Maritime Ireland / Wales
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The Fate of Nutrients in Estuarine Plumes

January 2000

R.Raine and P.J. LeB Williams.

Martin Ryan Institute, National University of Ireland, Galway.
School of Ocean Sciences, University of Wales, Bangor.

Martin Ryan Marine Science Institute
National University of Ireland, Galway
Galway, Ireland

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Measure 1.3: Protection of the Marine and Coastal Environment and Marine Emergency Planning

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Maritime (Ireland / Wales) INTERREG Programme- Building Bridges.

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The Fate of Nutrients in Estuarine Plumes

R. Raine[1] and P. J. leB. Williams[2].

[1]Martin Ryan Institute, National University of Ireland, Galway.
[2]School of Ocean Sciences, University of Wales, Bangor.

Maritime Ireland / Wales INTERREG Report No. 1

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Maritime (Ireland/Wales) INTERREG Programme (1994 – 1999)

The EU Maritime (Ireland / Wales) INTERREG II Programme (1994 - 1999) was established to:

1. promote the creation and development of networks of co-operation across the common maritime border.
2. assist the eligible border region of Wales and Ireland to overcome development problems which arise from its relative isolation within the European Union.

These aims are to be achieved through the upgrading of major transport and other economic linkages in a way that will benefit the constituent populations and in a manner compatible with the protection and sustainability of the environment. The Maritime INTERREG area includes the coastlines of counties Meath, Dublin, Wicklow, Wexford and Waterford on the Irish side and Gwynedd, Ceredigion, Pembrokeshire and Carmarthenshire on the Welsh side and sea area in between.

In order to achieve its strategic objectives the programme is divided into two Areas:

Sub-Programme 1: **Maritime Development:** transport, environment and related infrastructure (59 mEuro)

Sub-Programme 2: **General Economic Development:** Economic growth, tourism, culture, human resource development (24.9 mEuro)

The Marine and Coastal Environment Protection and Marine Emergency Planning Measure (1.3) has a total budget of 5.33 mEuro of which 3.395 mEuro is provided under the European Development Fund. EU aid rates are 75% (Ireland) and 50% (Wales).

The specific aims of Sub-Programme 1.3 are:

- to promote the transfer of information between the designated areas.
- to establish an in-depth profile of marine/coastal areas for conservation of habitat/species.
- to explore, survey, investigate, chart the marine resource to provide a management framework.
- to develop an integrated coastal zone management system.
- to improve marine environmental contacts and co-operation.
- to promote the sustainable development of the region.
- to improve nature conservation.

Joint Working Group

The Joint Working Group, established to oversee the implementation of Measure, consists of 5 Irish and 5 Welsh representatives.

Irish representation: Department of the Marine & Natural Resources, Department of the Environment & Local Government, Department of Transport, Energy & Communications, Local Authority and Marine Institute.

Welsh representation: National Assembly for Wales, Countryside Council for Wales, National Trust, Local Authority (Dyfed), Local Authority (Gwynedd).

This Report series is designed to provide information on the results of projects funded under Measure 1.3 Protection of the Marine & Coastal Environment and Marine Emergency Planning.

CONTENTS

ABSTRACT

Estuaries are highly biologically active zones lying between freshwater and marine systems. The classical view is that materials such as nitrates and phosphates which run into rivers as a result of man's activity are used by the planktonic algae, or phytoplankton, for growth – in some cases causing nuisance blooms of these organisms. The management of the reduction of these blooms is based on the classical assumption that the materials stimulating them are brought into the estuary by the river, and that effective control of the blooms can be achieved by setting limits on the initial discharge of these materials into rivers.

Funded under the EU INTERREG II (Ireland-Wales) programme, two groups of marine scientists from the University of Wales, Bangor and the National University of Ireland, Galway made a co-operative study of the Waterford (Ireland) and Conwy (Wales) estuaries. It was found that whereas the source of nitrogen for the estuarine phytoplankton was from the rivers, the main source of phosphate was from the sea. Phytoplankton blooms were being encouraged within the plume zone near the mouth of the estuaries, a region poised between a nitrate-rich freshwater and, relatively, phosphate-rich seawater.

The management consequences of the findings are profound. Phosphates contribute significantly to the pollution of rivers and lakes, systems where there is usually an abundance of nitrogen and algal growth is governed by the availability of phosphorus. Management of these freshwater systems is thus achieved through control of the input of phosphates. Results achieved during the present study show that this criterion does not apply to estuaries and estuarine blooms, as material (phosphate) supporting them comes from the seawater end of the system and is therefore obviously unmanageable. The requirement to control nitrogen (nitrate) levels in estuaries is therefore all the more important in order to properly manage phytoplankton blooms, and thus water quality, in estuaries.

EXECUTIVE SUMMARY

The flux of nutrients (nitrates, phosphates and silicates) through two estuaries in the INTERREG area, Waterford Harbour and the Conwy estuary, were studied over a seasonal cycle during 1997. Teams from the University of Wales, Bangor, the National University of Ireland, Galway, the Environment Agency (Warrington, UK) and the Environment Protection Agency (Kilkenny Laboratory) measured the distribution of nutrients, plant pigments (chlorophyll a) and phytoplankton along each estuary in April/May, July and October 1997. The results were supplemented by process rate measurements of primary production (light and dark bottle oxygen flux and 13CO2 uptake) and nutrient uptake (15NO3).

The results showed that whereas silicate and nitrate behaved essentially conservatively along both estuaries, anomalous distributions of phosphate were observed within the plume zone of Waterford Harbour and up-estuary of the plume in the Conwy estuary. These regions were also sites of enhanced levels of chlorophyll (and phytoplankton) and elevated rates of primary production and uptake. These blooms of phytoplankton separated a nitrate-rich environment on the freshwater side from a phosphate-rich seawater side. It was concluded from the data that in order to optimise their growth, phytoplankton were acting as a pump drawing phosphate from seawater into the estuary over the productive summer months.

Classically the management of the quality of freshwater systems is thought to rely on the levels and throughput of phosphorus. Nitrogen (as nitrate), on the other hand, is seldom regarded as a significant factor in controlling freshwater ecosystems or their trophic status. The results presented here show that estuarine phytoplankton blooms optimise the supply of nitrogen from freshwater run-off and the supply of phosphorus, as phosphate, from the sea. The maintenance of estuaries as a resource, from an economic or amenity aspect, or both, may therefore be significantly affected by nitrogen inputs from freshwater. Management systems must not therefore solely rely on phosphorus budgets in order to maintain water quality, as has often been the case.

1. INTRODUCTION

INTERREG II has as its primary objective :

> *"To promote the creation and development of networks of co-operation across the common maritime border and, where appropriate, extend these links to other European Countries."*

In the context of Measure 1.3 Protection of the Marine and Coastal Environment, INTERREG seeks to improve marine environmental contacts and promote the transfer of information in order to improve environmental management within the designated area.

Estuaries are systems at the interface between freshwater and marine environments. It is through estuaries that nutrients such as nitrogen and phosphorus are discharged from the terrestrial and freshwater systems into the sea. As the supply of nutrients exerts a significant and far-reaching influence on the biology of marine ecosystems, the fate of these elements as they pass through the estuarine system has a major bearing on the biology of inshore waters. As a by-product of the Natural Environment Research Council (UK) North Sea Programme, there have been major advances in our understanding of that system. By comparison, the final report of the Irish Sea Science Co-ordination Committee (Boelens, 1995) drew attention to the need to quantify the nutrient input through rivers in the area surrounding the Irish Sea. It noted a number of factors which had hampered progress in improving surveillance of environmental conditions in the Irish Sea which included : -

- *an emphasis on area-based monitoring with too little attention to natural features and processes;*
- *the absence of a bi-lateral programme, with common objectives and approaches, to integrate research and monitoring throughout the Irish Sea;*
- *disparities between Ireland and the UK with respect to the ranges of expertise available, and capacities, for marine science; and*
- *slow progress in defining measurable indicators of environmental quality*.

Boelens (1995) concluded that

"Many of these problems could be resolved through closer collaboration between Irish and UK scientists and agencies within the framework of a sharply focused, inter-disciplinary and basin-wide programme."

and that

With regard to the scientific elements of the programme, the report proposes stud ies that will provide more complete descriptions of the biological components of Irish Sea ecosystems and a better understanding of the processes and conditions which sustain them.

Work recently carried out under the 'JONUS' programme (a 4-year study of nutrients in estuaries on the eastern seaboard of the UK, funded by Ministry for Agriculture Fisheries and Food, the Department of the Environment, Transport and Regions, and the Environment Agency) identified the estuarine plume zone as an important site which influences the transfer of nutrients from rivers and estuaries to coastal seas (Morris et al., 1995). Of particular importance was the finding that, in summer, phytoplankton dynamics resulted in import of nutrients from the coastal zone into the plume of the Humber estuary, whereas in the winter months nutrients were transported passively into the North Sea.

Given the need identified by Boelens (1995) to accurately quantify the transport of nutrients from estuaries into the sea in order to improve the management of coastal waters, this project set out to test the hypothesis of Morris et al. (1995) that transfer of nutrients through estuaries is not always seaward. The role of phytoplankton in modifying and influencing this process was studied by making direct measurements of the rates of phytoplankton processes in estuarine plume zones in two case studies within the INTERREG area.

2. OBJECTIVES OF THE STUDY

The overall objective was to investigate the influence of coastal marine plankton on the flow of nutrients from estuaries into the sea by examining the seasonal dynamics between dissolved nutrients and the plankton within estuarine plume zones. Results from the study would :

(i) Investigate the hypothesis of Morris et al. (1995) that the transfer of nutrients is not always seaward.

(ii) Facilitate the construction of realistic budgets for the throughput of principal nutrient species (N, P, Si) through major Irish Sea estuaries.

(iii) In the light of findings, provide guidelines for nutrient management of coastal and estuarine areas.

3. THE PARTNERSHIP

The two lead institutes, the University of Wales, Bangor (UWB) and the National University of Ireland, Galway (NUIG), had a wide range of complimentary skills and facilities in place at the start of the programme. These were extended by the programme through the transfer of skills (Section 5.1). Value was added through the provision of shiptime, aerial and ground-based surveys by the UK Environment Agency, the Environment Protection Agency (Ireland) and the Marine Institute, Dublin. Facilities and analytical procedures contributed by each project partner are outlined in the Table 1.

Table 1. Facilities and Analysis Contributions from Project Partners.

Facility/Technology	**Provider** [1]
Autoanalyser Nutrient Analysis	EA
Continuous Chlorophyll Analysis	EA
Data logging	EA
Continuous Temp/Sal/O_2 Analysis	EA
Aerial Survey (Conwy)	EA
River surveys (Wales)	EA
Ship & Crew Provision (UK)	EA
Ship & Crew Provision (Ireland)	MI
River surveys (Ireland)	EPA
Low Level Nutrient Analysis	NUIG
Precision Salinity	NUIG
Chlorophyll by Extraction	NUIG
Plankton Analysis	NUIG
Suspended Matter	NUIG
High Precision Oxygen Analysis	UWB
^{13}C Productivity Analysis	UWB
^{15}N Nitrogen Analysis	UWB
Data Base & Assimilation	UWB
Particulate Organic Carbon/ Particulate Organic Nitrogen Analyses	UWB

The value of the contributions by the three statutory agencies (EA, EPA, MI) to the work cannot be overstated, as without them the study would not have been possible.

[1] see Appendix 1 for explanation of abbreviations

4. THE APPROACH

Boelens (1995) gave specific attention to topic 3.1(i) for the Irish Sea: -

> *'Construct realistic budgets for the throughput of principal nutrient species (N, P, Si) through major Irish Sea estuaries.'*

We noted the directives he gave for research involving estuarine nutrient fluxes:-

> *It is proposed that this study should apply the techniques developed under the UK's 'JONUS Programme' - a 4-year study of nutrients in estuaries on the eastern seaboard of the UK. These techniques have been successfully applied in estimating nutrient fluxes for estuaries with very different geo-chemical characteristics.*
>
> *Scientists with experience of the JONUS Programme will provide necessary guidance and supervision at all stages of the study. The work on Irish estuaries will require collaboration between Irish and UK laboratories.*

Given these requirements, we adopted the following approach.

4.1. MANAGEMENT OF THE PROGRAMME

A Steering Committee was established to oversee the programme. Its main responsibility was the establishment of linkages, and, through these, the dissemination of technologies and information. The Steering Committee comprised representatives from the Marine Institute, Welsh office, the JONUS programme and local environmental organisations in addition to a representative from each project partner (Table 2).

Meetings of the Steering Committee were held at the early and latter stages of the project, a series of planning and revue meetings were held by the experimenters during the course of the project.

A one-day presentation of the outcomes of the project was held at the Environment Agency in Bangor, Wales on 29th October 1997. In addition, a number of meetings between project participants took place. The dates and nature of these meetings, including participants, held during the programme are given in Table 3 below.

Table 2. The Steering Committee

Name	Affiliation
Dr. R. Fisher	Environment Agency, Bangor.
Dr. T. Jickells	University of East Anglia. JONUS programme
Dr. P. Jones	Environment Agency, Warrington
Dr. T. McMahon	Marine Institute, Fisheries Research Centre, Dublin.
Dr. S. Malcolm	CEFAS, Lowestoft. JONUS programme
Mr. M. Neill	EPA, Kilkenny Laboratory.
Mr. G. O'Sullivan	Marine Institute, Dublin
Dr. J. Patching	National University of Ireland, Galway
Dr. H. Prosser	Welsh Office, Cardiff
Dr. R. Raine	National University of Ireland, Galway
Mr. I. Thomas (later Dr. R. Stonehewer)	Environment Agency, Bangor
Prof. P. Williams	University of Wales, Bangor.

Table 3. Meetings held during the Project

Date	Location	Nature of Meeting	Present
23-Feb-97	Bangor	General Planning meeting	NUIG/UWB
24-Feb-97	Bangor	Meeting with Welsh Office/EA	EA/WO/EPA/NUIG/UWB
10-Mar-97	Bangor	Steering Committee & Fieldwork Planning Meeting	EA/EPA/NUIG/UWB/SSC
12-May-97	Bangor	Review of Waterford Fieldwork	NUIG/UWB
20-Oct-97	Bangor	Review of Spring & Summer Fieldwork	NUIG/UWB
28-Oct-97	Bangor	Review of Overall Results	NUIG/UWB
29-Oct-97	Bangor	INTERREG Workshop	EA/EPA/NUIG/UWB
26/7-Jan-98	Bangor	Review of Results & Consideration of Implications/ Publication	NUIG/UWB
08-May-98	Dublin	Steering Committee Meeting	EA/EPA/NUIG/UWB/WO/SSC

4.2. METHODOLOGY

The Waterford and the Conwy estuaries were chosen as fieldwork sites (Figures 1, 2), as their proximity and scale meant that the objectives could be achieved within the time and financial constraints of the project. In addition, these two estuaries complement studies carried out under the JONUS programme, such as those involving the Humber and Wash, as their nutrient regimes broaden the overall range (Table 4), thereby strengthening general conclusions achieved on nutrient transport and fate.

Table 4. Comparison of nutrient levels in selected estuaries.

Estuary	Freshwater end-member concentration range		Reference
	Nitrate (µM)	Phosphate (µM)	
Humber	600-900	20-100	Sanders *et al.*, 1997
Wash	200-750	15-30	Fichez et *al.*, 1992
Waterford	100-250	1-2	Current study
Conwy	40-80	0.5-1.5	Current study

The sampling programme consisted of rate measurements underpinned by conventional determination of nutrient and plant pigment distributions. The rate measurements (see below) were those that had been developed and evolved within the group at UWB prior to the current study. These techniques have been and are widely used by programmes such as the UK JONUS programme, thus ensuring compatibility. On-line nutrient analyses were supplemented by discrete sample analysis at NUIG, where phytoplankton species and plant pigments (chlorophyll a and phaeopigments) were also determined. Details of these analyses can be found in Table 6.

The two estuaries were the subject of three intensive studies made over a 13-month period (Table 5).

Table 5. Field Survey Dates

Date	**Location**	**Participant**
19-22 April 1997	Waterford	EPA/NUIG/UWB/MI
12-6 May 1997	Conwy	EA/NUIG/UWB
7-11 July 1997	Waterford	EPA/NUIG/UWB
21-24 July 1997	Conwy	EA/NUIG/UWB
7-10 Oct 1997	Waterford	EPA/NUIG/UWB/MI
21-24 Oct 1997	Conwy	EA/NUIG/UWB

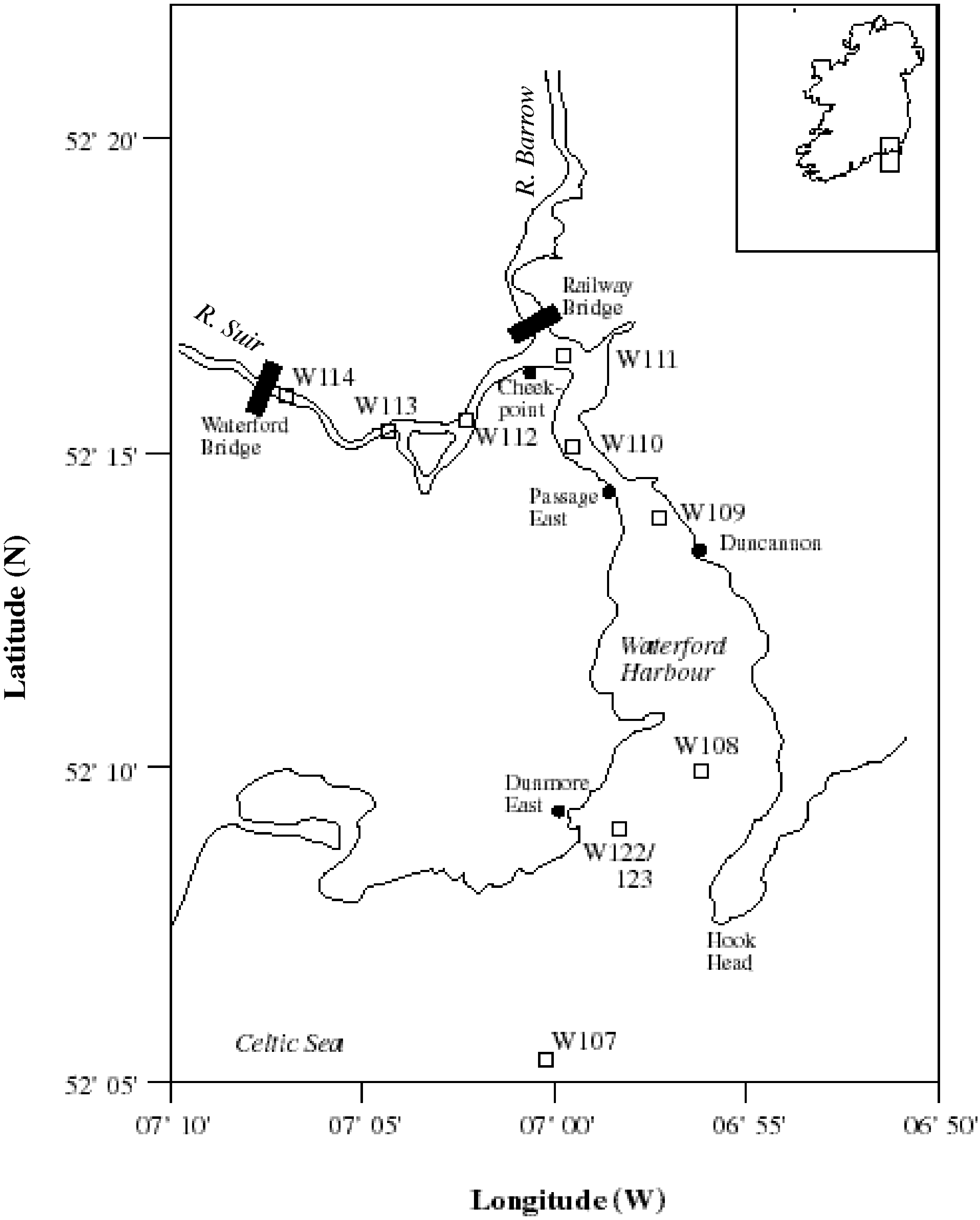

Figure 1. Map of Waterford Harbour showing locations referred to in the text and sampling positions (open squares).

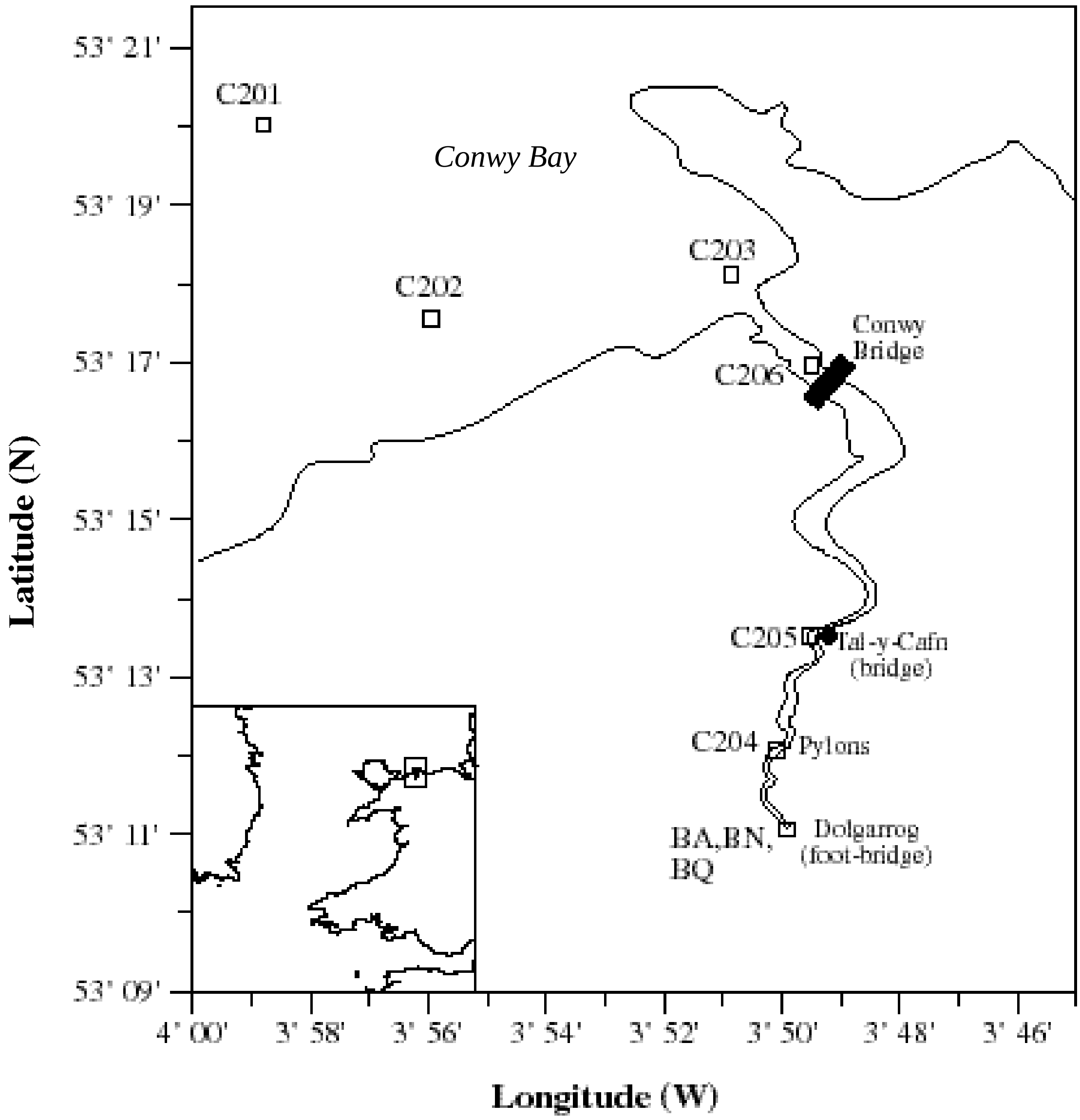

Figure 2. Map of the Conwy estuary, Wales, showing locations referred to in the text and sampling positions (open squares).

Table 6. Methodologies used during the study [2].

Property	Nature of Sampling[3]	Method	Reference
Rate Variables			
Gross and Net Production; Respiration	S	Light & Dark O_2 Flux/ $^{13}CO_2$ Uptake	Jenkinson & Williams, 1982; Blight *et al*., 1995
Nitrate assimilation	S	$^{15}NO_3$ Uptake	Dugdale & Goering, 1967.
State Variables			
Nitrate	SUT	Colorimetry	Grasshoff, 1976
Nitrite	SUT	Colorimetry	Grasshoff, 1976
Phosphate	SUT	Colorimetry	Grasshoff, 1976
Silicate	SUT	Colorimetry	Grasshoff, 1976
Chlorophyll a	SUT	Fluorometry	Tett, 1987
Plant Phaeopigment	SUT	Fluorometry	Tett, 1987
Particulate Organic Carbon (POC)	S	CN Analyser	Blight *et al*., 1995
Particulate Organic Nitrogen (PON)	S	CN Analyser	Blight *et al*., 1995
Phytoplankton	S	Inverted Microscopy	Hassle, 1978
Suspended Matter	ST	Gravimetry	Strickland & Parsons, 1972
Temperature	SUT	Thermistor; Thermometers	
Salinity	SUT	Inductively Coupled Salinometer	
Irradiance	S	Secchi Disc	

[2] Authors'note: In the case of the Conwy estuary, samples were taken as a precautionary measure against possible effects of enhanced copper levels. In the event, no anomalous features arose from the biological rate determinations that could be attributed to copper toxicity.

[3] S = Station measurements
U = Underway measurements
T = Measurements made over a tidal cycle

The overall fieldwork strategy is shown in Figure 3. This involved sampling a number of stations along the estuaries and in the estuarine plume zone for biological rate determinations (see e.g. Figure 1). At these stations, as well as along the cruise tracks, samples were taken for measurement of nutrients and plant pigment concentrations as well as phytoplankton species composition. The ship's track was designed to delineate features such as the plume zone and regions of maximum plant pigment concentrations. In addition to shipboard sampling, selected sites were sampled from the shore over a tidal cycle.

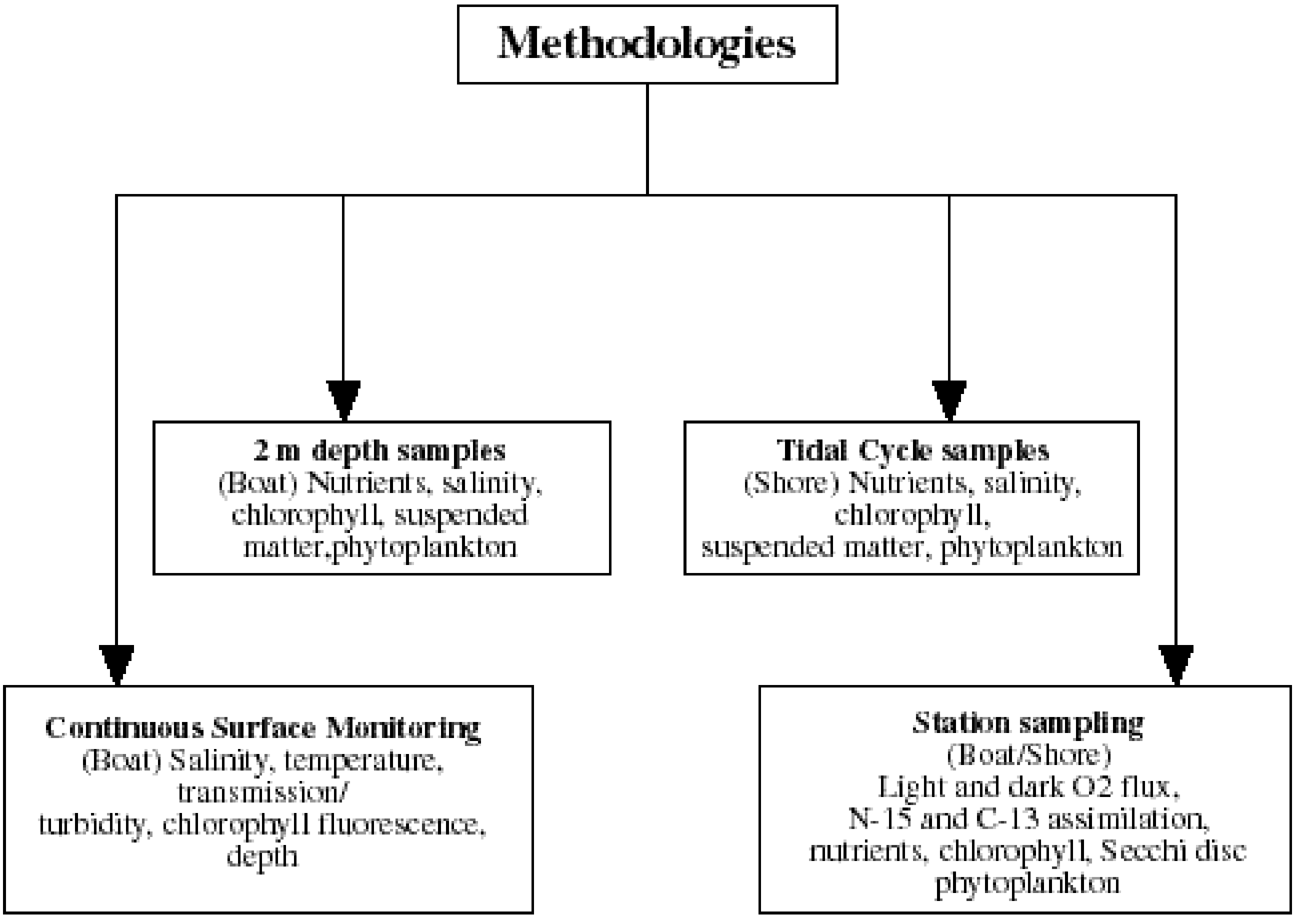

Figure 3. Outline of sampling procedures during fieldwork exercises.

5. OUTCOMES

5.1. TECHNOLOGY EXCHANGE, SHARING & TRAINING

Transfer of technologies between the participating institutes took place through the training of a NUIG researcher in the use of the techniques of high precision dissolved oxygen titrations and stable isotope analysis (^{13}C and ^{15}N) by mass spectrometry. Dr. B. Joyce from Galway was trained in all of these techniques, which were essential for biological process rate determinations, between 2-17th March 1997. In addition, all of the technological requirements for using high precision oxygen determinations was given to NUI, Galway by Prof. P. Williams.

5.2. SCIENTIFIC RESULTS

5.2.1. Distribution of properties

Longitudinal and horizontal salinity distributions

Both Waterford and Conwy estuaries are well-mixed estuaries. Salinity stratification in Waterford Harbour is absent with the exception of each extremity of the estuary where surface salinity values were either very low (<5) or high (>30; Figure 4). The plume zone for this estuary lies in the region between Dunmore East and Hook Head, where surface salinity values are in the range 30-34. Of significance for the phytoplankton is that the plume zone is a stratified region, which assists in keeping them suspended in the light-rich surface layers.

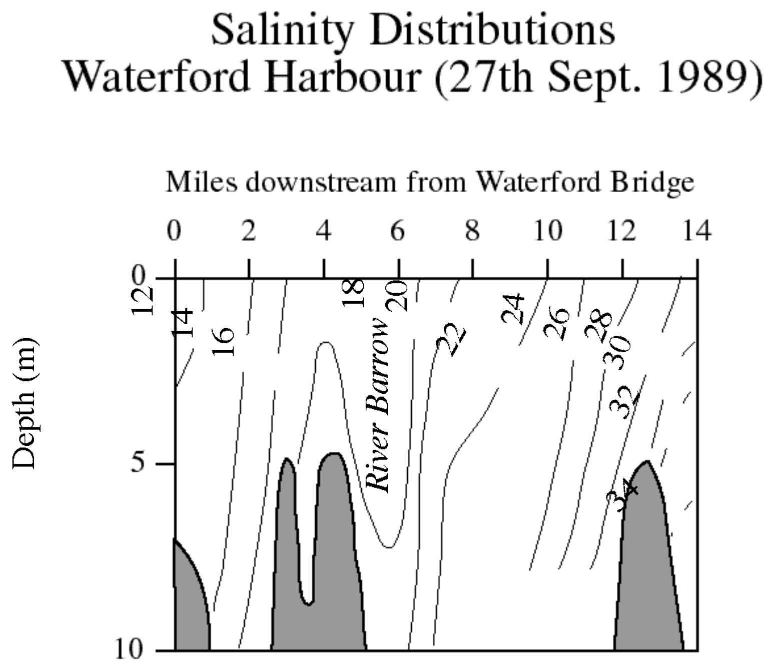

Figure 4. Vertical salinity section of Waterford Harbour, 27 September 1990. Note that salinity stratification is only found at each extremity of the estuary. Shaded areas are the Checkpoint Bar (mile 4) and the Duncannon Bar (mile 13) banks.

The outer reaches of Conwy estuary and the waters of Conwy Bay showed no vertical salinity structure. Results from surveys showed that on occasion, due to a combination of low run-off and strong tidal movement, high salinities could be found up-river. For example in June, salinity values as high as 30 were recorded 5 miles upstream at Tal-y-Cafn (Figure 2) at high tide.

Non-Anomalous Distributions Of Silicate And Nitrate

A constituent whose concentration in an estuary is passively diluted by increasing proportions of either fresh or salt water is referred to as conservative. The mixing curve approach (Figure 5) is a useful technique to locate regions in an estuary which are sources or sinks (removal) of any particular dissolved compound. An example of a source would be a single point discharge; physico-chemical processes such as desorption from or adsorption by suspended matter would represent either a source or a sink respectively; nutrient uptake by phytoplankton would represent a sink for that nutrient.

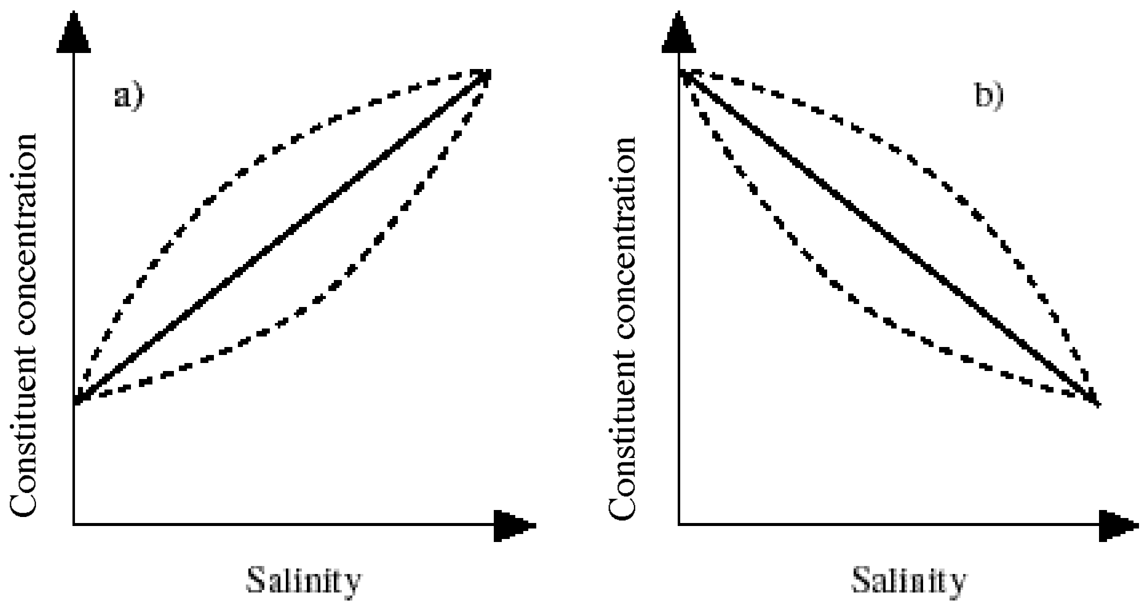

Figure 5. The use of mixing curves to demonstrate conservative and non-conservative behaviour of dissolved constituents in estuaries. Concentrations should fall on the straight (solid) line joining the freshwater and full salinity seawater if there are no sources or sinks for that constituent in the estuary (see text) a) for a constituent whose concentration is higher in seawater than freshwater and b) for a constituent whose concentration is higher in freshwater than seawater. Points will fall above or below these curves if there is a source (above) or sink (below) for the constituent within the estuary (dashed lines)

Silicate appeared to follow the classical dilution patterns of a conservative element in both Waterford Harbour and the Conwy estuary. In Waterford, the silicate data were consistent with the effect of a two-river (Suir-Barrow) system on a constituent-salinity relationship when the concentrations in each river differ considerably (Figure 6). For this reason, the distribution of constituents in Waterford Harbour when salinities are less than 20 will not be presented. The pattern of nitrate was similarly conservative (Figure 7).

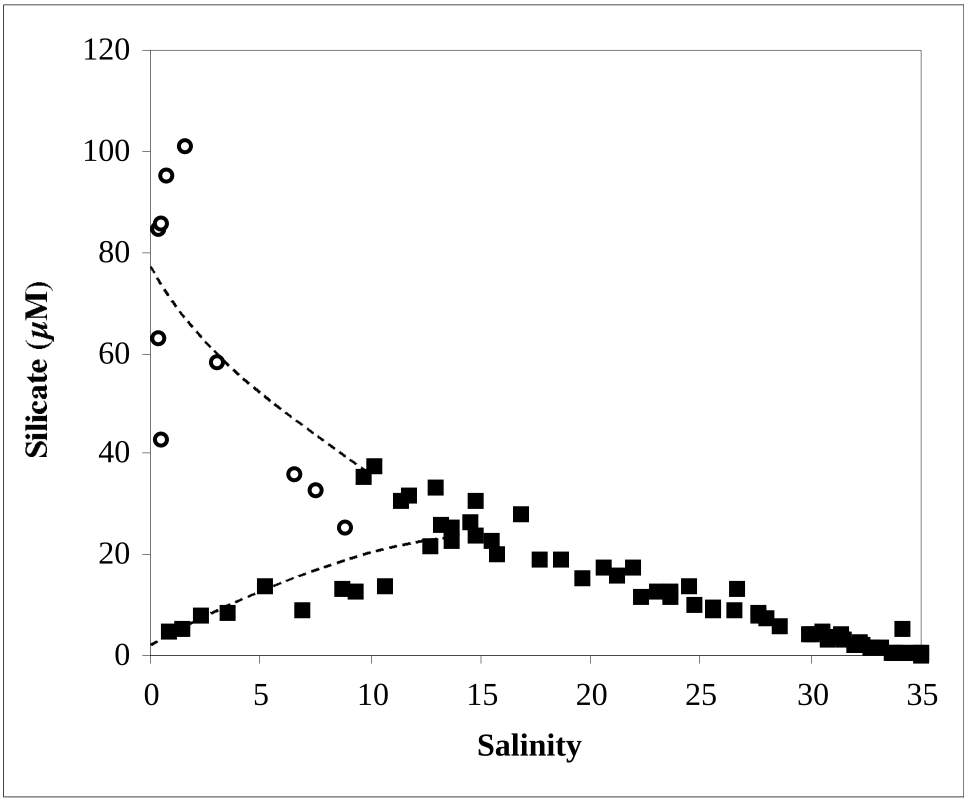

Figure 6. Relationship between salinity and the concentration of Silicate in Waterford Harbour. Open circles refer to samples taken within the tidal region of the river Barrow. Dashed lines represents theoretical mixing curves. Data are for 9-10th July 1997.

In the Conwy estuary, silicate always behaved conservatively (Figure 8), as did nitrate with the exception of results taken in May (Figure 8b), where values fell below the mixing curve. This was undoubtedly due to nutrient removal by an extensive bloom of Phaeocystis pouchettii [4] observed in Conwy Bay at this time.

[4] *P. pouchettii* is a Prymnesiophyte which does not require silicate and commonly blooms in May, utilising residual nitrate after the Spring Diatom Bloom has virtually stripped silicate from coastal waters. It has a colonial stage where cells are embedded in large gelatinous colonies which can be easily visible to the naked eye. It can greatly reduce water quality due to effects such as foaming, smell or visible deterioration.

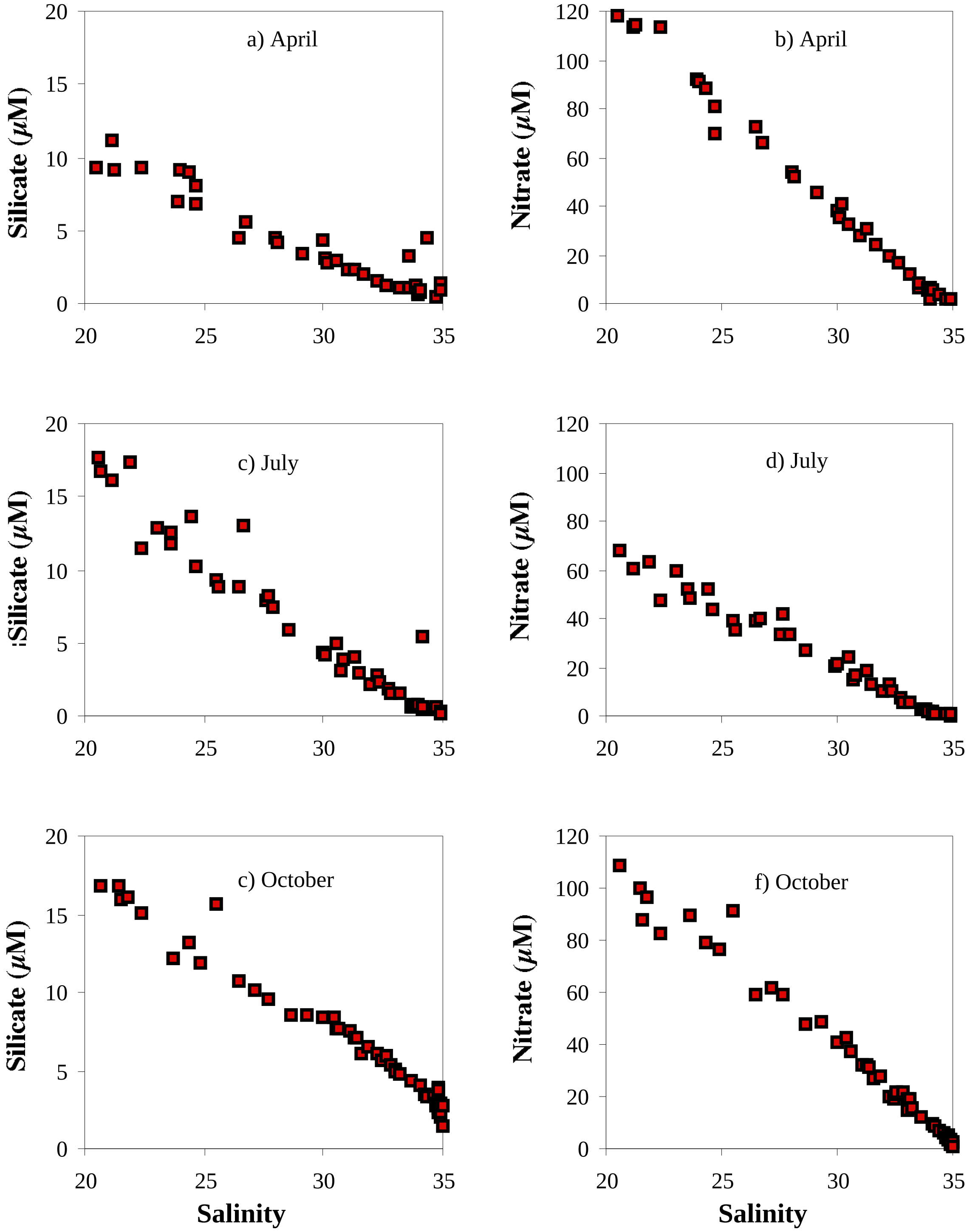

Figure 7. Relationship between salinity and nutrients (nitrate and silicate) in Waterford Harbour in a, b) April; c), d) July; e), f) October in 1997. Sampling dates may be found in Table 5.

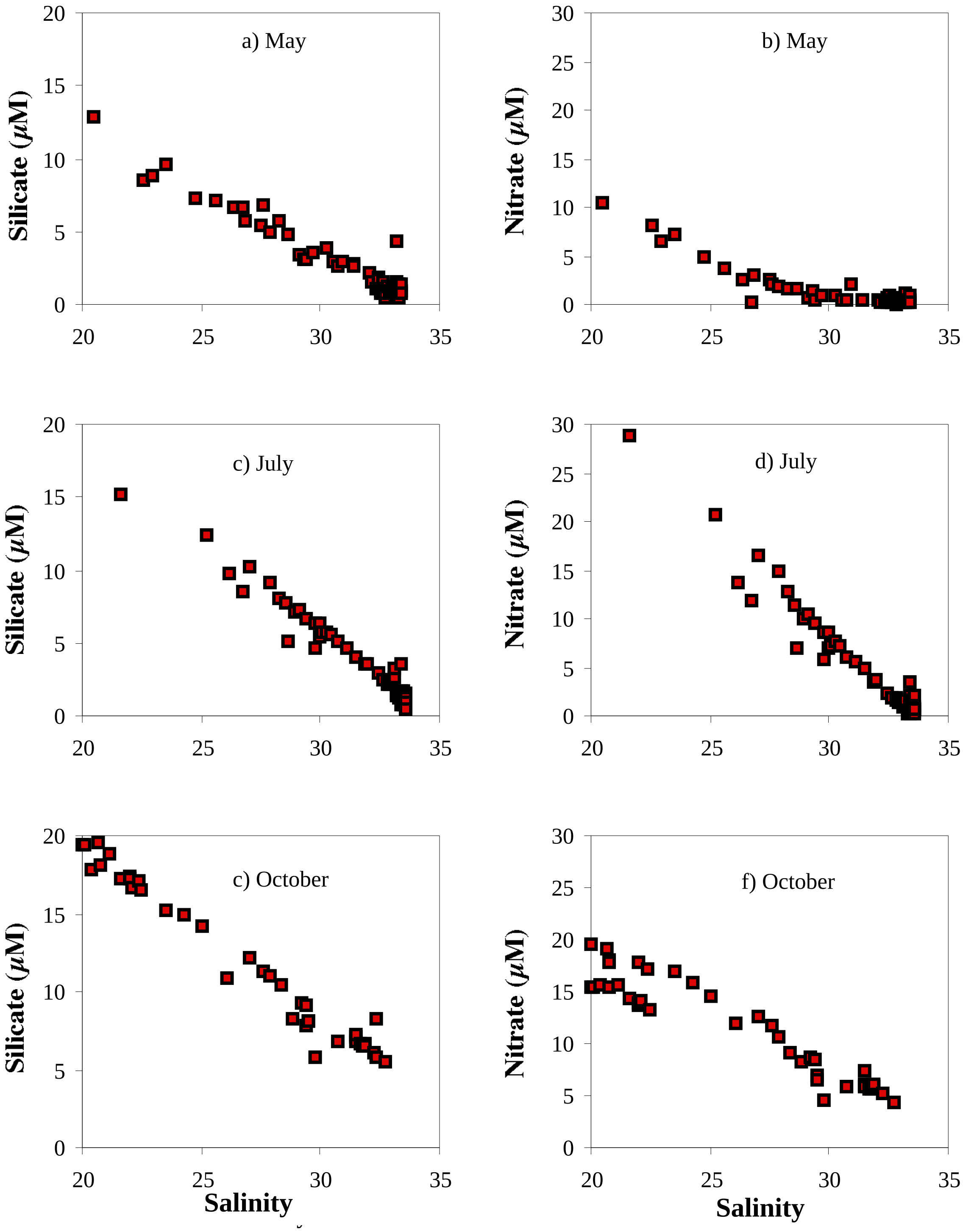

Figure 8. Relationship between salinity and nutrients (nitrate and silicate) in the Conwy Estuary in a, b) May; c), d) July; e), f) October in 1997. Sampling dates may be found in Table 5.

Anomalous distribution of Phosphate

The relationship between phosphate and salinity showed that this constituent was not behaving conservatively like silicate and nitrate, as anomalous features in the relationship were apparent. In Waterford, non-conservative behaviour of phosphate was observed at high (31-34) salinity in both April and July (Figure 9 a,b). The relationship showed an inversion in concentration over this salinity range suggesting a removal of this element in a region whose salinity corresponded to the plume zone. This was not the case in October, when the behaviour of phosphate was conservative (Figure 9 c).

Much larger inversions in the phosphate-salinity relationships were observed in the Conwy estuary. In May, the inversion was evident over a lower salinity range (15-30) than in Waterford Harbour (Figure 10a). In July, an inversion was apparent within the plume zone (S = 30-33; Figure 10b). This feature was not apparent in October (Figure 10c).

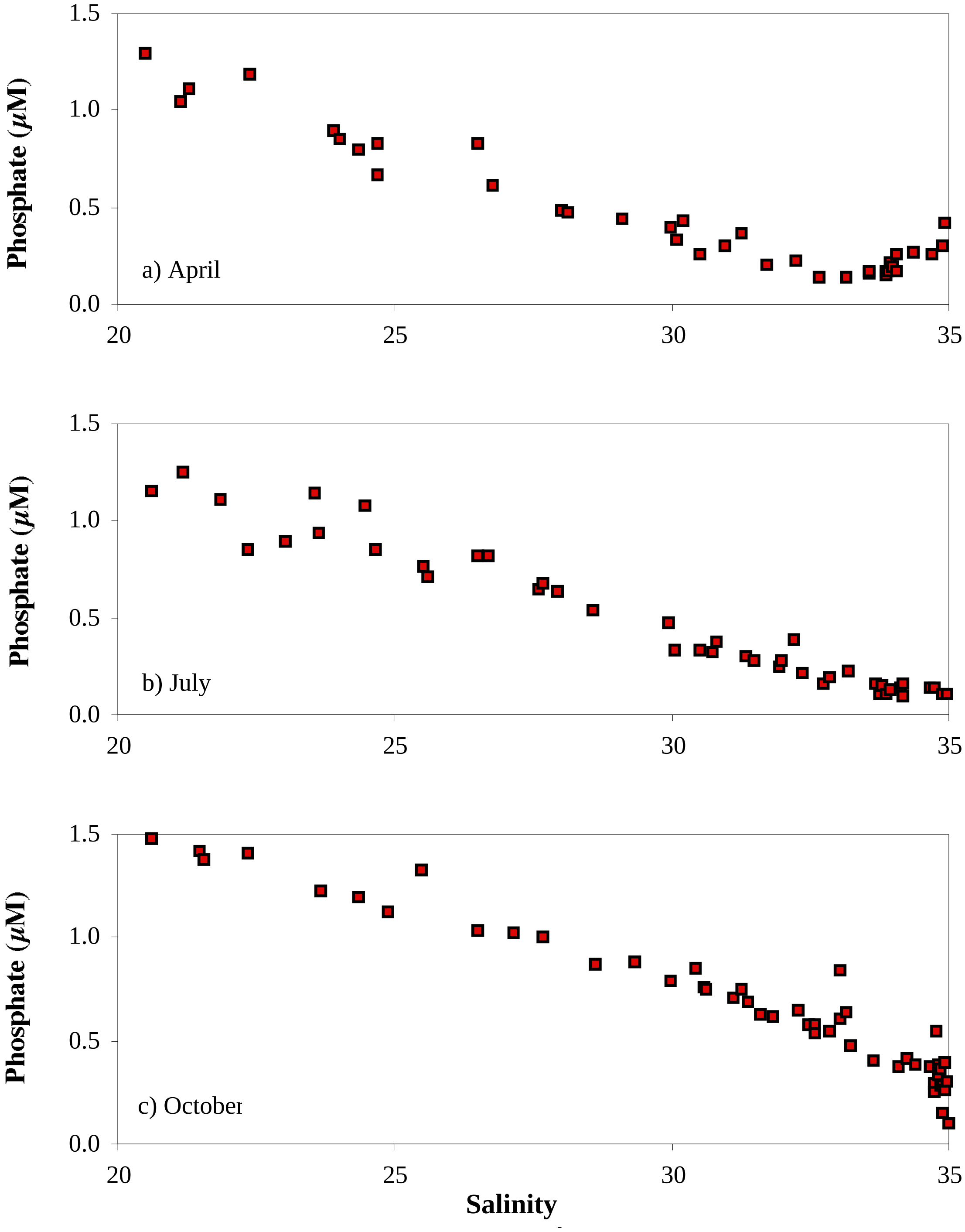

Figure 9 Relationship between salinity and phosphate in Waterford Harbour in a) April, b) July and c) October 1997. Note the anomalous inversion in the relation ship at high salinity values (32-34) corresponding to the plume zone in April and July.

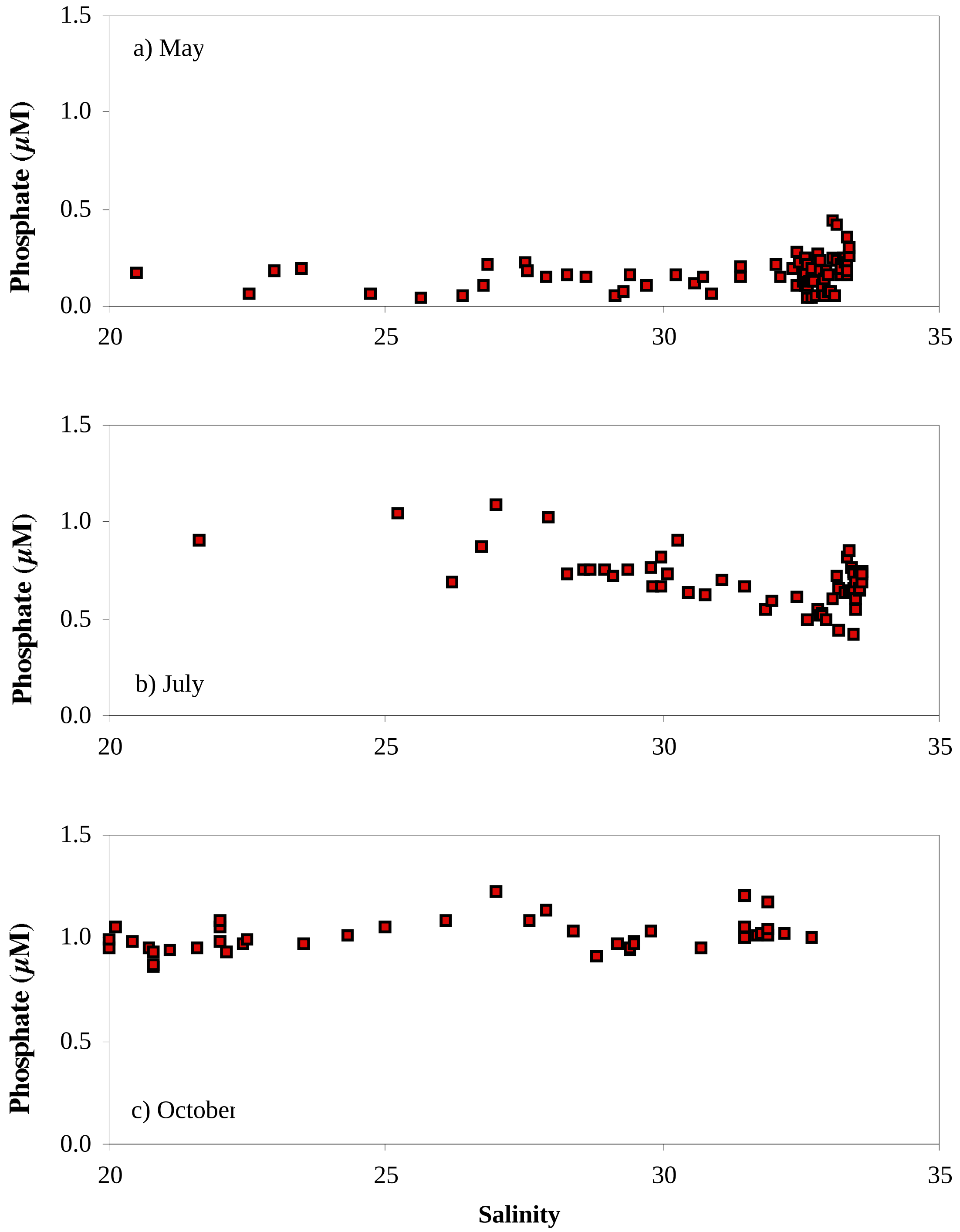

Figure 10. Relationship between salinity and phosphate in the Conwy estuary in a) May, b) July and c) October 1997. Note the anomalous relationships in May (freshwater concentration = 0.5 µM) and July (freshwater concentration = 1.2 µM)

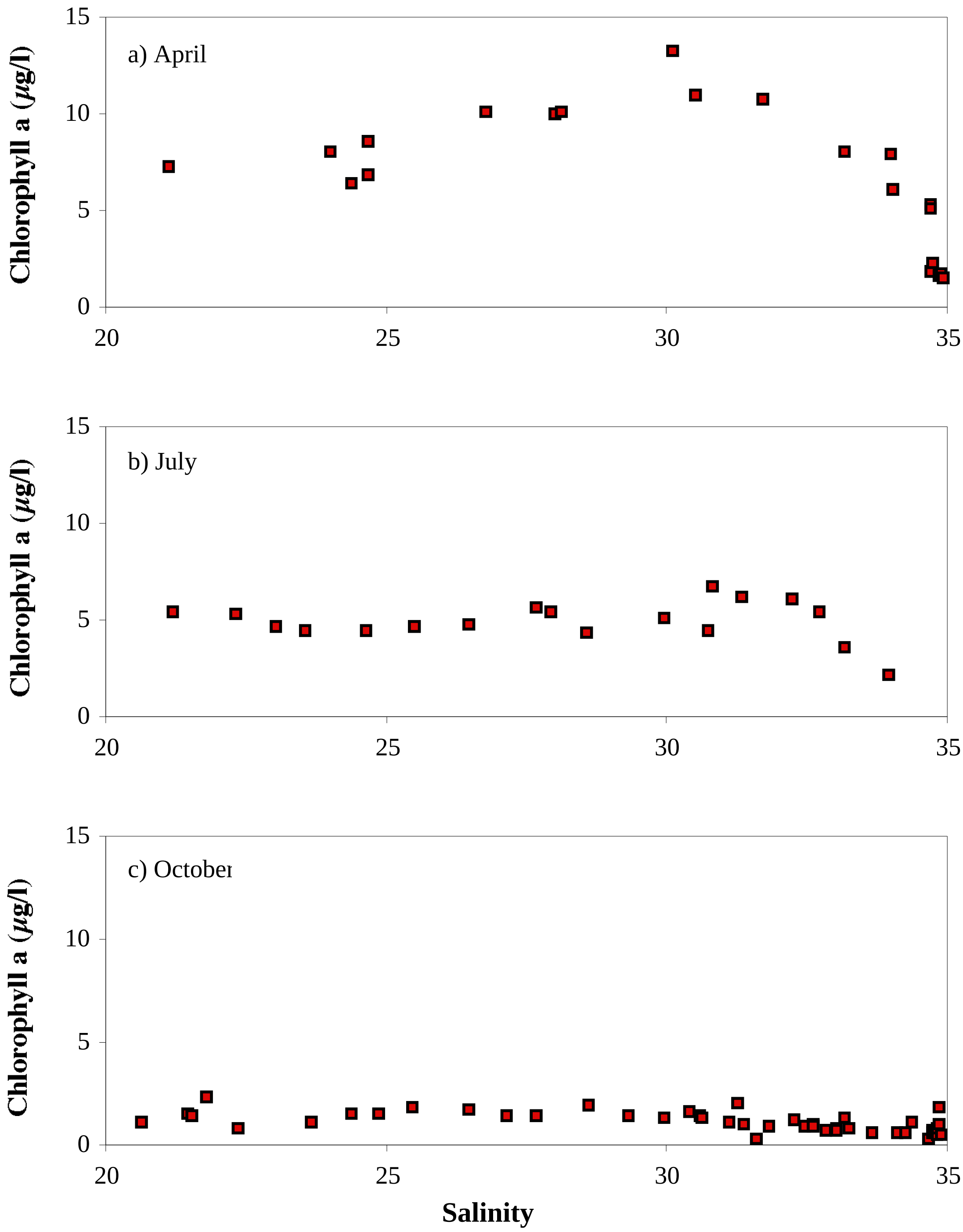

Figure 11. Distribution of chlorophyll with salinity in the outer section, plume zone and adjacent sea in Waterford Harbour in a) April, b) July and c) October 1997. Precise sampling dates are given in Table 5.

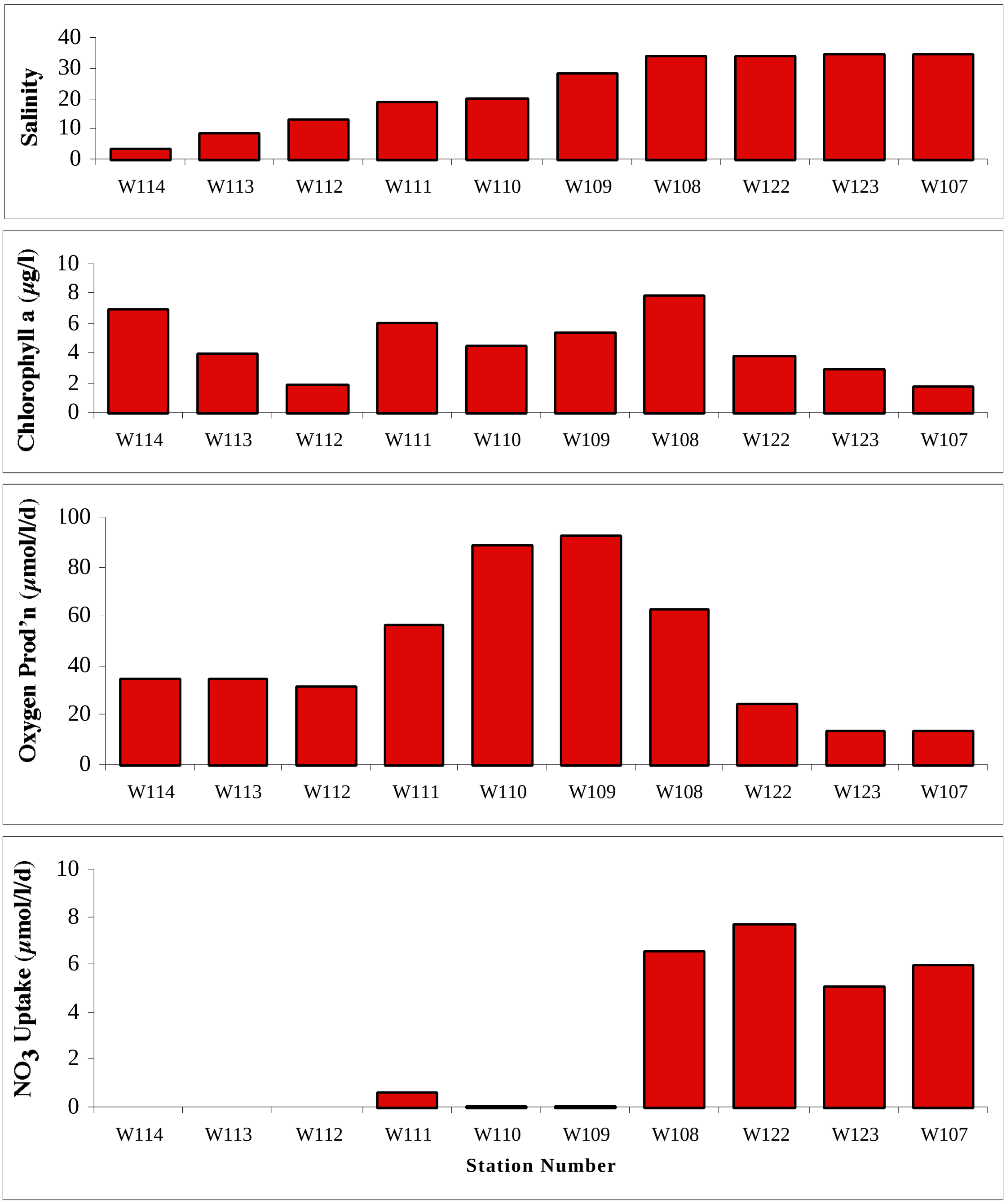

Figure 12. Salinity, Chlorophyll, Gross Production and Nitrate Uptake in Waterford Harbour in April 1997. Station positions are shown in Figure 1.

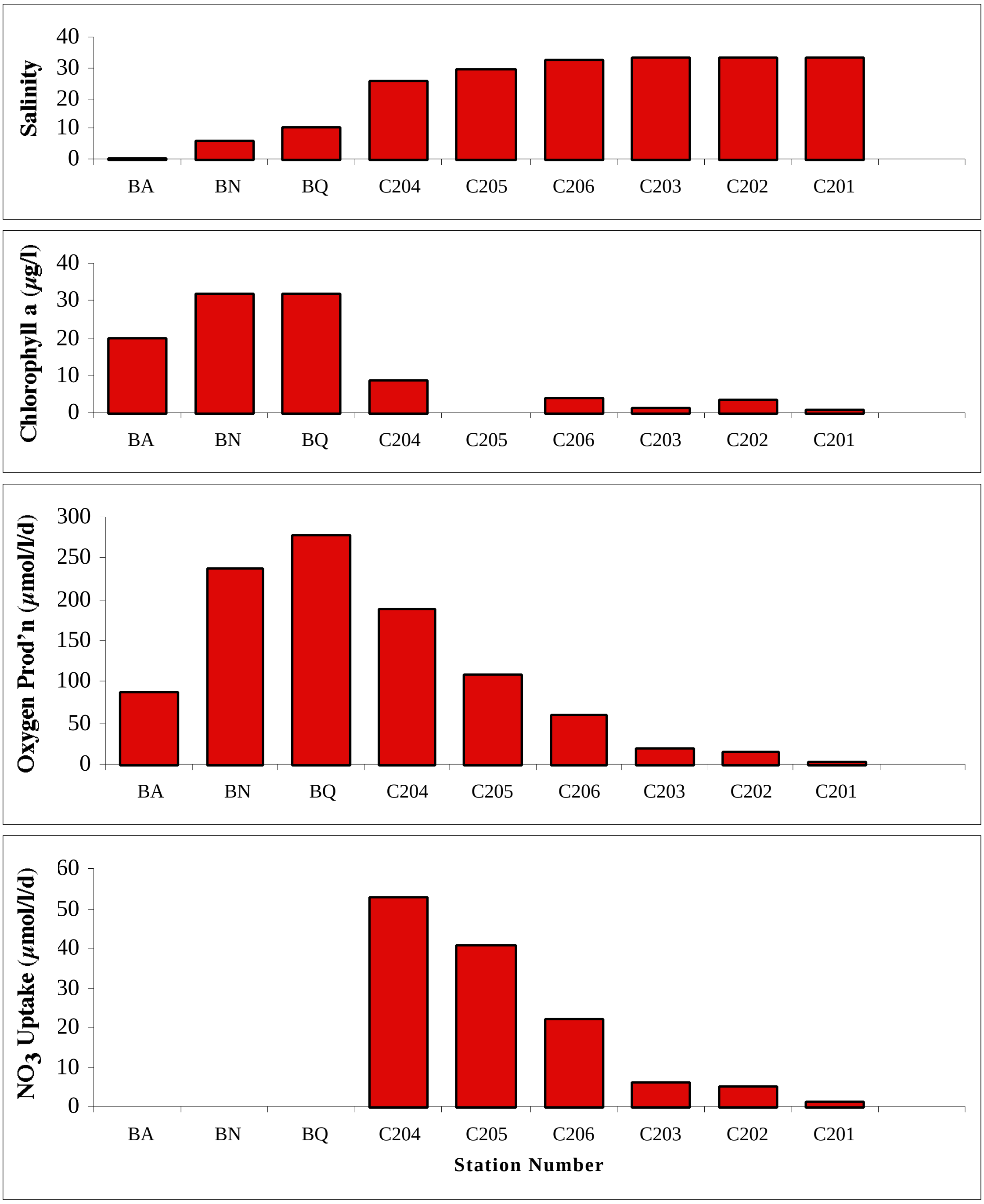

Figure 13: Salinity, Chlorophyll, Gross Production and Nitrate Uptake in the Conwy Estuary in July 1997. Station positions are shown in Figure 2.

Distribution of Chlorophyll, O2 production and 15N Uptake with Salinity

Chlorophyll a values tended to peak over the salinity ranges associated with the phosphate minima referred to above. For example, Figure 11 shows the substantial increases in chlorophyll encountered in spring and summer as one moves from the sea into the plume zone in Waterford Harbour. Here was the first evidence that we had indicating that the phosphate removal (deduced from the anomalous PO_4-S relationship) observed in the spring and summer months was controlled biologically. Note that there was no corresponding increase in chlorophyll in October (Figure 11c) when no anomalous behaviour of phosphate was apparent.

The distribution of the rates of primary production substantiated the view that the nutrient removal was biological. $^{15}NO_3$ uptake rates had maximum values at locations close to both maximum chlorophyll (biomass) but at marginally higher salinities (Figures 12 and 13). At slightly lower salinity values to the maximum chlorophyll concentrations were the maximum production rates. It may be concluded that this reflects the sequence:

[nutrient uptake] $\rightarrow$ [primary production] $\rightarrow$ [increase in phytoplankton biomass]

which progresses with decreasing salinity (i.e. landwards) within the plume zone. This is elaborated further below and is depicted graphically in Figure 14.

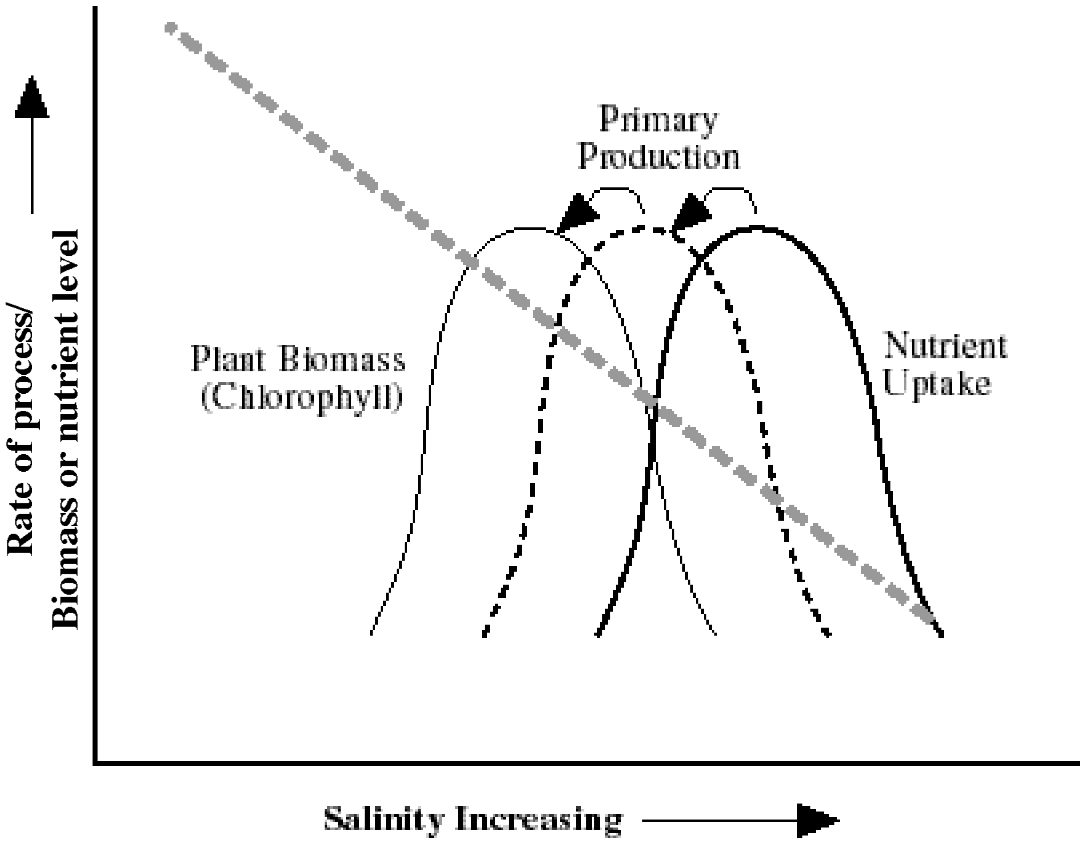

Figure 14. Phytoplankton processes occurring within the estuarine plume zone

5.2.2. Interpretation

Our data are not consistent with the classical view that the phytoplankton bloom [5] in an estuary is sustained by nutrients mixing down from the freshwater end-member. The anomalous behaviour of phosphate caused us to look more closely at the N:P ratio and the relationship of this ratio with salinity. The N:P ratio that is required to sustain phytoplankton growth (the so-called Redfield ratio) is in the region of 15:1 (N:P by atoms). The plots, of which examples are shown in Figure 15, showed first that the freshwater end-member is almost an order of magnitude above the Redfield ratio. That is to say that the freshwater end-member in both estuaries and on all occasions was rich in nitrogen and deficient in phosphorus as far as the phytoplankton are concerned.

The plots also show that the seawater end-member, by contrast, is richer in phosphorus than nitrogen. This is probably a consequence of the fact that the off-shore coastal bloom occurs before that in the estuaries. As a consequence nitrogen is exhausted and there is residual phosphate in coastal waters, either due to more rapid recycling or there was more phosphorus relative to nitrogen, in the sense of the Redfield ratio, prior to the bloom.

Our view of the nutrient dynamics of the phytoplankton in these estuaries is that the estuarine phytoplankton bloom, evident from elevated chlorophyll levels and seemingly persistent through the summer, is poised between two environments : one which is nitrogen-rich (originating from the freshwater end-member) and the other phosphorus-rich (the seawater end-member). The phytoplankton are apparently utilising nutrients from both sides in order to maximise their growth.

What we have been able to show in the two estuaries is that this is consistent with the distribution of the dynamic properties: production or nutrient uptake. Thus, the phytoplankton effect a net transport of phosphate from the sea into the estuary.

[5] The term 'bloom'is used in this report in a similar context to, for example, the Spring Bloom, referring to a proliferation of phytoplankton above typical background summer biomass levels of ca. 1 µg/l chlorophyll. It is not used as per the phrase 'exceptional bloom', which refers to a situation where cell concentrations are so elevated as to physically discolour seawater.

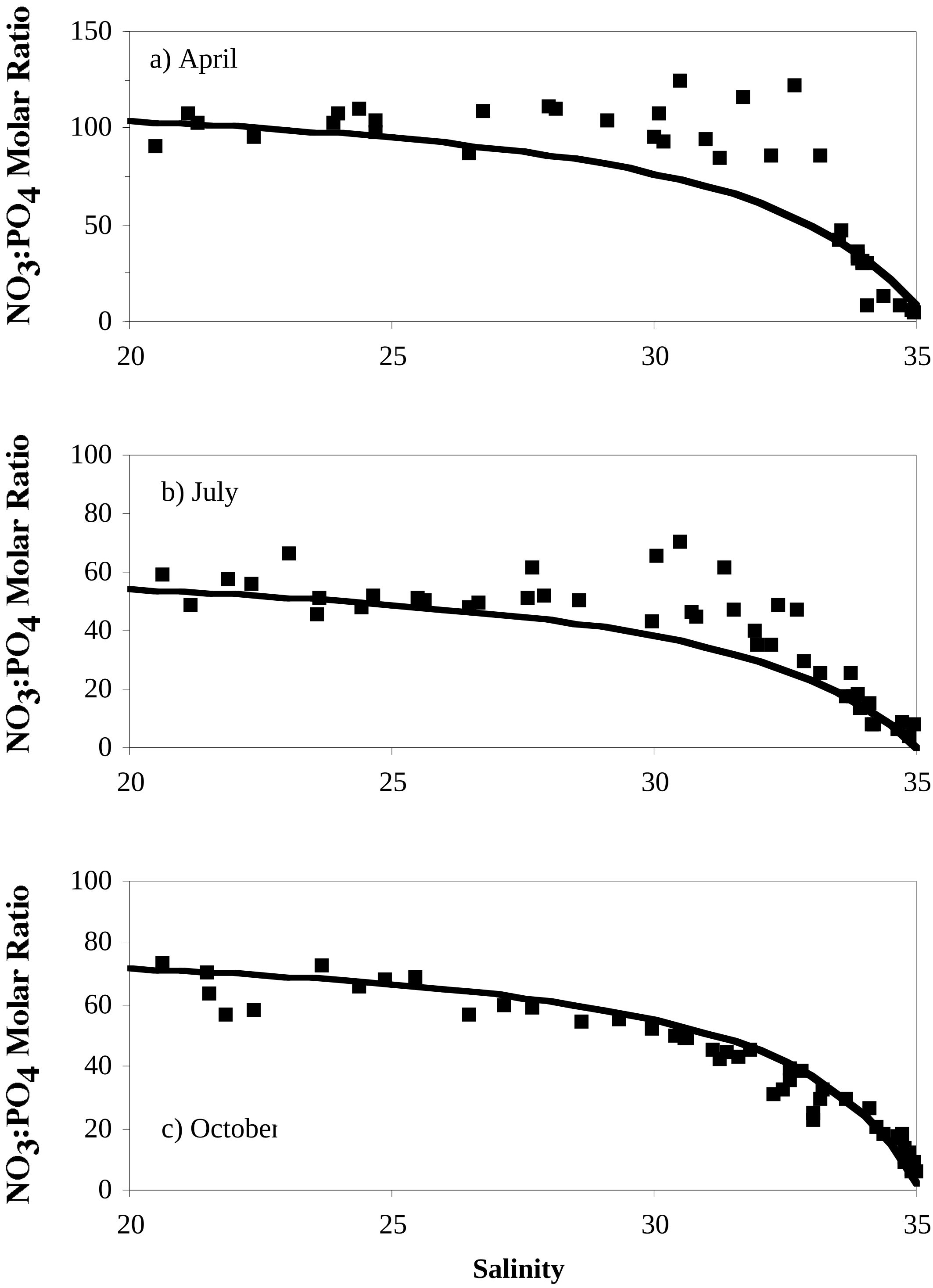

Figure 15. Observed (squares) and theoretical dilution lines (solid curves) for the N:P molar ratio in samples from Waterford Harbour taken in a) April, b) July and c) October 1997. Note how the points fall well above the line in the high (30-33) salinity range corresponding to the plume zone in April and July, indicating non-conservative behaviour of, in this case, phosphate.

5. CONCLUSIONS

We conclude from the results of this study that :

i) Silicate and Nitrate behave substantially conservatively in the Waterford and Conwy estuaries.

ii) This was not the case with phosphate, where systematic departures from conservative behaviour were evident both at the high salinity end of Waterford Harbour (the plume zone) and within the Conwy estuary.

iii) The phytoplankton blooms appeared to be poised between a freshwater nitrogen-rich zone and a seawater phosphorus rich zone.

iv) As a consequence, a biologically driven pumping of phosphate from the sea into the estuaries was observed. This is summarised in the diagram below.

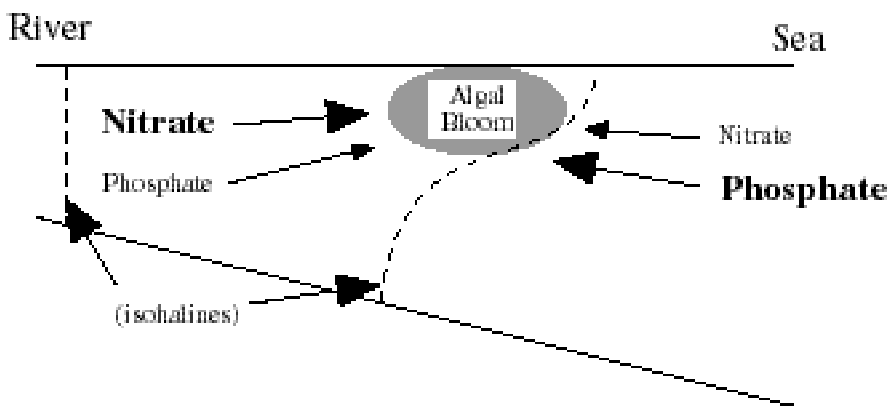

Figure 16. Salinity stratification, indicated by the shape of the isohalines, in the estuarine plume zone encourages growth of phytoplankton which utilise the river as their main source of nitrogen (nitrate) and the sea as the main source of phosphorus (phosphate). Up-estuary, vertical mixing and increased suspended matter levels prevent phytoplankton growth,

7. IMPLICATIONS

The biology of freshwater systems is often characterised by its trophic status – governed mainly by the concentration of available phosphorus. Although nitrogen is also required to drive aquatic biology, the former nutrient is nearly always the limiting of these two elements. As a consequence, the characterisation and management of freshwater systems is now based on the total phosphorus concentration along with levels of algae or phytoplankton, usually denoted as a concentration of the pigment chlorophyll a (see e.g. OECD, 1982)

By contrast, temperate coastal marine waters are often nitrogen depleted (relative to phosphorus). Estuaries are thus interfaces between nitrogen-rich freshwater systems and phosphorus-rich marine systems. The bloom in estuaries occurs typically at the seaward end where low suspended matter levels and salinity stratification greatly assist the growth of the phytoplankton community due to providing a local light-rich environment. Our results have shown that in this part of the estuary, the sea rather than the river, is important in supplying phosphate during the spring to autumn growing season. Thus the benefits derived from the management of phosphate input into rivers are, when these waters reach estuaries, are nullified due to the supply of phosphorus from the sea into the estuary.

Our results show that the supply of nitrogen, and the ratio of the amounts of nitrogen to phosphorus, are critical in promoting phytoplankton blooms in estuaries, in particular within the estuarine plume zone. We would recommend that statutory authorities take the present observations into consideration when developing water control measures by control of nitrate as well as phosphate levels in estuaries. For example, an immediate benefit for the two estuaries studied would be a reduction, as far as is possible, of nitrate towards the Redfield ratio equivalent (see Section 5.2.2) of current phosphate levels.

8. DATA REPORTING, MANAGEMENT & POLICY

Data arising from the fieldwork has been published as a data report. Copies are available for inspection at the Marine Institute, Dublin (G. O'Sullivan), NUI, Galway (R. Raine), University of Wales, Bangor (P. Williams), and the Welsh Office (H. Prosser). Data is in the process of being deposited in both the Irish Marine Data Centre, Dublin and the British Oceanographic Data Centre, Bidston. The data are also available as ASCII MS-DOS files from Dr. R. Raine, The Martin Ryan Institute, National University of Ireland, Galway. The Conwy data has been archived in the MicroSoft relational data base (ACCESS) at the School of Ocean Sciences, Menai Bridge.

Scientific output will be published with acknowledgement to the INTERREG programme in peer review journal(s).

9. ACKNOWLEDGMENTS

We are pleased to acknowledge the support we received from the INTERREG programme in carrying out this work. The UK Environment Agency, the Irish Environmental Protection Agency and the Irish Marine Institute provided assistance in the co-ordination of the fieldwork programme without which this project could not have been accomplished. A special mention is due to the Environment Agency, Warrington, UK for their willingness to provide the facilities of the *Coastal Guardian* for fieldwork in the Conwy estuary. The assistance of Capt. P. Baugh and the crews of the *Lough Beltra* and *Celtic Voyager* during fieldwork in Waterford Harbour, and Capt. M Castle and the crew of the *Coastal Guardian* is also gratefully acknowledged.

10. BIBLIOGRAPHY

Blight, S.P., Bentley, T.L., Lefevre, D., Robinson, C., Rodrigues, R., Rowlands, J. and P.J.leB. Williams. 1995. Phasing of autotrophic and heterotrophic plankton metabolism in a temperate coastal ecosystem. Marine Ecology Progress Series, 128, 61-75.

Boelens, R. 1995 An integrated science programme for the Irish Sea : Synthesis and Recommendations. Third Report of the Irish Sea Science Co-ordinator. Department of Environment, Dublin and Department of Environment, London. 36 + iii pp.

Dugdale, R. C. and Goering, J. J. 1967 Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol. Oceanogr. 12, 196-206.

Fichez, R., Jickells, T.D. and H.M. Edmunds 1992 Algal blooms in high turbidity, a result of the conflicting consequences of turbulence on nutrient cycling in a shallow water estuary. Estuarine, Coastal and Shelf Science, 35, 577-592.

Grasshoff, K. 1976 Methods of seawater analysis. Verl. Chemie, Weinheim, 317 pp.

Jenkinson, N. and P.J. leB. Williams. 1982 A transportable micro-processor controlled precise Winkler titration suitable for field station and shipboard use. Limnol. Oceanogr. 27, 576-584.

Morris, A.W., J.I. Allen, R.J.M. Howland and R.G. Wood. 1995. The Estuary Plume Zones : Source or Sink for Land-derived Nutrient Discharges. Estuarine, Coastal and Shelf Science, 40, 387-402.

OECD, (Organisation for Economic Co-Operation and Development) 1982 Eutrophication of Waters. Monitoring, Assessment and Control. Paris, OECD.

Sanders, R. Klein, C. and Jickells, T. 1997 Biogeochemical cycling in the upper Great Ouse Estuary, Norfolk, U.K. Estuarine, Coastal and Shelf Science, 44, 543-555.

Tett, P. 1987. Plankton. In Biological surveys of estuaries and coasts, pp. 280-341. Eds. J.M. Baker and W.J. Wolff, Cambridge University Press, Cambridge.

APPENDIX 1

Abbreviations and Addresses of Organisations involved

Abbreviation	**Organisation**
EA	Environment Agency (UK)
EPA	Environmental Protection Agency (Ireland)
MI	Marine Institute, Dublin
NUIG	National University of Ireland, Galway
SSC	Scientific Steering Committee
UWB	University of Wales, Bangor
WO	Welsh Office, Cardiff

APPENDIX 2 MARITIME INTERREG PROJECTS

The following co-operative projects and networks are supported under Measure 1.3 "Protection of the Marine and Coastal Environment and Marine Emergency Planning", of the Maritime (Ireland/Wales) INTERREG Programme (1994 – 1999):

Co-operative Projects

1. **Roseate Terns - The Natural Connection: A Conservation/Research Project linking Wales and Ireland.** Irish Wildbird Conservancy / North Wales Wildlife Trust.
2. **Marine Mammal Strandings - A Collaborative Study for the Irish Sea.** National University of Ireland, Cork / Countryside Council for Wales.
3. **South West Irish Sea Survey (SWISS).** Trinity College Dublin / National Museum of Wales, Cardiff.
4. **The Fate of Nutrients in Estuarine Plumes.** National University of Ireland, Galway / University of Wales, Bangor.
5. **Water Quality and Circulation in the Southern Irish Sea** National University of Ireland, Galway / University of Wales, Bangor.
6. **Grey Seals: Status and Monitoring in the Irish and Celtic Seas.** National University of Ireland, Cork/Dyfed Wildlife Trust.
7. **Sensitivity and Mapping of inshore marine biotopes in the Southern Irish Sea (SensMap).**Ecological Consultancy Services (Dublin), Dúchas / Countryside Council for Wales.
8. **Marine Information System: Scoping Study (Phase I).** Marine Institute, National Marine Data Centre/ Countryside Council for Wales.
9. **Achieving EU Standards in Recreational Waters.** National University of Ireland, Dublin / University of Wales, Aberystwyth.
10. **Irish Sea Southern Boundary Study** Marine Informatics Ltd (Dublin) / University of Wales, Bangor.
11. **Marine Information System: Demonstration (Phase II).** Marine Institute, National Marine Data Centre / Countryside Council for Wales.
12. **Emergency Response Information System (ERIS)** Enterprise Ireland, Compass Informatics, IMES/University of Wales, Bangor.
13. **Risk Assessment and Collaborative Emergency Response in the Irish Sea (RACER)** Nautical Enterprise Centre (Cork), National University of Ireland, Cork, University of Wales, Cardiff.

14. **Critical assessment of human activity for the sustainable management of the coastal zone.** National University of Ireland, Cork / University of Wales, Aberystwyth.
15. **SeaScapes – Developing a method of seascape evaluation** Brady Shipman Martin, National University of Ireland, Dublin / University of Wales, Aberystwyth.
16. **Ardfodir Glan – Clean Coasts/Clean Seas** CoastWatch Ireland / Keep Wales Tidy Campaign.

Co-operative Networks

17. **Irish Sea Hydrodynamic Modelling Network** Trinity College Dublin / University of Wales, Bangor.
18. **CoAST - Co-operative Action - Sustainability Network** Dublin Regional Authority / Isle of Anglesey County Council.
19. **ECONET - Erosion Control Network** Enterprise Ireland / Conwyn County Council.
20. **Navigate with Nature** Irish Sailing Association / Centre for Economic and Environmental Development (UK).
21. **"Land Dividing - Sea Uniting" Irish Seas Exhibition** Irish Seal Sanctuary, ENFO / National Assembly for Wales.
22. **From Seawaves to Airwaves** West Dublin Community Radio / Radio Ceredigion CYF.
23. **BENSIS – Benthic Ecology Network** Trinity College Dublin / National Museum of Wales, Cardiff.
24. **Remote Sensing of Suspended Sediment Load in the Coastal Zone** National University of Ireland, Galway / University of Wales, Bangor.
25. **Paving the Information Highway** Ecological Consultancy Services (Dublin) / Irish Sea Forum, University of Wales, Bangor.
26. **Inland, Coastal and Estuarine (ICE) Journal** National University of Ireland, Dublin / Centre for Economic and Environmental Development (UK).

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