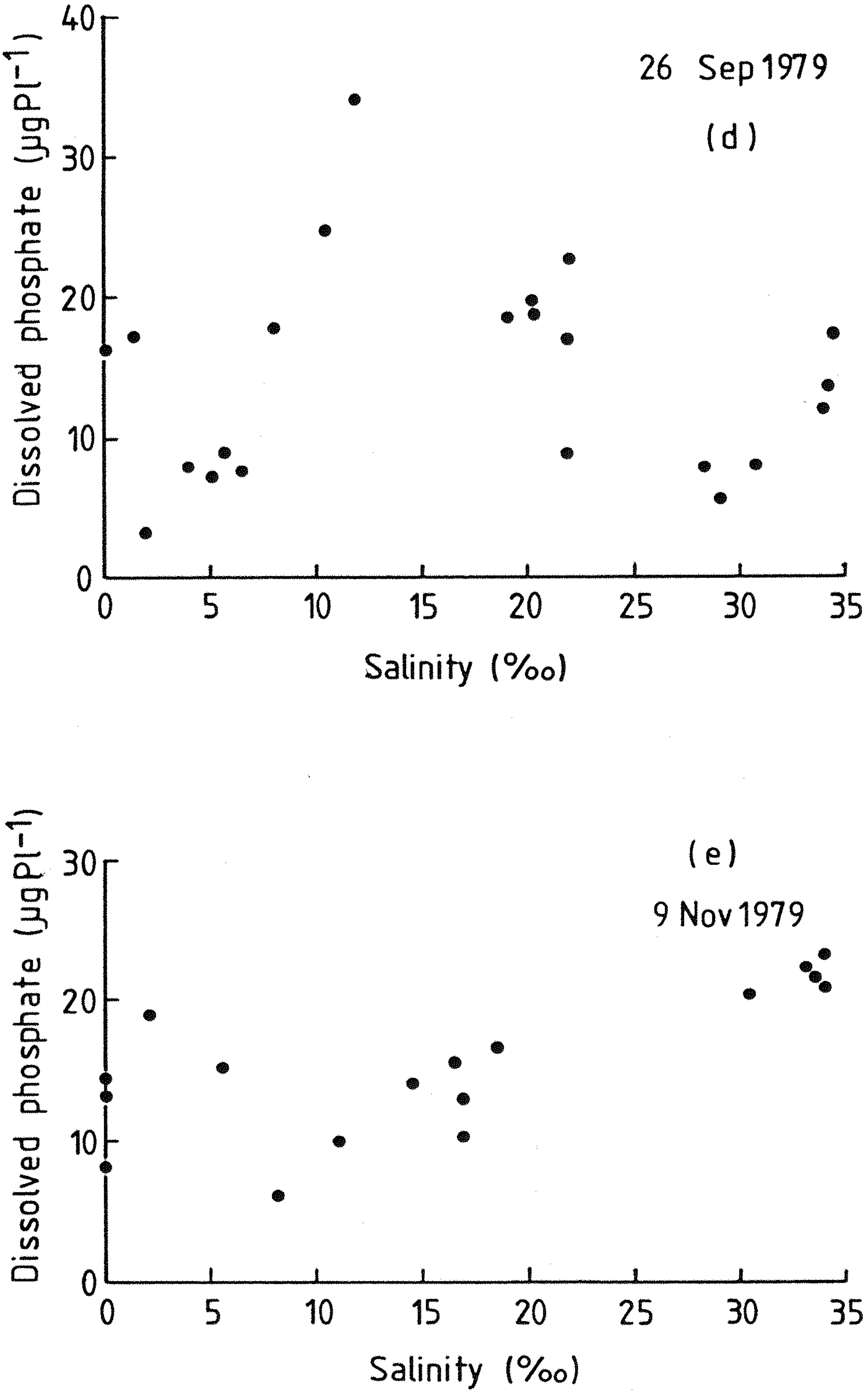


Figure 4-5. (d) 26 September, (e) 9 November, 1979.

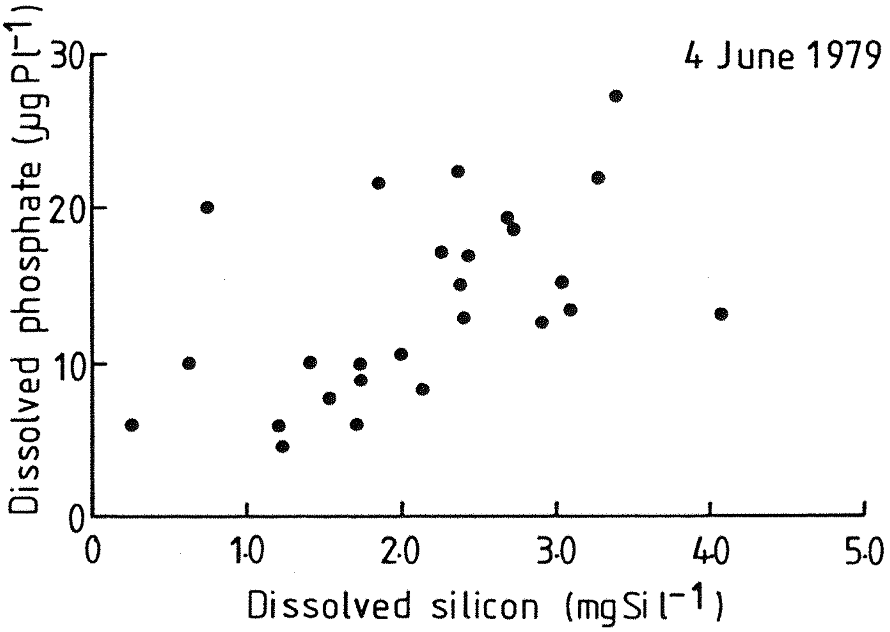


Figure 4-6. Relationship between concentrations of dissolved phosphate and dissolved silicon; survey of 4 June, 1979.

34 µg l^{-1} at salinity 12°/oo, compared to 53 µg l^{-1} at salinity 15.5°/oo on 16th August. The concentration of phosphate remaining at salinity 29°/oo was about 6 µg l^{-1}, which is similar to the pattern on 16th August. The marked increase in the concentration of phosphate at higher salinity coincided with a decrease in DOC content.

In the November survey the concentration in the sea water end-member was higher than elsewhere in the estuary and there was a fairly regular increase in concentration from the minimum value at about 8°/oo to this maximum. At lower salinities there were again trends which would be consistent with an initial stage of mixing in which release of phosphate exceeds removal followed by a stage in which removal dominates.

4.3 Discussion and Conclusions

A. River waters and Ultramembrane filtrations

The major finding from the ultramembrane fractionation experiments on dissolved iron and phosphate in River Beaulieu waters is the occurrence of some 50-85% of the reactive dissolved phosphate in association with, on average, more than 93% of the dissolved iron in the fraction of apparent molecular weight $>10^5$; this indicates that phosphate is mostly bound with colloidal iron hydroxide. The fraction retained on the XM-100 ultrafilter (M.W. cut-off 10^5) was reduced after photo-oxidation, the total concentration increasing. It is not possible to say from the data how much of the increase in phosphate concentration following photo-oxidation is released from the high molecular weight fraction and how much may have been associated with the organic material of lower molecular weight. Removal of phosphorus incorporated with iron hydroxide phases may be expected to occur along with iron removal by flocculation during estuarine mixing.

In contrast with iron and phosphorus, the DOC in waters of the Beaulieu River mostly occurred in the smaller molecular weight range ($<10^3$), which contained up to about 65%, with only $<5\%$ of the DOC presented in the high molecular weight range ($>10^5$). This fraction of DOC may arise from the association with iron colloids and may not reflect the presence of organic molecules of corresponding molecular weight. The dissolved silicon is almost wholly in true solution. This also appears to be true for a major fraction of manganese. Although only one sample was examined for manganese, the result supports by the findings of Moore *et al*. (1979).

B. Estuarine mixing

Extensive removal of dissolved iron was observed to occur in all the surveys of the Beaulieu Estuary, consistent with previous work (Holliday and Liss, 1976; Moore *et al*., 1979).

Most of the iron (90-95%) was removed in the earlier stages of mixing up to a salinity of 15^{o}/oo and the removal process was essentially complete as the salinity approached about 20^{o}/oo. The pattern of iron removal varied between different surveys and appeared to be influenced by the amount of DOC present in the water. A higher concentration of DOC in the river water tended to reduce the extent of iron removal with increase in salinity so that removal was still significant at higher salinity values. At the same time DOC behaved essentially conservatively except during the last survey in November in which non-linearity was observed in the relationship between DOC and salinity, corresponding to removal of about 20% of the DOC in the river input. This fraction exceeds the 5% of the DOC which occurs in the high molecular weight range ($> 10^5$) in which most of the iron occurs and the removal probably is amplified by an aggregation effect of DOC to form particulate organic matter (POC) during the removal of iron along the salinity gradient. In two surveys, the content of DOC in sea water samples was found to lie below the theoretical dilution line fitting the samples over the remainder of the salinity range; this corresponded to an increase in the concentration of dissolved phosphate. It is considered more likely to reflect a difference in the mixing history of the most saline water than a removal or release of these constituents at high salinities, although the possibility of such an effect through the decomposition of POC cannot be excluded.

Dissolved silicon showed conservative behaviour in one survey (November) but on other occasions there was evidence of removal during estuarine mixing. The extent of removal was generally in the range 10-25% but a much greater apparent removal up to about 70% was found in April coincident with a markedly lower than average concentration of silicon ($\sim$2.5 mg l^{-1}) in the river input.

The wide variation in behaviour of dissolved silicon is not readily explained. Biological utilization does not lead to non-conservative relationships between dissolved silicon and salinity in the considerably more eutrophic Test Estuary (Burton <u>et al</u>., 1970b) and is therefore unlikely to account for the observations in the Beaulieu Estuary. The large-scale removal found in the April survey is exceptional in the light of the other data and the dissolved silicon concentration in the river water was also exceptionally low at this time. It is possible that the concentration was then increasing from even lower values and that the intermediate salinity waters reflected this. There is, however, no evidence for this and this problem of interpretation emphasizes that sampling of the river input should ideally be undertaken over an extended period prior to an estuarine survey.

The behaviour of phosphate in Beaulieu Estuary was complex due probably to several controlling processes affecting the concentration. Desorption of phosphate from riverborne suspended solids may explain an initial increase in concentration usually observed in early estuarine mixing, which could result from the reaction of riverborne suspended solids in the saline water with the exchange of Cl^- ion for PO_4^{3-} ion. After this stage, removal of phosphate was generally observed. This is probably attributable to the coprecipitating of the phosphate with hydrous iron oxides as physicochemical parameters change during estuarine mixing. A considerable fraction of phosphorus, as shown above, occurs in the same molecular weight fraction as the bulk of the colloidal iron. Freshly precipitated iron hydroxide will present a lower surface area than that of the colloid. It may occlude phosphate but there will be a reduction in the number of adsorption sites. Whereas the removal of iron conforms to a general pattern that of phosphate is irregular and seem to be obscured by other processes which affect its concentration. No simple model can be advanced from the evidence of the surveys. Uptake on and release from suspended solids under different conditions may have occurred but it is not possible to exclude the possibility that mobilization from bottom sediments led to increase in concentration of dissolved phosphate which was not directly related to the mixing processes along salinity gradients.

The complex behaviour of phosphate suggested that interpretation might be assisted by laboratory experiments on the exchange of phosphate with sediments from the Beaulieu system. These are described in the following chapter.

CHAPTER V

LABORATORY EXPERIMENTS

5.1 Introduction

An understanding of the controlling mechanisms of phosphate levels in estuaries, and the various factors that affect the removal and release of phosphate, has been recognised to be particularly important, in order to determine, and predict, the fate and the distribution of anthropogenic inputs. There is evidence to show that exchanges by physicochemical processes such as adsorption,ion-exchange, and movement by sedimentation and resuspension (Hobbie and Copeland, 1977), are important controlling mechanisms for phosphate which can be held or released under changing environmental conditions such as salinity and pH in the estuary. The existence of equilibrium between the concentration of phosphate in the water and the bottom sediment ('buffering') has been observed (Rochford, 1951; Gessner, 1960; Pomeroy _et_ _al_., 1965; Butler and Tibbitts,1972).

The influence of suspended solids is also of considerable importance in regulating the dissolved phosphate exchange system in estuaries. There are numerous investigations on phosphate adsorption with a variety of well characterized solid materials, and environmental suspended solids and sediments. Among these investigations, most of the extensive work has been carried out in the field of soil fixation of phosphate and involved very high concentrations of phosphate. This limits the application, as one can hardly adopt this for study in different environmental conditions with the smaller amounts of phosphate in natural water systems.

To understand the role of adsorption processes in controlling the phosphate level in estuaries, a laboratory experimental approach is considered to provide a more significant picture since changes in physicochemical parameters such as occur during estuarine mixing can be more readily controlled in such experiments. The experimental results provide, however, only a static simulation which may not fit well the dynamical reactions in the estuary.

Phosphate adsorption by suspended sediments as an explanation of the controlling mechanism of the phosphate in estuaries has been previously studied. Carritt and Goodgal (1954) studied the adsorption of dissolved phosphate on suspended solids, from Roanoke river and Chesapeake Bay, under controlled condition (pH, salinity) and suggest that there was an ecological importance in the adsorption properties of suspended solids from Roanoke river but that this was not as evident for the sediment from Chesapeake Bay.

5.1.1 Adsorption and desorption mechanisms of phosphate

A. Effect of pH

Phosphate adsorption, on suspended sediments from Roanoke river, in fresh water conditions was observed to attain a maximum in the pH range 4-6 (Carritt and Goodgal, 1954). For estuarine mud (Swan River Estuary), the pH for maximum phosphate adsorption in the distilled water - mud suspension ranged from 3-7 (Jitts, 1959). Burns and Salomon (1969) found that the adsorption of phosphate on kaolin decreased as pH increased from acid to alkaline conditions, while Stumm and Zobrist (1971) suggested that the maximum adsorption of phosphate on goethite occurred at pH 2.5 by hydrogen bonding between the oxide ion of hydrous ferric oxide and the hydrogen of the hydrogen phosphate anion. The peak of maximum phosphate uptake on clays (illite and kaolinite) has been found to occur in the pH range 4-5 but for montmorillonite the adsorption of phosphate increased as pH increased to above 7 (Hall and Baker, 1971).

B. Effect of salinity

It has been suggested that an increase in salinity reduces the adsorption capacity of phosphate. Carritt and Goodgal (1954) observed the effect of salinity on river suspended solids and suggested that the adsorption of phosphate decreased as salinity of waters increased due to the competition with ions in sea water. This was also observed to happen on kaolin (Burns and Salomon, 1969).

These findings of pH and salinity effects lead to the conclusion that phosphate must have been adsorbed onto suspended solids in the pH range 4-6 in the river supply and could be released or regenerated from the adsorbed phase as it was transported from the river into the estuary under the influence of increasing salinity and pH. Carritt and Goodgal (1954) suggested that the desorption increased as the pH increased, resulting from the competition for OH^- ion. However Upchurch _et al_. (1974) suggested that the amount of phosphorus in estuarine sediments i.e. of the Pamlico Estuary, decreased as salinity increased, owing to the material which had been displaced by the Cl^- and SO_4^{2-} ions of sea water.

C. Effect of iron

Numerous studies have indicated that the presence of hydrous iron oxide may influence the amount of phosphate in estuaries. Iron in the estuaries is known to be supplied from the river input, in the form of colloidal hydrous iron oxides stabilized by dissolved organic matter, or as iron oxide coating on riverborne suspended solids (Gibbs, 1973, 1977). The high adsorption of phosphate on suspended solids in river water (Carritt and Goodgal, 1954) could result from the complex of phosphate ion with hydrous iron oxide phase coatings on riverborne suspended solids (Jenne, 1968; Gibbs, 1973; Hem, 1975; Lee, 1975), or held as iron-inorganic phosphorus complex (Upchurch _et al_., 1974). The less efficient adsorption of phosphate on kaolinite was found to be due to a very small amount of extractable iron content as compared to illite (Edzwald, 1977). Jitts (1959) also suggested that the adsorption of phosphate on estuarine silts was related to iron. Berner (1973) and Boström (1973) have demonstrated that the high phosphorus content of rapidly deposited metalliferous oceanic ridge sediments is associated with hydrogenous iron oxides. In an estuarine environment receiving iron-rich inputs, changes in physicochemical factors such as the increase in salinity and pH will result in an extensive removal of iron by flocculation of iron colloid or precipitation of the hydrous iron oxide.

Supporting the significance of iron in estuaries, Upchurch et al. (1974) and Edzwald (1977) observed, that, as the salinity of the water increased in the Pamlico Estuary the correlation between the amounts of inorganic phosphate, and oxalate extractable iron, was decreased, due to the breakdown of the iron-inorganic phosphorus complex which formed earlier in the river water, or the displacement of phosphate by Cl^- and SO_4^{2-} ions in the nonstabilized iron-phosphate complex as salinity increased.

In estuarine sediments, it is believed that iron also plays a dominant role in the sorption or release of phosphate, especially in the aerobic layer of the sediment. Iron plays a major role in the adsorption of phosphate from the overlying water and in the retention of phosphate ions, which diffuse from the deeper anaerobic layer of sediment. Phosphate is released by ferric complexes breaking down under anoxic conditions (Mortimer, 1941, 1971; Fillos, 1975); this phosphate may, depending upon conditions, be readsorbed in aerobic layers or released to the overlying water.

D. Effect of organic matter

Organic matter in the adsorbing material has been suggested to affect the adsorption of phosphate. Burns and Salomon (1969) suggest that the adsorption of phosphate was increased by a factor of two in pond sediment free from organic matter in 19^{o}/oo Cl artificial sea water, and a factor of about six was suggested by Meyer and Quinn (1974) for the increase in adsorption of organic-free bay sediment in saline solution. Jitts (1959) observed an inverse relationship of phosphate adsorption on organic-free sediment with particle size and concluded that the presence of organic matter reduces phosphate adsorption by a masking effect.

E. Biological effect

Biological effects on the exchange of phosphate between the water and the sediments in estuaries are also important in controlling the amount of phosphate. Among the microorganisms, bacteria are involved as conservators for phosphate. Aerobic bacteria can take up available phosphorus from the water (Johannes, 1964) and release phosphate by the process of autolysis. Bacteria are found attached to the particulate matter in estuaries and thus the adsorption of phosphate on suspended solids may result mainly from the uptake of phosphate by bacteria on the surfaces (Correll et al., 1975). Also, Thayer (1974) showed that bacteria can compete with the algae in taking up phosphorus. Furthermore, Pomeroy et al. (1965) observed the significance of biological effects in the distribution of ^{32}P between water and suspended estuarine muds, and suggested that for suspended sediments biological effects are large enough to exchange as much phosphate the exchange with clay minerals in the estuary. In the economy of phosphorus in high productivity salt marsh ecosystems, the effect of the river supply is usually trivial. Part of the phosphorus excess in the estuary is a result of exchange with sediments (Pomeroy et al., 1965) and part is brought about by the macrophytes in taking up and removing phosphorus from deep sediments and releasing into the water through bacterial degradation of the macrophytes (Pomeroy et al., 1969).

5.1.2 Removal and mixing experiment

Sholkovitz (1976) studied the removal of phosphorus in the flocculant forming during the mixing of filtered river water and sea water in laboratory experiments. The results indicated that the removal of phosphorus increased as salinity increased from 0 to 15-20°/oo. The extent of removal depended on the flocculation of the colloidal humic substances with associated phosphorus and iron. The nature and composition of dissolved organic matter in river waters will influence the holding capacity of suspended solids for phosphorus and the processes of uptake and desorption during estuarine mixing.

5.2 Experiments on adsorption of phosphate onto suspended solids

Experiments on adsorption of dissolved phosphate onto suspended solids from the Beaulieu River were carried out in order to study the behaviour of phosphate in adsorption on or release from riverborne suspended solids under the influence of changing physicochemical parameters (i.e. salinity, pH) and to observe the influence of organic matter and iron on the adsorption capacity of suspended solids for phosphate, using different molecular weight fractions of river water.

Surface sediment from Fawley Ford Bridge, Beaulieu River was sampled and wet sieved using river water collected at the same time. A nylon mesh was used to obtain the sediment size <54µ, and this sediment was kept in the refrigerator. It was used as a source of the suspended solids in the adsorption experiments, on the basis that it was representative of material which could occur also in suspension. It was not practicable to collect sufficient material directly from the suspended solids in the river.

In general, 0.45 µm filtered water samples with known concentrations of added standard phosphate were shaken with a small quantity of suspended solids, using a rotary mechanical shaker, or a magnetic stirrer. Aliquots were withdrawn, centrifuged and filtered through 0.45 µm Sartorius membrane filters, and the filtrates were analysed for dissolved phosphate by the method of Murphy and Riley (1962). The amount of the adsorbed dissolved phosphate was calculated relative to the initial concentration.

5.2.1 Effect of salinity

The kinetics of adsorption of phosphate on suspended solids as a function of contact time were measured in river water and saline water ($S = 17^{o}/oo$) from the Beaulieu Estuary (Figure 5-1). The initial concentration of phosphate was 46 µg l^{-1}. Samples were stirred with 196 mg l^{-1} of suspended solids using 2 litre water samples. Aliquots (100 ml) were sampled at various times, centrifuged, filtered, and analysed for the amount of dissolved phosphate. The results for the amount of dissolved phosphate remaining as a function of time, are summarized in Table 5-1. They show that the rate of adsorption is rapid in the first 15-30 min., with subsequently slower adsorption until equilibrium is obtained at about 2 hours. The percentage adsorption, calculated by comparing with the phosphate concentration at time zero, indicates slightly higher adsorption in river water than in saline water.

5.2.2 Effect of pH

The equilibrium adsorption of phosphate onto suspended solids at various pHs in river waters was examined by stirring 100 ml of sample with added phosphate (~100 µgP l^{-1}) with a quantity of 250 mg l^{-1} suspended solids for 24 hours. The pH of the river water was first adjusted by addition of dilute hydrochloric acid and sodium hydroxide solution and measured with the pH-meter before addition of suspended solids. The samples after equilibration were centrifuged and filtered through 0.45 µm Sartorius membrane filter and analysed for dissolved phosphate, and other aliquots were remeasured for pH. The results are summarized in Table 5-2 and in Figure 5-2. They show clearly that the maximum in phosphate adsorption was attained between pH 2.5-6, with an average of 91%; no adsorption was observed when the pH was as low as 1.7.

5.2.3 Effect of iron

The effect of dissolved iron in river water in controlling the adsorption behaviour of phosphate is shown in Figure 5-3, which gives the results of experiments carried out with two filtrates (1) that passing the 0.45 µm filter and (2) that passing an ultrafilter with a molecular weight cut-off of 10^5. The results are summarized also in Table 5-3. The higher percentage adsorption of phosphate in the 10^5 M.W. fraction river water showed that, as the amount of dissolved iron was reduced

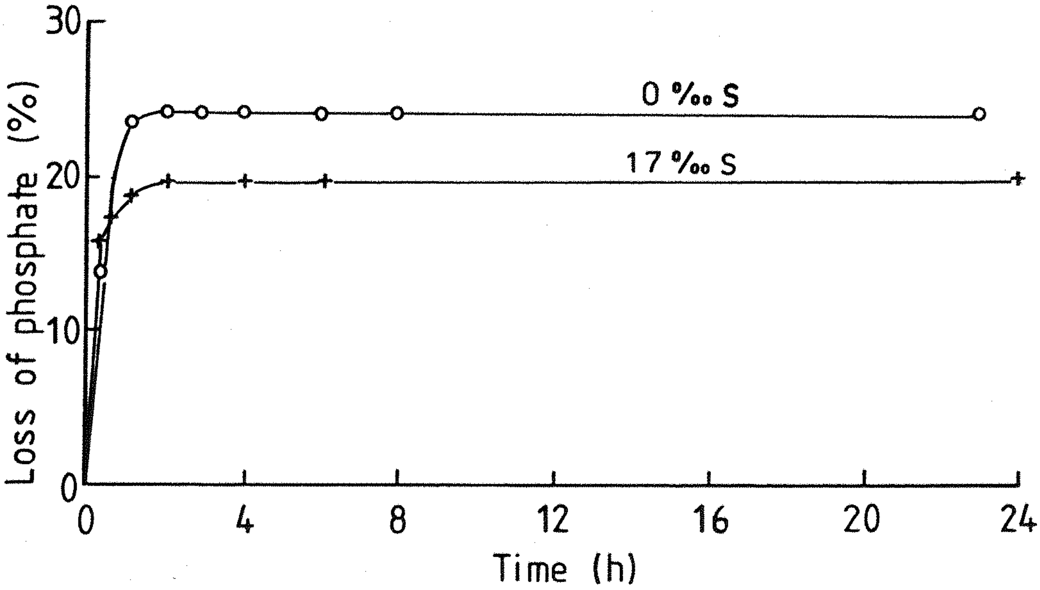


Figure 5-1. Adsorption of dissolved phosphate in river water and saline water (S = 17 ‰) as a function of time. Initial conditions; pH 5.0, solids 196 ppm, phosphate 46 μg Pl^{-1}, salinity as noted.

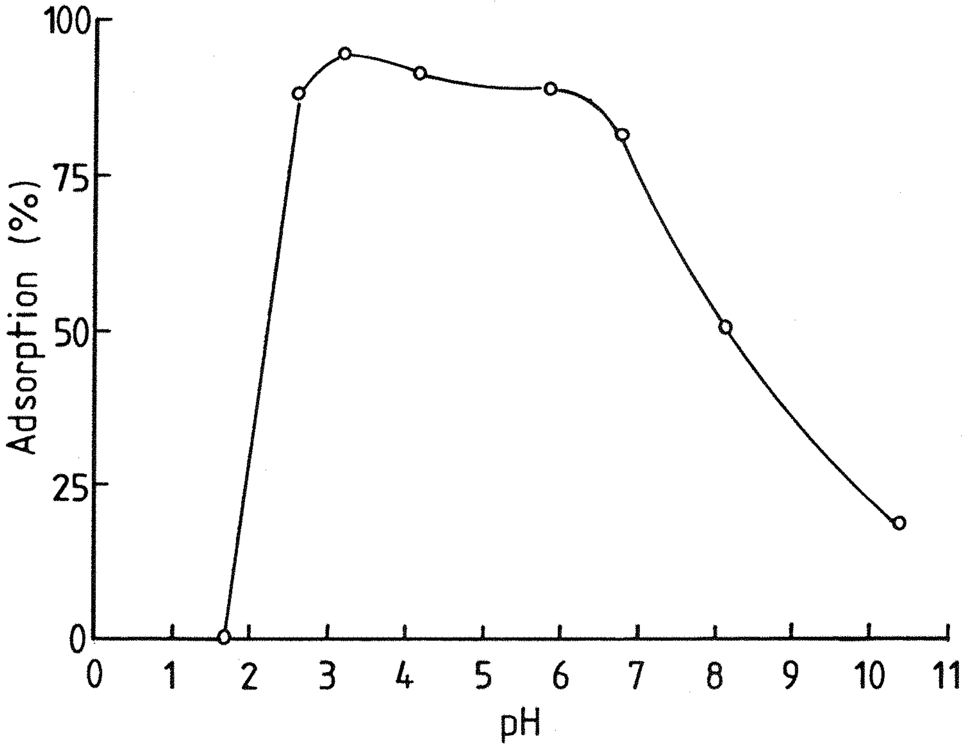


Figure 5-2. Adsorption of phosphate at various pH values on suspended solids in Beaulieu river water. Initial condition; suspended solids 250 ppm, phosphate 100 μg Pl^{-1}, temperature 22°C.

Table 5-1. Adsorption of dissolved phosphate in river water and saline water (S = 17°/oo) as a function of time.

Time (hr)	River Water (0°/oo) Concentration PO_4^{3-} remaining (μg l^{-1})	River Water (0°/oo) % Adsorbed	Saline water (17°/oo) Concentration PO_4^{3-} remaining (μg l^{-1})	Saline water (17°/oo) % Adsorbed
Initial	46.2	-	46.0	-
0.25	39.8	13.9	38.9	15.5
0.5	37.1	19.7	38.0	17.3
1	35.3	23.6	37.4	18.8
2	35.0	24.2	36.9	19.8
3	35.0	24.2	-	-
4	-	-	36.9	19.8
6	35.0	24.2	36.9	19.8
8	35.0	24.2	-	-
12	-	-	36.9	19.8
23	35.0	24.2	-	-
24	-	-	36.9	19.8

Suspended solids concentration 196 mg l^{-1}; pH 5.0

Table 5-2. Adsorption of phosphate at various pH values on suspended solids in Beaulieu river water

pH	Concentration phosphate remaining ($\mu g\ l^{-1}$)	% Adsorption
1.7	100	0
2.6	11.6	88.4
3.1	5.4	94.7
4.2	8.6	91.4
5.9	10.5	89.5
6.9	17.2	82.9
8.2	48.9	51.1
10.4	80.2	20.0

Initial phosphate concentration 100 $\mu g\ l^{-1}$

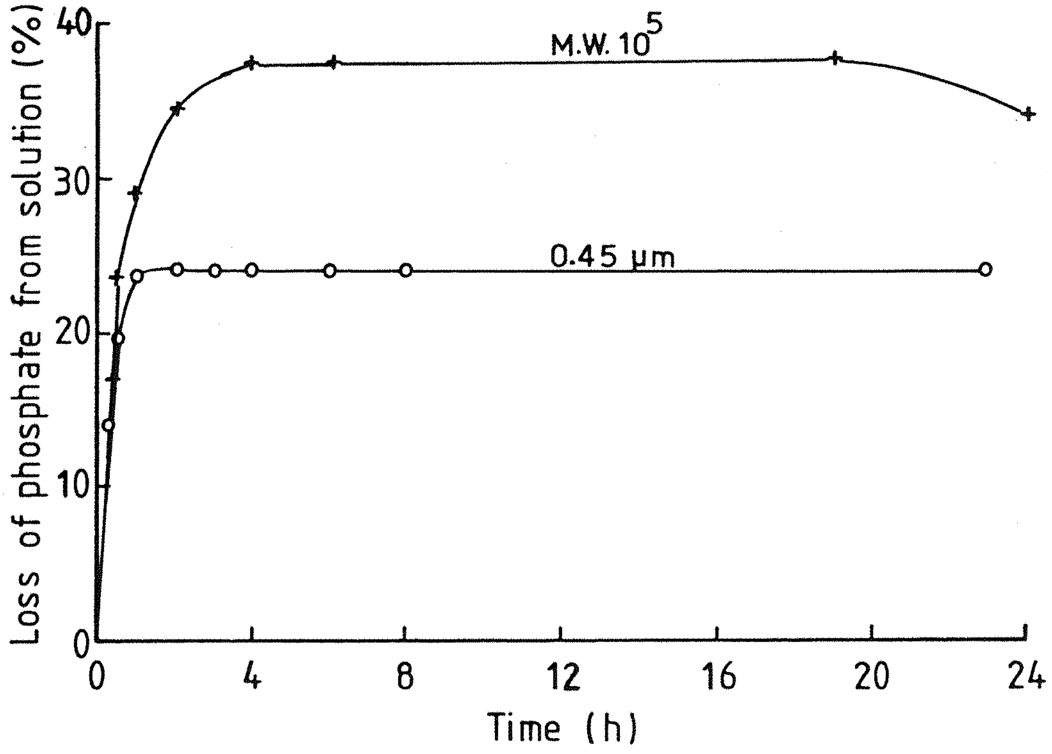


Figure 5-3. Adsorption of phosphate on normal suspended solids in 0.45 µm and XM 100 (M.W. < 10^5) filtrates of River Beaulieu water. Initial conditions; pH 4.5, solids 196 ppm, temperature 21° C , phosphate 46 µg P l^{-1} (0.45 µm fraction), 38 µg P l^{-1} (M.W.<10^5 fraction).

Table 5-3. Adsorption of phosphate on normal suspended solids in 0.45 µm and XM-100 filtrates of River Beaulieu water

Time (hr)	0.45 µm fraction		XM-100 ($<10^5$) fraction	
	Concentration PO_4^{3-} remaining (µg l^{-1})	% Adsorbed	Concentration PO_4^{3-} remaining (µg l^{-1})	% Adsorbed
Initial	46.2	-	38.3	-
0.25	39.8	13.9	31.8	16.9
0.5	37.1	19.7	29.3	23.5
1	35.3	23.6	27.3	28.7
2	35.0	24.2	25.0	34.7
3	35.0	24.2	-	-
4	35.0	24.2	24.0	37.3
6	35.0	24.2	24.0	37.3
8	35.0	24.2	-	-
19	-	-	24.0	37.3
23	35.0	24.2	25.3	33.9

Suspended solids concentration 196 mg l^{-1}; pH 5.0

Iron concentration 360 µg l^{-1} (0.45 µm filtrate)

95 µg l^{-1} (XM-100 filtrate)

DOC concentration 8.3 mg l^{-1} (0.45 µm filtrate)

8.1 mg l^{-1} (XM-100 filtrate)

from 360 $\mu g\ l^{-1}$ in the 0.45 μm filtrate to 95 $\mu g\ l^{-1}$ in the ultrafiltrate ($<10^5$ M.W.), the holding capacity for phosphate in the colloidal material was reduced, leading to an increase in adsorption on the suspended solids.

Also the equilibrium adsorption of phosphate in different fractions of river water filtrates from 0.45 μm membrane, XM-100 membrane (M.W. cut-off 10^5), PM-30 membrane (M.W. cut-off 3×10^4) and UM-10 membrane (M.W. cut-off 10^4) was examined by shaking 100 ml volumes of water samples with added standard phosphate with a small amount of suspended solids (90 mg l^{-1}) for 24 hours, the solutions then being analysed for the dissolved phosphate after filtration. The results, summarized in Table 5-4, clearly show that, as the amount of dissolved iron and to a lesser extent the amount of DOC, were reduced by ultrafiltration, the adsorption of phosphate on suspended solids was increased due to the loss of the holding capacity for dissolved phosphate in the solution.

The effect of iron oxide coating on the sediment in the adsorption of phosphate was next studied. Iron oxide free suspended sediment was obtained by using the hydroxylamine hydrochloric-acetic acid leaching technique of Chester and Hughes (1967). Experiments on equilibrium adsorption were performed in a similar way as for normal suspended solids. The results are summarized in Table 5-4. A marked reduction in the adsorption capacity was observed, uptake being about 60% less (with the 0.45 μm fraction) than with the normal suspended solids. The adsorption also decreased with decrease in molecular weight of the solution phase until no adsorption was observed using the filtrate from the ultrafilter with molecular weight cut-off of 10^4. This may result from the combined effect of the lack of dissolved iron in the solution and the absence of an iron phase in the suspended solids.

5.2.4 Effect of organic matter

The same suspended sediment was leached with 30% hydrogen peroxide in order to remove organic matter. The sediment was left to oxidize slowly overnight at room temperature, boiled for 2 hours at 90°C, centrifuged after cooling, and washed several times with 5% ethanol in distilled water. The leached suspended solid was left several days before using for the experiment.

The adsorption experiments were carried out using 100 ml volumes of the 0.45 μm filtrate and several fractions of ultrafiltered river water with added standard phosphate and the organic-free suspended solid. The solutions were centrifuged, filtered and analysed for dissolved phosphate after equilibrating with the solutions for 24 hours. The results, summarized in Table 5-4, showed that removal of organic matter from the suspended sediments reduces the efficiency of the adsorption of phosphate. The amount of dissolved iron and DOC in the solution influence the extent of adsorption, the adsorption tending to increase as dissolved iron is removed, i.e. from the larger M.W. fraction to the smaller M.W. fraction. Comparison of the percentage adsorption with the organic-free sediment and the normal sediment, shows that the capacity of adsorption was reduced from 29% (with the 0.45 μm filtrate) to 14% (with the ultrafiltrate using the membrane with M.W. cut-off 10^4).

Table 5-4. Comparison of the adsorption behaviour of phosphate on normal sediments, organic-free sediments and iron, manganese-free sediment in different molecular weight fractions of River Beaulieu water.

Fraction*	Initial added phosphate ($\mu g\ l^{-1}$)	Concentration phosphate remaining Normal sediment ($\mu g\ l^{-1}$)	Organic-free sediment ($\mu g\ l^{-1}$)	Iron, manganese-free sediment ($\mu g\ l^{-1}$)
0.45 μm	92.0	16.7(81)	42.7(53)	71.7(20)
10^5	79.8	10.8(86)	31.9(60)	70.5(11)
3×10^4	82.8	9.8(88)	19.0(77)	75.0(9)
10^4	76.8	8.0(89)	19.0(75)	76.8(0)

Values in parentheses are percentage adsorption (average of duplicates); 90 ppm suspended solids

* Filtrate	Iron ($\mu g\ l^{-1}$)	DOC ($mg\ l^{-1}$)
0.45	360	8.3
10^5	95	8.1
3×10^4	24	6.6
10^4	24	6.2

5.3 Mixing experiments

Mixing experiments using river water and sea water were carried out in order to study the removal of phosphate as a function of change in salinity. The experiments were performed under two conditions (1) without suspended material, and (2) with the suspended material and flocculants present.

5.3.1 Removal of phosphate as a function of salinity

The removal of phosphate as a function of salinity was studied by making a series of mixtures of filtered River Beaulieu water and filtered sea water from outside of the Beaulieu estuary. The mixed waters were filtered through 0.45 µm Sartorius membrane filters in order to remove the flocculants, after they had been reacted for a few hours. To duplicate aliquots (100 ml) of each mixture known amounts of phosphate were added and the solutions shaken for 24 hours. The filtered samples were analysed for phosphate. Results are summarized in Table 5-5 and in Figure 5-4. Phosphate removal of about 2 to 5% occurred over the salinity range 1.7 - 17°/oo. These experiments form a control for the following experiment in which iron was added.

5.3.2 Coprecipitation with iron as a function of salinity

The same set of mixed waters from the last experiment were used with 0.5 ppm of iron added. The amount of phosphate removed was calculated relative to the concentration in the sample of salinity ~ 0°/oo (Table 5-5); the values are plotted against salinity in Figure 5-4. It showed that in the presence of iron, dissolved phosphate can be removed from the water through coprecipitation with iron as the salinity increases. A pronounced removal of phosphate was observed to occur in the salinity range 0-5°/oo with a subsequent decrease in removal as salinity increases.

Table 5-5. Removal of phosphate and the effect of iron in mixing experiments

Salinity (°/oo)	No iron added			With 0.5 ppm iron	
	Concentration			Concentration	
	Initial ($\mu g\ l^{-1}$)	Final ($\mu g\ l^{-1}$)	% Adsorbed	Final ($\mu g\ l^{-1}$)	% Adsorbed
0	90.0	90.0	0	85.0	5.6
1.7	91.7	89.0	3.0	72.2	21.7
3.4	91.5	87.0	5.0	57.3	38.0
5.6	92.0	90.0	2.2	20.2	79.8
8.5	91.3	87.0	4.8	19.8	79.4
17.0	94.6	92.0	2.9	28.7	73.2
22.7	96.5	96.0	0.5	45.3	56.9
27.2	100	100	0	49.2	56.4
34.0	100	100	0	57.3	47.8

The flocculants were removed before experiments

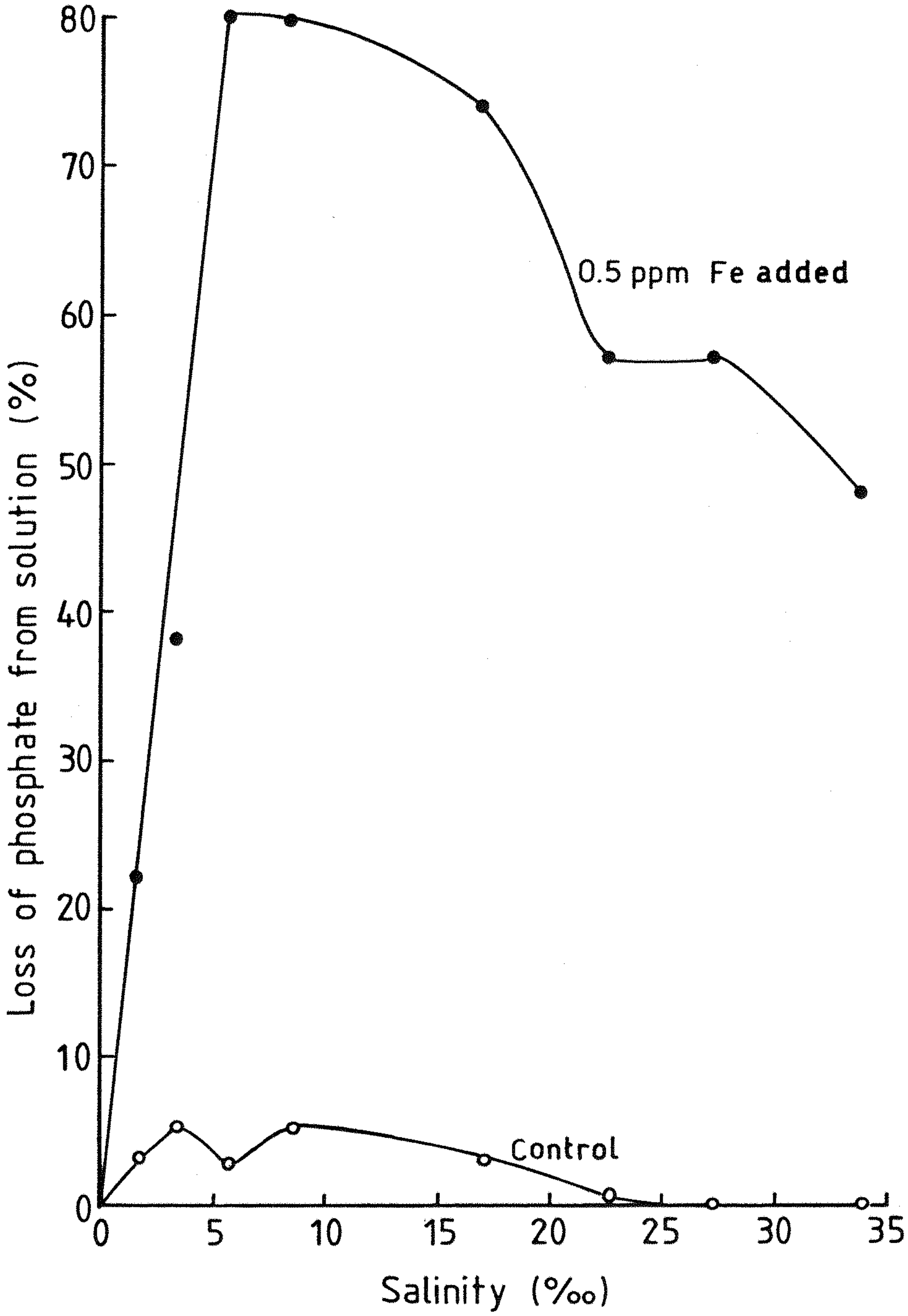


Figure 5-4. Removal of phosphate and the effect of iron in experimentally mixed waters, Initial conditions, phosphate 90 µg P l^{-1}, temperature 22°C, no flocculants present.

5.3.3 The removal of phosphate with suspended solids as a function of salinity

This experiment was performed by mixing the two end-member waters with their suspended solids still present, in order to study the adsorption behaviour of phosphate onto suspended solids under salinity changes. Biological effects were examined by comparing adsorption in sterilized water samples and in non-sterilized water samples.

Samples of the Beaulieu river water and the sea water from the Solent area were filtered through a nylon mesh (54 µ) in order to remove large particulate matter. A series of mixed samples of varying salinity were prepared, and as soon as they were mixed, 100 ml volumes were pipetted into conical flasks with standard phosphate added. The samples were then agitated for 24 hours on the mechanical shaker. The percentage of phosphate adsorption was calculated relative to the initial concentration plus the amount of standard phosphate added. The results are summarized in Table 5-6 and shown in Figure 5-5. A similar experiment was carried out using water samples sterilized by autoclaving for 15 minutes. The results of this experiment are also shown in Figure 5-5, for comparison with the non-sterilized samples. The difference in the percentage removed between the two experiments was observed to be about 15 to 25%, which may reflect the adsorption attributable to biological effects, especially through micro-organisms attached to the suspended solids. In general, removal occurred most markedly between salinity 0 to 5‰, and continued up to salinity >25‰. These removal patterns except at low salinity are consistent with the previous experiment without suspended solids (Figure 5-4). The river water solutions showed a large removal of phosphate which may reflect the high adsorption capacity of riverborne suspended solids in river water.

Table 5-6. The effect of biological activity on phosphate adsorption on suspended solids in waters at various salinities.

Salinity (°/oo)	Non-sterilized water samples*		
	Concentration		
	Initial (μg l^{-1})	Final (μg l^{-1})	% Adsorbed
0	59.3	39.3	33.7
	59.3	39.6	33.2
4.0	56.7	43.5	23.3
	58.1	44.1	24.1
6.7	55.6	44.7	19.6
	55.8	44.7	19.9
9.0	54.6	43.5	20.3
	55.1	44.3	19.6
11.0	54.4	41.5	23.7
	54.2	41.2	24.0
12.7	55.5	43.5	21.6
	55.3	42.7	22.8
15.0	55.5	44.1	20.5
	55.5	43.7	21.3
16.7	55.1	44.3	19.6
	55.1	43.7	20.7
19.0	56.2	43.7	21.7
	55.8	44.2	21.4
22.0	55.8	45.0	19.4
	55.8	45.2	19.0
26.5	57.8	49.3	14.7
	57.5	49.0	14.8
32.4	59.1	53.0	10.3
	59.3	53.0	10.3

Initial concentration after adding 49 μg l^{-1} standard phosphate

Continued

Table 5-6 (Continued)

	Sterilized water samples*		
Salinity (°/oo)	Concentration		
	Initial ($\mu g\ l^{-1}$)	Final ($\mu g\ l^{-1}$)	% Adsorbed
0	72.1	65.0	9.9
	72.1	65.0	9.9
4.0	70.4	69.6	1.1
	70.5	69.6	1.1
7.0	73.1	69.6	4.8
	73.5	69.6	5.3
9.4	72.1	68.6	4.9
	72.1	69.2	4.0
11.4	72.7	69.2	4.8
	72.7	69.2	4.8
14.4	70.5	66.2	6.1
	70.5	65.7	6.8
17.2	72.1	69.1	4.1
	71.7	68.7	4.2
23.2	71.0	67.8	4.5
	71.2	68.2	4.2
25.0	70.3	67.8	3.6
	70.5	68.6	2.7
32.4	69.3	75.8	9.4) Excess
	69.3	75.5	8.9)

Initial concentration after adding 56 $\mu g\ l^{-1}$ standard phosphate

*Suspended solids and flocculants present

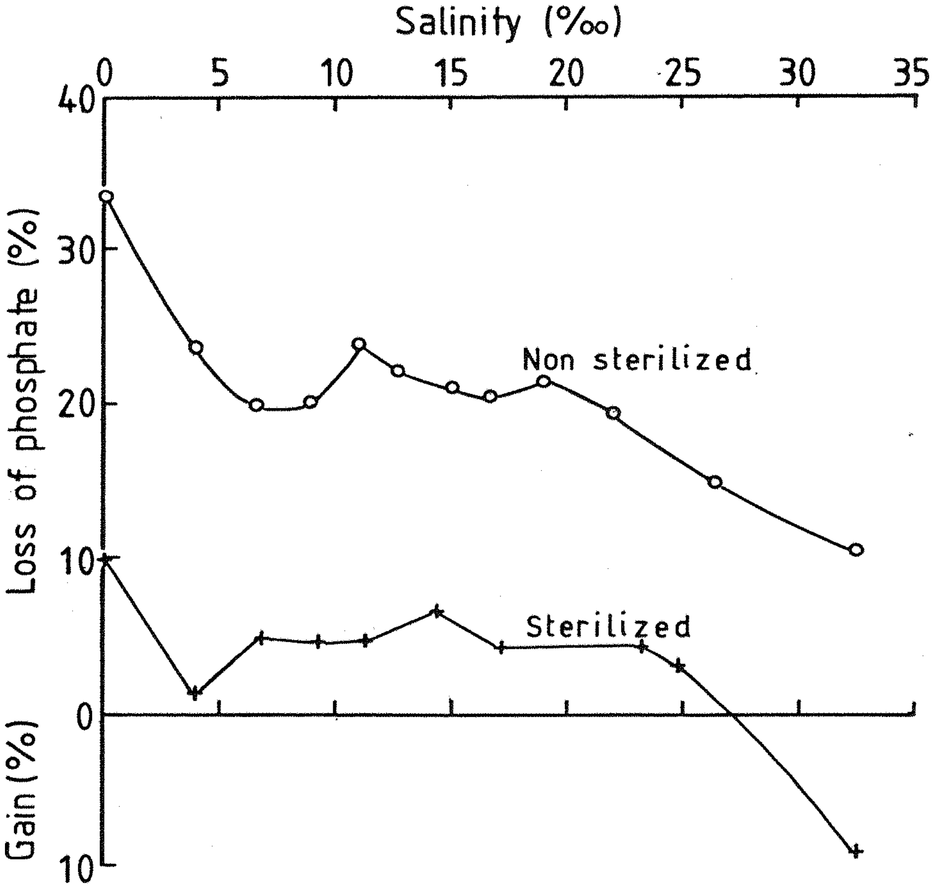


Figure 5-5. The effect of biological activity on phosphate adsorption on suspended solids in mixed waters at various salinities; Initial conditions; phosphate 90 µg P l^{-1}, temperature 21° C.

5.4 Discussion and conclusions

It can be seen that the suspended solids especially in the river can play a major role in their effect on the supply of available reactive phosphate to the estuary, through the processes of transport of the adsorbed phosphate and its release in the estuary in which the ionic strength, pH and other properties differ from the source. From the findings in the experiments on the phosphate in the river water, some 60% is in the dissolved/colloidal form with iron, and another part is adsorbed on the surface of riverborne suspended solids. The amount of dissolved iron in the river water will also control the distribution of phosphate between the suspended solids and the water; as the dissolved iron in the river water is lowered (Figure 5-3) the holding capacity of phosphate in the solution is reduced, and the reaction is shifted to adsorb more phosphate on the suspended solid. So the ratio of dissolved phosphate/adsorbed phosphate in the river water is controlled mainly by the amount of dissolved iron (and organic matter) in the colloid. From the experiments, the maximum adsorption of phosphate in river water occurs between pH 3-6 (Figure 5-2), and less adsorption occurs in more saline water (Figure 5-3, 5-5). As the adsorbed phosphate on the suspended solids in river waters is transported to the estuary, on early contact with higher ionic strength water, some of it will be released into the estuarine water. The phosphate incorporated in the colloid will be removed from the water by the process of flocculation with the iron; the presence of iron will control the removal of dissolved phosphate (Figure 5-4). The salinity of maximum removal in the experiment in which most of the dissolved iron (with some dissolved organic matter) was as a flocculate, was observed to be in the range 0-5°/oo, compared with the range of 0-15°/oo in the real estuarine system. With salinity increase from about 7°/oo (Figure 5-4) to the highest salinity of 34°/oo, the adsorption of phosphate was found to decrease. The lesser adsorption of phosphate as the salinity increases in the presence of solid materials (Figure 5-5), probably reflects the effects of the

Cl^- and SO_4^{2-} ions in sea water taking up adsorption sites on the suspended solids, as suggested by Upchurch (1974).

The presence of iron on the suspended solids is a main control of the adsorption capacity of phosphate onto their surfaces. A marked reduction of the adsorption capacity of iron-free suspended solids was observed (Table 5-4), to 25% of the value for the normal suspended sediment. In estuarine mixing, where the river water with riverborne suspended solid mixes with sea water and its suspended solids, it has been observed that the non-lattice iron in the suspended solids decreases, as the salinity increases (Moore _et al._, 1979), suggesting that as the salinity increases, the suspended solids present will have less capacity to adsorb phosphate.

A short summary can be made that, as the dissolved phosphate in the river water enters the estuary, removal will occur in early mixing by the process of flocculation, the magnitude of removal depending on the concentration of dissolved phosphate in the river water which is influenced by the concentration of dissolved iron. In contrast, the phosphate adsorbed on suspended solids will tend to be released into the water as the salinity increases.

The effect of organic matter on the adsorption of phosphate in the experiment was found to be different than suggested from other work, in that the removal of the organic matter in the sediment tended to decrease the adsorption capacity for phosphate. This may be due to indirect effects, e.g. changes in the adsorption capacity of the iron colloid, rather than a direct result of the oxidation of organic material, and further work would be needed to determine the role of organic matter in affecting adsorption.

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APPENDIX I

Beaulieu estuary survey: 10 April 1979

The following data, as presented, correspond to the stations which are shown in Figure 2-2.

Station	Salinity (o/oo)	Dissolved Phosphate ($\mu g\ l^{-1}$)	Dissolved Silicon ($\mu g\ l^{-1}$)	Dissolved Iron ($\mu g\ l^{-1}$)
1	32.0	3.8	48	10.2
2	31.5	6.2	49	11.0
3	30.5	1.1	61	10.5
4	29.4	4.3	75	14.5
5	28.8	2.0	87	11.2
6	27.9	1.2	101	8.5
7	26.8	1.1	120	16.0
8	28.5	2.0	92	10.5
9	28.4	1.2	89	10.5
10	27.1	1.2	116	9.5
11	26.7	3.7	121	11.0
12	25.0	5.3	161	7.5
13	24.2	3.3	180	8.5
14	21.9	5.6	243	11.0
15	21.4	8.5	264	13.0
16	21.2	3.5	236	12.5
17	21.0	6.0	266	12.5
18	20.5	9.6	283	14.5
19	18.0	9.6	345	18.5
20	4.0	8.2	1,330	109
21	3.9	8.2	1,545	167

Cont'd

APPENDIX I (Cont'd)

Station	Salinity (o/oo)	Dissolved Phosphate ($\mu g\ l^{-1}$)	Dissolved Silicon ($\mu g\ l^{-1}$)	Dissolved Iron ($\mu g\ l^{-1}$)
22	2.5	9.2	1,000	78
23	1.5	17.0	1,835	280
24	1.8	9.0	1,680	-
25	1.9	10.8	1,695	134
Fawley Ford Bridge*	0	20.5	2,625	320

* see Figure 2-1

APPENDIX II

Beaulieu estuary survey: 4th June 1979

The following data, as presented, correspond to the stations which are shown in Figure 2-3.

Station	Salinity (°/oo)	DOC (mg l^{-1})	Dissolved Phosphate ($\mu g\ l^{-1}$)	Dissolved Silicon ($\mu g\ l^{-1}$)	Dissolved Iron ($\mu g\ l^{-1}$)
FIXED: A					
Time 1100	7.1	7.9	12.6	2,925	126
" 1200	7.0	8.9	18.5	2,750	97
" 1300	7.7	7.1	13.0	2,437	40
" 1400	4.7	8.4	15.0	3,065	162
" 1500	8.9	6.6	22.2	2,375	48
" 1600	14.0	6.3	21.4	1,885	38
B_1	0.8	9.2	19.0	3,700	395
B_2	2.6	9.5	27.2	3,400	345
B_3	3.6	8.6	21.7	3,275	275
B_4	6.5	7.9	17.1	2,287	138
C_1	11.8	6.6	15.0	2,445	23
C_2	17.3	5.2	9.8	1,735	15
C_3	21.3	4.0	4.5	1,245	15
C_4	15.4	5.7	10.3	2,000	21
C_5	12.3	6.3	16.8	2,455	25
C_6	9.5	7.2	8.3	2,130	56
2	29.5	1.8	5.9	270	12
3	26.2	2.7	-	635	14

Cont'd

APPENDIX II (Cont'd)

Station	Salinity (°/oo)	DOC (mg l^{-1})	Dissolved Phosphate (μg l^{-1})	Dissolved Silicon (μg l^{-1})	Dissolved Iron (μg l^{-1})
4	25.1	3.2	-	755	15
6	21.2	4.2	6.0	1,220	15
7	16.4	5.3	8.8	1,765	25
8	19.7	4.8	10.1	1,420	16
9	16.8	5.4	6.0	1,735	17
10	18.7	5.0	7.7	1,540	16
Fawley Ford Bridge*	0	9.2	13.0	4,087	435

Fixed Station A at various times

B_1 - B_4 areas are above Station A

C_1 - C_6 areas are below Station A

* see Figure 2-1

APPENDIX III

Beaulieu estuary survey: 16th August 1979

The following data, as presented, correspond to the stations which are shown in Figure 2-3.

Station	Salinity ($^0/oo$)	DOC (mg l^{-1})	Dissolved Phosphate ($\mu g\ l^{-1}$)	Dissolved Silicon ($\mu g\ l^{-1}$)	Dissolved Iron ($\mu g\ l^{-1}$)
FIXED: A					
Time 1100	18.4	4.3	28.8	2,260	9.5
" 1200	19.9	3.7	31.5	1,935	10.5
" 1300	20.7	3.7	29.1	1,820	12.5
" 1400	22.3	3.5	25.7	1,610	10.0
" 1500	17.9	4.1	42.4	2,310	10.5
" 1600	19.4	4.3	47.5	2,090	9.0
B_1	14.3	-	51.7	3,000	11.0
B_2	15.7	4.3	53.3	2,870	10.5
B_3	18.1	4.3	28.8	2,170	11.0
1	34.5	0.9	11.2	150	5.5
2	34.4	1.2	8.2	140	5.5
3	33.8	1.4	4.5	189	6.5
4	32.0	2.1	2.5	315	6.0
5	30.4	2.4	5.2	490	6.0
6	28.9	2.6	7.7	630	7.0
7	27.3	2.8	10.2	860	7.2
8	26.6	3.3	12.3	965	7.0
9	26.0	2.8	12.3	1,040	7.0

Cont'd

APPENDIX III (Cont'd)

Station	Salinity (°/oo)	DOC (mg l^{-1})	Dissolved Phosphate (µg l^{-1})	Dissolved Silicon (µg l^{-1})	Dissolved Iron (µg l^{-1})
10	25.5	3.1	13.8	1,120	8.0
Fawley Ford Bridge *		6.5	15.8	5,725	437

* see Figure 2-1

APPENDIX IV

Beaulieu estuary survey: 26th September 1979.

The following data, as presented, correspond to the stations which are shown in Figure 2-4.

Station	Salinity (°/oo)	DOC (mg l^{-1})	Dissolved Phosphate (μg l^{-1})	Dissolved Silicon (μg l^{-1})	Dissolved Iron (μg l^{-1})
1	34.3	0.9	17.5	117	6.0
2	34.3	1.1	13.8	124	6.0
3	34.1	1.2	12.3	143	6.0
5	30.8	2.2	8.2	320	7.5
E_1	17.2	3.3	-	2,430	12.0
E_2	19.3	3.0	18.7	2,050	8.5
E_3	20.3	2.8	19.8	1,900	8.5
E_4	22.0	2.8	23.0	1,750	7.5
E_5	28.5	2.4	7.0	545	7.0
E_6	29.2	2.2	5.8	545	7.0
P_1 Surf.	20.5	2.7	18.8	1,785	8.0
Bot.	26.0	2.5	13.3	890	14.5
P_2 Surf.	22.0	2.6	17.0	1,560	30.0
Bot.	26.5	2.4	12.3	885	14.0
P_3 Surf.	12.0	3.5	34.3	3,375	32.0
Bot.	25.7	-	22.8	990	7.5
P_4 Surf.	10.5	3.0	24.3	3,750	12.0
Bot.	24.4	2.6	24.0	1,140	25.5
P_5 Surf.	8.2	3.4	18.0	4,375	19.5
Bot.	22.4	2.6	20.4	1,590	20.5

Cont'd

APPENDIX IV (Cont'd)

Station	Salinity ($^{o}/oo$)	DOC (mg l^{-1})	Dissolved Phosphate (ug l^{-1})	Dissolved Silicon (ug l^{-1})	Dissolved Iron (ug l^{-1})
P_6 Surf.	6.4	3.2	7.8	4,825	41.0
Bot.	21.7	2.4	16.2	1,785	23.0
P_7 Surf.	21.9	2.8	9.0	-	43.0
Bot.	21.6	2.8	14.3	1,830	19.5
P_8 Surf.	4.1	3.4	7.9	5,275	62.0
Bot.	21.0	2.5	16.2	1,980	31.0
P_9 Surf.	5.2	3.3	7.5	4,975	30.0
Bot.	19.0	2.5	17.5	2,350	16.1
Museum Bridge	2.1	3.9	3.5	5,450	111
Private Bridge	1.4	3.9	17.5	5,600	280
Fawley Ford Bridge	0	3.6	16.5	5,900	437

E_1 - E_6	Varies salinity from Bailey's Hard up to the sluice.
P	Samples in the pond and along the stream up to Private Bridge, (see Figure 2-1).

APPENDIX V

Beaulieu estuary survey: 9th November 1979

The following data, as presented, correspond to the stations which are shown in Figure 2-4.

Station	Salinity (^{o}/oo)	pH	DOC (mg Cl^{-1})	Diss. Phos. (μg l^{-1})	Diss. Silicon (μg l^{-1})	Diss. Iron (μg l^{-1})
1	34.0	7.7	1.4	23.2	227	5.0
2	34.0	7.7	1.5	21.0	241	6.0
3	33.6	7.7	1.4	22.0	280	5.0
4	33.2	7.7	1.5	22.5	335	6.0
5	30.5	7.6	2.4	20.5	695	11.0
E_1	0	7.0	9.3	13.2	4,700	385
E_2	0	6.9	9.4	10.3	4,400	450
E_3	8.3	7.1	7.0	6.3	3,500	131
E_4	2.3	6.8	8.6	19.0	4,225	350
E_5	11.2	6.7	5.8	10.3	3,125	62.0
E_6	17.1	7.1	4.3	13.2	2,500	19.5
P_1 Surf.	17.0	6.9	3.7	10.2	2,450	33.0
Bot.	17.4	6.8	3.7	16.3	2,300	29.0
P_2 Surf.	18.5	6.9	4.7	16.7	2,125	25.0
Bot.	18.5	7.0	3.7	16.6	2,150	19.0
P_3 Surf.	16.7	6.8	4.1	15.8	2,225	30.5
Bot.	17.6	6.9	4.3	10.2	2,100	22.5
P_4 Surf.	14.7	6.8	5.6	14.3	2,475	48.5
Bot.	17.0	7.0	6.6	12.4	2,200	23.0
P_5 Surf.	6.5	6.4	6.4	15.3	3,650	200
Bot.	14.0	7.0	4.9	13.5	2,725	63

Cont'd

APPENDIX V (Cont'd)

Station	Salinity (°/oo)	pH	DOC (mg C l^{-1})	Diss. Phos. (µg l^{-1})	Diss. Silicon (µg l^{-1})	Diss. Iron (µg l^{-1})
P_6 Surf.	0	6.5	9.8	8.2	4,550	402
Bot.	8.0	6.4	6.2	13.2	3,550	175
P_7 Surf.	0	6.5	9.5	14.3	4,550	475
Bot.	0	7.1	9.4	13.3	4,600	407
P_8 Surf.	0	6.8	9.5	13.6	4,525	447
Bot.	4.3	6.3	7.2	14.7	4,025	302
P_9 Surf.	0	7.2	9.5	15.3	4,600	475
Bot.	6.1	6.6	7.1	13.8	3,840	220
Private Br.*	0	6.6	10.3	9.3	4,400	390
Hartford Bridge*	0	6.6	11.1	7.8	4,350	387
Fawley Ford Br.*	0	6.6	10.3	14.5	4,450	470

* see Figure 2-1