

# Biogeochemical Controls on Phosphorus Cycling between Sediment and Water in Estuaries

University of East Anglia

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# Biogeochemical Controls on Phosphorus Cycling between Sediment and Water in Estuaries

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This report is a summary of work carried out for a PhD at the University of East Anglia as part of the Agency's contribution to the DoE and MAFF funded JoNuS programme. The Executive Summary identifies the elements of JoNuS available separately to Agency staff. These were not part of the R&D Project but are made freely available to participants of the JoNuS programme.

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\* Available from the Environment Agency Project Manager; they do not form part of this research report.

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<sup>1</sup> "Establishing the Nutrient Status of UK Coastal Waters - The JONUS Programme"; Brochure compiled by Bob Dickson, Martin Roche and Nick Faber, formerly MAFF/DFR, now CEFAS

<sup>2</sup> The JoNuS Project - Full Report; A computer-based summary of all the JoNuS exercises, comprising two 3½ inch MS-DOS disks and a 53 page guide.

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# Executive Summary

The Joint Nutrient Study (JoNuS) was a Programme set up in response to international pressure to limit the risks of pollution due to excess nutrients entering the North Sea. Its purpose was to establish the nutrient status of UK Coastal Waters and was aimed at understanding nutrients in the southern North Sea, primarily in the Humber, Wash and Thames. It was also hoped to estimate the flux of phosphorus from the land to the coastal zone. Fieldwork took place between 1990 and 1993. The Programme was principally funded by DoE and MAFF, with a small contribution from the then NRA via the R&D programme. Anglian Region additionally contributed to the sampling programme. Figure 1 shows the extent of the full sampling programme.

This report covers the NRA funded Ph.D. at UEA which was a part of the JoNuS Programme, having been identified as a discrete element for the purposes of R&D administration. It provides some understanding of processes in estuaries, an essential feature of the JoNuS Programme.

The primary goal was to assess the behaviour of phosphorus in the intertidal areas of the Wash system. Some of the work, including methodology, was described in progress reports. Experimental work focused on sediment samples from the Great Ouse and Nene estuaries, which drain to the Wash in Anglian Region.

These studies demonstrated that passive diffusion studies such as conventionally used in studies of fluxes from sediments, may not adequately mimic the environmental situation in intertidal systems since the regular tidal excursions can actively force exchange of overlying and pore waters at rates that could be 10 times those predicted from molecular diffusion. In the case of phosphorus, this active “tidal pumping” probably acts to increase the rates of diffusion of oxygen into the sediments and thus acts to retain phosphorus within the sediments rather than promote its release.

Thus it seems likely that diagenetic processes within sediments can act to redistribute phosphorus within sediments but do not result in fluxes of DIP into the water column. If sedimentary phosphorus is re-suspended and transported to an area of low DIP, desorption will occur, resulting in a potentially large source of DIP to the water column. In the U.K. most estuaries are effective traps and hence this particulate export process may not represent an important source of DIP to coastal waters. However, in some estuaries such as the Great Ouse there is evidence that winter storm flows may flush particulate matter out of the estuary.

## Context within the JoNuS Programme

The ultimate aim of the Programme has been to provide managers and policy makers with a soundly-based assessment of the nutrient status of that stretch of the North Sea coast which receives the bulk of UK nutrient inputs, while at the same time developing a sufficiently detailed understanding of the factors controlling these inputs to advise on the most appropriate remedial measures, should these prove necessary.

The philosophy behind the experiment is that we cannot assess eutrophication from ill-defined, low amplitude trends of nutrient concentrations in coastal waters, or from the trends in nutrient loads reaching the so-called “tidal points” of rivers since these loads are known to be

subject to radical geochemical transformations in passing through the estuaries on the way to the sea. Instead, the JoNuS experiment sought to identify the budgets and dominant controls acting on three key nutrients as they pass through three large estuaries of contrasting character: the industrial Humber, the agricultural Wash and the urban Thames. This “estuary budget” approach to the problem has since been commended by the North Sea Quality Status Report.

### JoNuS Outputs

The main benefit of this joint collaboration was the access to the very large data set and wide range of skills of the entire Programme. Although the principal outputs of the JoNuS Programme were not identified as part of the R&D Project, they are accessible to the Agency as a collaborator. These include:

- a FoxPro database of Humber, Wash and related coastal data over 3 years, using a purpose designed graphical interface;
- scientific collaboration of a high order, leading to the development of good sampling protocols and analytical techniques within Anglian Region;
- interim reports identifying the elements of the project and progress;
- a glossy brochure describing the purpose and outcome of the Project. The Agency (as NRA) is listed as one of the 3 sponsors; however its financial contribution was only about 5% of the total;
- ultimately there will be a final report; the completion of which is outside the Agency’s influence;
- at least 3 publications in the scientific press.

The JoNuS Programme Brochure makes recommendations for a Phase II of JoNuS, covering the Thames Estuary and Irish Sea. The Environment Agency has been approached with a view to joint participation.

Following the successful conclusion of JoNuS (phase I) the “estuary budget” approach is further recommended for future studies involved with establishing the nutrient status of coastal waters.

Although the final report on the original JoNuS Programme has still to be issued by MAFF, DoE are happy with the final result and have already commenced the funding for parts of Phase II of JoNuS (from April, 1996).

**Keywords:** JoNuS, phosphorus, nutrients, Wash, Humber, North Sea, sediment, database.







# Glossary of Terms

**Anoxic** - The opposite of *oxic*, this is a condition in sediments or water where there is a complete lack of oxygen, often caused by the oxidative decomposition of organic matter. Such conditions are ideal for the proliferation of sulphate-reducing bacteria, which are attached to sediments. Anoxic sediments often appear black (due to iron) and smell of hydrogen sulphide.

**Anthropogenic** - A loose description of a process or artifact not considered to be of natural origin, but caused by the activities of industrialised man.

**Biogeochemical** - A description of a chemical change process occurring in the geology (e.g. sediments) that is influenced by the presence of biological organisms. An example is sulphate-reducing bacteria in *anoxic* sediments leading to the production of iron pyrites.

**Bioturbation** - The reworking and further degradation of sediment by the action of organisms moving through it and feeding on it.

**Diagenesis** - A collection of processes by which loose accumulated sedimentary material becomes sedimentary rock.

**Eutrophication** - The enrichment of water by *nutrients*, especially compounds of nitrogen and/or phosphorus, causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms present in the water concerned. Whilst not necessarily harmful in itself, further processes can lead to problems such as loss of dissolved oxygen and fish mortality.

**Flocculation** - The coagulation of finely divided particles into particles of greater mass.

**Geomorphology** - The study of the evolution of landforms, excluding the major forms of the earth's surface, such as mountain chains and ocean basins.

**JONUS** - Acronym for **JO**int **NU**trient Study Programme which took place between 1990 and 1993, primarily funded by DoE and MAFF, with a contribution and participation by the Environment Agency, principally through the funding of this Ph.D at University of East Anglia.

**Nutrients** - These are substances needed for the growth of phytoplankton and benthic plants and which are often scarce, in relation to demand, in seawater. For present purposes, they are compounds of nitrogen, phosphorus and silicon (mostly in the oxidised, inorganic form).

**Oxic** - The condition of a water or sediment with a surfeit of oxygen. It is the "normal" state and is the opposite of *anoxic*.

**Pore Water** - Also known as Interstitial water, this is the water trapped within the accumulating sediment. There is interaction between this water and the sediment, giving rise to very localised chemical changes.

**Stratification** - The condition in an estuary or other saline water body in which there is a detectable change in salinity between the surface and the bottom. Strongly stratified water will have a interface layer with a rapid change in salinity, restricting mixing between the upper and lower layers. It can be caused by river or estuary water flowing over more dense seawater or be generated by thermal heating of the sea surface.

# **1. INTRODUCTION**

## **1.1 The Rationale Behind This Project**

An estimation of the flux of phosphorus from the land to the world's ocean is necessary in calculating the world's nutrient budgets and the ocean's long term productivity. On a smaller scale inputs of phosphorus from estuaries have an important impact on the productivity of local coastal areas. Raised levels and skewed ratios of nutrients can have serious consequences, such as toxic algae blooms.

Measuring fluxes of nutrients from estuaries is complex, and a thorough knowledge of sources and sinks within an estuary is necessary to predict how fluxes may react to environmental changes. Estuarine nutrient cycling can be affected by small alterations within the estuary and its catchment, such as changes in inputs into the estuary or different land use in the catchment area. Large scale changes such as climate and sea level change will also have an important impact.

As phosphorus is very particle reactive, intertidal sediments may represent a significant sink for phosphorus entering an estuary. Much of this phosphorus is derived from anthropogenic point sources such as sewage works in the catchment and estuary and intertidal sediments may store this phosphorus preventing it from entering coastal waters and eventually the oceans. The importance and stability of this store is poorly understood because intertidal sediments are so variable and dynamic and phosphorus chemistry complex. However an understanding of phosphorus cycling in intertidal sediments is necessary to quantify and understand fluxes of phosphorus from rivers to the sea.

## **1.2 The Structure of This Report**

This report aims to summarise the results of a three year research project on phosphorus in intertidal sediments. The primary goal of this project was to assess the behaviour of phosphorus in the intertidal areas of the Wash system. This has been addressed by a number of different approaches and the results of these have been reported in previous reports. In the first section of this report the results are drawn together to produce an overall synthesis. For details of the methods and individual results, the reader is referred to the earlier reports. Experimental work has focused on sediment samples collected in the Gt. Ouse and Nene estuaries (Figure 1.1) because their accessibility allows regular sampling and rapid return of material to the laboratory, but the results obtained allow general patterns of phosphorus cycling to be identified applicable beyond the specific area studied. The second section of this report therefore contains a synthesis of the present knowledge of estuarine phosphorus cycling. This will form part of a larger paper on aquatic phosphorus cycling to which the authors of this report are contributing.



## 2. DISCUSSION OF PROJECT RESULTS

Our results clearly demonstrate that particle water exchange is a critical control on phosphorus behaviour. In laboratory experiments using freshly collected sediments we have investigated the sorption and desorption of dissolved inorganic phosphorus (DIP). At high DIP concentrations, the sediments sorb phosphorus and at low concentrations they release it on time scales of several hours (Figure 2.1). It takes 24 - 48 hours for a quasi-steady state to be reached after which adsorption rates slow. The first period represents the exchange of phosphorus with the surface of the particles and the second a slower diffusion of the phosphorus into the interior of the particles. These relatively slow kinetics mean that in the highly dynamic environment of intertidal and near tidal areas, and particularly in estuaries with steep chemical gradients, these particle water interactions may not have time to come to steady state. This factor could greatly complicate modelling these interactions.

The rate of uptake can be mathematically described by a modified Elovich equation (House, 1995) (Equation 1, below) as illustrated in Figure 2.2.

$$n(t) = \frac{1}{b} \ln \left( 1 + k_p (\text{DIP}_0 - \text{EPC}_0)^2 b t \right) \quad \text{Equation (1)}$$

$n(t)$	-	Uptake of phosphorus ( $\mu\text{mol g}^{-1}$ )
$b$	-	Variable ( $\text{g}^{-1} \mu\text{mol l}^{-1}$ )
$k_p$	-	The rate constant ( $\mu\text{mol h}^{-1}$ )
$t$	-	Time (hours)
$\text{DIP}_0$	-	Initial concentration of Dissolved Inorganic Phosphorus ( $\mu\text{mol l}^{-1}$ )
$\text{EPC}_0$	-	Equilibrium Phosphate Concentration (defined below)

As the sorption reactions approach steady-state concentrations of DIP in natural waters maybe buffered by these sorption/desorption reactions within a relatively narrow range. Although the sediments all tend to buffer DIP concentrations at similar levels as measured by  $\text{EPC}_0$ , the capacity of this buffer ( $K^*$ ) varies considerably (Table 2.1) and hence the possibility that the buffer capacity will be exceeded varies.

**Table 2.1      The Equilibrium Phosphate Concentrations ( $\text{EPC}_0$ ) and the Linear Adsorption Coefficient ( $K^*$ ) measured using sediments from the top mms of the mudflats at King's Lynn, Denver, Sutton Bridge and Wisbech.**

River	Site	$K^* \text{ l g}^{-1}$	$\text{EPC}_0 \mu\text{mol l}^{-1}$
Great Ouse	King's Lynn	0.045	5
	Denver	0.40	3
Nene	Sutton Bridge	0.050	5
	Wisbech	0.87	6

These values of the  $EPC_0$  were similar to those reported for Intertidal sediments of the Wadden Sea (Raaphorst and Kloosterhuis, 1994) which ranged from 5 - 10  $\mu\text{mol l}^{-1}$ . Sediments from other marine and freshwater sites give similar values (Froelich, 1988). However, lower values for  $EPC_0$  have also been reported, (Froelich, 1988). Notably values for the Amazon range from 0.5 - 1.5  $\mu\text{mol l}^{-1}$  (Froelich, 1988) and Slomp and Raaphorst (1993) reported values for North Sea sediments ranging from 0.2-1.5  $\mu\text{mol l}^{-1}$ . This may well reflect the different histories of the particles at the different sites. For example the estuarine sediments of the Amazon are in contact with lower concentrations of DIP than those in the Great Ouse. Therefore there are more sites available to take up phosphate but less phosphate available on the particle to desorb. The result is a lower  $EPC_0$  concentration than that for Great Ouse sediments, which have been in contact with a higher concentration of DIP, and are therefore less able to take up DIP but, are more able to release it.

The sites at the seaward end of the estuaries have a lower value of  $K^*$  than those at the freshwater end. Therefore sediments at King's Lynn ( $K^* = 0.045 \text{ g l}^{-1}$ ), and Sutton Bridge: ( $K^* = 0.05 \text{ g l}^{-1}$ ) can be said to have a greater capacity to sorb phosphorus than those at the freshwater end (Denver 0.40  $\text{g l}^{-1}$ , Wisbech 0.87  $\text{g l}^{-1}$ ). This was despite the fact that the salinity of the experiments were kept approximately constant.

The  $K^*$  values at King's Lynn and Sutton Bridge were similar to a wide range of  $K^*$  values found for oxic marine/estuarine sediments:

- Raaphorst and Kloosterhuis (1994), 0.0068-0.0227  $\text{l g}^{-1}$  (Wadden Sea)
- Krom and Berner (1980), 0.05  $\text{l g}^{-1}$  (Long Island Sound)

$K^*$  values at Denver and Wisbech were similar to the few values that could be found in the literature for stream and lake sediments:

- Mayer and Gloss (1980), 0.6  $\text{l g}^{-1}$  (Colorado River sediments)
- Wauchope and McDowell (1984), 0.3  $\text{l g}^{-1}$  (Lakes and streams in the Mississippi river flood plain)

This suggests that there may be a fundamental difference in the composition of the particles present in the marine and estuarine environments affecting the ability of the particles to buffer DIP concentrations. It is hard to confirm this from the literature because experiments have been undertaken with different ranges of initial DIP concentrations, temperature, ionic strength and pH.



In almost all profiles, dissolved phosphorus concentrations are higher than in the overlying water and higher than predicted from the laboratory oxic studies of phosphorus buffering. This observation provides further evidence of the central role of iron and reflects the reduction of  $\text{Fe}^{3+}$  in pore water systems mobilising adsorbed phosphorus and decreasing adsorption, in effect lowering  $\text{K}^*$ .

Direct measurements of fluxes from sediment cores collected in the field and returned to the laboratory have always yielded very low dissolved phosphorus fluxes (Table 2.2) and these have been both into and out of the sediments.

**Table 2.2**      **The range of DIP fluxes going into (negative) or out (positive) of the sediments measured from cores incubated in the laboratory.**

River	Site	Range of DIP fluxes $\mu\text{mol m}^{-2} \text{ day}^{-1}$
Great Ouse	King's Lynn	200 - -300
	Denver	25 - -290
Nene	Sutton Bridge	0 - -260
	Wisbech	-90 - -400

The fluxes measured at other estuarine and coastal sites were also variable and in some cases the range of fluxes reported for other sites were similar to those reported for the Great Ouse and Nene. Flux rates were lower than those found in the Potomac River estuaries and measurements made in flux chambers ranged from  $-600$  -  $4000 \mu\text{mol m}^{-2}$  (Callender and Hammond, 1982). In the Ems Dollard fluxes were low and sometimes negative apart from in July when they rose to  $1000 \mu\text{mol m}^{-2} \text{ day}^{-1}$ . Intertidal sediments of the Wadden Sea (Raaphorst and Kloosterhuis, 1994) had similar measured fluxes ranging from  $-4.8 \mu\text{mol m}^{-2} \text{ day}^{-1}$  in April to  $106 \mu\text{mol m}^{-2} \text{ day}^{-1}$  in July. Fluxes from sediments from Warnow River (North Germany) under oxygenated conditions varied from  $34$  -  $1030 \mu\text{mol m}^{-2} \text{ day}^{-1}$  (Kleeburg and Schlunbaum, 1993).

Calculation of the diffusive flux of DIP from the pore waters of these sediments compared to the measured flux show the importance on the reactions occurring at the sediment-water interface on controlling sediment-water fluxes of DIP. The flux appears to be a balance of regeneration of organic phosphorus and sorption of phosphorus at the sediment surface. The calculated diffusive fluxes tend to be into the sediments and we believe they demonstrate the critically important role of an oxidised surface layer on these intertidal sediments. Such a layer will cause iron to be reduced and mobilised at depth to re-precipitate and hence to trap phosphorus mobilised at depth along with iron. This process appears to be capable of preventing release of phosphorus almost entirely from intertidal systems. In laboratory simulations we have been able to isolate a core and allow the whole core, including the sediment water interface, to go anoxic and under these conditions there is an increase in phosphorus fluxes out of the sediments (Figure 2.7). There is not a parallel increase in DIP in the pore waters of these cores suggesting that the DIP was released from reduced iron oxides at the sediment-water interface (Figure 2.8).



However, in the relatively coarse sediments with relatively low organic carbon loadings which characterise this area (0.5 - 3 % organic carbon), it takes several days for the rate of oxygen consumption by the sediments to be able to reduce water column oxygen concentrations sufficiently to create conditions appropriate for  $\text{Fe}^{3+}$  reduction in surface sediments. In intertidal systems, and probably all shallow marine areas, tidal activity will mean that isolation of the system will take place only for a few hours at most, and thus the sediments are likely to remain oxygenated at the surface and to retain phosphorus.

### 3. PHOSPHORUS IN THE ESTUARINE ENVIRONMENT

Riverine phosphorus species enter the marine environment through estuaries of one sort or another. In these environments the phosphorus is subjected to an extreme chemical gradient. Freshwater composition is highly variable but on a global average stream waters are about 1mM in ionic strength and dominated by calcium bicarbonate, by contrast seawater has an ionic strength of about 500 mM and is dominated by sodium chloride (Andrews *et al.*, 1995). Mixing of only 1 part of seawater with 99 parts of freshwater results in a solution dominated by sodium chloride and hence the change from a freshwater to a marine chemical environment occurs very early in the mixing process and usually on a time scale of minutes. This extreme change causes a number of related processes to occur that can alter the efficiency of phosphorus transport. The sudden change in ionic strength will cause colloidal species to flocculate (Olsen *et al.*, 1981; Sholkovitz, 1978; Eckert & Sholkovitz, 1976). This will convert any colloidal phosphorus to a particulate form and in addition colloidal iron will precipitate which may have the effect of removing DIP by coprecipitation. In addition colloidal clay material will precipitate, so sediment will be trapped at the freshwater seawater interface. This effect is exacerbated by the sedimentation of suspended material associated with the decline in unidirectional flow on entering the marine environment. Thus particulate phosphorus is likely to be efficiently trapped though it could be subsequently remobilised during storms (Boynton *et al.*, 1995, Fichez *et al.*, 1993, Magnien *et al.*, 1992).

Although unidirectional flow reduces, tidal energy is high in many estuary systems, so the sedimented material is regularly resuspended and moved up and down the estuary by tidal flows. This process creates a region near the head of the estuary known as the turbidity maximum (Postma 1986). In this region suspended solids concentrations can often increase dramatically. For instance in the Great Ouse estuary in south east England, riverine suspended solid concentrations are usually several 10s of  $\text{mg l}^{-1}$  but increase to several 100s  $\text{mg l}^{-1}$  in the turbidity maximum (Fichez *et al.*, 1993). Since DIP is particle reactive, the turbidity maximum offers another site for conversion of dissolved to particulate forms. Thus in the early stages of mixing, conversion of dissolved to particulate phosphorus is anticipated and hence estuaries are a trap for both DIP and particulate phosphorus. Removal in the low-salinity regions is seen in many estuarine systems; for example, The Humber (Prastka & Malcolm, 1994; - Figure 3.1), The Delaware (Lebo, 1991), The Clyde (Mackay & Leatherland, 1976) and the St Lawrence (Lucotte & d'Anglejan, 1988) estuaries. So overall, this implies that estuaries are a long term phosphorus sink.

There are however, further factors operating in the estuarine system which complicate this picture. There is for example evidence of mid-estuarine inputs of DIP through dissolution of calcite mid-estuary and release of carbonate-bound phosphate (De Jonge & Villerius, 1989). However most processes altering DIP concentrations in estuaries have been attributed to sorption and desorption. For example suspended sedimentary material can release phosphorus throughout the mid and high salinity region of estuaries. The extent of this desorption depends on the dissolved phosphate concentration and the mineralogy and past sorption history of the particles. The time in which the particles are in contact with the water and the extent of particle resuspension are also important. It has been argued in some estuaries that after suspended solid concentrations are greater than 100  $\text{mg l}^{-1}$  adsorption becomes independent of suspended load (Fox *et al.*, 1986).

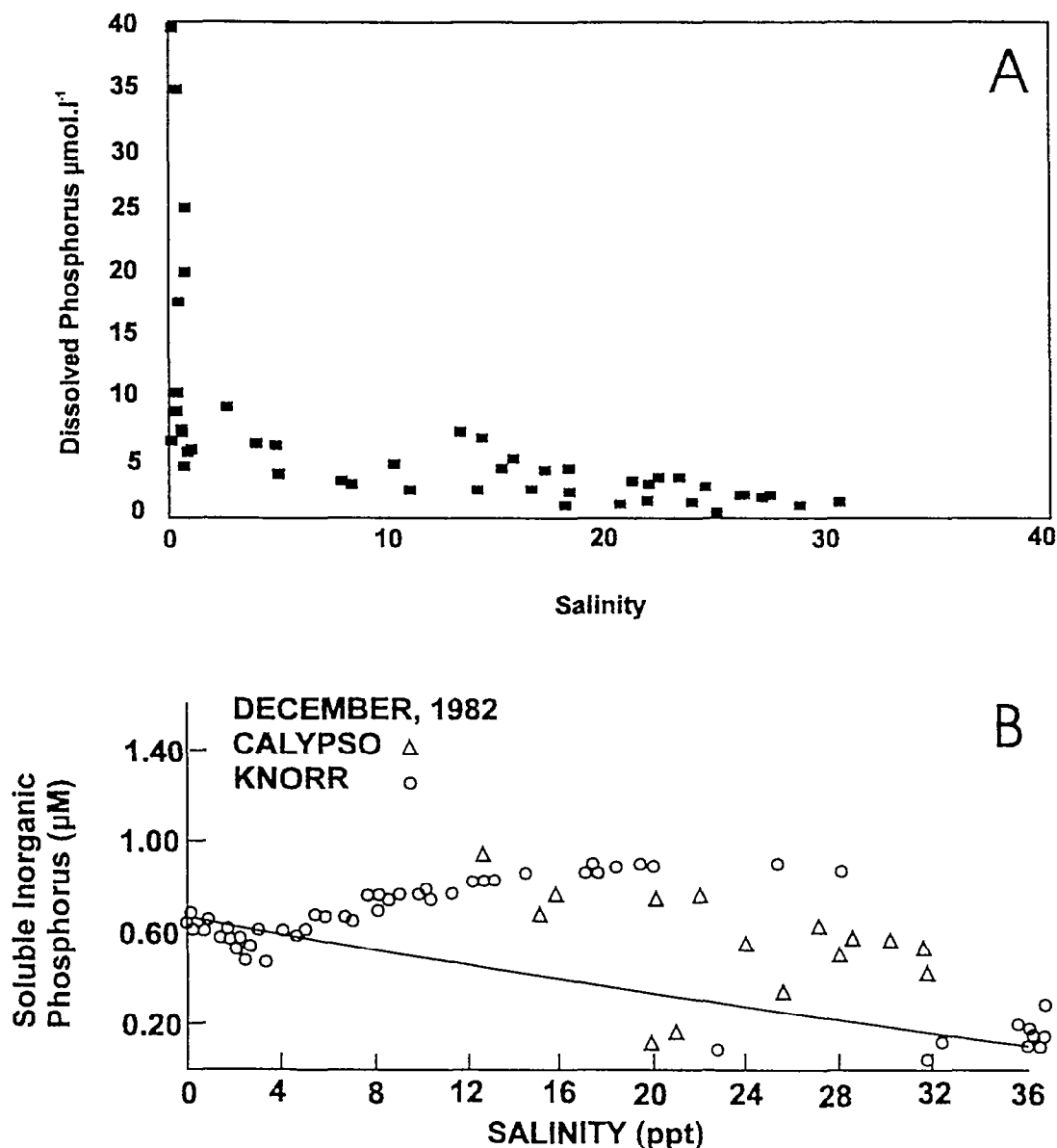


Figure 3.1 DIP as a function of salinity in (A) The Humber estuary, June 1992 (Prastka & Malcolm, 1994) and (B) The Amazon estuary, December 1992.<sup>6</sup>

<sup>6</sup> The straight lines represent the concentration of DIP that would be expected if the DIP in the river water simply mixed with the seawater (conservative mixing). Extrapolation of the linear partition of the mixing relationship at high salinities gives an effective zero salinity end-member. Comparison of this with the observed concentration at zero salinity allows an estimation of estuarine removal (or input). It should be noted that this approach to quantifying estuarine processing can be very sensitive to short term changes in river concentration (Lebo *et al.*, 1994) The DIP concentrations in the Humber shows a negative deviation from the conservative line suggesting that the estuary is a sink for DIP. The Amazon DIP concentrations show a positive deviation suggesting a source of DIP within the estuary from desorption. (Redrawn from Fox *et al.*, 1986).

Seawater DIP concentrations are generally much lower than freshwater concentrations and hence desorption is likely to be favoured. Such release is seen in the Amazon for example and can be rationalised in terms of the measured sedimentary buffering capacity (Froelich, 1988) (Figure 3.1).

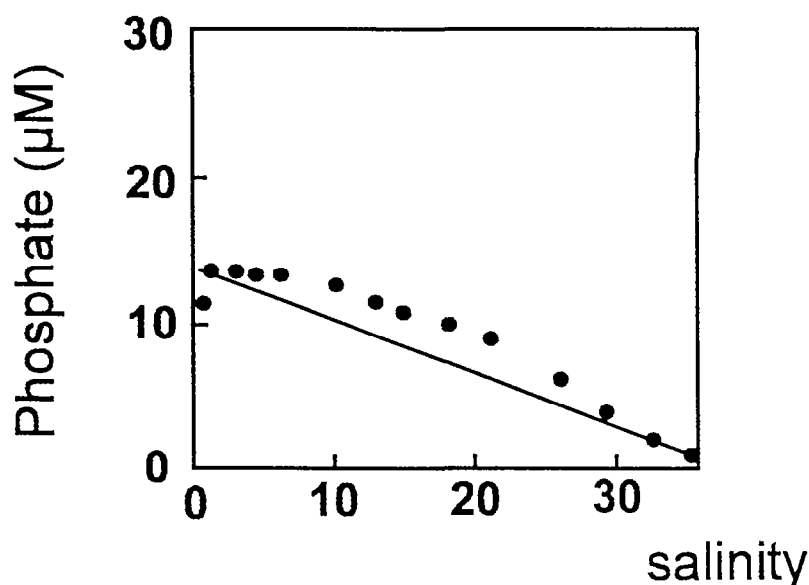
Changes in ionic strength on the mixing of seawater with freshwater within an estuary will also play an important part in the extent of phosphate sorption. As ionic strength increases ions such as sulphate in the seawater will compete with the inorganic phosphorus ions for sorption sites, leading to a decrease in the ability of the particles to sorb DIP. It has even been suggested that this mechanism is one of the reasons phosphorus limitation is rare in marine systems compared to freshwater environments (Caraco *et al.*, 1987, 1990).

To understand the impact of anthropogenic inputs on the phosphorus cycling in estuaries it is necessary to understand processes occurring in relatively pristine estuaries. Unfortunately rather little data exists on phosphorus behaviour in unperturbed systems, since such systems are now few and far between and also situated in remote areas. In the Amazon removal of DIP is seen in the early stages of mixing, followed by a greater amount of release at higher salinities (Froelich, 1988). On this basis Froelich (1988) has suggested that the desorption of particulate phosphorus within the Amazon estuary could increase the flux of DIP from this estuary into the ocean by 50 %. Froelich (1988) also, based on the rather limited available data, concluded that desorption and resuspension processes in these estuaries “buffer” DIP at about 2  $\mu\text{M}$ . Human intervention in the phosphorus cycle can alter this picture considerably. In many fluvial systems today, as a result of human impact, DIP concentrations are much higher and this buffer systems is either overwhelmed or shifted to higher steady-state DIP concentrations (see Section 2). Under these conditions, adsorption will be favoured and desorption discouraged. Thus in the Chesapeake and Delaware estuary systems on the east coast of the USA 50-70% of DIP inputs are retained within the estuary (Boynton *et al.*, 1995). In the Humber, similar proportions of removal have been reported (Sanders *et al.* .. in prep.) though this estuary is particularly complex and removal in one of the two tributaries is higher than this (Sanders *et al.*, in prep). Similar large scale low salinity DIP removal is evident in the Forth estuary in Scotland though in other less contaminated Scottish estuaries, desorption and buffering are evident (Balls, 1992 & 1994). Balls (1994) notes 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 hence removed from exchange with the water column. Thus there is also the 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, 1994). Such a large scale process therefore has a major impact on global phosphorus budgets.

One effect of increased DIP concentrations in rivers may be to push estuaries from being inefficient phosphorus sinks as is currently the case for pristine systems, toward being major sinks (Billen *et al.*, 1991). An important question then arises of whether this represents a stable long term sink, hence implying a negative feedback on human perturbations of the system or whether the stored phosphorus can be re-released, “chemical bombs” in the terminology of Liss *et al.*, (1991).

Balls (1992) work on the Forth estuary illustrates a major complication involved in assessing the behaviour of phosphorus in any industrialised estuary, inputs within the estuary itself. Estuaries often offer protection from the open sea and hence have been the site of port developments. These coupled to the areas being foci for transport routes via the lowest bridging points on the rivers has lead to many of the world's estuaries being the centres of population, e.g. London, New York, Hamburg. The discharges from these centres were historically discharged directly to the estuary. Nowadays they may be routed via sewage works but these still represent point source discharges of phosphorus and other contaminants. The use of property salinity plots (Sanders *et al.*, in prep.) in such circumstances is problematic and must be augmented by other mass balance modelling approaches. The discharge of sewage effluents has lead to low oxygen conditions in many estuaries, though the details vary depending on the discharge, river flow and estuarine residence time. Improvements in sewage treatment has lead to improvements in estuarine oxygen regimes in some systems (Jickells *et al.*, 1990) but problems persist in many estuaries. These problems can be exacerbated by the decomposition of organic matter introduced from the river either as a result of algal blooms in the river system or from the direct discharge of effluents into the river. The relatively long residence times of water in estuaries as a result of tidal flows and possibly density stratification (Bowden, 1980) make the development of low oxygen conditions in the water column, and more particularly in the sediments of estuaries an important issue.

The development of low concentrations of oxygen at the sediment-water interface are of vital importance in determining the release of DIP from sediments to the overlying water. In all sediments, the decomposition of organic matter will consume oxygen and at some depth in the sediments, this will lead to low oxygen conditions since oxygen diffusion into sediments is usually slow compared to the rate of oxygen consumption. At a certain depth  $\text{Fe}^{3+}$  will then be utilised by the microbes as an oxidising agent and phosphorus will be released into the sediment pore water. Whether this DIP escapes to the overlying water column is an important concern and depends on a number of factors. If the anoxia occurs at the sediment surface there is no barrier to diffusion of DIP into the overlying water. If there is an oxic layer, this can limit diffusion of DIP by reoxidising  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  and coprecipitation of the DIP. Active processes such as bioturbation and/or tidal pumping can increase the rate of diffusion of DIP. This will also however increase the amount of oxygen in the sediments leading to a thicker oxic zone. So the rate of transport of the DIP ions from the pore waters 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 (Prastka, 1996; Klump and Martens, 1981). In most intertidal systems and probably other near shore environments an oxic surface layer probably prevents release of large amounts of DIP (Prastka and Jickells, *in press*). (Krom and Berner, 1980). Some estuaries however do show possible fluxes of DIP from the sediments due to low oxygen conditions. These are the Scheldte estuary (Zwolsman, 1994, Figure 3.2), the Humber (Prastka and Malcolm, 1994) and Narragansett Bay (Pilson, 1985, Boynton *et al.*, 1980).



**Figure 3.2** DIP as a function of salinity in the Scheldte showing evidence of addition of DIP into the water column from the sediments in the upper reaches of the estuary.<sup>7</sup>

In most estuarine systems, primary productivity is limited by light availability due to the high turbidity. Algal blooms can occur and significantly affect the behaviour of phosphorus and other nutrients. These blooms may occur at low salinities if the light regime is appropriate (Fichez *et al.*, 1992; Monbet, 1992) but are more often restricted to higher salinities where suspended solids concentrations decrease due to sedimentation, though this does depend greatly on the tidal regime with micro-tidal estuaries being able to sustain high phytoplankton biomass due to lower turbidity (Monbet, 1992). In these situations there will be relatively high nutrient concentrations and hence large scale blooms can occur which can in turn consume large amounts of nutrients, though much of this may be recycled (e.g. Lebo and Sharp, 1992). As the DIP concentration falls as a result of phytoplankton uptake, desorption of phosphorus from sediments will occur, though this released phosphorus may be taken up immediately by phytoplankton. A similar picture is seen in the offshore plume region of estuaries with productivity increasing as turbidity decreases, release of particulate phosphorus into the dissolved phase (Morris *et al.*, 1995) and intense regeneration of biologically fixed phosphorus. Hence despite high productivity the Amazon plume, for example, is not an efficient nutrient trap (Demaster and Pope, 1996), though overall coastal waters sediments are an important global nutrient sink (Walsh, 1991; Jickells *et al.*, 1991). In addition within the plume region, the supply of nutrients from coastal and offshore waters become important to the overall productivity (Morris *et al.*, 1995, Demaster and Pope, 1996). Although low in nutrients, the large fluxes of such waters into the plume zone make such inputs important.

The sedimenting particulate organic phosphorus will be decomposed on or within the underlying sediments. The DIP subsequently mobilised is often readsorbed to various degrees.

<sup>7</sup> (Redrawn from Zwolsman, 1993).



A number of studies suggest about 30 % of sedimenting particulate organic phosphorus is retained in sediments but the fraction may be higher in rapidly sedimenting areas. The retention of phosphorus during this process may be greater than that of carbon as a result of the reactions of phosphorus with iron and formation of apatite. In the Chesapeake Bay system net retention is estimated to be greater than 100 % of terrestrial inputs as the result of efficient removal of particulate and dissolved phosphorus by chemical, physical and biological processes plus net import of particulate matter (Boynton *et al.*, 1995). These authors argue that the percentage of phosphorus retained with an estuary depends critically on the retention of particulate matter (which is controlled by the geomorphology of the system) rather than phosphorus loading.

Moving offshore from the estuarine zone, the cycling of phosphorus becomes more and more dominated by cycling associated with phytoplankton activity and less influenced by exchange with both suspended and bottom sediments as water depths increase and turbidity decreases (e.g. Jickells *et al.*, 1986). In temperate regions this results in strong seasonality in dissolved phosphorus concentrations in coastal waters (Brockman *et al.*, 1988, Howarth *et al.*, 1995), while in tropical regions where conditions favour all primary productivity throughout the year concentrations remain low (e.g. Jickells *et al.*, 1986). Phosphorus cycling in oceanic waters is almost entirely dominated by internal cycling processes with an oceanic residence time of about 100,000 years, of which only a few years are spent in the surface waters (Broecker and Peng, 1982).

In addition to riverine inputs of freshwater to coastal areas, groundwater discharges are thought to be an important source of freshwater. The magnitude of such fluxes, unfortunately is not known. They have however, been shown to be of particular importance in tropical island ecosystems (D'Elia and Jickells *et al.*, 1986). Such groundwater inputs are also subject non-conservative mixing processes which may take place within the pore waters of the aquifer or as the water issues into the marine system. Groundwater systems are characterised by the interaction of water with a very large solid surface area which will act to promote DIP removal via sorption, or in the case of limestone areas by the precipitation of calcium phosphates.

Phosphorus is involved in a vast complex global cycle dominated by a large particulate phosphorus reservoir (Mackenzie *et al.*, 1991). The amounts of phosphorus involved in the vast nutrient cycle in oceanic waters means that the increased phosphorus fluxes through coastal waters will have very little impact on deep ocean DIP concentrations, as is also the case for nitrogen (Andrews *et al.*, 1996). However the situation is different in coastal areas. Impacts in coastal waters are clearly seen as a result of increasing fluxes of nutrients (Nixon, 1995, Turner and Rabalais, 1994, Reid *et al.*, 1990). Since nitrate/DIP levels in contaminated rivers are substantially above that required by phytoplankton and estuarine DIP removal further enhances this nutrient imbalance, attention in investigations of coastal eutrophication problems has focused particularly on the role of nitrogen which is generally considered the limiting nutrient for marine systems. However, the massive enrichments of nutrients may be altering this. Perturbations in dissolved N/P ratios have been implicated in the formation of nuisance algal blooms (Riegman *et al.*, 1992, Justic *et al.*, 1995) and therefore perturbations of the phosphorus cycles are of considerable concern.

## 4. CONCLUSIONS

Our studies have demonstrated that passive diffusion studies such as conventionally used in studies of fluxes from sediments, may not adequately mimic the environmental situation in intertidal systems since the regular tidal excursions can actively force exchange of overlying and pore waters at rates that could be 10 times those predicted from molecular diffusion. In the case of phosphorus, this active “tidal pumping” probably acts to increase the rates of diffusion of oxygen into the sediments and thus acts to retain phosphorus within the sediments rather than promote its release.

Thus it seems likely that diagenetic processes within sediments can act to redistribute phosphorus within sediments but do not result in fluxes of DIP into the water column. If sedimentary phosphorus is re-suspended and transported to an area of low DIP, desorption will occur, resulting in a potentially large source of DIP to the water column. In the U.K. most estuaries are effective traps and hence this particulate export process may not represent an important source of DIP to coastal waters. However, in some estuaries such as the Great Ouse there is evidence that winter storm flows may flush particulate matter out of the estuary.

### The JoNuS Programme Outputs

The main benefit of this joint collaboration was the access to the very large data set and wide range of skills of the entire Programme. Although the principal outputs of the JoNuS Programme were not identified as part of the R&D Project, they are accessible to the Agency as a collaborator. These include:

- a FoxPro database of Humber, Wash and related coastal data over 3 years, using a purpose designed graphical interface;
- scientific collaboration of a high order, leading to the development of good sampling protocols and analytical techniques within Anglian Region;
- interim reports identifying the elements of the project and progress;
- a glossy brochure describing the purpose and outcome of the Project. The Agency (as NRA) is listed as one of the 3 sponsors; however its financial contribution was only about 5% of the total;
- ultimately there will be a final report; the completion of which is outside the Agency's influence;
- at least 3 publications in the scientific press.

## 5. RECOMMENDATIONS

This work documents and quantifies the processes regulating phosphorus in the Wash systems and provides evidence that the results are likely to be widely applicable. Two findings from the work raise larger questions that require further study.

The first issue arises from the evidence of efficient storage of DIP by adsorption to sediments at high sediment and DIP concentration. This result leads to questions about the long term stability of this adsorbed phosphorus. The data presented suggest that release to the overlying waters as a result of iron reduction is only likely to be an issue if the whole sediment and overlying waters become devoid of oxygen. However, if the sediments are resuspended and transported to a region of lower ambient DIP concentration, the adsorption will reverse with resultant release of DIP to the waters. Transport of sediments from an estuary as a result of winter storms, dredging or other processes might create this situation, though the associated release of DIP may be masked by phytoplankton uptake in the estuarine plume.

It should be possible to build on the results of this study to model the DIP release that might result, but such an exercise would need to be coupled to an estuarine sediment storage model.

The second issue arises from the evidence presented that tidal pumping of sediments can greatly increase sediment water exchange over that predicted based on laboratory studies using static exchange. If this effect is widespread for intertidal sediments it will have important implications for the exchange of a range of contaminants between sediments and the overlying water column. The study of such phenomena will require some innovative new techniques, probably working in difficult field environments.

### The JoNuS Programme

The following recommendations, taken from the 1993 North Sea Quality Status Report, are also a statement of the JoNuS approach:

“Reliable data on eutrophication are still required. They should include phytoplankton time-series in the open sea to supplement land-based surveys and a better quantification of nutrient budgets and production, recycling and circulation processes. Research should be intensified in order to improve risk assessment capability.

In future, assessments for estuaries which take into account local dynamics and fluxes should be used to provide calculated input budgets to the North Sea that can serve as a basis for control policies”.

Following the successful conclusion of JoNuS (phase I) this approach is further recommended for future studies involved with establishing the nutrient status of coastal waters.

Additionally, the other research recommendations of the North Sea QSR, viz:

“Further studies are also needed on plankton to determine any shift in species composition in the plankton community and at other trophic levels. The contribution of atmospheric inputs of nitrogen should also be investigated in greater detail with a view to identifying possible options for further reductions”.

are also supported by the outcome of the JoNuS Programme.

The JoNuS Programme Brochure makes recommendations for a Phase II of JoNuS covering the Thames Estuary and Irish Sea. The Environment Agency has been approached with a view to joint participation.

The final report on the original JoNuS Programme has still to be issued by MAFF, at a date to be determined by them. DoE are happy with the final result and have already commenced funding for parts of Phase II of JoNuS (from April, 1996).

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