This thesis is dedicated to my parents ,
the people whom I love and who love me

University of Southampton

Phosphorus biogeochemistry and models in estuaries:

Case study of the Southampton Water system

By

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ABSTRACT
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Phosphorus biogeochemistry and models in estuaries: Case study of the Southampton Water system

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Various factors may increase the supply of organic matter content (*eutrophication status*) of estuarine and coastal systems. The most common cause of eutrophication is considered to be nutrient enrichment. In this study data has been collected in monthly surveys from January 1998 to April 1999 in the Southampton Water system, and the major features of nutrients (nitrogen, phosphorus and silicon) and suspended particulate matter (SPM) thus obtained. Additionally phosphorus in porewaters, and the solid phase in sediments were measured. The forms of phosphorus in the solid phase of sediment (deposited and suspended) were also measured using a modified sequential phosphorus extraction protocol (SPEPs) method.

The ranges of the dissolved inorganic phosphorus (DIP) and other nutrients are similar to the data from the SONUS investigations. The overall distribution of DIP are strongly influenced by the sewage inputs to the system, with a peak in concentration in the River Itchen from the sewage works followed by apparently conservative behaviour. The concentration of dissolved organic phosphorus (DOP) were often low (rarely exceeded 5 μM) and irregularly distributed in the system. The concentrations of particulate phosphorus in the water column and in the particles decreased seaward. The P:Fe ratio in the bicarbonate-dithionite released phase from particles implied that the phosphorus "saturated" particles near the sewage outfall are likely buried before they reach the high salinity waters and the particles in the high salinity waters are mainly from sediment resuspension, the detritus of phytoplankton or from offshore. The N/P ratios obtained implies that the system has potential phosphorus limitation of phytoplankton growth.

The concentrations of the forms of inorganic phosphorus in the sediment generally decreased seaward. The Ca-bound phosphorus appears to be the dominant form of inorganic phosphorus (about 55%-85% of total inorganic phosphorus) in most of the sediments in the system. Benthic flux measurements revealed that the sediments in the system generally act as a sink of dissolved inorganic phosphorus and a source of dissolved organic phosphorus. This is in contrast to the fluxes of DIP predicted from the pore-water concentration gradients and implied the presence of a ferric iron-rich oxidising cap on the sediment surface.

The results of a K_d model applied on the freshwater-sea boundary revealed that within the range of the riverine DIP concentration only a small amount of removal or addition of DIP is likely to occur. The K_d model is useful in predicting the influence of resuspended particles on DIP in the water column after resuspension "events" caused by storm and dredging activities.

The total phosphorus input to the system is estimated as 144 ± 23.7 tonnes per year. The riverine input is the major source of phosphorus (about 69% of the total inputs). The direct sewage input (30% of the total phosphorus inputs) is also an important source of phosphorus in the system, especially in summer. The atmospheric input (1% of the total phosphorus inputs) is small. A considerable exchange flux with adjacent coastal waters (about 40% of total phosphorus inputs) reveals that the system is a phosphorus source to the English Channel and adjacent areas. The particle burial is an important process and retains about 60% of the phosphorus entering the system. However, significant removal of phosphorus from the water column was not obviously observed, suggesting that there are other sources of phosphorus in the system or the estimate of internal loss is overestimated.

Further study is needed to reaffirm the behaviour of all forms of phosphorus in the system, and assess their yearly variation. An investigation of the forms of particulate phosphorus and phosphorus in surfacial sediments on better temporal and spatial resolution is also needed together with more geological information on the origin and sizes of particles.

CONTENTS

Chapter 1: General introduction

Chapter 2: Overview of analytical methods for the determinations of phosphorus in marine waters and sediments

Chapter 3: Study of water column phosphorus in the Southampton Water system: sampling, analysis and results

Chapter 4: Study of water column phosphorus in the Southampton Water system: comparison with historical data and discussion

Chapter 5: Study of phosphorus in the sediments of Southampton Water and the Itchen Estuary

Chapter 6: The Phosphorus budget in the Southampton Water system

Chapter 7: Conclusions and further work

Appendices:

Abbreviations

BD	Bicarbonate-dithionate
C	Carbon
CaP	Ca-bound phosphorus
Chl *a*	Chlorophyll *a*
Corg	Organic carbon
DIN	Dissolved Inorganic Nitrogen
DIP	Dissolved Inorganic Phosphorus
DOP	Dissolved Organic Phosphorus
EA	Environment Agency
FeP	Fe-bound phosphorus
GMT	Greenwich mean time
LOICZ	Land-Ocean Interaction in the Coastal Zone
N	Nitrogen
P	Phosphorus
Porg	organic phosphorus
PIP	Particulate inorganic phosphorus
Poly P	Polyphosphate
POP	Particulate organic phosphorus
PTP	Particulate Total Phosphorus
PTP(c)	Particulate Total Phosphorus in water column
PTP(m)	Particulate Total Phosphorus on particles
PWD	Portswood wastewater discharge
RI	River Itchen
S	Sulphur
Sal	Salinity
Si	Dissolved silicon
SIP	Sediment inorganic phosphorus

SONUS	Southern nutrient study
SPEPs	Sequential phosphorus extraction protocols
SPM	Suspending Particulate Matter
SRP	Soluble reactive phosphorus
SW	Southampton Water
Temp	temperature
TP	total phosphorus
TDP	total dissolved phosphorous
UV	Ultraviolet

List of Figures

List of Tables

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Chapter 1: General introduction

1.1 Phosphorus (P) sources, sinks and global cycles

Phosphorus is the tenth most abundant element on Earth with an average crustal abundance of 0.1% (Brinck, 1978; Jahnke, 1992). Phosphate was first determined in seawater in 1865 (Gulbransen and Roberson, 1972). The concentration of phosphorus in seawater is small, with an average of about 2.3 μM (Redfield, 1958). It is an essential element in many of the biogeochemical processes occurring in the biosphere, such as photosynthesis, metabolism, storing of chemical energy and energy transfer (Jahnke, 1992). The global cycle of phosphorus has many poorly quantified steps, such as burial of phosphorus in oceanic and estuarine sediments, and the atmospheric input of phosphorus to oceans and *vice versa* (Jahnke, 1992). The global occurrence of phosphorus differs from that of the other major biogeochemical elements, C, N, S and Si, in several aspects. First, oxidation-reduction reactions play a minor role in controlling the reactivity and distribution of phosphorus in the environment. So that in general, the biogeochemical cycle of phosphorus is synonymous with that of phosphate (Williams, 1977; Jahnke, 1992). The second difference between phosphorus and the other biogeochemical elements is that unlike N (or S) P has no stable gaseous phase in the atmosphere. Thus although phosphorus is transported in the atmosphere on dust particles and dissolved in rain and at certain locations the small atmospheric source of phosphorus can be important (Duce *et al.*, 1991), the atmosphere generally plays a minor role in the phosphorus global cycle (Berner and Berner, 1987; Jahnke, 1992). Duce *et al.* (1991) estimated the atmospheric inputs of phosphorus as 0.95 Tg/y, compared to the global riverine phosphorus flux of 22 Tg/y (Howarth *et al.*, 1992) and the atmospheric N flux of 96.7 Tg/y (Mackenize *et al.*, 1993).

Phosphorus cycles slowly through the ocean and atmosphere (4.73×10^4 years)(Emsley, 1980). The primary inorganic phosphorus cycle consists of three major components:

1. Phosphorus is leached from the land by weathering and carried by rivers to the sea; rivers are the main source of phosphorus to the oceans. Published estimates of the annual world phosphorus riverine flux are between 21 Tg P/y (Meybeck, 1982) and 39 Tg P/y (Froelich *et al.*, 1982). Most recently Howarth *et al.* (1995) gave a global estimate of 22 Tg/y.
2. Phosphorus is precipitated in the sea as calcium phosphates (apatites). This produces deposits that are mostly found on continental shelves. The ultimate fate of most phosphorus entering the ocean is burial in sediments. Ruttenberg (1990) estimated phosphorus burial on the continental margin as 6.9 Tg/y and in deep-sea sediments as 0.5 Tg/y, while Howarth *et al* .(1995) estimated the burial rates of phosphorus as 3.3 Tg /y in the continental margins and 0.95 Tg/y in the deep sea .
3. The geological uplifting of marine deposits, prior to weathering starts the cycle again.

Most of the phosphorus in the primary inorganic phosphorus cycle is tied up as insoluble calcium phosphates (apatites) in sedimentary deposits. The dominant origin of phosphate in the cycle is igneous rock (Emsley and Hall, 1976), which contains about 0.2% phosphate. Whether it is phosphate fresh to the primary cycle, from igneous rocks, or phosphate having already been through the cycle, from sedimentary rocks, the solid phase of phosphorus is predominantly present as apatite.

Secondary cycles of phosphorus involve the movement of phosphorus through life cycles on land and in the sea as follows:

1. The uptake of phosphate by plants.
2. The phosphate in plants is then released again to the environment by bacteria and higher organisms.

The secondary cycles are linked with the primary cycles by rivers that wash soluble phosphates from land and thereby replenish the phosphate of lakes and seas, from which phosphate is continually lost by sedimentation, either as precipitated calcium phosphate or organic debris (excreta and dead organisms). The global cycle of phosphorus can be seen in Fig.1.1 (an example global budget after Richey, 1983; Howarth *et al.* 1995; Delaney, 1998) and the details with the comments of each estimation are shown in Table 1.1-1.3 and summarised in Table 1.4.

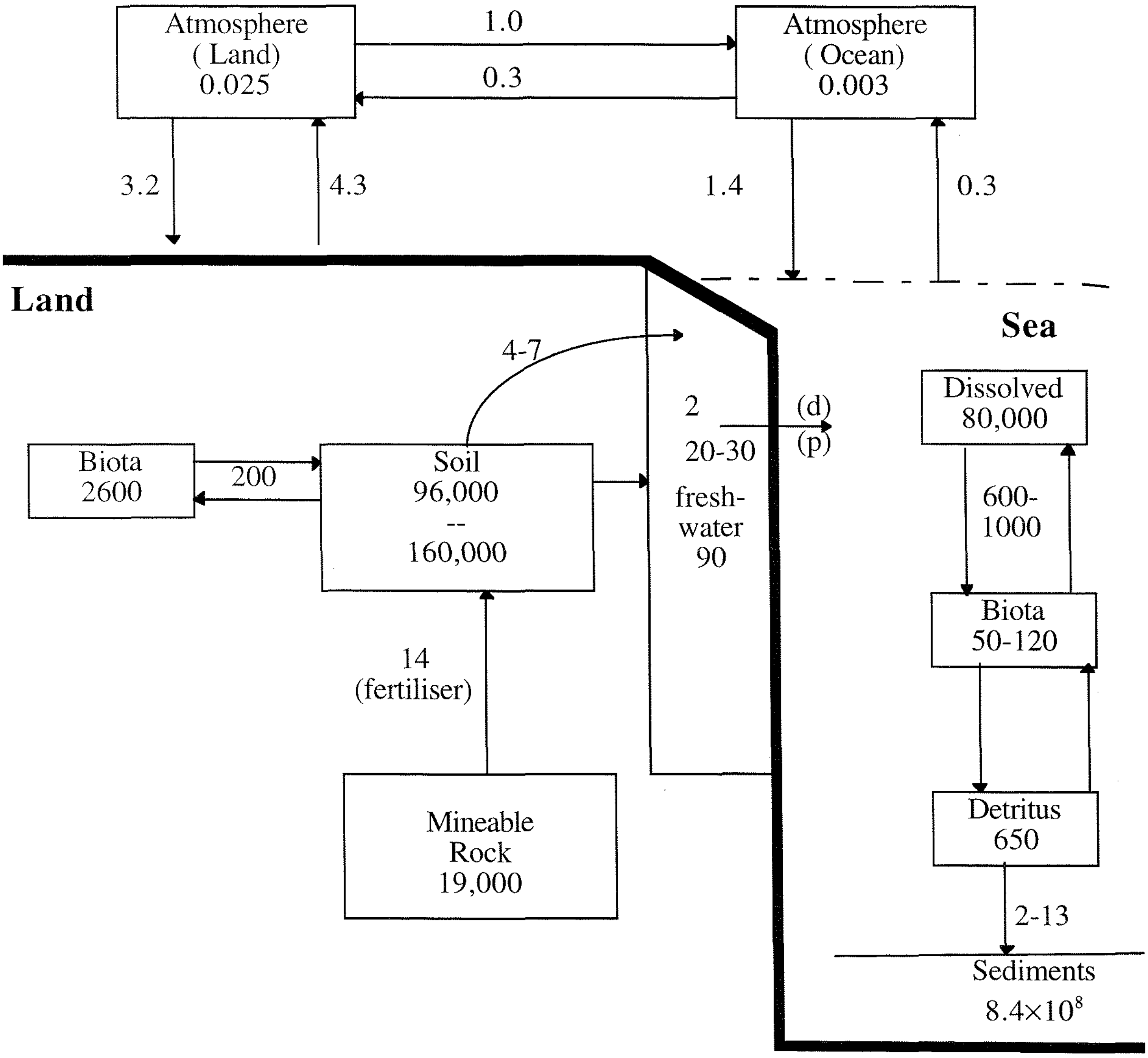


Figure1.1. The global phosphorus cycle.

after Richey (1983); Howarth *et al.* (1995); Delaney, (1998) (Fluxes are in Tg P/yr and reservoirs are in TgP); (d)for dissolved; (p) for particles.

Table1.1 Primary estimates of global river flux of dissolved phosphorus to the ocean

Reference	**Reactive P flux 10^{10} mol P yr^{-1}**	**Comments**
Meybeck (1982, 1993)	3.2	dissolved inorganic P flux based on estimates of total water input and of average dissolved inorganic phosphorus concentrations for undisturbed river systems (0.8 μM); dissolved organic phosphorus (DOP) based on a fixed ratio of DOP/TP; does not include P desorbed from particles.
Froelich *et al.* (1982)	3.6 ± 1.8	dissolved P flux based on estimates of dissolved P concentrations in undisturbed river (~1μM) also on estimate of continental denudation rates
Froelich (1984)	5(+/-50%)	"total reactive" P flux, based on estimates of dissolved flux of 3.6×10^{10} mol P yr^{-1} as given by Froelich *et al.* (1982) and Froelich (1984) plus soluble fraction of particulate P equivalent to 2 to 5 times dissolved flux; up to 25% of total P weathered from continent is delivered to ocean as reactive P.
Ramirez and Rose (1992)	8.1	"total reactive" P flux, based on estimates of dissolved flux from Meybeck (1982, 1993) plus the soluble portion of particulate organic P (POP) and particulate P; estimate of POP based on riverine particulate organic carbon (POC) numbers from Meybeck (1982) and on POP/POC from Delaney (1998).
Berner and Rao (1994)	6.8-9.4	"solubilised sediment" P flux, based on the study of transformation of various forms of particulate phosphorus within the estuary.

Table 1.2 Estimates of total phosphorus delivery to the sediments

Forms of delivery	Reactive P flux, 10^{10} mol P yr^{-1}	Source of estimate
Particulate organic carbon flux	32	Delaney (1998); based on POC flux from Jahnke (1996) to oceanic sediments > 1000m water depth and on Redfield $P/C_{org}/O_2$ from Anderson and Sarmiento (1994).
Hydrothermal plume particulates	0.77	Wheat *et al.* (1996): based on estimates of Fe flux from ridge-axis hydrothermal systems to nonbuoyant plumes and on the average P/Fe of plume particulates.
Phosphorus burial	26 (22± 50%, continental margin; 4, deep-sea)	The continental flux: Ruttenberg (1990) base on the difference between total sediment delivery to oceans in rivers and the rate of sediment accumulation . The deep sea flux: Howarth *et al.* (1995) multiplying an estimate of total sediment reaching the deep-sea by the phosphorus content in the surface sediments from deep-sea.

Table1.3 Estimates of different forms of P burial fluxes in marine sediments

Form of burial	Reactive P flux, 10^{10} mol P yr^{-1}	Comments
Authigenic apatite formation and burial		
Froelich *et al.* (1982)	<0.4	Based on estimate, from difference between estimated regenerated organic phosphorus and diffusive phosphorus loss in several west African margin cores (deepest core samples from < 9m subbottom depth), that maximum fraction of initial organic phosphorus trapped as apatite is 25% and on estimated organic phosphorus burial flux
Froelich *et al.* (1983), as corrected by Froelich *et al.* (1988)	at least 0.4	Based on interstitial water fluoride uptake in Peru margin cores, extrapolated to global ocean area of organic-rich shelf sediments (deepest core samples from <6m subbottom depth)

Ruttenberg (1993)	9.1	Based on sequential extraction data from two shallow, nonupwelling continental margin cores (deepest core samples from 3m subbottom depth) and from an equatorial Atlantic core (up to 5cm subbottom depth) extrapolated to global ocean.
Filippelli and Delaney (1996)	up to 8 (open ocean);	Based on total phosphorus accumulation rates for past 1 m.y. for various regions (including those for equatorial Pacific sites) and areal extent of different oceanic provinces, assuming 80-90% of total burial at depth is as authigenic phosphorus.
Burial of P with organic carbon -- global estimates		
Froelich *et al.* (1982)	1.45	Organic phosphorus concentration in sediments approximately constant; based on organic carbon burial of 3.58×10^{12} mol C yr^{-1} and assuming Porg / Corg ratio of 4×10^{-3} for typical burial.
Froelich (1984)	1.6	As in Froelich *et al.* (1982), but using larger Corg burial of 4×10^{12} mol C yr^{-1}.
Mach *et al.* (1987)	2.0	Reconsideration of analytical data used in Froelich estimates; based on constant sedimentary Porg/Corg ratio of 2.1×10^{-3} and Corg burial of 10×10^{12}molC yr^{-1}.
Delaney (1998)	1.1	Based on Corg burial of 1.25×10^{12}molC yr^{-1} from Jahnke (1996) and Redfield Porg/Corg of 8.5×10^{-3} from Anderson and Sarmiento (1994); maximum estimate because lower Porg/Corg ratios would result in lower burial flux.
Hydrothermal processes		
high-temperature oceanic crust alteration	0.01	Wheat *et al.* (1996); based on 24% of global convective heat loss in high temperature alteration processes, 76% in low temperature processes.
low-temperature oceanic crust alteration	0.65 (range 0.28-1.16)	

Adsorbed and oxyhydroxide-associated		
Ruttenberg (1993)	5.3	As for authigenic apatite burial estimate.
Delaney (1998)	up to 40% of total reactive phosphorus burial in young sediments(<5Ma); 5-15% of total reactive P burial in older sediments	Based on fraction of total reactive P present as adsorbed plus oxyhydroxide-associated in equatorial Pacific and Atlantic sites.
Calcium carbonate	<0.009	Delaney (1998); based on Holocene calcium carbonate burial flux of 8.6 $\times 10^{12}$molC yr^{-1} from Catubig *et al.* (1998) and on maximum P concentration in foraminiferal calcite from Palmer (1985).

There are a wide range of anthropogenic phosphorus sources to surface water including fertilisers, detergents, animal feeds, metal surface treatments, deflocculants, insecticides, and oil additives (Emsley and Hall, 1976). Some 12.6 Tg/y (Pierrou, 1976) to 15 Tg/y (Froelich *et al.,* 1982) of phosphorus are mined for fertiliser and industrial needs, although probably only part of this actually reaches the oceans (Meybeck and Helmer, 1989). The Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP, 1987) suggested that human activity has increased the riverine phosphorus flux by 50%, which is about 10 Tg/y. Municipal sewage makes a greater contribution to phosphorus pollution than agricultural sources in developed area like Europe, compared to developing area like Asia where agriculture is perhaps the largest factor affecting the movement of phosphorus (Howarth *et al.*, 1995). Howarth *et al.* (1995) estimated the total phosphorus inputs to the ocean prior to agricultural development were probably in the range of 8 to 9 Tg P/y. Some 70% of the total global riverine discharge of sediments (mainly due to agricultural development) is thought to come from south Asia and Oceania (Milliman, 1991). The riverine flux of phosphorus may be substantially transformed in estuaries by the deposition of particles (Lucotte and d'Anglean, 1983; Froelich 1988;

Prastka and Malcolm, 1994; Conley *et al.*, 1995). About 6 to 7 Tg P/y inputs to the ocean are from south Asia and Oceania.

Table 1.4 Summary of reservoir amounts, fluxes and residence times of phosphorus (Jahnke, 1992)

Reservoir	Size (Tg)	Σflux through reservoir (Tg/year)	Residence time τ (years)
Atmosphere	2.8×10^{-2}	4.5	6×10^{-3} (53hours)
Land biota	3.0×10^{3}	63.5	47.2
Land	2.0×10^{5}	88.1-100.1	2.27×10^{3}-2.0×10^{3}
Surface ocean	2.7×10^{3}	1058	2.56
Ocean biota	138	1040	0.13 (48 days)
Deep ocean	8.7×10^{4}	60	1.45×10^{3}
Sediments	4.0×10^{9}	21.4	1.87×10^{8}
Total ocean system	9.0×10^{4}	1.9	4.73×10^{4}

1.2 Phosphorus speciation in the marine environment

Phosphorus can exist in a range of oxidation states from -3 to +5 (PH_3 to P_2O_5) and can form relatively stable chemical bonds to a wide variety of elements. However, the thermodynamic stability of the phosphorus compounds in water is limited and this limitation restricts the biogeochemistry of phosphorus (Williams, 1977; Chameides and Perdue, 1997).

In the oceans phosphorus can be regarded arbitrarily as being partitioned amongst a dissolved inorganic phosphorus (DIP) pool, a dissolved organic phosphorus (DOP) pool, and a particulate total phosphorus pool (PTP) which consists of an inorganic and an organic fraction. The concentrations of DOP in seawater in some specific areas (e.g. lagoons) can be twice the levels of DIP (Smith *et al.*, 1986) but elsewhere the DOP : TDP ratio is lower (e.g.

Southampton Water, see Chapter 3). Evidence has suggested that as DIP is depleted the DOP pool is likely utilised by micro-organisms present in the system (Smith *et al.*, 1986; Ormaza-González and Statham, 1991).

Many phosphorus compounds exist in the terrestrial environment. This study only considers those phosphorus compounds that have been known to, or likely to occur in the aquatic environment, and more importantly the marine environment. The main phosphorus compounds found in the aquatic environment are orthophosphate and pyrophosphate, as well as their cyclic polymers, polyphosphate and their respective organic esters (Cembella *et al.*, 1984). Reduced phosphorus compounds, such as phosphite, are rarely reported in the literature, presumably because they have been overlooked in the reducing environments where they might be expected to play a role in the phosphorus oxidation-reduction cycle in an analogous way to similar compounds in the N and S cycles (Foster *et al.*, 1988). Reduced phosphorus compounds have been recorded in both aerobic and anaerobic situations. Hypophosphite, for example, has been recorded in soil bacteria (Heinen and Lauwers, 1974; Foster *et al.*, 1988). Devai and co-workers (1988) have demonstrated under lab conditions that phosphine is released by bacterial reduction from a medium containing inorganic phosphorus. Phosphine has been detected in the fluvial and marine hydrosphere in the River Elbe and the German Bight , where phosphine in the picomolar range was detected in particles and sediments, but was not detected in water samples (Gassmann, 1994).

Large amounts of the inorganic phosphorus in algae occur as polyphosphates. Solorzano and Strickland (1968) reported appreciable quantities of polyphosphate in waters of red-tide bloom, but they are thought to be present in most unpolluted marine and estuarine waters in variable quantities under normal circumstances. Also the use of polyphosphate in detergents means this can be a potential source of polyphosphate to surface waters (Head, 1985).

In an aquatic system the ratio of individual inorganic phosphorus species present is a function of pH as well as the concentration and relative proportions of cation species, competitive complexing anion ligands, temperature and pressure. Interaction of inorganic phosphorus with metal cations, especially Mg^{2+} and Ca^{2+} can result in complexation and surface adsorption onto inorganic particles. Loss of phosphorus in this way may remove a large part of the biologically available phosphorus pool (Cembella *et al.*, 1984). In seawater (pH 7.0 ~ 8.5) the orthophosphate ions are $[H_2PO_4]^-$, $[HPO_4]^{2-}$, $[PO_4]^{3-}$, with $[HPO_4]^{2-}$ being the dominant form. Orthophosphate ions form metallophosphate complexes and chelates, such that free orthophosphate represents less than half of the total inorganic phosphorus in seawater (Cembella *et al.*, 1984).

There has been little work on the structures of organic phosphorus compounds and more importantly their role in a metabolic sense within biological cycling and recycling. The main organic phosphorus compounds and groups that are known to exist in the aquatic environment are adenosine 5'- monophosphate (AMP), adenosine 5'- diphosphate (ADP), adenosine 5'-triphosphate (ATP), cytidine monophosphate, guasine monophosphate, glycerophosphate, glucose-1-phosphate, glucose-6-phosphate, polyphosphonates, phosphonate and uridine- (3' or 5') -monophosphate (Cembella *et al.*, 1984).

The natural organic derivatives of phosphorus that are present as total dissolved phosphorus (TDP) and particulate total phosphorus (PTP), include the phosphonates, in which carbon of the organic moiety is bound directly to phosphorus rather than through an ester bond (Cembella *et al.*, 1986). Phosphonates have an almost ubiquitous occurrence in algae (Baldwin and Braven, 1968; Kitteredge and Roberts, 1969), protozoa (Kennedy and Thompson, 1970), a wide range of marine invertebrates (Quin, 1965, 1967; Quin and Shelburne, 1969), and marine sediments (Ellery *et al.*, 1990). These types of compounds have also been found in seawater in the dissolved phase (Cembella and Antia, 1986). Dissolved polyphosphonate levels can be as high as 50% of the organic phosphorus pool. Phosphate esters have also been identified as the major form of phosphorus in many marine sediment extracts (Ellery *et al.*, 1990). It has been suggested that polyphosphonates associated with high levels of DOP are an indication that this fraction is derived from zooplankton and phytoplankton excretion, the persistence of both phosphonates and phosphate esters at depth in marine sediments suggests that these compound classes include undegradable forms of organic phosphorus that represent a potentially important sink for phosphorus in the ocean (Ellery *et al.*, 1990). However, large fraction of organic phosphorus is still uncharacterised.

1.3 Phosphorus processes in the marine environment

Phosphorus in natural waters is kept at low concentrations by two processes which remove it, inorganic precipitation of apatite and biological uptake and subsequent sedimentation of organic debris. In the sea precipitation is probably the more important; in lakes the lose via organic debris is possibly the greater (Emsley and Hall, 1976). Estuaries transform both the quantity and composition of nutrients through biogeochemical processes. The riverine flux of phosphorus may be substantially transformed in estuaries by the deposition of particles, and the formation and/or dissolution of phosphorus compounds through both biological and chemical processes. In estuarine and coastal areas, especially where there are high amounts of suspended particulate matter, reversible adsorption/desorption is a major process in the phosphorus cycle. This phenomenon has become known as the 'phosphate buffer mechanism' (Froelich, 1988) and has been suggested as an important process in maintaining the dissolved inorganic phosphorus concentration at fairly constant values (about 1 μM, Froelich, 1988). In estuaries dissolved phosphorus may be removed from solution onto the particulate phase and deposited in the sediments. On the other hand, the change in the solution composition may cause phosphorus to be released from the particulate load and thereby provided a large and potentially available reservoir of reactive phosphorus, for phytoplankton growth.

The phosphorus transported from the estuaries to the ocean in particulate form will rapidly settle to the sea floor and may be released via diagenesis. The dissolved phosphorus will enter the surface ocean and participate in the biological cycles. In the oceanic system, the dominant forms in which phosphorus is removed from seawater appear to be: (1) the burial of organic phosphorus; (2) the burial of phosphorus absorbed onto $CaCO_3$ surface; (3) the formation of apatite in continental margin sediment (Jahnke, 1992; Ruttenberg and Berner, 1993).

One of the dominant themes in estuarine research has been the non-conservative behaviour of dissolved inorganic phosphorus (DIP), especially in reference to the ability of particles to 'buffer' phosphorus concentration (Conley *et al.*, 1995). Phosphorus interacts with particles via essentially abiogenic adsorption and by active biological uptake. The two processes are not entirely separated since almost all particles in the marine environment are coated with an organic coating (Loder and Liss, 1984) which is ultimately derived from biological sources and phosphorus can also adsorb to biological particles. However, for convenience active biological phosphorus cycling has been separated from passive physico-chemical processes in the literature. The latter dominate in inshore systems such as estuaries where light limitation reduces phytoplankton activity (Mombret, 1992) and steep gradients in ionic strength together with high and variable suspended solid concentrations maximise the importance of abiogenic particle water interactions.

The interaction between particle and solution is dependent on the chemical environment. Increasing salinity of a solution, for example, will have two effects on the DIP sorption. At low salinity the sorption will increase as the negative organic coatings on the particles are disrupted. At higher salinity however, specific anions (e.g. Cl^-, SO_4^{2-}, F^-, $B(OH)_4^-$, OH^-) will compete with phosphate for surface sorption sites thereby inhibiting adsorption. The conversion of dissolved phosphorus in water column to PTP has been recorded in the low-salinity regions of many estuarine systems, for example, the Humber (Prastka and Malcolm, 1994; Sanders *et al.*, 1997), the Delaware (Lebo, 1991), the Clyde (Mackay and Leatherland, 1976) and the St Lawrence (Lucotte and d'Anglejan, 1988a) estuaries. Such removal is also evident in the Amazon, although it is reversed at high salinity (Froelich, 1988). Processes which lead to the removal of dissolved phosphorus in water column include flocculation, when colloidal phosphorus will be converted to a particulate form possibly by interaction with colloidal iron (Bale and Morris, 1981). In addition colloidal clay material may flocculate, thus trapping sediment at the freshwater-seawater interface. Also a turbidity maximum can form near the head of the estuary (Postma, 1967) which offers another site for conversion of dissolved phosphorus to particulate forms via adsorption to the high concentrations of suspended sediment.

The effect of pH on sorption is dependent on the substrate onto which the phosphate is sorbed. DIP can adsorb to calcite and hence may be released at low pHs due to calcite dissolution (de Jonge and Villerius, 1989). If the phosphate is sorbed onto clay minerals or metal oxy-hydroxides, an increase in pH would result in decreased sorption and an increase in the bioavailable DIP (Froelich, 1988). On the other hands, the redox state of a system strongly influences the ability of particles to adsorb phosphate (Krom and Berner, 1980; Slomp and van Raaphorst, 1993). Redox is an important control on phosphate sorption as phosphate is strongly associated with iron(III) oxides (Danen-Louwerse, 1993). Phosphate sorbed onto iron(III) oxides during aerobic conditions can be released with the reduction of Fe(III) to Fe(II) under anaerobic conditions (Froelich, 1988; Jensen *et al.,* 1995).

Total dissolved phosphorus reacts readily with a wide variety of surfaces, being taken up by and released from particles through a complex series of sorption reactions “playing hide and seek with both plankton and experimentalist ” (Froelich, 1988). The rates of adsorption process have been investigated recently (e.g. Slomp and van Raaphorst, 1993; van Raaphorst and Kloosterhuis, 1994). The simplest model of DIP adsorption involves the uptake and release of phosphate via a two-step process (Bowden, 1980; Barrow, 1983). The first stage is the adsorption of phosphate ions onto oxy-hydroxides at the surface of the particles which takes minutes to hours. The second process is a diffusive step where the ions move into the interior of the particles, which occurs over weeks to months. As the latter process can take weeks to months to reach equilibrium and in estuaries, where particles are exposed to varying concentrations of DIP over short timescales, sorption will be kinetically controlled and steady-state conditions will seldom be reached (Webster 1975; Elwood *et al.,* 1981).

Human intervention in the phosphorus cycle can alter the processes of phosphorus in estuaries considerably. In many fluvial system today, as a result of human impact, the concentrations of DIP are much higher and the buffer systems are either overwhelmed or shifted to higher steady-state DIP concentrations. Under these conditions, adsorption will be favoured and desorption discouraged. In the Chesapeake and Delaware estuary systems on the east coast of the USA 50-70% of DIP inputs are retained within the sediments of the estuaries (Boynton *et al.,* 1995). Balls (1994) noted that the expression of these various processes is a function of residence time within the estuary. In small estuary systems, there may be insufficient time for the desorption processes to reach steady state. However, this does not imply such desorption will not occur, but rather that it will be postponed to waters further offshore, unless the particulate matter is very rapidly buried and removed from the water column. There is a suggestion that export of particles containing desorbable phosphorus may increase the flux of bioavailable phosphorus 2-5 fold compared to the export of dissolved phosphorus alone (Froelich, 1988; Rao and Berner, 1993). Nixon *et al.* (1997) suggested that residence time is the major factor regulating the retention of phosphorus (and fixed nitrogen) in coastal ecosystems. This control is clearly important in their consideration which extends the definition of estuaries to include large coastal seas such as the Baltic. In such large systems removal of DIP by primary production becomes dominant as in the oceans, and hence residence time increases the likelihood of burial, and hence retention, rather than regeneration (Broecker and Peng, 1982).

The exchange of phosphorus at the sediment-water interface also plays an important role in the regeneration of phosphate (Sundby *et al.*, 1992). Sediments receive a mixture of labile and refractory organic and inorganic phosphorus compounds from the overlying water. Some of these compounds behave as inert material and are simply buried in their original form. Others decompose and release the phosphate to the sediment pore water. The regenerated phosphate may be released to the overlying water, or reprecipitated within the sediment as an authigenic phase, or adsorbed by other constituents of the sediment.

Adsorption on metal oxides (e.g. Fe, Mn) in the sediment has been identified as one of the principal reactions involving phosphate (Krom and Berner, 1981; Froelich, 1988). The redox conditions at the sediment-water interface are of vital importance in determining the release of DIP from sediments to the overlying water. An oxidised surface layer can be a trap for phosphate. In all sediments, the decomposition of organic matter consumes oxygen. At a certain depth manganese oxides and then iron oxides, after exhaustion of oxygen and nitrate will be utilised by the bacteria as oxidising agents. Surface-adsorbed phosphate is released to the pore water as needed to replace dissolved phosphorus that escapes to the overlying water (Sundby *et al.,* 1992). If the sediment surface is anoxic there is no barrier to diffusion of DIP into the overlying water. An oxic layer at the sediment-water interface however, can limit diffusion of DIP by re-oxidising Fe^{2+} to Fe^{3+} and coprecipitation of the DIP. In most intertidal systems and probably other near shore environments an oxic surface layer probably prevents release of large amounts of DIP (Krom and Berner, 1980). Active process such as bioturbation and/or tidal pumping can increase the rate of diffusion of DIP. This will also increase the amount of oxygen in the sediments leading to a thicker oxic zone if the overlying water is oxic. So the rate of transport of the DIP from the porewaters coupled with the rate of adsorption of these ions onto the particles and regeneration of phosphorus from organic particulate phosphorus at the sediment surface will determine the flux of phosphorus from the estuarine sediments (Klump and Martens, 1981). Some estuaries do show fluxes of DIP from the sediments due to low oxygen conditions. These are the Scheldte estuary (Zwolsman, 1994), the Humber (Prastka and Malcolm, 1994) and Narragansett Bay (Boynton *et al.,* 1995). The diffusion of the organic or colloidal forms of phosphorus into the overlying water may also be important but little work has been done on this subject (Williams, 1996).

Phosphorus is removed from the oceans in a variety of forms. These include organic phosphorus compounds (esters, diesters, phospholipids, phosphonates), phosphorus associated with hydrous ferric oxides (Fe-P), authigenic carbonate fluorapatite (francolite), hydroxyapatite of skeletal debris, phosphorus incorporated in $CaCO_3$, and phosphorus adsorbed on other substances such as clay minerals. An idea of the relative abundance of these various forms has been estimated using a sequential phosphorus extraction protocols (SPEPs) (Lucotte and d'Anglejan, 1983; Ruttenberg 1992; Berner *et al.*, 1993). The details will be discussed in Chapter2.

1.4 Phosphorus budgets in coastal and shelf seas, and estuaries (LOICZ biogeochemical model)

The world's coastal zone forms a long narrow boundary between land and ocean that is highly valued by man. The Land-Ocean Interactions in the Coastal Zone (LOICZ) is an international project that is studying this relatively small but highly dynamic and sensitive area. The primary interest of LOICZ is the role of the coastal zone in processing the nutrients elements carbon, nitrogen, and phosphorus, including the fluxes of these elements across the boundaries, their impact on man's activities, and the impact of man on these fluxes. Three spatial scales (local / site-estuaries and mangrove forests; regional--coastal seas; global), defined in terms of linear coastline length, have been identified in the Implementation Plan as being of primary interest to LOCIZ.

An early activity within the LOICZ project has been the development of the *LOICZ Biogeochemical Modelling Guidelines* (Gordon *et al.*, 1996). Four areas were chosen as case studies: East China Sea, North Sea, Peru-Chile Coast, Gulf of Guinea Shelf. The budgeting procedure is to develop a coupled water and salt budget to estimate water exchange. After water exchange is estimated, nutrient budgets are calculated in order to describe the uptake or release of carbon, nitrogen, and phosphorus. Then the uptake or release of these nutrients and simple stoichiometric reasoning surrounding composition of organic matter produced in the system (the local Redfield ratio) is used to calculate net production minus respiration for the system. Further stoichiometric considerations allow estimates of nitrogen fixation minus denitrification and, in some cases, CO_2 gas flux, calcium carbonate reactions, and sulphate reduction.

At steady state, a simple box model describes salt flux in the LOICZ biogeochemical model:

$$V_{syst} \times dS_{syst}/dt = 0 = V_Q S_Q - V_R S_{syst} + V_x (S_{ocn} - S_{syst}) \qquad (1)$$

where V_Q is freshwater delivery from runoff (m^3/s); V_R is the residual flow into the system (m^3/s); V_x is a mixing volume which exchanges estuary and ocean water but does not affect net flow (m^3/s); S_{syst} ,$S_{Q,}$ $S_{ocn,}$ are the salinities in the system, in the runoff and in the adjacent ocean. Equation (1) represents a salt balance for the system. Materials which are not conservative with respect to water and salt can be assumed to be represented by the same hydrographic inputs and outputs as govern the water and salt. Thus, the equation (1) can be applied to other dissolved materials (equation (2)).

$$V_{syst} \times dY_{syst}/dt = 0 = V_Q Y_Q - V_R Y_{syst} + V_x (Y_{ocn} - Y_{syst}) + \Delta Y \qquad (2)$$

Y is the concentration of any dissolved material (μM) which has a source (+) or sink (-) in the system. The ratio of C:P in the particulate material $(C:P)_{part}$, multiplied by the nonconservative flux of DIP (ΔDIP), gives an estimate of net metabolism (ρ-γ).

$$-\Delta DIP \times (C:P)_{part} = (\rho - \gamma) \qquad (3)$$

Assuming that the N:P ratio of particulate material $(N:P)_{part}$ in the system is known, the dissolved nitrogen flux associated with production and decomposition of particulate material is the dissolved phosphorus flux ($\Delta P = \Delta DIP + \Delta DOP$) multiplied by $(N:P)_{part}$. It follows, that (nfix - denit) is the difference between the measured dissolved nitrogen flux ($\Delta N = \Delta NO_3 + \Delta NH_4 + \Delta DON$) and that expected from production and decomposition of organic matter:

$$(\text{nfix - denit}) = \Delta N - \Delta P \times (N{:}P)_{\text{part}} \qquad (4)$$

(nfix - denit) represents the net sum of nitrogen fixation, where *nfix* represents the flux of nitrogen fixation and *denit* is the flux of denitrification.

More details of the equations can be found in LOICZ reports & studies No. 5 (1996).

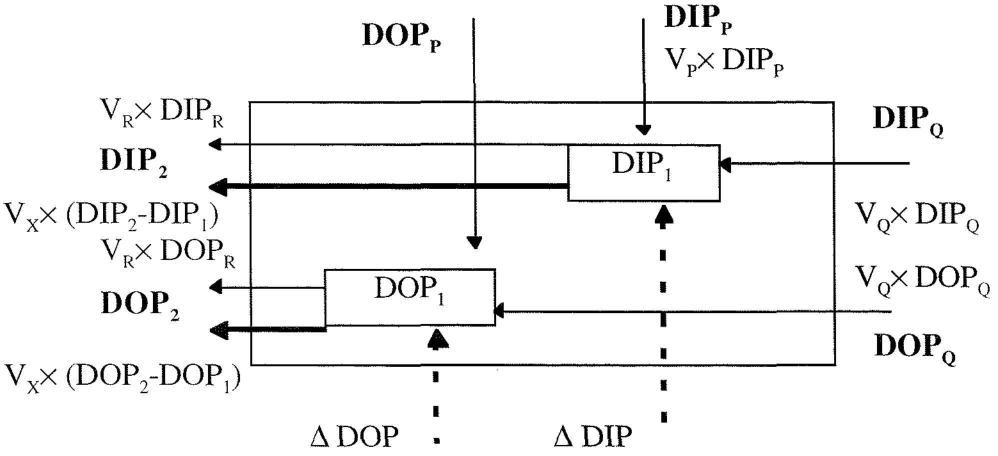


Figure1.2. Generalised box diagram illustrating the budget for phosphorus in LOICZ model

Nutrient regional budget calculations using the LOCIZ model can be useful for the management of coastal and estuarine ecosystems, but they only describe a static nutrient situation in the area. Budget and empirical relationships can be merged into dynamic simulation (Gordon *et al.,* 1996). The question is how will the nutrient budget of a coastal system be affected by environmental change, e.g. climate and nutrients load. What are the minimum key processes that have to be included in the model (e.g. DIP adsorption to the particles and subsequent burial)? How big will the error be if we use the Redfield ratio of C:N:P as 106:16:1 which is recommended by Smith (1996) instead of local ratio of C:N:P ?

1.5 The study area

The Southampton Water system is a good site for the studies of nutrient biogeochemistry because it is a representative macrotidal partially mixed estuary and has both natural and authropoganic nutrient inputs. Some limited earlier studies (See Chapter 3 and Chapter 4) are helpful to set the scene. The Solent area has also been one of the selected sites for LOICZ modelling, although the data base and the biogeochemical processes understanding for this modelling are currently limited. Additionally geographically it is very convenient with ready access using the School of Ocean and Earth Science boat, and adjacent laboratory.

The Southampton Water system consists of Southampton Water, the Test Estuary and Itchen Estuary. This study is mainly focused on Southampton Water and the River Itchen. Southampton Water (from Dockhead to Calshot Buoy) is a drowned river valley about 10 km long and 2 km wide, forming a north westerly extension of the central Solent. It is the site of the UK largest oil refinery with smaller satellite industries and one of the UK's major ports. This is also a popular recreational area for sailing and fishing.

Southampton Water is fed by two main rivers, the River Test and the River Itchen, which have a combined average annual discharge equivalent to 1.54×10^6 m^3/day (Hydes and Wright, 1999). The river input is small in comparison with its volume with 5.4×10^8 m^3 at high water and 2.7×10^8 m^3 at low water (Blain, 1980). The estuary was described as "partially mixed" and "macrotidal" by Dyer (1970). The maximum tidal range is about 4.5 m, and the tidal excursion is 2.5 km. In addition to the river flow, the Southampton Water system receives a consented sewage discharge of about 0.1×10^6 m^3/day directly from Southampton's population of 400000. Sewage outfall can contribute up to 25% of the total flow during periods of low river discharge (Hydes and Wright, 1999). Salinities in the main body of Southampton Water vary between 30 and 34. At high water there is little stratification but at low water the vertical salinity difference, surface to bottom, at the seaward end ranges from 0.5 to 2.3 (Soulsby, 1981).

1.6 Objectives

The objectives of this study are aimed at improving the understanding of the Southampton Water biogeochemical system with respect to the role of phosphorus. Earlier studies in the Southampton Water system have revealed that a significant number of different processes determine the distribution of dissolved inorganic phosphorus in this urbanised ecosystem. The main target of this research is to produce a budget for phosphorus flows through the system by quantifying the different pathways of supply and removal.

The construction of the biogeochemical budget of an element requires information on all important reservoirs and their seasonal variations. Information on processes that result in mass transport between reservoirs is also needed. To understand the phosphorus biogeochemical cycle in estuarine and coastal areas a range of reservoirs of phosphorus (DIP, DOP, PTP, phosphorus in sediments) must be quantified. The SONUS project (Hydes and Wright, 1999) has supplied a good dataset of the measurements of nutrients in the water column in the Southampton Water system, but the sizes of many other reservoirs of phosphorus (including DOP, PTP and phosphorus in deposited sediments) have not been quantified, or have rarely been looked at at the same time. The forms of phosphorus in the solid phase in the sediments (suspended and deposited) have not been looked at at all. In this study, the reservoirs are quantified and the seasonal variations of the reservoirs are monitored. The forms of phosphorus in the sediments (suspended and deposited) are measured.

Phosphorus is involved in many biogeochemical processes (photosynthesis and respiration; adsorption and desorption; burial and resuspension) in estuarine and coastal area. The study of the phosphorus transport between reservoirs (different phases and different forms) and their rates is essential. Research to date illustrates the important role of suspended particles and depositional sediment in the phosphorus biogeochemical cycle in estuarine and coastal areas. The processes determining the concentration of bioavailable phosphorus in the Southampton Water system are poorly understood and quantified (see Section 4.1). Recent study in the

Southampton Water system (Hydes and Wright, 1999) suggested that the exchange of phosphorus between suspended particles and solution is apparently not significant (i.e. no "buffering" observed) in the Southampton Water system compared to other estuaries. The benthic process is another important process which has not been highlighted and quantified in the Southampton Water system must be identified and quantified. The study on phosphorus in sediments is to be done not only to estimate the benthic fluxes but also to identify and quantify the distribution of the different forms of phosphorus within the sediments.

In summary, the main objectives of this work are:

1. to quantify and monitor the reservoirs of phosphorus in the Southampton Water system during an annual cycle.
2. to identify and quantify the biogeochemical processes of phosphorus leading to exchanges between the major reservoirs in the Southampton Water system.
3. to produce a biogeochemical budget of phosphorus in the Southampton Water system based on the studies of 1 and 2.

Specific tasks to achieve the objectives of this research are:

1. The measurement of phosphorus reservoirs (DIP, DOP and PTP) in the estuary. The size of the phosphorus reservoirs in the water column are calculated from the concentrations and the volume of water mass. The distribution of phosphorus species in suspended particulate matter and deposited sediments are determined at a series of stations along the estuary.
2. The benthic fluxes of phosphorus are calculated from the porewater phosphorus data using the empirical equation of Ullman and Aller (1987) and the calculations are compared with the direct measurements from sediment incubation experiments.
3. A selective sequential phosphorus extraction protocols (SPEPs) is used to identify and quantify the chemical forms of phosphorus in suspended particulate matter and deposited sediments in the system. The results from SPEPs are used to supply information on sediments as the potential phosphorus reservoirs in the system and to understand the exchange of phosphorus between the water and solid phase.

4. The K_d (K_d = DIP / PTP) model (Prastka, *et al.*, 1998) is applied to the survey data to interpret and rationalise the DIP behaviour in the system. The validity of the application of the model is discussed.
5. A conceptional budget of phosphorus in the Southampton Water system is produced. The budget uses the present phosphorus inputs and accounts for the different pathways and reservoirs of phosphorus in the system. The internal cycling of phosphorus between the reservoirs is also considered. The budget is compared to the budget of phosphorus in Chesapeake Bay. The budget is also compared with the result using LOCIZ model on the same dataset. The validity of the LOCIZ model is then discussed.

Chapter 2: Overview of analytical methods for the determination of phosphorus in marine waters and sediments

2.1 Introduction

In the marine environment detectable phosphorus compounds are grouped into three broad bands by different analytical procedures: Dissolved Inorganic Phosphorus (DIP), Dissolved Organic Phosphorus (DOP), and Particulate Total Phosphorus (PTP). The dissolved fraction of phosphorus can consist of compounds such as orthophosphate, inositol phosphates, nucleic acids, sugar phosphates and condensed phosphates (Thurman and Malcoln, 1983). The analytical differentiation amongst the groups is usually based upon the reactivity with molybdate, ease of hydrolysis, and particle size (Strickland and Parsons, 1972).

Two of the most frequently determined forms of dissolved phosphorus are soluble reactive phosphorus (SRP) and total dissolved phosphorus (TDP). Operationally, SRP is defined as that portion of the dissolved phosphorus which will react to produce phosphomolybdenum blue, and consists of orthophosphate and organic phosphorus which are easily hydrolysed. As the latter fraction is normally small, DIP will be used instead of SRP in this study although the difference must always be kept in mind. The TDP includes the SRP fraction and unreactive forms of phosphorus that must be subjected to rigorous hydrolysis and oxidation prior to determination by the formation of phosphomolybdate and subsequent spectrophotometic analysis.

This chapter reviews the available analytical procedures of phosphorus and indicates which are used in this study and why it is used.

2.2 The determination of Dissolved Inorganic Phosphorus (DIP)

There are many methods for the analysis of DIP, which are based on different techniques such as spectrophotometry, fluorometry, atomic absorption spectrometry, and enzymatic analysis (Kimerie and Rorie, 1973; Burton, 1973; Kubota *et al.*, 1988). Amongst the methods the phosphomolybdenum blue spectrophotometric technique is the most popular method due to its ease of use, limited interference, good precision and detection limits and its adaptability to both manual and automated systems (Murphy and Riley, 1962; Mee, 1986). The determination (normally named as Murphy and Riley method) is carried out by treating an aliquot of seawater with an acidic molybdate reagent containing ascorbic acid and a small amount of potassium antimonyl tartrate. The resulting phosphomolybdic acid is reduced to give a blue-purple complex. The complex is then analysed spectrophotometrically. The Murphy and Riley method has been modified many times (Strickland and Parsons, 1972; Johnson, 1979; Koroleff, 1983). A recent re-investigation of this method carried out by Pai *et al.* (1990) confirmed the suitability of the method and revealed that the acid / molybdenum ratio in the Murphy and Riley method is crucial, influencing not only the composition of the final reduced complex, but also playing an important role in the reaction kinetics. Kirkwood *et al.* (1991) included a survey of phosphate methodology and warned that any arbitrary changes to the Murphy and Riley method may cause substantial divergence from the expected behaviour of the method.

In this study, the DIP analyses were performed on a segmented continuous flow analyser (Mee, 1986) linked to a Digital-Analysis Microstream data capture and reduction system. The samples were measured using a Burkard Scientific SFA-2 Auto-analyser (See Appendix A), which is based on the traditional spectrophotometric method of Murphy and Riley (1962). The details of the determination of DIP can be found in Chapter 3.

2.3 The determinations of Total Dissolved Phosphorus (TDP) and Dissolved Organic Phosphorus (DOP)

The measurement of total dissolved phosphorus in seawater is normally based on the oxidative liberation of the organically bound and other forms of phosphorus and subsequent analysis of the phosphate by the method of Murphy and Riley (1962). A common drawback for all these methods is the estimation of organic phosphorus by difference between TDP and DIP fractions in a single sample. Liberation of the organically bound phosphorus and other forms of phosphorus has been carried out by a variety of methods, including sulphuric acid (Harvey, 1948) and perchloric acid digestion (Hansen and Robinson, 1953), persulphate oxidation (Menzel and Corwin, 1965), UV irradiation (Armstrong and Tibbits, 1968) and dry combustion (Solorzano and Sharp, 1980). The most commonly used methods are acid-base extraction or ignition. Anderson (1976) and Olsen and Sommers (1982) summarised the advantages and disadvantages of both methods. The ignition method is simpler, less tedious and more precise, but the acid-base extraction is more accurate.

Ridal (1992) compared different oxidation-hydrolysis methods for TDP analyses. The methods included UV irradiation, acid persulphate digestion, and a rigorous method that combined the UV and persulphate treatment (combination method). It was found that the UV irradiation and autoclaving times commonly used with the standard methods did not fully release the dissolved organic phosphorus in the open ocean surface seawater samples (Ridal and Moore, 1990). Recently Ormaza-Gonzalez and Statham (1996) reported a comprehensive comparison of five decomposition methods used for the determination of TDP. The five decomposition methods were: (1) Magnesium nitrate high-temperature oxidation (Cembella *et al.*, 1986); (2) Magnesium persulphate high-temperature oxidation (Solorzano and Sharp, 1980); (3) Acidified potassium persulphate with autoclaving (Koroleff, 1983); (4) Basic potassium persulphate with autoclaving (Valderrama, 1981); (5) Ultraviolet oxidation (Armstrong *et al.*, 1966). Overall, the magnesium nitrate method was recommended as the best technique by the authors on the basis of high recoveries for a range of organic phosphorus compounds, and concentrations in natural water samples. The magnesium nitrate method described as one of the "Ash/Hydrol method" was also recommended by Monaghan and Ruttenberg (1999) for routine

TDP analyses. They found no phosphorus loss due to volatilisation in seawater samples, which was mentioned by Ormaza-Gonzalez and Statham (1996).

A gas chromatographic, hydride generation method was introduced by Hashimoto *et al.* (1987), but this method used complicated equipment, and comparability with conventional methods is not obvious. A rapid in-line photochemical digestion for use with flow injection (FI) was also introduced by Mckelvie *et al.* (1989) in order to enable a rapid determination of TDP in natural waters, but this method appears likely to have restricted decomposition efficiency as indicated for UV methods above. A method based on ultraviolet oxidation under successive acid and alkaline conditions and using continuous-flow techniques was also described by Collos and Mornet (1993), but poor recoveries were obtained.

Some methods have been designed for specific organic phosphorus groups. A method was presented by Cembella and Antia (1986) for the determination of phosphonates, which are organic phosphorus compounds in which the phosphorus is bound directly to carbon of the organic moiety. It takes advantage of their chemically strong carbon-phosphorus bond being resistant to phosphatase action and acid hydrolysis. Phosphatase-hydrolyzable phosphorus has potential use as an indicator of bioavailability of dissolved phosphorus other than orthophosphate in natural waters. Methods for determining enzymatically hydrolyzable phosphate in natural waters were also introduced by Chrost *et al.* (1986) and Shan *et al.* (1994).

On the basis of efficiency of decomposition of organic phosphorus compounds (92 ± 7%)(Ormaza-Gonzalez and Statham, 1996), the concentrations of TDP are measured in this study using the magnesium nitrate high-temperature oxidation method (Cembella *et al.*, 1986) as developed and evaluated by Ormaza-Gonzalez (1990). The sample are dried and heated with $Mg(NO_3)_2$, prior to hydrolysis with HCl. After the oxidation step, HCl is added to hydrolyse the sample prior to the subsequent colormetric determination step. Details of the determination for TDP and DOP in this study are described in Chapter 3.

2.4 The determinations of phosphorus in bottom sediments and suspended sediment (PTP)

The determination of phosphorus in sediments is usually a two-step procedure including the determination of total phosphorus, and inorganic phosphorus before calculating "organic" phosphorus by the difference (Aspila *et al.,* 1976; Ruttenberg and Berner, 1993). In all instances the concentrations in leaching or digest solutions are determined as orthophosphate by using manual or automated systems based on the traditional Murphy and Riley (1962) spectrophotomatric method.

The determination of the concentration of total phosphorus in sediment usually involves a strong acid / oxidant attack, such as digestion by $HClO_4$, HF-HNO_3, H_2SO_4 / $K_2S_2O_8$, dry ashing / HCl-digestion, or Na_2CO_3 fusion (Olsen and Dean, 1965; Aspila *et al.* 1976; Agemian 1997). Amongst these methods, fusion with sodium carbonate and digestion with perchloric acid were the two most used methods. For most sediments these two methods give similar results (Jackson, 1958). Olsen and Dean (1965) recommended digestion by $HClO_4$. Since the $HClO_4$ method gave low results on strongly weathered samples Syer *et al.* (1968) preferred Na_2CO_3 fusion. Sommers and Nelson (1972) found digestion by $HClO_4$ underestimated the concentrations of total phosphorus by 1% to 6% compared to Na_2CO_3 fusion. The digestion using HF-HNO_3 was rejected by Aspila *et al.* (1976) because of the need of special handling and the potential hazards involved. The digestion using H_2SO_4-$K_2S_2O_8$ has been recommended to determine the concentrations of total phosphorus in aquatic sediments (Fishman and Friedman, 1989). Aspila *et al.* (1976) used the digestion with H_2SO_4-$K_2S_2O_8$ at 135°C in a sealed PTFE-lined Parr bomb to measure the total concentrations of phosphorus in lake and river sediments, and suggested it is a practical method when only a few samples are to be analysed. It is not convenient for routine measurements.

The safe and simple ignition, or dry ashing method to destroy organic phosphorus followed by digestion in HCl (1M) for 16 hour has been used to successfully determine the concentrations of total phosphorus in sediments (Anderson, 1976; Aspila *et al.* 1976). It was found that this method gave a close estimation of the concentration of total phosphorus in the sediments, and the results were comparable with the H_2SO_4-$K_2S_2O_8$ digestion method. This method is more applicable to large numbers of samples.

The determination of "inorganic" phosphorus in sediment is done by extraction of the unashed dry sediment with HCl (1M) for 16 hour (Aspila *et al.,* 1976). The C-P bonds are resistant to 1M HCl extraction (Cembella and Antia, 1986), as are the C-O-P bonds in phosphate esters (adenosine monophosphate and ribonucleic acid). Thus, the inorganic fraction measured here does not included most organic phosphorus compounds. Nucleotide diphosphates and triphosphates partially react with weak acids and therefore will be partially included in the inorganic fraction (Liebezeit, 1991). An alternative method using 0.5 M sulphuric acid for the extraction has been reported by Wildung *et al.* (1974). The concentration of organic phosphorus (Aspila *et al.*, 1976) is calculated as the difference between total phosphorus (ashing +1M HCl) and inorganic phosphorus (1M HCl). Another approach to estimate the concentration of organic phosphorus is by the difference between the results obtained by extraction with $HClO_4$ for total phosphorus and consecutive HCl and NaOH extraction for organic phosphorus (Sommers *et al.* 1970). An alternate method involves removing inorganic iron- and calcium- bound phosphorus with Ca-nitrilotriacetic acid / dithinoite and Na-ethylenediaminetetraacetic acid, with subsequent fractionation of the organic phosphorus into acid-soluble organic phosphorus, residual organic phosphorus, and humic and fulvic acids by sequential extraction with HCl (0.5M), NaOH (2M), and concentrated H_2SO_4, respectively (De Groot and Golterman, 1990).

The Aspila *et al.* (1976) method has been shown to be as a simple, safe approach to measure the total phosphorus and inorganic phosphorus in marine sediments (Prastka and Jickells, 1995), and it is the approach chosen in this study to measure the inorganic and organic phosphorus in the bottom sediments. Details of the method can be found in Chapter 5.

Phosphorus in suspended sediments (particulate total phosphorus, PTP) can be estimated directly or indirectly. An indirect estimate can be given by measuring the total phosphorus (TP) concentration of an unfiltered, and a filtered sub-sample of water; the difference between these measurements is estimated as PTP. A direct measure is given by digesting the particulate matter which has been collected onto a filter, and then analysing the phosphorus content of the resulting solution by spectrophotometric technique based on the phosphor-molybdenum blue method of Murphy and Riley (1962). Extraction methods for the determination of the concentration of total phosphorus in suspended sediments are similar to the methods used to measure total phosphorus in the bottom sediments. Ormaza-Gonzalez and Statham (1996) compared different methods for the determination of phosphorus in suspended sediment (PTP). Magnesium nitrate high-temperature oxidation method reported by Cembella *et al.* (1986) was recommended as the method to determine the concentration of PTP. The magnesium nitrate high-temperature oxidation method is simple and promising (Ormaza-Gonzalez and Statham, 1996). It was operated by the same mechanism: dry ashing/ oxidation with post-ashing acid hydrolysis. The time required for the magnesium nitrate high-temperature oxidation method (3 hours) is more economic than Aspila's method (1976) (24 hours). The measurement for PTP in this study is routine and in high frequency. Hence, the magnesium nitrate high-temperature oxidation method modified by Ormaza-Gonzalez (1990) is used to determine the concentrations of PTP in this study. Details of the method are shown in Chapter 3.

2.5 Sequential Phosphorus Extraction Protocols (SPEPs) for different forms of solid phase phosphorus

In order to understand the processes of influencing the distribution of phosphorus between water and sediments (suspended and bottom), it is necessary to identify and quantify the different forms of solid phase phosphorus (suspended and deposited) in the estuary. There are four approaches to determining the identity and size of sedimentary phosphorus reservoirs.

1. Use of observed correlation or anticorrelation between total phosphorus (TP) and mineral components or major element chemistry of bulk sediment (Baturin, 1988).
2. Physical separation of different sedimentary fractions, usually by grain size, and measurement of total phosphorus in the different fractions (Froelich *et al.*, 1982).
3. Use pore-water profiles to infer the nature of chemical reaction occurring in the sediments. (Gaudette and Lyons, 1980).
4. Active chemical investigation of the phosphorus contents -----SPEPs method (e.g., Williams *et al.*, 1971; de Lange, 1992; Ruttenberg, 1992; Agemian, 1997).

Numerous different extraction schemes have been developed for soil science and limnological studies since the 1950's (e.g. Chang and Jackson, 1957; Syers *et al.*, 1973; Hieltjes and Lijklema, 1980) to differentiate mainly between calcium phosphate, iron phosphate, reductant soluble phosphate and organic phosphorus. SPEPs method defines the phosphorus fractions on the basis of reactivity of a particular phase in a given extractant, and hence quantify the various phosphorus reservoirs in marine sediments (Ruttenberg, 1992). SPEPs are regularly used in the study of lakes, rivers, and soils (Williams *et al.* , 1976; Lucotte and d'Anglejan, 1985), modified schemes have been applied to marine sediment by many scientists (e.g. Balzer, 1986; Ruttenberg, 1992; Jensen and Thamdrup, 1993). A SPEPs method (the SEDEX method, Ruttenberg, 1992) consists of five steps which separate the major reservoirs of sedimentary phosphorus into five pools: loosely sorbed or exchangeable phosphorus; ferric Fe-bound phosphorus; authigenic carbonate fluorapatite + biogenic apatite + $CaCO_3$-associated phosphorus; detrial apatite phosphorus of igneous or metamorphic origin; and organic phosphorus. The SEDEX technique is capable of measuring concentrations as low as 1/20 of the average abundance of phosphorus when 0.5 g sediment samples are measured (Ruttenberg, 1992).

The series of papers published by Ruttenberg (1990, 1992) and Ruttenberg and Berner(1993) have focused on the method development and its application in continental margin sediments. The generalised sequential extraction scheme is shown as Figure 2.1. Details of SPEPs (the modified SEDEX scheme used in this study) are given in Section 4.3.2 and Section 5.2.4.

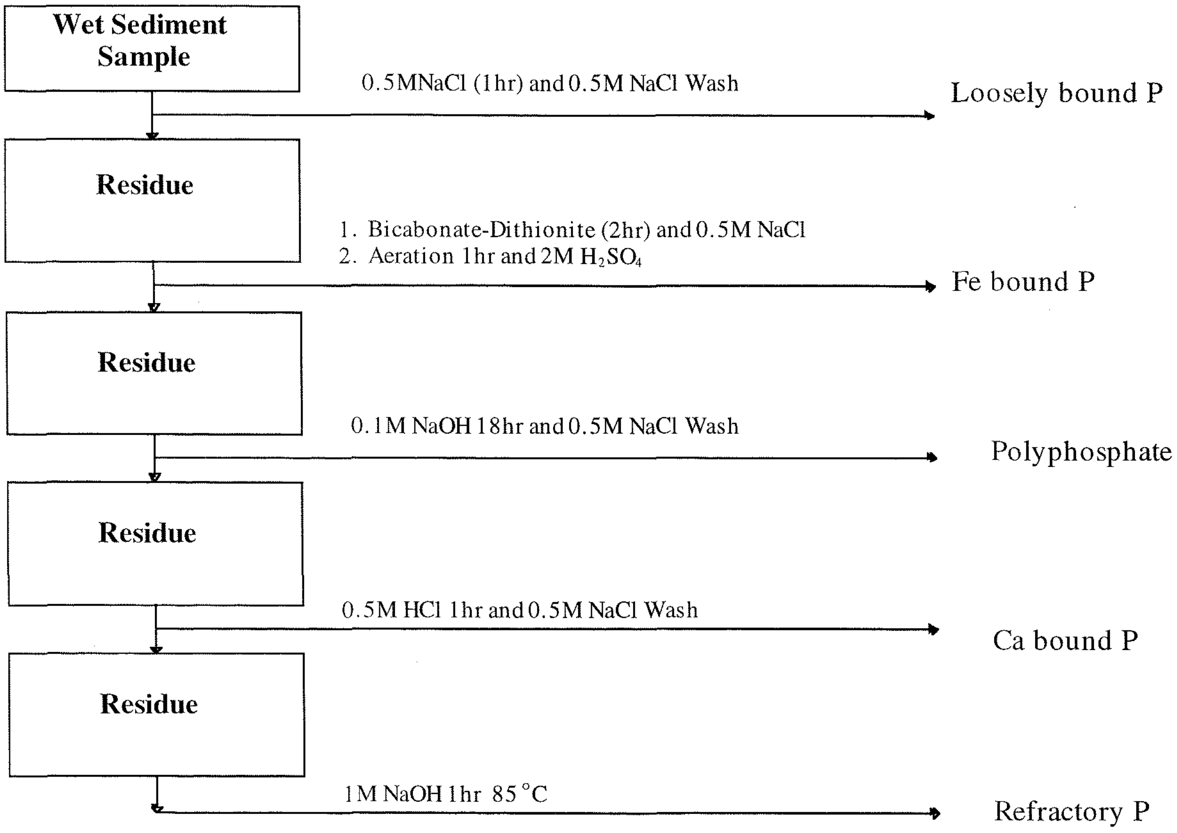


Figure 2.1 Flow chart for the fractionation of phosphorus species in marine sediments

Chapter 3: Study of water column phosphorus in the Southampton Water system: sampling, analysis and results

3.1 Introduction

Dissolved inorganic nutrients (DIN, DIP, Si) in the water column are taken up into biological material during the growth of micro and macro algae in estuaries, when light levels are high enough for photosynthesis to occur (Redfield, 1958). Monitoring the spatial and seasonal distributions of dissolved nutrients in the water column is essential to describing the context of nutrient biogeochemical cycles within an estuary, and subsequently to revealing any relationship between high inputs of nutrients to the system and hypernutriphication and eutrophication phenomena in a system. Dissolved nutrients have been monitored in the Southampton Water system since the 1970s. Since the establishment of the National River Authorities (NRA) in 1974, data for the concentrations of nutrients in the Southampton Water system, which includes the Test Estuary and the Itchen Estuary, has been collected systematically through the Harmonised Monitoring Scheme (Hydes and Wright, 1999). Some individual surveys have also been carried out in the Southampton Water system (e.g. Collins, 1978; Ormaza-Gonzalez, 1990; Kifle and Purdie, 1993; Williams, 1996). In 1997 the Southern Nutrient Study (SONUS) project finished a systematic two-year long nutrient field study in the Southampton Water system. The data set from the SONUS project consists of twenty four monthly surveys of dissolved inorganic nutrients. As less dissolved organic phosphorus and particulate phosphorus measurements were made this part of the dataset is incomplete. In order to update and extend the SONUS database over a longer period of time, and to obtain a more complete dataset for phosphorus species through a complete annual cycle, the research described here was carried out on a monthly basis for sixteen months from January 1998 to April 1999.

The main focus of this study is the biogeochemical cycle of phosphorus in the Southampton Water system. The River Itchen contributes more phosphorus to the Southampton Water system than other tributaries of Southampton Water (Hydes and Wright, 1999). Hence, the surveys of this study were only carried out in Southampton Water and the River Itchen. Data for the River Test was taken from the SONUS dataset when it was needed. The sampling strategy was designed to collect samples under consistent hydrodynamic conditions. The sampling periods were chosen to coincide with the spring tide in each month. In order to diagnose the nutrient status of the water column during the phytoplankton - bloom season, and the impact of changing intensity of the tidal flows to the nutrient cycles, four neap tide surveys were added in April, May, June of 1998 and April of 1999.

Table 3.1 Location of the sampling stations

Name	Area	location
Calshot Buoy	SW	50.48N 117.04W
Calshot Castle	SW	50.49N 118.53W
Fawley Power Station	SW	50.49N 118.8W
Hamble Point	SW	50.50N 118.67W
BP Jetty	SW	50.50N 119.58W
Greenland Buoy	SW	50.50N 120.39W
Hound Buoy	SW	50.50N 121W
NW Netley Buoy	SW	50.52N 122.7W
Weston Shelf Buoy	SW	50.52N 123.25W
Dockhead	SW	50.52N 123.24W
Itchen Bridge	RI	50.53N 123.04W
Shamrock Quay	RI	50.54N 123.02W
Oil Spill Centre	RI	50.54N 123W
Northam Bridge	RI	50.55N 122.09W
St Denys	RI	50.55N 122.8W
Itchen Rail Bridge	RI	50.55N 122.76W
Cobden Bridge	RI	50.54N 122.75W
Portswood Sewage Discharge	RI	50.53N 122.77W
Rowing Hard	RI	50.53N 122.76W
Woodmill Lane	RI	50.53N 122.69W

* SW: Southampton Water; RI: the Itchen Estuary

The sampling stations were located along the main channel of the Itchen Estuary and Southampton Water at intervals of 0.5~1.0 km (Table 3.1 and Appendix B). The samples were all collected within one day. The sampling dates are shown in Table 3.2.

The whole database for the water column in this study included:

- 590 salinity and temperature measurements;
- 590 nitrate + nitrite, phosphate, silicate analyses;
- 590 dissolved organic phosphorus analyses;
- 550 chlorophyll *a* analyses;
- 321 suspended particle matter analyses;
- 321 particulate phosphorus analyses.

Table 3.2 Dates of the surveys

Survey	Date	Tide
S1	16/1/98	Spring
S2	26/2/98	Spring
S3	30/3/98	Spring
S4	21/4/98	Neap
S5	28/4/98	Spring
S6	12/5/98	Spring
S7	19/5/98	Neap
S8	5/6/98	Neap
S9	12/6/98	Spring
S10	23/7/98	Spring
S11	12/8/98	Spring
S12	24/9/98	Spring
S13	21/10/98	Spring
S14	2/12/98	Spring
S15	19/1/99	Spring
S16	16/2/99	Spring
S17	19/3/99	Spring
S18	27/4/99	Neap

Table 3.3 Summary of the measurements made during the surveys

Survey	DIP	DOP	PTP	DIN	Si	SPM	Chl *a*	O_2	Temp	Sal
S1	√	√	√	√	√	√	√	√	√	√
S2	√	√	√	√	√	√	√	√	√	√
S3	√	√	√	√	√	√	√		√	√
S4	√	√	√	√	√	√	√		√	√
S5	√	√	√	√	√	√	√		√	√
S6	√	√	√	√	√	√	√	√	√	√
S7	√	√	√	√	√	√		√	√	√
S8	√	√	√	√	√	√	√	√	√	√
S9	√	√	√	√	√	√	√	√	√	√
S10	√	√	√	√	√	√	√	√	√	√
S11	√	√	√	√	√	√	√	√	√	√
S12	√	√	√	√	√	√	√	√	√	√
S13	√	√	√	√	√	√	√	√	√	√
S14	√	√	√	√	√	√	√	√	√	√
S15	√	√	√	√	√	√	√	√	√	√
S16	√	√	√	√	√	√	√		√	√
S17	√	√	√	√	√	√	√	√	√	√
S18	√	√	√	√	√	√	√		√	√

* Temp: surface water temperature; Sal: salinity of the water samples.

3.2 Sampling and storage procedures

Water samples were collected in Southampton Water and the Itchen Estuary from the School of Ocean and Earth Science research vessel *Bill Conway*. Surface water samples were collected via a bucket that was fed by the launch's deck wash. The intake for the deck wash is at approximately 1m depth. Bottom water samples about 1m above the bed of the estuary were collected using a 5-litre conventional Niskin water sampler. The salinity of the surface water samples was measured by an independent salinometer (model WTW L320) in the bucket and the salinity of bottom water samples was measured by the same salinometer after subsampling the sample in a container. All salinity measurements were completed on the boat just after water sampling.

The filter used for the filtering of samples for nutrient analyses is important, especially for the PTP analysis. Ormaza-Gonzalez (1990) compared different filter materials and concluded that the most suitable material is glass fibre. Compared to other materials glass fibre has a higher flow rate and can be subjected to high suspended particle loads and has no detrimental effects on the chemistry of colour formation for the phosphorus analysis. Hence, the GF/F (nominal cut-off 0.7 μm) glass fibre filter was used through all the nutrient filtration in this study. The water samples for dissolved nutrients analysis were filtered via a plastic syringe and a GF/F filter (Whatman) of 25 mm diameter held in a "Swinex" unit, into a new 30 ml polystyrene "diluvial". Each receptacle for water samples was washed three times with filtered sample before filling. Separate water samples were taken for inorganic and total dissolved - phase analysis.

The glass fibre filters for particle analyses were prepared by heating at 500 °C for 2 hours in a muffle furnace and were individually weighed before the cruises. The filters were placed in a marked clean plastic Petric dish. The filters were rinsed with ultrapure water just after the filtration to minimise the interference caused by the salt in the water. Filtration for particle analyse was done under low vacuum (< 200 mm Hg) through GF/F filter (Whatman) of 47 mm diameter as suggested by Ormaza-Gonzalez (1990). The volume of water (250~500 ml) to be filtered at each station was depended on the suspended load of the samples at the station.

The type of storage vessel used for the nutrient samples must be carefully considered (Williams, 1996), due to the potential for phosphate adsorption on the plastic surface, and silica dissolving from the walls of glass bottles. However, the data from Hydes and Wright (1999) indicated that for phosphate and nitrate analyses, there is little difference between glass and plastic stored samples, while dissolved silicon did show a distinct difference between glass and plastic storage vessels. Hence, virgin polystyrene containers ("diluvals") were used to collect water samples throughout the cruises. The new clean "diluvals" were only used and washed by the sample three times before filling.

No single universal preservation method for nutrients has been reported in the literature as being suitable for all types of aquatic waters, although filtration prior to storage and either rapid freezing or addition of a chemical preservative appears to be the preferred method (Williams, 1996). Although mercuric chloride was suggested by Williams (1996) as a very effective chemical preservative for phosphorus compounds, due to its impact on the sensitivity of the cadmium column in nitrate analysis and serious health risks, this preservative was not applied in this study. Dissolved inorganic nutrient samples were analysed immediately after the cruise (normally on the same day) without adding any chemical preservative. It has been reported that freezing can lead to the precipitation of forms of dissolved silicon, which may be recovered only by slow thawing (Dore *et al.,* 1996). Hence water samples were kept in the refrigerator without freezing before the measurement were carried out. The total dissolved phosphorus and particle-bound phosphorus analyses were carried out later the same day or one day after the survey, and freezing was not used. The filter papers with particle samples were placed in a dissicator individually and dried in an oven at 80 °C for twenty four hours immediately after the cruise. The filters were weighed one day after the cruise.

3.3 Methods

The rationale behind the choice of methods used here is given in Chapter 2. Precision of the analytical methods for DIP, DOP and PTP has been assessed on the basis of the variation between replicate measurements of individual samples, and by the comparison with the historical data. The differences between duplicate measurements averaged 1.6%, 1.8% and 2.0% for DIP, DOP and PTP.

Accuracy of the measurements should be carried out by measuring with respect to the reference standards. There is no reference standards available for PTP and DOP measurements and only low concentration reference standard for DIP is available. Hence the accuracy of the analytical methods for DIP, DOP and PTP in this study has only to be inferred from operational and environmental consistency of the data.

Blanks were run though with the measurements of DIP, DOP and PTP. The final results were correted by the relative blanks. No detectable blank was observed for DIP measurements and only few blanks for DOP measurement were detectable. The maximum blanks for DOP measurement can be as high as 0.29 µM, it probably due to the contamination in the flask. Unused filters were run as the blanks for PTP measurements and high blanks of up to 0.58 µM were observed. This was also reported by Ormaza-Gonzalez (1990) and Williams (1996). It was also observed that blanks of the GF/F filters differed little within the same batch but could differ considerably between batches. Thus the blanks of the GF/F filters were always monitored through the PTP measurements of every survey.

3.3.1 Dissolved inorganic phosphorus (DIP)

Dissolved inorganic nutrient analyses in this study were performed on a Burkard Scientific SFA-2 Auto-analyser linked to a Digital-Analysis Microstream data capture and reduction system. The protocols are similar to those described in the final SONUS report (Hydes and Wright, 1999). The analytical chemistry background to the methods used in this study can be found in Grasshoff *et al.* (1983). Basically a chemical reaction is carried out with the nutrient in the seawater to produce a coloured solution and the optical density of the colour is proportional to the concentration of the nutrient in the samples (where the Beer-Lambert law holds). In the auto-analyser the output from the photometer is fed through a logarithmic converter to give a signal which is proportional to the concentration. The linear working range has to be determined empirically for each series of measurements. The gain on the colorimeter for each channel has to be adjusted to give full scale deflection on the chart recorder for the most concentrated samples. The ratio of sample to wash times in this study was set as 60 seconds to 30 seconds. Artificial seawater made of NaCl (20 g/l) was used as a wash solution and matrix of analytical standards to minimise the potential interference caused by the varying salinity of the water samples. Analytical grade chemicals were used throughout for the preparation of reagents. Ultrapure - water of 18.2 MΩ.cm was used .

3.3.2 Dissolved organic phosphorus and particulate total phosphorus

Dissolved organic phosphorus was estimated as the difference between the total dissolved phosphorus (TDP) and DIP fractions in a single sample. The measurement of TDP in this study was carried out by using the magnesium nitrate high-temperature oxidation method (Cembella *et al.*, 1986) as described by Ormaza-Gonzalez (1990).

Method: To 20 ml of filtered water sample in a 250 ml Erlenmeyer flask, 1 ml oxidising reagent solution reagent (20 g of magnesium nitrate hexahydrate dissolved in 95% ethanol) was added. The flask was placed on a hot plate (temperature set at 200 °C) inside a fume hood. When the volume is approaching 10 ml, diminish the heat and put loose fitting glass balls on the top of flasks to prevent spluttering of material out of the flasks but also allowing some ventilation. When the samples were boiled to dryness and the brown nitrous oxides smoke start to evolve, take the balls off. Let the flask cool and after the nitrous oxides have dissipated, add 20 ml of 0.1 M HCl. Heat the solution at 80 °C for 30 min. Move the solution to a 15 ml plastic tube (rinse the solid residue with small volume of water if it is needed) and centrifuge the tubes at 3000 rev/min for 5 min to separate the solid residue. Dilute the supernatants to suitable concentrations based on the estimation of the concentration range present, and analyse using the same procedure as the DIP measurement on the auto-analyser.

Particulate phosphorus was determined by a slight modification of the method as described above for TDP:

The dried filters with particle samples were weighed and placed at the bottom of a 250 ml Erlenmeyer flask containing several glass boiling chips. 20 ml of ultrapure water was added and place the flask on a hot plate (temperature was set at 200°C) inside a fume hood. The same procedure as for TDP is then followed, except the concentration of HCl used to hydrolyse the samples is 0.4 M HCl rather than the 0.1 M HCl used in the determination of TDP. Knowing the SPM concentration from the separate gravimetric determination, it is possible to calculate particulate phosphorus on a mass / mass, as well as mass / volume basis.

3.3.3 Chlorophyll *a*

Chlorophyll *a* was measured from 50 ml duplicate samples filtered onboard. All these samples were taken on the monthly surveys of Southampton Water and the River Itchen. Chlorophyll *a* samples were taken in the same way as the other water samples. The volume of the water samples for chlorophyll analysis were measured using a plastic 50 ml volumetric flask cut off at the calibration mark, that had been previously rinsed with sample. The 50 ml chlorophyll sample was filtered onto a 25 mm GF/F filter under a low vacuum. The filtration was not more than 200 mm Hg pressure as any more would have caused cell damage. The filter was not rinsed as this could rupture the cells. The filter was carefully removed from the filter funnel using forceps, folded in half to protect the sample from the light and then placed in labelled plastic bags. The chlorophyll samples were stored immediately in the freezer compartment of the refrigerator onboard and transferred into the laboratory freezer just after the cruises. The first step in the analysis was to remove the filters from the bag and place them into the base of a 13 ml polypropylene sample tube. Five ml of 90% acetone was added, and the parafilm was placed over the top of the tube. The samples were sonicated to break up the cells, by inserting a sonicator probe into the tube with a sound reduced cabinet and pressing start. The sonicator was pre-set to operate for 30 seconds with the pulse on and off at 1 second intervals. The sonicator probe was cleaned between each sample. A single fluorescence curvette was used throughout the analyses, with rinsing between samples. 90% acetone was used for the blank measurement. The stock chlorophyll standard was prepared from an ampoule of chlorophyll (Sigma; approximately 1 mg) by applying the Beer - Lambert Law. It was then diluted into an acceptable working range and stored in a refrigerator. The concentration was determined spectrophotometrically on a multi-wavelength spectrophotometer. An Aminco fluro-colorimeter was used to measure the fluorescence of the acetone extracted samples, and was switched on at least 1/2 hour before the measurement. The fluorescence measurement was recorded together with the sensitivity setting used. The curvette was washed thoroughly with distilled water and then 90% acetone to remove all traces of sample and acid. The details of chlorophyll sample collection and analysis can be found in the report of Holley (1999).

3.4. Results

The median values of the data are shown instead of mean values, for the histogram of the observations is skewed. It was obtained by placing the observations in ascending order of magnitude and then picking out the middle observation (Chatfield, 1983).

3.4.1 Salinity

The salinity of the water sample generally increased seaward in the Southampton Water system and covered the range from 0.0 (upper estuary, e.g. the Woodmill Lane site) to 34.7 (bottom of the estuary, e.g. the Calshot Buoy site). In the 18 cruises the median values for salinity of the samples did not show any significant changes through the year. The salinity data for each survey is summarised in Table 3.4 and the range of salinity for each survey throughout the year is shown in Figure 3.1 refer to full datasets in Appendix C. Due to the limited access upstream of the boat during the neap tide periods, the range of salinity for neap tide survey is smaller compared to the spring tide survey in the same month.

Table 3.4 Salinity data summary

Date	Max	Min	Median
Jan-98	34.5	0.9	28.1
Feb-98	33.9	2.0	29.1
Mar-98	32.0	0.1	20.1
Apr-98 (neap)	32.8	7.2	30.1
Apr-98	33.5	0.0	29.0
May-98	33.7	0.0	30.4
May-98 (neap)	32.3	17.3	30.3
Jun-98 (neap)	33.4	8.3	31.7
Jun-98	33.8	0.1	31.9
Jul-98	34.6	0.4	31.2
Aug-98	34.7	1.1	33.0
Sep-98	34.4	2.1	31.6
Oct-98	34.4	0.5	30.2
Dec-98	34.2	2.0	31.9
Jan-99	32.4	0.0	17.3
Feb-99	33.2	8.0	31.4
Mar-98	33.2	0.1	30.2
Apr-99 (neap)	33.6	4.7	29.4

3.4.2 Temperature

The temperature of the water taken from each survey in the Southampton Water system varies seasonally, and is high in summer and low in winter (Figure 3.2). The highest temperature (21 °C) was observed on August 12^{th} 1998, whilst the lowest one (6.2 °C) was observed on

February 16th 1999. The air temperature and the general weather description of the sampling days are shown in Table 3.5 (No data available for 1999).

Table 3.5 Air temperature and the weather conditions on the sampling days (1998)

Sampling date	Air temperature (∞C)	Weather
16/1/98	7~10	dry
26/2/98	6~10	cloudy
30/3/98	11~14	rain
21/4/98	8~13	cloudy
28/4/98	7~14	cloudy
12/5/98	11~25	dry
19/5/98	12~25	dry
5/6/98	11~22	dry
12/6/98	7~18	dry
23/7/98	15~22	dry
12/8/98	14~23	dry
24/9/98	12~22	cloudy
21/10/98	9~18	cloudy
2/12/98	1~5	cloudy

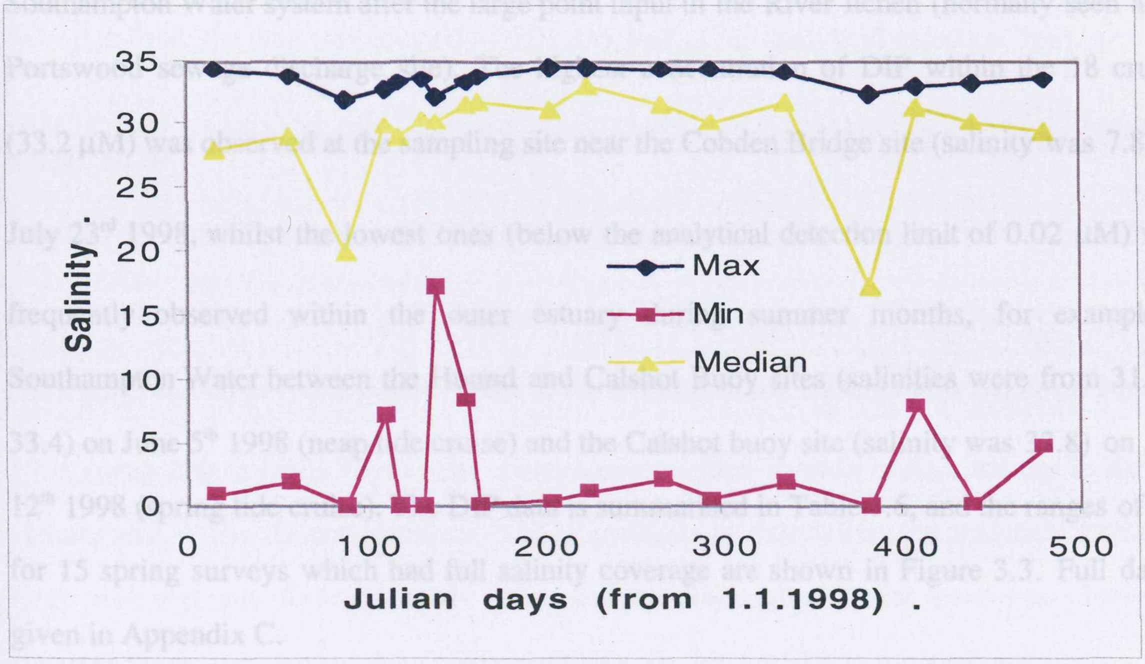


Figure 3.1 The range and seasonal variation of salinity for the surveys

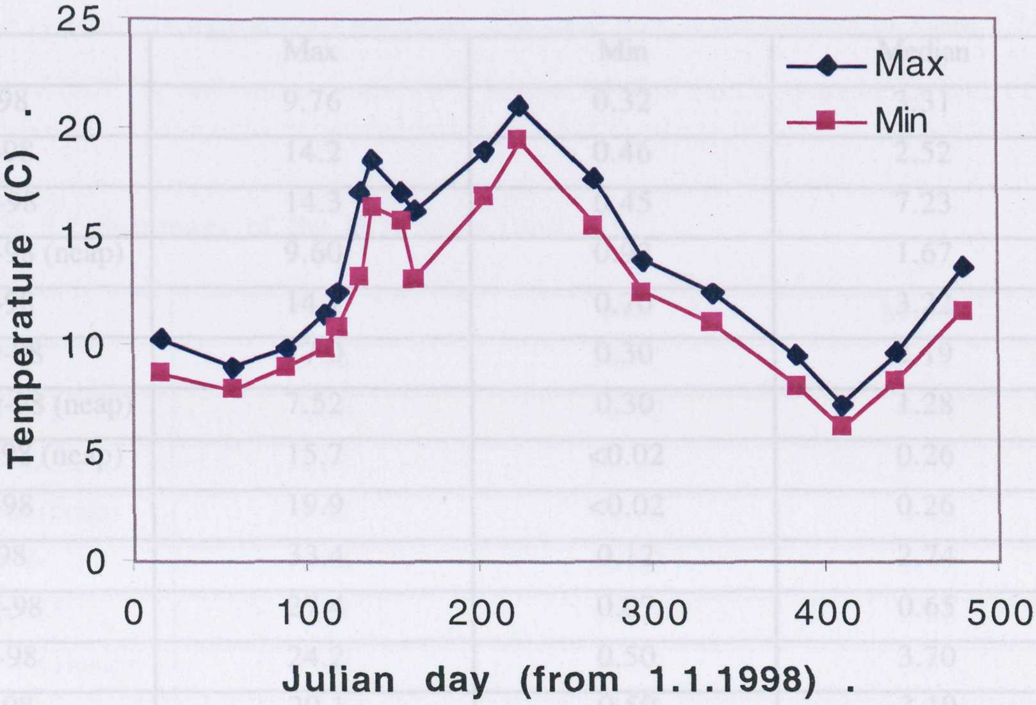


Figure 3.2 Surface water temperature of the surveys

3.4.3 DIP (SRP)

Dissolved inorganic phosphorus (DIP) appears to decrease conservatively seaward in the Southampton Water system after the large point input in the River Itchen (normally seen at the Portswood sewage discharge site). The highest concentration of DIP within the 18 cruises (33.2 µM) was observed at the sampling site near the Cobden Bridge site (salinity was 7.8) on July 23rd 1998, whilst the lowest ones (below the analytical detection limit of 0.02 µM) were frequently observed within the outer estuary during summer months, for example in Southampton Water between the Hound and Calshot Buoy sites (salinities were from 31.8 to 33.4) on June 5th 1998 (neap tide cruise) and the Calshot buoy site (salinity was 33.8) on June 12th 1998 (spring tide cruise). The DIP data is summarised in Table 3.6, and the ranges of DIP for 15 spring surveys which had full salinity coverage are shown in Figure 3.3. Full data is given in Appendix C.

Table 3.6 DIP data summary (unit: μM)

Date	Max	Min	Median
Jan-98	9.76	0.32	3.31
Feb-98	14.2	0.46	2.52
Mar-98	14.3	0.45	7.23
Apr-98 (neap)	9.60	0.92	1.67
Apr-98	14.1	0.70	3.22
May-98	27.0	0.30	2.19
May-98 (neap)	7.52	0.30	1.28
Jun-98 (neap)	15.7	<0.02	0.26
Jun-98	19.9	<0.02	0.26
Jul-98	33.4	0.12	2.74
Aug-98	27.4	0.07	0.65
Sep-98	24.2	0.50	3.70
Oct-98	20.1	0.50	3.19
Dec-98	12.4	0.90	2.14
Jan-99	7.40	0.44	4.38
Feb-99	6.52	0.55	0.88
Mar-98	20.7	0.90	1.94
Apr-99 (neap)	11.4	0.55	1.57

* When calculating the median value of DIP, if the data was below the 0.02 μM analytical detection limit, the data was counted as 0.01 μM, half of the analytical detection limit.

3.4.4 DOP

Dissolved organic phosphorus (DOP) is often low and rarely higher than 5 μM in the Southampton Water system, and the spatial trend appears erratic. The highest concentration (20.0 μM) was observed in bottom water at the Dockhead site (salinity was 32.9) on June 5th 1998 (neap tide cruise). There were always several sites in each cruise, mainly in the low salinity area, where the concentration of DOP could not be detected by the analytical method. A large peak was only observed in one cruise in June, although a similar result was obtained in SONUS 1995 cruise (December 1995, 17.6 μM, the Portswood sewage discharge site). This may be due to an analytical error of the analytical method or truly reflect the variability of DOP in the system (discussion see Chapter 4). The DOP data is summarised in Table 3.7 and the range of DOP for each survey is shown in Figure 3.4. Full data is given in Appendix C.

Table 3.7 Summary of the DOP data (unit: μM)

Date	Max	Min	Median
Jan-98	3.14	<0.02	0.47
Feb-98	10.6	<0.02	0.35
Mar-98	2.51	<0.02	0.99
Apr-98(neap)	3.62	<0.02	0.22
Apr-98	1.54	<0.02	0.78
May-98	1.27	<0.02	0.68
May-98 (neap)	1.24	0.32	0.61
Jun-98 (neap)	20.0	<0.02	0.23
Jun-98	1.60	<0.02	0.43
Jul-98	4.91	<0.02	<0.02
Aug-98	3.78	<0.02	0.48
Sep-98	17.3	<0.02	0.34
Oct-98	3.36	<0.02	0.41
Dec-98	1.69	0.12	0.43
Jan-99	1.01	<0.02	0.41
Feb-99	0.68	<0.02	0.16
Mar-98	0.10	<0.02	<0.02
Apr-99 (neap)	0.81	0.27	0.54

3.4.5 DIN (nitrate plus nitrite)

DIN appears to behave less variably than phosphorus within the Southampton Water system. High river nitrate inputs dominate the sources of DIN within the system, while the domestic sewage outfall which has had nitrogen removed prior to discharge is the dominant source for phosphorus. The concentrations of DIN decreased seaward. In summer months low dissolved

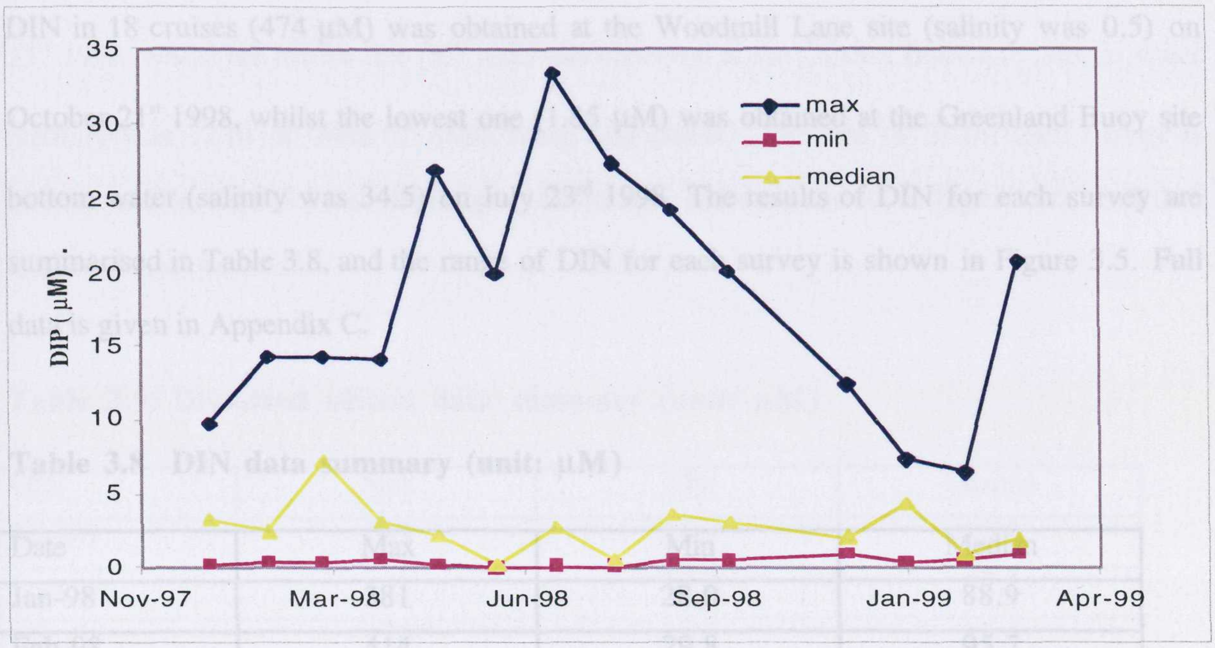


Figure 3.3 The range and seasonal variation of DIP for the spring tide surveys

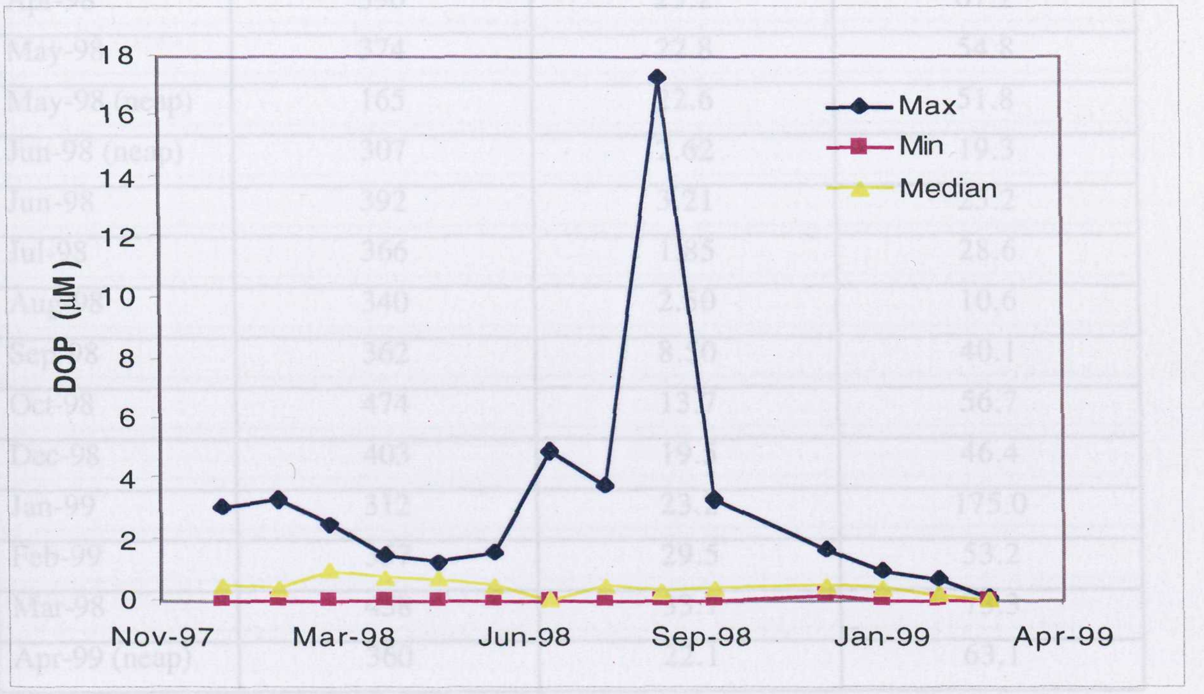


Figure 3.4 The range and seasonal variation of DOP for the spring tide surveys

inorganic nitrogen could be observed within the outer estuary. The highest concentration of DIN in 18 cruises (474 μM) was obtained at the Woodmill Lane site (salinity was 0.5) on October 21st 1998, whilst the lowest one (1.85 μM) was obtained at the Greenland Buoy site bottom water (salinity was 34.5) on July 23rd 1998. The results of DIN for each survey are summarised in Table 3.8, and the range of DIN for each survey is shown in Figure 3.5. Full data is given in Appendix C.

Table 3.8 DIN data summary (unit: μM)

Date	Max	Min	Median
Jan-98	381	28.0	88.9
Feb-98	414	29.8	95.7
Mar-98	400	50.8	176.4
Apr-98 (neap)	304	33.4	57.3
Apr-98	390	25.2	67.2
May-98	374	22.8	54.8
May-98 (neap)	165	22.6	51.8
Jun-98 (neap)	307	2.62	19.3
Jun-98	392	3.21	25.2
Jul-98	366	1.85	28.6
Aug-98	340	2.50	10.6
Sep-98	362	8.50	40.1
Oct-98	474	13.7	56.7
Dec-98	403	19.5	46.4
Jan-99	312	23.2	175.0
Feb-99	357	29.5	53.2
Mar-98	458	33.7	73.3
Apr-99 (neap)	360	22.1	63.1

3.4.6 Dissolved Silicon

Dissolved Silicon (Si) generally behaved conservatively throughout the Southampton Water system and the concentrations of Si decrease seaward. The highest concentration of dissolved silicon in 18 cruises (211 µM) was observed at the Rail Bridge site (salinity was 1.8) on July 23rd 1998, whilst the lowest one (5.7 µM) was observed at the Calshot Buoy site bottom water (salinity was 32.6) on June 5th 1998 (neap tide cruise). The data of Si for each survey is summarised in Table 3.9 and the range of Si for each survey is shown in Figure 3.6. Full data is given in Appendix C.

Table 3.9. Dissolved silicon data summary (unit: µM)

Date	Max	Min	Median
Jan-98	189	24.4	53.8
Feb-98	183	15.9	47.4
Mar-98	178	33.5	85.4
Apr-98 (neap)	132	13.7	22.4
Apr-98	169	11.3	31.8
May-98	158	8.2	25.2
May-98 (neap)	68.9	7.7	16.4
Jun-98 (neap)	143	5.7	8.5
Jun-98	202	9.8	13.0
Jul-98	211	7.6	21.9
Aug-98	167	8.1	11.5
Sep-98	183	11.6	25.6
Oct-98	164	5.4	29.1
Dec-98	204	13.8	28.5
Jan-99	174	17.3	98.5
Feb-99	154	17.2	29.2
Mar-98	176	13.5	28.3
Apr-99 (neap)	126	7.2	23.2

3.4.7 SPM

The suspended particle matter (SPM) was measured for 18 cruises. Higher concentrations of SPM can be found in the outer estuary. In spring and summer the SPM concentrations are generally lower than in winter when the river flow are high and resuspension of sediments caused by wind occurred. The highest concentration (83.4 mg/l) was observed at the Calshot Castle site(salinity was 32.4) on January 19th 1999, whilst the lowest concentration (2.6 mg/l) was obtained at the Hound site (salinity was 33.4) on August 12th 1998. The lower concentrations throughout the system usually could be observed in May and June. The SPM data is summarised in Table 3.10, and the range of SPM is shown in Figure 3.7. Full data is given in Appendix C.

Table 3.10 Summary of the SPM data (unit: mg/l)

Date	Max	Min	Median
Jan-98	54.2	9.0	19.7
Feb-98	76.0	8.6	23.4
Mar-98	59.6	12.2	36.1
Apr-98(neap)	54.6	10.0	39.2
Apr-98	65.8	8.8	39.2
May-98	29.4	4.6	14.8
May-98 (neap)	31.6	8.6	16.2
Jun-98 (neap)	23.0	3.8	11.1
Jun-98	23.2	6.6	14.5
Jul-98	55.8	7.4	43.8
Aug-98	35.0	2.6	18.8
Sep-98	61.4	3.2	39.2
Oct-98	68.0	5.4	23.0
Dec-98	37.6	4.6	12.2
Jan-99	83.4	25.0	48.4
Feb-99	54.2	17.3	45.0
Mar-98	73.0	9.6	16.6
Apr-99 (neap)	73.6	15.6	29.0

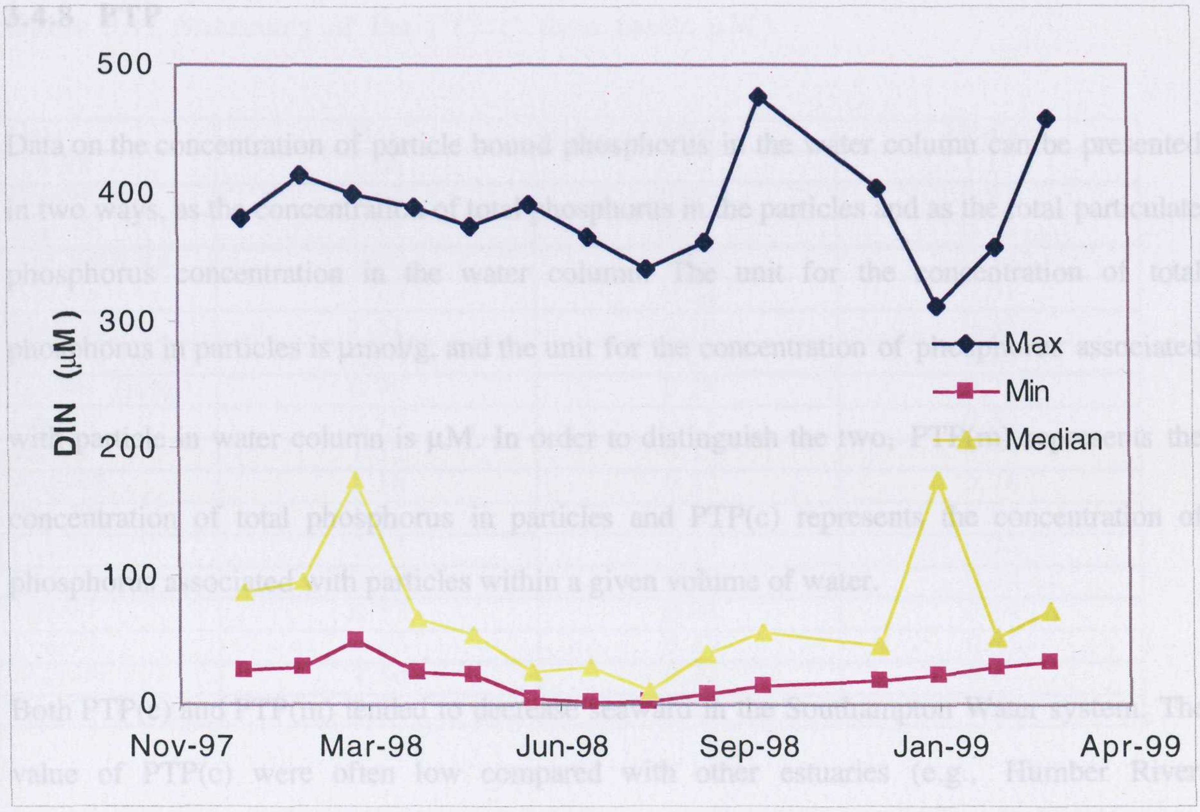


Figure 3.5 The range and seasonal variation of DIN for the spring tide surveys

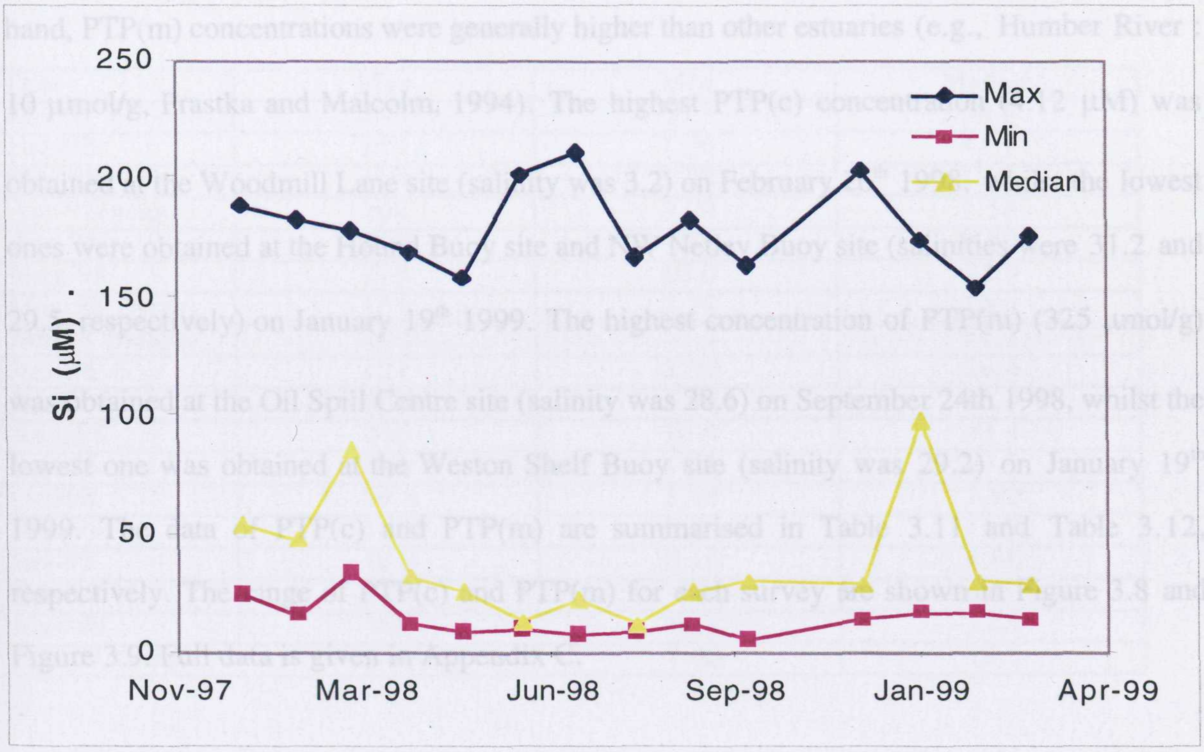


Figure 3.6 The range and seasonal variation of Si for the spring tide surveys

3.4.8 PTP

Data on the concentration of particle bound phosphorus in the water column can be presented in two ways, as the concentration of total phosphorus in the particles and as the total particulate phosphorus concentration in the water column. The unit for the concentration of total phosphorus in particles is μmol/g, and the unit for the concentration of phosphorus associated with particle in water column is μM. In order to distinguish the two, PTP(m) represents the concentration of total phosphorus in particles and PTP(c) represents the concentration of phosphorus associated with particles within a given volume of water.

Both PTP(c) and PTP(m) tended to decrease seaward in the Southampton Water system. The value of PTP(c) were often low compared with other estuaries (e.g., Humber River: 1.02~6.03 μM, Prastka and Malcolm, 1994) and were not higher than 5 μM. On the other hand, PTP(m) concentrations were generally higher than other estuaries (e.g., Humber River : 10 μmol/g, Prastka and Malcolm, 1994). The highest PTP(c) concentration (4.12 μM) was obtained at the Woodmill Lane site (salinity was 3.2) on February 26th 1998, whilst the lowest ones were obtained at the Hound Buoy site and NW Netley Buoy site (salinities were 31.2 and 29.5, respectively) on January 19th 1999. The highest concentration of PTP(m) (325 μmol/g) was obtained at the Oil Spill Centre site (salinity was 28.6) on September 24th 1998, whilst the lowest one was obtained at the Weston Shelf Buoy site (salinity was 29.2) on January 19th 1999. The data of PTP(c) and PTP(m) are summarised in Table 3.11 and Table 3.12, respectively. The range of PTP(c) and PTP(m) for each survey are shown in Figure 3.8 and Figure 3.9. Full data is given in Appendix C.

Table 3.11 Summary of the PTP(c) data (unit: μM)

Date	Max	Min	Median
Jan-98	3.06	0.81	1.17
Feb-98	4.12	0.03	0.91
Mar-98	1.91	0.21	0.63
Apr-98(neap)	1.06	0.16	0.33
Apr-98	1.24	0.22	0.51
May-98	1.27	0.16	0.35
May-98 (neap)	2.36	0.07	0.26
Jun-98 (neap)	0.98	0.18	0.71
Jun-98	0.95	0.12	0.32
Jul-98	1.52	0.25	0.73
Aug-98	1.30	0.37	0.76
Sep-98	1.37	0.13	0.94
Oct-98	0.93	0.13	0.34
Dec-98	0.74	0.12	0.34
Jan-99	0.53	0.01	0.18
Feb-99	0.45	0.17	0.31
Mar-99	1.56	0.21	0.84
Apr-99 (neap)	1.16	0.26	0.40

Table 3.12 Summary of the PTP (m) data (unit: μmol/g)

Date	Max	Min	Median
Jan-98	245	30.1	50.5
Feb-98	253	1.20	41.9
Mar-98	119	3.70	17.3
Apr-98(neap)	106	3.90	7.50
Apr-98	109	4.30	9.40
May-98	275	10.0	22.9
May-98 (neap)	131	2.70	16.4
Jun-98 (neap)	200	15.9	57.3
Jun-98	121	5.90	20.4
Jul-98	186	5.90	15.3
Aug-98	208	16.9	43.4
Sep-98	326	16.1	23.2
Oct-98	89.4	2.70	7.90
Dec-98	149	8.50	15.7
Jan-99	11.2	0.10	4.00
Feb-99	24.0	3.9	6.90
Mar-99	162	12.2	27.9
Apr-99 (neap)	74.5	7.00	12.5

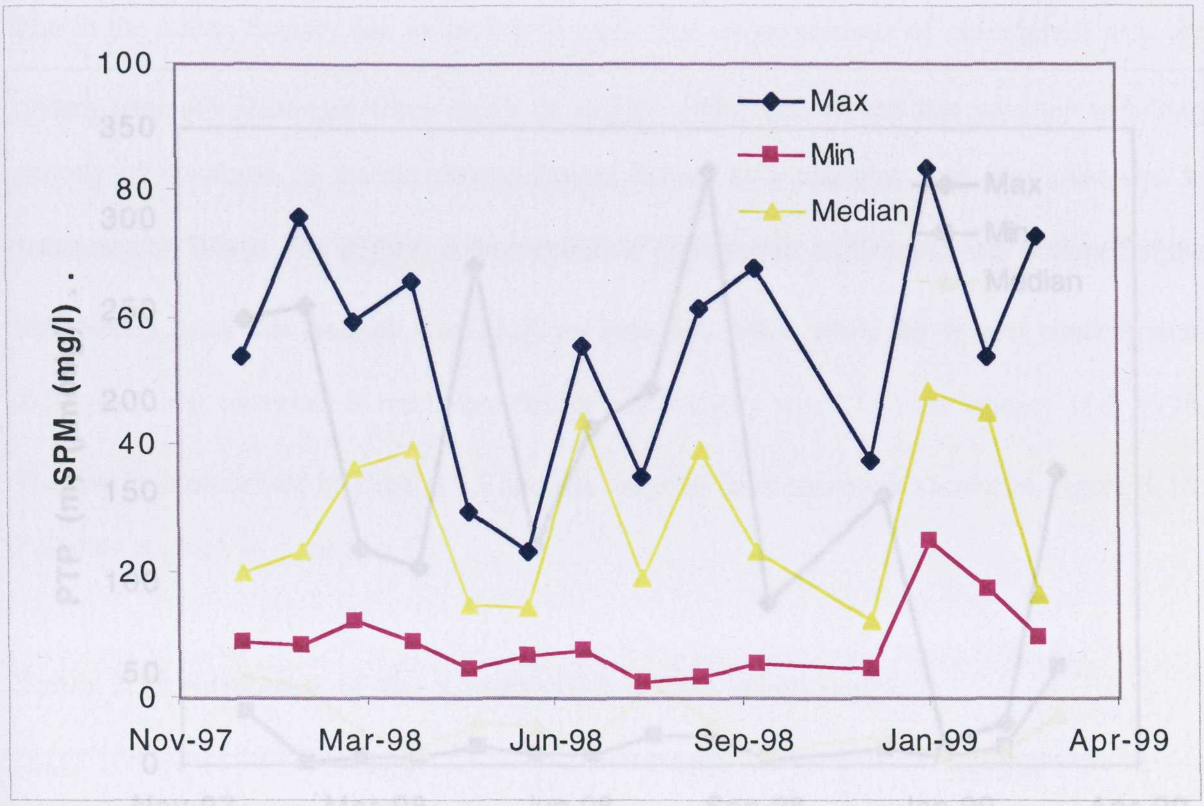


Figure 3.7 The range and seasonal variation of SPM for the spring tide surveys

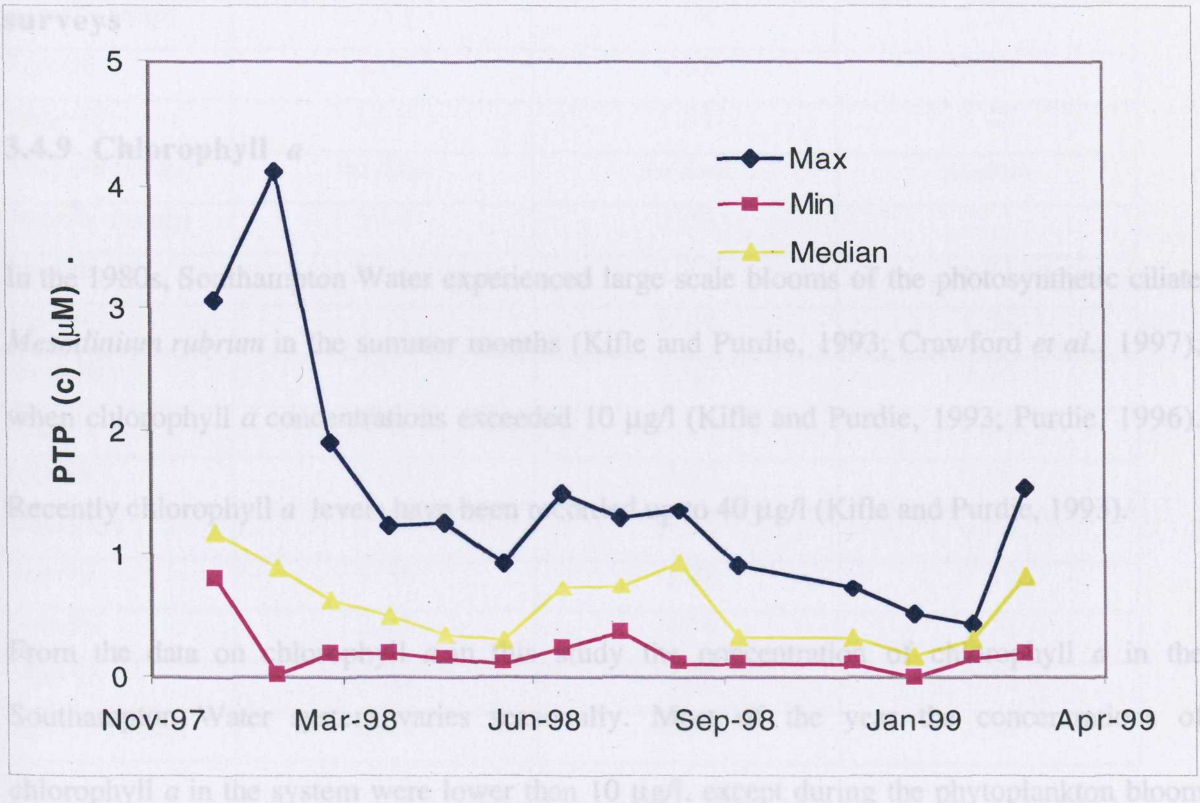


Figure 3.8 The range and seasonal variation of PTP(c) for the spring tide surveys

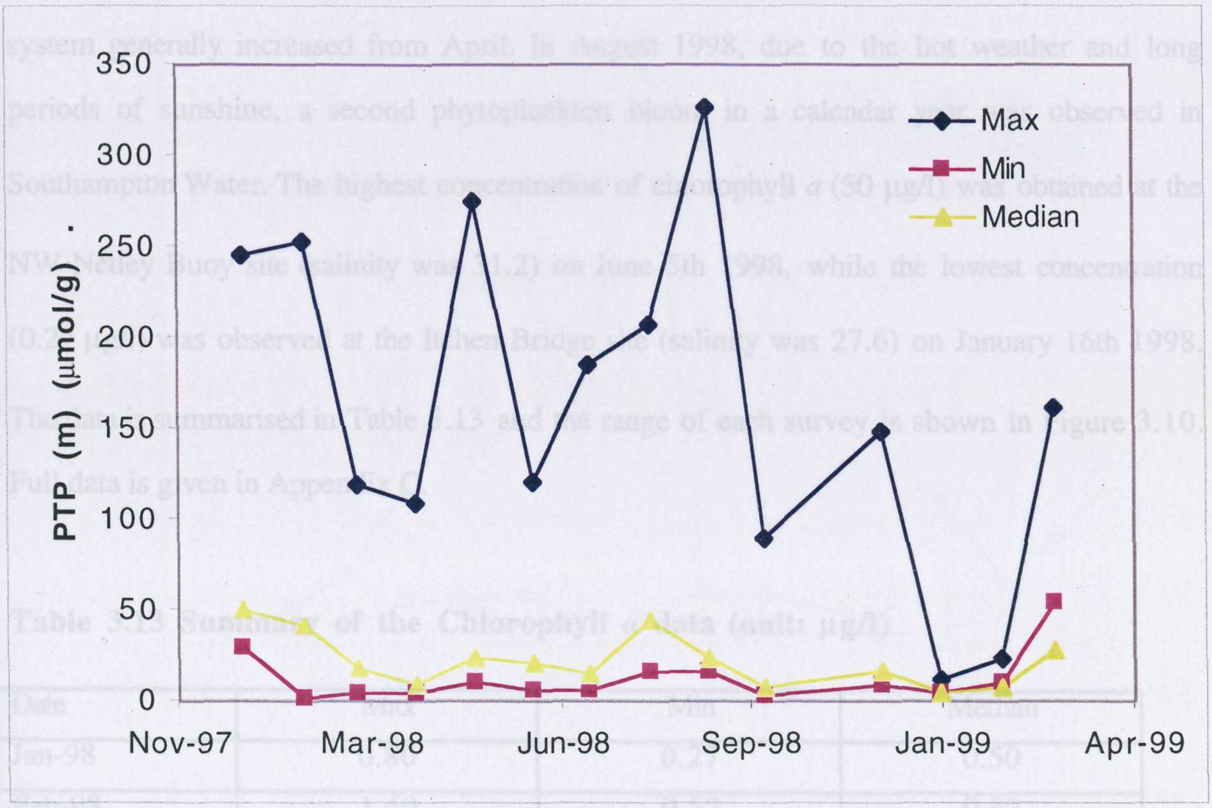


Figure 3.9 The range and seasonal variation of PTP(m) for the spring tide surveys

3.4.9 Chlorophyll *a*

In the 1980s, Southampton Water experienced large scale blooms of the photosynthetic ciliate *Mesodinium rubrum* in the summer months (Kifle and Purdie, 1993; Crawford *et al.*, 1997), when chlorophyll *a* concentrations exceeded 10 µg/l (Kifle and Purdie, 1993; Purdie, 1996). Recently chlorophyll *a* levels have been recorded up to 40 µg/l (Kifle and Purdie, 1993).

From the data on chlorophyll *a* in this study the concentration of chlorophyll *a* in the Southampton Water system varies seasonally. Most of the year the concentrations of chlorophyll *a* in the system were lower than 10 µg/l, except during the phytoplankton bloom period, when the concentrations of chlorophyll *a* in Southampton Water were generally higher than in the Itchen Estuary and exceeded 10 μg/l. The concentrations of chlorophyll *a* in the system generally increased from April. In August 1998, due to the hot weather and long periods of sunshine, a second phytoplankton bloom in a calendar year was observed in Southampton Water. The highest concentration of chlorophyll *a* (50 μg/l) was obtained at the NW Netley Buoy site (salinity was 31.2) on June 5th 1998, while the lowest concentration (0.27 μg/l) was observed at the Itchen Bridge site (salinity was 27.6) on January 16th 1998. The data is summarised in Table 3.13 and the range of each survey is shown in Figure 3.10. Full data is given in Appendix C.

Table 3.13 Summary of the Chlorophyll *a* data (unit: μg/l)

Date	Max	Min	Median
Jan-98	0.80	0.27	0.50
Feb-98	1.40	0.52	0.82
Mar-98	2.79	0.65	1.00
Apr-98(neap)	5.33	1.58	2.38
Apr-98	6.00	1.63	3.38
May-98	13.9	1.61	3.48
May-98 (neap)	no data	no data	no data
Jun-98 (neap)	50.0	2.53	21.1
Jun-98	14.2	1.87	6.71
Jul-98	1.79	0.89	1.30
Aug-98	23.7	1.00	9.75
Sep-98	2.13	0.67	1.50
Oct-98	1.98	0.49	0.99
Dec-98	0.93	0.35	0.66
Jan-99	5.56	0.74	1.78
Feb-99	2.48	0.96	1.74
Mar-98	4.29	0.86	1.53
Apr-99 (neap)	2.93	0.15	1.34

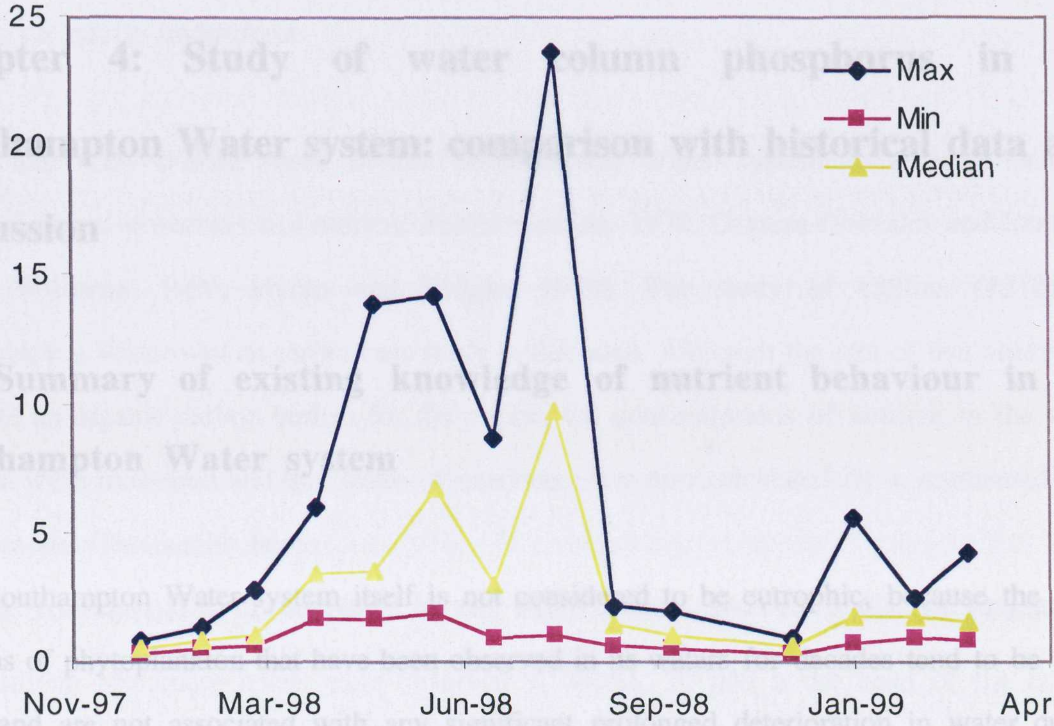


Figure 3.10 The range and seasonal variation of Chlorophyll *a* for the spring tide surveys

Chapter 4: Study of water column phosphorus in the Southampton Water system: comparison with historical data and discussion

4.1 Summary of existing knowledge of nutrient behaviour in the Southampton Water system

The Southampton Water system itself is not considered to be eutrophic, because the large blooms of phytoplankton that have been observed in its waters for decades tend to be short lived and are not associated with any significant prolonged deterioration in water quality (Hydes and Wright, 1999). However, high concentrations of nutrients are present in both the rivers draining into and the extensive sewage treatment plants discharging into Southampton Water making the system hypernutriphied. An almost annual recurrence of a marked "red tide" caused by the photosynthetic ciliate *Mesodinium rubrum* occurred in Southampton Water in the 1980s and early 1990s but had been absent for four years before 1998. A strong bloom of the organism occurred in August 1998 depleting the concentrations of nutrients in Southampton Water to levels lower than had been observed in the previous three years. These features make the Southampton Water system a suitable focus for the study of biogeochemical processes that lead to excessive algal growth (eutrophication) in estuarine and coastal waters (Wright and Hydes, 1997). Outside the estuary the inputs of nitrogen and phosphorus from the English Channel to the southern North Sea may be significant in comparison to other fluxes from the UK south coast (Wright and Hydes, 1997). At present the riverine, direct discharges and atmospheric sources of nutrients to the UK south coast and English Channel are not well quantified. In particular the large direct inputs from sewage discharges and subsequent influence on the Southampton Water ecosystem are not completely characterised and quantified. Similarly knowledge of the biogeochemical processes taking place in the estuary that potentially link the inputs of nutrients to the growth of planktonic organism in the water column are poorly understood.

There has been limited work in the Southampton Water system to evaluate nutrient biogeochemical processes and nutrient fluxes (Collins, 1978; Ormaza-Gonzalez and Statham, 1991; Williams, 1996; Hydes and Wright, 1999). The study of Collins (1978) on Southampton Water was an earlier case study in this area. Although the aim of that study was to make an organic carbon budget for the region, the concentrations of nutrient in the water column were measured and the fluxes of nutrients were also calculated by a segmented tidal prism model. The results were:

1. The concentrations of ammonia in the water column showed a distinct longitudinal gradient. Maximum levels were observed in winter, 20 μM at the head of the estuary falling to 5 μM in the Solent. All stations showed a yearly cycle falling to a minimum in August, 1 μM was observed along the length of Southampton Water. River input of ammonia is small, while industry provided the largest input of ammonia.
2. A longitudinal gradient in nitrite concentration was observed throughout the year, typically around 1 μM at the head of estuary (salinity was 25), 0.4 μM in the Solent (salinity was 34). The concentrations showed considerable scatter with no clear season cycle.
3. The concentration of nitrate showed a similar longitudinal and seasonal variation to ammonia. Maximum levels were observed in winter, 90 μM at the head (salinity was 26), 25 μM in the Solent (salinity was 34). Minimum levels were observed in August, 10 μM at the head (salinity was 31), 7 μM in the Solent (salinity was 34).
4. No clear seasonal cycle of phosphorus for the whole estuary was observed. A sharp drop over the whole of estuary was observed in August with minimum levels around 0.03 μM. Collins (1978) concluded that the main source of dissolved inorganic phosphorus in Southampton Water was from sewage. A smaller amount (about 10 %) came in with the

rivers, presumably originating from agricultural run-off and inland sewage inputs. A substantially constant level of DIP was found in the estuary, only exception was during the mid-summer plankton bloom when the concentrations were depressed. This non-conservative behaviour of phosphorus was thought to be caused by the apparent buffering mechanism of particulate phosphorus. There appeared to be fast initial surface adsorption of phosphorus onto surfaces of particulate material that could be readily desorbed in low phosphate waters.

Ormaza-Gonzalez and Statham (1991) expanded the survey to the Itchen Estuary and did two surveys in November 1988 and July 1989. They found that in the upper parts of the Itchen Estuary high concentrations of DIP (up to 55 μM, salinity around 5) dominated the forms of phosphorus, due to the large inputs from sewage treatment works. They also revealed that significant but variable amounts of DOP and PTP were present and these fractions of phosphorus became relatively important in the high salinity waters.

Phosphorus in the sediment porewaters and DIP, DOP, PTP seasonal variations in the Solent were reported by Williams (1996). The work consisted of a monthly study of phosphorus from February 1993 through January 1995 at a sampling site off the coast of Bembridge, Isle of Wright, which is at the geographical edge of the Southampton Water system. Over the 23 month sampling period a strong seasonal cycle of the concentrations of dissolved inorganic phosphorus in the water column was found. The concentrations of DIP were high during the winter / spring period and decreased during the algal bloom to below detection limit in early summer. It appeared that the rate of recycling and geochemical supply did not meet the biological demand. The deficit in DIP was overcome by utilising DOP as a source of phosphorus for phytoplankton via the action of phosphatase enzymes. Particulate total phosphorus increased in the spring / early summer due to biological particles in the water column, but high concentration of PTP in winter was caused by sediment resuspension.

In 1994 the Department of the Environment set up the SOuthern Nutrients Study (SONUS) project. The SONUS study was the first systematic study on the nutrient biogeochemistry in this region and it aimed to estimate the nitrogen and phosphorus inputs to the English Channel from UK south coast estuaries between Poole and Dover. A field work programme was developed to measure nutrient biogeochemical processes and fluxes, movement of associated water and suspended matter from the Solent / Southampton Water system into the English Channel over two annual cycles.

In Spring 1995, the SONUS project started a two-year long field study through the Southampton Water system. The work was based on quasi-synoptic sampling along the length of the estuary (including the Itchen Estuary, the Test Estuary, Southampton Water). Twenty four monthly surveys were conducted using the School of Ocean and Earth Science boat "*Bill Conway* " and sampling from the shore. Chemical analyses included dissolved nitrogen (nitrate, nitrite, ammonium, organic nitrogen) and phosphorus (DIP and DOP) species, as well as periodic measurement of PTP, oxygen and urea.

Conservative mixing of nutrients was generally found in Southampton Water by the SONUS project. This appears to be the prevalent situation within Southampton Water, whereas the distributions of the concentrations of phosphorus and ammonia within the River Itchen (above Dockhead) are altered by the sewage inputs from Portswood waste water treatment works (Hydes and Wright, 1999).

Ordinarily, ammonia, nitrite and phosphate levels were higher around the Portswood sewage outfall, with organic nitrogen being low. Distributions of phosphate are dominated by such point sources, with dilution by fresh river water low in phosphate. It was observed that as the river discharge began to increase during the year, the peak concentrations of phosphate generally decreased.

For dissolved inorganic nitrogen (DIN) (nitrate + nitrite + ammonia), the highest concentration (1040 μM) was observed at the Portswood sewage discharge site (salinity was 3.5) on November 24th 1995, whilst the lowest one (1.1 μM) was obtained at the Calshot Buoy site (salinity was 34.1) on August 30th 1995. The highest concentration of DIP (91 μM) was observed at the Portswood sewage discharge site (salinity was 8.9) on October 27th 1995 and the lowest DIP (0.1 μM) was observed at the Calshot Buoy site (salinity was 33.2) on March 21st 1996. The highest concentration of Si (231 μM) was observed at the Rowing Hard site (salinity was 1.7) on February 22nd 1996 and the lowest one of Si (4.2 μM) was observed at the Calshot Buoy site on August 30th 1995.

When predicting which nutrient is the major limiting factor in one ecosystem the Redfield ratio (Redfield, 1958) has proved useful, although the Redfield ratio was calculated for open ocean and not coastal waters (Williams, 1996). The Redfield ratio of Carbon : Nitrogen : Phosphorus as 106 : 16 : 1 indicates the overall required ratio of nutrients in the system for primary production to occur. Any move away from the ratio indicates the potential limiting nutrient (Redfield, 1958). However, the Redfield ratio does not take into account the possibility of short term regeneration or the consumption of organic forms of nutrients by phytoplankton (Veldhuis and Admiraal, 1987). The variation of N / P ratio in terms of DIN : DIP in the Southampton Water system, ranging from 2 to 268, is large compared to most of the major rivers in the world. Table 4.1 shows the comparison of DIN : DIP ratio within a variety of estuaries. N / P ratios generally decrease seaward in the whole Southampton Water estuary. The mean value of N / P ratios in the Southampton Water system is 41. It is higher than the Redfield Ratio, which is 16 (Redfield, 1958). Therefore the Southampton Water system likely has potential phosphorus limitation of phytoplankton growth.

In summary, the SONUS study and other previous studies all pointed out the importance of high phosphorus inputs from the sewage works and phosphorus biogeochemical processes

Table 4.1. Ratios of dissolved inorganic nitrogen to dissolved inorganic phosphorus (DIN : DIP) in a variety of estuaries.

Most data from Boynton *et al.*, 1982. Data for Chinese rivers from Zhang (1996). Data for the Southampton Water system from the provisional SONUS research and this study. Data are given in order of increasing values

Estuary	DIN:DIP ratio at time of maximum productivity	Annual range in DIN:DIP ratio
Pamlico River, USA	0.2	~0-3
Roskeeda Bay, Ireland	0.3	~0-1
Narragansett Bay, USA	0.5	0.5-14
Dedford Basin, USA	0.8	0.5-8
Beaufort sound, USA	1.0	0.5-16
Chincoteague Bay, USA	1.2	1-10
Western Wadden Sea, Netherlands	1.3	1.3-120
Eastern Wadden Sea, Netherlands	1.5	1.5-56
Peconic Bay, USA	1.5	1-4
Mid-Patuxent River, USA	1.8	1.8-53
S.E.Kancohe Bay, USA	2.0	not reported
St. Margaret Bay, USA	2.2	1-7
Central Kaneohe Bay, USA	2.8	not reported
Long Island Sound, USA	3.9	1-6
Lower San Francisco Bay, USA	6.0	4.5-8.5
Upper San Francisco Bay, USA	6.0	0.5-16
Barataria Bay, USA	6.2	6-16
Victoria Harbour, Canada	6.2	6-15
Mid-Chesapeake Bay, USA	7.6	7-225
Duwamish River, USA	8.5	8-16
Upper Patuxent River, USA	9.2	9-61
Baltic Sea	15	not reported
	Redfield N:P=16:1	
Loch Etive, Scotland	18	12-125
Hudson River, USA	20	16-30
Vostock Bay, USSR	20	5-22
Apalachicola Bay, USA	31	8-62
High Venice Lagoon, Italy	48	48-190
ChangJiang, China	not reported	84(mean)
Yellow River, China	not reported	335(mean)
The Southampton Water system, UK	34	2-268

within the estuary to the whole Southampton Water ecosystem, although the phosphorus biogeochemical processes in the system have not been well interpreted. The potential importance of phosphorus as the limiting nutrient in the Southampton Water ecosystem has been suggested by the SONUS study by examining the DIN : DIP ratio in the system, although in Collins (1978) study phosphorus limitation was not determined due to the complicated buffering of the particles. In contrast to the study of Collins (1978) Ormaza-Gonzalez (1990) discussed the suggestion of Collins (1978) that "buffer" was an important mechanism controlling the concentrations of phosphorus in water column in Southampton Water and found that no significant phosphorus " buffer " phenomenon can be seen through the system. This was maybe due to the narrow salinity range (25 ~ 34) in Collins (1978) study while the study of Ormaza-Gonzalez (1990) covered the salinity range from 0 to 34. Ormaza-Gonzalez (1990) also revealed the significant but variable amounts of DOP and PTP were important in the high salinity waters. In contrast to Collins (1978), Williams (1996) found a strong seasonal cycle of the concentrations of DIP in water column, although this conclusion was based on only one open water site in the Solent. This seasonal variation was again shown by the SONUS study through the whole system; in low salinity water the seasonal variation was controlled by the seasonal river input and in high salinity waters the biological activity played the main part.

Due to only occasional measurements of DOP and PTP in the SONUS study and other previous studies in the system, the discussion above shows that the dataset for phosphorus in this system is incomplete but indicates a better understanding could be gained from extended study of DOP and PTP. The biogeochemical processes of phosphorus in the system therefore needed further investigation and the budget of phosphorus of the region needed evaluation.

4.2. Nutrient distributions and nutrient-salinity relationships

Evidence of active nutrient biogeochemical processes in estuaries can be found in the salinity-nutrient relationships during the mixing of nutrient-rich freshwater and nutrient-poor seawater (Burton, 1973; Hydes and Liss, 1977; Sanders *et al.*, 1997). This method involves back extrapolation of the regression of nutrient with salinity to zero salinity to derive an effective freshwater end-member concentration. This concentration is then compared with the measured freshwater end-member to estimate the degree of removal or addition within the estuary. When the influence of estuarine biogeochemical processes is small, a linear relationship between the nutrient concentrations and salinity can be found. However, when the transformation processes strongly influence nutrient concentrations, this nonconservative behaviour is indicated by a non-linear relationship. For example, van Beusekom and Brockmann (1998) found that the formation and retention of apatites was a major process in the Elbe Estuary withdrawing phosphorus from the biogeochemical cycle and making the nonconservative behaviour of phosphorus occur by the non-linear phosphorus-salinity relationship. These relationships are also useful to demonstrate the distributions of nutrients in the estuary.

Figures 4.1 to 4.4 and Figure 4.6 to 4.8 show representative examples of the data expressed in terms of their relationships to salinity for the surveys undertaken in this study. The rest of these relationships are shown in Appendix D. The trends of the distributions of each nutrient and chlorophyll *a* are analysed as following.

1. **DIP**: the distributions of concentrations of dissolved inorganic phosphorus in the system are generally influenced by the sewage inputs. When the DIP data from each survey is plotted against the salinity of the sample, the general pattern seen in the distribution in the River Itchen is a peak associated with the sewage discharge at Portswood and followed by apparent conservative behaviour in Southampton Water through the year except during the periods of algal blooms. Concentrations of DIP drop to below the detection limit in high salinity waters (salinity > 33) during the period of the phytoplankton bloom, when DIP was consumed by the phytoplankton.

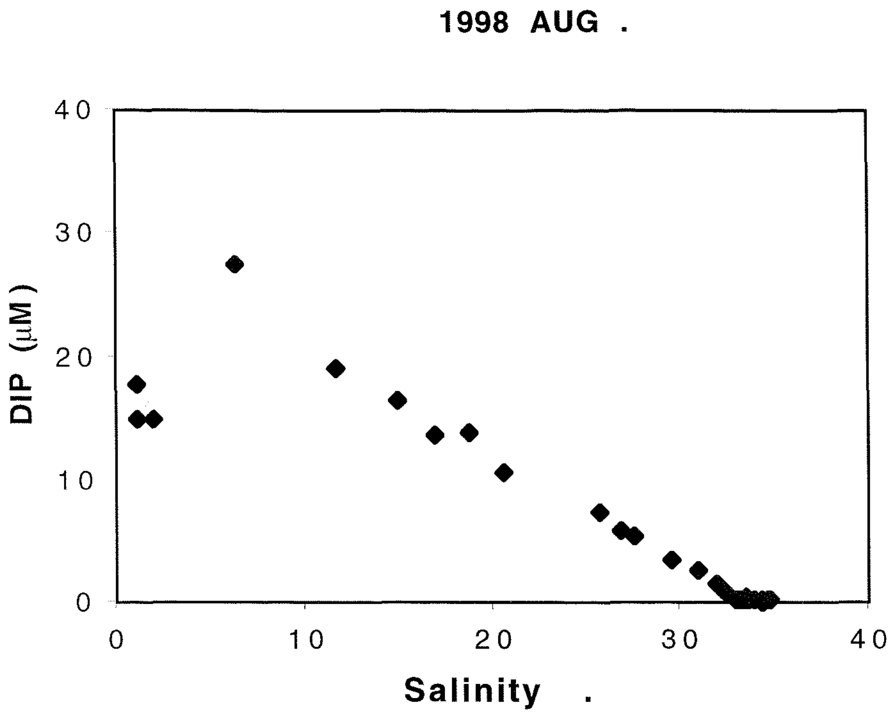


Figure 4.1 An example of DIP- Salinity relationship in the system

2. **DIN** (NO_3^- + NO_2^-): the distributions of the concentrations of dissolved inorganic nitrogen with respect to salinity tend to be conservative within the system. There appears to be no significant influence from the sewage discharges. When the phytoplankton bloom occurred the DIN concentrations were below detection limit at high salinity waters (salinity > 33), which reflected the significant biological activity in those waters.

3. **Si**: the distributions of the concentrations of dissolved silicon with respect to salinity are conservative within the system throughout the year and no significant influence from sewage discharges can be observed. The seasonal variation of Si is similar as DIN.

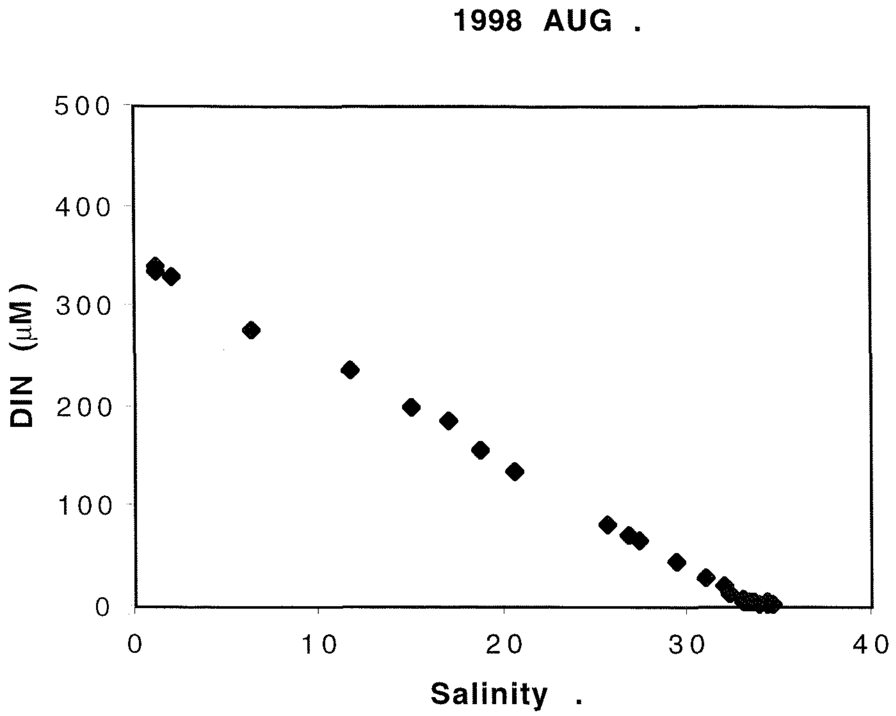


Figure 4.2 An example of DIN- Salinity relationship in the system

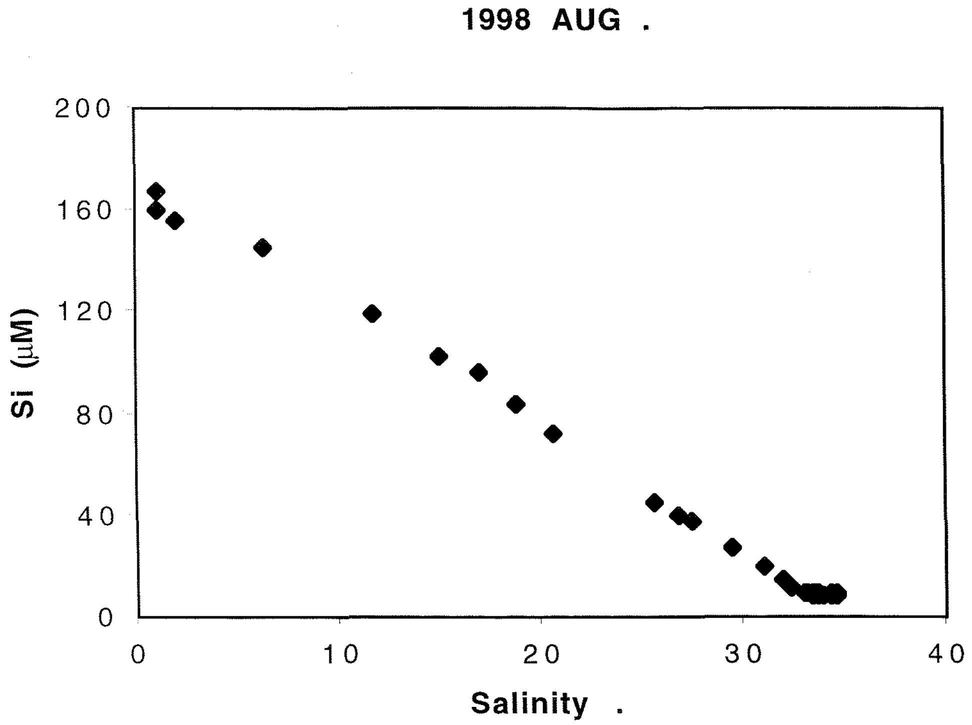


Figure 4.3 An example of Si-Salinity relationship in the system

4. **DOP**: patterns of distributions of the concentrations of dissolved organic phosphorus were generally variable in the system. Concentrations were often low, and rarely exceeded 5μM. In June 1998 and September 1998, two high concentrations (20 μM and 17.3 μM), were obtained at the Dockhead and Itchen Bridge sites, respectively. Such a large peak of DOP concentration was also observed in the SONUS study (July 1996, the Rail Bridge site, 17.6 μM) (Hydes and Wright, 1999). Williams (1996) suggested that the sources of DOP in water column may consist of a combination of the following sources: 1) advection of material into the area; 2) immediate biological supply of material from organisms in the water column; 3) supply of material to the water column from the sediments. Statham (pers.com.) suggested that most of the DOP in the water column is derived from the phytoplankton in estuarine and coastal waters, and particularly just after / about the time of peak biomass. Williams (1996) also revealed that DOP in the water column can increase from phytoplankton cell exudates and excretion after the phytoplankton bloom. In the Southampton Water system the phytoplankton bloom normally occurs in later May or early June. Hence, these high concentrations of DOP in the water column after the phytoplankton blooms may be expected. Further work is needed to explain why this phenomenon only occurs at few sites rather than the whole system.

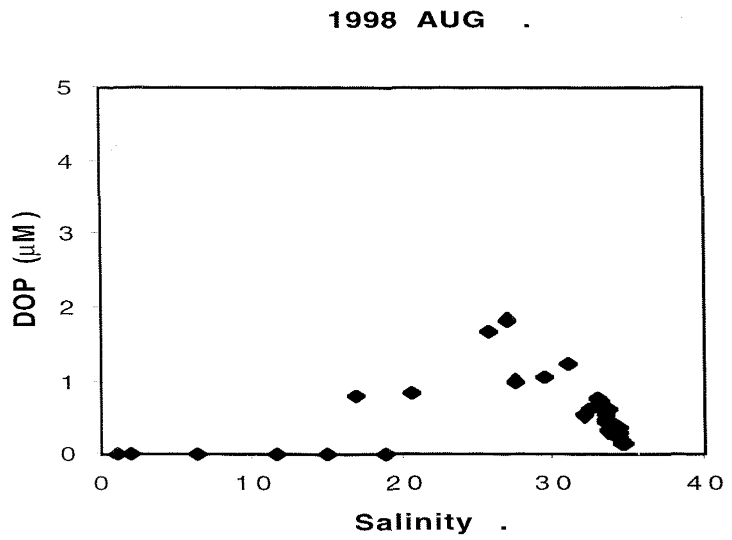


Figure 4.4 An example of DOP - Salinity relationship in the system

5. **PTP**: the concentrations of particulate phosphorus in water column PTP (c) and phosphorus on the particle PTP (m) generally all decreased when the salinity increased along the estuary. Similar phenomenon was also observed by van Beusekom and Brockmann (1998) in the Elbe Estuary. If the particle population is consistent down estuary, this phenomenon implies that: 1) in low salinity waters where there are high DIP inputs and high DIP concentrations in the water column, the particles appear to sorb the DIP in the water column and become "saturated" with phosphorus. When the particles "saturated" with phosphorus were transported to low DIP and high salinity waters phosphorus on the particles is released and the concentration of PTP(m) decreased. 2) the riverine particles buried before they reached the high salinity water and the particles in the high salinity waters were mainly from the sediment resuspension, the detritus of phytoplankton or offshore waters. The mixing with these low phosphorus content particles decreased the concentrations of PTP(m) in the high salinity waters. If it was caused by the first processes, the concentration of DIP in high water ought to increase due to the release of phosphorus. But the data of DIP from the surveys shows conservative mixing in the high salinity waters, which implied the second process was more likely the dominant one. The significance of particles in phosphorus cycling in the system is estimated and discussed in Section 4.3. Figure 4.5 shows the proportion of phosphorus in the water column in the system (Calshot buoy site and Portswood sewage discharge site as the examples for seaside and upstream side of the system ,respectively). DIP is dominant on the upstream side while DOP and PTP are important on the sea side.

6. **Chl *a* :** the concentrations of Chl *a* were generally homogeneous throughout the estuary at most times of the year except during the phytoplankton bloom season (June and August in 1998) when the concentrations of Chl *a* in high salinity waters (salinity > 33) increased from normally 1 μg/l up to 25 μg/l reflecting the biological activity in those area.

Figure 4.5 Proportion of phosphorus in the water column in the system

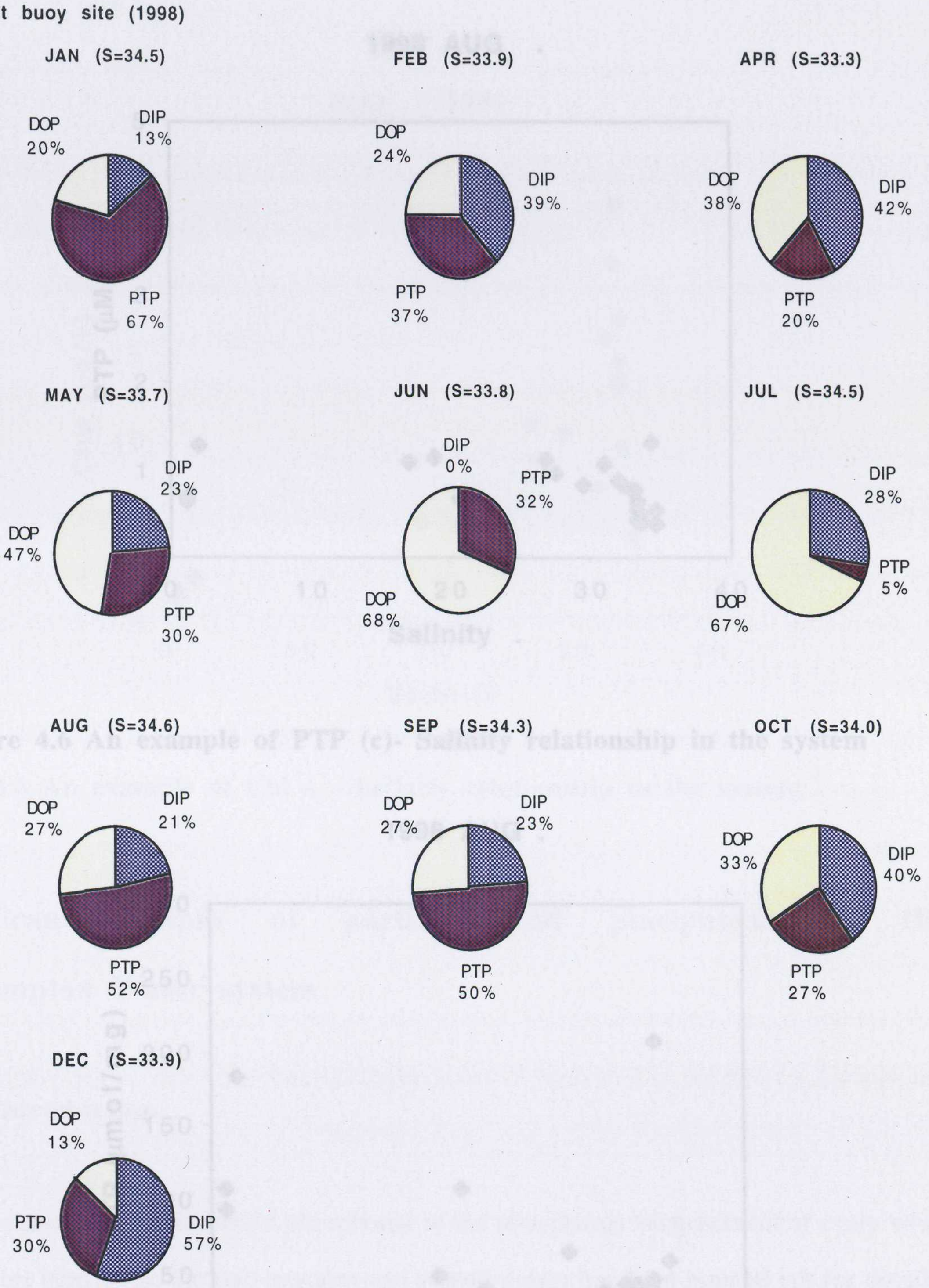


Figure 4.5 (cont.) Proportion of phosphorus in the water column in the system

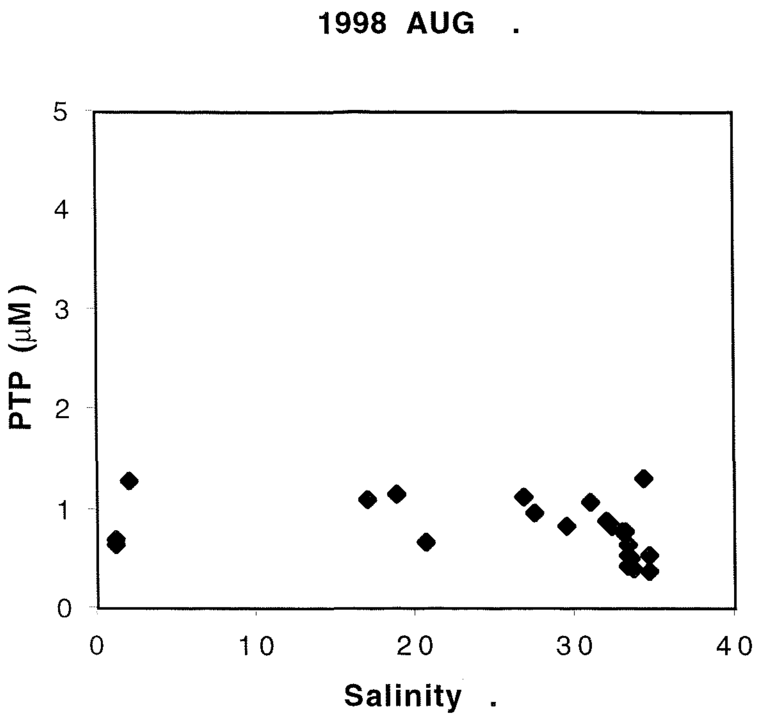


Figure 4.6 An example of PTP (c)- Salinity relationship in the system

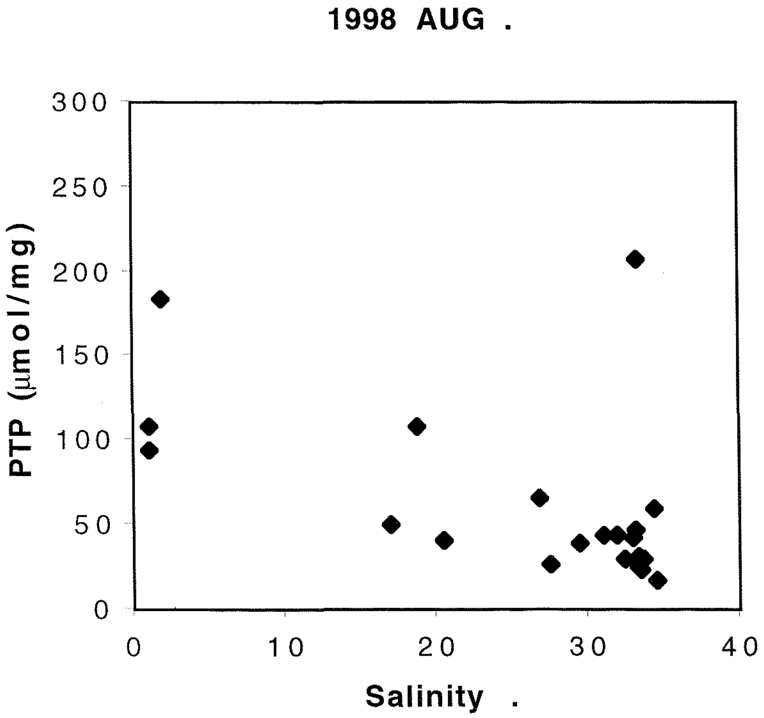


Figure 4.7 An example of PTP(m)-Salinity relationship in the system

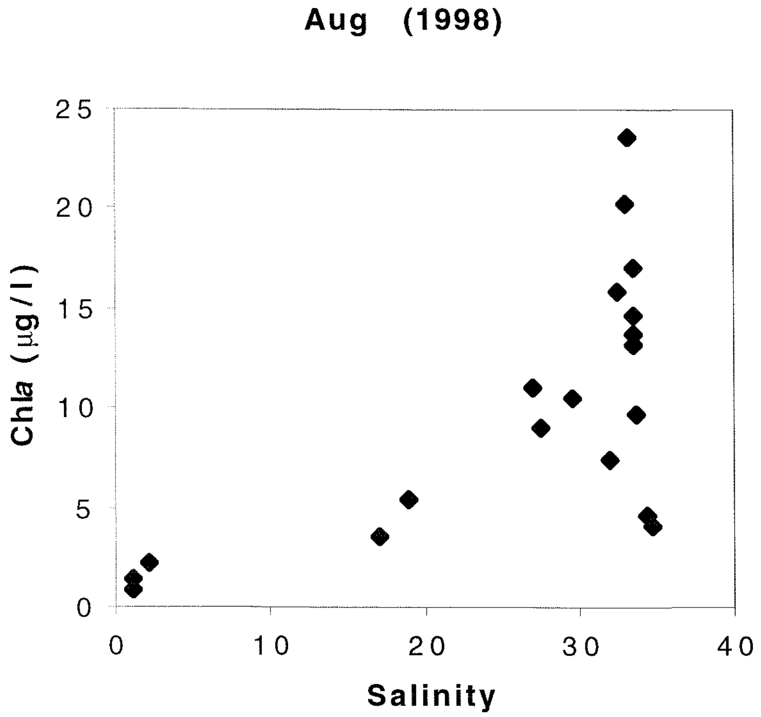


Figure 4.8 An example of Chl *a* - Salinity relationship in the system

4.3 Transformation of particle-bound phosphorus in the Southampton Water system

4.3.1. Introduction

The importance of particle-bound phosphorus to the phosphorus biogeochemical cycle when particles are transported through estuarine and coastal waters has been pointed out for decades (e.g. Froelich, 1988; Conley *et al.*, 1995). It has been observed that the concentrations of dissolved inorganic phosphorus in some turbid estuaries with short residence times and low biological activity were influenced by suspended sediment concentrations (Pomeroy *et al.*, 1965; Froelich, 1988). Phosphorus contained in the suspended particulate matter in estuarine waters are derived from many sources, including phytoplankton production (Fisher *et al.*, 1988), seston of landward and / or seaward origin (Kaul and Froelich, 1984), resuspension of surface sediments (Biggs *et al.*, 1983), shoreline erosion (Biggs *et al.*, 1983) and benthic production of seagrasses and algae (Boynton *et al.*, 1982). There have been several investigations, at various spatial and temporal scales, of particulate phosphorus distributions in estuarine waters (e.g. van Bennekom *et al.*, 1978; Sharp *et al.*, 1982). However, little information is available concerning the partitioning of phosphorus between inorganic and organic fractions (Froelich, 1988; Lebo, 1991).

Recent studies have shown that a significant fraction of biologically available inorganic phosphorus present in estuarine and coastal waters is held in particulate suspended matter in the water column (Lucotte and d'Anglejan, 1983; Lebo, 1991; Conley *et al.*, 1995). Surface adsorption on hydrous ferric oxide precipitates has been suggested as the main cause of phosphorus bounding to particles and subsequently nonconservative behaviour of phosphorus in estuaries (Froelich, 1988; Fox, 1991; Conley *et al.*, 1995; van Beusekom and Brockmann, 1998). Within the salinity gradient of the Delaware estuary, USA, particulate phosphorus associated with iron oxides and aluminium oxides decreased with increasing salinity, suggesting that DIP concentrations in the water column may be partly buffered by desorption from aluminium and iron oxide phases (Lebo, 1991). In the St Lawrence estuary, Canada, a significant portion of the particle-bound phosphorus is also observed to adsorb on iron hydroxide precipitates and is retained within the turbidity maximum of the estuary (Lucotte and d'Anglejan, 1983). By contrast, in Chesapeake Bay, USA, due to the low capacity of particles to adsorb phosphorus through interactions with iron, the biological processes in the bay were much more important to the biogeochemical cycle of phosphorus (Conley *et al.*, 1995). The study of the Elbe estuary, Germany, (van Beusekom and Brockmann, 1998) concluded that the ambient salinity in the estuary influenced the adsorption on and desorption from Fe (oxy) hydroxides processes and sets an upper limit to the capacity of Fe (oxy) hydroxides to adsorb inorganic phosphorus. In fresh water this capacity is about two times higher than in coastal water (van Beusekom and Brockmann, 1998). They also suggested during the remineralization of particulate organic phosphorus inorganic phosphorus is not directly released into solution but first adsorbed onto Fe(oxy) hydroxides. Only when the adsorption capacity — set by the ambient salinity — is exhausted, is the inorganic phosphorus released to the solution.

In the Southampton Water system, the SPM input is small and DIP concentration is high compared to the other systems. The particles in low salinity waters near the sewage works are apparently phosphorus saturated. The transformation of these particles when they are transported through the system is important to the phosphorus cycle in the system and has not been diagnosed. It may be useful to know the distribution of particulate phosphorus speciation and therefore to interpret the transformation and distinguish the source of particles in different parts of the system (Conley *et al.,* 1995; van Beusekom and Brockmann, 1998). The information taken from the SPEPs data on particles supply a useful tool for these tasks.

4.3.2. Sampling and methods

Sampling:

Samples were collected during the April 1999 survey of this study. The sampling sites were the same as for the water column chemistry surveys shown in Appendix B. The dissolved nutrient samples were taken by the same method as in Chapter 3. For the speciation of particulate phosphorus, the samples were collected via a bucket which was fed by the launch's deck wash and filled a 5 litre plastic bottles for subsequent filtration. Filtration was done under low vacuum (< 200mm Hg) through GF/F filter (Whatman) of 47 mm diameter as suggested by Ormaza-Gonzalez (1990). The filtration of most of the samples were carried out onboard the vessel just after the sampling. When the filtration could not be finished during the survey, it was completed in the lab just after returning to Southampton Oceanography Centre. The bottles of sample were shaken to make the sample homogeneous before the filtration. The volume of water (1 l ~ 1.5 l) filtered at each site depended on the suspended load of the samples at the station. Duplicate filter wereproduced from each individual water sample. One was used to measure the suspended particulate matter and total particulate phosphorus of the sample, while another was used to determine the speciation of particulate inorganic phosphorus. The glass fibre filters were used and prepared by heating at 500°C for 2 hours in a muffle furnace and weighed before the survey. The filters were placed in a marked clean Petric dish. The filters were rinsed with ultrapure water just after the filtration to minimise the interference caused by the salt in the water.

In this study due to the low SPM concentration in the system, it is difficult to obtain enough particles to measure the concentrations of PIP (particulate inorganic phosphorus) directly by the Aspila method (1976) at the same time as determining the speciation of particulate inorganic phosphorus by the SPEPs method. However, van Beusekom and Brockmann (1998) have reported that 93% of the PIP measured by the traditional Aspila *et al.* (1976) combustion method could be recovered during their sequential extraction. In this study the sequential extraction procedure was the same as van Beusekom and Brockmann (1998). Hence, in this study the sum of the sequential extraction steps which was assumed to be 90% PIP was used to estimate the concentrations of PIP. POP (particulate organic phosphorus) was calculated from the difference between PTP and PIP.

Methods:

Salinity, dissolved nutrients, suspended particulate matter (SPM) and particulate total phosphorus (PTP) of the samples were measured as described in Chapter 3. The investigation of speciation of particulate inorganic phosphorus was carried out using a sequential extraction method based on Psenner and Pucsko(1988) and modified by Agemian (1997) at room temperature. The scheme comprises the extraction of loosely adsorbed phosphorus with NaCl, of Fe (oxy) hydroxide bound phosphorus with bicarbonate-dithionate, of reduction resistant phosphorus (polyphosphate) with NaOH, and of Ca-bound phosphorus with HCl. The composition of the extractants and the extraction times are given in Table 4.2. The details of the sequential extraction procedure can be found in Chapter 2.

The amount of Fe(oxy)hydroxides removed by reduction with dithionite (Fe_{BD}) was measured by analysing the Fe content of the extractant on an atomic absorption spectrophotometer (Pye Unicam Ltd., Model SP9). A 1000 μg/ml iron standard solution (Merck Com.) in 1 M HNO_3 was diluted to make 100 μg/ml standard solution in 2 % v/v HNO_3 as a working standard. This standard was diluted to a standard series as (0, 2.0, 5.0, 10.0, 20.0 μg/ml). The matrix influence was tested by comparing the blank of 2 % v/v HNO_3 and BD reagent (0.11M $Na_2S_2O_4$, + 0.11M $NaHCO_3$). There was no significant difference observed, so the standards were in 2 % v/v HNO_3 solution. A calibration curve was constructed. From the calibration curve the concentrations of the sample can be calculated.

The sum of the sequential steps was assumed to equate to 90% PIP based on the conclusion of van Beusekom and Brockmann (1998) using the same sequential extraction procedure. POP was calculated from the difference of PTP and PIP.

Table 4.2 Sequential extraction of solid phase inorganic phosphorus in particles. After Agemian (1997).

	Extractant	Volume of extractant (ml)	Extraction time	Phase extracted
filter	0.5M NaCl, pH 7	5	1 hour	loosely sorbed DIP
residue	BD reagent (0.11M $Na_2S_2O_4$, + 0.11M $NaHCO_3$)	5	1 hour	Fe-bound phosphorus
residue	0.1M NaOH	5	18 hour	Polyphosphate + DIP from clay minerals
residue	0.5 M HCl	5	1 hour	Ca-bound phosphorus

4.3.3 Results and discussions

The detailed results can be found in Appendix E.

POP, which was calculated from the difference between PTP and PIP, was the dominant phosphorus species on the particles at the seaward end of the estuary (82%), decreasing to 36% upstream (Figure 4.9). Iron bound phosphorus (extracted with BD reagent) dominated the particulate inorganic phosphorus fractions at most sites in the system, except where at some sites loosely absorbed phosphorus (extracted with NaCl) and Ca-bound phosphorus (extracted with HCl) were most important. The contribution of Fe -bound phosphorus increased upstream from 13% of PIP at the Hamble Point site (salinity was 31.9) to 60% at the Portswood sewage works site (salinity was 8.8). The contribution of loosely adsorbed P to PIP generally increased seaward, although the highest (39%) at the Hound Site (salinity was 30) and lowest (13%) at the Weston Shelf site (salinity was 31) were all in high salinity waters. The contribution of the polyphosphate fraction (extracted with NaOH) is generally constant through the system, with a range between 6% (salinity was 4.7) and 14% (salinity was 30.8). The Ca-bound fraction (extracted with HCl) increased seaward from 16% (salinity was 17.4) to 56% (salinity was 31.9). All distributions of forms of inorganic phosphorus and its contributions to PIP are shown in Figure 4.10 and Figure 4.11.

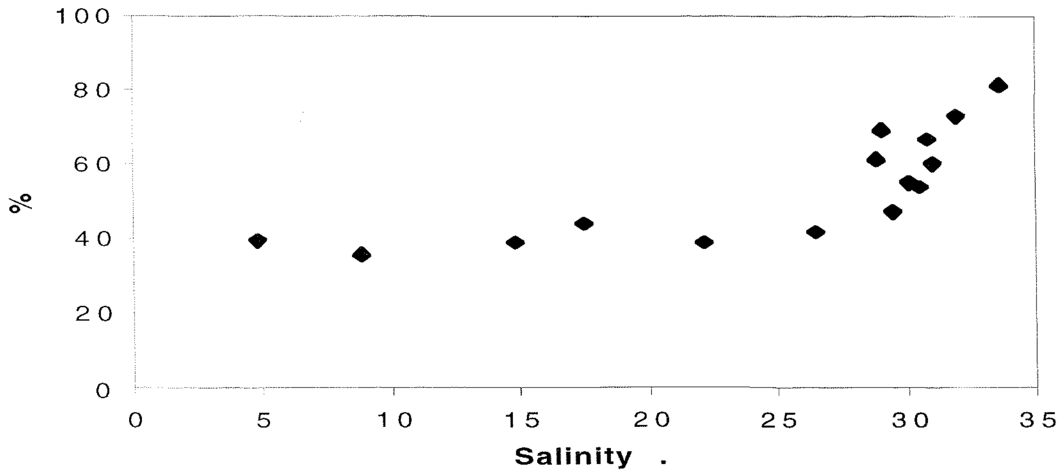


Figure 4.9 The distribution of POP in the system

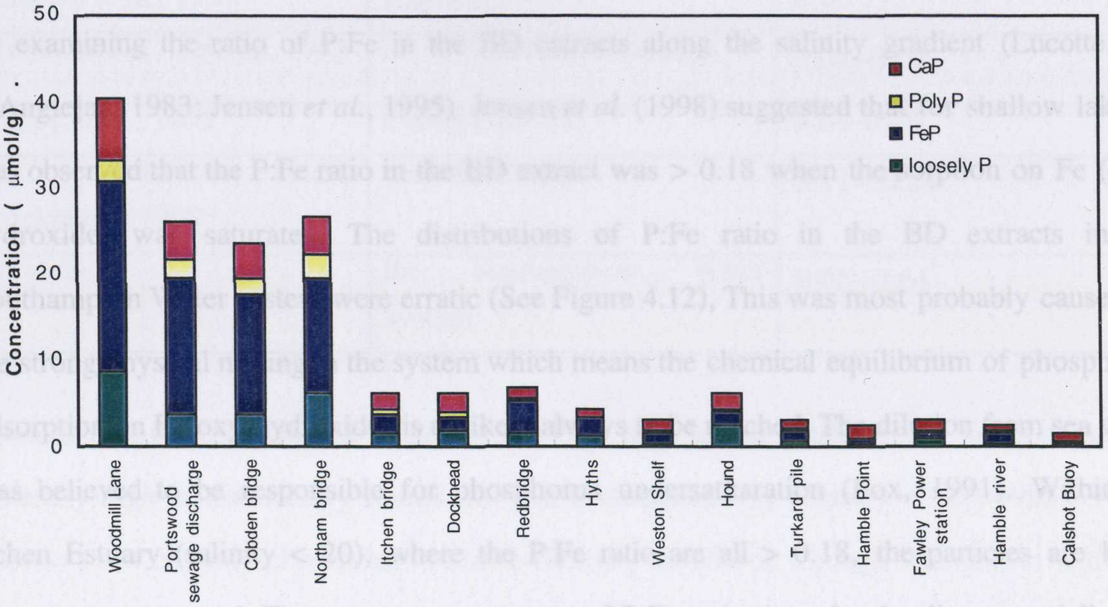


Figure 4.10 The distributions of forms of inorganic particulate phosphorus (April 1999).

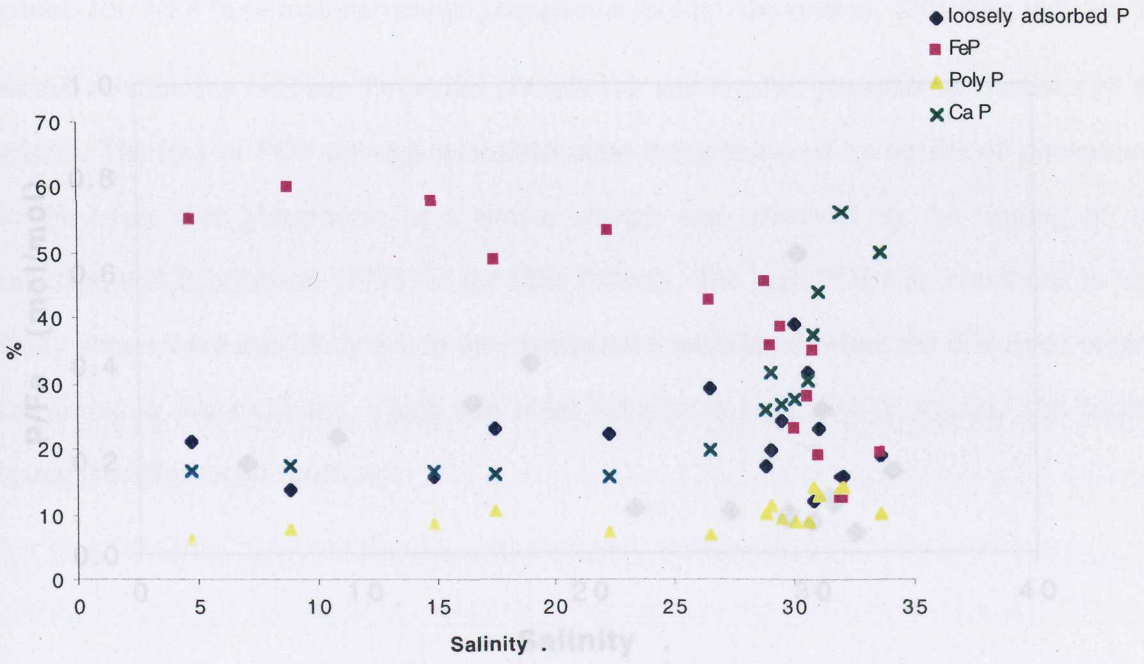


Figure 4.11 The contribution of forms of inorganic particulate phosphorus.

An index of the capacity of suspended particles to transfer DIP from the waters to the particulate matter, or vice versa, during transport across the land-sea interface can be evaluated by examining the ratio of P:Fe in the BD extracts along the salinity gradient (Lucotte and d'Anglejan, 1983; Jensen *et al.*, 1995). Jensen *et al.* (1998) suggested that for shallow lakes it was observed that the P:Fe ratio in the BD extract was > 0.18 when the sorption on Fe (oxy) hydroxides was saturated. The distributions of P:Fe ratio in the BD extracts in the Southampton Water system were erratic (See Figure 4.12), This was most probably caused by the strong physical mixing in the system which means the chemical equilibrium of phosphorus adsorption on Fe(oxy)hydroxides is unlikely always to be reached. The dilution from sea water was believed to be responsible for phosphorus undersatuaration (Fox, 1991). Within the Itchen Estuary (salinity < 20), where the P:Fe ratio are all > 0.18, the particles are likely phosphorus saturated. The apparent two groups of P:Fe ratio data also implies potentially two sources of particle (riverine, and marine resuspension) which may have different P:Fe ratio.

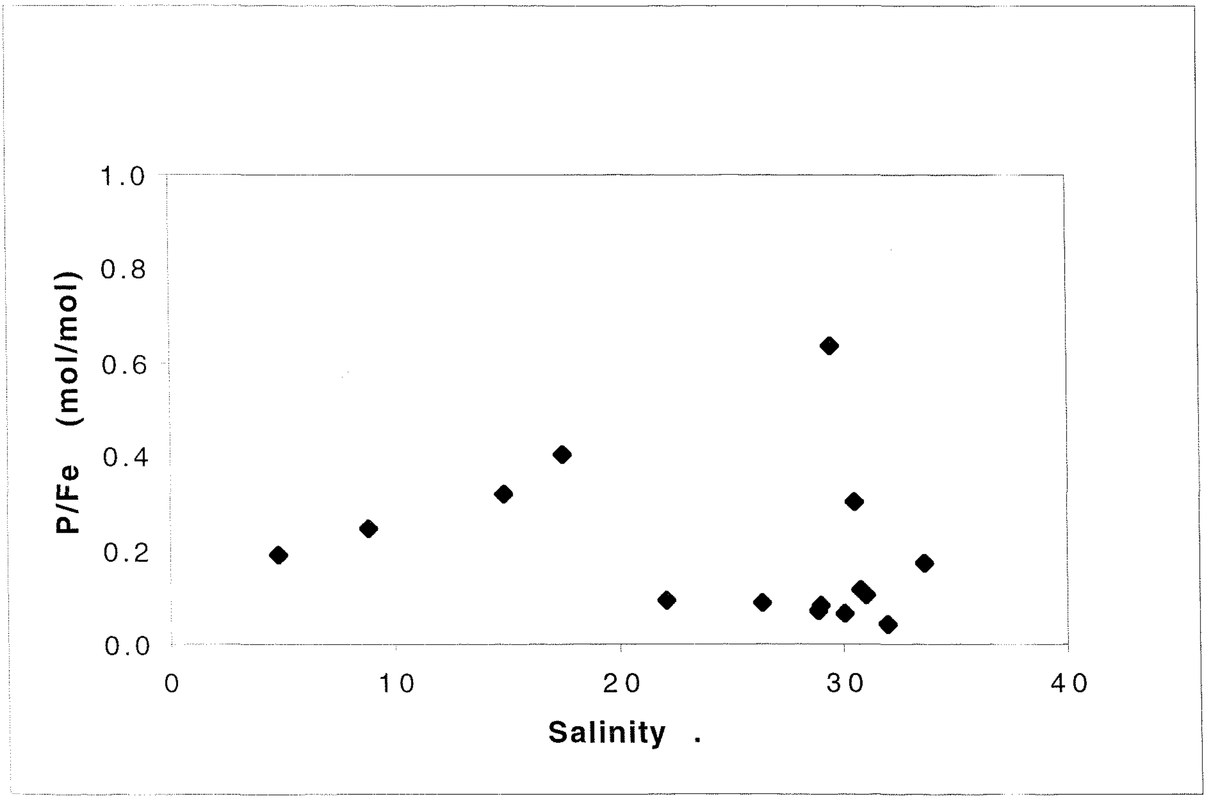


Figure 4.12 The distribution of P : Fe in BD extracts of particles

Table 4.3 Comparison of P:Fe in this study with other water systems, in BD extracts.

Source	Water system	P:Fe
Williams *et al.*, 1976	Lake Erie	0.03
Lucotte and d'Anglejan, 1983	the St. Lawrence Estuary	0.04~0.08
Conley *et al.*, 1995	Chesapeake Bay	0.09-0.48
van Beusekom and Brockmann, 1998	the Elbe estuary	0.11~ 0.24
this study	the Southampton Water system	0.05~0.64

Compared to the other aquatic systems, the P:Fe ratio in the Southampton Water system is generally high in low salinity waters, as with Chesapeake Bay (Conley *et al.*, 1995), which implies a low capacity of particles to adsorb further phosphorus through interactions with iron when it enters the high salinity waters.

The organic phosphorus fraction and the Fe-bound phosphorus fraction showed opposite distribution with salinity (Figure 4.13). The sum of both fractions remains constant and accounts for 70±9 % of total particulate phosphorus through the system. This may indicate the potential relationship between Fe-bound phosphorus and organic phosphorus fractions in the particles. The loss of POP through remineralisation being balanced by uptake of phosphorus onto Fe oxide sites phosphorus as a similar change was observed by the finding of van Beusekom and Brockmann (1998) in the Elbe Estuary. The high POP concentrations in high salinity waters were also likely due to the resuspended particle adsorbed the dissolved organic phosphorus in water column, which was observed high in high salinity waters, and became organic phosphorus rich particles.

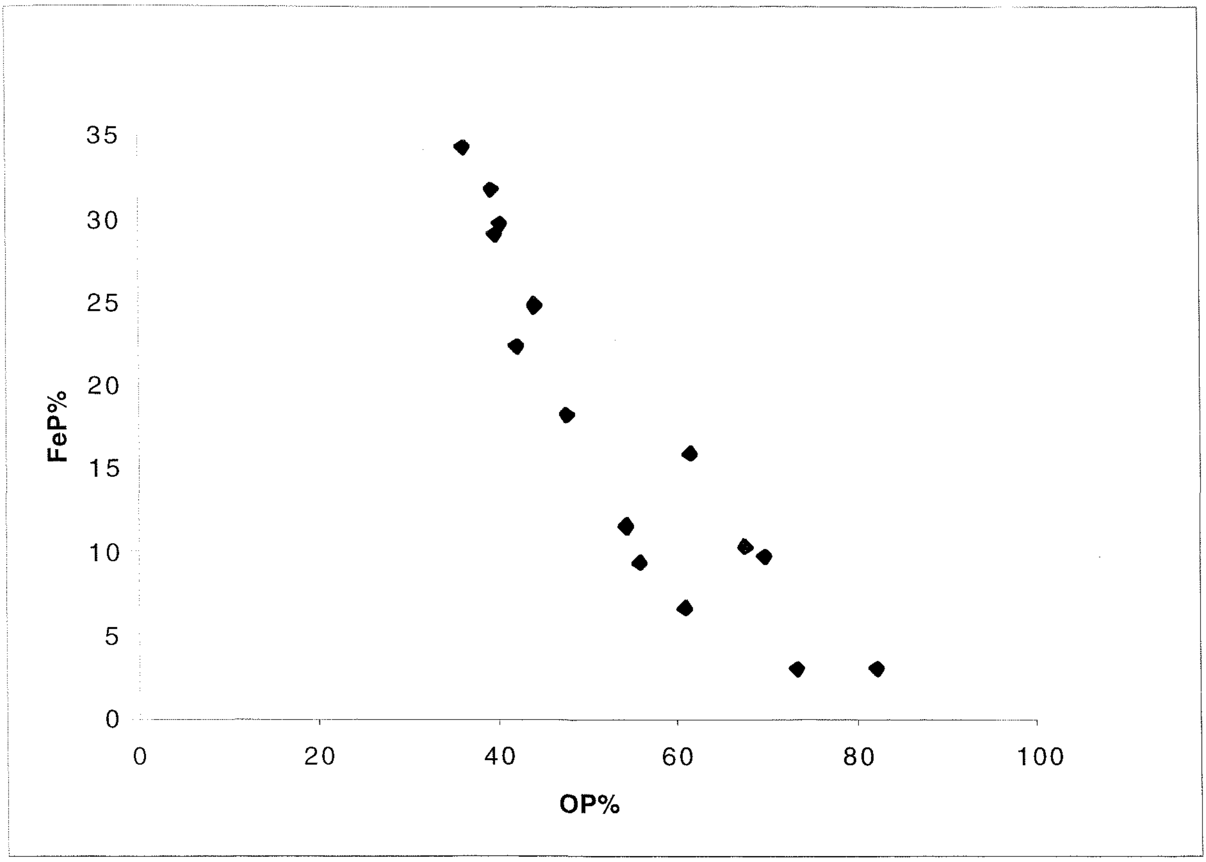


Figure 4.13 The comparison of the contributions of POP and Fe-bound phosphorus on the particles

4.4. Dissolved inorganic phosphorus pattern in the Southampton Water system — application of the K_d model

4.4.1. Introduction

The biogeochemical processes involving phosphorus in estuaries, which govern the levels of dissolved phosphorus in the water column and its fluxes to coastal seas and oceans, have not been well elucidated and rationalised. This is due to the complicated mix of hydrological and biological factors. One theme in estuarine research has been the behaviour of dissolved inorganic phosphorus, especially in reference to the ability of particles to "buffer" phosphorus concentrations in water column (Sharp *et al.*, 1982; Froelich, 1988). Froelich (1988) outlined the geochemical principles underling this complex particle-water interactions and Fox (1989) presented a thermodynamic model in terms of solid state activity coefficients relating to iron and phosphorus. However, a simple and practicable model such as that developed by Prastka *et al.* (1998) is needed to rationalise the specific mechanism and reactions at the particle-water interface on the transport of dissolved inorganic phosphorus through estuaries (Froelich, 1988; Conley *et al.*, 1995).

Solid-solution interactions of the elements are often interpreted and quantified in terms of a conditional particle-water partition coefficient, K_d (e.g., Olsen *et al.*, 1982; Morris, 1986; Prastka *et al.*, 1998), defined as

$$K_d = M_p / M_s$$

where M_p (w/w) and M_s (w/v) are the element concentrations in the particulate and solution phases, respectively. Such ratios have been proven to be useful in rationalising elemental removal reactions and residence times in the coastal and open ocean (e.g., Fisher, 1986; Morris, 1986; Prastka *et al.*, 1998; Wen *et al.*, 1999). However, the determination of K_d values in estuarine and coastal waters has been criticised for failing to discriminate between different solid phase associations (Balls, 1989; Turner *et al.*, 1993), particularly the solid component available for exchange processes between the carrier phase and solution (Martin *et al.*, 1987). The K_d model also assumes an instant equilibration and steady state, which means it is not a kinetic model. The application of a K_d model is often additionally limited by using the average of the data in the estuary where there is normally a big spatial variation of the element through the estuary.

K_d has been widely used to interpret the solid-solution interactions of metals (Morris, 1986; Wen *et al.*, 1999). Recently a simple K_d model presented by Prastka *et al.* (1998) appears to be able to rationalise different patterns of phosphorus behaviour in the estuary and estimate the removal of dissolved inorganic phosphorus in an estuary. This model is simple and practicable in contrast to other complex approaches (e.g. Fox, 1993; Turner, 1996), although some assumption in the model need to be treated very cautiously. It has been applied in the Humber and other estuaries (Prastka *et al.,* 1998). Here the K_d model is applied to the data collected from the surveys of this study to attempt to predict the patterns of dissolved inorganic phosphorus in the Southampton Water system and estimate the likely significance of the removal or addition of DIP in the water column.

The K_d definition for phosphorus is given by Prastka *et al.* (1998) as follow [equation (1)]:

$$K_d = P_{es} / C_{es} \tag{1}$$

where

P_{es} : the average concentration of particulate phosphorus (PTP) in the estuary (μmol/g);

C_{es}: the average concentration of DIP in the estuary (μM).

Assuming the phosphorus input to the low salinity region is equal to the sum of the estuarine DIP and the estuarine particulate phosphorus after equilibration reaction has occurred, and also that the higher salinity water component is insignificant.

$$C_r + (P_r S_r) + (P_{UP} S_{UP}) = C_{es} + (P_{es} S_{es}) \tag{2}$$

where,

C_r: river DIP concentration (μM);

P_r: river particulate phosphorus concentration (μmol/g);

S_r: river suspended solid concentration (mg/l);

P_{UP}: resuspension phosphorus concentration (μmol/g) in estuary;

S_{UP}: resuspension solid concentration (mg/l) in estuary ;

S_{es}: estuarine suspended solid concentration (mg/l);

Assume that the suspended solid in the estuary is only from river and resuspension:

$$S_r + S_{UP} = S_{es} \tag{3}$$

Considering the contribution of resuspension to the particulate phosphorus concentration in the estuary, a parameter α is introduced as equation (4):

$$\alpha = P_{UP} / P_{es} \tag{4}$$

This parameter, α, describes the fractional concentration of exchangeable phosphorus on the resuspended particles (P_{UP}) before equilibration reactions, relative to this concentration following equilibration reactions (P_{es}). Morris (1986) suggested an α value of $\alpha = 0.5$ for trace metals while Prastka *et al.* (1998) used an α value of 0.9 basis that sediments continuously resuspended in the turbidity maximum zone of an estuary will tend to saturation. The value of α has been determined arbitrarily, although the variation of α was tested by Prastka *et al.* (1998) and showed no signs of significant influence on the result. However, the direct measurement of α was recommended by Prastka *et al.* (1998).

Combine equation (1) ~ (4) to yield equation (5):

$$\Delta DIP = C_r - C_{es} = [(C_r K_d S_{es}) - (\alpha K_d C_R (S_{es} - S_r)) - (S_r P_r)] / [1 + (K_d S_{es}(1-\alpha) + (\alpha K_d S_r)] \quad (5)$$

The removal of dissolved inorganic phosphorus can be calculated from equation (6)

$$\%DIP\ removal = (\Delta DIP / C_R) \times 100 \quad (6)$$

Prastka *et al.* (1998) concluded that as C_r increases, estuaries gradually move from being sources of DIP to sinks for DIP. Variations in S_{es} are also an important factor in governing the removal of phosphorus as they mentioned. While the exact value of removal varies with the values of the various parameters chosen, the general pattern of behaviour does not change. Variations in S_r have, in general, little effect, since in most cases systems are considered in which the total suspended load is dominated by estuarine resuspended sediment. A key factor controlling the extent of estuarine DIP removal is the riverine DIP concentration.

Many K_d values in the literature (e.g. van Bennekom *et al.* 1978; Edmond *et al.* 1981; Laslett, 1993) were estimated from the total particulate phosphorus concentrations in the estuaries. Prastka *et al.* (1998) argued that total particulate phosphorus is an inappropriate term for estimating K_d. A comparison of K_d estimate of the Humber River using total particulate phosphorus concentrations as well as inorganic particulate phosphorus concentrations (measured by Aspila method, same as Chapter 2) was done. An appropriate value for K_d estimated by inorganic particulate phosphorus concentrations is found to be only 25-50% of the K_d value estimated by the total particulate phosphorus. The data from sequential extraction scheme of Ruttenberg (1992) also showed that only 5% of total particulate phosphorus is exchangeable. Hence, field campaigns should measure both labile and total particulate phosphorus, and the K_d value should consider the fractions of phosphorus in the particles. The fractions of phosphorus from the sequential extraction protocol on the particles are considered to estimate the K_d value in this study.

The results of a K_d model (Prastka *et al.*, 1998) demonstrated that the concentrations of suspended particulate matter in estuaries are an important regulator of DIP behaviour. The modification of suspended solids via dredging and land reclamation activities in estuaries can alter the DIP removal capacity. As far as environmental management is concerned, reduction in the DIP loading to estuaries may promote desorption of DIP from relict high phosphate sediments deposited under periods of higher riverine DIP inputs, if phosphorus behaviour in the estuary follows the K_d model (Prastka *et al.*, 1998).

The comparison of C_R, S_{es}, S_R, K_d, P_R in the K_d model in this study and with other estuaries is shown in Table 4.4. The data for other estuaries in Table 4.4 are taken from the summary of Prastka *et al.* (1998), and the values of K_d were all calculated using the concentrations of total particulate phosphorus. Compared to the other aquatic systems, the Southampton Water system has high DIP river input and low riverine particle input. The value of K_d in the Southampton Water system was general low, although in summer the value of K_d in high salinity waters can be high due to the depletion of DIP causing by the phytoplankton bloom (details of seasonal and spatial variation can be found in Appendix F). The value of C_R in Table 4.4 was taken from the Department of Environment river survey data (1997). Other data are from the surveys of the current study. Due to the lack of river data for S_R, and P_R values were taken as the mean value of the data collected from the surveys of this study where the salinity was below 0.5.

Table. 4.4 The comparison of C_r, S_{es}, S_r, K_d, P_r in the K_d model in this study and with other estuaries

Estuary	C_r (µM)	S_{es} (mg/l)	S_r (mg/l)	P_r (µmol/g)	K_d (l/kg)
Southampton Water	3.71~15.3 (high)	2.60~83.4 (low)	5.4~14.6 (lowest)	61.5~119 (high)	456~842000* (low)
Humber	6-40	1200	60-200	75-110	39000±6696
Gt. Ouse	8	125	75	20	2500
Amazon	0.5	400	130	34	42000
Zaire	0.7	NA	32	32	38000
Tay	0.7	18	33	96	77500

* In order to be able to compare to other estuaries, this value is derived from the data of PTP rather than PIP, which is used in Table 4.5. The mean value of K_d in the Southampton Water system is 9600.

The application of the K_d model in this study was carried out to

1) examine the fate of the riverine derived particles in the Itchen Estuary;

2) study the importance of resuspension of surfacial sediment in Southampton Water on DIP concentrations.

A critique of the K_d model is then provided.

4.4.2 Dissolved inorganic phosphorus behaviour in the low salinity waters in the River Itchen --- application (I) of the K_d model

1) the value of α

In this study the value of α is derived from the data of particle and sediment analyses and is estimated by the concentrations of particulate inorganic phosphorus and inorganic phosphorus in the surficial sediment (depth < 2cm).

The value of α can be estimated from eqn (7) which assumes that the concentration of phosphorus on the resuspended particles is the same as the concentration of phosphorus on the solid phase in the surfacial sediment at the same site:

$$\alpha = SIP / (PIP + SIP) \qquad (7)$$

where: SIP is inorganic phosphorus in the surface sediment and PIP is particulate inorganic phosphorus in the water column. The units are all μmol/g.

Table 4.5 Data used for calculation of the α value (from April 1999 survey)

Site	Sal	SPM (mg/l)	DIP (μM)	PTP (μmol/g)	PIP (μmol/g)	SIP (μmol/g)	K_{d1} (l/kg)	K_{d2} (l/kg)	α
Woodmill Lane	0.7	15.6	7.05	74.5	40.1	18.8	10600	5690	0.32
Portswood sewage discharge	4.8	21.6	6.34	45.8	26.2	22.2	7220	4140	0.46
Cobden Bridge	14.8	22.2	10.1	43.2	23.6	23.7	4280	2340	0.50
Hythe Pier	26.4	47.0	1.98	8.60	4.48	11.6	4340	2261	0.72
Weston Shelf	30.8	36.6	1.44	10.4	3.07	11.6	7230	2129	0.79
Turkard Pile	29	32.0	1.57	11.6	3.17	12.1	7400	2017	0.79
Hamble Point	31.9	28.0	0.91	10.5	2.54	12.6	11600	2790	0.83
Fawley Power station	31	29.0	0.84	9.12	3.22	9.88	10900	3828	0.75
Average							7946	3150	0.65

* K_{d1} and K_{d2} are calculated from PTP and PIP respectively.

There was only one survey (April 1999) when all the data required for the estimation of α values are available (for details of the survey see Chapter 3 and Section 4.3). The data used for the estimation of α are shown in Table 4.5. The data reveals that the values of K_d can vary by using PTP or PIP data as mentioned above. The K_{d2} value which is calculated from the PIP data is only about 40% of the K_{d1} value which is calculated from the PTP data. No significant trend of the K_{d1} value occurs along the salinity gradient while the K_{d2} value generally decreases seaward. The value of α generally increases seaward. In this study, 0.32 of α is used when examining the DIP pattern in the Itchen River and 0.6 of α is used to asses the influence of resuspension in the system in later Section.

2) The behaviour of dissolved inorganic phosphorus in the low salinity waters of the Itchen Estuary

The K_d model was used to examine the behaviour of dissolved inorganic phosphorus in the low salinity waters of the Itchen Estuary in this section.

Considering that the K_d model is only applicable to a low salinity water where the mixing of other water masses can be ignored (Morris, 1986) and the interaction between riverine particle and water phase normally happens at low salinity, in this study the waters where salinity is below 2 in the Itchen Estuary are considered only to exam the behaviour of DIP at this freshwater -seawater boundary. The data for the application of the K_d model in this study are shown in Table 4.6. The data for C_r are taken from the Environment Agency (1997, no data is available for 1998 or 1999). No data is available for S_r and P_r from the Environment Agency. The estimations of these data are therefore based on the data collected from the surveys of this study (1998). The data from the site where the salinity is < 0.5 is used. The data of S_{es} and K_d are all derived from the data of surveys of this study (1998) where the salinity is between 0.5 and 2. These data were used to select values of parameters for the model runs.

Table 4.6 Data for the K_d model application

	C_r (μM)	S_r (mg/l)	S_{es} (mg/l)	P_r (μmol/g)	*K_d (l/kg)
Range	9.35~14.5	5.4~21.2	4.6~17.4	61.5~119	5750~34500
Mean	11.2	10.6	8.88	93.9	12700

* K_d is calculated by the data of PTP due to lack of PIP data for the surveys.

In this study different values of riverine component (C_r, S_r, P_r) as well as the value of K_d are tested to examine the pattern of DIP in the Itchen Estuary under different conditions. The results are shown in Figure 4.14. Figure 4.14a shows that within the range of concentration of DIP in the River Itchen (9.35~14.5 μM) the release of DIP from the particles increases when the concentration of SPM in the river increases. If the DIP riverine concentration increases the DIP pattern can be changed from addition to remove. The same pattern can be found in Figure 4.14b, where removal/addition of DIP is examined as a function of phosphorus concentration on the particles. In Figure 4.14c, when the K_d value increases the DIP in the water column is more likely to be removed. From Figure 4.14a, Figure 4.14b and Figure 4.14c within the range of the riverine DIP concentration it can be predicted that only a small amount (< 20%) of removal or addition of DIP is likely to occur.

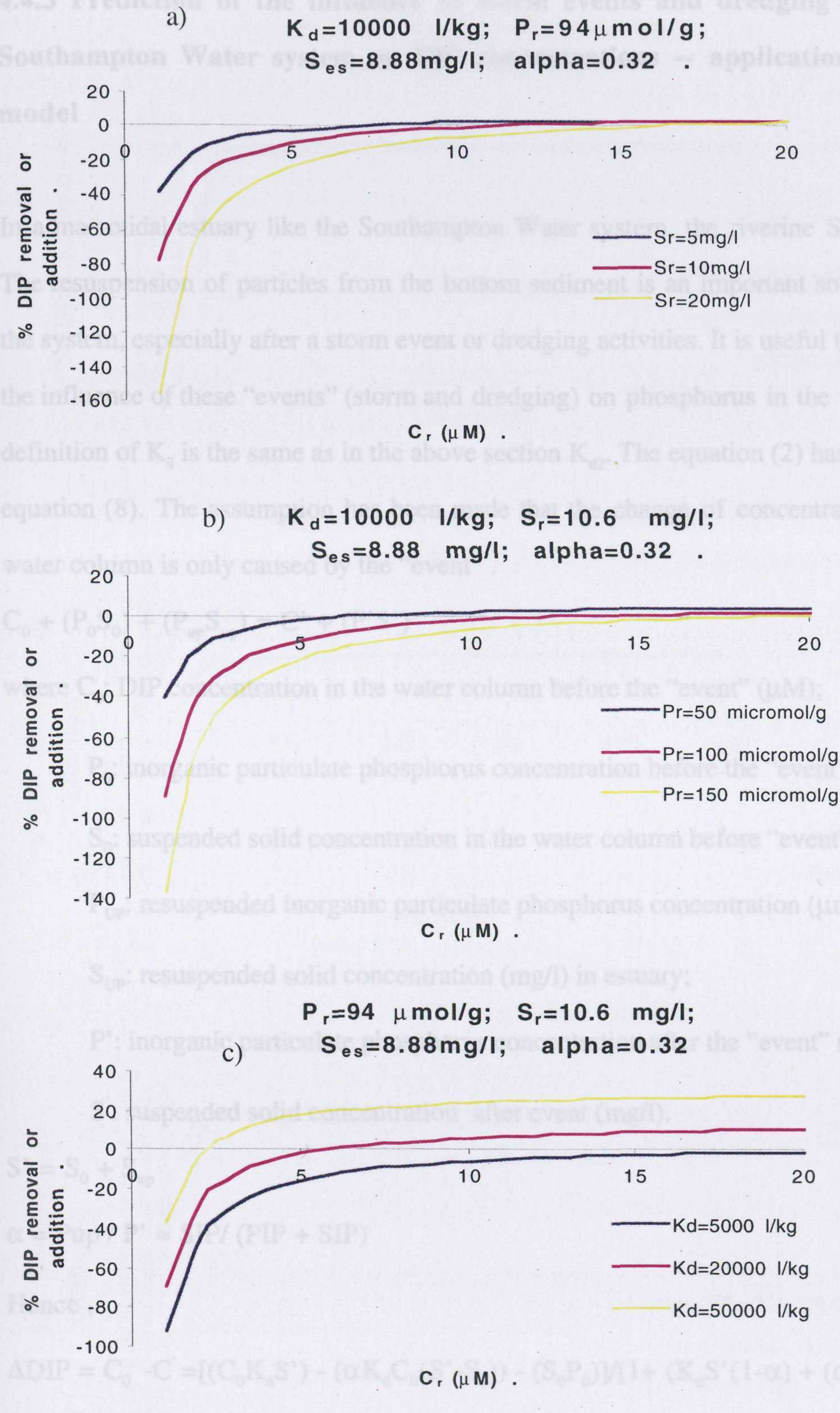


Figure 4.14 The behaviour of DIP in the low salinity waters of the Itchen Estuary using the K_d model, under different conditions (negative values correspond to the DIP release from the particles).

4.4.3 Prediction of the influence of storm events and dredging activities in the Southampton Water system on DIP concentrations -- application (II) of the K_d model

In a macrotidal estuary like the Southampton Water system, the riverine SPM load is small. The resuspension of particles from the bottom sediment is an important source of particles in the system, especially after a storm event or dredging activities. It is useful to asses and predict the influence of these "events" (storm and dredging) on phosphorus in the water column. The definition of K_d is the same as in the above section K_{d2}. The equation (2) has been converted to equation (8). The assumption has been made that the change of concentration of DIP in the water column is only caused by the "event".

$$C_0 + (P_0S_0) + (P_{up}S_{up}) = C' + (P'S') \quad (8)$$

where C_0: DIP concentration in the water column before the "event" (µM);

P_0: inorganic particulate phosphorus concentration before the "event" (µmol/g);

S_0: suspended solid concentration in the water column before "event" (mg/l);

P_{UP}: resuspended inorganic particulate phosphorus concentration (µmol/g) in estuary;

S_{UP}: resuspended solid concentration (mg/l) in estuary;

P': inorganic particulate phosphorus concentration after the "event" (µmol/g);

S': suspended solid concentration after event (mg/l).

$$S' = S_0 + S_{up} \quad (9)$$

$$\alpha = Pup / P' \approx SIP/ (PIP + SIP) \quad (10)$$

Hence ,

$$\Delta DIP = C_0 - C' = [(C_0K_dS') - (\alpha K_dC_0(S'-S_0)) - (S_0P_0)]/[1+ (K_dS'(1-\alpha) + (\alpha K_dS_0)] \quad (11)$$

and the change of DIP in the water column can be calculated by eqn(12).

$$\% \text{ DIP removal} = \Delta DIP / C_0 \times 100 \quad (12)$$

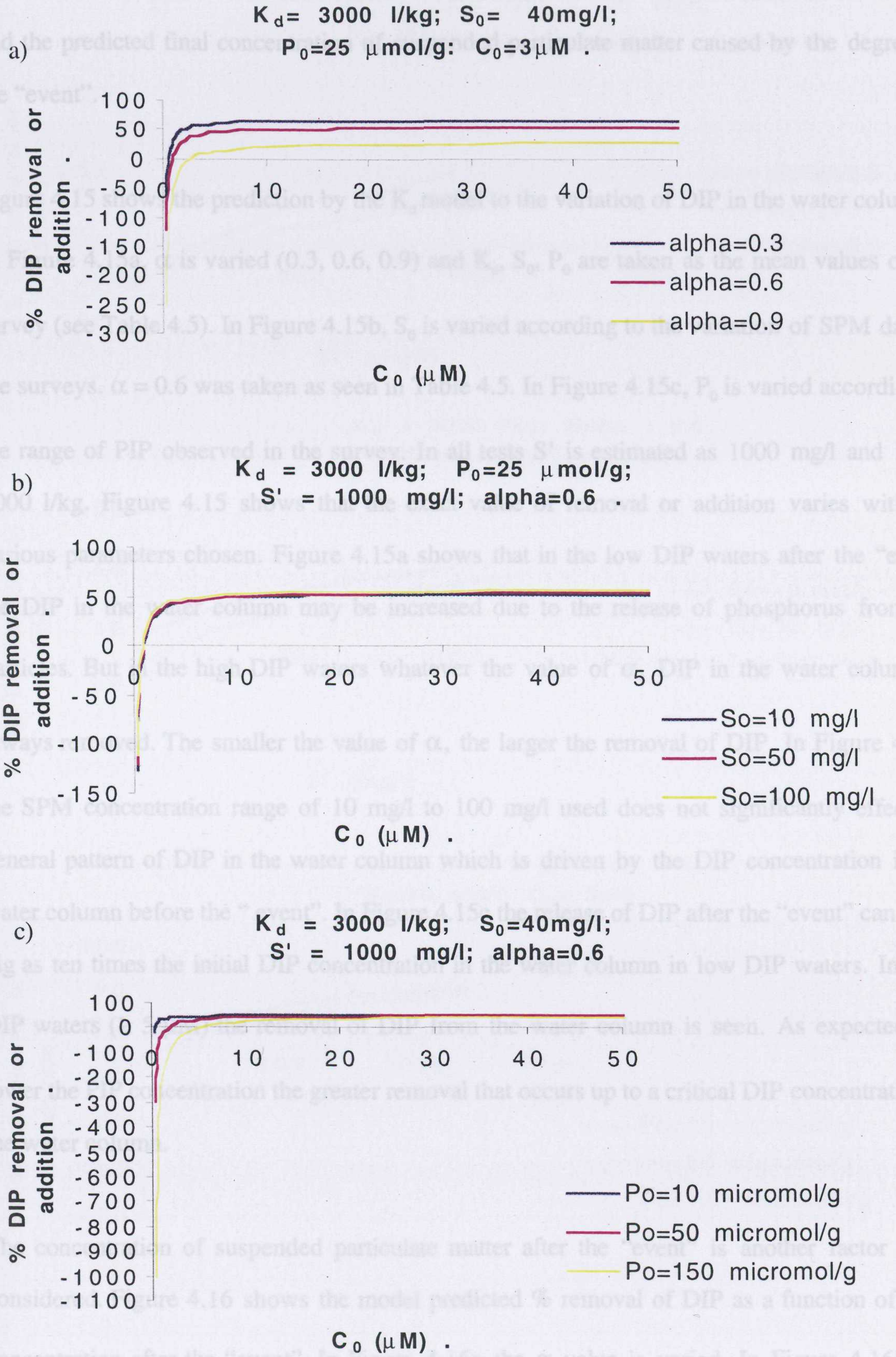


Figure 4.15 The prediction of the DIP change caused by a resuspension "event' in the estuary, under different conditions (negative values correspond to the DIP release from the particles).

The tests of the model were done based on the variation of DIP concentrations in the estuary and the predicted final concentration of suspended particulate matter caused by the degree of the "event".

Figure 4.15 shows the prediction by the K_d model to the variation of DIP in the water column. In Figure 4.15a, α is varied (0.3, 0.6, 0.9) and K_d, S_0, P_0 are taken as the mean values of the survey (see Table 4.5). In Figure 4.15b, S_0 is varied according to the variation of SPM data in the surveys. $\alpha = 0.6$ was taken as seen in Table 4.5. In Figure 4.15c, P_0 is varied according to the range of PIP observed in the survey. In all tests S' is estimated as 1000 mg/l and K_d is 3000 l/kg. Figure 4.15 shows that the exact value of removal or addition varies with the various parameters chosen. Figure 4.15a shows that in the low DIP waters after the "event" the DIP in the water column may be increased due to the release of phosphorus from the particles. But in the high DIP waters whatever the value of α, DIP in the water column is always removed. The smaller the value of α, the larger the removal of DIP. In Figure 4.15b the SPM concentration range of 10 mg/l to 100 mg/l used does not significantly effect the general pattern of DIP in the water column which is driven by the DIP concentration in the water column before the " event". In Figure 4.15c the release of DIP after the "event" can be as big as ten times the initial DIP concentration in the water column in low DIP waters. In high DIP waters (≥ 5 μM) the removal of DIP from the water column is seen. As expected, the lower the PIP concentration the greater removal that occurs up to a critical DIP concentration in the water column.

The concentration of suspended particulate matter after the "event" is another factor to be considered. Figure 4.16 shows the model predicted % removal of DIP as a function of SPM concentration after the "event". In Figure 4.16a the α value is varied. In Figure 4.16b and Figure 4.16c the concentrations of S_0 and P_0 are varied, respectively.

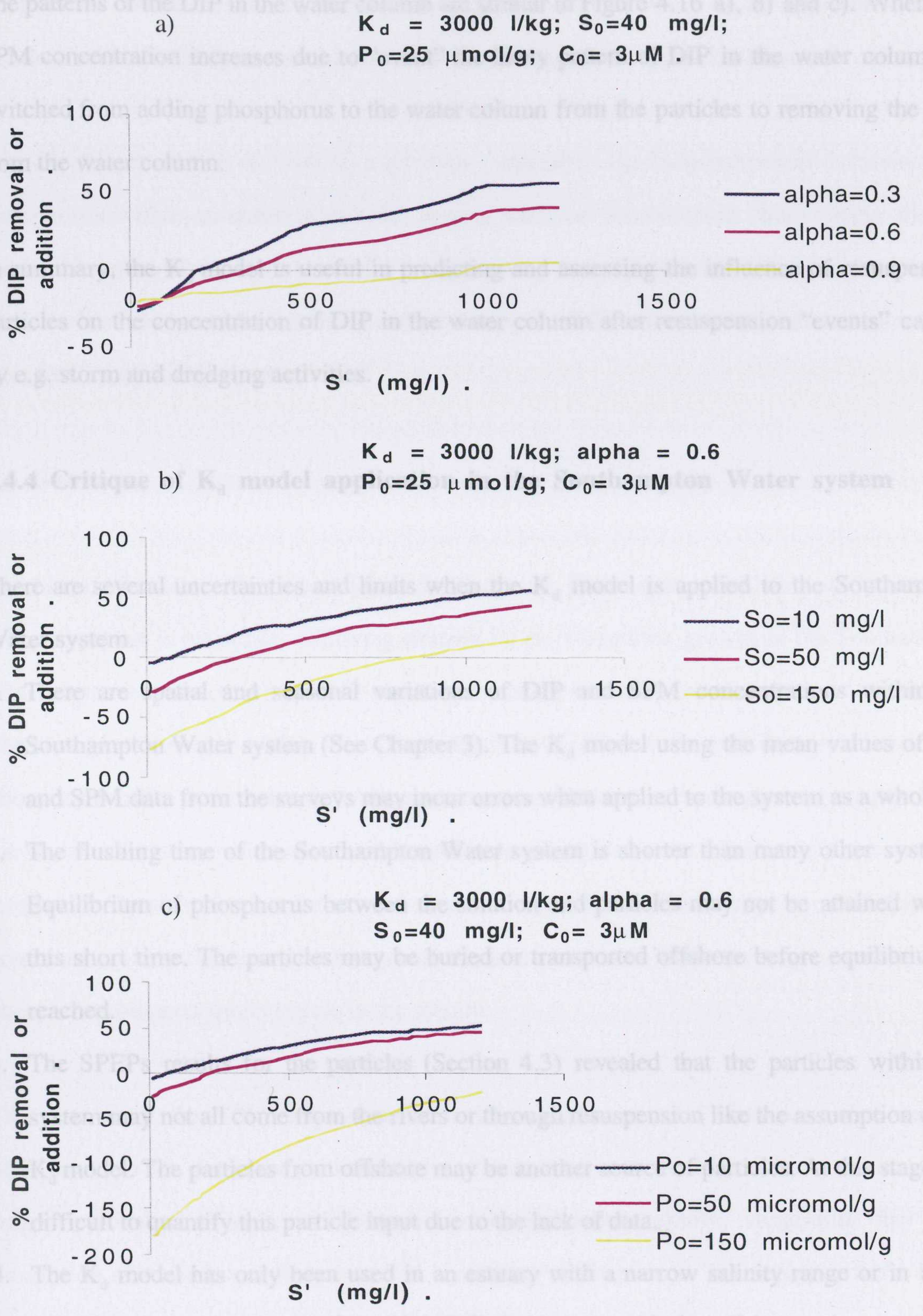


Figure 4.16 Model predicted % removal or addition of DIP as a function of SPM concentration after the "event", under different conditions.

The patterns of the DIP in the water column are similar in Figure 4.16 a), b) and c). When the SPM concentration increases due to "event" the likely pattern of DIP in the water column is switched from adding phosphorus to the water column from the particles to removing the DIP from the water column.

In summary, the K_d model is useful in predicting and assessing the influence of resuspended particles on the concentration of DIP in the water column after resuspension "events" caused by e.g. storm and dredging activities.

4.4.4 Critique of K_d model application in the Southampton Water system

There are several uncertainties and limits when the K_d model is applied to the Southampton Water system.

1. There are spatial and seasonal variations of DIP and SPM concentrations within the Southampton Water system (See Chapter 3). The K_d model using the mean values of DIP and SPM data from the surveys may incur errors when applied to the system as a whole.
2. The flushing time of the Southampton Water system is shorter than many other systems. Equilibrium of phosphorus between the solution and particles may not be attained within this short time. The particles may be buried or transported offshore before equilibrium is reached.
3. The SPEPs results for the particles (Section 4.3) revealed that the particles within the system may not all come from the rivers or through resuspension like the assumption of the K_d model. The particles from offshore may be another source of particles. At this stage it is difficult to quantify this particle input due to the lack of data.
4. The K_d model has only been used in an estuary with a narrow salinity range or in a low salinity, where the mixing of the high DIP river water with the offshore seawater of low DIP concentration is not a significant process. In a macrotidal system like Southampton Water the salinity range is big and the physical mixing is likely a dominant dynamic

process. Hence the assumption of most removal/addition being in the low salinity zone may not be perfectly met in this system when the K_d model applied to the whole estuary.

Overall, therefore it is difficult to rigorously rationalise the biogeochemical behaviour of phosphorus within an entire macrotidal system such as Southampton Water using the K_d model. However the K_d model is useful for examining the behaviour of DIP at the freshwater-seawater boundary, and for assessing and predicting the DIP concentration in the water column after storm and dredging activities.

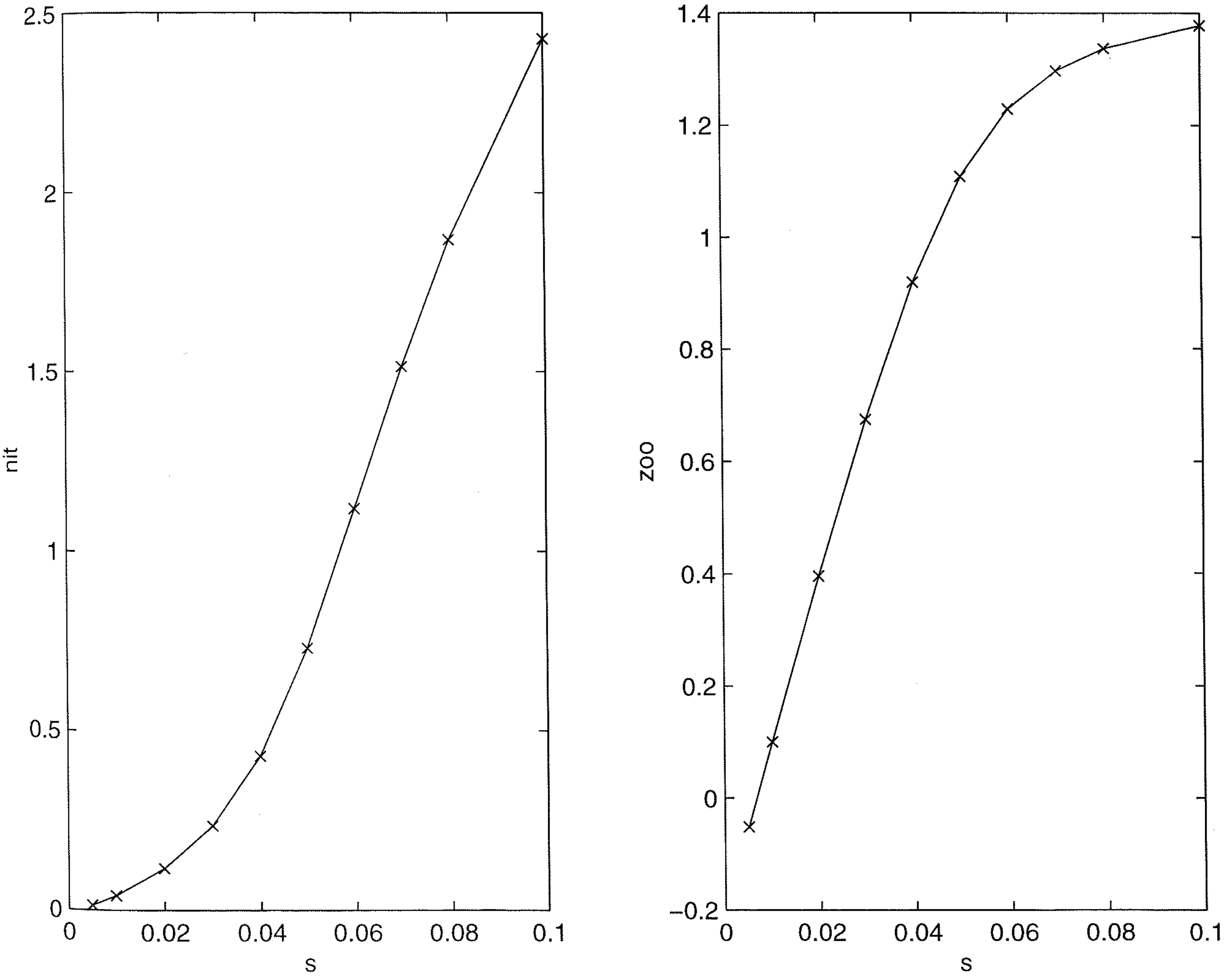
4.5 Summary

The historical studies of nutrients in the Southampton Water system and this study revealed that phosphorus is potentially a limiting element for phytoplankton growth in the Southampton Water system. which has high DIP inputs and relative low suspended matter concentrations. The sewage discharges within the system significant influence the distribution of dissolved phosphorus in the water column. In the estuarine environment, particulate matter suspended in the water column can be sources of bioavailable phosphorus, or alternatively can actively remove phosphorus from solution and render it unavailable. This study revealed that both processes occur in Southampton Water and the later process is likely the major process in the phosphorus biogeochemical cycle in the system.

The data from the SPM sequential extraction scheme revealed that particulate organic phosphorus is the dominant particulate phosphorus species in the high salinity waters. Iron-bound particulate phosphorus decreased with increasing salinity, suggesting the likely desorption of phosphorus from iron and aluminium oxide phases. The analysis of the P : Fe ratio in the BD extract suggested that in low salinity waters where the concentrations of DIP in the water column were high, the particles were probably saturated with dissolved inorganic phosphorus from the water column. The generally lower P : Fe ratio in the BD extract of particles in high salinity waters suggested that the particles either released the phosphorus they adsorbed in low salinity waters or the particles in high salinity waters were mainly from offshore and resuspension where the particles were "fresh" and unsaturated. The particles in the high salinity waters consist mainly of resuspended matter. Due to the high biological activity in this area and relatively high DOP concentration in the water column, it is likely that the phytoplankton growth and subsequently decay offshore may produce both DOP and PTP.

The data for PTP(c) decreased seaward which revealed that when the particles are transported into the estuary, the estuary generally behaves as a sink of dissolved inorganic phosphorus which may be through burial of the estuarine particles. Desorption of DIP from particles was not supported by the data from the water column where no significant removal or addition processes were observed. This in part may reflect the weak signal from this desorption process compared to the dominant physical mixing processes occurring.

The K_d model is useful for examining the behaviour of DIP at the freshwater-seawater boundary, and for assessing and predicting the DIP concentration in the water column after storm and dredging activities. The K_d model may also be able to use to examine the DIP behaviour at the sewage -river boundary. However, currently due to lack of the necessary data on particulate and dissolved phosphorus in the sewage outfall, it is difficult to examine the behaviour of DIP at this boundary. In the future this work would be useful to asses the influence of the sewage works on the system when data becomes available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Chapter 5: Study of phosphorus in the sediments of Southampton Water and the Itchen Estuary

5.1 Introduction

In the marine environment, dissolved phosphorus is consumed during the growth of phytoplankton and is regenerated during bacterial decomposition of organic matter. Much of this regeneration take place in the water column. In relatively shallow environments, such as estuaries and continental shelves, due to the large storage capacity for organic matter and nutrients, sediments may play an important role in the biogeochemical cycle of phosphorus (Fisher *et al.,* 1982; Sundby *et al.*, 1992). In fact the efficiency of sediments in retaining phosphorus is not well known (Jensen *et al.*, 1995). While some estuarine studies (e.g. Chesapeake Bay) indicated that nearly 100% of the phosphorus from sedimenting organic matter is regenerated to the water column during a single year (Nixon, 1981; Billen *et al.,* 1991), other studies (e.g. Baltic Sea) shown that significant amounts of phosphorus can permanently accumulate in the sediments (Klump and Martens, 1983; Sundby *et al.*, 1992). Over short time scales, the remineralization of phosphorus from the sediments can provide a significant proportion of phosphorus required by the primary production (Boynton *et al.*, 1982; Klump and Martens, 1983). Over longer time periods, the balance between phosphorus deposition and phosphorus remineralization determines the availability and fate of phosphorus in an ecosystem (DeMaster *et al.*, 1985). Different approaches have been used to study the phosphorus dynamics in sediments including the measurement of the vertical and horizontal variations of solution and solid phase concentrations of phosphorus, phosphorus exchange rates and the factors controlling them, and studies of the chemical fractions of phosphorus in sediments for revealing the chemical nature of phosphorus.

Many factors control the fluxes of nutrients between water column and sediments. There is a direct relationship between the depositional flux of organic matter to bottom sediments and subsequent benthic nutrient regeneration (Nixon, 1981; Jensen *et al.*, 1990; Billen *et al*, 1991), suggesting that there may be distinct differences in nutrients regeneration rates associated with specific geomorphological types of estuaries where the depositional flux of organic matter may vary. In deltaic environments, the reactivity of organic matter deposited and the ratio of organic to inorganic sediment input determine the rates of benthic phosphorus regeneration (Canfield, 1989). In river-dominated coastal environments, sedimentation of terrigenous materials and water column turbidity dilute the labile or reactive organic matter reaching bottom sediments and inhibit the production in overlying water by decreasing light penetration. The reactivity (relative to decomposition) of bottom sediments in these environments is inversely proportional to the sedimentation rate (Berner, 1978; Aller *et al.* 1985). In lagoons with minor river input and more wind and tidal impact the regeneration rates are lower due to the lack of organic matter deposition (Corredor and Morell, 1989). Temperature and subsequent stratification in the water column also influence the benthic fluxes of nutrients. As temperatures increase during the summer, the regeneration processes in sediments release nutrients to water column (Kemp and Boynton, 1984). In deeper estuaries, summer stratification traps the regenerated nutrients below the pycnocline, while in shallow water the lack of stratification allows the nutrients to be transported to the surface water column where they may enhance the rates of phytoplankton growth (Kemp and Boynton, 1984). Stratification also controls the redox condition of the bottom waters and sediment and then influences the chemical sorption / desorption processes of sediments for phosphorus (Sundby *et al.*, 1992).

Three mechanisms for transfer of phosphorus to and from sediments have been reviewed by Williams and Mayer (1972). Transfer of phosphorus from sediment to overlying water can occur if the sediment is disturbed and mixed by wave action and current. This mechanism is more significant for shallow waters than for relatively deep waters. The second mechanism for phosphorus regeneration between sediment and overlying water is diffusion of soluble phosphorus out of the sediments as a result of a difference in concentration of soluble phosphorus between the interstitial water of the sediment and the overlying water.

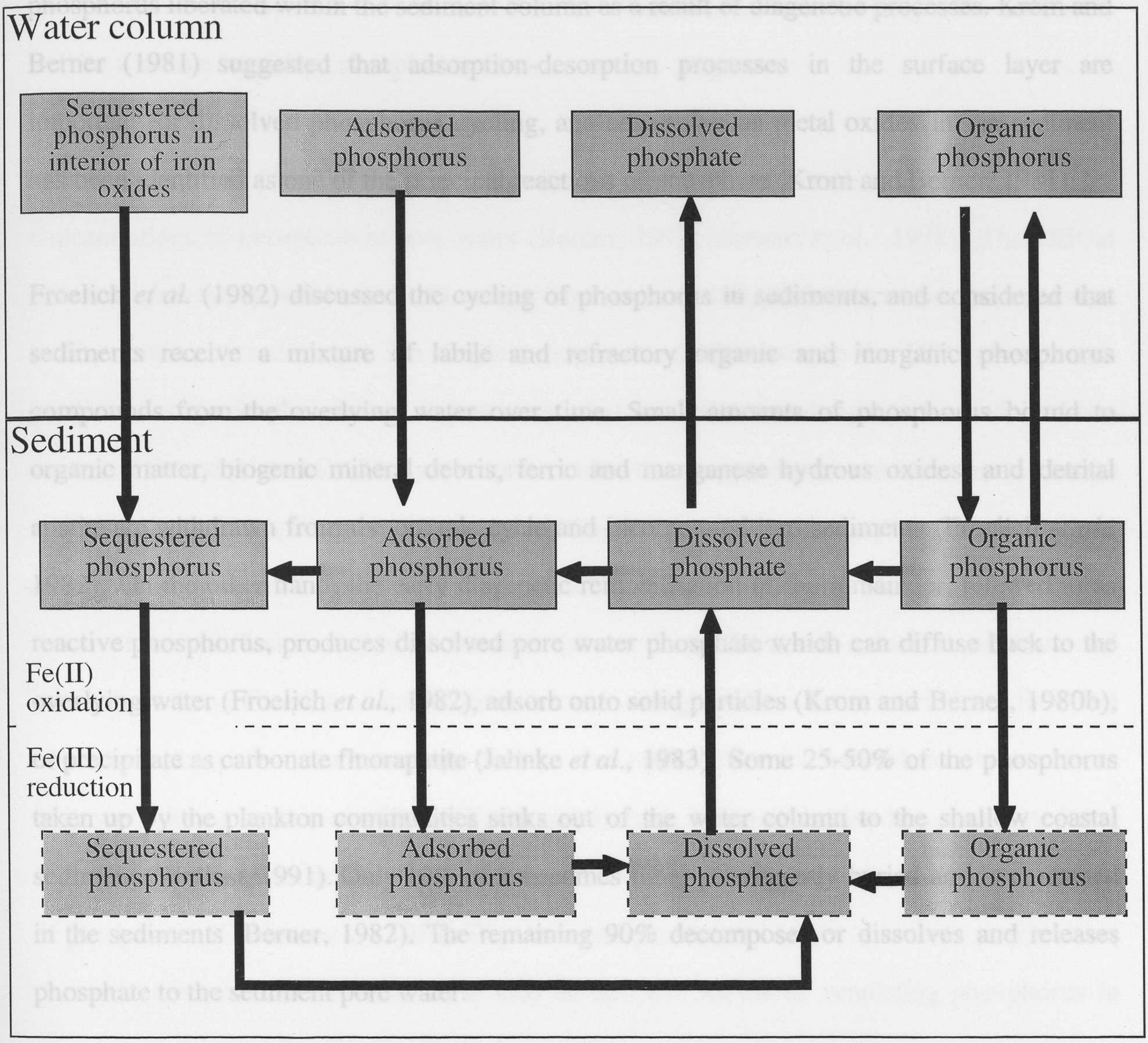

Figure 5.1 Summary diagram of P fluxes within the sediment and across the sediment-water interface. Inert P is not shown. (adapted from Sundby *et al.*, 1992).

The third mechanism by which phosphorus may travel from sediment to overlying water is incorporation into organisms (e.g. bottom-feeding fish). Amongst the three mechanisms the first mechanism is of greatest importance (Williams and Mayer, 1972; Syers *et al.*, 1973). Two stages of regeneration of phosphorus from sediments on the basis of kinetic factors were suggested by Williams and Mayer (1972). The first stage is the conversion of sediment phosphorus into soluble phosphorus at the interface without incorporation of the sediment material into the sediment column proper. The second stage is the regeneration of soluble phosphorus liberated within the sediment column as a result of diagenetic processes. Krom and Berner (1981) suggested that adsorption-desorption processes in the surface layer are important for dissolved phosphorus cycling, and adsorption on metal oxides in the sediment has been identified as one of the principal reactions of phosphate (Krom and Berner, 1981).

Froelich *et al.* (1982) discussed the cycling of phosphorus in sediments, and considered that sediments receive a mixture of labile and refractory organic and inorganic phosphorus compounds from the overlying water over time. Small amounts of phosphorus bound to organic matter, biogenic mineral debris, ferric and manganese hydrous oxides, and detrital apatite are withdrawn from the oceanic cycle and incorporated into sediments (Froelich *et al.*, 1982). On the other hand, the early diagenetic remobilisation of the remainder, referred to as reactive phosphorus, produces dissolved pore water phosphate which can diffuse back to the overlying water (Froelich *et al.*, 1982), adsorb onto solid particles (Krom and Berner, 1980b), or precipitate as carbonate fluorapatite (Jahnke *et al.*, 1983). Some 25-50% of the phosphorus taken up by the plankton communities sinks out of the water column to the shallow coastal sediment (Wollast, 1991). Only 10% of it becomes more permanently buried and is contained in the sediments (Berner, 1982). The remaining 90% decomposes or dissolves and releases phosphate to the sediment pore water.

The movement of phosphorus in marine sediments is influenced by advective and diffusive transport. The occurrence of high benthic primary production has also impacted the movement of phosphorus in marine sediments (van Raaphorst and Kloosterhuis, 1994). Two closely interrelated factors play a major role in controlling the chemical and physical mobility of phosphorus in sediment (Syers *et al.*, 1973), these are

1. Oxidation-reduction potential
2. Rates of transport within the sediments via diffusion, turbulent mixing and possibly the upward movement of groundwater through the sediment column.

Generally, sediments can be either a source of bioavailable phosphorus to overly waters, or a sink of phosphorus from bottom waters. The depositional environment, and the consequent early diagenetic reactions which occur within the sediment, determine whether the sediments will be a source or sink of phosphorus.

Many studies of phosphorus dynamics in the sediments have been focused on the concentrations of phosphate in pore-water (Berner, 1977; Martens *et al.,* 1978). The DIP in porewater has two possible fates: 1) escape from sediments by various transport mechanisms or 2) retention by sediments. The simplest mechanism is diffusion up the DIP concentration gradient. Inorganic phosphorus in porewater also can be retained by oxides and hydrous oxides of Fe and Al and $CaCO_3$ by a sorption rather than a precipitation mechanism (de Jonge and Villerius, 1989). Carritt and Goodgal (1954) indicated that the sorption (adsorption) of inorganic phosphorus is initially rapid but the additional inorganic phosphorus is sorbed by a much slower diffusion-controlled reaction (absorption). Chemical reduction of iron and subsequent demobilisation of sorbed phosphorus is thought to be a major control on dissolved interstitial phosphate concentrations and to be responsible for phosphate release from sediments during anoxic conditions (Krom and Berner, 1981). It is also been suggested that bacteria in the sediment are important not only as reducers of iron but also as temporary stores of phosphorus (Gachter *et al.*, 1988). Physical resuspension of bottom sediments under wave, current, or organismal disturbance, is also an effective means of ventilating phosphorus in porewater into overlying waters (Ruttenberg, 1993).

Molecular diffusion provides the foundation for assessing and describing the transport of phosphorus in sediment porewaters and across the sediment-water interface. The theoretical fluxes of phosphate from the sediments to overlying water were estimated from the porewater phosphate concentrations using Fick's first law and the vertical gradients of the porewater phosphate concentrations. The benthic fluxes of phosphorus across the water-sediment interface can also be assessed by sediment incubation. In the regions dominated by molecular diffusive transport, these estimates are in reasonable agreement. In areas with sufficient macrofaunal activity, the fluxes estimated by the sediment incubation often exceed those calculated from porewater gradients, indicating that non-molecular diffusion is also important

(Jahnke, 1992). Klump and Martens (1983) found that the fluxes of dissolved phosphate from organic-rich sediments were often less than predicted by porewater concentration gradients when oxygen was present in the overlying water. Sundby *et al.* (1986) even observed no release of phosphate from a shallow coastal sediment when the overlying water contained oxygen, even though the measured pore-water profile predicted a flux out of the sediment. This observation implied that sorption in the oxygenated surface layers of the sediments, presumably by iron hydroxyoxides, may trap the phosphate produced through mineralisation. In principle, the presence of oxygen in bottom waters should minimise the release of sediment phosphorus but the release of phosphorus may increase if the oxygenation process involved turbulence at the sediment-water interface (Sundby *et al.,* 1992). It is possible that eutrophic estuaries with large sediment phosphorus stock will remain in a eutrophic condition through release of sediment phosphorus for some time after external sources of phosphorus are eliminated.

For the DOP in porewater, Ruttenberg (1993) suggested that a similar concentration gradient to DIP would be established for DOP due to the same source for DIP and DOP being remineralised organic matter. It is proposed that the flux of dissolved organic phosphorus from the sediment is potentially high and can supply phosphorus to phytoplankton when the dissolved inorganic phosphorus is depleted (Williams, 1996). Balzer (1984) in the Kiel Bight calculated that about 66% of the organic phosphorus reaching the sediments returned as inorganic phosphorus to the water column. In fact, little is known of the cycling of organically associated phosphorus in sediments, or its significance in fluxes of phosphorus between sediments and overlying water due to infrequent measurements.

To estimate the potential flux of phosphorus from or into the sediment and the reservoirs of phosphorus, it is important to measure the concentrations of solid phase inorganic and organic phosphorus in the sediments. The factors controlling solid phase inorganic and organic phosphorus levels in sediments are relatively independent. Differences in sediment organic phosphorus are more a function of general organic matter transformation dynamics than of differences in the nature of the specific organic phosphorus compounds and complexes constituting the sediment organic phosphorus fraction. Studies (Williams *et al.*, 1971) on organic matter in terrestrial soils have shown that much organically bound phosphorus is present in high-molecular-weight compounds comprising part of the humic and fulvic acid fractions of soil organic matter. In turn, organic compounds of this type are frequently intimately associated with alumino-silicate clay minerals. The displacement of organic phosphorus from sediment sorption sites by more strongly bound inorganic phosphorus was also suggested (Williams *et al.,* 1971). Amongst inorganic phosphorus reservoirs, "loosely absorbed phosphorus" represents solid phase phosphorus which is directly bioavailable and ready to release as phosphate; "Fe bound phosphorus" is a measure of potential bioavailable phosphorus which can be released to the solution when the ambient condition is met; "Ca-bound phosphorus" (apatite) is considered as permanent sink of phosphorus from the system. Overall, it is clear that a knowledge of the solid phase speciation of phosphorus is needed to help understand the role of sediments as a source or a sink of phosphorus.

Different forms of sediment phosphorus can be determined by different sequential extraction procedures (e.g. Williams *et al.*, 1971; Psenner *et al.*, 1988; Ruttenberg, 1990; Jensen and Thamdrup, 1993; Agemian, 1997). Williams *et al.* (1971) firstly divided sediment phosphorus into four categories:

1. Inorganic phosphorus presents as orthophosphate ions sorbed on the surfaces of P-retaining components ("non-occluded P").
2. Inorganic phosphorus presents as orthophosphates ions within the matrices of P-retaining components ("occluded").
3. Orthophosphate phosphorus presents in discrete phosphate minerals such as apatite and vivianite ("discrete P").
4. Organic esters of phosphoric acid (" organic P").

Five sediment phosphorus forms (exchangeable phosphorus; Fe bound phosphorus; authigenic apatite and $CaCO_3$ bound phosphorus; detrital phosphorus; organic phosphorus) were also distinguished by the sequential method of Ruttenberg (1990), while recently Agemian (1997) modified a sequential extraction procedure to determine five sediment reservoirs i.e. loosely bound phosphorus, Fe-bound phosphorus, polyphosphates, Ca-bound phosphorus and refractory phosphorus. A more detailed discussion is given in Section 2.6.

The one previous investigation of phosphorus sedimentary chemistry in the Southampton Water system was reported in Williams (1996). Williams (1996) investigated the fluxes of DIP and DOP at the sediment-water interface through incubation of sediment cores and measurement of the concentrations of phosphate in the pore and overlying waters. The sediment cores in the study of Williams (1996) were collected off the coast of the Isle of Wright at Bembridge, where is at the margin of the Southampton Water system. Williams (1996) indicated that the sediments might act as a sink for phosphate, while they also acted as a significant source of organic phosphorus in winter. He also concluded that the sedimentary source of phosphorus would become more significant during storm events. However, the site where the sediments was taken from was located in a shallow bay and has little influence on Southampton Water. Hence, it is questionable to use the data from this individual site to estimate the benthic fluxes of phosphorus in the Southampton Water system as a whole No data of the speciation of solid phase phosphorus in the sediments of the system has been available so far. Therefore further work was undertaken in this study to cover the possible area of the sediments in the system and measure the speciation of solid phase phosphorus in the sediments.

The sampling strategy and experiments conducted in this study were designed to 1) gain a better understanding of the magnitudes of reservoirs of phosphorus in the sediments of the Southampton Water system and 2) establish the magnitude of potentially important phosphorus fluxes across the sediment-water interface which may vary the concentrations of phosphorus in the water column. The investigation of porewater chemistry of phosphate in the sediments was carried out in the Itchen Estuary. The distribution of inorganic and organic phosphorus in the sediments were investigated throughout the Southampton Water system. The forms of inorganic phosphorus in the sediments were measured via a modified sequential extraction method. The information of the sedimentary chemistry of phosphorus from this study has been incorporated into the regional phosphorus budget (See Chapter 6).

The details of the sediment surveys are shown in Table 5.1

Table 5.1 Sediment survey summary

Date	Sampling area	Sampling method	Number of sites	Sampling purpose
15.4.1997	Itchen Estuary	Muti-corer	4	Phosphorus porewater chemistry
30.3.1998	Itchen Estuary and Southampton Water	Van Veen grab sampler	7	Phosphorus distributions in the sediments
3.12.1998	Itchen Estuary and Southampton Water	Van Veen grab sampler	3	Phosphorus flux at sediment -water interface
18.3.1999	Itchen Estuary and Southampton Water	Hand-taken intact core	2	Phosphorus flux at sediment -water interface and phosphorus vertical distribution in the sediments
27.4.1999	Itchen Estuary, Southampton Water and Test Estuary	Van Veen grab sampler	9	Phosphorus distributions in the sediments

5.2 Sampling and methods

5.2.1. Porewater chemistry investigation

The investigation of porewater chemistry of phosphorus in the sediments was carried out in the Itchen Estuary(the main phosphorus source within the Southampton Water system). The location of the sampling stations are shown in Appendix B. They were chosen in order to give a representative transect of the Itchen Estuary. Details of the sampling stations can be seen in Table 5.2.

Table 5.2 Details of the sampling stations for phosphate porewater chemistry sediment survey in the Itchen Estuary (April 13, 1997)

Sampling Station	Location	Sampling time (GMT)	Overlying-water Depth	Distance to Portswood Sewage outfall
Station 1	50°54.152"N 1°22.112"W	11:15	5.5m	3.33 km
Station 2	50°54.922"N 1°23.253"W	12:33	2.9m	0.88 km
Station 3	50°55.112"N 1°22.122"W	16:20	1.6m	1.67 km
Station 4	50°55.777"N 1°28.36"W	13:00	0.9m	0.02 km

Sampling took place on April 15th 1997 on the *R.V. Bill Conway*. A Bowers and Connelly multicorer with four perspex coring tubes, 5 cm in diameter, and 38 cm in length was used to collect sediment cores at each station. The core tubes were carefully removed, capped and sealed immediately after collection to prevent loss of sediment and overlying water, and prevent the contact of air with the samples. After the cruise they were transferred to a cold store (4°C) at Southampton Oceanography Centre. The sediment cores were sectioned into horizontal layers in a nitrogen-purged glovebox to prevent oxidation and contamination of the sediments. Cores were sectioned into slices 1-3 cm in thickness, with a higher resolution near the sediment-water interface. Each slice was placed in a polycarbonate centrifuge tube, which was tightly closed, and then centrifuged at 3000 rev/min at 15 °C for 30 min. The tubes were then returned to the glovebox, and after purging of any oxygen, where the supernatant was decanted and sequentially filtered through 0.47 μm polycarbonate membrane filters, and then through 0.2 μm polypropylene membrane filters to remove particles still in the porewater. The concentration of DIP in the pore waters was immediately measured by the standard colorimetric procedure as modified by Strickland and Parsons (1972). The solid phase was kept in the tube, and also stored at 4 °C. The solid phase samples were oven-dried at 80 °C for 24 hours and placed in a desiccator for storage. A Tema Laboratory disc mill was used to grind the dried solid phase samples, using a large agate barrel and puck, which was thoroughly cleaned and dried after each use.

5.2.2 Direct measurement of phosphorus fluxes across the sediment-water interface

Three cores were taken from the Van Veen grab cores on December 3rd 1998. Perspex coring tubes, 5 cm in diameter, and 38 cm in length were carefully pushed into the mass of sediment. In order to get longer undisturbed sediment vertical profiles, four other sediment cores were taken by hand on two intertidal flats within the system on April 17th 1999. Two of the intact cores were used to measure benthic fluxes and two were used to measure vertical distribution of phosphorus in the sediments. The location of the sites are given in Table 5.1

There are several methods designed to measure benthic fluxes of phosphorus, including batch incubations of cores in laboratory (van Raaphorst and Kloosterhuis, 1994; Cowan *et al.*, 1996); continuous flow with shipboard incubations (Miller-Way *et al.*, 1994) and *in situ* benthic chambers with no flow (Sundby *et al.*, 1986). This study used the more traditional batch incubations described in van Raaphorst and Kloosterhuis (1994). Cores and water samples from each site were placed in a temperature controlled room which was maintained and monitored at the temperature of the site at the time of sampling. The water overlying the intact cores was carefully siphoned off to exclude possible effects due to suspended matter and algae. Approximately 500 ml water from the same site was carefully poured over the top of the cores with minimal disturbance of the sediment. In parallel control of water were made in water collected from same site incubated in a polythene bottle in the absence of sediment. The oxygen concentration in the overlying water was kept near saturation by continuously bubbling air at a constant flow rate through a filtered air supply system. The air was bubbled through a plastic tube approximately 2 cm above the sediment surface and the control incubation as well. The flow of air bubbles provided sufficient mixing to give a homogeneous overlying water column, whilst the resulting turbulence near the sediment surface did not give visible resuspension of bottom material. 10 ml subsamples of overlying water were siphoned off through plastic tubes at 1 hour interval during the first incubation day and one day intervals afterwards. The subsamples were filtered through 25 mm GF/F filters and stored in the refrigerator, and dissolved inorganic phosphorus and dissolved organic phosphorus were measured within one week using the same method as in the water column. The changes of DIP and DOP concentrations during the core incubations were converted into cumulative benthic fluxes with time after correction for the changes in overlying water volume and the changes of the concentrations in the water collected without contacting the sediments. The incubation time for the fluxes calculation was set at one day, the same as the estimated flushing time of the system (Wright and Hydes, 1997) and comparable with the results from other systems (van Raaphorst *et al.,* 1990; Prastka and Jickells, 1995).

5.2.3 Inorganic and organic phosphorus distributions in the sediments

Sediment samples for the investigation of phosphorus distributions in the sediments were taken during two cruises (March 30th 1998 and April 27th 1999) using a Van Veen grab sampler. The 1998 cruise contained seven sites within the Itchen Estuary and Southampton Water, while the 1999 cruise contained 9 sites within the Itchen Estuary, the Test Estuary and Southampton Water. The details of the sites can be found in Table 5.1. The analytical methods of solid phase inorganic and organic phosphorus in sediments were chosen as described in Chapter 2.

The investigation of vertical distributions of phosphorus in the sediments were carried out on the same core sediment samples used for the benthic flux incubation measurement. The sediment cores were sectioned into horizontal layers in a nitrogen-purged glovebox to prevent oxidation and contamination of the sediments. Cores were sectioned into slices 1~3 cm in thickness, with a higher resolution near the sediment-water interface. Each slice was placed in a zig-sealed plastic bag, which was tightly closed in the glovebox. The bags were stored at 4°C.

Between 0.5 g and 1.0 g of each wet sample was placed in a separated plastic container, and accurately weighed. The containers with the sediment were then dried in an oven at 80 °C overnight and weighed again. The water content of the sediment was estimated by the weight difference before and after drying. The samples were ground using the same procedure as Section 5.2.1.

Aliquots (0.3-0.5 g) of the dry sediments were accurately weighed and then transferred into 10 cm^3 silica crucibles. The crucibles on a suitable tray were placed into a muffle furnace and ignited at 550 °C; the tray was carefully but loosely covered with a piece of aluminium foil to avoid possible disturbance of samples by the hot air current in the furnace. The rate of heating of the furnace was not controlled, and it normally took 15 min to get to 550 °C. The samples were maintained at 550 °C for an additional 1.5 hours, and were then carefully removed from the muffle furnace, allowed to cool to the room temperature and transferred into 100-ml calibrated flasks. Small amount of ultrapure water was used to wash any residue in the crucible into the flasks. 50.0 ml of 1.0 M hydrochloric acid was then added to each flask. The mixture in the flasks were then agitated for 18 hours on an orbital shaker (Model: MK V Shaker, L.H. Engineering Co.) at the ambient room temperature (around 22 °C).

The method chosen for the determination of "inorganic phosphorus" in the sediments was to measure the phosphate released by extraction of the unignited dry sediment with 1M hydrochloric acid over 18 hours. The organic phosphorus was determined from the difference between the phosphorus extracted with 1M hydrochloric acid before and after igniting the sediment for 1h at 550°C. After extraction, aliquots of the ignited and non-ignited mixture were transferred into 15 ml tubes and centrifuged at 3000 rev/min for 10 min. The clarified extracts were finally diluted to varying extents dependent on the anticipated concentration range, and analysed by the autoanalyser automated procedure used for the phosphate measurement in the water column. The final results are reported in units of μmol phosphorus per dry gram of sediment.

Precision of the measurement of phosphorus in the sediment by Aspila method (1976) has been assessed on the basis of the variation between duplicate measurements of individual sediment samples. The duplicate measurement were carried out on the grounded sediment samples. The precision of the phosphorus measurements in the sediments averaged 6.5%. Due to the different type of the sediments, the difference of the duplicate measurements can be up to 10%. Since no sediment standard is available, it is impossible to assess the accuracy of the measurement of phosphorus in sediments in this study directly. Instead, the recovery of the measurement was carried out by adding known amount of phosphorus into the sediment. The average recovery was 99%.

5.2.4 Forms of inorganic phosphorus in the sediments

The aim of this part of the study was to investigate in different sediment types the significance and distribution of various fractions in which phosphorus occurs. Samples were from the two cruises as in Section 5.5, as well as the intact cores from the incubation flux study. Between 0.5 and 0.8 g of wet homogeneous grab sediment, or sediment sample from intact cores were subsampled and placed into 15 ml polyethylene centrifuge tubes.

The extraction scheme in this study is a modification of those of Psenner *et al.* (1988), Ruttenberg (1990), Jensen and Thamdrup (1993) and Agemian (1997). The SPEPs scheme contains four extraction steps, which divided inorganic phosphorus in the sediment into four categories : 1) loosely exchangeable phosphorus; 2) Fe bound phosphorus; 3) polyphosphate, and 4) Ca bound phosphorus. The extraction scheme, extractants and extraction times used in the study are presented in Table 5.3.

Table 5.3 Sequential extraction of solid phase inorganic phosphorus in sediments. After Agemian (1997).

	Extractant	Volume of extractant (ml)	Extraction time	Phase extracted
0.5 ~ 1 g fresh sediment	0.5 M NaCl, pH 7	10	1 hour	loosely sorbed DIP and DIP in porewater
residue	BD reagent (0.11M $Na_2S_2O_4$, 0.11M $NaHCO_3$)	10	1 hour	Fe-bound phosphorus
residue	0.1M NaOH	10	18 hour	Polyphosphate + DIP from clay minerals
residue	0.5 M HCl	10	1 hour	Ca-bound phosphorus

* each step was all followed by a 10 ml of 0.5 M NaCl wash, except step two a BD reagent wash was added. The washes were then added to the supernatant.

In step one, which is to extract the pool of loosely sorbed SRP (DIP) and SRP (DIP) in porewater, 10 ml of 0.5 M NaCl solution was added and the tube was closed by an air-tight screw cap. The centrifuge tube was shaken for 1 hour and then centrifuged for 10 minutes at 3000 rev/min. The supernatant was collected in a "diluvial" and another 10 ml NaCl solution was used to wash the sample, followed by centrifugation for 10 minutes at 3000 rev/min. The supernatant was then added to the same “diluvial”.

In step two, which is to extract Fe bound phosphorus, 10 ml of BD-reagent (consisting of a pH 7.0 buffered solution of 0.11 M $Na_2S_2O_4$, 0.11 M $NaHCO_3$) was added to the sediment pellet. After 1 hour of shaking at room temperature the extraction was followed by one 10 ml BD wash and one 10 ml 0.5M NaCl wash. Each step was followed by 10 minutes centrifugation at 3000 rev/min. To the supernatant, 2 ml of 1M H_2SO_4 was added to avoid precipitation of Fe and Mn during the following 1 hour aeration step where any remaining dithionite was oxidised.

In step three, which mainly extracts polyphosphate and DIP from clay minerals, an 18 hour extraction (shaking) with 10 ml 0.1M NaOH was followed by one 10 ml 0.5M NaCl wash. The solution was centrifuged for 10 minutes at 3000 rev/min after the extraction and the wash. 1 ml of 1M H_2SO_4 was added to the mixed supernatants in the “diluval” to neutralise the sample.

In step four, a 10 ml 0.5M HCl solution was used to extract calcium-bound phosphorus (mainly apatite) by shaking for one hour. The extraction was also followed by a 10 ml 0.5M NaCl wash, and centrifugation for 10 minutes at 3000 rev/min after the extraction and the wash.

The precision assessment of SPEP’s experiment was difficult because the sequential extraction protocol was carried out on the wet sediments, it is impossible to obtain a proper duplicate sample. The difference between two subsamples of an individual sediment sample can be as high as 30%, which was even higher than the difference between different samples. For the same reason as for the other sediment measurement, due to the lack of suitable sediment standard it is impossible to assess the accuracy of the method. It was referred to the literature and each steps were strictly controlled to keep the consistency of data and to be comparative to the data in the literature.

5.3 Results and discussion

5.3.1. Porewater chemistry of phosphate in the sediments of the River Itchen

The concentrations of DIP in porewater in the sediments of the River Itchen can be found in Appendix G. They ranged from 0.1 μM to 1860 μM. The highest concentration of phosphate in porewater was observed between 15-20 cm in the core from Station 4, which maybe due to the proximity of the Portswood sewage outfall. The typical profile of the pore water DIP concentration from Station 4 is shown in Figure 5.2. The DIP profiles of the porewaters were found to be generally unchanging until a peak occurs just above the base of the cores and then the concentration of DIP in porewaters decreased. The positive gradient of DIP in porewater above the peak depth reflects the input to pore waters of DIP from remineralised organic matter. Below the peak depth the gradient reverses from positive to negative, indicating that DIP was being removed from porewater to the solid phase properly due to the early diagenetic reaction (Ruttenberg and Berner, 1993) that removed the dissolved phosphorus in the porewaters to the authigenic phase. The profile of porewater DIP is a result of two conflicting processes, input of DIP from remineralised organic matter to porewater and removal of DIP from porewater to authigenic phases.

Benthic fluxes of elements are calculated using Fick's first law of diffusion assuming steady state conditions (Aller, 1980; Froelich *et al.*, 1982; Sundby *et al.*, 1992):

$$J = - \phi \times D_s \times \partial C/\partial x \qquad (1)$$

where J is the diffusive flux of phosphate in mass per unit area per unit time; D_s is the molecular diffusion coefficient in the sediment in area per unit time; ϕ is the porosity, and

$\partial C/\partial x$ is the concentration gradient at the sediment-water interface. Taking tortuosity into account, the diffusion coefficient for phosphate in the sediment was calculated with the empirical equation of Ullman and Aller (1982):

$$D_s = \phi^{(n-1)} \times D_m \qquad (2)$$

where D_m is the molecular diffusion coefficient in water which was taken from Li and Gregory (1974) as 0.0231 m^2yr^{-1}, and n is a correction factor ($n=3$ if $\phi \geq 0.7$; $n=2$ if $\phi < 0.7$). A porosity of 0.85 can be presumed as a mean for the uppermost 0~0.5 m interval (Henson *et al.*, 1998). The concentration gradient ($\partial C/\partial x$) is determined by a two-point calculation between the uppermost concentration of phosphate in porewater and the concentration of phosphate in the bottom overlying water. The results calculated from the above equations are summarised in Table 5.4

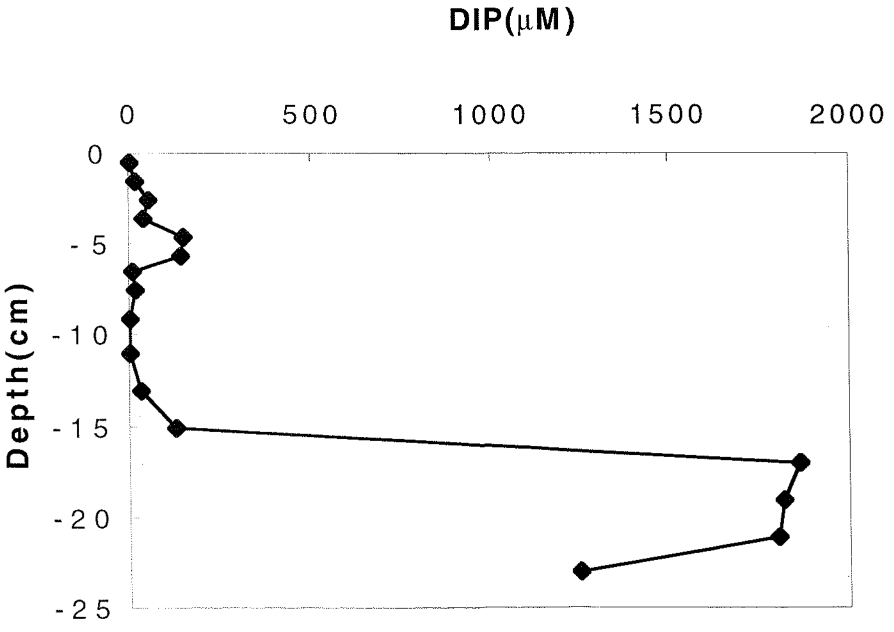

Figure 5.2 Porewater DIP concentrations of sediment from the Portswood sewage discharge site

Table 5.4 The benthic flux of DIP in the River Itchen

(+ out of sediment; - into sediment; unit: mmol $m^{-2}yr^{-1}$)

Station1	Station2	Station3	Station4
19.7	3.44	47.9	- 39.9

The results are about the same magnitude as results in the literature, 32 mmol m^{-2} yr^{-1} in the North Sea (-6.8 ~ 36.1 mmol $m^{-2}yr^{-1}$) (Nedwell *et al.*, 1993) and 34 mmol m^{-2} yr^{-1} in Aarhus Bay, Denmark (cumulative monthly efflux) (Jensen *et al.,* 1995). The concentration of porewater phosphate in sediment at Station 4 (near the Portswood sewage outfall) has a peak between 15~20 cm. The flux calculated from the concentration gradient in the porewaters was negative which means the DIP in water column was diffusing into the sediment.

The concentration of phosphate in the porewater is the result of the balance between input from microbially mediated organic matter decomposition, anoxic reduction of ferric iron phases with liberation of associated phosphate, plus fish-bone dissolution in some environments, and removal by diffusional loss or by immobilisation reactions (Ruttenberg and Berner, 1993). The results from this investigation suggest that in rapidly depositing organic-rich sediments (like Station 4) the removal of phosphate from the porewater by precipitation of authigenic minerals (Fe, Mn) under oxic conditions and release of phosphorus to the porewater under the reducing environment occur when the redox condition of sediments change. The trend of DIP in the porewater is accompanied by SO_4^{2-} reduction and Fe^{3+} profile in the same sediment samples reported by Paterson (1997).

The validity of modelling diffusive gradients to predict the benthic flux of dissolved phosphorus to overlying water has been tested by actual flux of phosphorus out of sediment either in a companion core which is incubated at *in situ* conditions (Aller, 1980, van Raaphorst and Kloosterhuis, 1994), or by *in situ* measurement of the flux out of sediments using benthic flux chambers lowered onto the sediment surface (Jahnke, 1990). Some studies (Klump and Martens, 1981; Sundby *et al.*, 1992) found that the fluxes of dissolved inorganic phosphorus from organic-rich sediments were often less than predicted by pore-water concentration gradients when oxygen was present in the overlying water and can change seasonally. Hence, the question should be asked are these theoretical benthic fluxes of phosphorus estimated from porewater DIP concentrations are realistic? An additional problem is that the DOP concentration in porewater was not measured due to the limited volume of porewater samples and a diffusive flux of DOP may probably contribute to the dissolved phosphorus benthic flux. Additionally other processes like tidal pumping and bioturbation may play considerable rule on the phosphorus recycling in the system.To provide an independent estimate, the actual fluxes of phosphorus from the sediments were measured by incubating the sediments taken by either grab sediment sampler or hand under *in situ* conditions. The results in the following section are compared with the above benthic flux calculations based on porewater concentration gradients.

5.3.2 Direct measurement of benthic fluxes of phosphorus by core incubations

The detailed results of the incubations are shown in Appendix H. and Figure 5.3. Table 5.5 shows the DIP fluxes calculated from the change of the concentration of DIP in the overlying water.

The results show that both cores from grab samples or intact long core samples all gave negative phosphate fluxes, which means that the concentration of phosphate in the overlying water during the incubation period decreased and the sediments apparently acted as a phosphate sink. The fluxes at sites decreased seaward and the biggest flux of phosphate was observed, not surprisingly, at the Portswood sewage discharge sampling site, where the concentration of phosphate in the water column is the highest one in the system (see Chapter 3). Phosphate fluxes estimated by a similar method in the Great Ouse estuary (Prastka and Jickells, 1995) at the same time of year, ranged from -110 μmol m^{-2} d^{-1} to -60 μmol m^{-2} d^{-1}, and are in a similar range to those in the Southampton Water system. The benthic fluxes of phosphate into the

Southampton Water system were bigger than the fluxes estimated for the Dutch coastal sites, -19.2 μmol m^{-2} d^{-1} (van Raaphorst and Kloostrhuis, 1994). In contrast, positive fluxes of DOP were observed in all cores. This maybe due to benthic diatoms activities (van Raaphorst *et al.*, 1988). Generally, muddy sediments have higher diatom biomass (Lucas, per. comm). In this study the muddy sediments taken from the Fawley power station, Northam Bridge and Hythe Pier sites were all observed to have fairly high DOP fluxes from the sediment. Compared to the benthic fluxes of DIP in the system, the benthic fluxes of DOP are generally small except Fawley power station, where the benthic flux of DOP is at the same magnitude of the benthic flux of DIP. This maybe due to the high bioactivity in that area.

The benthic fluxes of phosphate using diffusive modelling, and core incubations are generally different, although in shallower areas dominated by molecular diffusive transport (like the Portswood sewage discharge site) the estimates by the two methods were in reasonable agreement. This result may imply the presence of an iron-rich oxidising cap on the sediment surface which forms an efficient barrier for phosphate. This type of phosphorus-trapping by oxic surficial sediment has been observed in numerous places (Koop, 1990; De Lange, 1992) and is considered as a wide-spread phenomenon (Sundby *et al.*, 1992).

Table 5.5 benthic phosphorus fluxes
(+ out of sediment; - into sediment; unit: μmol m^{-2} d^{-1})

Grab sample (1998)			Intact cores (1999)	
Portswood sewage discharge	Itchen Bridge	Fawley power station	Northam Bridge	Hythe Pier
DIP				
-353	-100	-40.0	-291	-131
DOP				
7.82	10.9	51.8	32.5	26.9

5.3.3 Phosphorus distributions in the solid phases of sediments

The concentrations of inorganic and organic phosphorus in sediments from the Southampton Water system are shown in Figure 5.4 and 5.5. A full data set is given in Appendix I. The highest inorganic phosphorus concentration in the sediments (26.9 µmol/g) was obtained at the Portswood sewage discharge site in 1998, while the lowest concentration (6.07 µmol/g) of inorganic phosphorus was observed at the Greenland site in 1998. The highest concentration of organic phosphorus in the sediments (10.5 µmol/g) was obtained at the Itchen Bridge site in 1999, while the lowest concentration (1.33 µmol/g) was found at the Portswood sewage discharge site in 1999.

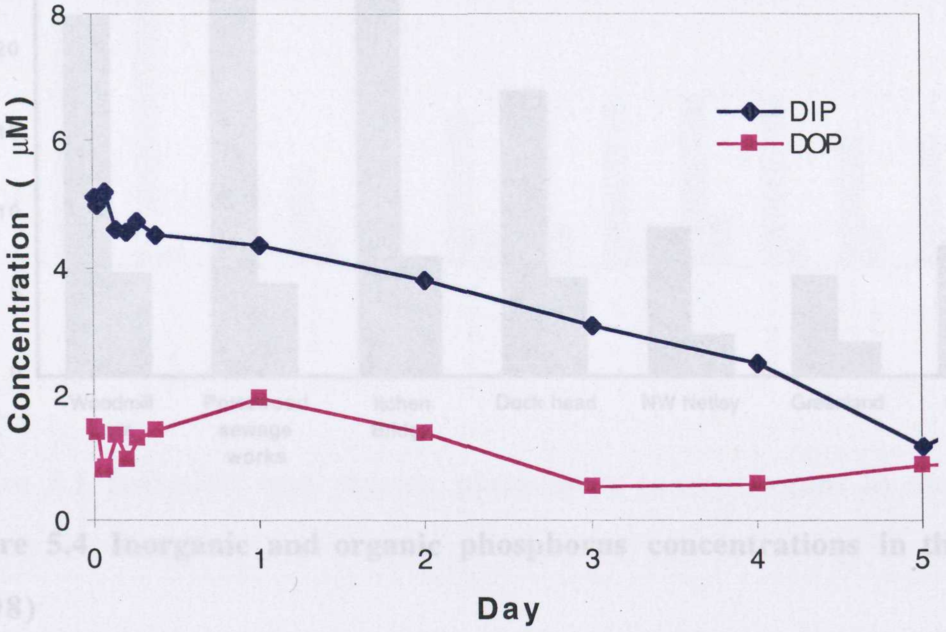

Figure 5.3 Phosphorus concentrations in the overlying water during incubation (sample from Portswood Sewage discharge site)

The horizontal trend of inorganic phosphorus in the sediments, and the corresponding dissolved inorganic phosphorus in the water column generally decreased seaward in the two cruises. The organic phosphorus in the sediments does not change significantly through the system, although some slight decrease can be observed when the results from sediments in the Southampton Water system are compared to the results from those in the Itchen Estuary.

The vertical distributions of inorganic and organic phosphorus in the sediments were investigated in the two intact cores, one from the Hythe Pier site in Southampton Water, and another from the Northam Bridge site in the Itchen Estuary. The results can be found in Appendix J. In order to estimate the change in phosphorus vertical distribution during the benthic flux incubation, the cores used in this experiment were sectioned in the same way as the replicate cores which had not been used in the incubation experiment.

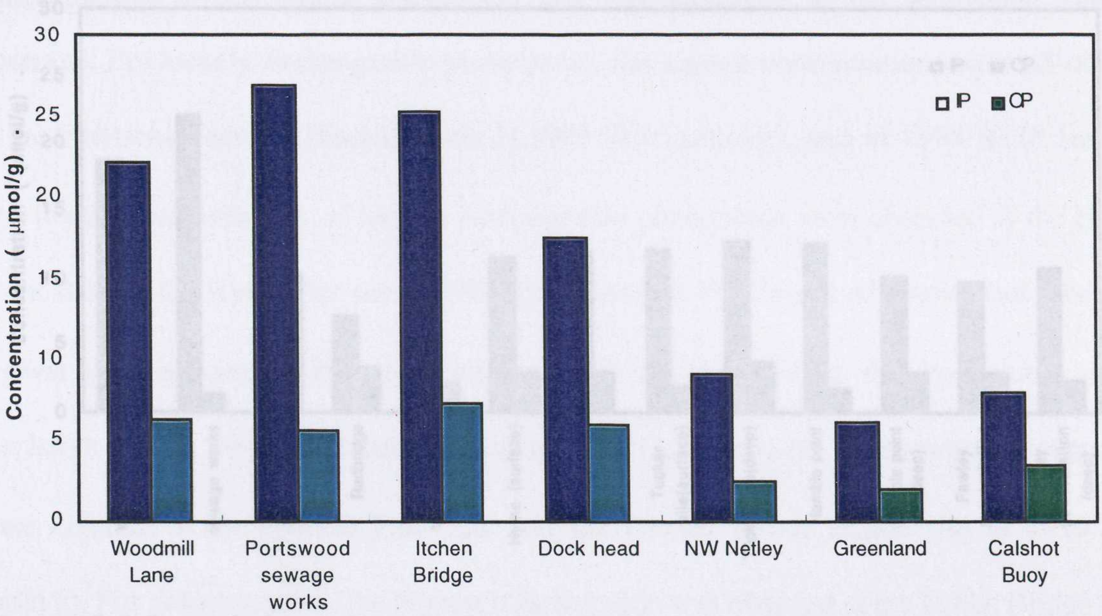

Figure 5.4 Inorganic and organic phosphorus concentrations in the sediments (1998)

In the Hythe Pier core, the highest inorganic phosphorus concentration (18.9 µmol/g) occurred in the surface layer, while the lowest value (10.0 µmol/g) was between 4 and 6 cm. The highest organic phosphorus concentration in the Hythe Pier core (8.3 µmol/g) was found between 4 and 6 cm, while the lowest one (below detection limit 0.05 µmol/g) was at 6~8 cm. The inorganic phosphorus in the sediments of the Hythe Pier generally decreased with depth, while organic phosphorus in the sediments behaved irregularly. In the Northam Bridge core, the highest inorganic phosphorus concentration (45.3 µmol/g) was observed in the surface layer, while the lowest (32.8 µmol/g) was in depth range of 5~7 cm. The highest organic phosphorus concentration in the Northam Bridge core (11.9 µmol/g) occurs at 5~7 cm, while the lowest (0.6 µmol/g) was obtained between 4 and 5 cm. The inorganic phosphorus in sediments of the Northam Bridge decreased slightly with depth, while organic phosphorus behaved irregularly.

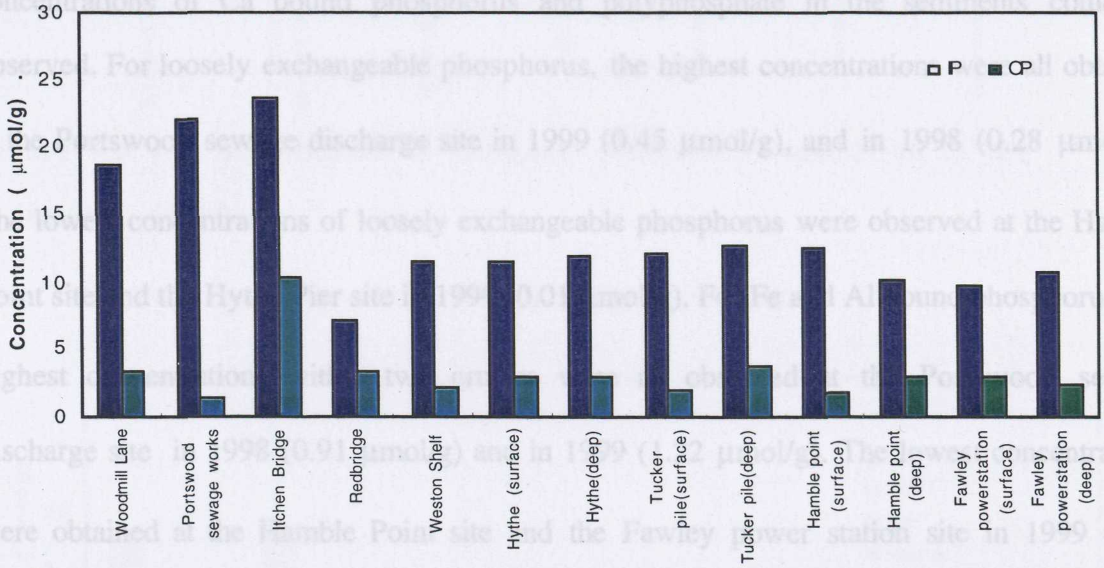

Figure 5.5 Inorganic and organic phosphorus concentrations in the sediments (1999)

5.3.4 Inorganic phosphorus speciation in sediments

In this section, the SPEPs method described in Chapter 2 and Section 5.2.4 was used to identify the speciation of the inorganic phosphorus in the sediment. The sum of the inorganic phosphorus pools from the SPEPs has been reported to agree fairly well with parallel measurements of total particulate phosphorus by the Aspila (1976) method, that were performed on replicates of dried ground sediment (Jensen *et al.*, 1995). However, since the inorganic phosphorus in the solid phase in sediments measured in Section 5.3.3 by the Aspila

(1976) method is thought to be more accurate than other methods (Jensen *et al.,* 1995; van Beusekom and de Jonge, 1997), the sum of inorganic phosphorus pools from SPEPs was normalised to that number by maintaining the percentage distribution of inorganic phosphorus among the various pools. The pool of organic phosphorus in the sediments is estimated from the Aspila (1976) method in Section 5.3.3. The sediment SPEP's results on grab sediment samples are shown in AppendixI and Figures 5.6 and 5.7.

The concentrations of all forms of inorganic phosphorus in the sediment generally decreased seaward through the Southampton Water system, although no significant change of the concentrations of Ca bound phosphorus and polyphosphate in the sediments could be observed. For loosely exchangeable phosphorus, the highest concentrations were all obtained at the Portswood sewage discharge site in 1999 (0.45 μmol/g), and in 1998 (0.28 μmol/g). The lowest concentrations of loosely exchangeable phosphorus were observed at the Hamble Point site and the Hythe Pier site in 1999 (0.01 μmol/g). For Fe and Al bound phosphorus, the highest concentrations within two cruises were all observed at the Portswood sewage discharge site in 1998 (0.91 μmol/g) and in 1999 (1.22 μmol/g). The lowest concentrations were obtained at the Hamble Point site and the Fawley power station site in 1999 (0.01 μmol/g). For polyphosphate, the highest concentration was obtained at the Itchen Bridge site in 1999 (7.86 μmol/g), while the lowest concentration was obtained at the Weston Shelf site in 1999 (0.80 μmol/g). For Ca bound phosphorus, the highest concentration was observed at the Woodmill Lane site in 1999 (11.8 μmol/g), while the lowest concentration (0.86 μmol/g) was observed at the Redbridge site in 1999.

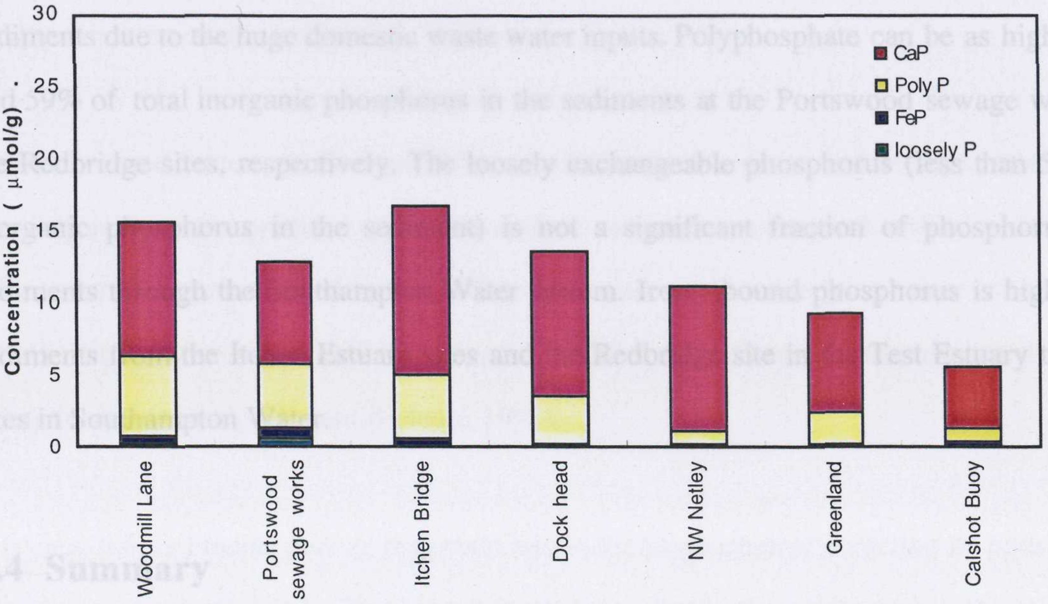

Figure 5.6 The distribution of inorganic phosphorus speciation in the sediments (1998).

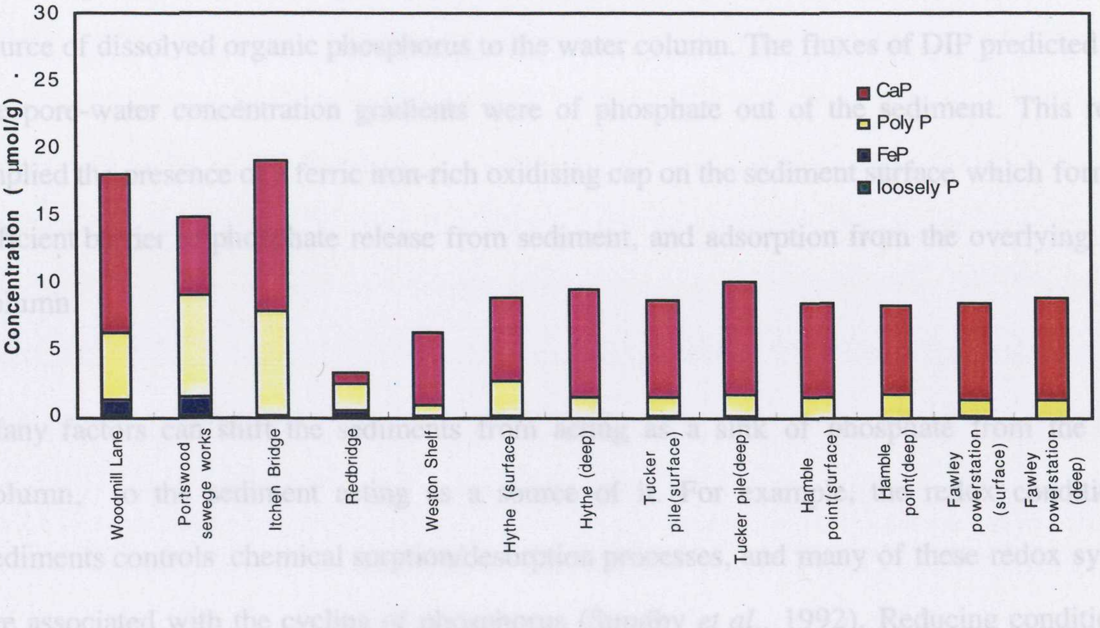

Figure 5.7 The distribution of inorganic phosphorus speciation in the sediments (1999).

The Ca-P is inferred to be mainly apatite, and appears to be the dominant form of inorganic phosphorus (about 55%-85% of total inorganic phosphorus) in most of the sediments in the

Southampton Water system. At some sites, such as the Portswood sewage works and the Redbridge site, polyphosphate is another important form of inorganic phosphorus in the sediments due to the huge domestic waste water inputs. Polyphosphate can be as high as 51% and 59% of total inorganic phosphorus in the sediments at the Portswood sewage works and the Redbridge sites, respectively. The loosely exchangeable phosphorus (less than 5% of the inorganic phosphorus in the sediment) is not a significant fraction of phosphorus in the sediments through the Southampton Water system. Iron - bound phosphorus is higher in the sediments from the Itchen Estuary sites and the Redbridge site in the Test Estuary than other sites in Southampton Water.

5.4 Summary

The direct measurement of the benthic fluxes of phosphate at the water-sediment interface in the cores taken from the River Itchen and Southampton Water revealed that the sediments in the Southampton Water system generally act as a sink of dissolved inorganic phosphorus and a source of dissolved organic phosphorus to the water column. The fluxes of DIP predicted from the pore-water concentration gradients were of phosphate out of the sediment. This results implied the presence of a ferric iron-rich oxidising cap on the sediment surface which forms an efficient barrier to phosphate release from sediment, and adsorption from the overlying water column.

Many factors can shift the sediments from acting as a sink of phosphate from the water column, to the sediment acting as a source of it. For example, the redox condition of sediments controls chemical sorption/desorption processes, and many of these redox systems are associated with the cycling of phosphorus (Sundby *et al.*, 1992). Reducing conditions at the sediment-water interface caused by an eutrophication event can alter the nature of nutrient flux at the interface by changing the specific nutrient geochemical processes. The presence of hypoxia in bottom waters will result in higher fluxes of phosphate from sediments to overlying water, promoting the input of nutrients that can contribute to overall poor water quality conditions. Hence, when eutrophication occurs, low dissolved oxygen concentration in the bottom water will trigger the release of phosphate from the sediments and make the water quality situation even worse.

Turbulence and bottom stress caused by occasional storm events and dredging activities can possibly remove the oxidised cap in the surface sediments, resuspend surface sediments and release the phosphate trapped in the surface porewaters to the overlying water column (Vidal, 1994). Bioturbation associated with macroinfaunal communities can also elevate the rates of nutrient release from sediment (Pelegri, 1995).

It is clear that sediments play an important role in the biogeochemical cycling of phosphorus in estuaries and coastal waters. The impact depends on, firstly, the tendency to retain phosphorus and thereby decrease the availability of phosphorus in the water column and, secondly, on the potential ability to release phosphorus when environmental conditions change.

Chapter 6: The phosphorus budget in the Southampton Water system

6.1 Introduction

Large amount of descriptive (e.g., nutrient concentrations) and process-oriented (e.g., rates of nutrients inputs and losses) data are now available for some estuarine and coastal ecosystems (e.g., Hager and Schemel, 1992; Rabalais *et al.*, 1996; Sanders *et al.*, 1997). However, much of the information has been interpreted in terms of relatively narrow issues such as nutrient seasonal variation and distribution (Lebo, 1990; Boynton *et al.*, 1995). Large scale analyses, such as the construction and evaluation of nutrient budgets at the scale of whole systems are needed to provide a conceptual framework (Gordon *et al.,* 1996).

Budget models are generally defined as mass balance calculations of specific variables for a defined geographic area and time period. A nutrient budget of an ecosystem requires major assessment of all known terms so that exchanges between them can be assessed but equally important so that the size of what is not known can be estimated. A few budgets have been developed in some estuarine and coastal ecosystems (e.g., Dutch Wadden Sea, Postma and Dijkema, 1983; Baltic Sea, Larsson *et al.*, 1985; Narragansett Bay, Nixon *et al.*, 1986; Chesapeake Bay and selected tributaries, Boynton *et al.*, 1995; Humber Estuary, Sanders *et al.*, 1997). In the Southampton Water system since the 1970's, especially after the SONUS (1995~1997) project and this study (1998~1999), a large amount of quality nutrient data have been collected. Additionally, major internal processes have been estimated in this study. A first order phosphorus budget can be made based on these in order to better quantify the human activity impact on the ecosystem and subsequently manage the coastal environment.

The quantification of nutrient fluxes from rivers to coastal regions is notoriously difficult (GESAMP, 1987); the problems include:

(1) Variability of freshwater discharge.

River flows vary as a function of season, and major runoff events can occur over only days and are often not sampled, but may dominate the input picture (Schubel and Pritchard, 1986).

(2) Concentration / flow relationships.

While nutrient concentrations are to some extent a function of river flow, they also tend to be a function of individual catchment and season (Webb and Walling, 1985).

(3) Tidal variability.

In macrotidal estuaries the flushing rate and residence time of nutrients are influenced by the tide (Griffiths, 1987).

(4) Estuarine processes.

Different kinds of biogeochemical processes affect the concentrations of nutrients in estuaries These may act as "filters" of nutrients before the remainder finally enters the coastal zone (Schubel and Pritchard, 1986). The processes are variable and often unknown or poorly quantified (Billen *et al.*, 1985; Froelich, 1988).

The biogeochemical processes of phosphorus within an ecosystem have been identified and estimated using a variety of methods. These include the analysis of property - salinity plots (Hydes and Liss, 1977; Officer, 1979; Billen *et al.*, 1985), the calculation of mean fluxes (Lebo and Sharp, 1992), the construction of chemical mass balance (Lebo and Sharp, 1992), the use of models which calculate the residual water transport within the estuary or across the estuary-sea boundary (Soetaert and Herman, 1995; Morris *et al.*, 1995) and a box model using nutrient stiochiometric relationships (LOICZ model, Smith, 1996). Amongst these methods nutrient - salinity relationships from the analysis of property salinity plots have been widely used (Sanders *et al.*, 1997; Hydes and Wright, 1999). This method provides a simple visual representation of the potential biogeochemical processes in the estuaries, but is susceptible to the changes in freshwater end-member concentration on timescales less than the flushing time of the estuary (Lebo *et al.*, 1994; Sanders *et al.*, 1997).

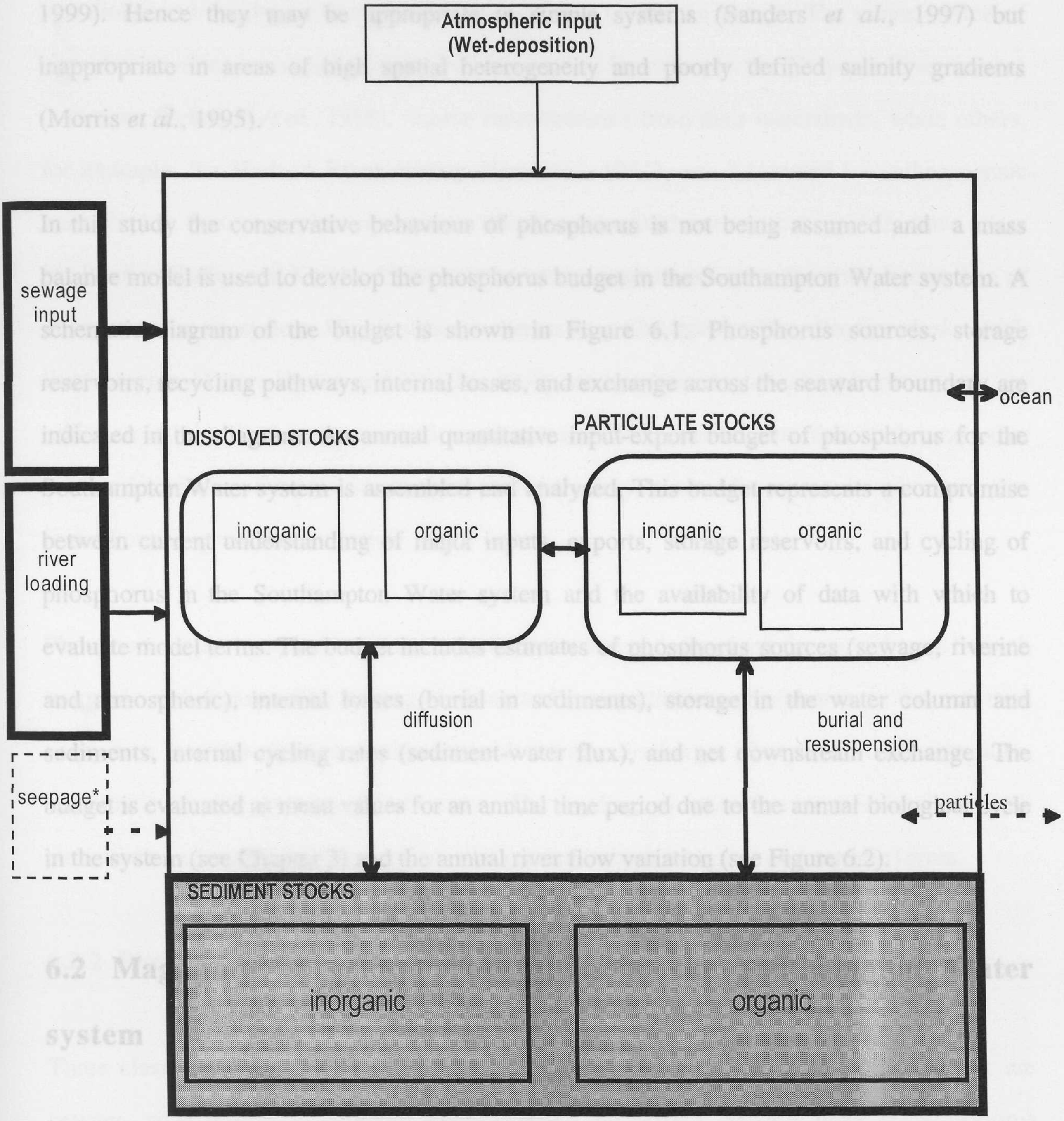

Figure 6.1 Schematic diagram of the phosphorus budget in the Southampton Water system.
* via ground water and other diffuse inputs

The chemical mass balance model and the LOICZ model make the assumption that the behaviour of nutrients within the estuaries are conservative (Smith, 1996; Hydes and Wright, 1999). Hence they may be appropriate in simple systems (Sanders *et al.*, 1997) but inappropriate in areas of high spatial heterogeneity and poorly defined salinity gradients (Morris *et al.*, 1995).

In this study the conservative behaviour of phosphorus is not being assumed and a mass balance model is used to develop the phosphorus budget in the Southampton Water system. A schematic diagram of the budget is shown in Figure 6.1. Phosphorus sources, storage reservoirs, recycling pathways, internal losses, and exchange across the seaward boundary are indicated in the diagram. An annual quantitative input-export budget of phosphorus for the Southampton Water system is assembled and analysed. This budget represents a compromise between current understanding of major inputs, exports, storage reservoirs, and cycling of phosphorus in the Southampton Water system and the availability of data with which to evaluate model terms. The budget includes estimates of phosphorus sources (sewage, riverine and atmospheric), internal losses (burial in sediments), storage in the water column and sediments, internal cycling rates (sediment-water flux), and net downstream exchange. The budget is evaluated as mean values for an annual time period due to the annual biological cycle in the system (see Chapter 3) and the annual river flow variation (see Figure 6.2).

6.2 Magnitude of phosphorus inputs to the Southampton Water system

6.2.1 Introduction

The inputs of dissolved phosphorus to estuaries is of significance to water quality as has been demonstrated many times (e.g. Nixon *et al.* 1996; Turner and Rabalais, 1999). In general phosphorus supply to an estuary has been found to be positively related to the level of primary, secondary, and fisheries production that is observed in the system (Nixon, 1982; Nixon, 1990). To quantitatively understand phosphorus biogeochemical processes, it is important to characterise and quantify the sources of phosphorus to the estuary, their spatial and temporal variations, and the degree to which they are affected by human beings. The major source of phosphorus varies amongst estuaries. Some estuaries, for example, the Umpqua River estuary in Oregon (Peterson *et al.*, 1988), receive most nutrients from their watersheds, while others, for example, the Hudson River estuary (Jaworski, 1981), are dominated by anthropogenic waste inputs. Sewerage plant operation within the urbanised estuary that typically have a low N : P ratio (Kadlec and Knight, 1996) may be a more important source for phosphorus than of nitrogen to the ecosystem. Highly urbanised areas (e.g. Chesapeake Bay, Boyton *et al.*, 1995; Southampton Water, Hydes and Wright, 1999) tend to have higher phosphorus inputs, as urban areas have discharges enriched in phosphorus. The results from this study and other studies described in the previous chapters reveal the importance of sewage phosphorus inputs to the Southampton Water system.

Phosphorus input to estuaries occurs in both particulate and dissolved forms and may be both inorganic and organic. The loading of dissolved and particulate phosphorus to the estuarine ecosystem is a function of freshwater and sewage discharge, phosphorus concentrations, estuarine area and the volume of water. The loading of phosphorus must include both particulate and dissolved forms and may be present in both inorganic and organic forms.

6.2.2 Phosphorus sources and inputs estimates

Three classes of phosphorus inputs, which are considered in this phosphorus budget are sewage, riverine and atmospheric sources within the system. Sewage input of phosphorus includes the major sewage discharges (Slowhill, Portswood, Woolston, Millbrook, Bursledon) to the system. Phosphorus associated with groundwater entering streams draining into the estuary is accounted for in the riverine source terms. The River Test and the River Itchen are the major riverine sources of phosphorus for the Southampton Water system (Hydes and Wright, 1999). Groundwater seepage of phosphorus directly into the system is not estimated because of a lack of data, but is assumed to be small. The atmospheric source of phosphorus is estimated according to the information from a similar urbanised area, the Wadden Sea (van Beusekom and de Jonge, 1997) and the result is compared to the atmospheric input estimate for Chesapeake Bay (Boyton *et al.,* 1995).

1. Riverine source of phosphorus

The riverine source of phosphorus in the Southampton Water system is estimated by combining the phosphorus fluxes from the River Test and the River Itchen. The flow in the River Hamble has been considered to be insignificant (Collins, 1978) (0.31 m^3/s). The variation of flows for the River Itchen and the River Test are illustrated in Figure 6.2, which shows the river flow to the Southampton Water system has a strong seasonal variation. The flows are generally big in winter and small in summer.

The fluxes of DIP for the River Test and the River Itchen are estimated by using the data from the Environment Agency (1990 -1997). Due to the lack of data for the concentrations of DOP and PTP in the rivers, the riverine DOP and PTP fluxes are estimated from the data obtained in this study. The DOP and PTP freshwater end-member concentrations are estimated from the data of low salinity (salinity < 1) in each survey of this study. The mean values of the whole dataset (salinity < 1) are used to present the concentrations of DOP and PTP in the freshwater end-member. The concentrations are multiplied by the mean monthly flow of the rivers to obtain the riverine phosphorus monthly fluxes and summed up for annual fluxes. The riverine phosphorus inputs are summarised in Table 6.1

The DIP input of the River Test estimated from EA data (1990-1997) is only about 70% of the DIP input of the River Itchen (this is due to the sewage input to the upstream of Itchen Estuary). The inputs of DOP and PTP from the River Test are estimated on the basis of the same proportion of phosphorus species in each river. The uncertainties of the estimation (±) shown in the Table 6.1 are a combination of the analytical errors and the error for the flow measurement. The analytical errors of DIP, DOP and PTP measurements are 5% each (See Chapter 3). The 2% error is added for the flow measurement.

Table 6.1 Summary of the riverine phosphorus inputs to the Southampton Water system

	Test	Itchen	Fluxes (tonne P / yr)
Flow (m^3 / s)	1.62-23.6	1.82-13.9	
DIP (μM)	2.58-7.23	5.55-15.3	86.8 (Test: 35.2; Itchen: 51.6) ± 15.0
DOP (μM)	NO Data	0.02- 0.66	2.71 (Test: 1.12*; Itchen: 1.59) ± 0.47
PTP (μM)	No Data	0.40-1.57	9.87 (Test: 4.07*; Itchen: 5.81) ± 1.71
		Total:	99.4 ± 15.1

* There is no DOP and PTP data available for the River Test.

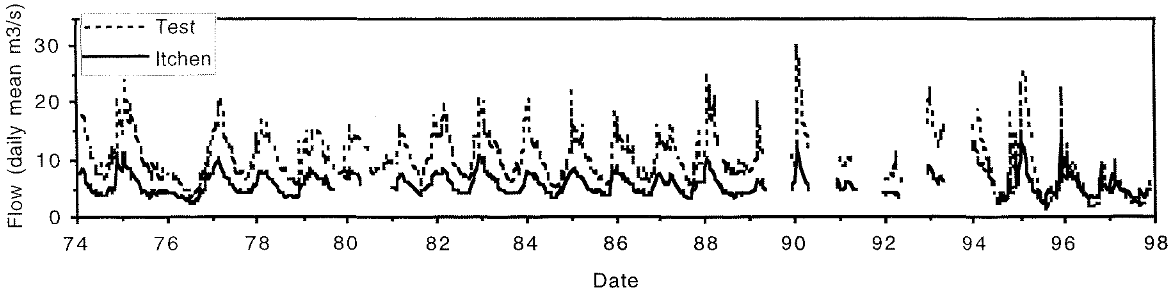

Figure 6.2 The flows of the River Itchen and the River Test (EA data, 1974 - 1998)

The phosphorus riverine input in the system is dominated by the DIP which is about 87% of the total phosphorus input. The River Itchen contributes about 59.4% of the phosphorus riverine inputs to the system. About 9.9 % of the total phosphorus input is in terms of PTP, which probably reflects the small input of SPM. Only 3 % of the total phosphorus transferred from the rivers is DOP, which implies that the relatively high DOP in the water column observed in high salinity waters (See Chapter 3) is likely produced by the biological activities in those waters, or transported from offshore.

2. Sewage inputs of phosphorus:

There are five major sewage works in the Southampton Water system. They are Slowhill Copse, Millbrook, Portswood, Woolston and Bursledon sewage discharge. The available details of the sewage works are shown in Table 6.2.

Table 6.2 Main sewage outfall in the Southampton Water system and the estimations of sewage phosphorus inputs in the SONUS study (Hydes and Wright, 1999)

Sewage outfall	Consented flow (m^3 / d)	Population equivalents	Phosphorus (tonne/y) (from SONUS study, based on per capita P of 0.4kg)
Slowhill Copse	14971	85900	34
Millbrook	40000	138700	55
Portswood	27700	67800	27
Woolston	15000	68000	27
Bursledon	1000	6600	4
Total	98671	367000	147

Phosphorus in the sewage outfall is mainly from human excrement, urine and domestic detergent. There are several methods to estimate the phosphorus sewage input in a system.

1) Multiply the coefficient of phosphorus discharge per person by the served inhabitant population of the sewage outfall to make the estimation. Different coefficients have been used in the literature. Excrement and urine from one person amounts to 0.6 kg phosphorus per year and phosphate used in washing powder amounts to 0.4 kg phosphorus per person per year (Lidgate, 1988). Lidgate (1988) estimated the sewage phosphorus inputs in the

North Sea by using the coefficient of 1.0 kg phosphorus per person per year. Hydes and Wright (1999), using the coefficient of 0.4 kg per person per year (Meybeck *et al.*,1989) estimated the phosphorus sewage input in the Southampton Water system as 147 tonnes per year. This estimation using a coefficient can be used as a general estimation of the sewage input of a region. Due to the variation of living standard and usage of detergent, the accuracy of the estimation by this method is questionable. However this value gives at least a maximum value for sewage input and the actual value would be expected to be lower due to sewage treatment and the potential for offshore dumping.

2) Multiply the typical concentration of phosphorus of the sewage discharge based on the level of treatment by the consented flow of each sewage discharge to make the total sewage input estimation. Somer (1988) has recommended the concentration of 1.5 mg / l (48 μmol P /l), which is a world wide average value, as the typical concentration of phosphorus in a sewage outfall. The estimation of phosphorus from sewage inputs for the Southampton Water system by this method is 54 tonnes per year. This value is expected to be high because the real flow of the sewage discharge should be less than the consented flow which is the maximum allowed.
3) The flux of DIP for sewage discharges is estimated in this study using the back extrapolating method of Wright and Hydes (1997). Here the difference between the back extrapolated and those fluxes calculated directly from the data of river DIP concentrations and river flows from the Environment Agency are obtained. The difference is estimated as the sewage input. The "pseudo" freshwater end-member concentration of DIP obtained by this method for each spring survey is calculated by the method of Wright and Hydes (1997). Regression lines are drawn from the most seaward sample, to the next most saline sample. The Pearson's moment correlation coefficient for each iteration is computed and its significance assessed. Once the change in coefficient becomes insignificant, the previous regression equation is used to calculate the intercept of the line and get a zero salinity theoretical end-member concentrations ("pseudo" freshwater end-member concentration). The "pseudo" freshwater end-member concentration of DIP is multiplied with the monthly

freshwater flow (from Environment Agency) to obtain the "pseudo" monthly DIP fluxes, and the sum of the monthly fluxes used to get the annual "pseudo" flux. There is no significant sewage input of phosphorus observed in the Test Estuary from the previous SONUS study (Hydes and Wright, 1999). The same phenomenon was also observed in the SONUS project and this study around the Woolston sewage discharge in the Itchen Estuary. This may be due to the more effective removal of phosphorus by the sewage treatments (Collins, 1978) and subsequently offshore dumping.

Table 6.3 The estimation of "pseudo" riverine input of the River Itchen

(the data are taken from the surveys in 1998 of this study)

Month	"pseudo" DIP concentration (μM)	river flow (m^3/s)	monthly fluxes (tonnes)
Jan	11.0	6.7	6.12
Feb	13.3	8.78	8.75
Mar	15.7	7.36	9.59
Apr	13.6	6.14	6.70
May	22.4	5.26	9.78
Jun	18.9	4.37	6.64
Jul	31.1	3.62	9.35
Aug	30.4	2.90	7.32
Sep	33.4	3.23	8.67
Oct	20.1	3.40	5.67
Nov	No Data	No Data	6.19*
Dec	14.3	5.65	6.71
		Annual total:	91.5 ± 15.8

* There was no survey in November, 1998. Hence, the flux of November is estimated as the average value of fluxes for December and October. The final error estimate is summed up the error of monthly flux.

There is no data available from the water companies about these sewage plants. Hence the sewage input in the Test Estuary is estimated here by the concentration of DIP in the River Test (Environment Agency data) with the consented flows of the sewage discharge works in the Test Estuary.

Due to the lack of data for DOP and PTP in the sewage outfalls and rivers, it is impossible to estimate the sewage input of these phosphorus species at this stage. However, inorganic phosphorus is likely the major part of sewage inputs to the system, as shown by the data of phosphorus in the water column from the surveys of this study around the Portswood sewage work site (See Chapter 3). Hence, the estimation of the sewage input of the Southampton Water system only consider inorganic phosphorus.

From Figure 6.3, the "pseudo" DIP concentration of the freshwater end-member appears high in summer and low in winter. There is no significant seasonal variation of the "pseudo" riverine flux through the year, although the river flow is high in winter and low in summer. The "pseudo" phosphorus concentration of the freshwater end-member is likely controlled by the consistently sewage input, especially in summer.

The riverine phosphorus input of the River Itchen is calculated above as 51.6 ± 8.8 tonne per year. The sewage input in the River Itchen is estimated by the difference between the annual "pseudo" riverine DIP flux and the real riverine input, which is 39.9 ±18.1 tonne a year. The estimation of sewage input in the Test Estuary is estimated as 3.30 ± 0.23 tonne a year (method see above). The total sewage input of phosphorus in the system is the combination of inputs to these two estuaries and is estimated as 43.2 ± 18.2 tonne a year.

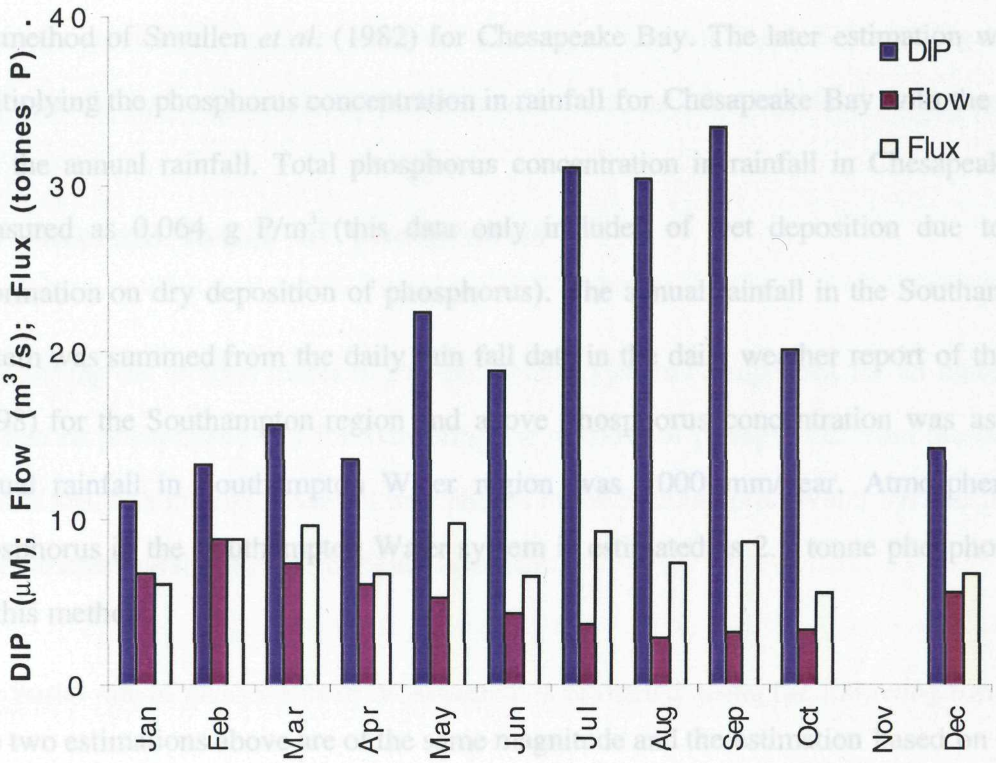

Figure 6.3 The monthly variation of river flow (m^3/s), the "pseudo" river DIP concentrations (μM), and the estimations of "pseudo" riverine monthly DIP fluxes (tonnes).

3. Atmospheric phosphorus input

Information on the atmospheric input of phosphorus for urbanised estuaries is rare in the literature. No phosphorus atmospheric deposition data is available in the Southampton Water system. In this study the phosphorus atmospheric deposition is estimated from the data of van Beusekom and de Jonge (1997) for the Wadden Sea, which is 0.04 tonne phosphorus km^{-2}y^{-1} based on wet-fall measurement. This estimation of atmospheric input of phosphorus was made by multiplying the phosphorus atmospheric deposition rate (0.04 tonne phosphorus km^{-2}y^{-1}) by the surface area of the system. The surface area of the Southampton Water system is 3.975×10^7 m^2 (Barne *et al.*, 1996). Therefore the atmospheric phosphorus input is estimated as 1.6 tonnes per year.

This estimation of atmospheric input of phosphorus can be compared with the estimate using the method of Smullen *et al.* (1982) for Chesapeake Bay. The later estimation was made by multiplying the phosphorus concentration in rainfall for Chesapeake Bay with the surface area and the annual rainfall. Total phosphorus concentration in rainfall in Chesapeake Bay was measured as 0.064 g P/m^3 (this data only included of wet deposition due to a lack of information on dry deposition of phosphorus). The annual rainfall in the Southampton Water system was summed from the daily rain fall data in the daily weather report of the Met office (1998) for the Southampton region and above phosphorus concentration was assumed. The annual rainfall in Southampton Water region was 1000 mm/year. Atmospheric input of phosphorus in the Southampton Water system is estimated as 2.5 tonne phosphorus per year by this method.

The two estimations above are of the same magnitude and the estimation based on the Wadden Sea data has been used in the phosphorus budget in this study as it is up to date and geographically similar to the Southampton Water system.

A small part of the phosphorus input may be lost to the atmosphere by reduction to phosphine (PH_3) (Section 6.2). Using the estimate taken from van Beusekonm and de Jonge (1997) for the Wadden Sea of 0.013 tonne phosphorus km^{-2}y^{-1}, the phosphorus atmospheric loss in terms of phosphine emission in the system is estimated as 0.52 tonne phosphorus per year. Currently due to lack of the information on the atmospheric phosphorus, it is difficult to estimate the error of this estimation but believe it is small compared with other estimates of inputs. Hence the net phosphorus atmospheric input in the system is estimated as 1.07 tonne phosphorus per year.

In summary, the total phosphorus input in the Southampton Water system is estimated as 144±23.7 tonne per year (the final error is combined the errors for all the inputs). Comparing the three phosphorus inputs in the system, the riverine input is the major input which is about 69% of the total phosphorus inputs. The direct sewage input contributes about 30% of the total phosphorus inputs to the system. Sewage input is an important source of phosphorus in the system, especially in summer when the river input is small (Table 6.3 and Figure 6.3). The atmospheric input of phosphorus is small and only about 1% of the total phosphorus inputs.

6.3 Internal losses of phosphorus

Quantifying the internal losses of phosphorus in a system is important for an understanding of the fate of phosphorus and for estimating the outflow of phosphorus from the estuary to the coastal sea. The internal losses of phosphorus in the Southampton Water system include burial in sediments and the regular dredging activities.

The burial rate of phosphorus in the sediment is estimated using the following formula:

Annual phosphorus burial in sediments = depositional area × annual deposition rate of dry sediments × % phosphorus in dry sediments

Dyer (1969) calculated semi-empirically a range of 2-6 mm sedimentation rate in Southampton Water. Croudace and Cundy (1995) used a combination of heavy metal analyses with radiochronology (using ^{137}Cs, ^{80}Co, and $^{210}Pb_{XS}$) to determine sediment accumulation rates in Southampton Water. Indications were that following dredging activities, accompanying the refinery expansion, there was a relatively rapid sedimentation rate of approximately 20 mm per year (1950's), which decreased with time to approximately 5 mm per year (1990's). There is a considerable variation of the sedimentation rate within the system due to hydrographic difference. In this study 5 mm per year is used as the current representative sedimentation rate in the system. The annual deposition rate of dry sediments is to multiply the sedimentation rate by the density of the sediments (0.58 g/cm^3, Cundy, 1994).

The mean content of phosphorus in the sediments in the Southampton Water system taken from the 1998 and 1999 sediment surveys of this study (for details of the surveys see Chapter5) is 18.6 μmol / g (0.057 % wt) (range: 7.97 - 34.2 μmol / g). The depositional area in the system is 3.975×10^7 m^2 (Barne *et al.*, 1996). An error of 50% based on the analytical error (See Chapter 5) is added on the estimation due to the variation of sediments. Therefore the burial rate of total phosphorus in the Southampton Water system is estimated as 66 ± 33 tonne phosphorus per year.

The Ca-bound phosphorus in terms of apatite is considered as permanent burial of phosphorus in the sediments (Ruttenberg and Berner, 1993). From SPEPs results in this study (see Chapter 5), the median value of Ca-bound phosphorus content in the sediments is 8.3 μmol / g (0.026 %wt). Therefore, in the Southampton Water system about 35.5 % of the phosphorus buried is estimated as remaining permanently in the sediments, which equates to 23.4 ± 11.7 tonnes phosphorus per year (error is estimated to be 50% of the value).

Data on annual dredging and dumping offshore for the system is not available. Therefore, the current estimation of phosphorus removal by dredging activities is based on the data from Dyer (1980) and Collins (1978). The annual regular maintenance dredging in the system amounts to about 50000 m^3, although the dredging of the shipping channel is variable. This removal is equivalent to the loss of 20.9 tonnes phosphorus per year. This amount of phosphorus is transported to other areas for commercial use.

The total internal loss of phosphorus is estimated by combining the burial of phosphorus in the sediment and the dredging removal; and equals 86.9 ± 33 tonnes per year (the error of the dredging estimation is presumably small compared to the sediment burial error and is ignored).

6.4 Exchange of phosphorus across seaward boundary

Estimate of the exchange of phosphorus across the seaward boundary was made by subtracting all internal losses from total terrestrial and atmospheric inputs, and is estimated by the following formula:

$\mathbf{I_o = I_p + I_r + I_a - L_b}$

where: $\mathbf{I_p}$ is annual phosphorus loads from sewage inputs; $\mathbf{I_r}$ is annual phosphorus loads from rivers; $\mathbf{I_a}$ is annual phosphorus from atmospheric deposition; $\mathbf{L_b}$ is annual phosphorus burial in sediments. The unites are all of tonne P. These estimates are given below in Table 6.4

Hence, the exchange of phosphorus across the seaward boundary is estimated as 57.1 ± 40.6 tonnes per year, which means that about 39.7% of the total phosphorus input is transported to the English Channel and adjacent areas and 60.3% of the phosphorus input is apparently retained in the system. Although some of the sediments which fills all of the inlets may come from the rivers, the greatest proportion was suggested probably derived from the sea and enters on the estuarine circulation (Dyer, 1980). The potential input of the particles from the sea needs to be investigated in the future. At this stage it is impossible to estimate the proportion of the sediment input from offshore. Hence this estimate is potentially overestimated (more discussion see Section 6.7).

6.5 Reservoirs of phosphorus

Annual stocks of phosphorus in this study included phosphorus in the water column (DIP, DOP, PTP) and sediment (top 5 cm of the sediment column). Each reservoir is considered in text below.

1. **DIP in water column**:

   The volume of water in the Southampton Water system is taken from Blain (1980) as 108×10^6 m^3 and 54×10^6 m^3 for a typical spring and neap tide, the mean value of these data (81×10^6 m^3) is used as the volume of the water mass for the Southampton Water system. The mean value of the concentrations of DIP of 18 surveys in this study is 2.40µM (0.02 - 33.4 µM), and is multiplied by the volume of water to estimate the reservoir of DIP in the system (6.03 tonnes). It is simplistic to estimate the storage by this method. The different behaviour of DIP in the Itchen Estuary and Southampton Water is obviously. Southampton Water has the large water mass, relative low DIP concentration the range of the concentration for DIP is small. In the Itchen Estuary the concentration of DIP is high, the gradient of DIP throughout the estuary is steep and the volume of water mass is small. Hence, further information on the volume of water mass for the Itchen Estuary and Test Estuary is needed to better estimate the pool of DIP in the system.

2. **DOP in water column**:

   The method used to estimate the storage of DOP in the system is as the same as DIP above. The mean value of DOP in the water column is 0.42 µM (0.02 ~20.0 µM) and the estimate of the reservoir is 1.05 tonnes.

3. **PTP in water column**:

   The method used to estimate the storage of PTP is as the same as DOP and DIP. The mean value of PTP-- PTP(c) in water column is taken as 0.56 µM (0.03 ~ 4.12 µM). The estimate of the PTP reservoir is 1.41 tonnes.

4. **Inorganic phosphorus in sediment**:

   The content of inorganic phosphorus in the sediments calculated from the data taken from the sediment surveys in this study (1998 and 1999) is 14.5 µmol / g (7.18 ~ 26.9 µmol/g). The sediment mass in the system (only considering top 5 cm depth, where phosphorus is more likely to be resuspended or released to the water column) is estimated by the following formula :

   $M = H \times G \times S$

   where :

M: the surficial sediment mass in the system (m^2);

H: the sediment depth (5 cm in this study);

G: the density of the sediments (0.58 g/cm^3);

S: the area of the sediment (3.975×10^7 m^2).

The surficial sediment mass in the system is estimated as 1.154×10^{12} g. The inorganic phosphorus storage in the sediments is thus estimated as 520 tonnes.

5. **Organic phosphorus in sediment**:

The average content of organic phosphorus in the sediment is 4.33 μmol / g (1.33 ~ 10.5 μmol/g) obtained from the 1998 and 1999 sediment surveys. The organic phosphorus storage in the sediments is estimated as 155 tonnes (the method of estimate is as the same as the estimation of inorganic phosphorus storage in the sediments). Phosphorus in the sediments in the system is mainly as inorganic phosphorus (about 77% of the total phosphorus). Organic phosphorus is only about 23% of the total stock.

6.6 Water column and sediment recycling rates

As mentioned in Chapter 5, the recycling rates across the sediment - water interface are important to the understanding of the phosphorus cycling within the system. The estimates of recycling rates across sediment-water column interface were obtained from the experimental incubation flux measurement (see Chapter 5). The results showed that the sediments in the Southampton Water system apparently acted as a sink for DIP and a source for DOP in the water column. The mean value of benthic flux of DIP is +183 μmol m^{-2} d^{-1}. Thus in the whole Southampton Water system about 2.66 tonnes of DIP are lost to the sediments per year. The mean value of benthic flux for DOP is 26 μmol m^{-2} d^{-1}, which means that about 0.38 tonnes of DOP are released to the water column from the sediments within a year. Due to the large variation amongst different sediment samples, these results can only be considered as a magnitude estimation. However, compared to the internal processes such as burial, the water column-sediment recycling caused by the diffusion of dissolved phosphorus is a minor component in the budget.

6.7 Budget summary and discussion

6.7.1 Summary of phosphorus budget in the system

Over the past several years new information on phosphorus has become available that is essential for making the phosphorus budget in the Southampton Water system presented here. This budget provides a framework to examine the manner in which phosphorus is processed as it passes through the system and also to diagnose the fate of phosphorus within the system. The phosphorus budget for the Southampton Water system is summarised in Table 6.4 and Figure 6.4.

Table 6.4. Summary of the phosphorus budget for the Southampton Water system

Category	General description	Data sources	Annual results (tonne P/year)
River inputs	Includes River Test and River Itchen	This study, freshwater data taken from EA (1990-1997)	99.4 ± 15.1
Sewage inputs	Includes all major point discharges in the system	1. Designed sewage served inhabitant population and potential discharge of phosphorus per person	367 (coefficient : 1.0 kgP/person/year, Lidgate, 1988); 147 (coefficient: 0.4 kgP/person/year, Meybeck *et al.*, 1989)
		2. Consented sewage flow and typical total phosphorus concentration in the sewage discharge after secondary treatment	54
		3. This study.	43.2 ± 18.2

Atmospheric input	Includes whole Southampton Water surface.	Atmospheric data taken from van Beusekom and de Jonge (1997) for the Wadden Sea, 0.04 tonne phosphorus km^{-2}y^{-1}. Surface area data from JNCC report (Barne *et al.,* 1996)	1.07
Burial in sediment	Estimate by the permanent burial of phosphorous in the intact sediment cores and the sedimentation rate	Permanent burial of phosphorus from SEDEX (Ca-bound P) data in this study.	104 ± 41.5 23.4 ± 11.7 (permanent)
Ocean exchange	Estimate of the annual net exchange of TP across the seaward boundary	This study (difference between terrestrial and atmospheric inputs and internal losses)	57.1 ± 40.6
Dissolved and particle stocks	Dissolved stocks include DIP and DOP in water column; particle stock estimated by the data as TP.	This study.	6.03 (DIP) 1.05 (DOP) 1.41 (PTP)
Sediment stocks	Consider inorganic and organic phosphorus in the sediment. The sediment mass is calculated to the depth of 5 cm	This study	520 (IP) 155 (OP)
Recycle terms	net sediment-water fluxes of DIP and DOP is evaluated	This study (incubation benthic fluxes measurement)	183 µmol m^{-2} d^{-1}(DIP) ------2.66 26 µmol m^{-2} d^{-1} (DOP) ------0.38

Riverine sources of phosphorus are the dominant input within the system and contribute about 69% of the total phosphorus inputs. Sewage input of phosphorus is comparable and important (30%), especially in summer when the river input is small. The atmospheric phosphorus input is small in this system, although in some other areas the dry deposition of phosphorus can be important and should be considered in the estimation of atmospheric phosphorus input (Duce, 1991). The estimate of the phosphorus sewage input still needs to be improved in the future. The real time concentration of phosphorus in the sewage discharge is needed together with discharge volume. The investigations of DOP and PTP in the sewage outfall are also important to complete the estimation of sewage inputs of phosphorus.

There is a considerable exchange flux with adjacent coastal waters (about 39.7% of total phosphorus inputs) which reveals that the Southampton Water system is likely to be a phosphorus source to the English Channel and adjacent areas. Retention of phosphorus causing by particle burial is an important process in the system. This process retains about 60.3% of the phosphorus entering the system. However, from the surveys in this study significant removal of phosphorus from the water column was not observed (Chapter 4), suggesting that there are other sources of phosphorus in the system or the estimate of internal loss is overestimated. While there is undoubtedly some error associated with all terms, none appear large enough to balance internal losses with the inputs of phosphorus in the system. It appears more likely that phosphorus is imported from coastal waters or adjacent areas via deep water flows associated with two-layer estuarine circulation. The P:Fe ratio of particles in BD extracts reported in Chapter 4 revealed the likelihood of the existence of an offshore input of particles. However, due to the lack of data on these particles, it is difficult to estimate the magnitude of this input of phosphorus at this stage. Hence the estimate of the exchange of phosphorus across seaward boundary in this study must be considered as a conservative estimation.

Due to the large population, the potential risk of large phosphorus sewage input exists during the waste water treatments accident. Because of the small suspended matter loading (see Chapter 3), the particles in low salinity waters are saturated with phosphorus. It is unlikely therefore that the burial of these particles can retain more phosphorus in the sediments.

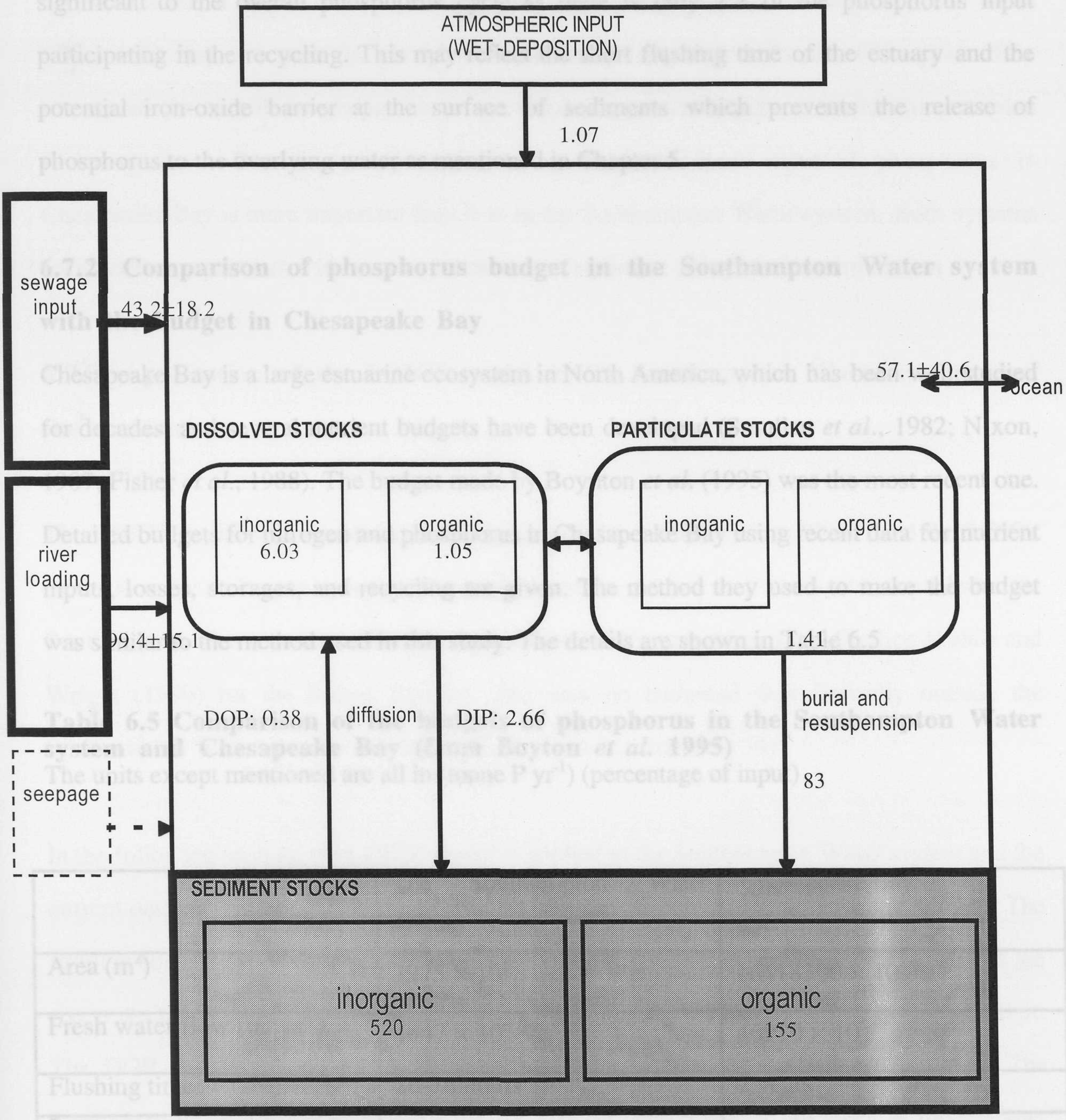

Figure 6.4 The budget of phosphorus in the Southampton Water system (units in diagram are all tonne P yr^{-1})

Sediment in the system is generally a diffusive sink of DIP in the water column, while the sediment is also a moderate source of DOP. The recycling of phosphorus in the system is not significant to the overall phosphorus cycle as there is only 2% of the phosphorus input participating in the recycling. This may reflect the short flushing time of the estuary and the potential iron-oxide barrier at the surface of sediments which prevents the release of phosphorus to the overlying water as mentioned in Chapter 5.

6.7.2 Comparison of phosphorus budget in the Southampton Water system with the budget in Chesapeake Bay

Chesapeake Bay is a large estuarine ecosystem in North America, which has been well studied for decades, and several nutrient budgets have been developed (Smullen *et al.*, 1982; Nixon, 1987; Fisher *et al.*, 1988). The budget made by Boynton *et al.* (1995) was the most recent one. Detailed budgets for nitrogen and phosphorus in Chesapeake Bay using recent data for nutrient inputs, losses, storages, and recycling are given. The method they used to make the budget was similar to the method used in this study. The details are shown in Table 6.5

Table 6.5 Comparison of the budgets of phosphorus in the Southampton Water system and Chesapeake Bay (from Boyton *et al.* 1995)
The units except mentioned are all in (tonne P yr^{-1}) (percentage of input)

	The Southampton Water system	Chesapeake Bay
Area (m^2)	3975×10^4	16418300×10^4
Fresh water flow ($m^3\ yr^{-1}$)	4447×10^6	46910×10^6
Flushing time	26-76 hours	2 years
Input		
Sewage	43.2(30%)	3960 (35.2%)
River	99.4 (69%)	6560 (58%)
Atmospheric	1.07(0.7%)	730 (6.5%)
Loss (bury in sediment)	86.9 (60.3%)	14488 (129%)
Ocean exchange	57.1 (39.7%)	-4110 *

* the negative value means phosphorus is transported from adjacent coastal waters.

Comparing to Chesapeake Bay, due to the shorter flushing time, the Southampton Water system is likely a source of phosphorus to the English Channel and the adjacent area while Chesapeake Bay is a sink for phosphorus and retains more phosphorus. Chesapeake Bay sewage works contribute comparable proportional phosphorus inputs as in the Southampton Water system. Due to the big surface area, the atmospheric input of phosphorus in Chesapeake Bay is more important than it is in the Southampton Water system. Both systems seem to have a problem with an over estimation of sediment phosphorus accumulation

6.7.3 Application of the LOICZ model in the Southampton Water system and the comparison

The LOICZ model was introduced in Chapter 1 of this study. Smith (1996) used the LOICZ model to make a nitrogen and phosphorus budgets for the Solent Estuary, which includes the Southampton Water system. The data Smith used (1996) was taken from Phillips (1980) and Wright (1980) for the Solent Estuary. The area he budgeted was basically outside the Southampton Water system (salinity for the budgeted system was 34).

In the following section, the LOICZ model is applied to the Southampton Water system and the current data obtained in this study is used to make the phosphorus budget for the system. The result is compared to the budget result above. The DIP concentrations and the flow data of the rivers are taken from Environment Agency (1990-1997) for the River Itchen and River Test. The DOP and PTP data of the rivers are estimated as the method in Section 6.2. The concentrations of DIP, DOP and PTP for the adjacent coastal waters are taken as the averages of the surveys in this study at the Calshot Buoy site which is at the mouth of the Southampton Water system and the highest salinity observed in the system. The concentrations of DIP, DOP and PTP for the budgeted system are obtained indicated in Section 6.5. The data used for the budget calculation is summarised in Table 6.6.

Table 6.6 Summary of data used for the budget calculation

	DIP (μM)	DOP(μM)	PTP(μM)	Salinity
River	5.63	0.32	0.91	0
Budgeted system composition (syst)	2.40	0.42	0.56	29.7
Adjacent coastal composition (ocn)	0.44	0.41	0.55	34

The equations used here are the same as described in Chapter 1.

$$V_{syst} \times dS_{syst}/dt = 0 = V_Q S_Q - V_R S_{syst} + V_x (S_{ocn} - S_{syst}) \quad (1)$$

$$V_{syst} \times dY_{syst}/dt = 0 = V_Q Y_Q - V_R Y_{syst} + V_x (Y_{ocn} - Y_{syst}) + \Delta Y \quad (2)$$

The descriptions of the items are the same as Chapter 1. Freshwater flow (V_Q) for the system estimated by combining the flow of the River Test and River Itchen is 4.64×10^8 m^3/yr. The direct precipitation (V_P) is estimated by multiplying the rain fall rate (1000 mm/y) with the surface area of the system (3.75×10^7 m^2) as 3.75×10^7 m^3/yr. Due to the lack of data for the evaporation in the system, the evaporation (V_E) in the system is unable to be estimated. But compared to the freshwater flow, the direct precipitation is less than 10% of the freshwater flow. V_E is assumed small and of the same magnitude as V_P. In this calculation, these flows (V_E and V_p) are not considered:

$$V_R = V_{in} - V_{out} = -V_Q - V_P + V_E \approx -V_Q = -4.64 \times 10^8 \text{ m}^3/\text{y} \quad (3)$$

V_R is negative indicating residual outflow.

$$V_x = (V_Q S_Q - V_R S_{syst}) / (S_{syst} - S_{ocn}) = 3.20 \times 10^9 \text{ m}^3/\text{y}$$

1)DIP:

Freshwater inflow delivers ($V_Q Y_Q = V_Q DIP_Q = 119$ tonnes /yr)

Residual outflow removes ($V_R Y_{syst} = V_R DIP_{syst} = 34.5$ tonnes /yr)

Mixing removes (V_x (Y_{ocn} - Y_{syst}) = V_x (DIP_{ocn} - DIP_{syst}) =194 tonnes /yr)

$\Delta DIP = -V_Q Y_Q + V_R Y_{syst} - V_x (Y_{ocn} - Y_{syst}) = -V_Q DIP_Q + V_R DIP_{syst} - V_x (DIP_{ocn} - DIP_{syst}) = 110$ tonnes /yr.

2) DOP:

Freshwater inflow delivers ($V_Q Y_Q = V_Q DOP_Q = 2.60$ tonnes /yr)

Residual outflow removes ($V_R Y_{syst} = V_R DOP_{sys} = 6.05$ tonnes/yr)

Mixing removes (V_x (Y_{ocn} - Y_{syst}) = V_x (DOP_{ocn} - DOP_{syst}) = 0.99 tonnes/yr)

$\Delta DOP = -V_Q Y_Q + V_R Y_{syst} - V_x (Y_{ocn} - Y_{syst}) = -V_Q DOP_Q + V_R DOP_{syst} - V_x (DOP_{ocn} - DOP_{syst}) =$ 4.44 tonnes /yr.

3) PTP:

Freshwater inflow delivers ($V_Q Y_Q = V_Q PTP_Q = 7.47$ tonnes /yr)

Residual outflow removes ($V_R Y_{syst} = V_R PTP_{sys} = 8.06$ tonnes/yr)

Mixing removes (V_x (Y_{ocn} - Y_{syst}) = V_x (PTP_{ocn} - PTP_{syst}) = 0.99 tonnes/yr)

$\Delta PTP = -V_Q Y_Q + V_R Y_{syst} - V_x (Y_{ocn} - Y_{syst}) = -V_Q PTP_Q + V_R PTP_{syst} - V_x (PTP_{ocn} - PTP_{syst}) =$ 1.58 tonnes /yr.

From the results above it appears that there are significant sources of phosphorus within the Southampton Water system. $\Delta P = \Delta DIP + \Delta DOP + \Delta PTP = 116$ tonnes/yr. If the sewage inputs are considered as an additional sources to the system, the sewage input in the system is estimated in Section 6.2. as 43.2 tonnes per year, there are about 72.8 tonnes phosphorus added in the system for which the source is unknown. The DIP release from the sediments to the overlying water is not significant in the system from the observation in this study. It seems hard to find any other sources to explain this gap. In the LOICZ model calculation, the result is very much reliant on the concentrations of phosphorus in the water of the budgeted system and the adjacent area. A seasonal variation in the high salinity waters, due to the seasonal biological activities, was observed in this study (Chapter3), and so the concentrations of phosphorus in the high salinity waters can change dramatically. When we estimated the concentration of the adjacent coastal waters, we used the annual median value of the samples taken from the Calshot Buoy site (salinity around 34). The range of DIP concentration at the Calshot Buoy site, for example, was from below the analytical detection limit to 1.28 μM. If 1 μM is used as the oceanic concentration of DIP in the model to estimate ΔDIP, the result is contrary. Due to the high DIP input into the system from sewage works, the concentration of phosphorus species in the whole estuary is varied and the median value used as the representative concentration for the whole estuary when the LOICZ model is applied, is questionable (in same survey the highest concentration of DIP can be hundreds times the lowest value). For DOP and PTP, no conservative mixing in the system was observed, and their estimations become even more difficult. Hence, in a system like the Southampton Water system, which has big tidal variations and complicated biogeochemical processes, the LOICZ model is not applicable.

Chapter 7: Conclusions and further work

This section summaries the main findings from the work reported here, and brings this together in an overview of the behaviour of phosphorus in the Southampton Water system. The remaining significant questions within the study are then considered and further works are suggested.

7.1 Phosphorus distribution in the Southampton Water system

7.1.1 Phosphorus in the water column

1. **Dissolved inorganic phosphorus (DIP)**: The overall distributions of concentrations of dissolved inorganic phosphorus in the system are influenced by the sewage inputs. The general pattern seen in the distribution in the River Itchen is a peak in concentration associated with the sewage discharge at Portswood and followed by apparent conservative behaviour in Southampton Water throughout the year except during algal blooms. Concentrations of DIP drop to below the detection limit (0.02 µM) in high salinity waters (salinity > 33) during the phytoplankton bloom in summer, when DIP in the water column was likely depleted by the phytoplankton growth.
2. **Dissolved organic phosphorus (DOP)**: The patterns of distributions of the concentrations of dissolved organic phosphorus were generally very variable in the system. Concentrations were often low, and rarely exceeded 5 µM. Occasionally a large peak in DOP in the water column was observed in the summer of 1998 which may result from phytoplankton cell exudates and release as the bloom crashed.
3. **Particulate phosphorus**: The concentrations of particulate phosphorus in water column $PTP_{(c)}$ (mass / volume) and phosphorus on the particle $PTP_{(m)}$ (mass / mass) generally all

decreased when the salinity increased along the estuary. This phenomenon and the DIP data in the water column suggest that in low salinity waters near the sewage outfall where the concentrations of DIP in the water column are high, the particles appear to adsorb the DIP in the water column and become "saturated" with phosphorus. The P:Fe ratio in bicanbonate-dithionite extractant in the SPEPs experiment (see Chapter 4) on particles implied that these particles are likely buried before they reach the high salinity waters and the particles in the high salinity waters were mainly from sediment resuspension, the detritus of phytoplankton or from offshore. The mixing with these low phosphorus content particles decreased the concentrations of $PTP_{(m)}$ in the high salinity waters. Particulate organic phosphorus (POP), which was calculated as the difference between $PTP_{(m)}$ and particulate inorganic phosphorus (PIP), was the dominant phosphorus species on the particles at the seaward end of the estuary (82%), decreasing to 36% upstream. This also reflected that the particles in high salinity waters are mainly detritus of phytoplankton or from offshore. Iron bound phosphorus (extracted with bicarbonate-dithionite reagent) dominated the particulate inorganic phosphorus fractions in most sites in the system, except where at some sites loosely absorbed phosphorus (extracted with NaCl) and Ca-bound phosphorus (extracted with HCl) were most important. The contributions of loosely adsorbed phosphorus and Ca-bound phosphorus to PIP generally increased seaward. The contribution of the polyphosphate fraction (extracted with NaOH) to PIP is generally constant through the system. The contribution of the iron -bound fraction to PIP phosphorus increased upstream.

7.1.2 Phosphorus in the sediments

Due to the limitation of sediment sampling technique used in this study only similar type of accessible sediments (mud or sandy mud) were sampled. Hence, presumably all the trends of phosphorus in sediments observed in this study were not due to different mixtures of sediment type.

1. **Organic and inorganic phosphorus in the sediments**. The horizontal trend of inorganic phosphorus in the sediments generally decreased seaward. The organic phosphorus content of the sediments does not change significantly through the system, although some slight decrease can be observed when the results from sediments in the Southampton Water system are compared to the results from those in the River Itchen. The vertical distributions of inorganic and organic phosphorus in the sediments were investigated. The inorganic phosphorus in the sediments generally decreased with depth, while organic phosphorus in the sediments behaved irregularly.
2. **Inorganic phosphorus species in the sediments**. The concentrations of all forms of inorganic phosphorus in the sediment generally decreased seaward through the Southampton Water system, although no significant change of the concentrations of Ca-bound phosphorus and polyphosphate in the sediments could be observed. The Ca- bound phosphorus appears to be the dominant form of inorganic phosphorus (about 55%-85% of total inorganic phosphorus) in most of the sediments in the Southampton Water system. At some sites, such as the Portswood sewage works and the Redbridge site, polyphosphate is another important form of inorganic phosphorus in the sediments due to the huge domestic waste water inputs. The loosely exchangeable phosphorus (less than 5% of the inorganic phosphorus in the sediment) is not a significant fraction in any of the sediments in the Southampton Water system. Iron bound phosphorus is higher in the sediments from the River Itchen sites and the Redbridge site in the River Test than other sites in Southampton Water. This results with the high iron bound phosphorus of the particles in these area reflect the likely immediate burial of the particles.

7.2 Application of the K_d model to the Southampton Water system

The application of the K_d model to the Southampton Water system revealed that it is difficult to rigorously rationalise the biogeochemical behaviour of phosphorus within an entire macrotidal system such as Southampton Water using this modelling approach. However, the K_d model is useful for examining the behaviour of DIP at the freshwater-seawater boundary, and for assessing and predicting the DIP concentration in the water column after storm and dredging activities could lead to particle resuspension.

The application of the K_d model in the Itchen Estuary shows that within the range of concentration of DIP in the Itchen Estuary the release of DIP from the particles increases when the concentration of SPM in the river increases. If the DIP riverine concentration or the phosphorus concentration on the particles increase the DIP pattern can be changed from release to removal. When the K_d value increases the DIP in the water column is more likely to be removed. Within the typical range of riverine DIP concentration it can be predicted that only a small amount of removal or addition of DIP is likely to occur at the freshwater-seawater boundary of the River Itchen.

The K_d model was used to predict the influence of sediment resuspension caused by storm events and dredging activities in the Southampton Water system on DIP concentrations. The tests of the model were done based on the variation of DIP concentrations in the estuary over typical ranges of values and the predicted final concentration of suspended particulate matter caused by the degree of the "event".

The results show that in the low DIP waters after the "event" the DIP in the water column may be increased due to the release of phosphorus from the particles. But in the high DIP waters DIP in the water column is always removed. The release of DIP after the "event" can be as big as ten times the initial DIP concentration in the water column in low DIP waters, while in high DIP waters (≥ 5 μM) the removal of DIP from the water column is seen. The concentration of suspended particulate matter after the "event" is another factor considered. The results show that when the SPM concentration increases due to the "event", the likely pattern of DIP in the water column is switched from adding phosphorus to the water column from the particles to removing the DIP from the water column.

7.3 Phosphorus budget of the Southampton Water system

In this study, a conceptual mass balance model was used to develop the phosphorus budget of the Southampton Water system. The budget provides an ecosystem-level framework to examine the manner in which phosphorus is processed as it passes through the system and also to diagnose the fate of phosphorus within the system. An annual quantitative input-export budget of phosphorus for the Southampton Water system was assembled and analysed. The budget includes estimates of phosphorus sources (sewage, riverine and atmospheric), internal losses (burial in sediments), storage in the water column and sediments, internal cycling rates (sediment-water flux), and net fluxes at estuary-sea boundary.

Riverine sources of phosphorus are the dominant input within the system and represent about 69% of the total phosphorus inputs. Sewage input of phosphorus is comparable in magnitude and importance (30%), especially in summer when the river input is small. The atmospheric phosphorus input is small in the system (1%).

There is a considerable exchange flux with adjacent coastal waters (about 40% of total phosphorus inputs) which reveals that the Southampton Water system is likely to be a source of phosphorus to the English Channel and adjacent areas. Retention of phosphorus caused by particle burial is an important process in the system. This process retains about 60% of the phosphorus entering the system. However, from the surveys in this study significant removal of phosphorus from the water column was not observed, suggesting that there are other sources of phosphorus to the system, or the estimate of internal loss is overestimated. It appears more likely that some of particulate phosphorus is imported from coastal waters or adjacent areas via deep water flows associated with two-layer estuarine circulation. However, due to the lack of data on these particles and their fluxes, it is difficult to estimate the magnitude of this input of phosphorus at this stage. Hence the estimate of the exchange of phosphorus across seaward boundary in this study is conservative. Sediment in the system is found to be a diffuse sink of DIP in the water column and a moderate source of DOP.

In a comparison with Chesapeake Bay, due to the shorter flashing time, the Southampton Water system appears to be a source of phosphorus to the English Channel and the adjacent area, while Chesapeake Bay is a sink for phosphorus. This difference reflects the longer residence time of water in Chesapeake Bay relative to the Southampton Water system, and hence a longer period for removal processes to occur. Sewage works in Chesapeake Bay contribute comparable proportional phosphorus inputs as in the Southampton Water system. Due to the big surface area, the atmospheric input of phosphorus in Chesapeake Bay is more important than it is in the Southampton Water system. Both systems seem to have a problem in the budgets with an over-estimation of accumulation of sediment phosphorus.

The LOICZ model has been applied to the Southampton Water system. The results appear to show that there are significant sources of phosphorus in addition to the sewage works within the Southampton Water system, which are hard to identify. The calculation of the LOICZ model very much relies on the concentrations of phosphorus in the water of the budgeted system and the adjacent area. In fact the concentrations of phosphorus in the high salinity waters can change dramatically. Due to the high DIP input into the system from sewage works, the concentrations of phosphorus species in the whole estuary also varied. Hence, the use of single median value of the data as the representative concentration for the whole estuary when the LOICZ model is applied, is questionable (in one survey the highest concentration of DIP can be hundreds times the lowest value). For DOP and PTP, no conservative mixing in the system was observed, and their estimations become even more difficult. In a system like the Southampton Water system, which has big tidal variations and complicated biogeochemical processes, the simple LOICZ model is not applicable.

7.4 Summary of the behaviour of phosphorus in the Southampton Water system

The analysis of historical studies of the Southampton Water system and this study revealed that phosphorus is potentially a limiting element for phytoplankton growth (Hydes and Wright, 1999). The Southampton Water system has high DIP inputs and relatively low suspended particulate matter concentrations. The "buffer" mechanism phenomena for phosphorus which has been observed in many estuaries and was discussed in detail by Froelich (1988) was not clearly observed in the Southampton Water system from the survey data. The test of the K_d model on the boundary of freshwater and seawater also proved that only small amount of DIP in the water removal or addition can possible occur over the typical range of riverine DIP concentration. The sewage discharges within the system significantly influence the pattern of phosphorus in the water column and contribute inputs of phosphorus to the system comparable in magnitude to those of rivers.

High particulate phosphorus (mass / mass and mass / volume) concentrations near the Portswood sewage works suggest that small amount of particles in the water column likely adsorb dissolved inorganic phosphorus in the water column and become "saturated". The high concentration of phosphorus in the sediments at the same area suggest that these particles are buried quickly after the adsorption of the phosphorus. The estuary likely retains dissolved inorganic phosphorus in the water column through burial of these particles. Major desorption of DIP from particles was not supported by the field data from the water column in this study, where no significant removal or addition processes were observed. This in part may reflect the weak signal from this desorption process compared to the dominant physical mixing processes occurring which influence phosphorus concentrations. The P:Fe ratio from the SPEPs experiment implied that the particles in high salinity waters are generally from the resuspension of the sediments or offshore. The noise in DIP / salinity relationship analysis could also reflect the influence of temporary particle resuspension due to " event" which are tested by the K_d model.

7.5 Further work

Further interdisciplinary studies are required to fully understand the interaction between the biological and geochemical processes that are occurring in the Southampton Water system. This study provided an annual data set for all forms of phosphorus in the Southampton Water system for the first time. Since the data for DOP and PTP were only obtained for one year, further study is needed to reaffirm the behaviour of these forms of phosphorus in the system, and assess their yearly variation.

The forms of suspended particulate phosphorus has been investigated for the first time in the Southampton Water system in this study. However, there was only one survey carried out, and hence the representativeness of the results is questionable. Further investigation of the forms of particulate phosphorus and phosphorus in surfacial sediments on better temporal and spatial resolution is needed. More geological information on the origin and sizes of particle are needed to better interpret the behaviour of the particulate phosphorus within the system in order to identify origins of particles. More studies on the P:Fe index as an indicator of the origin for the particles may provide clearer information on particle sources.

Phosphorus in the sediments has been measured for the first time in the Southampton Water system. More representative samples of different types of sediments from the estuary are needed. New technologies of the measurement of porewater phosphorus such as the DET gel technique should be applied to the system, to allow better understanding of phosphorus geochemistry in sediments.

The first regional budget of phosphorus has been made in this study for the Southampton Water system. Several points that need to be improved are outlined below :

1. River inputs. More riverine DIP, DOP, PTP, SPM data are needed, that can be coupled with real time flow measurement.
2. Sewage inputs. More information on sewage discharges is needed, especially for the DIP, PTP, DOP concentrations in the sewage outfall. Potential offshore dumping and changes in practices need to be monitored and assessed.
3. Atmospheric inputs. Data of the phosphorus concentration in rainfall in the Southampton Water region is needed to test the assumption made in this study (see Chapter 6).

More accurate estimate on internal losses is needed. The potential two layer offshore input is needed to be quantify.

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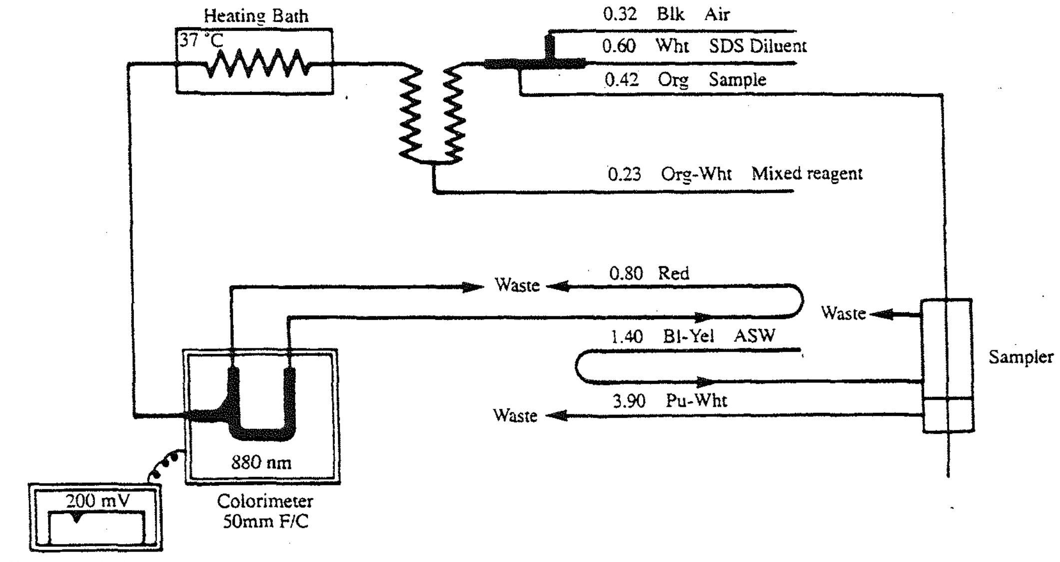
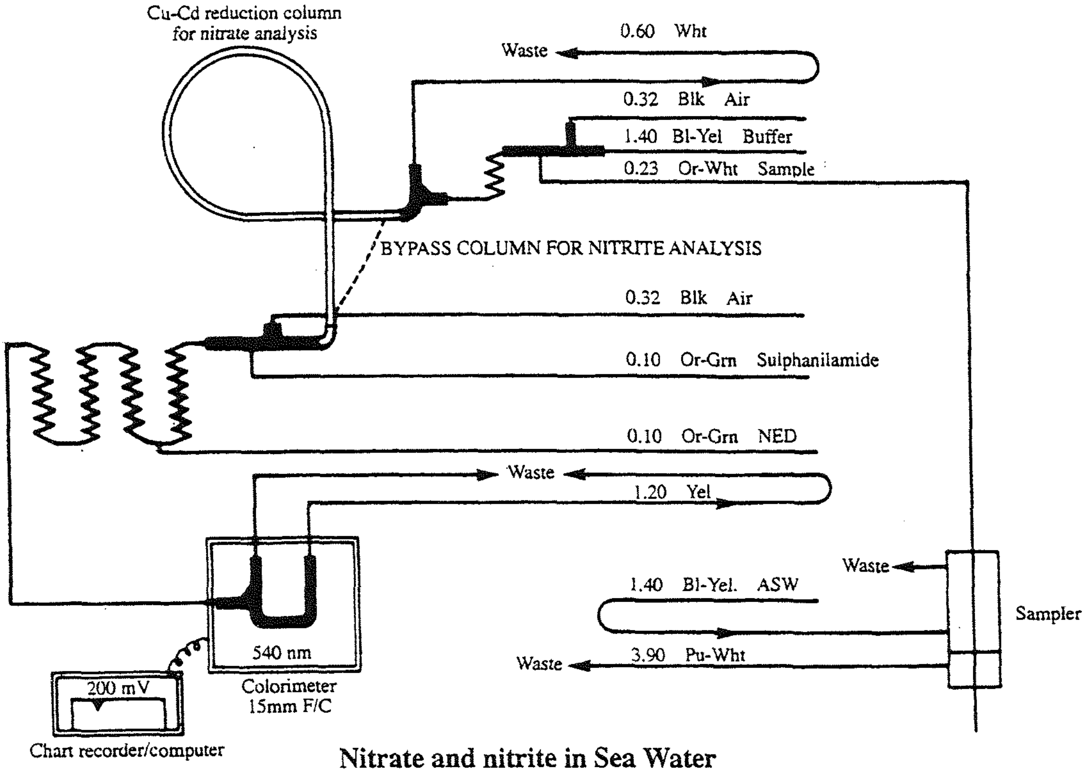
Appendices

Auto-analyser manifold for the determination of Phosphate



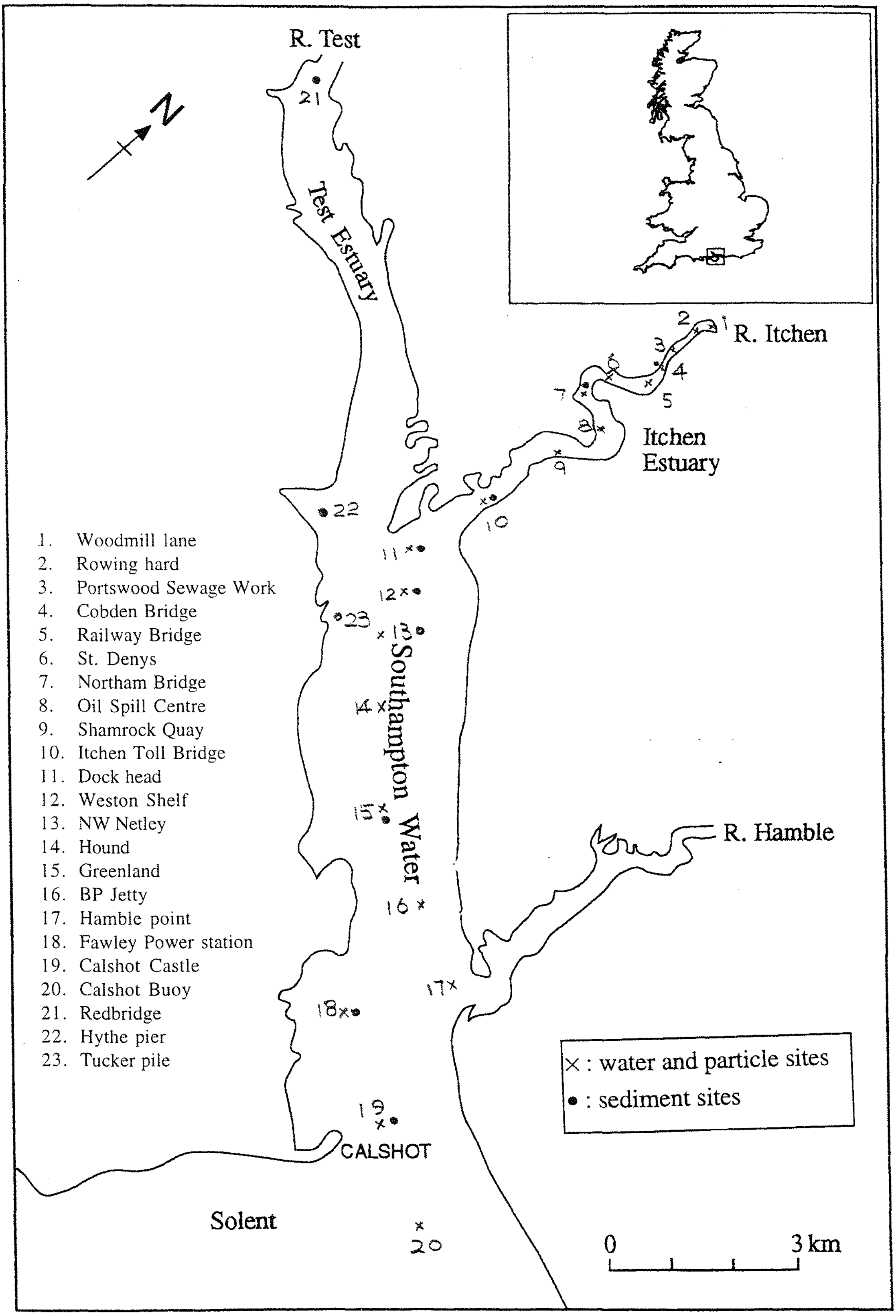
Phosphate in Sea Water

Auto-analyser manifold for determinations of Nitrate and Nitrite



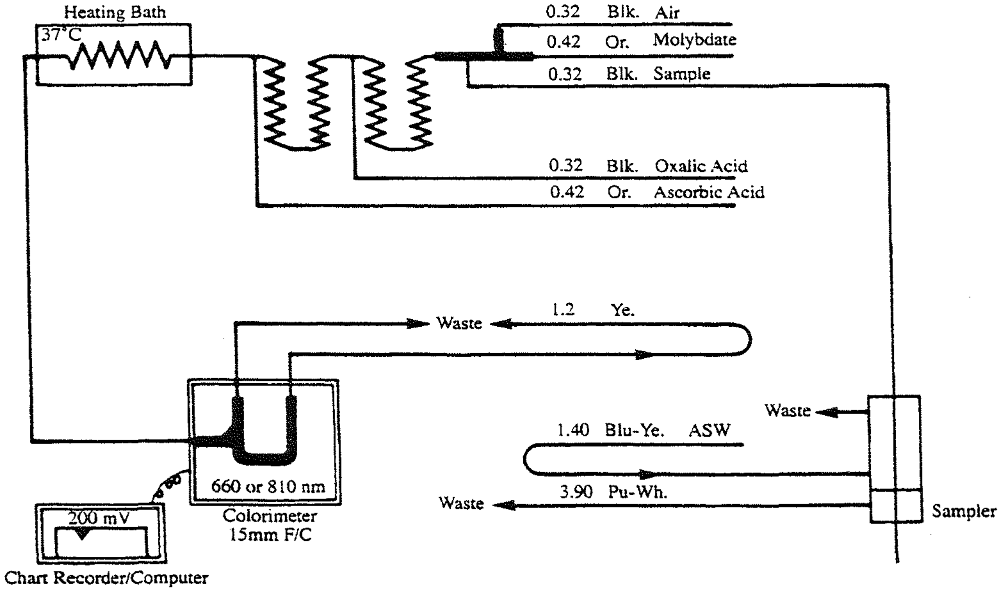
Nitrate and nitrite in Sea Water

Sampling Sites in the Southampton Water system



1. Woodmill lane
2. Rowing hard
3. Portswood Sewage Work
4. Cobden Bridge
5. Railway Bridge
6. St. Denys
7. Northam Bridge
8. Oil Spill Centre
9. Shamrock Quay
10. Itchen Toll Bridge
11. Dock head
12. Weston Shelf
13. NW Netley
14. Hound
15. Greenland
16. BP Jetty
17. Hamble point
18. Fawley Power station
19. Calshot Castle
20. Calshot Buoy
21. Redbridge
22. Hythe pier
23. Tucker pile

Auto-analyser manifold for dtermination of dissolved Silicon



Silicate in Sea water

SONUS 1998 JAN NUTS DATA											
Station	**Name**	**Salinity**	**SPM(mg/l)**	**Si**	**DIP**	**DIN**	**DIN/DIP**	**PTP (c)**	**PTP(m)µmol/g**	**DOP**	**Kd**
980101	Calshot Buoy	34.5	54.2	26.5	0.32	28.0	87	1.63	30.1	0.5	94027
980102	Calshot Castle	30.5	19.8	28.6	0.85	53.7	63	0.99	50.0	0.71	58871
980103	Fawley PS	30.4	23.6	28.7	0.90	53.5	59	0.89	37.6	1.22	41751
980104	Hamble Point	29.8	24.8	30.0	1.01	52.8	52	0.89	35.8	0.65	35404
980105	BP Jetty	30.4	21.8	28.5	0.98	53.0	54	1.11	50.8	0.31	51807
980106	Greenland	31.2	22.0	24.4	1.06	47.6	45	1.11	50.3	0.21	47461
980107	Hound	29.7	22.2	48.9	1.09	63.4	58	0.91	40.8	0.43	37474
980108	NW Netley	29.2	26.2	52.9	1.06	70.2	66	0.81	30.8	1.16	29051
980109	Weston Shelf	28.5	19.0	54.7	1.11	71.6	65	0.84	44.1	0.82	39772
980110	Dockhead	29.1	18.8	36.2	1.83	95.8	52	0.93	49.5	<0.02	27055
980111	Itchen Toll Bridge	27.6	28.2	43.2	7.02	82.1	12	1.09	38.7	<0.02	5510
980112	Woodmill Lane	2.0	14.6	185.6	7.33	367.5	50	3.06	209.8	<0.02	28619
980113	Rowing hard	0.9	17.4	189.4	7.31	380.8	52	2.30	132.3	<0.02	18105
980114	PWD	3.4	14.6	173.7	9.76	341.8	35	2.54	173.9	<0.02	17817
980115	Cobden Bridge	5.8	10.0	164.7	8.88	318.7	36	2.08	207.9	3.14	23410
980116	Rail Bridge	4.5	13.0	173.1	9.76	324.7	33	1.79	138.1	<0.02	14146
980117	St Denys	4.8	9.0	167.4	9.14	371.1	41	2.20	244.8	1.96	26779
980118	Northam Bridge	6.7	16.0	154.5	9.20	294.8	32	2.01	125.4	<0.02	13633
980119	Oil Spill Centre	13.8	20.6	116.2	6.41	224.4	35	1.73	84.2	0.52	13138
980120	Shamrock Quay	19.8	19.6	91.6	4.78	167.8	35	1.23	63.0	0.55	13180

SONUS 1998 FEB NUTS DATA											
Station	**Name**	**Salinity**	**SPM (mg/l)**	**Si**	**DIN**	**DIP**	**DIN/DIP**	**PTP (c)**	**PTP(m)µmol/g**	**DOP**	**Kd**
980201	Woodmill lane	3.2	26.2	173.9	367.8	7.20	51	4.12	157.36	<0.02	21855
980202	Rowing hard	2.0	11.8	174.1	414.0	7.33	56	2.98	252.78	5.98	34486
980203	PWD	9.9	12.6	129.8	305.1	7.02	43	2.21	175.14	<0.02	24949
980204	Cobden bridge	6.8	9.8	158.6	358.5	12.78	28	2.23	227.22	<0.02	17780
980205	Rail bridge	2.5	8.6	183.1	369.0	13.67	27	2.15	249.63	0.46	18261
980206	St denys	6.1	11.2	169.0	341.0	14.20	24	1.61	144.18	<0.02	10153
980207	Northam bridge	18.6	15.8	105.4	208.7	6.98	30	0.99	62.71	<0.02	8984
980208	Oil spill centre	24.1	18.4	62.2	141.9	5.34	27	0.83	44.93	<0.02	8415
980209	Shamrock quay	26.4	20.6	49.0	112.7	4.40	26	0.36	17.42	0.39	3959
980210	Itchen toll bridge	30.8	26.8	28.2	62.7	2.52	25	0.03	1.15	<0.02	456
980211	Calshot buoy	33.9	76.0	15.9	29.8	0.49	61	0.47	6.14	0.31	12535
980212	Calshot castle	33.2		16.0	32.1	0.51	63			1.42	
980213	Fawley ps	33.0		17.1	34.4	0.46	75			1	
980214	Hamble point	32.8	57.8	17.7	36.5	0.54	68	0.16	2.75	0.23	5088
980215	Bp jetty	32.0	58.2	27.9	56.2	0.67	84	2.26	38.88	0.39	58029
980216	Greenland	31.3	54.8	25.5	57.4	1.02	56	0.36	6.55	0.68	6419
980217	Hound	31.3	56.8	49.2	74.2	0.78	95	0.22	3.85	0.93	4939
980218	NW netley	30.2		45.7	83.6	0.73	115			0.69	
980219	Weston shelf	30.0		34.1	77.3	1.41	55			0.19	
980220	Dockhead	28.1	51.6	38.5	95.7	2.18	44	0.29	5.71	10.57	2621
980201*					390.1	6.86	57				

SONUS 1998 MAR NUTS DATA

Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m)μmol/g	DOP	Kd
980301	Hound	31.0	52.4	43.7	0.45	50.8	113	0.24	4.63	0.99	10297
980302	NW Netley	32.0	59.6	33.6	0.77	52.5	68	0.35	5.82	0.98	7557
980303	Weston Shelf	30.6	55.8	53.2	0.87	57.1	66	0.31	5.57	1.34	6402
980304	Dockhead	29.0	57.2	37.9	1.88	76.8	41	0.21	3.69	1.43	1960
980305	Itchen Toll Bridge	27.3	54.6	66.3	4.30	92.3	21	0.21	3.93	1.79	915
980306	Woodmill lane	24.1	40.8	64.1	5.48	129.5	24	0.41	9.97	1.74	1819
980307	Rowing Hard	22.6	46.2	73.6	6.26	149.0	24	0.59	12.87	1.25	2057
980308	PWD	20.0	34.4	84.9	7.25	176.9	24	0.66	19.27	1.67	2658
980309	Cobden Bridge	20.1	37.8	85.9	7.21	175.9	24	0.58	15.31	2.51	2124
980310	Rail bridge	8.2	29.8	146.6	11.47	309.8	27	1.07	35.87	<0.02	3127
980311	St Denys	5.0	14.4	167.9	13.83	361.3	26	0.94	65.06	<0.02	4704
980312	Northam Bridge	0.1	13.8	174.8	13.06	388.7	30	1.07	77.88	<0.02	5964
980313	Oil Spill Centre	0.1	12.2	178.1	10.65	399.6	38	1.45	118.75	<0.02	11151
980314	Shamrock Quay	0.1	21.2	175.5	14.25	396.6	40	1.91	89.94	<0.02	6312
980315	PWD-Corden	15.0	14.0	131.6	9.98	221.1	16	1.24	88.63	<0.02	8881
980316	After railway	2.2	31.6	168.6	9.35	358.9	38	0.98	30.97	0.25	3313

SONUS 1998 APR NUTS DATA

Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) μmol/g	DOP	Kd
980401	Woodmill Lane	0.0	13.4	166.46	7.15	389.7	55	0.91	68.27	0.61	9548
980402	Rowing hard	0.1	8.8	164.36	7.43	390.3	53	0.87	98.32	1.44	13233
980403	PWD	0.3	10.4	169.18	14.14	370.7	26	1.13	108.58	0.20	7679
980404	Cobden Bridge	2.9	18.8	154.83	12.44	345.2	28	1.24	65.77	0.45	5287
980405	S7	7.0	16.8	133.87	9.97	298.4	30	0.68	40.55	1.54	4067
980406	Rail Bridge	16.0	33.4	90.38	6.90	199.4	29	0.78	23.27	1.50	3372
980407	St Denys	18.8	38.0	83.56	6.33	182.2	29	0.62	16.41	1.26	2593
980408	Northam Bridge	22.2	31.2	65.42	5.59	141.1	25	0.51	16.40	1.25	2933
980409	Oil Spill Centre	23.4	33.4	55.51	4.70	119.6	25	1.01	30.17	1.12	6419
980410	Shamrock Quay	28.0	56.6	48.04	3.22	74.8	23	0.51	8.93	1.23	2772
980411	Itchen Toll B	29.0	54.4	31.82	3.56	67.2	19	0.51	9.40	0.95	2642
980412	Dockhead	30.6	39.2	23.67	1.66	51.4	31	0.26	6.52	0.67	3928
980413	Weston Shelf	30.7	50.6	22.97	1.48	49.8	34	0.31	6.16	0.94	4161
980414	NW Netley	30.8	47.2	22.92	1.43	49.8	35	0.34	7.18	0.00	5020
980415	Hound	32.2	44.0	16.98	1.01	35.8	35	0.26	5.92	0.63	5860
980416	Greenland	32.6	40.8	15.20	0.85	31.2	37	0.22	5.48	0.78	6448
980417	BP Jetty	33.2	25.6	14.75	0.85	30.4	36	0.24	9.42	0.58	11085
980418	Hamble Point	33.2	65.8	12.72	0.70	25.2	36	0.50	7.53	0.49	10760
980419	Fawley PS	33.4	58.8	14.30	0.75	26.9	36	0.25	4.29	0.48	5723
980420	Calshot Castle	33.5	55.6	11.28	0.70	25.9	37	0.31	5.66	0.79	8088
980421	Calshot Buoy	33.3	54.4	14.94	0.72	26.2	36	0.34	6.23	0.66	8650

SONUS 1998 APR (neap) NUTS DATA

Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m)μmol/g	DOP	Kd
N980401	Calshot Buoy	32.8	41.2	18.97	0.92	33.4	36	0.16	3.91	0.24	4253
N980402	Calshot Castle	32.1	53.2	13.69	1.00	33.9	34	0.37	6.88	0.48	6880
N980403	Fawley PS	31.6	46.4	24.50	1.36	44.0	32	0.33	7.16	0.2	5267
N980404	Hamble Point	30.4	41.0	29.33	1.60	54.6	34	0.28	6.94	<0.02	4335
N980405	BP Jetty	30.3	40.2	17.81	1.58	58.2	37	0.31	7.83	<0.02	4956
N980406	Greenland	30.2	54.6	18.13	1.60	55.5	35	0.22	4.10	0.02	2560
N980407	Hound	30.7	50.4	16.97	1.48	50.4	34	0.27	5.36	<0.02	3620
N980408	NW Netley	30.2	34.2	17.99	1.63	54.5	33	0.24	7.01	<0.02	4298
N980409	Weston Shelf	30.0	51.8	18.81	1.70	56.5	33	0.32	6.26	0.08	3684
N980410	Dockhead	29.3	29.0	20.25	2.02	61.6	30	0.33	11.24	<0.02	5565
N980411	S25	25.5	38.2	35.23	4.57	107.3	23	0.44	11.55	1.15	2527
N980412	Itchen Toll Bidge	20.1	33.8	56.10	8.62	145.8	17	0.51	15.18	2.74	1761
N980413	Shamrock Quay	12.9	22.2	84.65	7.51	241.1	32	0.82	37.03	1.43	4930
N980414	Oil Spill Centre	8.8	10.0	104.00	9.08	288.1	32	1.06	106.20	3.62	11696
N980415	Northam Bridge	7.2	15.0	131.60	9.60	303.8	32	0.95	63.44	2.34	6608
N980416	S16	16.0	31.2	76.36	7.11	199.9	28	0.83	26.76	2.57	3763

SONUS 1998 MAY NUTS DATA

Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) μmol/g	DOP	Kd
S980501	Woodmill Lane	0.0	11.0	145.39	7.36	374.3	51	1.01	92.18	1.02	12525
S980502	Rowing hard	0.1	9.2	157.83	9.40	368.7	39	0.82	89.00	0.3	9468
S980503	PWD	3.2	4.6	124.48	26.97	290.6	11	1.27	275.04	<0.02	10198
S980504	Cobden Bridge	13.2	13.4	97.58	11.61	250.3	22	1.08	80.81	0.27	6960
S980505	Rail Bridge	9.0	9.2	110.12	12.94	278.3	22	0.93	101.00	<0.02	7805
S980506	St Denys	18.2	9.0	79.08	8.63	202.9	24	0.75	82.98	0.13	9615
S980507	Northam Bridge	22.2	10.8	54.65	5.95	137.5	23	0.60	55.96	0.93	9406
S980508	Oil Spill Centre	26.8	18.2	41.78	4.00	94.2	24	0.50	27.23	0.97	6808
S980509	Shamrock Quay	29.0	14.8	24.35	2.55	67.3	26	0.35	23.54	1.27	9232
S980510	Itchen Toll B	30.4	17.4	19.03	2.19	53.0	24	0.32	18.55	1.12	8471
S980511	Dockhead	31.6	17.6	25.72	1.13	42.6	38	0.34	19.34	0.8	17116
S980512	Weston Shelf	30.6	14.4	17.62	1.32	54.8	42	0.33	22.86	0.82	17319
S980513	NW Netley	31.7	18.2	14.01	0.94	44.8	48	0.24	13.16	0.64	14005
S980514	Hound	32.5	18.0	25.19	0.66	33.6	51	0.18	10.20	0.67	15455
S980515	Greenland	32.7	21.8	10.74	0.55	31.8	58	0.22	9.96	0.77	18115
S980516	BP Jetty	32.7	15.4	10.47	0.54	32.8	61	0.25	16.18	0.68	29966
S980517	Hamble Point	32.8	11.8	10.31	0.52	31.9	61	0.16	13.80	0.68	26532
S980518	Fawley PS	33.0	15.6	9.69	0.46	30.2	66	0.18	11.46	0.77	24916
S980519	Calshot Castle	32.4	23.0	11.45	0.62	35.5	57	0.25	10.70	0.66	17251
S980520	Calshot Buoy	33.7	29.4	8.21	0.30	22.8	76	0.39	13.21	0.6	44036

SONUS 1998 MAY (neap) NUTS DATA											
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m)μmol/g	DOP	Kd
S980501*	Calshot Buoy	32.3	16.2	14.18	0.48	34.8	73	0.14	8.59	0.47	17901
S980502*	Calshot Castle	31.2	8.6	15.46	0.75	44.5	59	0.23	26.60	0.91	35473
S980503*	Fawley PS	31.1	16.2	15.08	0.75	42.5	57	0.21	12.94	0.59	17251
S980504*	Hamble Point	30.2	13.4	14.84	0.84	43.1	51	0.22	16.36	0.62	19474
S980505*	BP Jetty	30.5	13.6	13.94	0.83	43.1	52	0.26	19.29	0.58	23246
S980506*	Greenland	29.5	16.8	19.53	1.26	60.6	48	0.31	18.57	0.84	14739
S980507*	Greenland(bottom)	31.9	23.2	9.12	0.30	22.6	75	0.26	11.38	0.5	37931
S980508*	Hound	30.5	16.2	19.96	1.36	65.3	48	0.26	16.10	0.63	11837
S980509*	NW Netley	30.3	18.2	16.40	1.36	51.8	38	0.22	11.87	0.7	8727
S980510*	NW Netley(bottom)	31.5	25.0	10.16	0.59	30.9	52	0.26	10.43	0.57	17681
S980511*	Weston Shelf	30.7	20.0	14.97	1.28	46.5	36	0.24	12.08	0.61	9438
S980512*	Dockhead	29.8	25.4	37.68	1.94	56.6	29	0.07	2.71	0.7	1396
S980513*	Dockhead(bottom)	32.2	31.6	7.70	0.38	23.7	62	0.44	13.97	0.52	36775
S980514*	Itchen Toll B	24.0	11.4	36.43	3.78	94.0	25	0.33	28.91	0.32	7649
S980515*	Shamrock Quay	19.3	9.8	67.36	7.35	160.8	22	0.43	43.59	0.94	5931
S980516*	Sharmark Quay (b)	29.5	15.4	29.38	3.49	80.0	23	0.50	32.52	0.55	9318
S980517*	Oil Spill Centre	17.8	10.8	57.18	6.22	137.9	22	0.49	45.78	1.24	7360
S980518*	Northam Bridge	17.3	12.2	68.87	7.52	165.2	22	0.69	56.39	0.61	7499
S980519*	Notham Bridge(b)	27.7	18.0	37.57	4.14	97.9	24	2.36	131.11	0.36	31669

SONUS 1998 JUN NUTS DATA											
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) μmol/g	DOP	Kd
S980601	Calshot Buoy	33.8	19.8	13.0	<0.02	6.2		0.12	5.90	0.26	
	bottom	33.7	21.8	10.0	<0.02	3.2		0.23	10.53	0.35	
S980602	Calshot Castle	33.4	16.6	10.6	0.02	8.3		0.12	7.23	0.37	
S980603	Fawley PS	32.6	15.8	12.1	0.14	13.9	99	0.19	12.20	0.43	87161
S980604	Hamble Point	32.6	17.0	11.6	0.12	13.7	114	0.17	9.84	0.35	81961
	bottom	33.5		10.1	0.00	16.6				0.81	
S980605	BP Jetty	32.6	16.0	11.3	0.17	14.3	84	0.23	14.30	0.44	84118
S980606	Greenland	32.5	23.2	11.1	0.20	14.8	74	0.24	10.28	0.53	51379
	bottom	33.1		10.0	0.04	9.6				0.58	
S980607	Hound	32.4	6.6	11.1	0.24	16.5	69	0.22	33.58	0.45	139899
S980608	NW Netley	32.4	13.6	11.2	0.26	24.4	94	0.26	19.06	0.56	73303
	bottom	32.7		9.8	0.22	14.2	65			0.57	
S980609	Weston Shelf	32.1	7.0	11.4	0.36	19.3	54	0.32	45.49	0.59	126349
S980610	Dockhead	31.9	17.2	11.6	0.41	21.0	51	0.25	14.65	1.6	35735
	bottom	32.0	19.6	10.9	0.45	25.2	56	0.35	18.04	0.61	40091
S980611	Itchen Toll B	30.0	15.4	21.9	1.89	41.5	22	0.33	21.30	0.24	11269
	bottom	32.4		12.5	0.48	17.9	37			0.6	
S980612	Shamrock Quay	29.8	16.2	24.8	1.84	52.5	29	0.31	19.41	0.54	10548
S980613	Oil Spill Centre	26.8	10.4	41.2	3.72	67.0	18	0.37	35.15	0.06	9450
S980614	Northam Bridge	23.5	9.6	62.3	5.54	109.2	20	0.52	54.08	0.31	9762
	bottom	28.7		30.6	2.78	55.2	20			0.51	
S980615	St Denys	21.4	7.2	70.6	6.60	139.1	21	0.48	67.11	0.08	10168
S980616		15.0		113.9	9.12	221.2	24			0.04	
S980617		9.5		147.5	11.93	261.6	22			<0.02	
S980618	Rail Bridge	5.3	8.6	174.0	15.32	316.4	21	0.86	99.81	<0.02	6515
S980619		2.8		190.7	17.39	356.1	20			<0.02	
S980620	Cobden Bridge	1.9	7.8	195.7	19.87	364.5	18	0.95	121.74	<0.02	6127
S980621	PWD	1.6	9.4	193.0	13.80	365.4	26	0.83	87.83	<0.02	6364
	bottom	19.1		86.9	8.75	170.5	19			0.47	
S980622	Rowing hard	0.1	7.2	201.8	9.95	392.1	39	0.81	112.11	0.65	11267
S980623	Woodmill Lane	0.8	7.8	199.1	11.45	386.2	34	0.79	101.13	<0.02	8832

SONUS 1998 JUN (neap) NUTS DATA											
Station	**Name**	**Salinity**	**SPM(mg/l)**	**Si**	**DIP**	**DIN**	**DIN/DIP**	**PTP (c)**	**PTP(m) µmol/g**	**DOP**	**Kd**
*S980601	Cobden Bridge	18.2	3.8	127.08	15.68	286.1	18	0.76	200.32	0.41	12775
	bottom	27.0	7.8	87.56	7.55	174.5	23	0.66	84.05	0.97	11133
*S980602	Rail Bridge	27.2	5.2	40.28	4.02	76.0	19	0.77	147.92	0.05	36797
*S980603	St Denys	10.0	8.8	135.48	11.71	286.4	24	0.77	87.14	0.00	7441
*S980604	Northam Bridge	8.3	7.6	143.35	13.08	307.0	23	0.81	106.89	0.00	8172
	bottom	30.5	8.8	21.46	2.45	44.9	18	0.69	78.77	0.42	32152
*S980605	Oil Spill Centre	15.0	10.4	93.19	8.51	193.3	23	0.74	71.35	0.27	8384
*S980606	Shamrock Quay	21.8	20.4	68.13	6.52	136.4	21	0.98	48.02	0.21	7365
*S980607	Itchen Toll B	26.0	5.0	29.14	2.75	61.8	22	0.76	151.92	0.32	55244
	bottom	31.8	11.8	13.03	0.97	26.8	28	0.58	49.53	0.61	51057
*S980608	Dockhead	27.7	8.4	29.35	2.17	62.9	29	0.74	88.43	0.41	40750
	bottom	32.9	16.8	6.70	0.26	6.5	25	0.27	15.93	20.01	61264
*S980609	Weston Shelf	29.4	10.0	20.10	1.60	44.0	28	0.66	66.04	1.28	41275
*S980610	NW Netley	31.2	23.0	8.52	0.14	19.3	138	0.94	40.78	0.75	N/A
	bottom	33.0		6.83	0.05	4.4	88			0.36	N/A
*S980611	Hound	31.8	11.8	7.53	0.02	14.2	N/A	0.72	61.12	0.25	N/A
*S980612	Greenland	32.2	14.0	6.59	<0.02	10.1	N/A	0.75	53.40	0.10	N/A
	bottom	32.7		6.31	<0.02	4.4	N/A			0.08	N/A
*S980613	BP Jetty	31.7	12.6	6.30	<0.02	9.0	N/A	0.51	40.41	0.22	N/A
*S980614	Hamble Point	32.7	12.4	6.92	<0.02	8.9	N/A	0.58	46.74	0.08	N/A
	bottom	32.6		6.58	<0.02	4.3	N/A			0.09	N/A
*S980615	Fawley PS	32.4	12.8	6.26	<0.02	8.0	N/A	0.64	49.72	0.13	N/A
*S980616	Calshot Castle	32.9	14.8	5.88	<0.02	6.2	N/A	0.51	34.73	0.23	N/A
*S980617	Calshot Buoy	33.4	14.8	5.83	<0.02	4.8	N/A	0.28	18.73	0.12	N/A
	bottom	32.6	7.6	5.74	<0.02	2.6	N/A	0.18	24.05	<0.02	N/A

SONUS 1998 JUL NUTS DATA											
Station	**Name**	**Salinity**	**SPM(mg/l)**	**Si**	**DIP**	**DIN**	**DIN/DIP**	**PTP (c)**	**PTP(m)µmol/g**	**DOP**	**Kd**
S980701	Woodmill Lane	0.7	14.6	190.83	10.12	362.5	36	0.90	61.53	<0.02	6080
	S1.8	1.8		187.93	10.68	354.5	33			2.18	
S980702	Rowing hard	0.5	10.4	196.71	11.56	366.2	32	0.88	84.62	0.49	7320
S980703	PWD	0.4	7.4	199.95	13.64	364.3	27	1.04	140.54	<0.02	10304
	S9.3	9.3		149.43	13.12	196.2	15			0.76	
S980704	Cobden Bridge	2.8	18.6	196.18	27.08	251.9	9	1.52	81.59	1.29	3013
	S7.8	7.8		171.62	33.24	269.7	8			4.91	
	bottom	17.9		99.89	14.00	164.0	12			<0.02	
S980705	Rail Bridge	1.8	8.2	210.85	32.32	247.6	8	1.52	185.76	4.12	5747
	S6.1	6.1		185.40	26.92	303.0	11			<0.02	
S980706	St Denys	10.0	13.2	158.41	19.12	196.6	10	1.46	110.85	<0.02	5798
S980707	Northam Bridge	23.4	34.8	68.75	9.54	108.6	11	0.83	23.82	<0.02	2496
	bottom	30.7	47.6	23.93	3.53	35.7	10	0.73	15.31	<0.02	4337
S980708	Oil Spill Centre	25.0	41.6	58.73	7.58	89.2	12	0.90	21.69	<0.02	2862
S980709	Shamrock Quay	24.5	38.4	61.84	8.05	95.2	12	0.82	21.46	<0.02	2666
S980710	Itchen Toll B	31.5	45.0	19.51	2.74	28.6	10	0.82	18.15	0.39	6624
	bottom	32.4	54.4	14.60	1.66	19.7	12	0.57	10.47	<0.02	6308
S980711	Dockhead	32.8	46.2	12.62	1.10	14.8	13	0.47	10.18	<0.02	9256
	bottom	33.5		9.37	0.53	8.0	15			<0.02	
S980712	Weston Shelf	31.2	52.6	21.86	1.10	26.5	24	0.54	10.28	<0.02	9347
S980713	NW Netley	31.2	54.4	21.03	1.03	25.8	25	0.47	8.63	<0.02	8381
	bottom	34.1		8.18	0.27	5.0	19			<0.02	
S980714	Hound	31.9	49.4	16.75	1.10	21.5	20	0.43	8.62	0.08	7832
S980715	Greenland	32.4	43.8	12.94	0.97	17.2	18	0.37	8.53	0.07	8793
	bottom	34.5		7.55	0.17	1.8	11			0.06	
S980716	BP Jetty	32.5	55.8	13.51	0.97	17.0	18	0.33	5.92	<0.02	6104
S980717	Hamble Point	33.2	50.2	10.11	0.53	9.4	18	0.46	9.08	0.11	17139
S980718	Fawley PS	33.9		9.43	0.72	6.3	9			1.58	
S980719	Calshot Castle	33.5	48.0	10.08	0.29	6.7	23	0.35	7.37	0.38	25402
S980720	Calshot Buoy	34.5	40.8	7.79	0.12	2.5	21	0.25	6.06	0.29	50490
	bottom	34.6		7.70	0.83	5.7	7			<0.02	

SONUS 1998 AUG NUTS DATA											
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) µmol/g	DOP	Kd
S980801	Hill head34.7			52.44	0.20	3.9	20			0.15	
S980802	Calshot Buoy	34.6	21.6	8.84	0.15	2.5	17	0.37	16.94	0.19	112963
	bottom	34.6	31.0	9.72	0.15	3.6	24	0.53	16.97	0.15	113118
S980803	Calshot Castle	34.3		9.07	0.10	3.3	33			0.23	
S980804	Fawley PS	34.3	22.0	9.14	0.07	2.7	38	1.30	58.96	0.29	842338
S980805	Hamble Point	33.7	13.2	9.07	0.14	4.1	29	0.40	30.45	0.63	217532
	bottom	34.3		8.71	0.15	4.2	28			0.37	
S980806	BP Jetty33.4		17.6	9.23	0.18	5.0	28	0.44	25.02	0.45	139015
S980807	Greenland	33.5	21.6	9.16	0.27	4.4	16	0.50	23.06	0.48	85391
	bottom	33.9		8.28	0.14	3.6	26			0.44	
S980808	Hound	33.4	2.6	8.80	0.15	4.9	33	0.54	207.85	0.5	139000
S980809	NW Netley	33.4	19.8	8.80	0.14	5.0	36	0.63	31.86	0.48	227561
	bottom	33.7		8.14	0.17	4.4	26			0.33	
S980810	Weston Shelf	33.2	16.4	8.96	0.20	5.8	29	0.76	46.51	0.74	232561
S980811	Dockhead	33.0	17.8	9.18	0.23	6.6	29	0.76	42.85	0.75	186321
	bottom	33.1		9.26	0.31	7.4	24			0.64	
S980812	Itchen Toll B	32.4	27.8	11.93	0.97	13.7	14	0.83	29.86	0.62	30780
	bottom	33.5		9.92	0.33	6.2	19			0.56	
S980813	Shamrock Quay	32.0	19.8	14.79	1.43	21.1	15	0.88	44.38	0.53	31038
S980814	Oil Spill Centre	29.5	20.6	26.98	3.53	44.5	13	0.82	39.75	1.05	11260
S980815	Northam Bridge	27.5	35.0	37.98	5.32	65.2	12	0.95	27.19	1.01	5111
	bottom	31.0	24.2	19.93	2.69	30.2	11	1.06	43.98	1.25	16351
S980816	St Denys	26.9	17.2	40.29	5.73	71.8	13	1.13	65.42	1.84	11417
S980817	Rail Bridge	17.0	21.6	96.16	13.68	186.9	14	1.09	50.39	0.8	3683
	S11.7	11.7		119.45	19.10	235.5	12			<0.02	
S980818	Cobden Bridge	18.8	10.6	83.27	13.76	157.1	11	1.15	108.87	<0.02	7912
	bottom	25.7		45.41	7.36	82.9	11			1.68	
	S6.3	6.3		145.56	27.43	275.4	10			<0.02	
S980819	Woodmill Lane	2.0	7.0	155.94	14.98	330.1	22	1.29	183.94	<0.02	12279
S980820	Rowing hard	1.1	7.4	160.55	14.90	340.3	23	0.70	94.43	<0.02	6338
S980821	PWD	1.1	6.0	167.08	17.65	334.7	19	0.65	108.33	<0.02	6138
	S15	15.0		102.86	16.38	199.7	12			<0.02	

SONUS 1998 SEP NUTS DATA											
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) µmol/g	DOP	Kd
S980901	Calshot Buoy	34.3	58.8	11.60	0.50	8.5	17.06	1.06	17.95	0.57	35905
	bottom	34.4	60.0	12.32	0.64	10.4	16.28	1.22	20.25	0.71	31646
S980902	Calshot Castle	34.0	40.4	13.26	1.28	12.8	10.03	0.94	23.16	0.12	18093
S980903	Fawley PS	34.1	56.4	12.11	0.82	11.0	13.38	0.97	17.16	0.36	20931
S980904	Hamble Point	33.6	48.0	14.19	1.04	15.8	15.22	0.93	19.37	0.34	18622
S980905	BP Jetty33.1		59.2	16.91	1.03	22.1	21.42	0.96	16.29	1.07	15816
S980906	Greenland	33.2	57.2	16.17	1.09	20.5	18.76	0.94	16.36	0.73	15006
	bottom	33.4		20.15	0.67	16.4	24.49			0.49	
S980907	Hound	33.0	53.2	16.47	1.14	20.8	18.21	0.95	17.83	0.49	15644
S980908	NW Netley	32.8	61.4	18.45	1.79	25.4	14.19	0.99	16.14	0.28	9015
	bottom	33.2		16.25	1.41	20.0	14.16			0.32	
S980909	Weston Shelf	32.6		19.28	1.70	26.3	15.45			0.75	
S980910	Dockhead	31.9	39.2	22.72	2.49	34.5	13.86	0.98	24.97	0.26	10028
	bottom	33.2		16.13	1.52	19.8	12.99			0.34	
S980911	Itchen Toll B	31.6	54.8	25.64	3.70	40.1	10.83	1.23	22.42	0.17	6058
	bottom	32.0		22.70	3.11	35.4	11.39			0.61	
S980912	Shamrock Quay	30.0	35.2	34.62	4.51	56.3	12.48	1.16	33.06	0.15	7330
S980913	Oil Spill Centre	28.6	4.2	40.02	5.81	68.3	11.76	1.37	325.90	0.13	56094
S980914	Woodmill Lane	2.1	4.6	92.25	16.89	254.7	15.08	0.70	152.26	<0.02	9015
	bottom	6.5		150.95	16.83	306.8	18.23			<0.02	
S980915	Rowing hard	2.5	11.2	92.24	17.17	361.6	21.06	0.86	76.68	<0.02	4466
S980916	PWD	2.8	19.4	183.36	16.59	339.9	20.49	0.80	40.99	0.19	2471
	bottom	22.3		75.85	11.31	143.3	12.67			1.23	
	S6	6.0		150.66	16.31	306.9	18.82			2.53	
S980917	Cobden Bridge	3.0	23.6	119.77	17.57	252.9	14.39	0.91	38.42	4.57	2187
	S10	10.0		138.54	24.17	264.1	10.93			<0.02	
S980918	Rail Bridge	9.8	12.6	139.24	23.86	278.5	11.67	0.89	70.63	7.18	2960
	S20	20.0		83.94	14.04	159.4	11.36			17.32	
S980919	St Denys	20.9	24.6	84.68	13.18	159.1	12.07	0.82	33.25		2523
S980920	Northam Bridge	26.5	3.2	51.27	8.28	92.8	11.21	0.70	217.37	<0.02	26253
	bottom	30.0	20.4	41.65	5.09	69.2	13.60	0.13	6.51	<0.02	1279

SONUS 1998 OCT NUTS DATA											
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) μmol/g	DOP	Kd
S981001	Calshot Castle	34.0	40.0	5.68	0.50	13.7	28	0.34	8.44	0.42	17051
	bottom	34.4	63.8	6.25	0.58	14.1	24	0.24	3.83	0.40	6610
S981002	Fawley PS	34.3	57.6	5.46	0.52	14.0	27	0.35	6.06	0.40	11652
S981003	Hamble Point	34.3	55.0	5.35	0.51	14.0	27	0.27	4.92	0.46	9640
S981004	BP Jetty	33.7	25.0	8.98	0.76	19.5	26	0.20	7.86	0.53	10347
S981005	Greenland	33.6	17.0	9.21	0.79	19.5	25	0.13	7.51	0.98	9501
	bottom	34.0		7.25	0.63	16.4	26			0.43	
S981006	Hound	33.3	23.0	10.54	0.79	42.9	55	0.18	7.61		
S981007	NW Netley	33.1	36.2	11.38	0.93	23.2	25	0.25	6.86	0.81	7372
S981008	Weston Shelf	32.8	43.0	12.99	1.08	25.7	24	0.22	5.12	0.84	4737
S981009	Dockhead	32.8	68.0	13.93	1.17	26.7	23	0.18	2.65		2277
	bottom	33.2		13.05	1.12	25.7	23			0.89	
S981010	Itchen Toll B	31.7	65.0	19.99	2.02	36.8	18	0.25	3.78	<0.02	1877
	bottom	32.5		16.04	1.35	30.0	22			3.36	
S981011	Shamrock Quay	26.9	16.8	42.60	4.58	80.6	18	0.26	15.20	1.44	3319
S981012	Oil Spill Centre	25.2	50.2	57.18	5.87	113.3	19	0.37	7.30	0.73	1244
S981013	Northam Bridge	23.8	13.4	58.62	6.05	116.7	19	0.35	26.04	<0.02	4308
	bottom	28.7		38.28	4.37	70.4	16				
S981014	St Denys	19.0	19.4	86.84	8.97	193.9	22	0.50	25.63	0.41	2857
S981015	Rail Bridge	3.5	10.4	106.66	20.09	336.1	17	0.93	89.35	<0.02	4448
S981016	Cobden Bridge	2.2	8.4	142.47	13.00	425.0	33	0.75	89.26	<0.02	6866
S981017	Woodmill Lane	0.5	5.4	163.99	13.51	474.4	35	0.43	79.63	<0.02	5894
S981018	Rowing hard	0.7	6.8	153.95	12.92	434.7	34	0.58	85.38	0.32	6611
S981019	PWD	1.2	8.2	149.43	12.09	423.7	35	0.64	78.34	<0.02	6480
	bottom	8.0	10.8	149.90	13.68	448.6	33	0.67	61.70	<0.02	4511
S5		5.0		133.29	15.99	387.5	24			1.26	
S9		9.0		124.56	16.06	336.4	21			<0.02	
S11		11.0		123.18	13.48	317.0	24			<0.02	

SONUS 1998 DEC NUTS DATA											
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) μmol/g	DOP	Kd
S981201	Woodmill Lane	2.4	6.4	202.80	8.18	395.4	48	0.74	115.81	0.57	14158
S981202	Rowing hard	2	4.6	203.75	8.29	402.9	49	0.68	148.61	0.40	17926
S981203	PWD	2.6	4.8	200.78	8.39	399.2	48	0.60	124.04	1.38	14793
S981204	Cobden Bridge	4.9	4.8	191.35	12.24	362.0	30	0.69	143.42	0.74	11722
S981205	Rail Bridge	6.2	5.0	183.66	11.44	348.6	30	0.64	127.96	0.43	11185
S981206	St Denys	8	6.0	175.89	12.14	326.7	27	0.69	115.33	1.69	9504
S981207	Northam Bridge	10.5	5.6	159.05	9.80	303.3	31	0.45	80.61	0.40	8229
	bottom	31.6	17.4	32.04	2.33	55.4	24	0.45	25.87	0.43	11105
S981208	Oil Spill Centre	24.5	8.6	71.72	4.92	126.2	26	0.31	36.09	0.26	7336
S981209	Shamrock Quay	25.6	14.6	66.58	4.66	116.8	25	0.20	13.95	0.23	2996
S981210	Itchen Toll B	31.3	9.8	32.22	2.31	54.1	23	0.24	24.14	0.50	10451
S981211	Dockhead	31.9	12.6	28.53	2.14	46.4	22	0.17	13.59	0.12	6364
	bottom	33.2	22.2	20.73	1.45	32.0	22	0.34	15.41	0.35	10667
S981212	Weston Shelf	32.3	12.2	25.86	1.68	42.2	25	0.16	12.70	0.77	7562
S981213	NW Netley	32		27.43	1.84	44.2	24			0.26	
S981214	Hound	32.8	11.8	22.41	1.48	34.7	23	0.16	13.64	0.34	9219
S981215	Greenland	33.1	13.6	21.05	1.39	32.0	23	0.17	12.81	0.92	9248
S981216	BP Jetty	33.4	13.8	18.54	1.22	27.4	23	0.12	8.45	0.88	6954
S981217	Hamble Point	33.5	15.2	18.87	1.20	27.6	23	0.15	10.00	0.38	8368
S981218	Fawley PS	33.3	13.2	19.11	1.24	28.9	23	0.16	12.06	0.44	9766
S981219	Calshot Castle	33.6		17.83	1.15	26.2	23			0.52	
S981220	Calshot Buoy	33.9	33.6	16.24	0.98	23.4	24	0.53	15.74	0.23	16059
	bottom	34.2	37.6	13.82	0.90	19.5	22	0.59	15.66	0.41	17497

SONUS 1999 JAN NUTS DATA										
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) µmol/g	DOP	Kd
S990101	Calshot Buoy	32	81.6	18.96	0.47	26.3	57	0.05	0.63	0.30	1356
S990102	Calshot Castle	32.4	83.4	29.73	0.44	23.8	54	0.05	0.61	0.31	1377
S990103	Fawley PS	32.4		17.34	0.44	23.2	53			0.30	
S990104	BP Jetty	31.5	82.4	21.46	0.69	31.1	45	0.05	0.66	0.53	964
S990105	Greenland	31.2	71.2	22.17	0.65	32.5	50	0.02	0.25	0.47	381
S990106	Hound	31.2	63.6	22.41	0.67	33.5	50	0.01	0.13	0.40	201
S990107	NW Netley	29.5	66.2	29.77	0.90	45.0	50	0.01	0.13	0.42	146
S990108	Weston Shelf	29.2	56.6	31.54	0.99	48.9	49	0.09	1.58	0.46	1599
S990109	Woodmill Lane	0	48.4	168.06	4.89	297.0	61	0.43	8.82	0.36	1805
S990110	Rowing hard	0		167.67	5.04	296.1	59			0.98	
S990111	PWD	0	48.0	174.22	4.82	292.2	61	0.40	8.27	0.88	1716
S990112	Cobden Bridge	0.1	25.0	168.32	7.40	297.5	40	0.24	9.52	<0.02	1286
	bottom	14.4	46.3	120.53	5.96	216.5	36	0.18	3.95	0.69	664
S990113	Rail Bridge	0.2		171.15	7.37	301.5	41			0.43	
S990114	St Denys	1.2	28.0	173.11	7.05	312.1	44	0.31	11.16	0.60	1583
S990115	Northam Bridge	3.6	29.0	165.70	7.23	302.1	42	0.31	10.60	0.22	1467
S990116	Oil Spill Centre	8.6	35.7	144.35	7.04	263.7	37	0.21	6.02	0.32	855
S990117	Shamrock Quay	12	38.3	128.65	6.53	233.3	36	0.18	4.73	1.01	725
S990118	Itchen Toll B	20.1	45.0	76.54	3.94	133.5	34	0.08	1.83	0.46	465
S990119	Dockhead	26.2	49.4	47.27	1.99	82.0	41	0.53	10.66	0.35	5373
	S5.2	5.2		160.79	7.18	293.7	41			<0.02	
	S25	25		50.97	2.41	87.8	36			0.20	

SONUS 1999 FEB NUTS DATA										
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m)µmol/g	DOP	Kd
S990201	Calshot Buoy	33.2	54.2	17.23	0.55	29.5	54	0.45	8.21	0.30	15072
S990202	Calshot Castle	33		19.26	0.60	32.4	54			0.15	
S990203	Fawley PS	33.1		18.94	0.61	32.2	53			0.11	
S990204	Hamble Point	33		18.70	0.60	31.9	54			0.17	
S990205	BP Jetty	32.5	44.7	18.57	0.58	32.1	55	0.31	6.94	0.14	11966
S990206	Greenland	32		36.29	0.75	45.5	61			0.24	
S990207	Hound	32		22.73	0.74	43.9	60			0.31	
S990208	NW Netley	31.5		25.58	0.86	51.9	61			0.14	
S990209	Dockhead	31.4	45.0	26.23	0.90	54.4	61	0.17	3.87	0.38	4320
S990210	Itchen Toll B	30.4		32.08	1.52	66.4	44			0.35	
S990211	Shamrock Quay	23.7		66.65	3.01	150.9	50			<0.02	
S990212	Oil Spill Centre	24	47.3	66.18	3.09	150.2	49	0.30	6.25	<0.02	2027
S990213	Northam Bridge	8	17.3	154.26	6.52	357.2	55	0.42	24.00	<0.02	3684
S10		10		141.31	6.18	329.6	53			0.40	
S15		15		114.74	5.25	270.4	52			<0.02	
S18		18		98.06	4.67	230.5	49			0.68	

SONUS 1999 MAR NUTS DATA

Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m) µmol/g	DOP	Kd
S990301	Woodmill Lane	0.1	15.4	169.17	6.08	454.9	75	1.33	86.18	<0.02	14186
S990302	Rowing hard	0.1		170.07	6.16	457.6	74			<0.02	
S990303	PWD	0.5	9.6	175.80	20.69	407.1	20	1.56	162.13	<0.02	7838
S990304	Cobden Bridge	2.2		166.26	12.13	419.0	35			<0.02	
S990305	Rail Bridge	6.2		148.82	9.23	381.3	41			<0.02	
S990306	St Denys	19.0		86.07	5.79	214.8	37			<0.02	
S990307	Northam Bridge	20.0	16.4	82.28	5.74	205.4	36	0.70	42.51	<0.02	7413
S990308	Oil Spill Centre	26.1		47.11	3.07	118.3	39			<0.02	
S990309	Shamrock Quay	28.7		34.06	3.06	86.2	28			<0.02	
S990310	Itchen Toll B	29.7		31.76	2.30	81.5	36			<0.02	
S990311	Dockhead	31.5	27.4	20.80	1.42	54.7	39	0.34	12.53	<0.02	8852
S990312	Weston Shelf	31.5		21.43	1.36	56.8	42			<0.02	
S990313	NW Netley	31.6		20.05	1.28	52.9	41			<0.02	
S990314	Hound	30.7		24.80	1.58	65.1	41			<0.02	
S990315	Greenland	32.3	16.8	17.25	1.10	44.2	40	0.21	12.21	<0.02	11104
S990316	BP Jetty	32.5		16.31	1.02	41.2	40			<0.02	
S990317	Hamble Point	33.0		14.05	0.90	35.2	39			<0.02	
S990318	Fawley PS	33.0		14.39	0.90	36.2	40			<0.02	
S990319	Calshot Castle	33.0		15.33	0.94	52.5	56			<0.02	
S990320	Calshot Buoy	33.2	73.0	13.50	0.92	33.7	37	0.97	13.35	0.1	14509

SONUS 1999 APR (neap) NUTS DATA

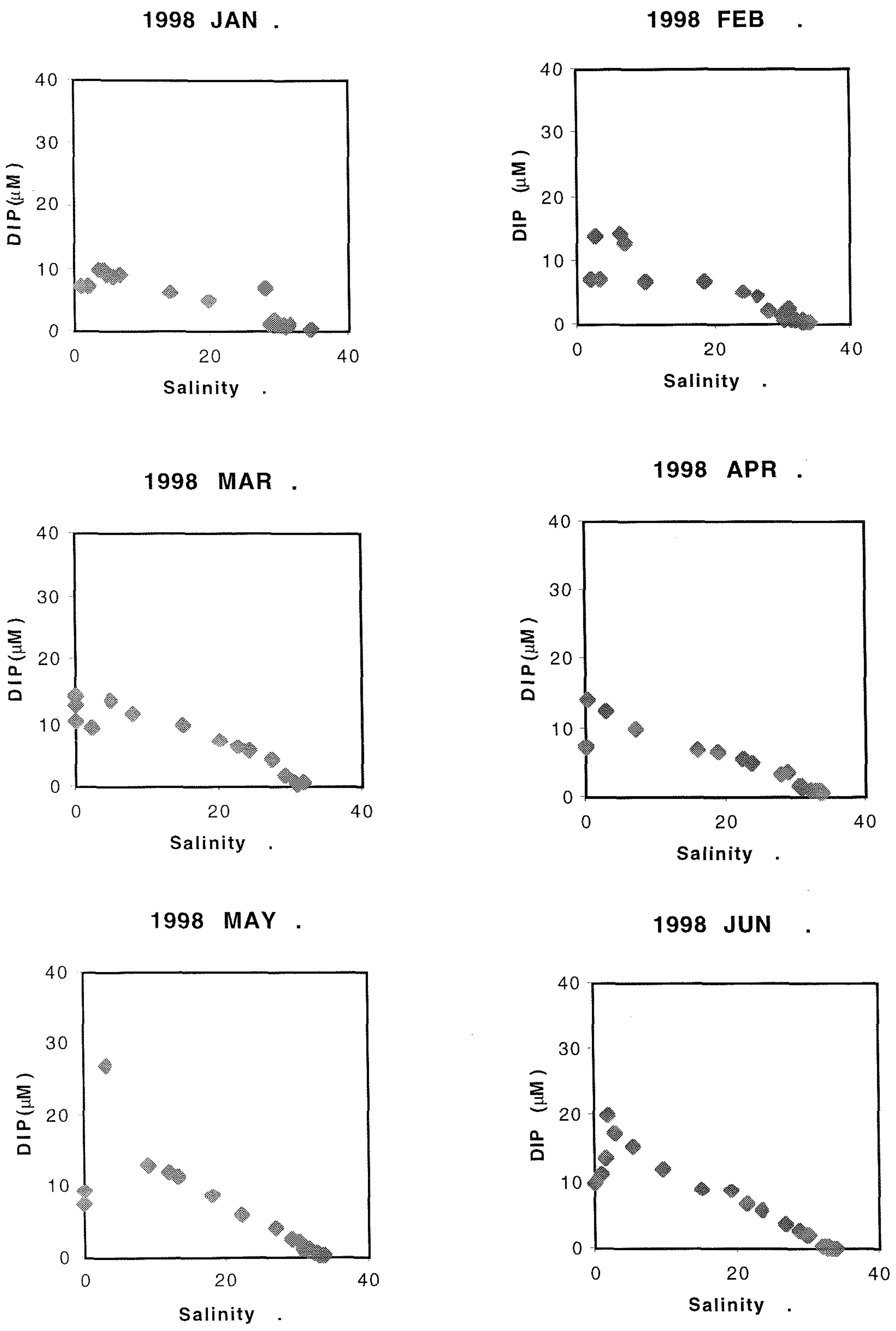
Station	Name	Salinity	SPM(mg/l)	Si	DIP	DIN	DIN/DIP	PTP (c)	PTP(m)µmol/g	DOP	Kd
S990401	Woodmill Lane	4.7	15.6	125.53	7.05	360.3	51	1.16	74.53	0.27	10571
S990402	PWD	8.8	21.6	105.91	6.34	294.8	47	0.99	45.77	0.54	7219
S990403	Cobden Bridge	14.8	22.2	108.25	10.09	290.6	29	0.96	43.23	0.46	4285
S990404	Rail Bridge	7.1		118.53	11.43	319.9	28			0.37	
S990405	St Denys	13.2		92.07	8.20	249.8	30			0.72	
S990406	Northam Bridge	17.4	17.2	86.01	7.35	232.2	32	0.91	53.05	0.80	7217
S990407	bottom	29.8		24.47	2.32	62.3	27			0.27	
S990408	Oil Spill Centre	21.3		62.41	5.10	162.9	32			0.81	
S990409	Shamrock Quay	27.4		33.29	3.06	88.3	29			0.75	
S990410	Itchen Toll B	29.4	35.8	24.68	2.22	67.1	30	0.46	12.87	0.59	5795
S990411	bottom	30.9		17.83	1.53	48.6	32			0.38	
S990412	Dockhead	30.5	24.4	19.35	1.67	52.0	31	0.36	14.65	0.46	8771
S990413	Redbridge	22.1	38.6	32.81	1.52	88.5	58	0.48	12.46	0.55	8198
S990414	hyths	26.4	47.0	36.03	1.98	92.9	47	0.40	8.60	0.68	4343
S990415	Weston Shelf	30.8	36.6	17.23	1.44	48.0	33	0.38	10.40	0.53	7225
S990416	bottom	30.9		17.06	1.43	47.6	33			0.72	
S990417	Hound	30	19.6	19.75	1.40	54.4	39	0.31	15.66	0.76	11188
S990418	Turkard pile	29	32.0	23.24	1.57	64.3	41	0.37	11.62	0.55	7400
S990419	bottom	29.8		22.44	1.55	63.1	41			0.60	
S990420	Greenland	30		19.23	1.43	54.6	38			0.54	
S990421	Hamble Point	31.9	28.0	12.26	0.91	35.8	39	0.30	10.54	0.41	11578
S990422	bottom	31.4		10.66	0.75	31.9	43			0.49	
S990423	Fawley PS	31	29.0	12.27	0.84	35.1	42	0.26	9.12	0.35	10854
S990424	Calshot Buoy	33.6	73.6	7.17	0.55	22.1	40	0.66	8.95	0.37	16270
S990425	Hamble river	28.8	48.6	22.32	1.43	53.3	37	0.34	7.01	0.72	4901

Chlorophyll a data

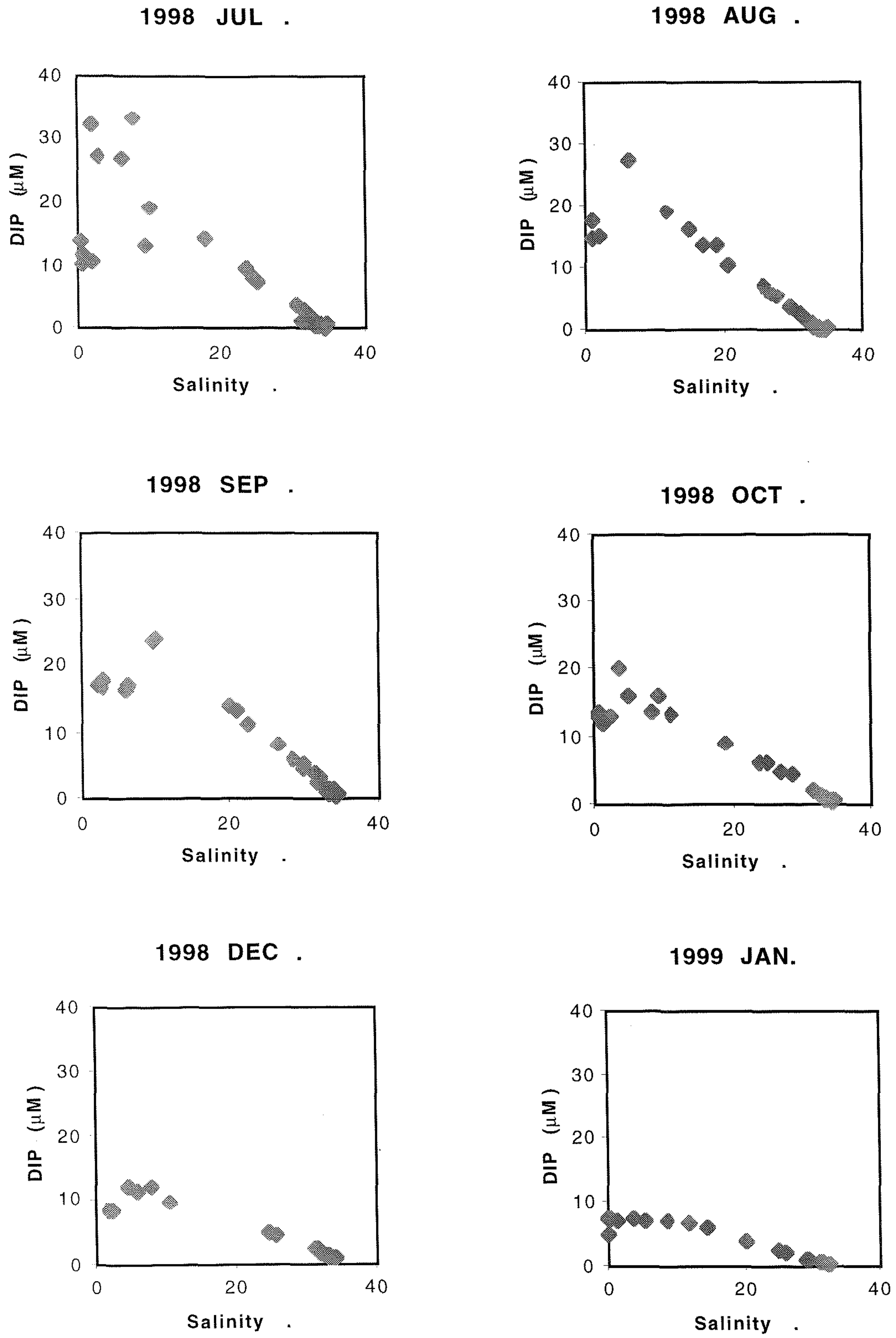
Sampling date	Station	Salinity	Chla (µg/l)	Sampling date	Station	Salinity	Chla (µg/l)	Sampling date	Station	Salinity	Chla (µg/l)
Jan-98	Calshot Buoy	34.5	0.80	28-Apr-98	St Denys	18.8	2.63	05-Jun-98	Cobden Bridge	18.2	4.33
	Calshot Castle	30.5	0.45		Rowing hard	0.1	5.50		bottom	27	6.53
	NW Netley	29.2	0.58		Shamrock Quay	28	3.19		Rail Bridge	27.2	2.53
	Dockhead	29.1	0.51		Northam Bridge	22.2	3.38		St Denys	10	3.60
	Itchen Toll B	27.6	0.27		Cobden Bridge	2.9	6.00		Northam Bridge	8.3	3.33
	Woodmill Lane	2	0.71		Dockhead	30.6	2.31		bottom	30.5	14.13
	Cobden Bridge	5.8	0.48		Itchen Toll B	29	2.00		Oil Spill Centre	15	7.47
	Northam Bridge	6.7	0.48		Fawley PS	33.4	3.44		Shamrock Quay	21.8	16.80
Feb-98	woodmill lane	3.2	1.13		Hamble Point	33.2	3.63		Itchen Toll B	26	21.07
	rowing hard	2	1.40		Hound	32.2	1.63		bottom	31.8	23.73
	pwd	9.9	1.37		Weston Shelf	30.7	1.88		Dockhead	27.7	29.33
	cobden bridge	6.8	1.01		Rail Bridge	16	2.69		bottom	32.9	6.93
	rail bridge	2.5	0.95		BP Jetty	33.2	5.06		Weston Shelf	29.4	27.33
	st denys	6.1	0.85		Oil Spill Centre	23.4	2.38		NW Netley	31.2	50.00
	northam bridge	18.6	0.58		Calshot Castle	33.5	3.94		bottom	33	12.80
	oil spill centre	24.1	0.73		Greenland	32.6	3.44		Hound	31.8	48.67
	shamrock quay	26.4	1.01		PWD	0.3	6.00		Greenland	32.2	48.67
	itchen toll b	30.8	0.82		Woodmill Lane	0	3.19		bottom	32.7	22.27
	calshot buoy	33.9	0.88		Calshot Buoy	33.3	5.94		BP Jetty	31.7	43.33
	hamble point	32.8	0.52	12-May-98	Woodmill Lane	0	13.94		Hamble Point	32.7	28.67
	bp jetty	32	0.73		Rowing hard	0.1	9.16		bottom	32.6	22.93
	greenland	31.3	0.55		PWD	3.2	7.87		Fawley PS	32.4	46.00
	hound	31.3	0.61		Cobden Bridge	13.2	6.32		Calshot Castle	32.9	32.00
	nw netley	30.2	0.73		Rail Bridge	9	3.61		Calshot Buoy	33.4	17.07
	dockhead	28.1	0.76		St Denys	18.2	3.35		bottom	32.6	9.87
Mar-98	Hound	31	1.05		Northam Bridge	22.2	3.23	12-Jun-98	Calshot Buoy	33.8	4.52
	NW Netley	32	0.95		Oil Spill Centre	26.8	2.97		bottom	33.7	5.81
	Weston Shelf	30.6	0.82		Shamrock Quay	29	2.77		Calshot Castle	33.4	6.32
	Dockhead	29	0.65		Itchen Toll B	30.4	2.45		Fawley PS	32.6	8.52
	Itchen Toll B	27.3	0.95		Dockhead	31.6	5.10		Hamble Point	32.6	6.71
	Woodmill lane	24.1	0.65		Weston Shelf	30.6	1.61		bottom	33.5	5.87
	Rowing Hard	22.6	0.92		NW Netley	31.7	3.03		BP Jetty	32.6	9.55
	PWD	20	0.92		Hound	32.5	2.39		Greenland	32.5	8.52
	Cobden Bridge	20.1	1.05		Greenland	32.7	3.94		bottom	33.1	9.55
	Rail bridge	8.2	1.19		BP Jetty	32.7	3.87		Hound	32.4	8.77
	St Denys	5	1.12		Hamble Point	32.8	3.29		NW Netley	32.4	12.13
	Northam Bridge	0.1	1.56		Fawley PS	33	3.81		bottom	32.7	6.19
	Oil Spill Centre	0.1	2.14		Calshot Castle	32.4	2.97		Weston Shelf	32.1	11.61
	Shamrock Quay	0.1	2.79		Calshot Buoy	33.7	5.35		Dockhead	31.9	10.32
21-Apr-98	Calshot Buoy	32.8	1.58						bottom	32	14.19
	Calshot Castle	32.1	2.50						Itchen Toll B	30	7.23
	Fawley PS	31.6	2.08						bottom	32.4	13.16
	Hamble Point	30.4	2.42						Shamrock Quay	29.8	9.55
	BP Jetty	30.3	2.08						Oil Spill Centre	26.8	5.94
	Greenland	30.2	2.00						Northam Bridge	23.5	4.77
	Hound	30.7	2.33						bottom	28.7	10.06
	NW Netley	30.2	2.67						St Denys	21.4	4.13
	Weston Shelf	30	2.92						Rail Bridge	5.3	1.87
	Dockhead	29.3	3.00						Cobden Bridge	1.9	1.87
	Itchen Toll B	20.1	5.33						PWD	1.6	2.71
	Shamrock Quay	12.9	3.50						Rowing hard	0.1	3.61
	Oil Spill Centre	8.8	2.08						Woodmill Lane	0.8	2.84
	Northam Bridge	7.2	1.83								

Chlorophyll a data (Cont.)

Sampling date	Station	Salinity	Chla (µg/l)	Sampling date	Station	Salinity	Chla (µg/l)	Sampling date	Station	Salinity	Chla (µg/l)
Sep-98	Calshot Castle	34	1.28	Oct-98	Rail Bridge	3.5	1.98	Feb-99	Calshot Buoy	33.2	2.19
	Calshot Buoy	34.3	1.40		Calshot Castle	34	0.99		Calshot Castle	33	0.96
	bottom	34.4	1.69		bottom	34.4	0.99		Fawley PS	33.1	1.70
	Fawley PS	34.1	0.67		*Northam Bridge*	23.8	0.74		*Hamble Point*	33	2.26
	Hamble Point	33.6	1.38		bottom	28.7	0.49		BP Jetty	32.5	1.74
	BP Jetty	33.1	1.46		calshot bouy	0	0.49		Greenland	32	1.33
	Greenland	33.2	1.54		Oil Spill Centre	25.2	0.99		Hound	32	1.33
	bottom	33.4	1.50		Woodmill Lane	0.5	0.99		NW Netley	31.5	1.56
	Hound	33	1.38		St Denys	19	0.49		Dockhead	31.4	2.00
	NW Netley32.8		1.86		Dockhead	32.8	0.49		Itchen Toll B	30.4	2.15
	bottom	33.2	0.70		Cobden Bridge	2.2	0.74		Shamrock Quay	23.7	2.04
	Weston Shelf	32.6	1.70		Weston Shelf	32.8	0.99		Oil Spill Centre	24	2.48
	PWD	2.8	1.28		Shamrock Quay	26.9	1.24		Northam Bridge	8	1.11
	Northam Bridge	26.5	2.06		Rowing hard	0.7	0.99				
	Dockhead	31.9	1.59		Itchen Toll B31.7		0.49	Mar-99	Woodmill Lane	0.1	4.29
	Woodmill Lane	2.1	1.64		bottom	32.5	1.48		Rowing hard	0.1	2.45
	Shamrock Quay	30	1.44		PWD	1.2	1.00		PWD	0.5	1.93
	Rail Bridge	9.8	1.69		bootom	8	1.45		Cobden Bridge	2.2	0.86
	Oil Spill Centre	28.6	1.69		Fawley PS	34.3	1.48		*Rail Bridge*	6.2	1.41
	Itchen Toll B	31.6	2.13		Hamble Point	34.3	1.11		St Denys	19	1.23
	Cobden Bridge	3	0.98		BP Jetty	33.7	1.04		Northam Bridge	20	1.29
	St Denys	20.9	1.96		Hound	33.3	1.07		Oil Spill Centre	26.1	1.75
	Rowing hard	2.5	1.00		Greenland	33.6	1.04		Shamrock Quay	28.7	1.56
23-Jul-98	Woodmill Lane	0.7	1.20		NW Netley	33.1	1.30		Itchen Toll B	29.7	1.50
	PWD	0.4	1.12	Dec-98	Dockhead	31.9	0.76		Dockhead	31.5	1.41
	Cobden Bridge	2.8	1.79		Shamrock Quay	25.6	0.48		Weston Shelf	31.5	1.63
	Rail Bridge	1.8	0.99		Oil Spill Centre	24.5	0.70		NW Netley	31.6	1.63
	St Denys	10	0.99		Woodmill Lane	2.4	0.85		Hound	30.7	1.50
	Northam Bridge	23.4	0.89		PWD	2.6	0.72		Greenland	32.3	1.32
	Oil Spill Centre	25	1.78		*Itchen Toll B31.3*		0.76		*BP Jetty*	32.5	1.59
	Shamrock Quay	24.5	1.28		St Denys	8	0.67		Hamble Point	33	1.66
	Itchen Toll B	31.5	1.67		Northam Bridge	10.5	0.52		Fawley PS	33	1.41
	Dockhead	32.8	1.51		bottom	31.6	0.78		Calshot Castle	33	1.47
	Weston Shelf	31.2	1.39		Cobden Bridge	4.9	0.35		Calshot Buoy	33.2	2.36
	NW Netley31.2		1.28		Rail Bridge	6.2	0.67	Apr-99	Woodmill Lane	4.7	2.59
	Hound	31.9	1.24		Weston Shelf	32.3	0.52		PWD	8.8	2.93
	Greenland	32.4	1.13		NW Netley	32	0.56		Cobden Bridge	14.8	2.09
	BP Jetty	32.5	1.33		Hound	32.8	0.63		Rail Bridge	7.1	2.26
	Hamble Point	33.2	1.32		Greenland	33.1	0.54		St Denys	13.2	1.42
	Fawley PS	33.9	1.40		Fawley PS	33.3	0.65		Northam Bridge	17.4	1.51
	Calshot Castle	33.5			*BP Jetty*	33.4	0.78		*Northam Bridge deep*	29.8	1.84
	Calshot Buoy	34.5	1.51		Calshot Castle	33.6	0.59		Oil spill Centre21.3		0.59
					Calshot Buoy	33.9	0.93		Shamack quay	27.4	0.90
12-Aug-98	Woodmill Lane	2	2.24		Hamble Point	33.5	0.65		Itchen toll bridge	29.4	1.05
	Rowing hard	1.1	1.43	Jan-99	Dockhead	26.2	1.20		Itchen toll deep	30.9	1.17
	PWD	1.1	1.00		St Denys	1.2	2.04		Dockhead	30.5	1.34
	Cobden Bridge	18.8	5.53		Oil Spill Centre	8.6	1.78		Redbridge	22.1	1.17
	Rail Bridge	17	3.57		Shamrock Quay	12	1.70		Hythe pier	26.4	1.00
	St Denys	26.9	11.07				1.22		Moorhead	30.8	0.15
	Northam Bridge	27.5	9.10		Northam Bridge	3.6	1.67		Weston shelf deep	30.9	0.95
	Oil Spill Centre	29.5	10.60		Hound	31.2	1.33		Hound	30	1.34
	Shamrock Quay	32	7.52		Rowing hard	0	5.56		Tucker Pile	29	1.09
	Itchen Toll B	32.4	15.96		Fawley PS	32.4	1.93		Tucker Pile deep	29.8	1.42
	Dockhead	33	20.29		BP Jetty	31.5	1.82		Greenland	30	1.34
	Weston Shelf	33.2	23.65		Cobden Bridge	0.1	2.78		Hamble	31.9	1.59
	NW Netley33.4		17.07				0.74		*Hamble deep*	31.4	1.51
	Hound	33.4	14.68		PWD	0	5.56		Fawley PS	31	1.67
	Greenland	33.5	13.28		Weston Shelf	29.2	1.11		Calshot buoy	33.6	2.17
	BP Jetty	33.4	13.75		Woodmill Lane	0	4.26		Hamble	28.8	1.17
	Hamble Point	33.7	9.75		Calshot Castle	32.4	1.78				
	Fawley PS	34.3	4.65		Calshot Buoy	32	2.00				
	Calshot Castle	34.3			NW Netley	29.5	1.52				
	Calshot Buoy	34.6	4.21		Greenland	31.2	1.45				



DIP -Salinity relationship .



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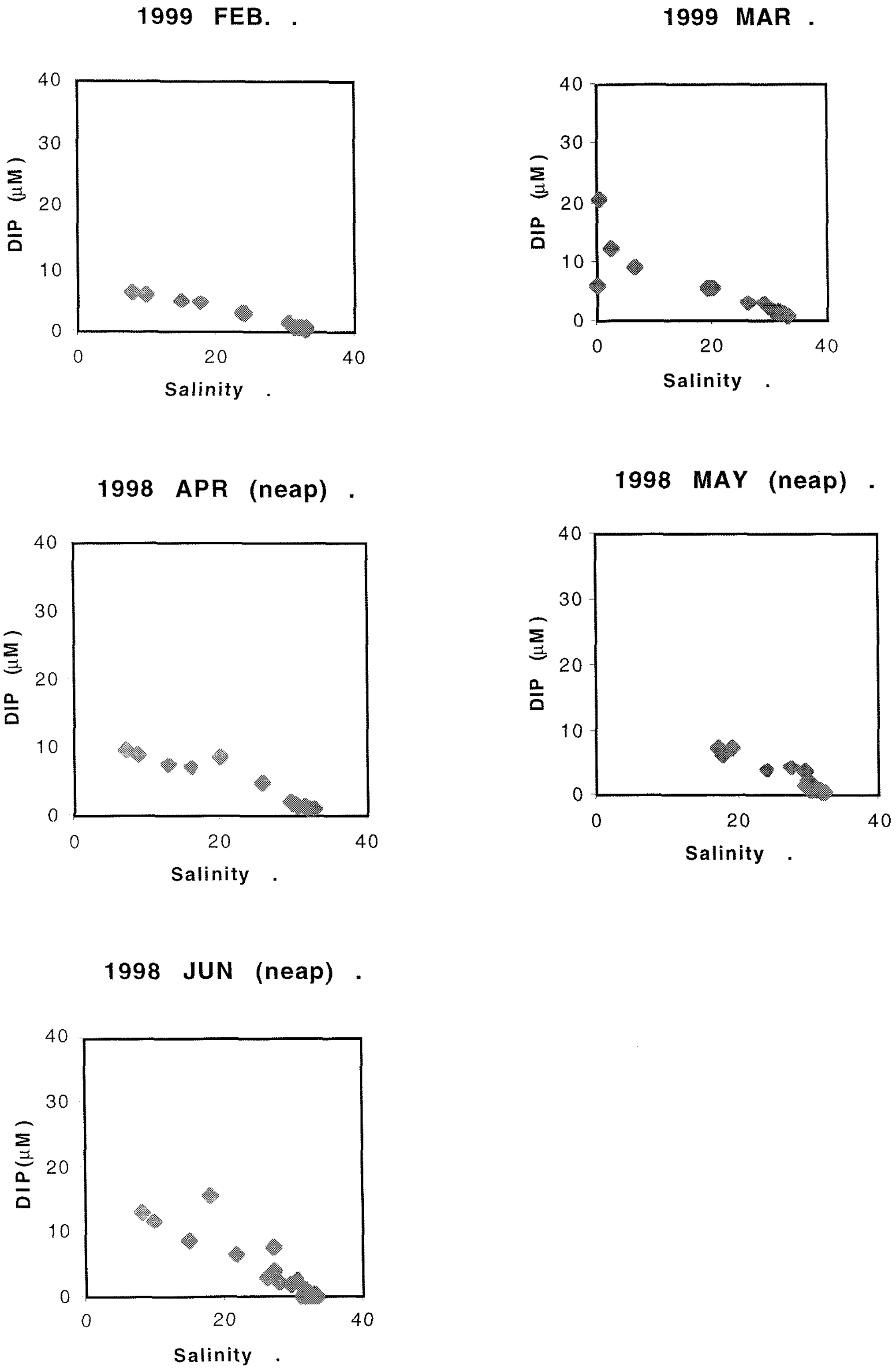

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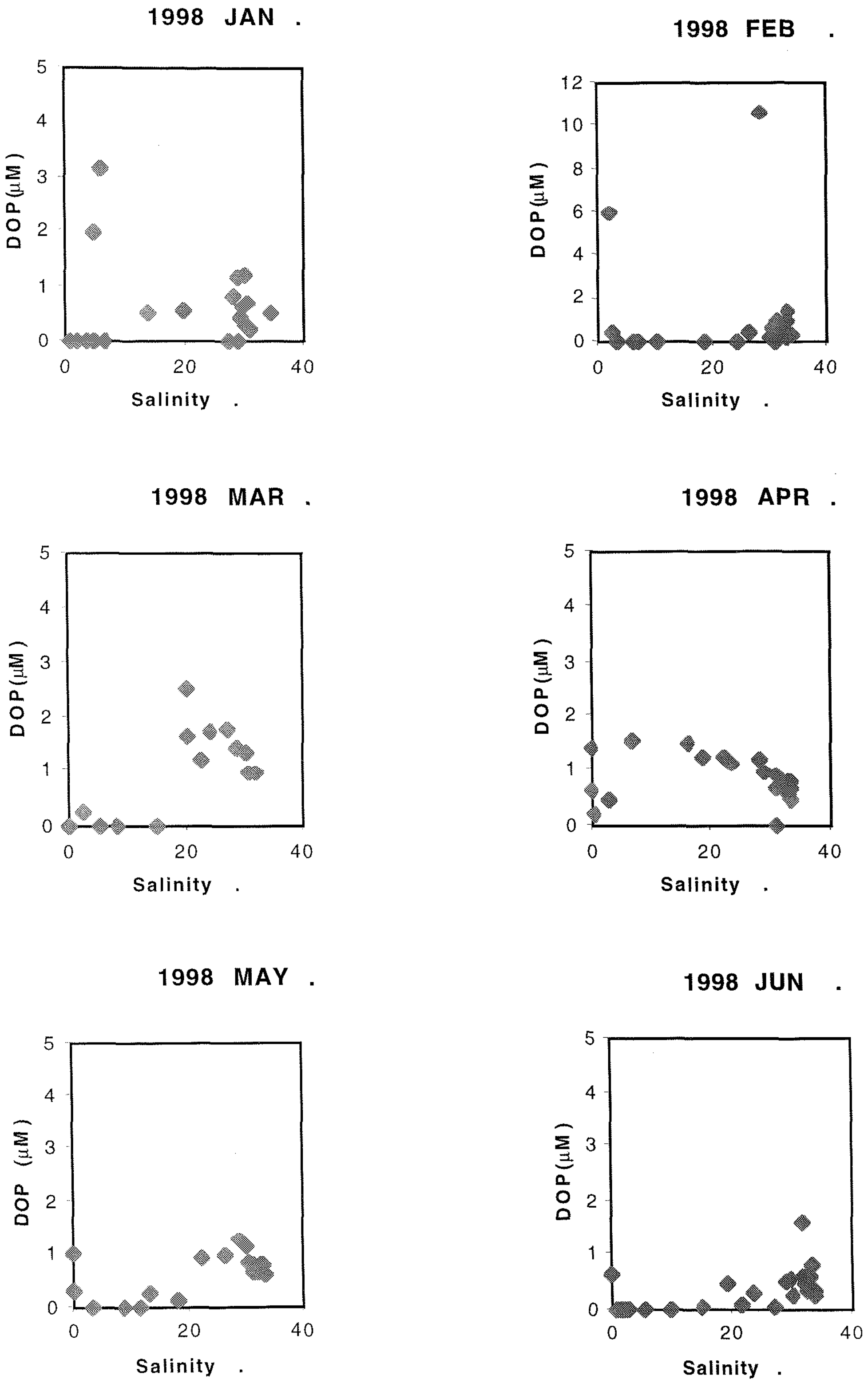

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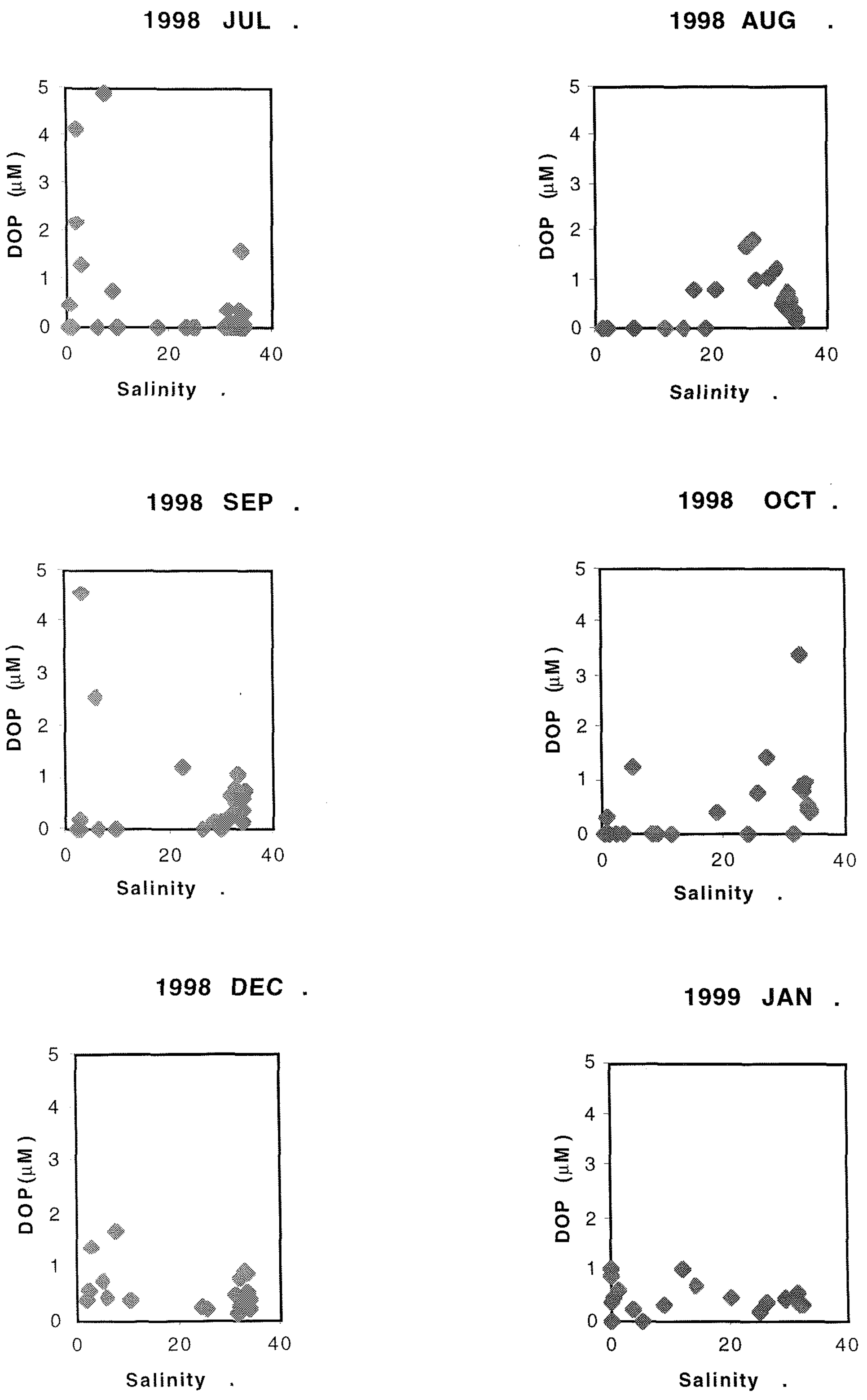
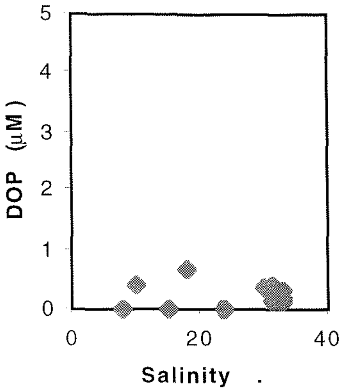
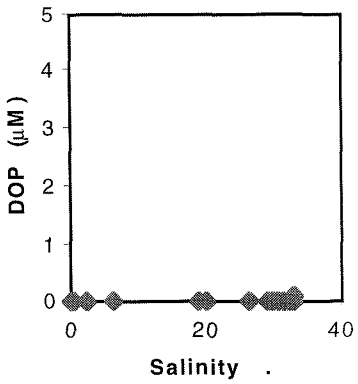


DOP-Salinity relationship (Cont.)

1999 FEB .



1999 MAR .



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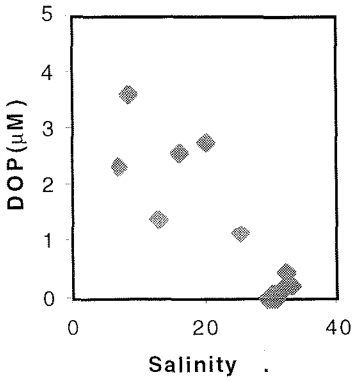

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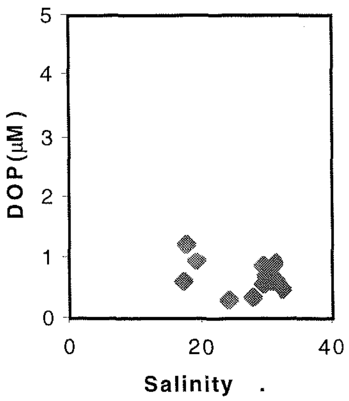

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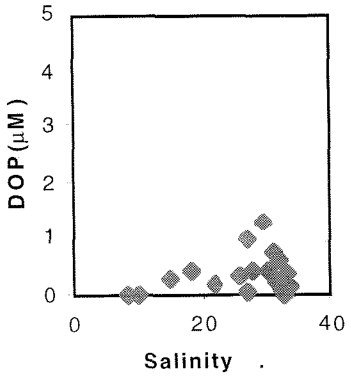

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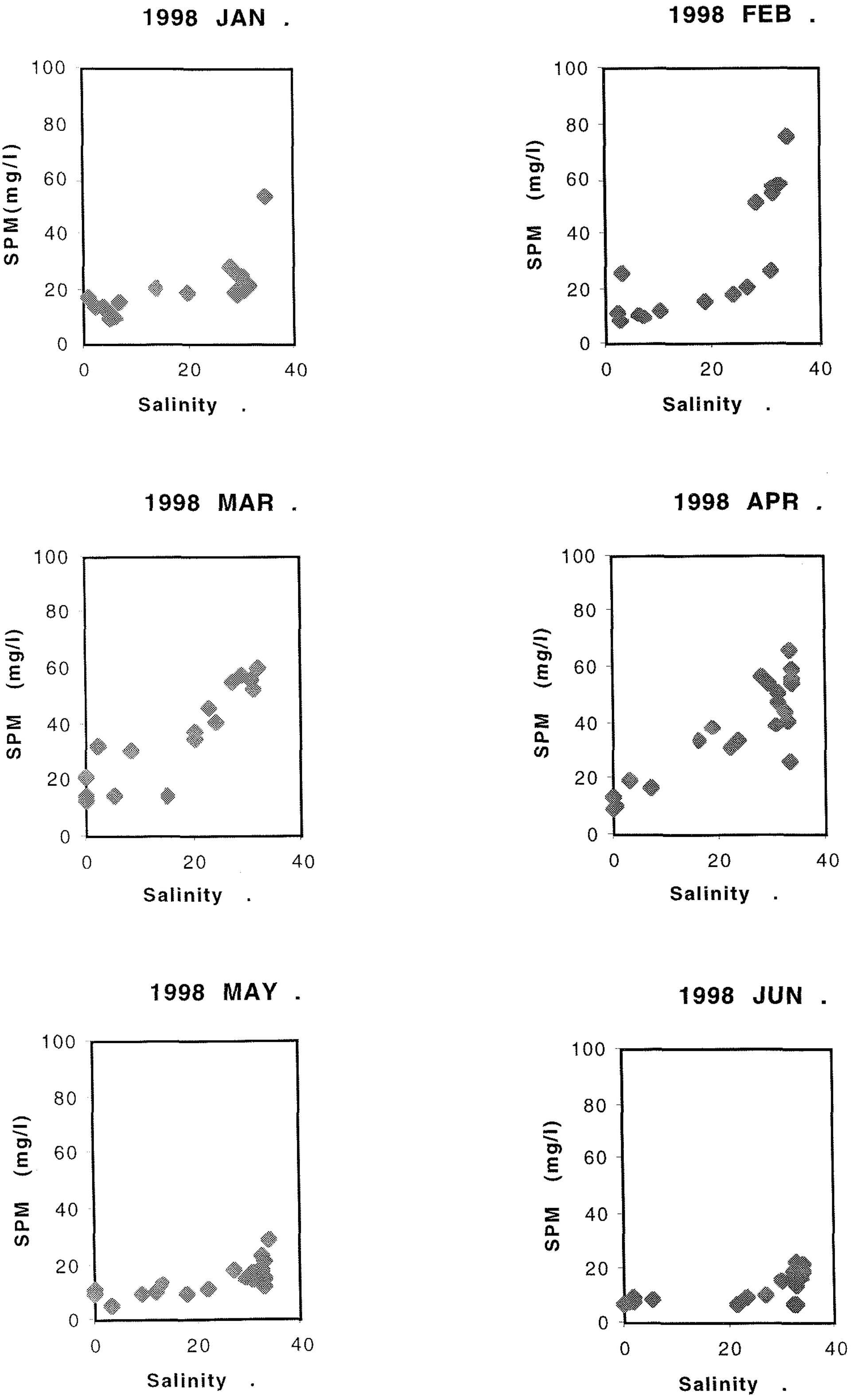
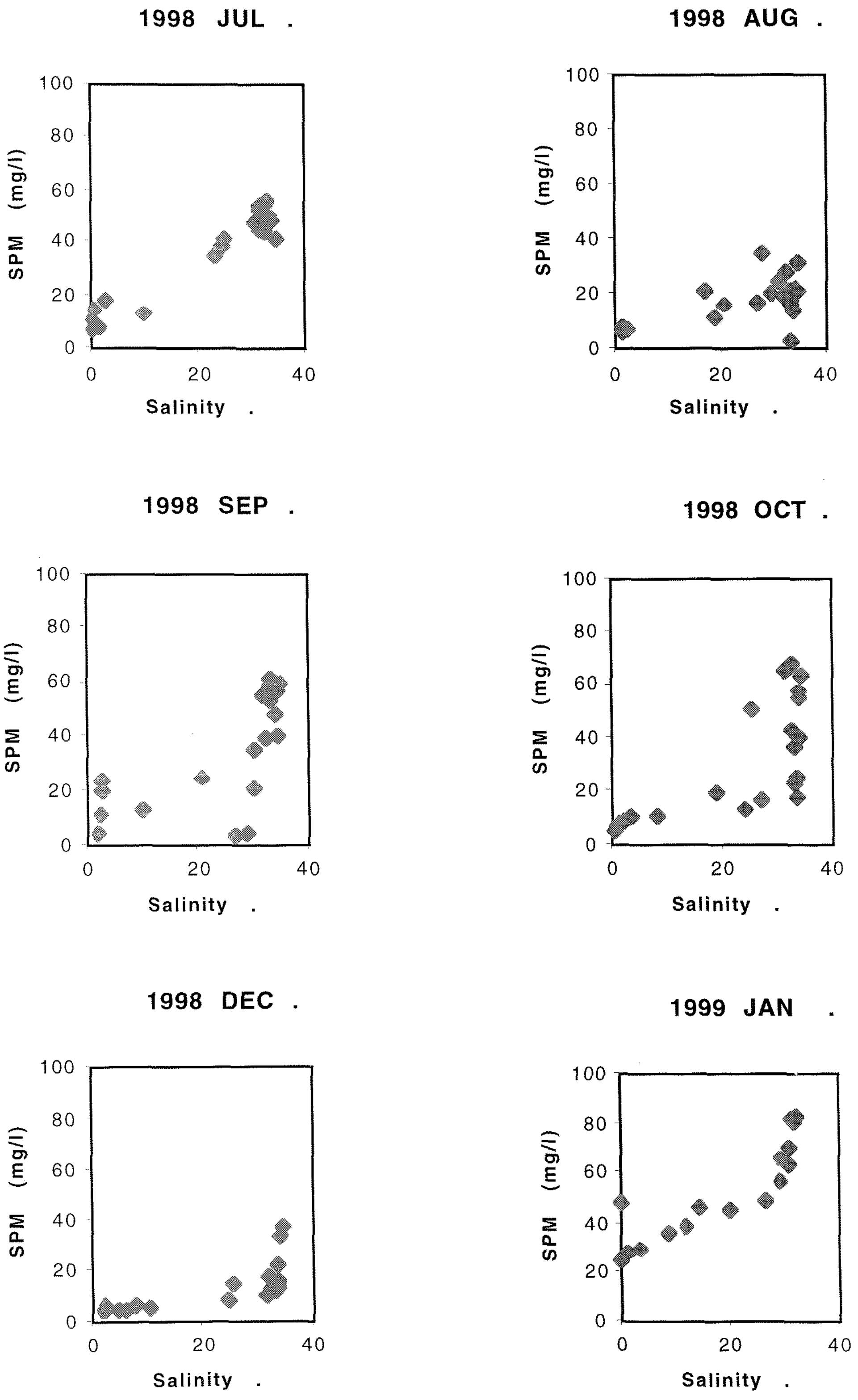
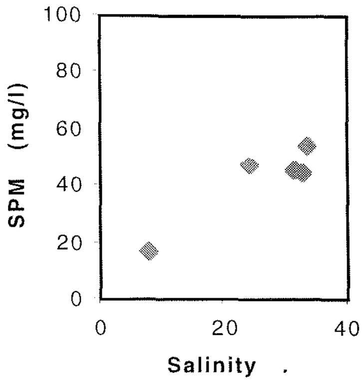


SPM-Salinity relationship .

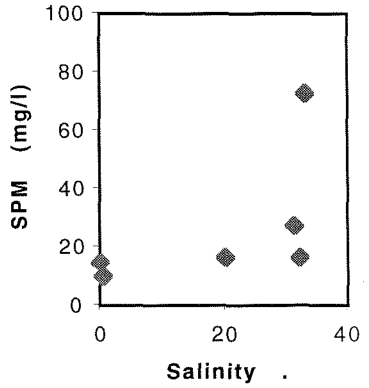


SPM-Salinity relationship (Cont.) .

1999 FEB .



1999 MAR .



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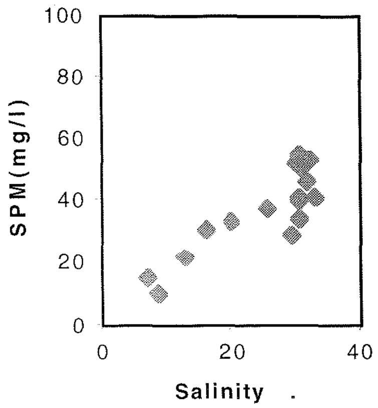

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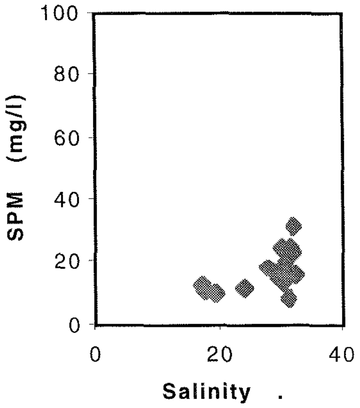

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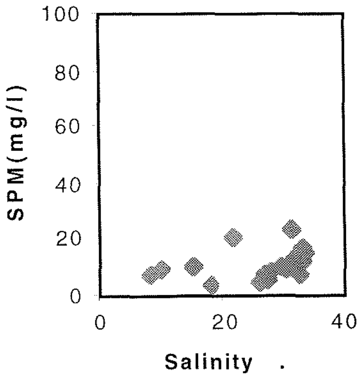
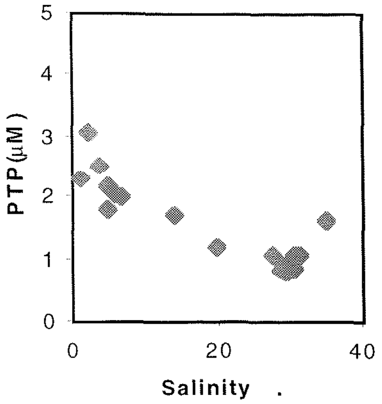


SPM-Salinity relationship (Cont.) .

1998 JAN .



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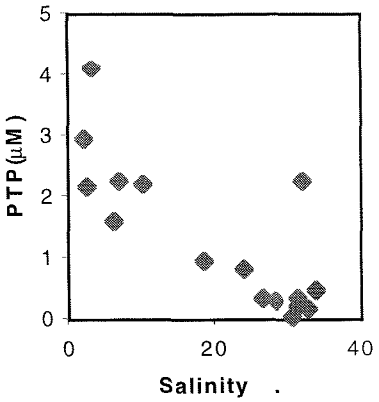

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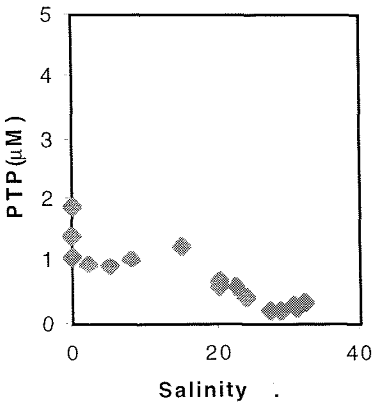

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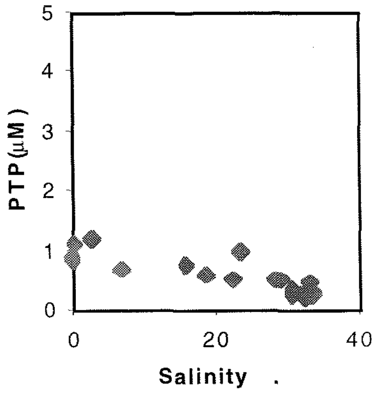

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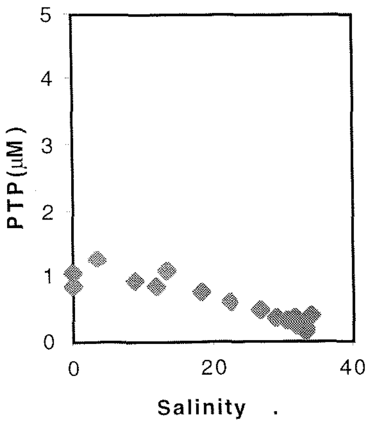

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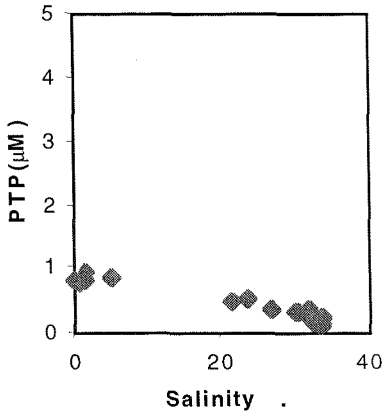
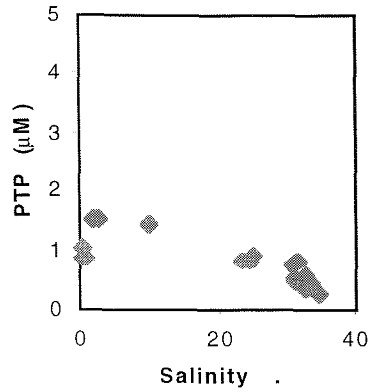
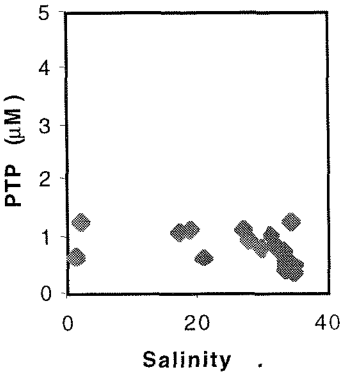


PTP(c) - Salinity relationship

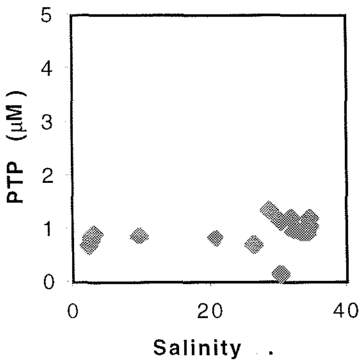
1998 JUL .



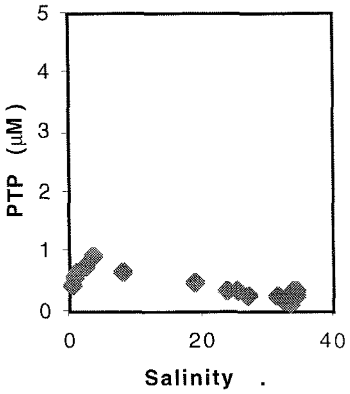
1998 AUG .



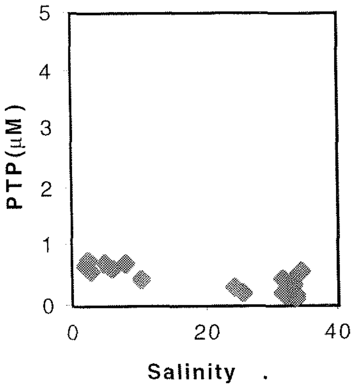
1998 SEP .



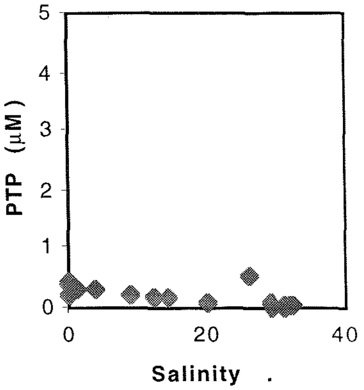
1998 OCT .



1998 DEC .

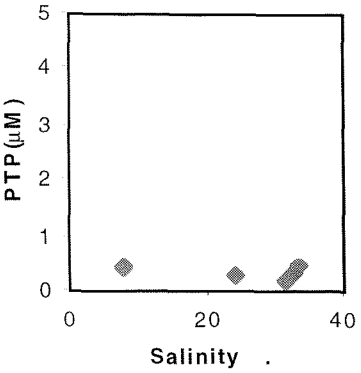


1999 JAN .

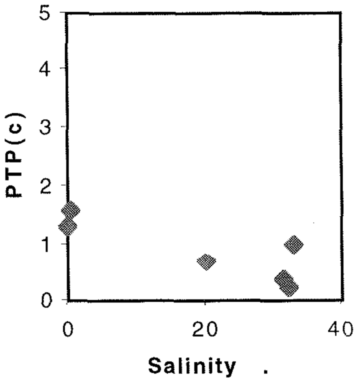


PTP(c) - Salinity relationship (Cont.)

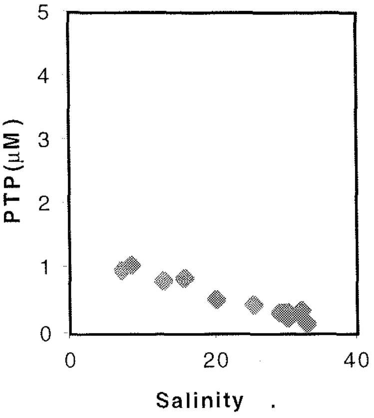
1999 FEB .



1999 MAR .



1998 APR (neap) .



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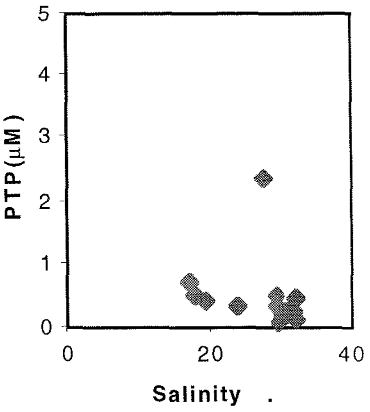

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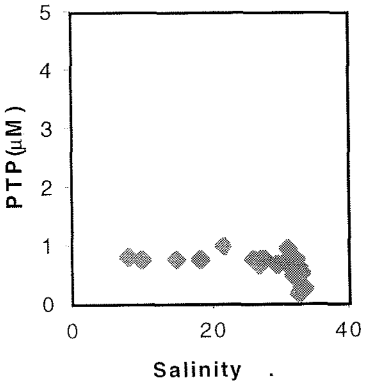
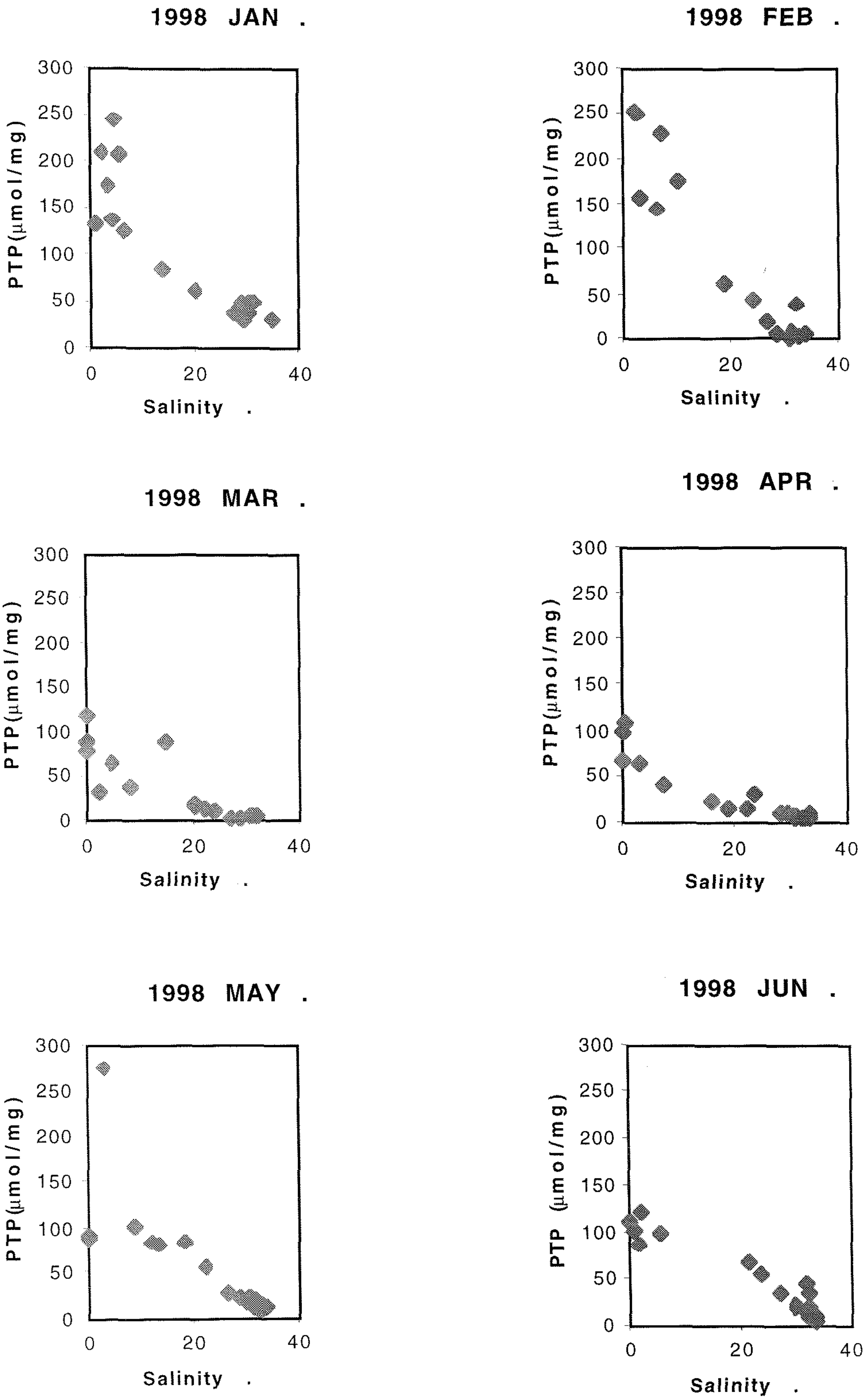


PTP(c) - Salinity relationship (Cont.)



1998 JAN .

1998 FEB .

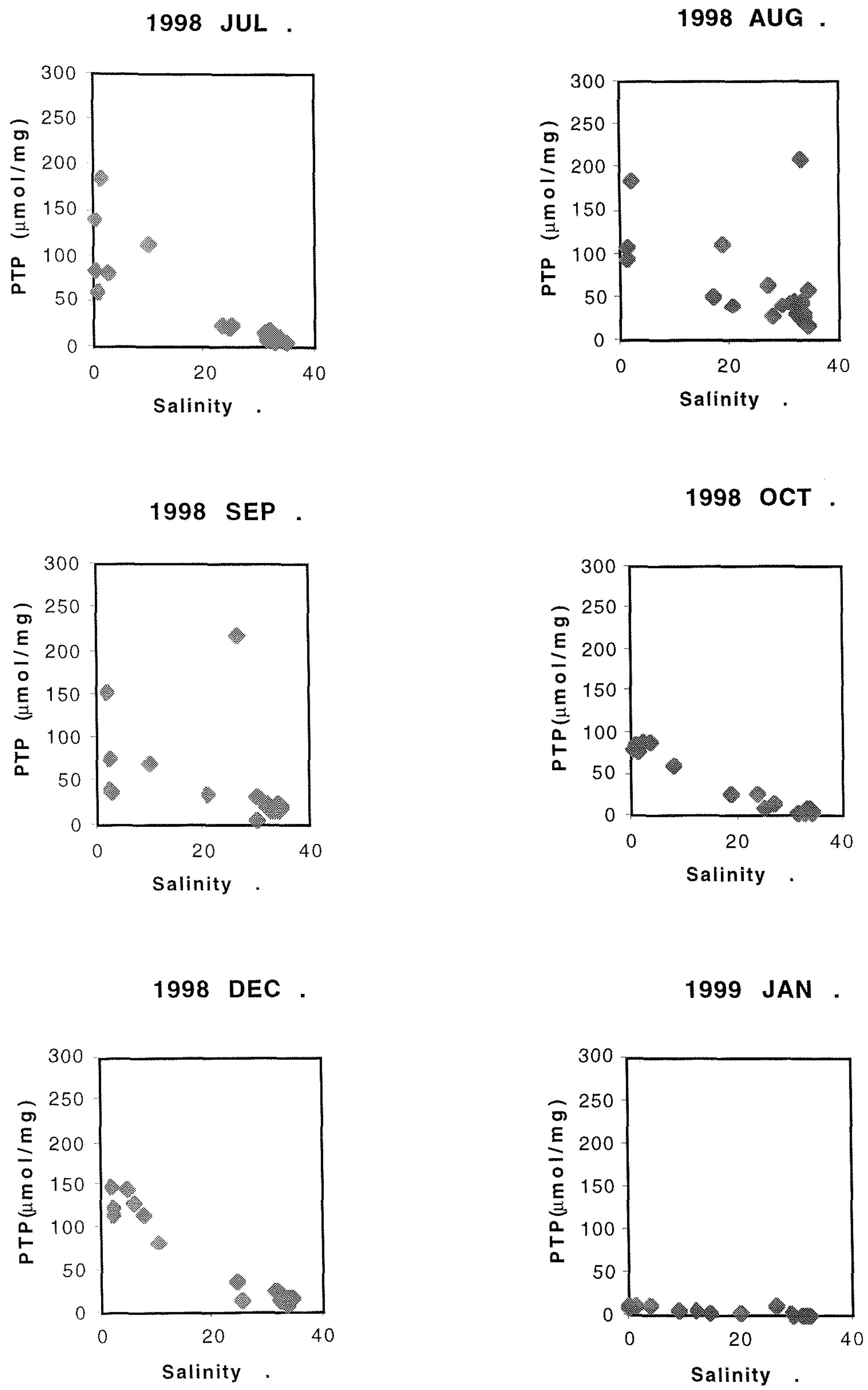
1998 MAR .

1998 APR .

1998 MAY .

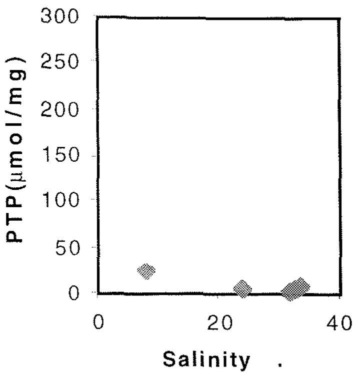
1998 JUN .

PTP(m)-Salinity relationship

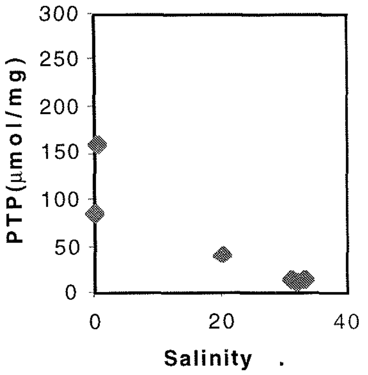


PTP(m)-Salinity relationship (Cont.)

1999 FEB .



1999 MAR .



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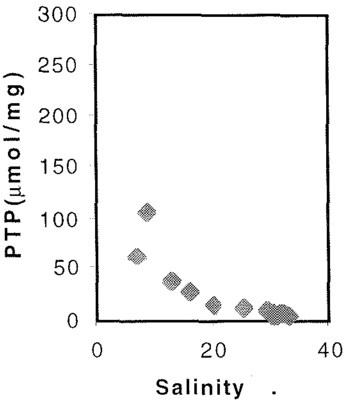

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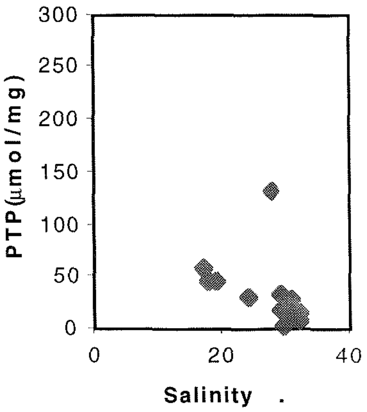

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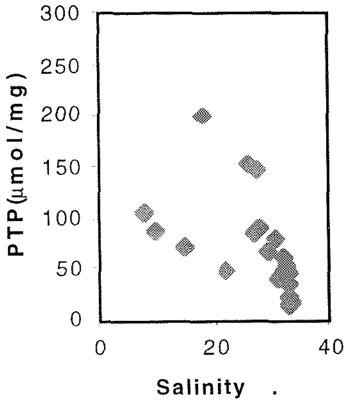
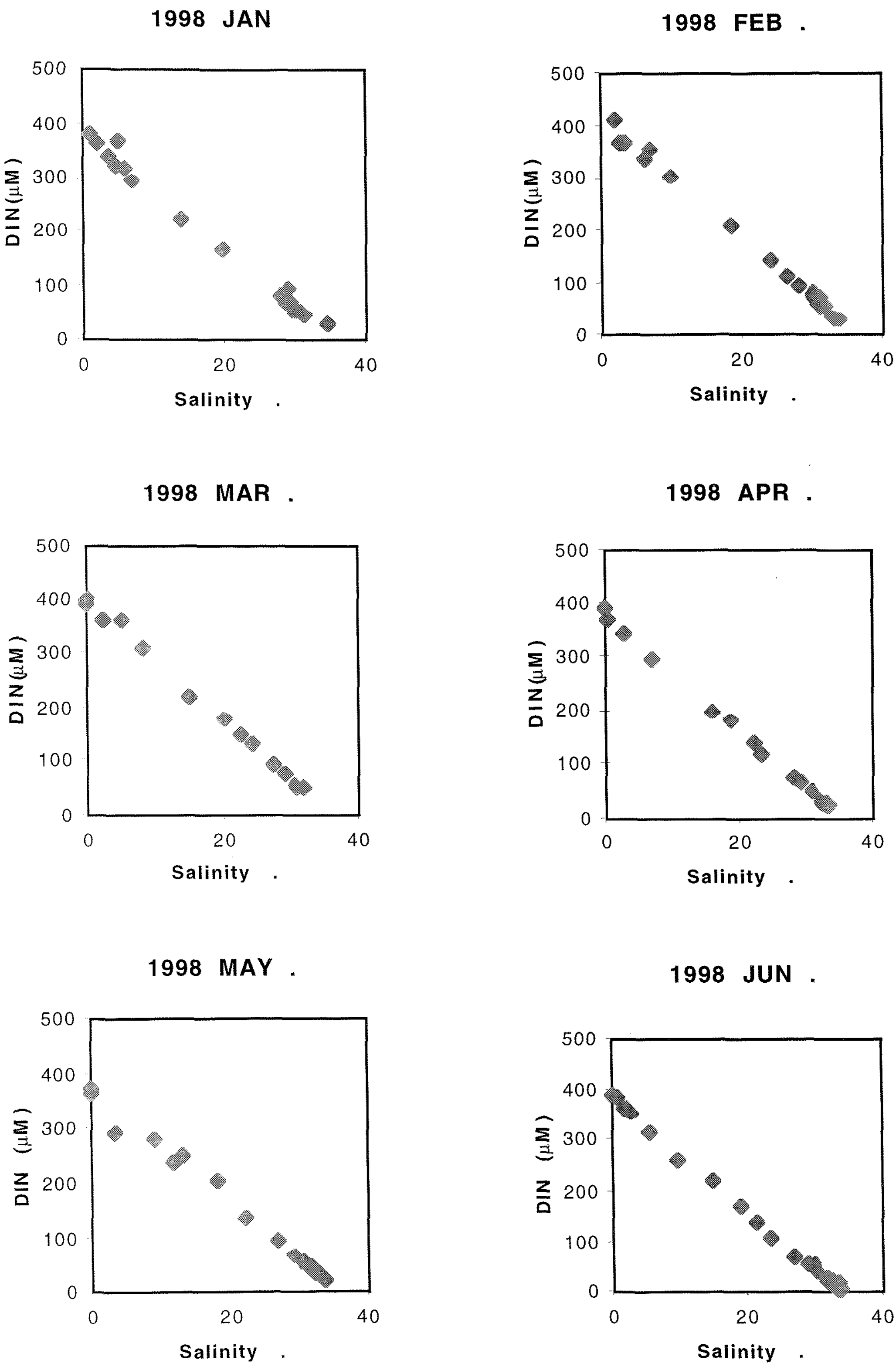
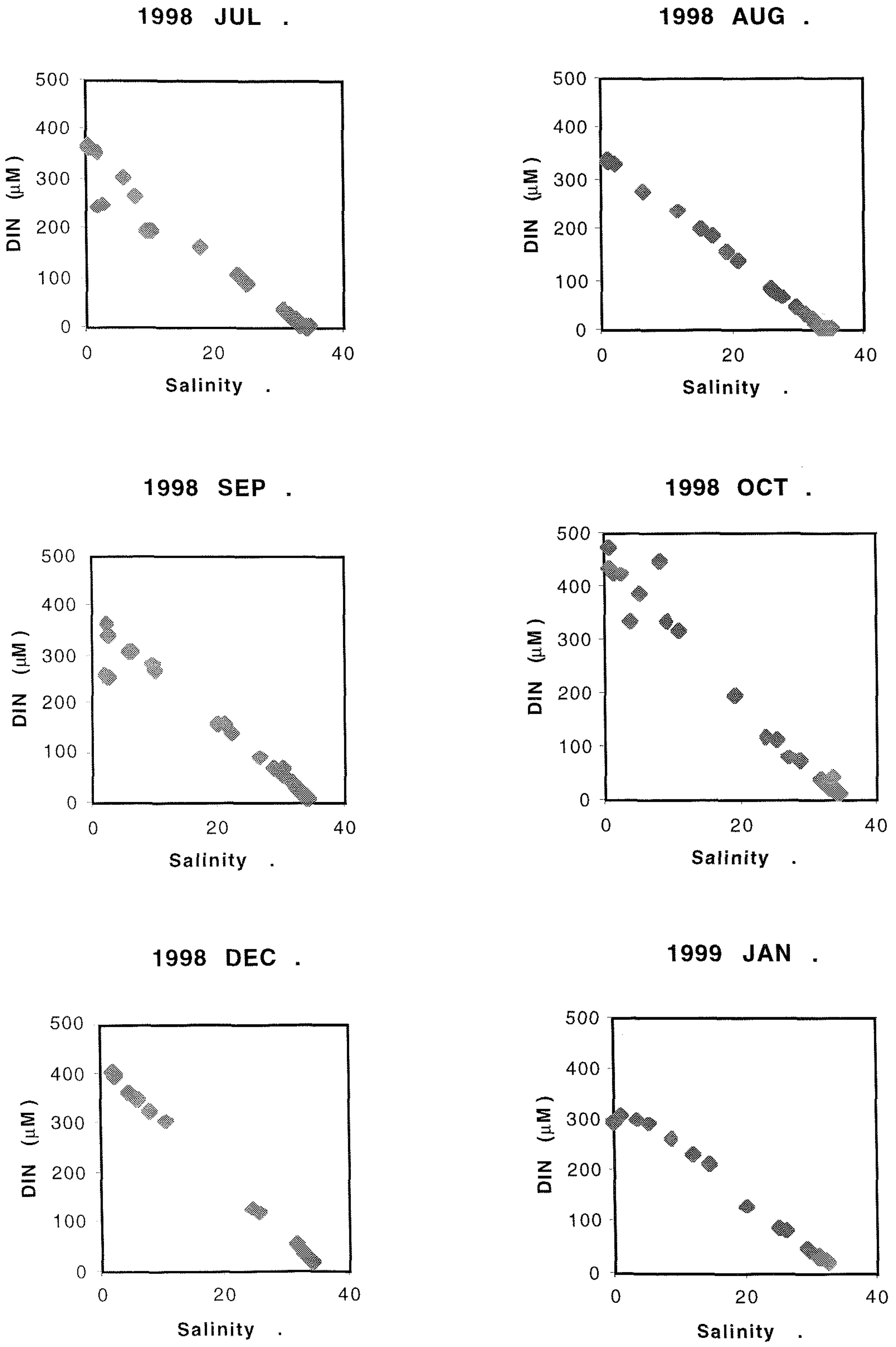


PTP(m)-Salinity relationship (Cont.)

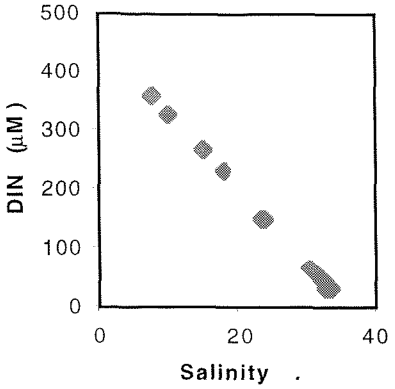


DIN-Salinity relationship

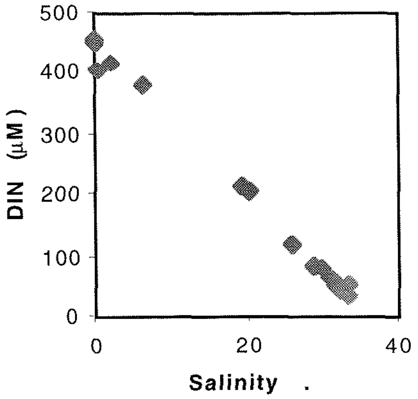


DIN-Salinity relationship (Cont.)

1999 FEB .



1999 MAR.



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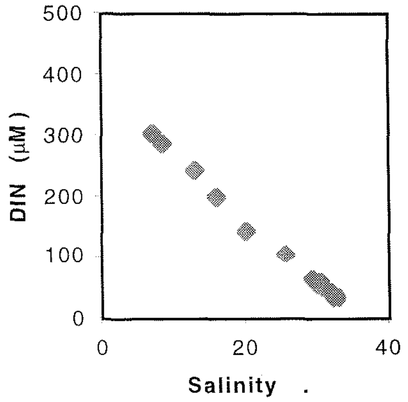

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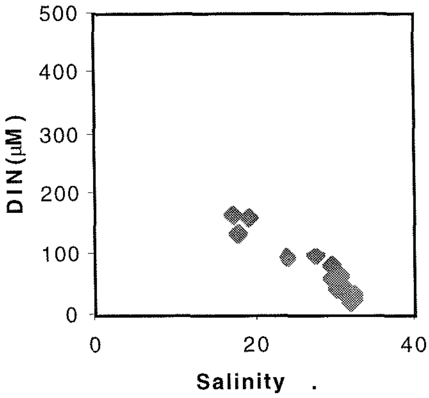

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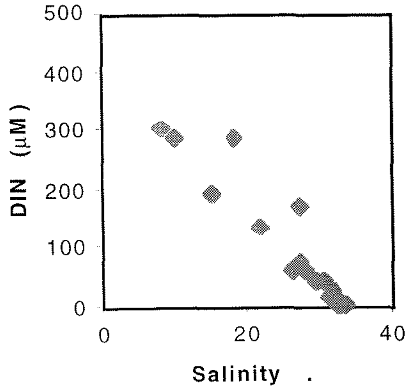
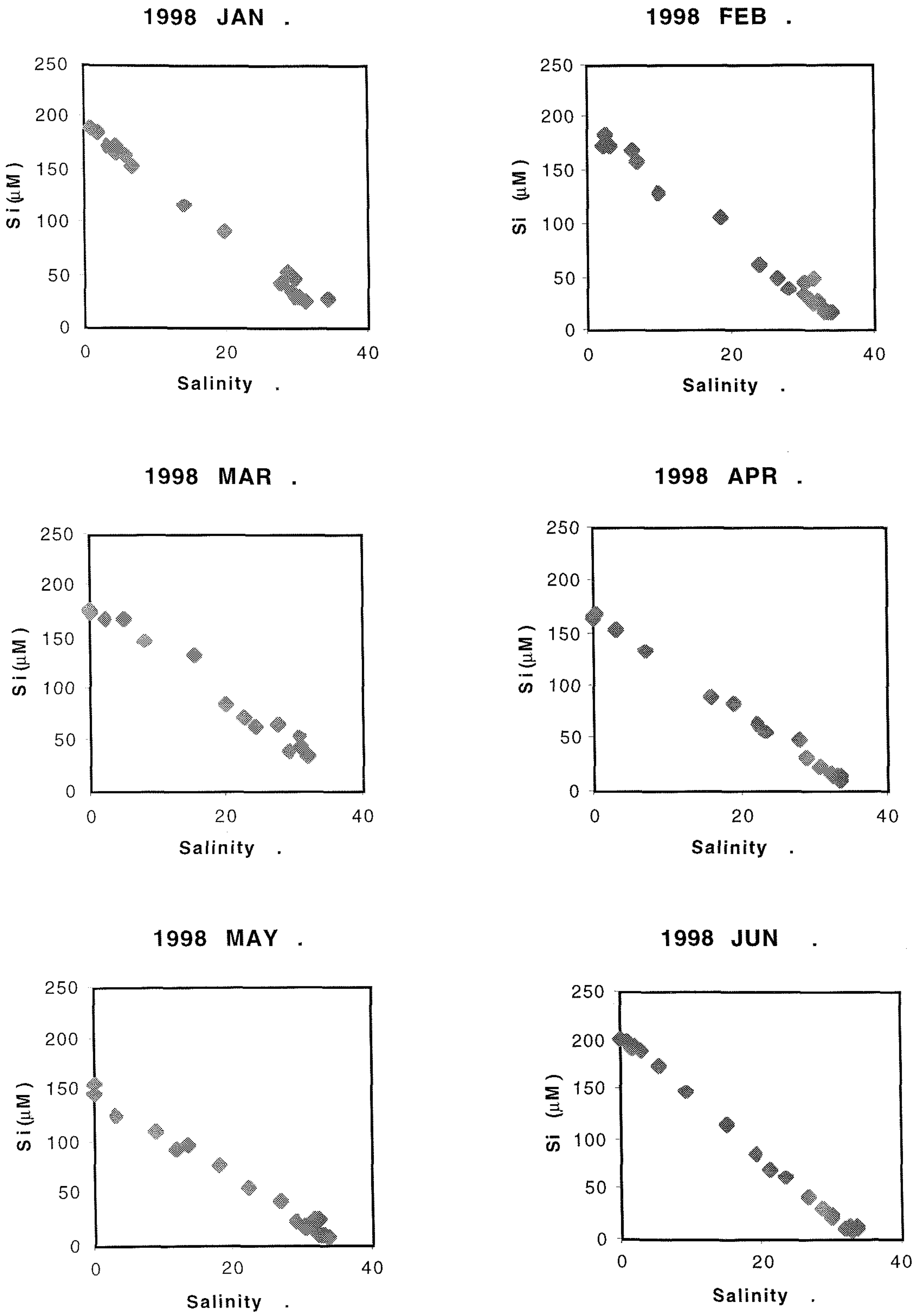
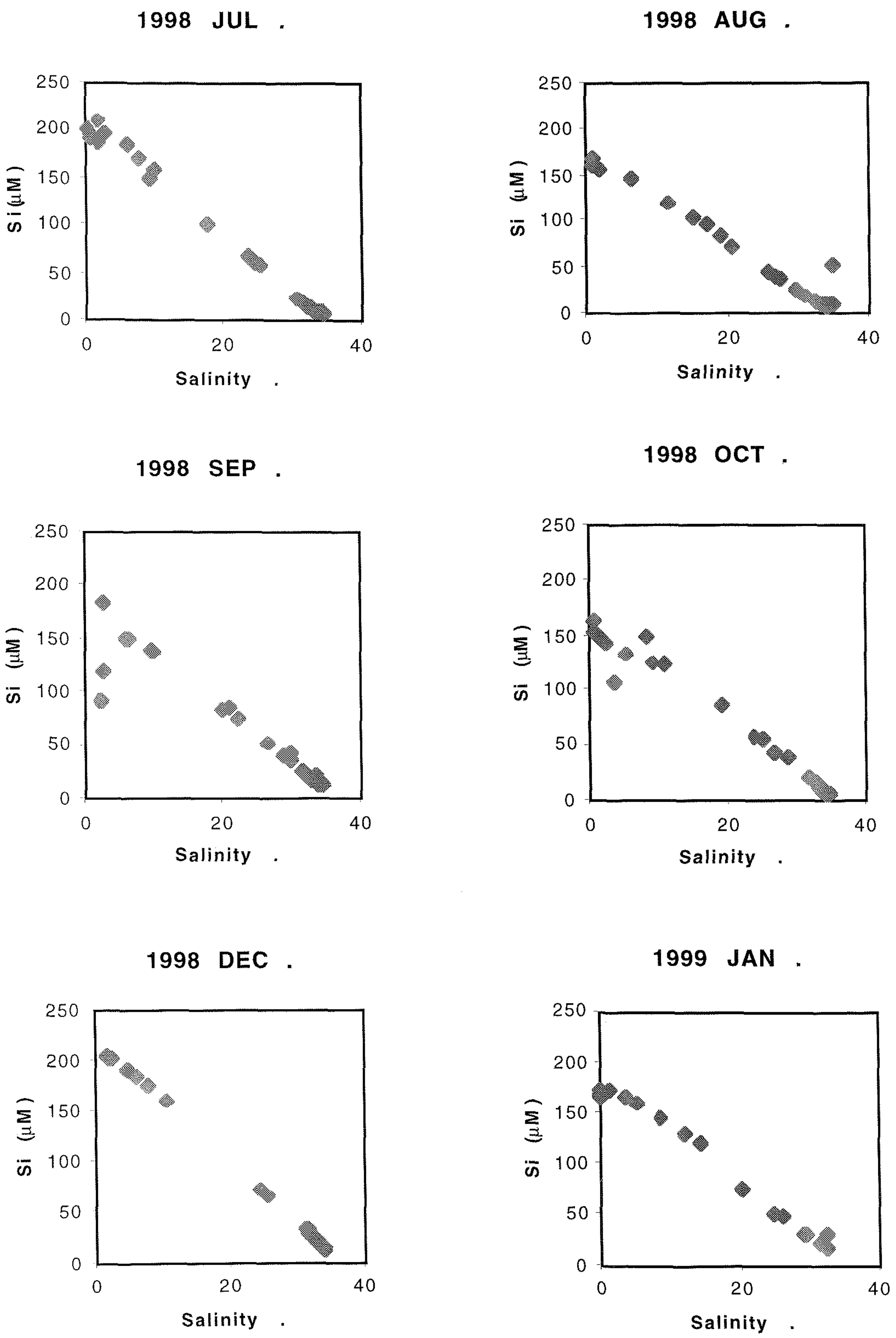


DIN-Salinity relationship (Cont.)

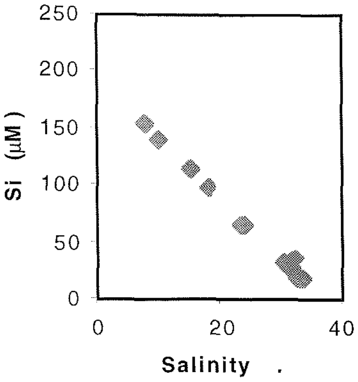


Si-Salinity relationship

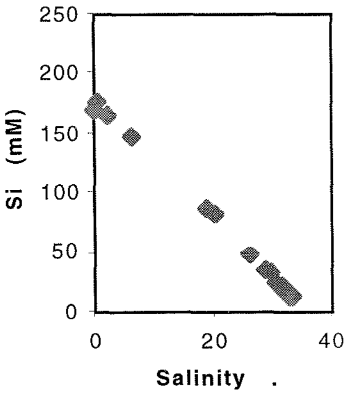


Si-Salinity relationship (Cont.)

1999 FEB .



1999 MAR .



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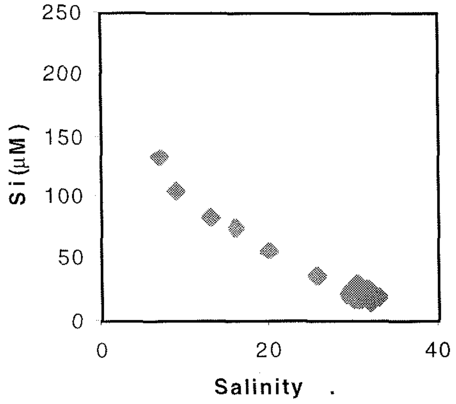

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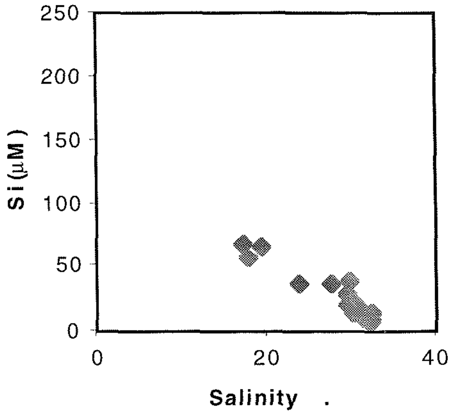

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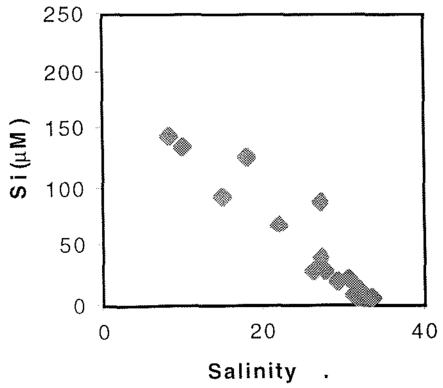
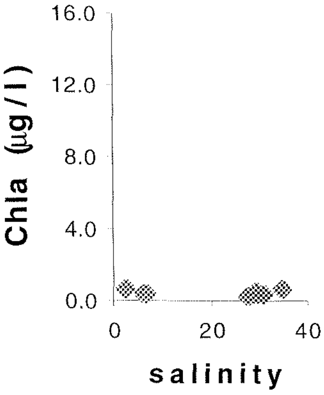
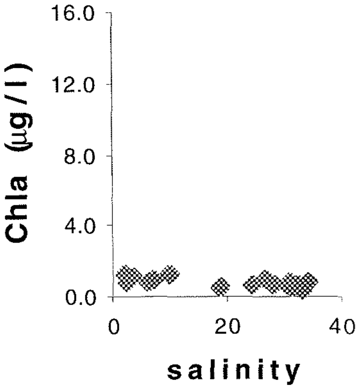


Si-Salinity relationship (Cont.)

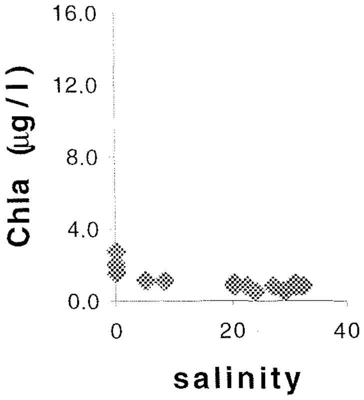
Jan (1998) .



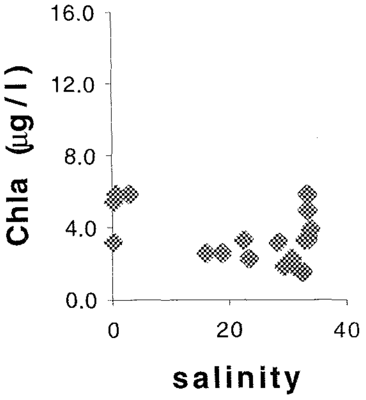
Feb (1998)



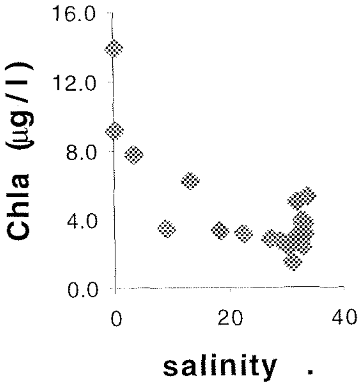
Mar (1998)



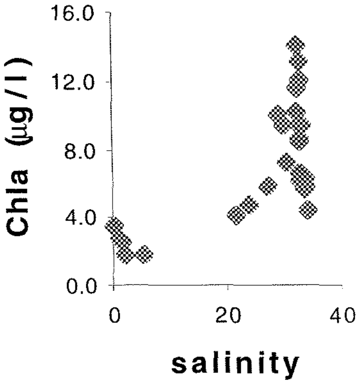
Apr (1998)



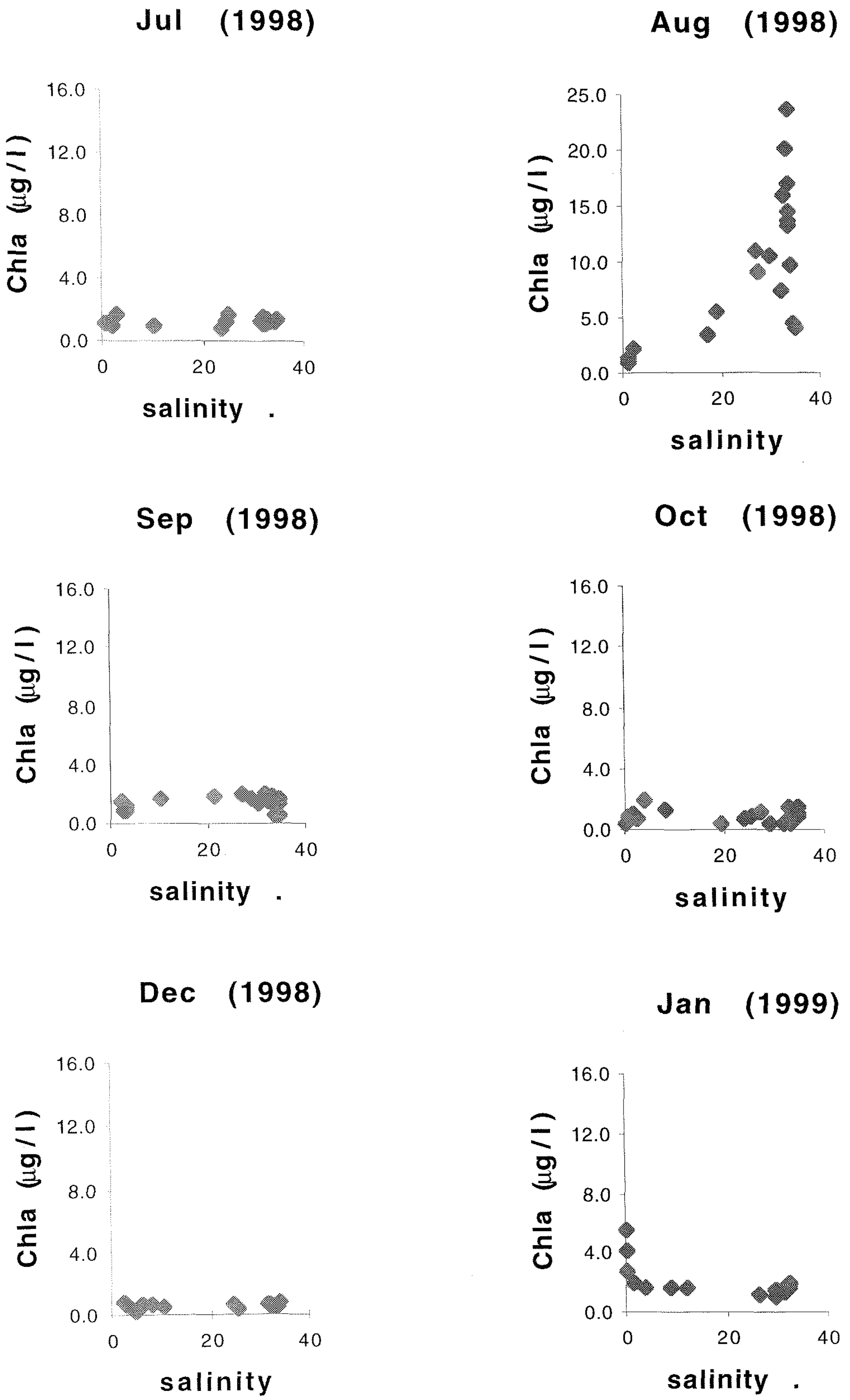
May (1998)



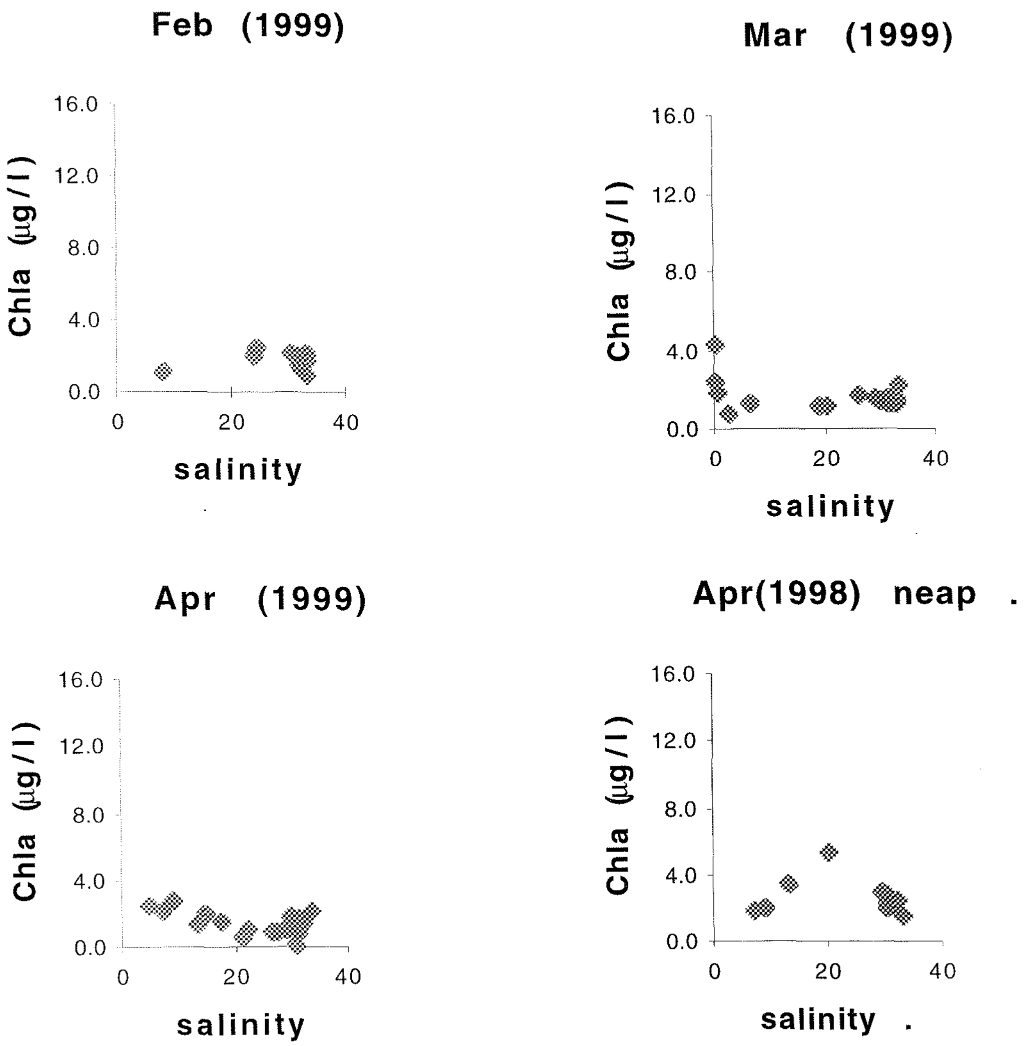
Jun (1998)



Chla -salinity relationship

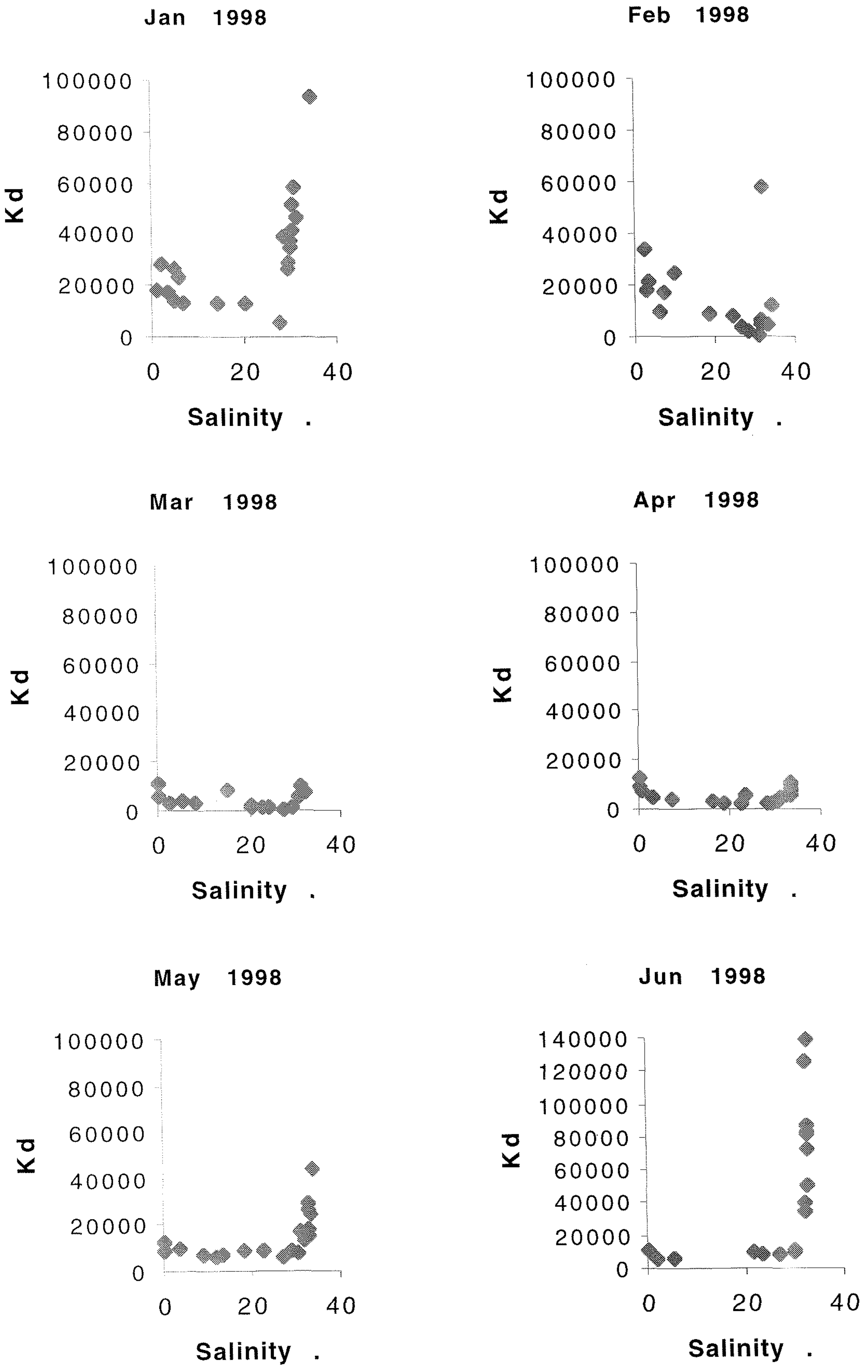


Chla -salinity relationship(Cont.)

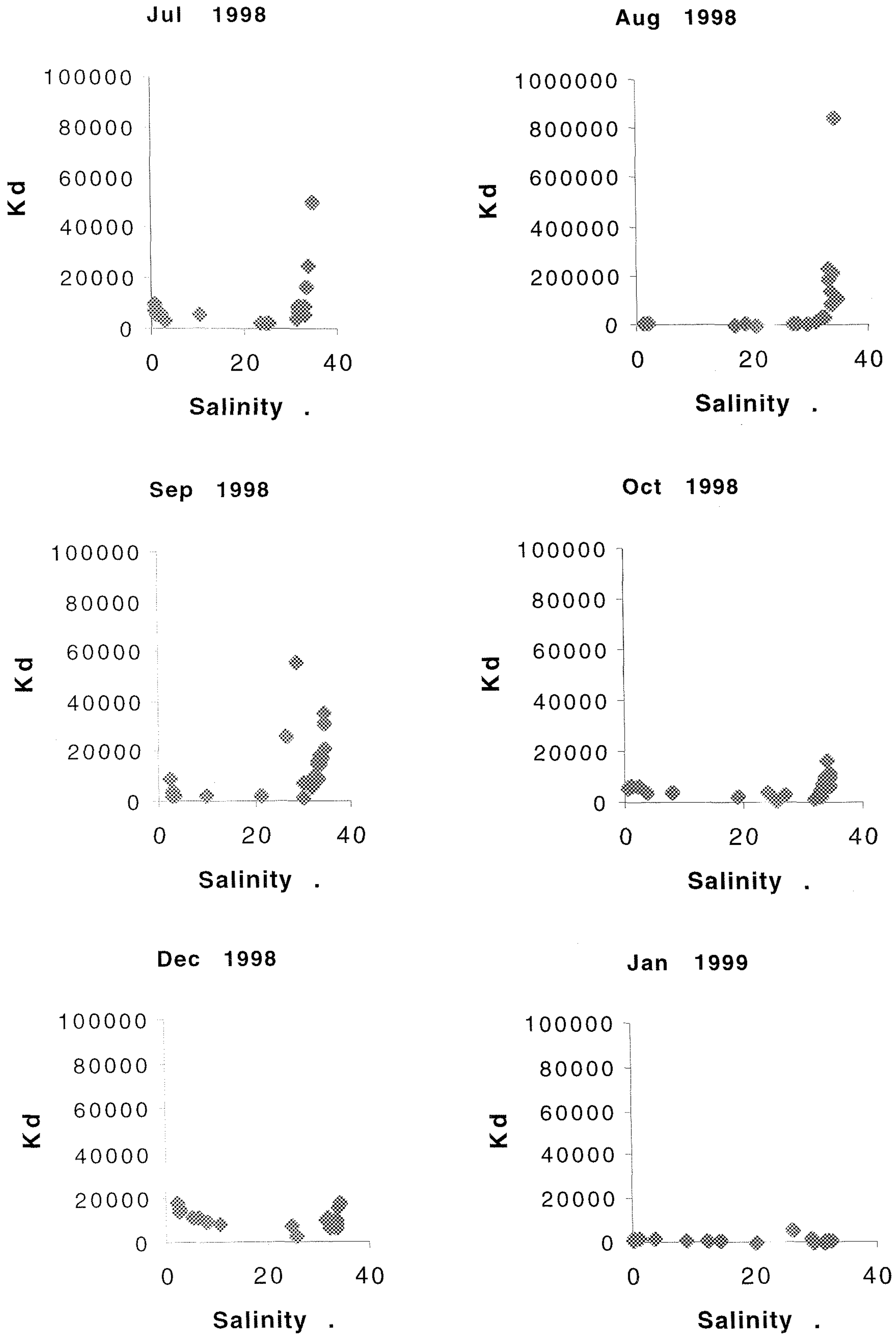


Chla -salinity relationship(Cont.)

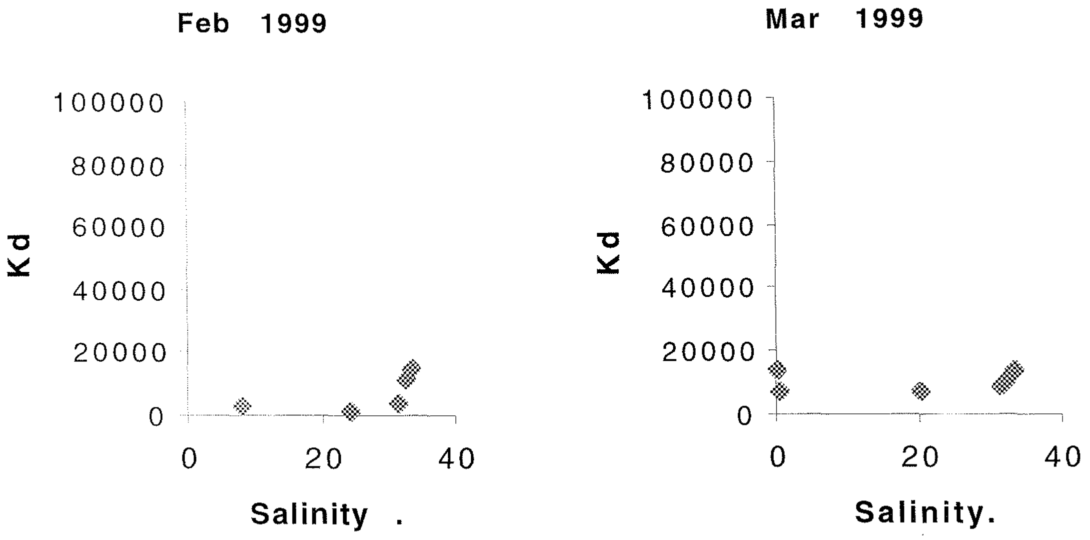
Particle SPEPs Result		(unite: µmol/g)					
Site	**PTP**	**loosely P**	**FeP**	**Poly P**	**CaP**	**OP**	**Fe**
Woodmill Lane	74.53	8.57	22.25	2.42	6.88	29.95	115.02
PWD	45.77	3.68	15.80	2.04	4.71	16.62	64.19
Cobden bridge	43.23	3.83	13.76	1.99	4.03	17.01	42.59
Northam bridge	53.05	6.24	13.18	2.85	4.38	23.43	32.21
Itchen bridge	12.87	1.51	2.36	0.57	1.63	6.12	3.70
Dockhead	14.65	1.92	1.70	0.55	1.85	7.95	5.61
Redbridge	12.46	1.54	3.62	0.51	1.10	4.94	36.66
Hyths	8.60	1.33	1.92	0.32	0.90	3.62	20.71
Weston Shelf	10.40	0.38	1.08	0.44	1.16	7.00	9.33
Hound	15.66	2.46	1.47	0.57	1.75	8.73	21.65
Turkard pile	11.62	0.64	1.14	0.37	1.02	8.10	13.20
Hamble Point	10.54	0.41	0.33	0.37	1.43	7.71	7.15
Fawley Power station	9.12	0.75	0.62	0.43	1.42	5.54	5.81
Hamble river	8.95	0.43	1.13	0.24	0.64	7.33	1.63
Calshot Buoy	7.01	0.28	0.29	0.15	0.74	4.30	15.18
	Salinity	**%looselyP/IP**	**%FeP/IP**	**%PolyP/IP**	**%CaP/IP**	**%OP/PTP**	**Fe/FeP**
Woodmill Lane	4.70	21.37	55.47	6.02	17.14	40.19	5.17
PWD	8.80	14.03	60.23	7.77	17.97	36.32	4.06
Cobden bridge	14.80	16.23	58.29	8.42	17.07	39.34	3.10
Northam bridge	17.40	23.43	49.45	10.68	16.44	44.18	2.44
Itchen bridge	29.40	24.79	38.90	9.39	26.91	47.55	1.57
Dockhead	30.50	31.87	28.21	9.16	30.76	54.27	3.30
Redbridge	22.10	22.77	53.48	7.46	16.30	39.63	10.12
Hyths	26.40	29.60	42.98	7.22	20.20	42.15	10.76
Weston Shelf	30.80	12.42	35.30	14.47	37.81	67.26	8.62
Hound	30.00	39.39	23.57	9.06	27.97	55.71	14.71
Turkard pile	29.00	20.24	36.05	11.64	32.07	69.71	11.56
Hamble Point	31.90	16.16	12.91	14.52	56.42	73.22	21.81
Fawley Power station	31.00	23.29	19.14	13.27	44.29	60.80	9.44
Hamble river	33.60	19.35	19.64	10.54	50.46	81.91	5.69
Calshot Buoy	28.80	17.64	46.22	10.04	26.09	61.39	13.49



Kd -Salinity relationship



Kd -Salinity relationship (Cont.)



Kd -Salinity relationship (Cont.)

* The units for Kd are all l/kg.

DIP Concentrations in the porewater of the River Itchen sediments

Depth(cm)	DIP (μM)		Depth(cm)	DIP(μM)
Station1			**Station3**	
0.5	10.5		0.5	20.1
1.5	5.2		1.5	9.6
2.5	5.5		3	9.8
4	4.3		5	11.8
6.6	4.1		7	16.6
9.5	6.8		9	19.8
12	3.9		11	25.1
14	38		13	17.7
15.5	20.1		**Station4**	
16.5	53.2			
17.5	91.9		0.5	0.1
18.5	158.3		1.5	15
19.5	421		2.5	54.8
21	510		3.5	35.2
22.5	357		4.5	151.2
24	160		5.5	141.8
Station2			6.5	8.4
			7.5	12
0	6.8		9	1.9
1.5	11.4		11	2.2
2.5	44		13	31.7
3.5	28		15	122.4
4.5	88.2		17	1860
6	106.7		19	1812
8	96.4		21	1801
9.5	63.7		23	1250

				Grab Sediment Incubation Experiment Result (from 10.12.98)												
Sampling time: 4.12.98																
Sample No.1: Fawley powerstation				d: 57mm. Sediment depth: 90mm overlying water salinity: 33.9 + water 500ml												
Sample No.2: Itchen Bridge				d: 57mm, sediment depth: 103mm. overlying water salinity: 31.5 + water 485ml												
Sample No.3: Portswood sewage discharge				*d: 57mm, Sediment depth: 93mm. overlying water salinity: 22.0 + water 490ml*												
each sampling takes overlying water 15ml and filter through GF/F filter paper								10ml water sample for DOP and 5ml water sample for DIP								
Sampling starts at 10:35 am 10.12.98																
Sample cup No.	*time(d)*	*1					*2					*3				
		DIP	TDP	DOP	DIN	Si	DIP	TDP	DOP	DIN	Si	DIP	TDP	DOP	DIN	Si
water100							1.79	2.66	0.87	47.37	27.48	5.08	5.51	0.43	149.44	83.09
101	0.00	1.03	1.58	0.55	48.61	35.36	1.67	2.17	0.5	70.71	32.51	5.14	6.61	1.47	169.41	88.37
102	0.02	1.18	1.9	0.72	50.84	15.51	1.64	2.57	0.93	64.54	38.85	4.99	6.39	1.4	168.14	107.87
103	0.04	1.19	1.79	0.6	27.92	19.21	1.7	1.96	0.26	48.08	30.84	5.13	5.93	0.8	148.38	85.24
104	0.06	1.4	2.12	0.72	31.74	19.94	1.67	2.28	0.61	46.49	28.25	5.2	6.05	0.85	163.77	84.5
105	0.13	1.8	2.56	0.76	50.37	30.98	1.72	1.97	0.25	51.11	31.95	4.63	5.97	1.34	139.4	83.54
106	0.19	1.13	1.63	0.5	25.85	17.09	1.53	2.22	0.69	51.93	32.38	4.58	5.57	0.99	137.36	84.48
107	0.25	1.14	1.54	0.4	26.04	20.96	1.61	2.37	0.76	54.7	31.81	4.72	6.04	1.32	143.93	85.67
108	0.38	1.12	1.92	0.8	25.52	20.9	1.56	2.18	0.62	54.36	33.15	4.51	5.93	1.42	140.1	88.27
109	1.00	1.07	2.09	1.02	25.94	21	1.5	2.65	1.15	54.73	33.61	4.37	6.33	1.96	137.06	88.94
110	2.00	0.99	2	1.01	27.29	26.25	1.46	2.66	1.2	54.38	39.45	3.82	5.2	1.38	127.52	95.78
111	3.00	0.11	1.05	0.94	25.46	28.65	1.01	1.43	0.42	50.37	40.75	3.08	3.62	0.54	119.7	99.24
112	4.00	0.13	0.57	0.44	27.31	35.93	0.92	1.32	0.4	54.66	50.07	2.48	3.06	0.58	104.61	112.58
113	5.00	0.12	0.57	0.45	26.72	32.93	0.47	1.31	0.84	52.39	48.14	1.17	2.08	0.91	77.63	117.58
114	6.00	0.06	0.34	0.28	25.6	53.68	0.81	1.34	0.53	52.64	71.48	2.36	3.34	0.98	70.24	147.94
115	7.00	0.12	0.31	0.19	22.66	47.04	0.94	1.32	0.38	47.09	76.05	4.35	5.27	0.92	62.94	167.56
116	8.00	0.12	0.47	0.35	20.4	56.92	1.16	1.21	0.05	42.8	84.55	3.94	4.5	0.56	53.84	189.43
117	9.00	0.18	0.51	0.33	19.83	62.11	1.27	1.32	0.05	37.39	90.33	4.19	3.37	<0.02	49.38	204.23
118	10.00	0.22	0.45	0.23	5.28	7.44	1.08	1.23	0.15	29.98	80.13	4.76	5.43	0.67	40.03	184.08
119	11.00	0.29	0.71	0.42	6.76	26.68	1.73	0.93	<0.02	34.74	97.18	5	3.54	<0.02	29.81	198.29
120	14.00	0.31	0.53	0.22	3.24	32.86	1.72	1.85	0.13	45.95	112.45					
water121	14.00	0.85	1.26	0	22.3	13.5	1.61	1.42	<0.02	45.56	25.35	5.05	4.82	<0.02	147.97	77.26

				Intact Cores incubation Experiment Result (from 7.4.99)					
Sampling time:1.4.1999				Sediments area:		0.00255176			
Sample No.1:Northam Bridge			**d: 57mm. Sediment depth: 95mm overlying water salinity: 19.5 + water 500ml**						
Sample No.2: Hythes Pier			**d: 57mm, sediment depth: 120mm. overlying water salinity: 27.5 + water 430ml**						
each sampling takes overlying water 20ml and filter through GF/F filter paper						10ml sample for DOP and 10ml sample for DIP			
Sampling starts at 11am 7.4.98									
Sample cup No.	time(d)	DIP	TDP	DOP	Sample cup No.	time(d)	DIP	TDP	DOP
A0	0.00	3.82	4.93	1.11	B0	0.00	1.15	1.85	0.7
A1	0.00	4.44	6.57	2.13	B1	0.00	1.48	1.66	0.18
A2	0.02	4.07	5.53	1.46	B2	0.02	1	1.38	0.38
A3	0.04	4.09	5.16	1.07	B3	0.04	0.42	1.76	1.34
A4	0.08	4.16	5.61	1.45	B4	0.08	1.09	0.99	0
A5	0.13	4.14	5.69	1.55	B5	0.13	0.27	1.64	1.37
A6	0.21	4.16	5.82	1.66	B6	0.21	0.77	1.71	0.94
A7	0.29	4.17	5.69	1.52	B7	0.29	0.83	1.36	0.53
A8	1.00	3.58	5.49	1.91	B8	1.00	0.61	1.18	0.57
A9	2.00	3.62	5.07	1.45	B9	2.00	0.57	1.34	0.77
A10	3.00	2.83	3.77	0.94	B10	3.00	0.64	1.13	0.49
A11	4.00	2.95	3.83	0.88	B11	4.00	0.51	1	0.49
A12	5.00	3.04	4.24	1.2	B12	5.00	0.4	0.44	0.04
A13	6.00	2.55	3.58	1.03	B13	6.00	0.35	1.1	0.75
A14	7.00	2.07	4.51	2.44	B14	7.00	0.05	1.15	1.1
A15	8.00	2.77	3.69	0.92	B15	8.00	0.23	1.59	1.36
A16	9.00	2.14	3.23	1.09	B16	9.00	0.04	1.55	1.51
A17	10.00	2.07	3.02	0.95	B17	10.00	0.03	1.29	1.26
A0'	10.00	4.8	5.93	1.13	B0'	10.00	1.23	2.38	1.15

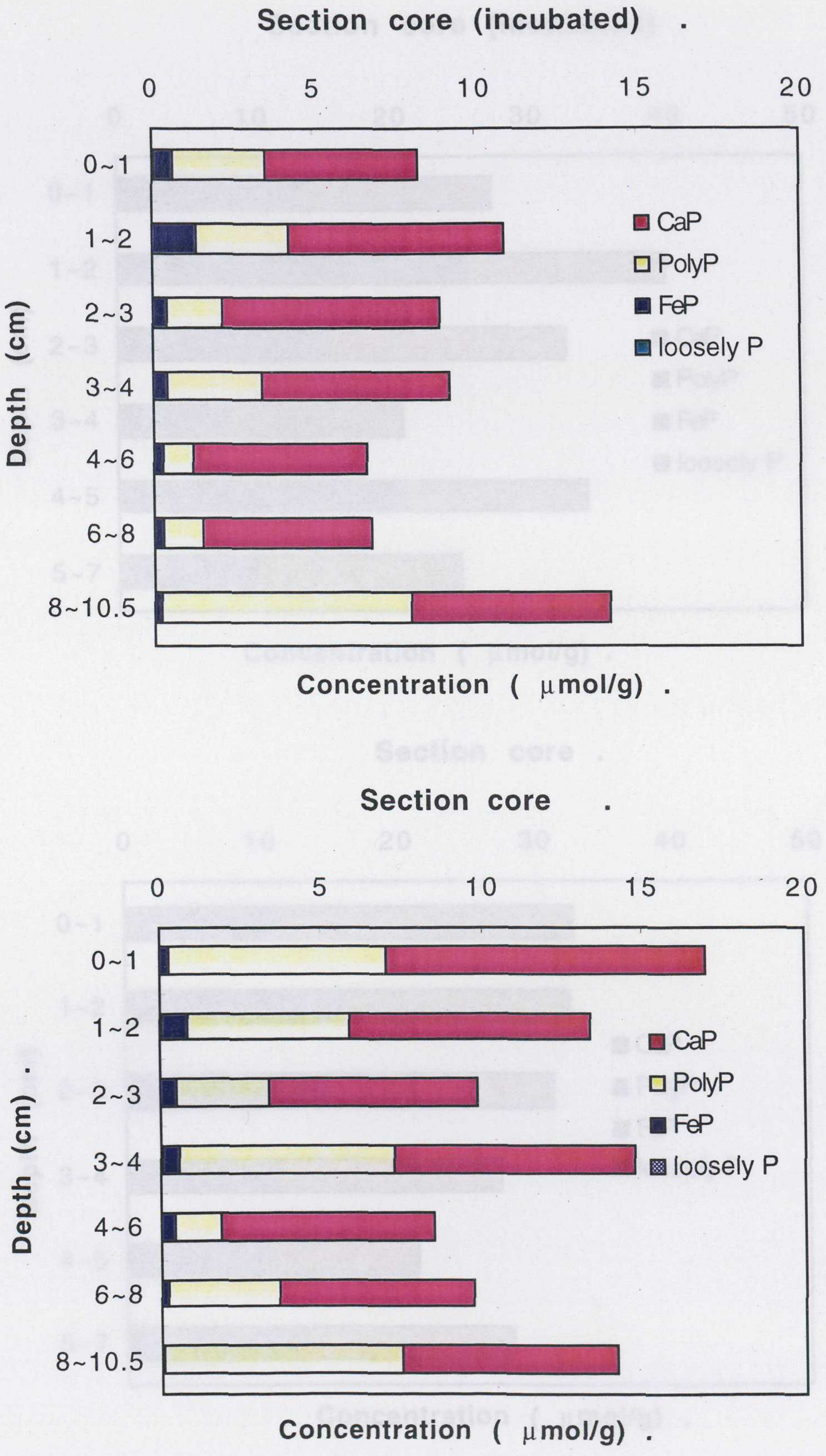
Sediments SPEPs results (1998)

Sample date:	30.3.1998						
Station	name	Water Conter	IP	loosely P	FeP	Poly P	CaP
1	Woodmilllane	44.34	**22.16**	0.30	0.47	5.48	9.37
2	PWD	26.38	**26.87**	0.45	0.91	4.43	7.10
3	Itchen Bridge	45.37	**25.37**	0.13	0.42	4.47	11.62
4	No1 SG	54.74	**17.52**	0.16	0.06	3.42	9.93
5	NW Netley	33.41	**9.12**	0.13	0.18	0.86	10.06
6	greenland	39.60	**6.07**	0.06	0.20	2.28	6.91
7	calshot buoy	34.96	**17.83**	0.08	0.26	0.88	4.49
Station	name		OP	loosely%	FeP%	PolyP%	CaP%
1	Woodmilllane		6.27	1.92	3.00	35.10	59.98
2	PWD		5.57	3.46	7.04	34.41	55.08
3	Itchen Bridge		7.26	0.78	2.55	26.85	69.83
4	No1 SG		5.83	1.20	0.44	25.20	73.17
5	NW Netley		2.40	1.16	1.58	7.63	89.63
6	greenland		1.90	0.67	2.07	24.15	73.11
7	calshot buoy		3.42	1.32	4.49	15.44	78.75

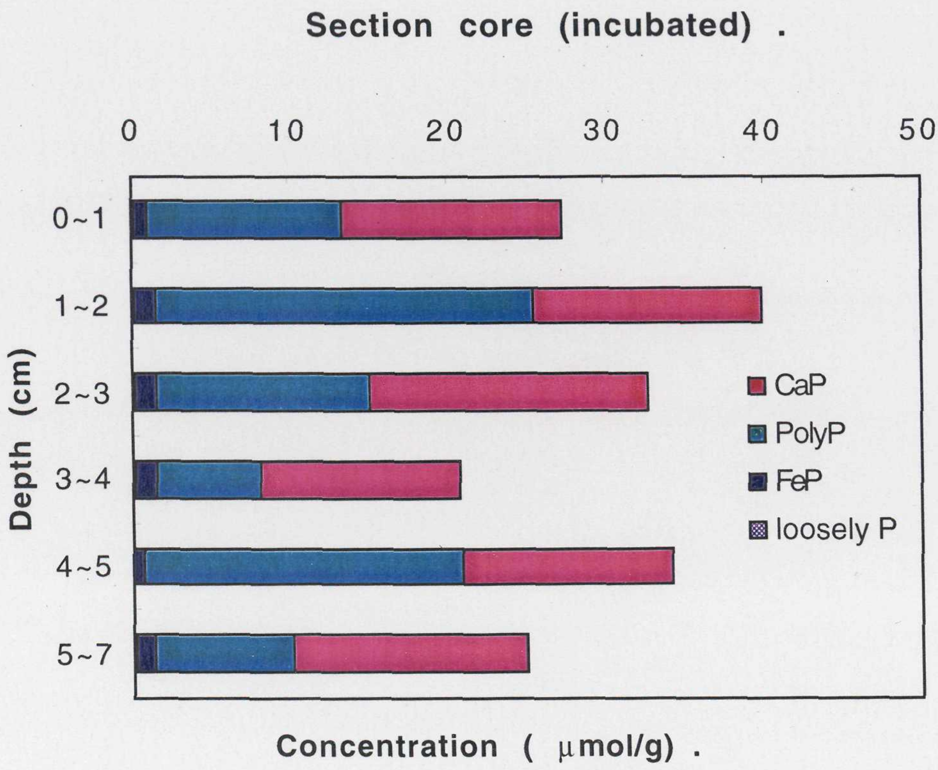
Sediments SPEPs results (1999)

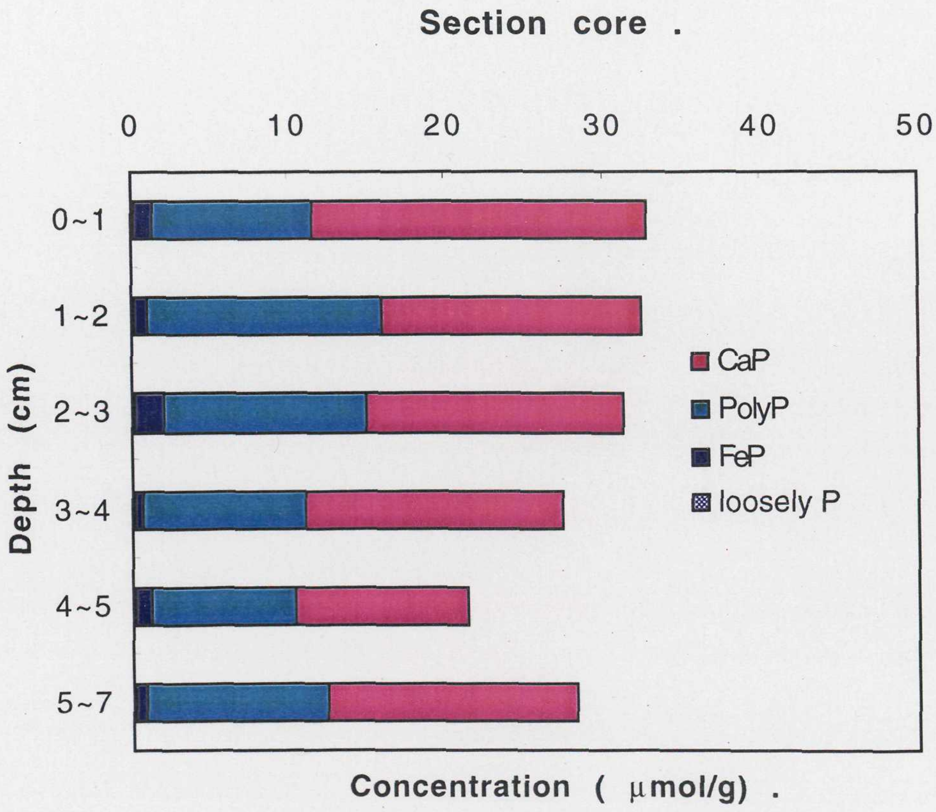
	water content(%)	IP	loosely P	FeP	Poly P	CaP
Woodmill lane	42.27	18.83	0.24	1.20	4.92	11.76
PWD	34.32	22.19	0.28	1.22	7.62	5.78
Itchen bridge	53.68	23.67	0.03	0.10	7.86	11.18
Redbridge	34.35	7.18	0.15	0.34	1.97	0.86
Westshelf	55.02	11.64	0.03	0.06	0.80	5.45
Hythe (surface)	59.38	11.60	0.05	0.07	2.54	6.32
Hythe (2)	40.06	12.00	0.01	0.03	1.54	8.01
Turkard pile(1)	52.39	12.07	0.03	0.07	1.46	7.15
Turkard pile(2)	56.09	12.79	0.02	0.07	1.76	8.33
Hamble point(1)	43.35	12.60	0.01	0.01	1.57	6.88
Hamble point(2)	47.08	10.19	0.01	0.01	1.64	6.59
Fowley power station	45.80	9.88	0.02	0.06	1.16	7.32
Fowley powerstation (2)	47.67	10.75	0.02	0.01	1.29	7.54
		OP	loosely P%	FeP%	Poly P%	CaP%
Woodmill lane		3.48	1.32	6.64	27.14	64.90
PWD		1.33	1.89	8.18	51.14	38.79
Itchen bridge		10.49	0.17	0.54	40.97	58.31
Redbridge		3.38	4.52	10.15	59.41	25.92
Westshelf		2.32	0.51	0.96	12.62	85.90
Hythe (surface)		3.12	0.52	0.80	28.25	70.44
Hythe (2)		3.12	0.09	0.33	16.05	83.53
Turkard pile(1)		2.08	0.33	0.84	16.76	82.07
Turkard pile(2)		3.91	0.22	0.64	17.29	81.85
Hamble point(1)		1.83	0.11	0.14	18.55	81.20
Hamble point(2)		3.09	0.18	0.15	19.90	79.78
Fowley power station		3.06	0.18	0.73	13.58	85.51
Fowley powerstation (2)		2.54	0.22	0.17	14.57	85.04

* Units are all μmol/g. % is percentage of inorganic phosphorus.



Hythe sediment SPEPs results





Northam Bridge sediment SPEPs results

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