

**NUTRIENTS AND EUTROPHICATION IN THE
TAW ESTUARY**

by

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ABSTRACT

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Increased inputs of nutrients to estuaries and coastal waters can cause undesirable effects associated with eutrophication, including nuisance and toxic algal blooms, reduced amenity value, changes in species composition, bottom anoxia and fish kills. The main sources of nutrients to estuaries are river runoff, sewage discharges, atmospheric inputs and possibly submarine groundwater discharges. For the UK, estuarine eutrophication has been shown to occur in at least 16 estuaries (including the Taw in North Devon). Consequently, these systems have been designated as '(Potential) Problem Area' under the OSPAR Common Procedure for the Identification of Eutrophication and also as a 'Eutrophic Water' under the EU's Nitrates Directive and / or a 'Sensitive Area (Eutrophic)' under the Urban Wastewater Treatment Directive or both. Significant reductions in N and P inputs have been realized following application of the EU's Urban Waste Water Treatment Directive. Atmospheric NO_x and NH_x emissions have also decreased and are expected to decrease further as implementation of existing legislation continues and new controls are introduced for activities such as shipping. The Nitrates Directive was introduced to tackle N discharges from agriculture but little change in N loads to estuaries has been recorded.

Using the Taw Estuary as an example, data routinely collected by the Environment Agency for England and Wales (EA) over the period 1990–2004 were interrogated to identify the drivers of excessive algal growth. The estuary was highly productive with chlorophyll *a* concentrations regularly exceeding 100 µg L⁻¹, mostly during periods of low freshwater input from the River Taw when estuarine water residence times were longest. The reported approach demonstrates the value of applying conventional statistical analyses in a structured way to existing monitoring data and is recommended as a useful tool for the rapid assessment of estuarine eutrophication.

However, understanding of primary production dynamics in the Taw was constrained because of the low temporal resolution, heterogeneity and gaps in the EA data. Therefore, a temporal high resolution monitoring campaign was conducted in summer 2008 to document the development and decline of three algal blooms. The significance of long water residence times following low freshwater inflow and neap tides was confirmed. During peaks in chlorophyll *a* concentration (max. 226 µg L⁻¹), nutrient limitation switched from P to Si and persisted for more than 2 weeks in the outer estuary. Signs of ammonium and phosphate (<0.2 µM) and silicate (<2 µM) depletion were also observed. Using multivariate statistics, five distinct sets of environmental conditions present in the Taw at different stages of algal growth were identified and directly linked to freshwater inflow.

UK Climate Impacts Programme scenarios predict a 30-50% decrease in Q95 flows (the flow which is exceeded 95% of the time) of rivers in south Britain by 2050. Under the current nutrient regime, this is likely to severely increase the severity and duration of symptoms of eutrophication in the Taw and favour potentially hazardous phytoplankton groups instead of diatoms.

To mitigate future eutrophication events in the Taw, it is recommended to further reduce N and P inputs. It is also crucial to perform a detailed assessment of potential climate change consequences for the Taw Estuary and similar systems.

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*Meeresleuchten
(Sea sparkle)*

*Aus des Meeres dunklen Tiefen
Stieg die Venus still empor,
Als die Nachtigallen riefen
In dem Hain, den sie erkor.*

*Und zum Spiegel, voll Verlangen,
Glätteten die Wogen sich,
Um ihr Bild noch aufzufangen,
Da sie selbst auf ewig wich.*

*Lächelnd gönnte sie dem feuchten
Element den letzten Blick,
Davon blieb dem Meer sein Leuchten
Bis auf diesen Tag zurück.*

Christian Friedrich Hebbel (1813-1863)

In this poem, Christian Friedrich Hebbel describes one particular interpretation of the nature of a harmful algal bloom, inspired by the bioluminescence of the dinoflagellate Noctiluca. One night, when the Goddess Venus left the sea to dwell henceforth in the skies, the sea calmed to capture for the last time -very much like a mirror- the light of the Goddess' smile. This was how the sea received its nocturnal luminescence.

AUTHOR'S DECLARATION

At no time during the registration for the degree of Doctor of Philosophy has the author been registered for any other University award without prior agreement of the Graduate Committee.

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The work presented in chapter 2 was developed from a study commissioned by DEFRA and carried out by myself in conjunction with Rebecca Nimmo Smith, Gillian A. Glegg, Alan D. Tappin and Paul J. Worsfold.

Relevant scientific seminars and conferences were regularly attended at which work was often presented and two papers were prepared for publication.

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PRESENTATIONS AND CONFERENCES ATTENDED

POSTERS

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Maier, G., Glegg, G.A., Tappin, A. and Worsfold, P.J., Eutrophication Events in the Taw Estuary (UK) – Suggestions for Future research. Understanding Marine Systems - the first Marine Institute Conference, Plymouth, UK (Dec. 2007).

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PEER REVIEWED PUBLICATIONS

Maier, G., Nimmo-Smith, R.J., Glegg, G.A., Tappin, A. and Worsfold, P.J., 2009. Estuarine eutrophication in the UK: current incidence and future trends. *Aquatic Conservation: Marine and Freshwater Ecosystems*, **19**(1): 43-56. doi:10.1002/aqc.982

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OTHER PUBLICATIONS

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Strategy for England. Report to UK Department of the Environment, Food and Rural Affairs. Defra contract NIT 18., University of Plymouth, Plymouth, UK.

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AWARDS

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GLOSSARY OF COMMONLY USED ABBREVIATIONS

| | |
|------------------|---|
| CAP | Common Agricultural Policy |
| CEH | Centre for Ecology & Hydrology |
| CLRTAP | Convention on Long Range Transboundary Air Pollution |
| CPR | Continuous Plankton Recorder |
| CRM | certified deep seawater reference material |
| DEFRA | Department for Environment, Food and Rural Affairs |
| DIN | dissolved inorganic nitrogen |
| DIP | dissolved inorganic phosphorus |
| DO | dissolved oxygen |
| DOC | dissolved organic carbon |
| DON | dissolved organic nitrogen |
| DOP | dissolved organic phosphorus |
| DP | dissolved phosphorus |
| EA | Environment Agency for England and Wales |
| EcoQOs | Ecological Quality Objectives |
| FSI | freshwater-saltwater interface |
| HAB | harmful algal bloom |
| HDPE | high density polyethylene |
| HPW | high purity water |
| HTCC - TOC | high temperature catalytic combustion of total organic carbon |
| IQR | interquartile range |
| LoD | limit of detection |
| NCD | nitrogen chemiluminescence detection |
| ND | Nitrates Directive |
| NH ₃ | ammonia |
| NH ₄ | ammonium |
| NH _x | ammonia and/or ammonium |
| NMDS | non-metric multidimensional scaling |
| NMMP | National Marine Monitoring Programme |
| NO ₂ | nitrite |
| NO ₃ | nitrate |
| NRFA | National River Flow Archive |
| NVZ | Nitrate Vulnerable Zone |
| OPA | orthophthaldialdehyde |
| OSPAR | Oslo and Paris Convention |
| PA | problem area |
| PC1, PC2, PCi... | principal component nr... |
| PCA | principal component analysis |
| PO ₄ | phosphate |
| PPA | potential problem area |
| RO-water | water obtained from a reverse osmosis system |
| SGD | submarine groundwater discharge |
| SiO ₂ | silicate |
| STW | sewage treatment works |

| | |
|-------------------|---|
| TDN | total dissolved nitrogen |
| TIN | total inorganic nitrogen |
| TOC | total organic carbon |
| TO _x N | total oxidised nitrogen |
| UKCIP | UK Climate Impacts Programme |
| UNECE | United Nations Economic Commission for Europe |
| UWWTD | Urban Waste Water Treatment Directive |
| WFD | Water Framework Directive |
| WR | working reagent |

**NUTRIENTS AND EUTROPHICATION IN
THE TAW ESTUARY**

INTRODUCTION



*Stranded Fucus
and Mytilus at
Airy Point*

1. Introduction

Eutrophication¹ was defined by Nixon (1995) as *an increase in the rate of supply of organic matter to an ecosystem*. Although this definition is value neutral as it describes a naturally occurring process (e.g. spring blooms in temperate waters or increased primary production following reduced grazing pressure), the term eutrophication has received a negative connotation as it has been used often synonymously for “(hu)man induced” or “cultural” eutrophication, which leads to undesirable effects in the aquatic environment (Tett *et al.* 2007). This development is also reflected in more recent definitions of de Jonge and Elliott (2001) or of the OSPAR commission (2003) which encompass the enrichment of anthropogenic nutrients, increased primary production and adverse environmental and ecological consequences.

In chapter 2, where estuarine eutrophication in the UK in the context of European legislation is reviewed, the definition of OSPAR (2003a) was used², as this and similar definitions from the Urban Waste Water Treatment Directive and the Nitrates Directive were employed throughout the policy related literature.

The archived data, which were collected by the Environment Agency for England and Wales (EA) and were used in chapter 3, did not contain information about the occurrence of ‘*undesirable disturbances to the balance of organisms*’ (e.g. changes in benthic community composition). In the absence of such data, employment of the OSPAR definition would have been inappropriate. Consequently, the more basic definition of Nixon (1995) was used for this there. To quantify the ‘*increase in the*

¹ Derived from Ancient Greek *εὖ* + *τροφή* = good, well + nourishment, food; + the Latin suffix *-tion* to generate a noun with a continuative aspect.

² “‘*Eutrophication*’ means the enrichment of water by nutrients 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 and to the quality of the water concerned, and therefore refers to the undesirable effects resulting from anthropogenic enrichment by nutrients as described in the Common Procedure”

supply of organic matter', chlorophyll *a* was used as a proxy for phytoplanktonic biomass. Accordingly, the same approach and definition were used in chapter 5.

1.1. Some stepping stones to the current understanding and management of eutrophication

Research linking organic pollution of freshwaters and the organismic and ecological response dates back to 1853, when the botanist Ferdinand Cohn investigated the relationship between the degree of pollution, the amount of organic material and the aquatic faunal and floral assemblage in freshwaters (Cohn, 1853). Einar Naumann first used the terms oligotrophic and eutrophic in 1917 (Naumann, 1917) when he described different types of lakes and 11 years later, August Thienemann (1928) first elucidated differences in dissolved oxygen concentrations between oligotrophic and eutrophic lakes. Research on nutrient limitation of arable crops was initiated by Justus von Liebig in his Law of the Minimum (1855), stating that the yield of crops was limited by the nutrient that is present in the environment in the least quantity relative to a plant's demands for growth. With the Redfield ratio (Redfield *et al.*, 1963) for the average atomic ratio of the elements C:N:P in marine seston of 106:16:1, the concept of nutrient limitation was introduced into biological oceanography. Its consequences for the shaping of benthic and planktonic algal communities are still being investigated extensively today.

The early driving force for research into freshwater quality was primarily hygienic problems and public health issues (*e.g.* cholera outbreaks) arising from polluted drinking waters. Research on coastal and estuarine eutrophication lagged considerably behind its freshwater counterpart for several decades, mainly because these waters were not used to supply drinking water, but also because the effects of organic pollution and

eutrophication where either masked by the sheer size and dynamics of the studied systems, or simply had not occurred yet. However, accelerated economic growth, increased agricultural production and urbanisation after 1945 led to such an increase in N and P inputs to coastal ecosystems that the buffering capacity of many of these was overcharged. In 1955 the first scientific documentation of red tides off the west coast of Florida was published (Feinstein *et al.*, 1955). Together with the emerging understanding of the links between imbalances in nutrient supply and excessive algal growth, by 1971, marine eutrophication was identified as a major threat to ecosystem integrity (Ryther and Dunstan, 1971).

Over the following decades, estuarine and coastal waters in many areas of the globe underwent cultural eutrophication (Gray *et al.*, 2006). For Europe the main areas affected were (and some still are) the northern Adriatic (*e.g.* Justić *et al.*, 1995a; Degobbis *et al.*, 2000) and other parts in the Mediterranean (*e.g.* Bethoux *et al.*, 2002; Perez-Ruzafa *et al.*, 2002), the Baltic (*e.g.* Bonsdorff *et al.*, 1997; Rosenberg *et al.*, 1990), the Black (Kideys, 2002) and the North Sea (*e.g.* Riegman *et al.*, 1992; Carstensen *et al.*, 2004; OSPAR, 2003a; 2008). Following the emerging understanding of the biogeochemical and physical processes governing coastal and estuarine eutrophication (Cloern, 2001; de Jonge *et al.*, 2002; Smith, 2006) it became clear that the detrimental environmental and economic consequences of eutrophication in marine and inland waters required a legal framework for the regulation and limitation of nutrient pollution. In the European Union this was done primarily via the Urban Wastewater Treatment Directive (91/271/EEC) and the Nitrates Directive (91/676/EEC). Both directives were initially targeted at inland waters but subsequently expanded to include estuaries and coastal waters. In 2000, the Water Framework

Directive (2000/60/EC) was introduced and now serves as an umbrella directive for the latter two and several other EU water quality policies.

1.2. Aims and objectives

Little is known about eutrophication dynamics in small, temperate estuaries like the Taw in North Devon (UK), but it is evident that anthropogenic eutrophication in the Taw Estuary is driven by a complex interaction of physical and chemical processes.

The overall aim was to identify and characterize the various physical and biogeochemical drivers influencing eutrophication dynamics over different temporal and spatial scales in the Taw Estuary.

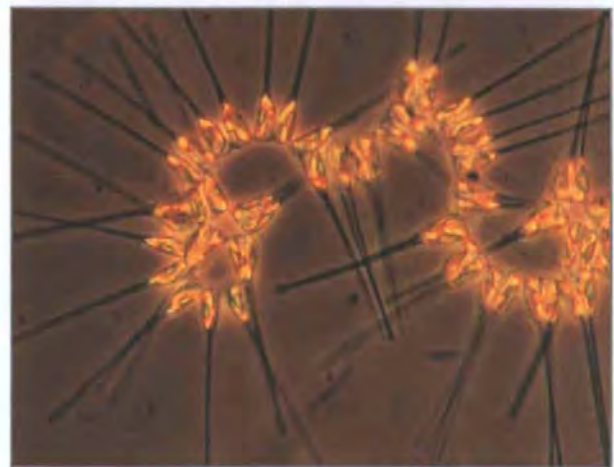
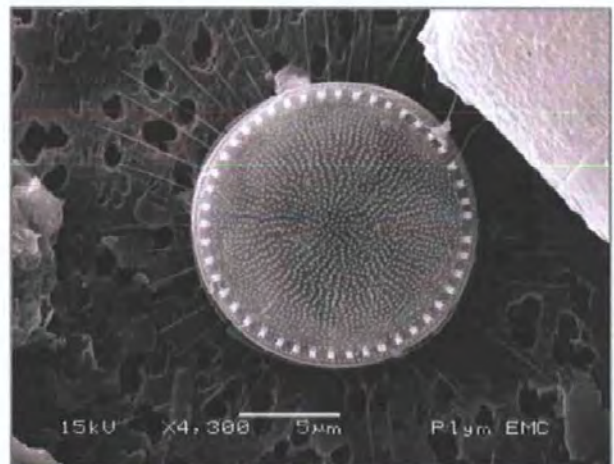
The objectives of this thesis are to:

1. Review and summarise the occurrence, management and future outlook of estuarine eutrophication in the UK (chapter 2).
2. Assess the suitability of regularly collected water quality monitoring data by the Environment Agency for England and Wales (EA) to identify the drivers of estuarine eutrophication, using the Taw as a case study (chapter 3).
3. Develop a reliable methodology for the collection and comprehensive chemical analysis of estuarine water samples for eutrophication studies (chapter 4).
4. Conduct a temporal high resolution survey to gain additional insights into bloom dynamics in the Taw and to assess potential climate change consequences for the Taw's trophic regime (chapter 5).
5. Generate a conceptual model of eutrophication in the Taw Estuary.

Specifically, the following hypotheses were tested:

- Data routinely collected by the Environment Agency are suitable to identify the drivers of eutrophication in the Taw Estuary (chapter 3).
- Phytoplankton growth in the Taw Estuary is governed by freshwater discharge from the River Taw (chapters 3 and 5).
- During phytoplankton blooms, silicon depletion and silicon limitation do occur (chapter 5).
- Multivariate analysis is suitable to identify distinct environmental conditions or states, which are characteristic for eutrophication events in the Taw (chapter 5).

**ESTUARINE EUTROPHICATION IN THE UK:
CURRENT INCIDENCE AND FUTURE TRENDS**



Thalassiosira guillardii
and *Asterionellopsis*
***glacialis*, two common**
diatom species in the Taw
Estuary.

2. Estuarine eutrophication in the UK: current incidence and future trends

2.1. Introduction

Eutrophication has been defined by OSPAR (2003b) as "... the enrichment of water by nutrients 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 and to the quality of the water concerned, and therefore refers to the undesirable effects resulting from anthropogenic enrichment by nutrients as described in the Common Procedure". Tett *et al.* (2007) defined an undesirable disturbance as 'a perturbation of a marine ecosystem that appreciably degrades the health or threatens the sustainable human use of that ecosystem', noting that the source of the problems arising from eutrophication is the uncoupling of production and use of organic matter in aquatic systems. This definition, like that of de Jonge and Elliott (2001), encompasses not simply the presence of excess nutrients but also adverse effects on the ecosystem such as enhanced algae growth, changing species composition, abundance and mass. This facilitates discrimination between eutrophication and hypereutrophication, in which excess nutrient inputs may not cause observable detrimental impacts within the estuary. This may often be the case in estuaries where, for example, high turbidity or rapid flushing times might limit primary production. However, estuarine environments are naturally stressed systems with an ecological assemblage reflecting the high degree of variability in physico-chemical characteristics, such as salinity, temperature and oxygen, as well as high organic productivity and inputs (Elliott and Quintino, 2007). This makes detecting the presence and extent of eutrophication resulting from anthropogenic

stressors in estuarine systems an important and challenging area of scientific debate (Dauvin, 2007; Tett *et al.*, 2007).

Eutrophication has been described as one of the greatest contemporary threats to the integrity of coastal ecosystems (Vitousek *et al.*, 1997; Vidal *et al.*, 1999) and it is widely accepted that the increased availability of nutrients (generally N and P) is a major factor that drives eutrophication in estuaries (Nixon, 1995; Nedwell *et al.*, 1999; Scott *et al.*, 1999; de Jonge and Elliott, 2001). Estuaries are among the marine systems most at risk, as they only have limited interaction with adjoining pelagic waters (Vollenweider, 1992). Rising global population and its associated activity has caused a substantial increase in inputs of N and P to estuarine and coastal waters. Although N and P inputs may decrease in industrialized countries, resulting from the implementation of new environmental legislation, this can be very slow and predictions for less industrialized countries are the reverse (Nixon 1995; Carstensen *et al.*, 2006; Gray *et al.*, 2006).

In the European Union (EU), eutrophication has been identified as a priority issue for fresh water protection for some years, but only recently concern has grown about transitional, coastal and marine waters (CIS, 2005). Two key policy instruments were introduced in the early 1990s to address the most significant pressures leading to eutrophication: the Nitrates Directive (ND, 91/676/EEC), which considers the agricultural contribution and the Urban Waste Water Treatment Directive (UWWTD, 91/271/EEC), which focuses on urban sewage discharges. The importance of atmospheric deposition has also been recognized and addressed most recently through the Thematic Strategy on Air Pollution, which notes the importance of agricultural sources of atmospheric nitrogen as well as combustion sources (principally energy and transport) to the eutrophication of surface waters (CEC, 2005). Now, the Water

Framework Directive (WFD, 2000/60/EC) has been introduced with new definitions of good ecological status and new goals for 2015. A Common Implementation Strategy for the EU is being developed for the WFD (CIS, 2005) and it seems an appropriate time to assess the current status of eutrophication in the UK, 20 years after the problem was first addressed, and to consider what progress has been made. The aims of this chapter are to summarize the occurrence of undesirable disturbance within UK estuaries and coastal waters, to identify the main drivers and pressures contributing to these occurrences, and to examine how the incidence of eutrophication may change in response to the application of the legislative framework outlined above.

2.2. Nutrient enrichment and the occurrence of eutrophic conditions in UK waters

The UK was required by both, the EU and OSPAR, to review its approach to eutrophication and its monitoring in the late 1990s/early 2000s, and this process has provided the rich source of data concerning the status of UK waters that has been distilled in this discussion. The occurrence of eutrophic waters within the OSPAR maritime area was reported in 2003, and was based on the first application of the Comprehensive Procedure (OSPAR, 2003a). The UK focused on offshore areas as part of this Procedure (all of which were classified as non-problem areas), but also included assessments of 16 estuaries and near-shore waters made under the UWWTD and the ND (Figure 2.1). Twelve sites were classified as problem areas and four as potential problem areas (Table 2.1). The OSPAR Comprehensive Procedure generally covered the years 1990 to 2001 and the results for the UK are shown in detail in Table 2.2. They can be summarized as follows (OSPAR, 2003a):

- (i) Several estuarine and coastal areas showed increased riverine N and P inputs.
- (ii) Several estuarine and coastal areas showed elevated concentrations of dissolved inorganic nitrogen (DIN, *i.e.* $\text{NO}_3 + \text{NO}_2 + \text{NH}_x$) and dissolved inorganic phosphorus (DIP, *i.e.* PO_4) in winter. Elevated concentrations (defined as >50% above salinity related and/or region specific background concentrations) of winter DIN are $>10 \mu\text{mol N L}^{-1}$ and winter DIP are $>0.8 \mu\text{mol P L}^{-1}$ for the UK.
- (iii) Many areas experienced elevated winter DIN:DIP ratios.
- (iv) Several areas showed elevated levels of chlorophyll *a*. Concentrations of chlorophyll *a* considered elevated (>50% above salinity related and/or region specific background concentrations) are $>10 \mu\text{g L}^{-1}$ for UK offshore waters (>34 salinity) and $>15 \mu\text{g L}^{-1}$ for UK coastal waters (<34 salinity). Region specific levels were used to assess elevated levels of chlorophyll *a*, but it was not specified whether reference values were defined for means or maxima. The UK did not derive its chlorophyll *a* definitions from background concentrations but from chlorophyll *a* concentrations expected based on nutrient concentrations found in adjacent Atlantic waters.
- (v) Available data on phytoplankton communities were examined in relation to perturbations of the balance of organisms resulting from nutrient enrichment. All areas were classified as non-problem areas, *i.e.* no evidence of impacts on the balance of organisms, despite the occurrence of elevated nutrient concentrations and/or DIN:DIP ratios. In the offshore southern North Sea, Continuous Plankton Recorder (CPR) data provided evidence of a changing

diatom to flagellate index, but this was explained by climate variability (Edwards *et al.*, 2001).

- (vi) Some areas showed shifts in macrophyte (including macroalgae) species and abundance, from long-lived species like eelgrass to nuisance short-lived species like *Ulva*.
- (vii) Dissolved oxygen concentrations were generally good, although a degree of oxygen deficiency occurred in one local case.

Considering the nutrient loads³ to coastal waters, the UK's National Marine Monitoring Programme (NMMP) identified that, from 1985–2001, annual inputs of DIP (river and direct discharges) to UK coastal waters fell by 40–50%, but there was no reduction in DIN inputs (MEMG, 2004). In relation to direct discharges, from 1990–2001, annual inputs of DIN and DIP have declined by 30–40%, reflecting the effectiveness of measures taken to control point source discharges direct to marine waters. It was added that the recent extension of Nitrate Vulnerable Zones (NVZ) and DIP stripping at inland sewage treatment works (STW) is expected to decrease diffuse inputs of N and direct inputs of DIP to rivers (MEMG, 2004). Monitoring the nutrient status of UK coastal waters is restricted to winter months, aiming to estimate maximum DIN and DIP concentrations, and hence indicate the concentration of nutrients available to support spring algal growth (MEMG, 2004). However, concentrations continue to rise during late winter and early spring until conditions are suitable for algal growth, and also vary considerably on a short-term basis. Annual winter nutrient samples for 37 sites around the UK, from 1999–2001, revealed the following (MEMG, 2004):

(Continued on page 16)

³ Nutrient load: the amount or mass of a given nutrient received by a body of water (*e.g.* an estuary) from a river over a certain time span, *e.g.* kg d⁻¹ or t a⁻¹.

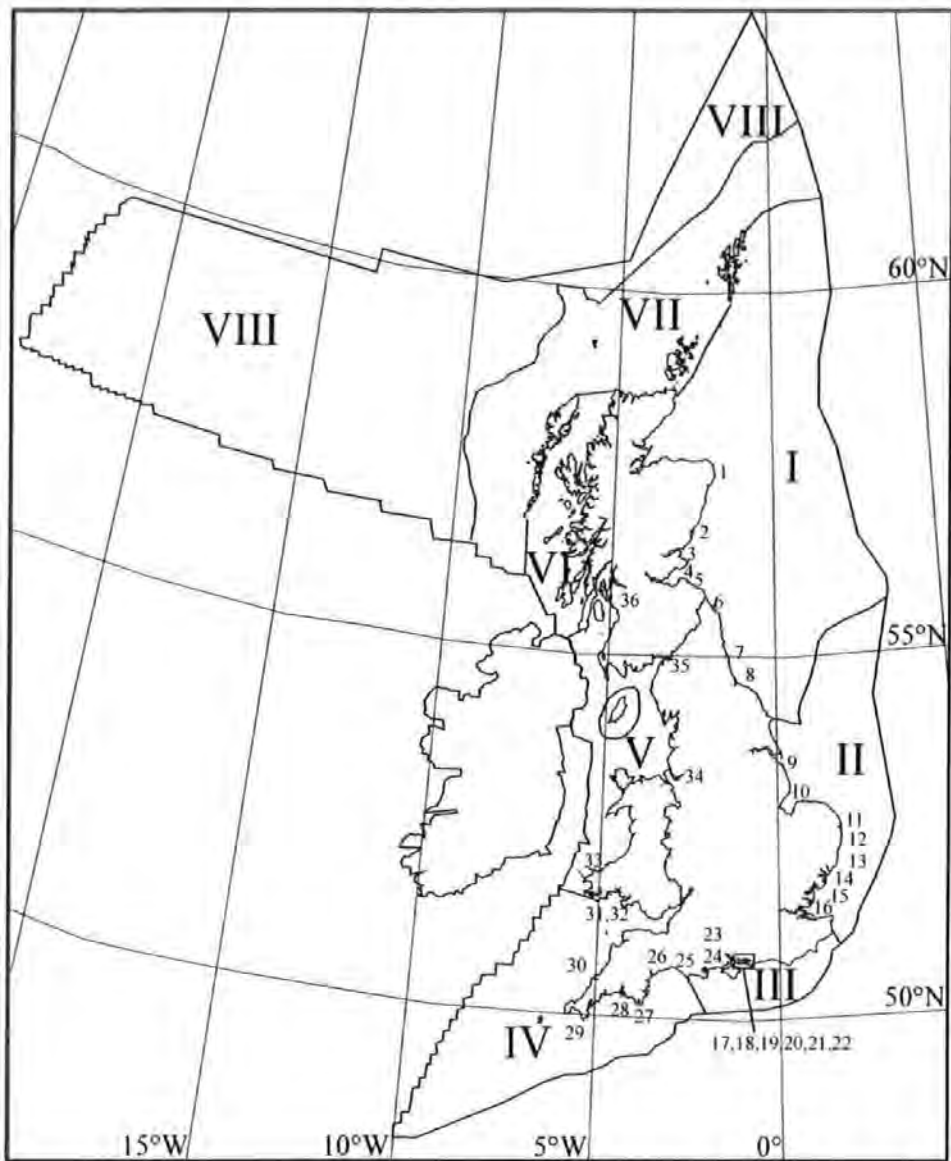


Figure 2.1. Locations of coastal and estuarine waters assessed for their eutrophic status as part of national and international monitoring programmes. UK regional seas: I-Northern North Sea, II-Southern North Sea, III-Eastern English Channel, IV-Western English Channel, Celtic Seas and South-West Approaches, V-Irish Sea and North Channel, VI-West Scotland including the Minch, VII-Scottish Continental Shelf, VIII-Atlantic North-West Approaches, Rockall Trough and Faroe/Shetland Channel. Estuarine waters: 1, Ythan Estuary; 2, Montrose Bay; 3, Tay Estuary; 4, Eden Estuary; 5, Forth Estuary; 6, Lindisfarne; 7, Tyne Estuary; 8, Seals Sands (Tees Estuary); 9, Humber Estuary; 10, Wash; 11, Deben Estuary; 12, Orwell Estuary; 13, Stour Estuary; 14, Colne Estuary; 15, Crouch Estuary; 16, Blackwater Estuary; 17, Pagham Harbour; 18, Selsey Bill; 19, Chichester Harbour; 20, Langstone Harbour; 21, Portsmouth Harbour; 22, Southampton Water; 23, Holes Bay; 24, Poole Harbour; 25, Fleet Lagoon; 26, Exe Estuary; 27, Erme Estuary; 28, Tamar Estuary; 29, Fal complex; 30, Taw Estuary; 31, Tawe Estuary; 32, Loughor Estuary; 33, Cardigan Bay (R. Teifi); 34, Mersey Estuary/Liverpool Bay; 35, Solway Estuary; 36, Clyde Estuary; 37, Belfast Lough; 38, Strangford Lough. From Nedwell *et al.* (2002), OSPAR (2003a), DEFRA (2004).

Table 2.1. UK estuarine and coastal waters and estuaries classified under the OSPAR Comprehensive Procedure, the Nitrates Directive (ND) and the Urban Waste Water Treatment Directive (UWWTD); Numbers indicate position of sites as shown on map in Figure 2.1. From OSPAR (2003a).

| No. | Water body | OSPAR | ND | UWWTD |
|-----|--|-------|---|----------------------------|
| 19 | Chichester Harbour (England) | PA | | Sensitive Area (Eutrophic) |
| 24 | Holes Bay - a small part of Poole Harbour embayment (England) | PA | Part of the Poole Harbour Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 37 | Inner Belfast Lough and Tidal Lagan Impoundment (Northern Ireland) | PA | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 20 | Langstone Harbour (England) | PA | | Sensitive Area (Eutrophic) |
| 6 | Lindisfarne NNR Area (England) | PA | Eutrophic Water NVZ | |
| 32 | Loughor Estuary (Wales) | PPA | | Sensitive Area (Eutrophic) |
| 17 | Pagham Harbour (England) | PA | | Sensitive Area (Eutrophic) |
| 24 | Poole Harbour (England) | PPA | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 21 | Portsmouth Harbour (England) | PPA | | Sensitive Area (Eutrophic) |
| 38 | Quoile Pondage - in Strangford Lough catchment (Northern Ireland) | PA | NVZ | Sensitive Area (Eutrophic) |
| 8 | Seal Sands, Tees Estuary (England) | PA | | Sensitive Area (Eutrophic) |
| 30 | Taw Estuary (England) | PA | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 31 | Tawe Estuary Impoundment (Wales) | PA | | Sensitive Area (Eutrophic) |
| 25 | The Fleet (England) | PPA | Eutrophic Water NVZ | |
| 29 | Truro, Tresillian and Fal Estuaries (England) | PA | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 1 | Ythan Estuary (Scotland) | PA | NVZ | Sensitive Area (Eutrophic) |

Table 2.2. UK waters assessed under the OSPAR Comprehensive Procedure. NI Riverine total N and total P inputs and direct discharges. DI = Winter DIN and/or DIP concentrations; NP = Increased winter N/P ratio; Ca = Maximum and mean Chlorophyll a concentration; Ps = Region/area specific phytoplankton indicator species; Mp = Macrophytes including macroalgae; O₂ = Degree of oxygen deficiency; Ck = Changes/kills in zoobenthos and fish kills; Oc = Organic carbon/organic matter; At = Algal toxins (DSP/PSP mussel infection events); + = Increased trends, elevated levels, shifts or changes in the respective assessment parameters; - = Neither increased trends nor elevated levels nor shifts nor changes in the respective assessment parameters; ? = Not enough data to perform an assessment or the data available is not fit for the purpose; NPA = Non-problem area; PPA = Potential problem area; PA = Problem area. Numbers indicate position of sites as shown on map in Figure 2.1. From OSPAR (2003a).

| Area | No. | NI | DI | NP | Ca | Ps | Mp | O ₂ | Ck | Oc | At | Class. |
|---|-------|----|----|----|----|----|----|----------------|----|----|----|--------|
| Offshore Central North Sea | I | - | - | - | - | - | - | - | - | - | - | NPA |
| Offshore Southern North Sea | II | - | - | - | - | ? | - | - | - | - | - | NPA |
| South East England coastal water - Humber to Norfolk area | 9-11 | + | + | + | + | - | - | - | - | - | - | PA |
| South East England coastal water - Norfolk to Thames | 11-16 | + | + | + | + | - | - | - | - | - | - | PA |
| Irish Sea / Liverpool Bay Region | V | + | + | - | + | - | - | - | - | - | - | PA |
| Mersey estuarine area | 34 | + | + | - | + | - | - | - | - | - | - | PA |
| Bristol Channel coastal water | 30-32 | + | + | - | - | - | - | - | - | - | - | PPA |
| East Coast of Scotland - Aberdeenshire Coast | 1-2 | - | - | - | - | - | - | - | - | - | - | NPA |
| East Coast of Scotland - Angus Coast | 2-3 | - | - | - | - | - | - | - | - | - | - | NPA |
| Montrose basin | 2 | - | - | - | - | - | + | - | - | - | - | PPA |
| East Coast of Scotland - Tay Estuary | 3 | + | - | - | - | - | - | - | - | - | - | PPA |
| East Coast of Scotland - Tay to Forth | 3-5 | - | - | + | - | - | - | - | - | - | - | PPA |
| East Coast of Scotland - Forth Estuary | 5 | - | - | + | - | - | - | - | - | - | - | PPA |
| East Coast of Scotland - Firth of Forth | 5 | + | - | - | - | - | - | - | - | - | - | PPA |
| Eden Estuary | 4 | + | + | - | - | - | - | - | - | - | - | PPA |
| East Coast of Scotland - Berwickshire Coast | 5-6 | - | - | - | - | - | - | - | - | - | - | NPA |
| Clyde Estuary | 36 | + | + | - | - | - | - | + | - | - | - | PA |
| Firth of Clyde | 36 | + | + | - | - | - | - | - | - | - | - | PPA |
| Solway Estuary | 35 | + | - | + | + | - | - | - | - | - | - | PA |
| Solway Firth | 35 | + | - | - | - | - | - | - | - | - | - | PPA |

- (i) Median total oxidized nitrogen (TO_xN , *i.e.* NO_3+NO_2) exceeded OSPAR assessment criteria in the inshore waters of the Wash, Clyde, Belfast Lough, Liverpool Bay, Cardigan Bay, Southampton Water and Thames (Figure 2.1).
- (ii) Median DIP concentrations exceeded OSPAR assessment criteria in the inshore waters of the Thames, Clyde, Belfast Lough, Liverpool Bay, Cardigan Bay, Forth and Humber.
- (iii) It is assumed that N is the limiting nutrient in coastal waters, but it was in excess when compared with DIP at 17 of the 37 sites sampled, and at almost all the sites when compared with Si. The Wash and Selsey Bill exhibited the greatest excess of N.
- (iv) The DIN:DIP ratio was greater than 25:1 in the Wash, Selsey Bill, Cardigan Bay, Celtic Deep and close to the Thames at South Varne. The NMMP did not collect data on the biological effects of nutrient inputs, but the report advised that future monitoring should include routine measurements of chlorophyll *a* and assessment of phytoplankton species composition.

DEFRA, reviewing the state of the UK's seas in 2005, identified the following for estuarine and coastal waters (DEFRA, 2005):

- (i) Since 1990 there has been a 35–50% reduction in direct inputs (*i.e.* loads) of N and P (similar to the 30–40% reduction stated in MEMG (2004)), although riverine inputs, which are in part dependent on river flows, have not shown any significant change.
- (ii) UK marine waters with significant freshwater influence, which are confined to estuaries and coastal waters close to large rivers, tend to have elevated

levels of nutrients but are often turbid, and so less susceptible to the risk of excessive growth of phytoplankton. This demonstrates the difference between hypernutrified and eutrophic waters since a secondary factor, turbidity, may limit primary productivity in these waters. DEFRA consider that waters beyond these areas are dominated by the movement of Atlantic waters and generally unaffected by direct anthropogenic nutrient inputs.

The threat posed by anthropogenic nutrient inputs to the ecological status of marine waters varies by region in the UK. The highest concentrations of nutrients occur in coastal areas off the south-east coast of England in Region II (Figure 2.1) but the indicative effects are generally below the OSPAR assessment criteria (OSPAR, 2005a). It is probable that tidal mixing, shallow water depth and turbidity prevent undesirable disturbance in this region. Riverine inputs from Region II account for about 40% of total UK nutrient inputs. These are affected significantly by flow variability and only marginal reductions in N inputs have been achieved in this area. In contrast, on the north-eastern coast of the UK (Region I), inputs of N have been reduced by 60% while in the north-west of Scotland (Regions VI, VII and VIII) no problems were evident and nutrient concentrations were low in the south-west (Region IV). The Irish Sea (Region V) and the Channel (Region III) both have enhanced nutrient inputs influenced by human activities. In terms of effects, the highest concentrations of chlorophyll occur in Region V (the north-eastern Irish Sea) where concentrations occasionally exceed the OSPAR assessment criteria. DEFRA (2005) noted that records from the CPR suggest that UK offshore waters are not generally affected by nutrient inputs from land based sources and effects are limited to localized inshore areas such as the Ythan Estuary, Chichester, Langstone and Portsmouth Harbours and inner Belfast Lough.

In view of the WFD, it will be necessary to standardize the definitions used to describe the boundaries between good and moderate ecological status (see section 2.4.2.2 and Table 2.3) to give clarity and ensure agreement throughout appropriate ecoregions in the EU. Multimetric indices are being developed for eutrophication that incorporate the causes and effects within estuaries and coastal waters. For example, Devlin *et al.* (2007a) propose incorporation of indices of pressure (nutrient concentrations), state (potential primary productivity) and impact (oxygen depletion) into a hierarchy, such that high nutrient inputs alone, without evidence of excessive primary production, will define water as good rather than high quality, while if there is also elevated primary production the water body will be defined as moderate or poorer quality. This enables the susceptibility of waters to respond to high nutrient inputs, identified by Painting *et al.* (2007), and linked to light availability and water residence times, to be taken into consideration. Similar indices are being developed with respect to a range of parameters that may be affected by excessive nutrient inputs, including benthos and attached macroalgae (Borja *et al.*, 2007; Wilkinson *et al.*, 2007).

2.3. Pressures leading to nutrient enrichment

Estuaries receive nutrient inputs from river and other runoff, the atmosphere, submarine groundwater discharges (SGD), waste discharges, mariculture and from adjacent coastal waters. Nutrient inputs to an estuary, either directly or via riverine inputs, can originate from either point (*e.g.* waste discharges) or diffuse sources (*e.g.* atmospheric, leaching from surrounding land). Point sources are localized and they are easier to monitor and control (Smith *et al.*, 1999), while diffuse sources are much more difficult to regulate (Scott *et al.*, 1999). The relative contribution of diffuse and point inputs to an estuary's nutrient load varies spatially, depending primarily upon local human population densities and land use. For the UK, a significant correlation between urbanization and

catchment area-normalized nutrient load⁴ has been seen for P, but no correlation was apparent for N (Nedwell *et al.*, 2002). Nedwell *et al.* (2002) attributed this to the significance of STW's as the major source of P in densely populated catchment.

2.3.1. Riverine inputs and direct discharges to estuaries

DEFRA reported estimates of the riverine and direct inputs of DIN, NH_x (separately) and DIP to UK estuaries and coastal waters for the period 1990–2003 as part of the OSPAR Comprehensive Study on Riverine Inputs and Direct Discharges (DEFRA, 2005; OSPAR, 2005a). Littlewood *et al.* (1998) also calculated river loads of these nutrient fractions to UK estuaries for the longer period of 1975–1994, using the National River Flow Archive and the Harmonised Monitoring Scheme databases. These time series are shown in Figure 2.2.

The river loads of DIN are approximate to 250 000 t a⁻¹, with NO₃ the dominant measured fraction. The largest inputs occurred in the high flow years, reflecting the importance of diffuse, agriculturally derived, sources of NO₃. Overall, however, there has been no underlying change in the magnitude of the loads (Littlewood *et al.*, 1998; DEFRA, 2005). In contrast, direct inputs of DIN decreased from 115 000 t in 1990 to 75 000 t in 2003, largely because of a reduction in NH_x discharges from 78 000 t to 43 000 t over the same period. River inputs of DIP showed no clear trends, with loads of ca. 15 000–20 000 t a⁻¹. Direct inputs of DIP have halved, however, from 22 000 t in 1990 to 10 000 t in 2003 (Figure 2.2), reflecting the change in sewage treatment works discharges to estuarine waters. On a regional basis, increasing loads of river DIN and

⁴ Catchment area-normalized nutrient load: Estuaries of large rivers with large catchments usually have greater annual nutrient loads than small rivers with small catchments. Following Nedwell *et al.* (2002), the catchment area-normalized loads permit comparisons by removing such differences in catchment size. The loads of nutrients derived per km² catchment gives information about the relative export loads of nutrients per unit of catchment area.

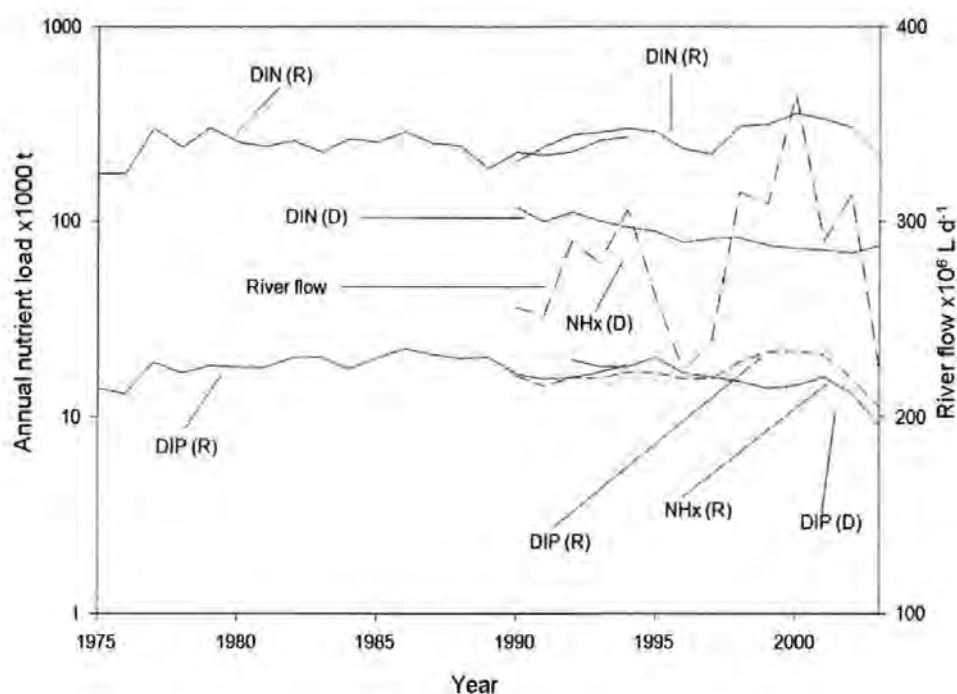


Figure 2.2. Annual estimates of river and direct discharges of DIN, DIP and ammonium (NH_4) and river flow (right hand axis) to UK coastal waters between 1975 and 2003. Data from 1975–1994 are from Littlewood *et al.* (1998); data from 1990–2003 are from DEFRA e-Digest Environmental Statistics, coastal and marine waters (accessed 25/5/06). R=river, D=direct.

DIP have been identified (OSPAR, 2005a). Nedwell *et al.* (2002) conducted an assessment of river nutrient inputs on a catchment basis and calculated that the average catchment area-normalized river DIN load to UK estuaries was $1570 \text{ kg N km}^{-2} \text{ a}^{-1}$. This was of the same order of magnitude found for other European catchments draining into the North Sea ($1450 \text{ kg N km}^{-2} \text{ a}^{-1}$; Howarth *et al.*, 1996). Total oxidised N loads were highest in areas draining high nitrate soils, which were often within Nitrate Vulnerable Zones (NVZs) (*i.e.* the Severn, Mersey, Clyde, Humber, Thames and around the Solent; Nedwell *et al.*, 2002). The majority of the UK's catchment area-normalized N loads were in the category 'moderately influenced by human activity' which was defined by Hessen (1999) to range from $500\text{--}2000 \text{ kg N km}^{-2} \text{ a}^{-1}$. In contrast, the average catchment-normalized river DIP load of $152 \text{ kg P km}^{-2} \text{ a}^{-1}$ was above the average load of $117 \text{ kg P km}^{-2} \text{ a}^{-1}$ for catchments around the North Sea, and was highest for the

Mersey and Thames catchments. Nedwell *et al.* (2002) also estimated estuary area-normalized loads⁵ based on the general assumption that a large estuary may be better buffered (*i.e.* less susceptible to detrimental effects) than a small estuary for a given nutrient loading. They found that there were large differences in the nutrient impact (*i.e.* increased or accelerated algal growth) on UK estuaries, with two orders of magnitude variation in the estuary area-normalized loads for the nutrients. Particularly high estuary area-normalized loads of TO_xN and DIP were found from the Tweed to the Humber and around the Solent. In contrast, most of the Welsh and north Scottish estuaries had much lower loads.

2.3.2. Aeolian inputs

Aeolian N is deposited via dry deposition of aerosols or wet deposition of rain, mist and cloud. Deposition can be from natural and anthropogenic sources, and will include the oxidized species nitric oxide, nitrous oxide, nitrogen dioxide and nitrate, and the reduced species ammonia and ammonium. The two main sources are nitrogen oxides from fossil fuel combustion and ammonia/ammonium and nitrate from agriculture (particularly N fertilizers and intensive livestock farming). The most recent estimate, from 1997, of N deposition in the UK is 380 000 t a⁻¹, of which 43% is oxidized N and 57% is reduced N (NEG-TAP, 2001). Areas of highest deposition include the uplands of northern England, Wales, regions of western Scotland, south-west England and East Anglia (Figure 2.3), and this is linked to ammonia emissions from cattle, pig and poultry farming in these regions.

⁵ Estuary area-normalized load: The amount or mass of received nutrients per unit area of estuary over time, *e.g.* kg km⁻² a⁻¹. This allows comparing the relative “nutrient pressure” that differently sized estuaries receive.

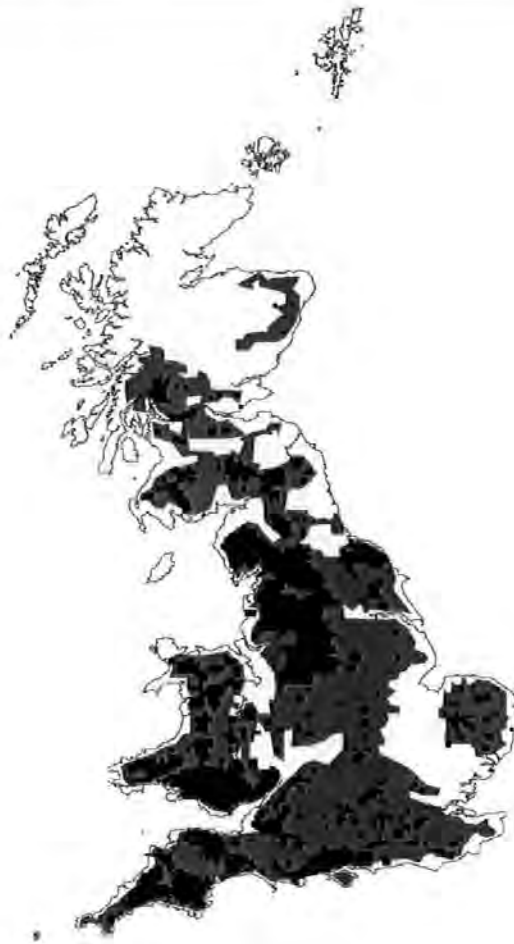


Figure 2.3. Total N deposition to the UK for 1997, calculated as the average deposition accounting for different land cover types. Grey=20–25 kg N ha⁻¹ a⁻¹; black=>25 kg N ha⁻¹ a⁻¹. Redrawn from NEG-TAP (2001).

The deposition patterns indicate that many catchments in the UK are receiving aeolian N inputs of similar magnitude as the area-normalized river inputs of N to estuaries (1570 kg N km⁻² a⁻¹). Resolving the proportion of the riverine N load, which originates from aeolian input in any one estuary is difficult and aeolian inputs may vary significantly geographically. A modelling study of sources of N to rivers in the Great Ouse, Nene, Welland and Witham catchments in East Anglia reported by DEFRA (2004) estimated that aeolian inputs contributed 5% of the total N river load, while agriculture accounted for 71% and point sources 24%. Reduced N is more reactive than oxidized N, its atmospheric residence time is much shorter (5 h compared with 30 h)

and most reduced N is deposited within 150 km of its source (NEG-TAP, 2001). However, it is likely that most of the major effects from ammonia occur in a very large number of small area deposition hot spots within a few hundred metres of intensive livestock units (Sutton *et al.*, 1998). Further afield, it has been reported that aeolian N accounts for 29–43% of total N inputs to the North Sea (OSPAR, 2005b).

Atmospheric inputs of P to surface waters are generally small, except perhaps in environments influenced by soil erosion (Sharpley *et al.*, 1995). However, there appear to be no data for the UK.

2.3.3. Submarine groundwater discharges (SGD)

Anthropogenic nutrient enrichment of groundwaters arises primarily from agriculture and urbanization. Globally, there is a paucity of data on SGD and their nutrient loads to near shore waters. Fluxes of N from SGD can vary over orders of magnitude (Slomp and van Cappellen (2004) reported N fluxes ranging from 160-72,000 $\mu\text{mol m}^{-2} \text{d}^{-1}$), and in some regions can rival river N inputs (Slomp and van Cappellen, 2004). The range in fluxes of P appears smaller (0.58-900 $\mu\text{mol m}^{-2} \text{d}^{-1}$; Slomp and van Cappellen, 2004), but is expected to be highest where the groundwater is anoxic (Krest *et al.*, 2000). DIN:DIP ratios in groundwaters are generally above the Redfield ratio, and therefore may have disproportionate impacts on N-limited receiving waters. Within the UK the influence of SGD on estuarine nutrient biogeochemistry is likely to be regionally variable (Nedwell *et al.*, 1999) although there appear to be no published data (Slomp and van Cappellen, 2004). It is likely that the largest SGD inputs of nutrients to estuaries and near shore waters will occur in regions of aquifer bearing strata outcropping at the coast and occurring within NVZs. These conditions are found in

north-east England, north and south of the Humber Estuary, north Norfolk, east Kent and along parts of the Channel coast, as shown in Figure 2.4.



Figure 2.4. Regions of aquifer bearing strata outcropping at the coast and occurring within Nitrate Vulnerable Zones. Grey=aquifer; black=groundwater NVZ. Reproduced with permission from UK Natural Environment Research Council and British Geological Survey.

2.3.4. Mariculture

Scotland contributes ca. 90% of all UK mariculture production (DEFRA, 2005), and the predominant farmed species is Atlantic salmon. The farms are mainly located in sea lochs of the west coast and Western Isles, Orkney and the voes of Shetland. Production increased from 80 000 t in 1996 to 150 000 t in 2002, with concomitant N inputs to coastal waters rising from 3200 t a⁻¹ to 6000 t a⁻¹ (Islam, 2005; SEPA, 2005). These estimates are based on 35–45 kg N t⁻¹ of fish produced, lower than the UK limit for salmon of 123 kg N t⁻¹ (Islam, 2005). In general, the impact of nutrients from

aquaculture in the UK is localized and where flushing is high the impact may be minimal, although the state of the marine environment around the islands is being studied for the OSPAR Comprehensive Review (SEPA, 2005).

2.3.5. Nutrient speciation and ratios

N and P fractions can be inorganic or organic and operationally defined as dissolved (<0.45 μm) or particulate (>0.45 μm). The inorganic species (*e.g.* NO_3 , NO_2 , NH_x , PO_4) are readily utilized by primary producers and appear to have more potential to limit plant growth. Dissolved and particulate organic N may be significant fractions of the total N load to estuaries (Bronk, 2002), and the extent of their bioavailability is only now beginning to be investigated. In relation to P, the quantity, composition and role of dissolved organic P requires further investigation (Nedwell *et al.*, 1999).

The concept of nutrient limitation is a keystone of eutrophication research (Smith *et al.*, 1999; Turner, 2002) and as important as element loads and concentrations. The average N:P atomic ratio of phytoplankton is 15.5:1 (Redfield *et al.*, 1963) and combined with the N:P ratio of 16.5:1 for zooplankton gives the Redfield ratio for marine seston of 16:1. It has often been postulated that this nutrient ratio is required for optimum growth of marine algae and biomass production would be limited by the nutrient that is first depleted (*i.e.* if ambient N:P ratios deviate widely from Redfield's ratio) and there is no other limiting factor (*e.g.* light or temperature). *In situ* growth rates are usually not affected by ambient nutrient ratios, as long as the absolute concentrations are high enough to sustain optimal growth. It is only after growth rates start to be limited by lowered nutrient concentrations that limitation of ultimate biomass production begins (Kocum *et al.*, 2002). Hecky and Kilham (1988) pointed out, however, that in order to determine which nutrient is possibly limiting, information on intracellular

concentrations should be favoured over nutrient concentrations in the water column, as it is often difficult to relate external concentrations to growth rates. For example, under conditions of ammonium-limited growth, *Thalassiosira pseudonana* (3H) and probably other small algae can grow at about 80% of their maximum growth rates while ammonium concentrations in the water column remain immeasurable (Kilham and Hecky, 1988). Biochemical composition of nutrient replete algae and cyanobacteria suggests that the critical N:P ratio that marks the transition between N- and P-limitation is likely to lie in the range between 15 and 30 (Geider and La Roche, 2002). Kamer *et al.* (2004) showed experimentally that *Enteromorpha intestinalis* (a ubiquitous nuisance species) from a southern Californian estuary with N:P tissue ratios of <26 was N limited, but they also raised the question that N:P ratios indicative of nutrient limitation may vary over regional and local scales and may be site- or species-specific. However, the general theory of nutrient limitation of algal growth has been demonstrated or inferred in many estuarine and marine ecosystems (Hecky and Kilham, 1988; Howarth, 1988; Vitousek and Howarth, 1991). In experiments, ambient nutrient limitation has been shown to have the potential to shape phytoplankton communities in fresh water (Tilman, 1977; Sommer, 1986) and estuarine environments (Piehler *et al.*, 2002) and it is known that the relative availability of Si determines the competitive success of diatoms (Hecky and Kilham, 1988 and literature cited therein).

Generally, N is the limiting nutrient in many coastal waters, P may limit the production in some estuarine systems, and nutrient limitation may switch seasonally in other estuaries (Howarth, 1988; Vollenweider, 1992; Vitousek *et al.*, 1997; Conley, 2000; Rabalais, 2002). However, this natural variation may be overridden by anthropogenic inputs and, for example, might be masked by inputs of STW effluents with relatively high P content (low N:P). In this case, the estuary might become N limited all year (*e.g.*

the Thames Estuary, Nedwell *et al.*, 2002). Seasonal switching has been related to sediment regeneration of P (Conley, 2000) and lack of N fixation by cyanobacteria in estuaries, combined with N loss by denitrification (Howarth, 1988). Nutrient limitation in UK estuaries is probably in the order $P > Si > N$ (Nedwell *et al.*, 2002). However, the potentially limiting nutrient indicated by nutrient ratios during the active growing season in the spring and summer may be quite different to that indicated by the mean annual nutrient ratio, as the peak fluvial inputs of NO_2 and NO_3 occur in the winter when growth is light limited (Nedwell *et al.*, 2002).

Estuaries are not only transitional waters in terms of salinity, but also by the decreasing degree of terrestrial influence towards the adjacent coastal waters. Terrestrial plants have high N:P ratios (up to 110; Hedin, 2004 and literature cited therein), which is reflected in the relative concentrations of N and P in the receiving rivers, where input of terrestrial plant debris plays an important role (Vannote *et al.*, 1980), while ocean water has N:P ratios approaching Redfield's. Consequently, estuaries exhibit steep gradients in nutrient concentrations and ratios between their fresh water head and their mouth. When the adjacent coastal water is potentially N limited (which is not always the case), a shift from potential P limitation to potential N limitation down estuary will probably occur. These inherent properties of estuarine environments often favour opportunistic, bloom-forming phytoplankton species and are likely to represent a natural state.

The terrestrial influence on estuaries is also reflected in nutrient pulses, following precipitation events in the catchment, which may account for 80–90% of the nutrient load delivered (Tappin, 2002). Experimental research on (temporal) nutrient patchiness (Sommer, 1986) has shown that individual species of algae respond quite differently to low, homogenous nutrient levels and to nutrient pulses. In an experiment with natural phytoplankton populations from Lake Constance, Sommer (1985) identified that in

populations exposed to static (*i.e.* unpulsed) Si and P inputs, only two species persisted, but in those with pulsed P and Si inputs between six and nine species survived. Kilham and Hecky (1988) assumed that both marine and freshwater algae respond to nutrient pulses in a similar manner. These findings may be important for the understanding of the processes behind algal blooms in UK estuaries, where nutrient inputs are often pulsed, following precipitation events in the catchment. During summer, when precipitation and consequently nutrient pulses are low or absent for weeks, these conditions, together with increased irradiation and temperature, might competitively enable one or two bloom-forming species, whereas under pulsed conditions a more diverse assemblage would persist.

2.3.6. Physical estuarine characteristics

In addition to the various forms of nutrient input to an estuary or coastal system, the physical characteristics of an estuary will influence its productivity and the likelihood that eutrophication as opposed to hypernutrification will occur (de Jonge and Elliott, 2001). High nutrient loads do not necessarily lead to undesirable disturbance in all estuaries, indicating the need for a comprehensive assessment to identify the risk of eutrophication in individual estuaries and coastal waters adjacent to hypernutrified estuaries.

Key variables affecting trophic status include the fresh water flushing time for the estuary, which dictates the residence time of the dissolved nutrients (Nedwell *et al.*, 1999; Scott *et al.*, 1999), the morphology of an estuary (including water depth) and its turbidity, which both have a controlling influence on light availability (de Jonge *et al.*, 2002), and the stratification of the estuary, which may support plankton in the surface layers while also facilitating the formation of bottom anoxia (Scott *et al.*, 1999). High

turbidity leading to a low light regime within estuarine waters frequently limits primary productivity in UK estuaries (Painting *et al.*, 2007).

Nutrients delivered to an estuary, which are not used for primary production can accumulate in the sediments or be transported into the coastal waters, but the relative importance of the roles played by these processes in individual estuaries is not well understood (Tappin, 2002). Estuaries are regions of sediment accumulation and both N and P can be retained within sediments, although this is more significant for P than for N. Depending on the nature of the estuary a significant proportion of the retained N may be removed from the system by denitrification within the sediments, while P may be temporarily stored and re-released in the future as conditions change (Tappin, 2002). Nutrients transported through hypernutrified estuaries may produce eutrophic symptoms in coastal waters. The WFD includes coastal waters to one nautical mile (three nautical miles in Scotland) offshore and hence these waters will also have to meet the required standard of good ecological status.

2.4.Potential future trends in eutrophication status

2.4.1. Impacts of existing legislation

2.4.1.1. OSPAR led activities

International agreements under the auspices of the EU and OSPAR have been crucial to the development of UK policy with regard to nutrient discharges and eutrophication. Three principal sources of nutrients to estuaries have been identified, each of which have separate control requirements: those discharged with urban wastes, those from agriculture and, for N discharges only, those entering via the atmosphere.

OSPAR adopted three recommendations concerning the reduction of nutrient (or nitrogen) inputs to estuaries and coastal waters in 1988, 1989 and 1992 (OSPAR, 2003a). However, it was not until the 'Strategy to Combat Eutrophication' adopted in 1997 and implemented through the Common Procedure, that the UK recognized a need to reduce nutrient discharges to coastal waters and eutrophication around its coasts. The Common Procedure identified those areas which clearly do not have a problem with respect to eutrophication and then required a comprehensive assessment of the remaining areas to categorize regions into problem, non-problem and potential problem areas as shown in Table 2.1.

Following the implementation of the Common Procedure, OSPAR is piloting an integrated set of Ecological Quality Objectives (EcoQOs) for eutrophication as part of an adaptive management approach to tackle the problem alongside its recommendations for reduction of pollution at source (OSPAR, 2005a). Based on the same classification process, these EcoQOs consider cause and effect criteria including winter nutrient concentrations (causes), phytoplankton indicator species and chlorophyll *a* concentrations (direct effects) and oxygen depletion and changes in zoobenthos (indirect effects). Atmospheric emissions of N are also recognized by OSPAR as a key input to marine waters which must be reduced if the aims of the Eutrophication Strategy are to be met. In their 2005 report they note the activities of the EU and other international fora, and point to their role in improving data collection and assessment (OSPAR, 2005b).

2.4.1.2. Urban Waste Water Treatment Directive (UWWTD)

The EU has adopted a multi-sectoral approach (Elliott and de Jonge, 2002) towards the control of anthropogenic nutrient enrichment that aims to combat both, point source

discharges, specifically sewage discharges under the UWWTD, and diffuse pollution, including agricultural pollution under the ND, and atmospheric discharges. To fulfil the requirements of the UWWTD it was necessary to assess the condition of water with respect to eutrophication, to determine whether action should be taken under the Directive to reduce inputs to a given water body. The selection methodology used to identify 'sensitive areas', with regard to nutrients, under the UWWTD is based on a water body being classed sensitive if it is, or is likely to become, eutrophic in the near future. There is also the possibility under the UWWTD of classifying areas, such as estuarial or coastal waters, as 'less sensitive areas' in which secondary treatment of sewage is not required.

From an initial selection of 38 sensitive areas in the UK under the UWWTD in 1995, there are now 347 across the UK, classified for reasons of eutrophication and as bathing waters (CEC, 2004). A number of areas not designated, including the Thames, Humber, Wash and some coastal waters, were subject to infringement proceedings (CEC, 2004). The designation of less sensitive areas (under the UWWTD), which allowed sewage treated to primary standard only to be discharged into areas classified as having 'High Natural Dispersion', was proposed when the UWWTD was introduced for the UK, but is no longer being applied (DEFRA, 2003). Therefore the application of the UWWTD with the Bathing Waters Directive (76/160/EEC) has been instrumental in improving the treatment of sewage effluent discharged to estuaries and coastal waters round the UK and has led to a reduction of NH_x and DIP, as already reported. However, while there has been a significant upgrading of sewage treatment works around the UK, to improve bathing waters, eliminate sewage sludge dumping at sea and tackle nutrient inputs, the European Commission is of the opinion that further upgrading the level of

sewage treatment and the performance of the facilities in sensitive areas is still necessary (CEC, 2004).

2.4.1.3. Nitrates Directive (ND)

As for OSPAR and the UWWTD, the ND requires water bodies to be classified according to current and likely future status. In the first instance the UK classified water bodies only for their impact on drinking waters and hence the emphasis was on classifying waters with a NO_3 concentration at or above 50 mg L^{-1} , the limit set by the World Health Organisation to protect human health. This led to 8% of England being classified as an NVZ. Following a judgement by the European Court of Justice that it was necessary to protect all surface and groundwaters, and not just those used for drinking, the UK Government broadened its classification to include surface waters which were, or were likely to become, eutrophic (EC, 2002). In October 2002 the UK Government classified 55% of the land area of England as NVZs (DEFRA, 2006), including five estuarine and coastal waters (see Table 2.1 and Figure 2.5). This land is now subject to action programme measures (see section 2.4.2.1) to reduce the losses of N and P compounds from agricultural land.

2.4.1.4. Policy on atmospheric inputs of nitrogen

The EU has recognized atmospheric inputs of nitrogen to ecosystems as a serious concern and in its Thematic Strategy on Air Pollution notes the scope for improvements in shipping, as a source of NO_x , and of farming, as a source of ammonia, to the atmosphere (CEC, 2005). The UK has met the emissions reductions for NO_x laid out in the UN CLRTAP (Convention on Long Range Transboundary Air Pollution) Nitrogen Oxide Protocol Target and the Fifth Environmental Action Programme, and NO_x emissions have decreased by *ca.* 45% since 1990. This trend has also satisfied the target

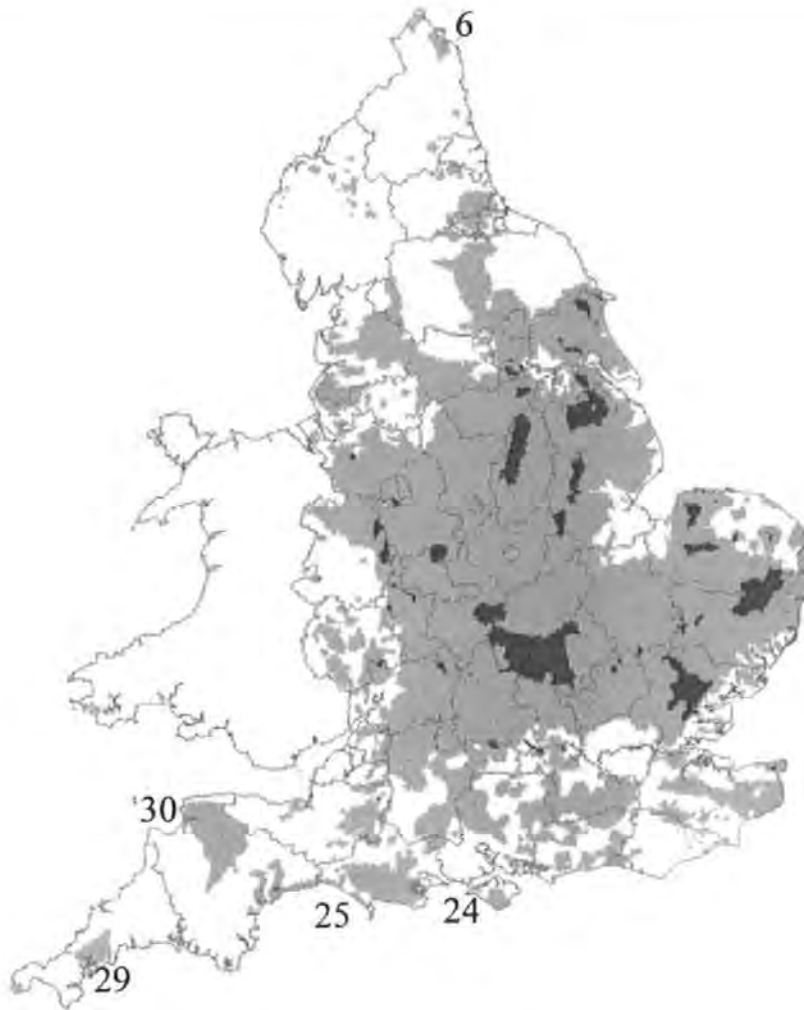


Figure 2.5. Nitrate Vulnerable Zones in England and Wales as designated in 1996 (dark grey) and 2002 (light grey). The numbers indicate the locations of the five estuaries designated as ‘Eutrophic Water NVZ’, see Figure 2.1 and Table 2.1. From DEFRA (2006).

of a 56% reduction in NO_x emissions over the period 1990–2010 under the UNECE Gothenburg Protocol (Cunha *et al.*, 2002). However, because only 20% of NO_x emissions are deposited in the UK, the wet and dry deposition of NO_x has shown only a small decrease since 1986 (NEG-TAP, 2001). Additional emissions policies for ammonia are found in the EC National Emission Ceiling Directive. The target of an 11% reduction in emissions between 1990 and 2010 is expected to be met (NEG-TAP, 2001). However, the strategy notes that even if existing legislation were fully implemented across Europe it is likely there would be only a 14% reduction on 2000

figures in the area affected by eutrophication. The strategy (CEC, 2005) calls for reductions of 60% in NO_x and 27% in NH₄ emissions relative to 2000 emissions and believes this can be achieved in part at least through streamlining and better managing existing legal instruments, including the Common Agricultural Policy (CAP), and also through introduction of new controls, such as those on shipping. In terms of the UK's estuarine and coastal waters the key is likely to lie with farming and the impact of the CAP is uncertain. It is proposed in the CAP strategy that additional controls on the N content in feedstuffs and action to prevent excessive use of nitrogen fertilizers may be appropriate (CEC, 2005).

2.4.2. The possible implications of future actions

2.4.2.1. NVZ Action Programme measures

The ND seeks to reduce and further prevent nitrate inputs from diffuse sources (*i.e.* agriculture) through the regulation of agricultural practices in 'vulnerable zones'. These (nitrate) vulnerable zones are areas which drain into waters (including estuaries, coastal waters and marine waters) that are found to be eutrophic, or may become eutrophic in the near future if no action is taken. The objectives of the ND are to be achieved through the implementation of Action Programme measures for the NVZs. These include rules concerning

- (i) seasonal periods considered suitable for application of organic fertilizer to sandy and shallow soils,
- (ii) the capacity of storage vessels for livestock manure in order to bridge closed periods (*i.e.* when manure must not be applied to land) and

- (iii) limitation on the quantity of fertilizers applied to land, taking into account (among other features) soil type and slope, N demand of the planted crop, and climate conditions. Appropriate record keeping detailing land use and management is also a requirement.

The UK was slow to implement controls on nutrients but now the Directive is being implemented over 55% of England (Figure 2.5).

The introduction of closed periods, when fertilizers may not be applied to land, may potentially have an impact during September in England and Wales, when light and temperature conditions are suitable for primary production. Reduction of N loads may limit the possibility of autumn phytoplankton blooms. However, this would depend on the residence time and losses of N within the estuary's catchment, which will vary spatially (*e.g.* according to soil type and topography) and temporally (*e.g.* weather/climate variability). In relation to manure specifically, the closed period would be most effective if applicable to all soil types (rather than just sandy or shallow soils), so that groundwater and surface water inputs to estuaries are protected from nitrate leaching. For example, in an arable or grassland area where clay soils dominate, the application of slurry during August or September prior to a high rainfall event is a potential source of nutrient enrichment.

Restricting the application of N fertilizer and organic manure when the soil is waterlogged, flooded, frozen or snow covered may reduce winter nitrate losses from the land to the estuary. This could potentially reduce spring N concentrations in the estuary, as less N will have been percolated in the soil during the preceding winter. This would be important in estuaries that are not P limited in spring. However, our understanding of the temporary burial of organic N and its release is limited. Inhibiting the application of

N fertilizer and organic manure on steep slopes will reduce N loss via runoff in certain catchments, and potentially reduce N inputs to estuaries in those catchments. During the summer and early autumn, a reduction in N loads to estuaries is likely to diminish the occurrence of nutrient enrichment. Spreading fertilizer or manure evenly and accurately, which is dependent on machinery being calibrated regularly, has the potential to reduce N loss, as has the regulation specifying that water courses should be protected from contamination by N fertilizer and organic manure by, for example, the use of buffer strips alongside streams. The NVZ measure on waste storage capacity will ensure that farmers can comply with the closed period regulations, which may contribute towards a reduction in nitrate leaching to ground and surface waters during the winter months when precipitation is highest.

Capping the total amount of N which can be applied to agricultural land also has the potential to reduce the amount lost to surface water. However, the limits set in England are high and for inorganic fertilizer application rates are based on crop requirements that relate to an economic optimum. This is likely to lead to high losses, as the residual soil N concentrations will be high and available for leaching. It has been noted that this implementation of the ND will require little change in practice for farmers in NVZs (Nimmo-Smith *et al.*, 2007).

It is possible that annual N loads to estuaries may be reduced as a result of NVZ Action Programme measures, but there is concern that this reduction may be too small to have any significant effect (ADAS, 2007; Nimmo-Smith *et al.*, 2007). The operation and interactions of environmental processes over a range of temporal and spatial scales may mask anticipated beneficial changes in water quality. These measures are fundamentally designed to impact on groundwater concentrations of N to protect drinking water quality and so they should, eventually, also lead to a reduction in submarine inputs but

the timescale for this is unknown. In 2007, DEFRA consulted on revisions to the Action Programme measures (DEFRA, 2007), which resulted in 'The Nitrate Pollution Prevention Regulations 2008' to be issued (Anonymous, 2008), where the maximum permitted amount of nitrogen to be spread was set ($0\text{-}330 \text{ kg N ha}^{-1}$, depending on crop).

2.4.2.2. Water Framework Directive (WFD)

Two key policy drivers can be expected to steer the change in the nutrient status of the UK's estuarine waters in the first decade of the 21st century: the first is the Water Framework Directive and the second is the Common Agricultural Policy. The WFD clearly addresses the status of transitional waters (such as estuaries, rias and coastal lagoons), integrating these with groundwater and inland surface water management. It requires member states to achieve 'high' or 'good ecological status' in all surface waters by 2015 (Table 2.3) and to ensure that there is no deterioration in water quality, is a far higher aspiration than has been the case in the past. It bases its assessment on ecological quality status, requiring evidence of impacts on biological quality elements, as well as supporting physico-chemical data to confirm the likely cause of the impacts.

Currently the European Commission is developing the Common Implementation Strategy for the WFD and in this it considers the implications of other initiatives and directives (CIS, 2005) to ensure the classifications are compatible. The WFD classification scheme for water quality is compared in Table 2.3 with those developed for the ND, the UWWTD and by OSPAR. This shows that all water bodies that are classified as 'sensitive' under the UWWTD, 'polluted' under the ND or a 'problem area' under OSPAR will need to be considered in a programme of measures alongside those which, even though they are currently classified as of 'good' or 'high' ecological status, may become eutrophic in the near future (CIS, 2005). The WFD specifically

Table 2.3. Comparison of assessment results under various policies for waters responding to nutrient enrichment (based on the assumption that the WFD classification is the starting point and that the different sources of pollution are relevant) From: CIS (2006)

| ASSESSMENT OF CURRENT STATUS | | | | |
|-------------------------------------|---|---|--|------------------|
| Ecological status | WFD normative definition | UWWT Directive | Nitrate Directive | OSPAR |
| High | Nearly undisturbed conditions | Non Eutrophic, designation of sensitive area is not required | Non Eutrophic, not a polluted water, designation of NVZ not required | Non-Problem area |
| Good | Slight change in species composition, biomass | Non Eutrophic, designation of sensitive area is not required | Non Eutrophic, not a polluted water, designation of NVZ not required | Non-Problem area |
| Moderate | Moderate change in species composition, biomass | Eutrophic or may become eutrophic in the near future, designation of sensitive area is required | Eutrophic or may become eutrophic in the near future, polluted water, designation of NVZ is required | Problem area |
| Poor | Major change in biological communities | Eutrophic, designation of sensitive area is required | Polluted water, designation of NVZ is required | Problem area |
| Bad | Severe change in biological communities | Eutrophic, designation of sensitive area is required | Polluted water, designation of NVZ is required | Problem area |

mandates the control and mitigation of diffuse pollution impacts (Haygarth *et al.*, 2003), and it is likely that the drive to achieve ‘good ecological status’ will override the implementation of the ND in many locations: the N application limitations laid out in The Nitrate Pollution Prevention Programme 2008 (Anonymous, 2008) may not be sufficient to achieve measurable improvements in an estuary’s trophic status and actions additional to those outlined in the NVZ action programme measures may be required. Ensuring clarity concerning these action levels and harmonizing the quality indices used will be key to ensuring efficient and effective management.

2.4.2.3. Common Agricultural Policy reform

The Common Agricultural Policy has been in existence for 40 years and during that time subsidies from the EU encouraged increased production partly by excessive use of fertilizers (de Clercq *et al.*, 2001). Now, recognition that supporting such intensive systems is expensive in terms of economic, social and environmental costs, the CAP is being revised. Some of the key elements of the CAP reform are

- (i) the decoupling of subsidies for farms from production,
- (ii) linking the payment to respect for environmental, food safety, animal and plant health and animal welfare standards, as well as the requirements to keep all farmland in good agricultural and environmental condition ('cross-compliance'),
- (iii) a reduction in direct payments for bigger farms, and
- (iv) asymmetric price cuts in the milk sector (CEC, 2003).

The aim of these reforms is, in part, to reduce the pressure on the environment.

GFA-RACE Partners Ltd (2004) investigated the potential impacts of the CAP reform on N and P losses in the UK and concluded that the losses to ground and surface waters are likely to be reduced. For example, farmers may be more focused on reducing input costs and targeting N and P use to crop requirements in the future. However, N and P losses will increase in certain regions where further specialization will occur, such as concentration of dairy production in the Southwest, Northwest and west Midlands. The study (GFA-RACE Partners Ltd, 2004) also considered how organic wastes will be affected by the reforms, suggesting that livestock numbers will decline overall, leading to a reduction in organic wastes in areas where livestock farming is predominant,

although consolidation within the dairy sector may present specific problems in some catchments as farm size and herds increase. Furthermore, investment in infrastructure on larger farms may help to reduce problems from organic wastes, but nutrient loading will remain a problem.

Therefore, at a national level, it would appear that CAP reforms will reduce N and P losses to the aquatic environment, but in relation to estuarine eutrophication, the picture is less clear. The location of the eutrophic estuaries is critical; if they are located in regions where dairy production concentrates for example, then it is possible that nutrient enrichment will increase. The Taw Estuary in Devon is one such example: it is classified as being eutrophic under the ND and UWWTD and the predominant land use in the catchment is dairy and livestock farming.

The UK's DEFRA recognizes diffuse water pollution from agriculture to be the greatest threat to the successful implementation of the WFD (DEFRA, 2007) and sees the implementation of the CAP reform as an important opportunity to reduce this threat. A modelling exercise by Haygarth *et al.* (2003) undertaken for DEFRA considered the likely interaction between the CAP and WFD requirements and identified that substantial changes in agricultural land use and management will be required to achieve 'good ecological status' in all waters by 2015. They propose for example, that to meet this goal it may be necessary to reduce stocking densities and to take certain sensitive areas out of production altogether (Haygarth *et al.*, 2003). Therefore, it is suggested that implementation of the WFD may require significant changes in agricultural practice if it is to achieve its aim to reduce nutrient enrichment and possibly estuarine eutrophication.

2.5. Do nutrient control measures work?

There is conflicting evidence on the ability of nutrient load control measures to reduce nutrient enrichment and the impact of eutrophication. Following a marked decrease in the use of commercial fertilizers in Eastern Europe in the late 1980s, European rivers responded only slowly and to a limited degree (Grimvall *et al.*, 2000). This could reflect residence time in the system or the importance of other nutrient sources (Grimvall *et al.*, 2000). The narrow, coastal inlets of the Bodden (Baltic Sea) have not shown recovery, despite decreases in nutrient inputs during the 1990s (Meyer-Reil and Köster, 2000). De Jonge (1997) concluded that there was no evidence that reduced loads of DIP from the River Rhine or Lake IJssel had proportionally reduced primary production in the western part of the Dutch Wadden Sea. In contrast, a clear relationship between partial recovery of the Black Sea's pelagic and benthic communities, seriously damaged by eutrophication, and reduced nutrient inputs has been reported (Rabalais, 2002). Tampa Bay (USA) experienced symptoms of over-fertilization in the 1970s, and remedial action included the installation of sewage treatment works and a decreased P loading from fertilizer applications. By 1980 the annual wastewater loading of N had decreased 10-fold and by 1990 the mean annual chlorophyll *a* biomass had decreased by more than half (Cloern, 2001). It appears that the use of nutrient load control measures is not straightforward in terms of reducing nutrient enrichment down-estuary. It is likely that effective water quality management requires both, a multi-dimensional approach to controlling nutrient discharges within catchments, and also a general multi-sectoral management strategy towards N and P, as demonstrated in the following examples.

Denmark's control of agriculturally-derived nutrient inputs to estuarine and coastal waters has been in development since 1987, when its first Action Plan for the Aquatic Environment was devised, and can be described as a multi-dimensional approach. The

Danish Action Plan measures go beyond the requirements of the Nitrates Directive, and include the reestablishment of wetlands, afforestation, improved feed utilization, and optimized livestock density requirements (Iversen *et al.*, 1998). These measures have led to farms' utilization of 65–75% of the N content in their organic manure (Winther, 2002), which has subsequently contributed towards a 37% decrease in the use of manufactured N fertilizer between 1985 and 2000 (Grant and Blicher-Mathiesen, 2004). Nitrate leaching from agricultural fields (the root zone) has been modelled for seven agricultural catchments in Denmark and the results showed a reduction of 32% over the period 1990–2000 (Grant and Blicher-Mathiesen, 2004). In addition, Andersen *et al.* (2004) stated that a 30% reduction of annual mean nitrate concentrations in streams within cultivated areas, over the period 1989–2002, was mainly due to reduced leaching from cultivated fields. Recently, it has been reported that total N concentrations in Danish estuaries and coastal waters have decreased by up to 44% over the period 1998–2003 (climate variability taken out), primarily in response to reduced diffuse inputs of nutrients (Carstensen *et al.*, 2006). The response time of Denmark's estuarine and coastal waters to controls on nutrient inputs has been longer than 10 years, reflecting the historical legacy of increased nutrient inputs, and the subsequent storage of nutrients in sediments and their long-term recycling to the water column.

Efforts to manage nutrient inputs from agriculture to the Chesapeake Bay have focused on Best Management Practices (Soil and Water Conservation Plans, Nutrient Management Plans, and state agricultural cost-share programmes) that aimed to prevent soil erosion, reduce nutrient application and control nutrient movement (Boesch *et al.*, 2001). Reduction of nutrient inputs by 40% was required to improve water quality in the Chesapeake Bay, yet reductions of non-point inputs of P and N, under the Chesapeake Bay's soil conservation-based management strategies, were projected by models to

achieve only 19% and 15% reduction (Boesch *et al.*, 2001). Strategies were successful in reducing P transport in areas of the Bay catchment predisposed to high erosion rates, but less effective in addressing dissolved nutrient transport in surface runoff or leaching to groundwater. Subsequently, there has been a lack of reduction in nutrient concentrations in streams and tidal waters in some areas of the Chesapeake Bay. It is suggested that a multi-sector approach is required to control nutrient inputs to the Chesapeake Bay in the future, including the development of more effective agricultural practices, reduction of atmospheric sources of N, enhancement of nutrient sinks, and control of suburban development (Boesch *et al.*, 2001). This perspective is also advocated by Whitall *et al.* (2004) who evaluated a variety of management strategies for reducing N export to four east coast US estuaries, concluding that comprehensive, multi-sector management is critical to effective N reduction and can result in 35–58% reductions in N loads to coastal ecosystems. In comparison, specifically in less urban catchments, reductions in agricultural loading alone can result in 5–56% reductions.

2.6. Scope for improvement in the UK

Whereas some UK estuaries undoubtedly do suffer from eutrophication (*sensu* de Jonge and Elliott, 2001; Table 2.1), a number of other UK systems have elevated nutrient inputs but do not present symptoms of eutrophication. This is largely owing to high tidal range, large fresh water flows and high estuarine turbidity. These characteristics result in a hypernutrified estuary which, while it does not present ecological symptoms of eutrophication, such as excessive algal growth or changes in species composition, will export the high nutrient load to the coastal waters, where such symptoms may be encountered. The UK has only slowly come to accept the need to implement strategies to protect estuaries from eutrophication, but under the WFD, as the definitions for the

new ecological status classifications are refined, the requirement for improved protection is apparent.

The UWWTD has been highly significant in reducing P and NH_x inputs to estuaries but there is limited scope for further reductions. Current implementation of the ND may have some impact on the nutrient status of estuaries, as the Action Programme measures are introduced across the catchments designated as NVZs following the European Court of Justice judgement in 2000, but on their own they are unlikely to enable estuaries to meet the WFD classification of 'good' or better (ADAS, 2007).

Significant improvements could be made through the current revision of the Action Programme measures by DEFRA following the examples of countries such as Denmark, but this will require a significant change in attitudes towards farming activities (Nimmo-Smith *et al.*, 2007). There is an opportunity now to make that change through the implementation of the CAP single payment scheme. Waterborne and atmospheric inputs from agriculture pose the most significant pressure on eutrophication in transitional waters in the UK and the CAP is a key policy driver, which could be addressed in association with the WFD to modify this pressure.

However, research is needed to observe the impacts of changes in policy and legislation on nutrient loads and estuarine eutrophication. Not only is the impact of changes to the Action Programme measures and the Single Farm Payment on farm practices uncertain, but also the effect of changes in practice on actual concentrations in surface water and their export to coastal waters is not easily predicted.

The significance of submarine groundwater discharges to eutrophication of estuarine and coastal waters is relatively unknown, whilst the importance of aeolian inputs of N to estuaries is poorly quantified. Responses to a change in emissions of nutrients from

agriculture may be slow and natural characteristics of estuaries may result in complex responses to this change. For example, nutrient storage in sediments, seasonal changes in primary production and responses to flash flood events all complicate assessments of the impact of changes in the drivers and pressures acting on the estuary.

The ability to make these connections between the policy drivers and the environmental impacts is critical to successful environmental management and, given the economic (and environmental) importance of sectors such as agriculture, fishing and tourism, the need for more research is very clear.

**THE USE OF MONITORING DATA FOR IDENTIFYING FACTORS
INFLUENCING PHYTOPLANKTON BLOOM DYNAMICS IN THE
EUTROPHIC TAW ESTUARY, SW ENGLAND**



Crab at Crow Point

3. The use of monitoring data for identifying factors influencing phytoplankton bloom dynamics in the eutrophic Taw Estuary, SW England

3.1. Introduction

For estuaries, which are highly dynamic environments, the links between nutrient inputs and organism response are not straightforward. Although N and P can be related to an increase in chlorophyll *a* concentrations in coastal and estuarine waters on a general basis (Smith, 2006), estuarine eutrophication is regulated through a range of ‘filters’ (Cloern, 2001). The relative contribution of each filter is system specific, which makes it difficult to relate biological responses linearly to nutrient inputs (Cloern, 2001). The two most important filters are probably light availability as a function of turbidity and freshwater flushing time. In nutrient rich, light-limited estuaries, symptoms of eutrophication may not develop at all and the estuary is termed hypernutrified (De Jonge and Elliott, 2001). Flushing time strongly controls primary production in an estuary (Painting *et al.*, 2007) and also shapes phytoplankton biodiversity (Ferreira *et al.*, 2005), simply by determining how long the cells remain in the estuary to reproduce before being flushed out to the sea.

The Taw Estuary was selected for this study as it is one of the few UK estuaries to be designated under both the UWWTD (as a “Sensitive Area (Eutrophic)”) and the ND (as a “Polluted Water (Eutrophic)”). In 1996 the Environment Agency for England and Wales (EA), during an assessment under the UWWTD, found evidence for eutrophication in the Taw including undesirable symptoms such as surface algal scum, concentrations of suspended chlorophyll *a* exceeding the OSPAR threshold of 15 $\mu\text{g L}^{-1}$

(OSPAR Commission, 2003), and diurnal fluctuations in concentrations of dissolved oxygen. Subsequently (1998), the estuary was designated a Sensitive Area (Eutrophic), with the requirement that inputs of nutrients from the main sewage treatment works (STW) at Ashford (Figure 3.1) be reduced by the end of 2004. In 2005 the EA estimated that diffuse sources of inorganic N to the estuary were significant throughout the year, contributing 99% of the N loading in the winter and up to 40% during the summer. On the basis of this assessment, the EA recommended that the Taw Estuary be classified as a Polluted Water (Eutrophic) under the ND. However, nutrient stripping following Action Plans under either Directive can be very expensive and for small catchments, such as the Taw, costs can quickly approach several million Euros (Atkins and Burdon, 2006; Gren, 2000). It is therefore clear that a sound understanding of the drivers that trigger algal blooms in an estuary is required to justify investment of public funds, particularly because the support of the local community for eutrophication management measures is imperative (Atkins *et al.*, 2007).

The main objectives of this chapter were to assess the potential of the large monitoring datasets, developed by the EA as a result of its statutory sampling obligations, to identify the drivers of excessive algal growth in the Taw Estuary, and to provide a template for further eutrophication assessments of UK estuaries using existing water quality monitoring data. To achieve these objectives, the specific aims of the study were to:

- (i) optimize data pre-treatment in order that the maximum amount of good quality information could be extracted,
- (ii) enhance information recovery from the dataset using appropriate statistical methods, and

- (iii) based on (i) and (ii), highlight where monitoring-type data collection (*i.e.* as opposed to surveillance, with monitoring being an assessment against some preconceived (*a priori*) standard; Elliott and de Jonge, 1996) under the ND and UWWTD can be improved in order to provide more robust eutrophication assessments of UK estuaries.

3.2. Materials and methods

3.2.1. Site description

The Taw Estuary is located in the south-west of England, draining an area of 1211 km² (Environment Agency, 2000) and forms, together with the Torridge Estuary, a twin estuarine system that discharges into the Bristol Channel (Figure 3.1).

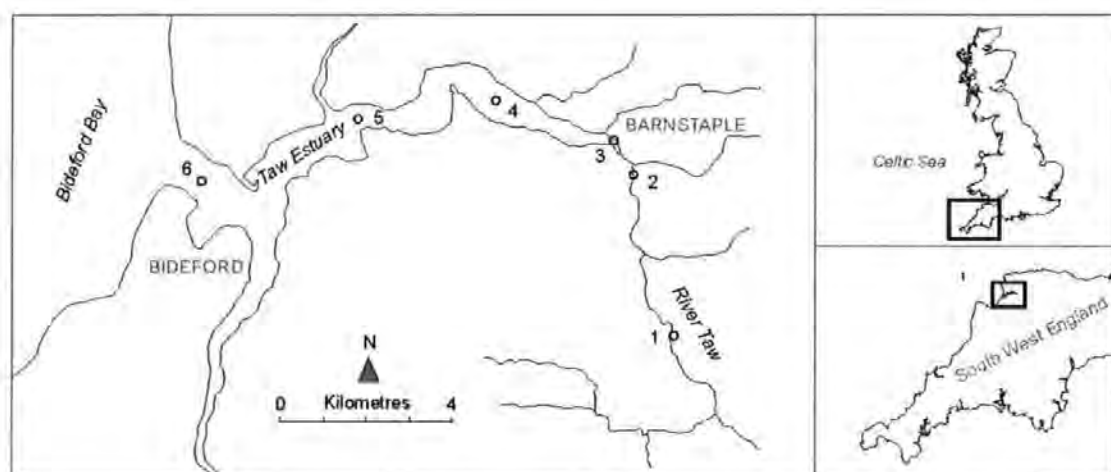


Figure 3.1. Location of the Taw Estuary. Circles represent Environment Agency water quality monitoring sites. (1) Newbridge; (2) Little Pill; (3) Barnstaple; (4) Ashford STW; (5) RAF Chivenor; (6) Airy Point.

The Taw Estuary is 23 km in length, extending from its tidal limit at Newbridge to its mouth. The estuary is macro-tidal (tidal range >4 m), with a tidal range at the mouth during spring tides of *ca.* 7 m and ≤ 5 m during neaps. Further up-estuary, at Barnstaple, the tidal range is *ca.* 4 m during springs and can be <1 m during neaps. The approximate

flushing time of the system is 2–3 days (Sturley, 1990) but may be considerably longer during neap tides and dry weather or shorter during spring tides and heavy rain. There are extensive intertidal sand and gravel beds (with some mud) at the mouth, and mud flats in the upper reaches. Above Barnstaple the estuary is dominated by freshwater, whilst the mid and lower reaches are usually influenced by coastal water, as shown in Figure 3.2a. However, at low tide during high river flows, the freshwater plume can extend as far as site 5. The main freshwater inflow to the estuary is from the River Taw. Average annual rainfall in the Taw catchment is highest near the source on Dartmoor (~2200 mm) and below 940 mm at the river mouth (Haygarth *et al.*, 2005). Precipitation is strongly seasonal and hence the River Taw has a distinct annual flow pattern with maximum mean flow in December ($\sim 40 \text{ m}^3 \text{ s}^{-1}$) and minimum flow in August ($5 \text{ m}^3 \text{ s}^{-1}$). The bedrock in the Taw catchment consists of granite in the south and Devonian shale and sandstones of Exmoor in the north. In the central area, the catchment is underlain mainly by Culm shale and Carboniferous sandstones (Marsh and Hannaford, 2008). The type of soil and subsoil, and the low groundwater storage in the catchment, means that the river responds quickly to rainfall, with rapid rises in river levels (Environment Agency, 2000); over 95% of the catchment is covered by clay and clay loam soils (Lord *et al.*, 2007). Although groundwater reserves are generally low, they do contribute to river base flows (base flow index of 0.47 at Umberleigh gauging station; Marsh and Hannaford, 2008) during dry periods (Haygarth *et al.*, 2005).

About 75% of the catchment area is used for agriculture (59% grassland, 14% arable), 12% woodland and forest and 9% rough grassland (Williams and Newman, 2006). An estimated 77% of the grassland is used for beef cattle and sheep, whilst the remainder is used for dairy cattle (Lord *et al.*, 2007). Given the relatively low population density ($\sim 80 \text{ km}^{-2}$) in the catchment, it can be assumed that most of the inorganic nutrient inputs

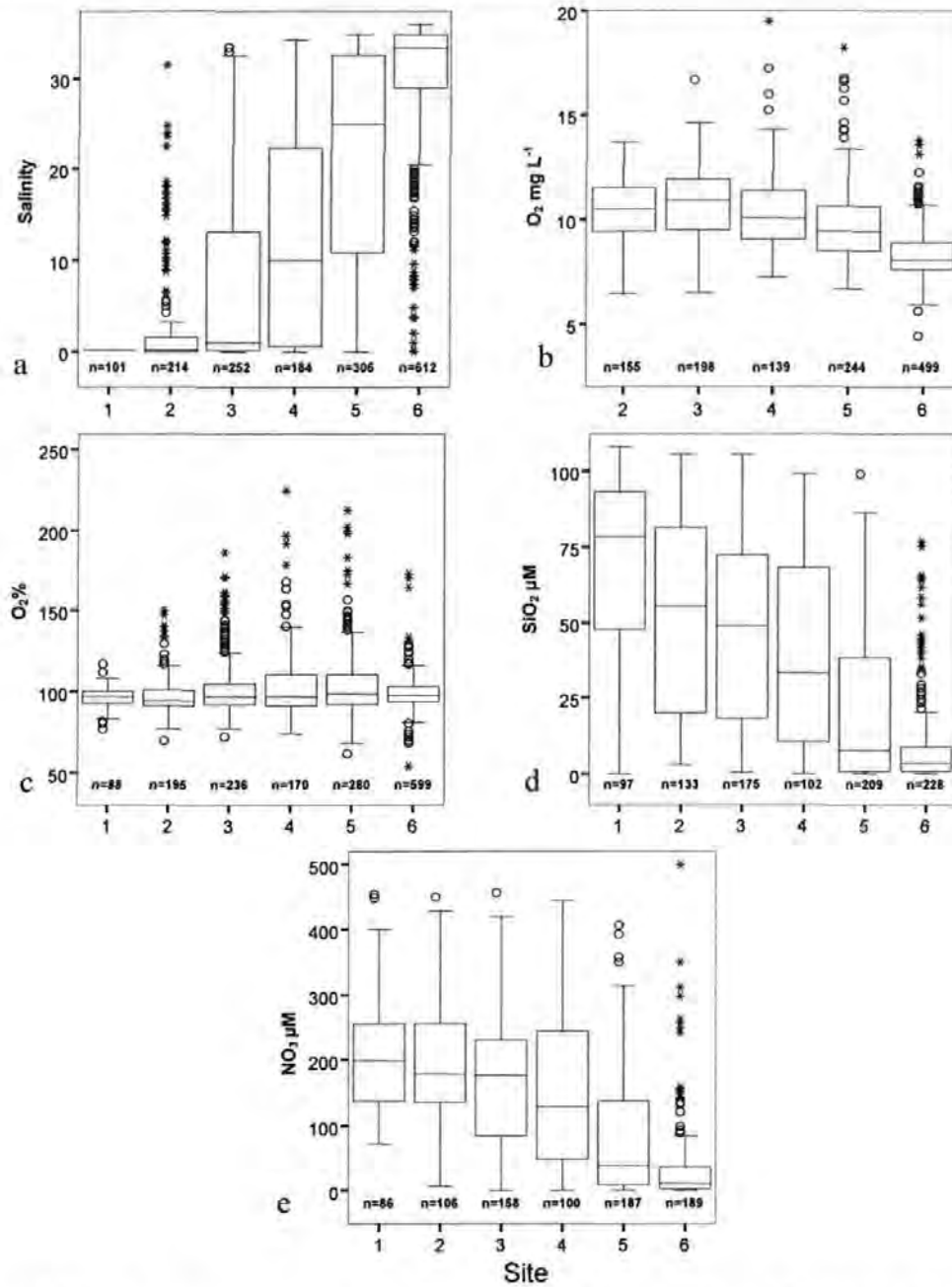


Figure 3.2. Box plots estuarine data at individual sample sites, collected by the EA between 1990 and 2004. Within the box are all observations between the first and third quartile (50% of total observations), the solid line inside each box is the second quartile (median). The whiskers represent 1.5x the interquartile range (IQR) from the box or, in the absence of values at the 1.5x IQR, the maximum and minimum value. Values outside the 1.5x IQR are shown in open circles, values outside the 3x IQR are depicted as stars. No data were available for O₂ mg L⁻¹ at site 1.

originated from diffuse agricultural sources. The main point source of nutrients to the estuary is the sewage treatment works at Ashford, processing the sewage from the town of Barnstaple (pop. 46,000).

3.2.2. Data sources

Physical, chemical and biological water quality data for the Taw Estuary were collected by the EA for routine monitoring purposes and later adapted to the monitoring required under the ND and UWWTD. Sampling was undertaken from the six sites shown in Figure 3.1 on a fortnightly to monthly basis over the period 1974–2004. In the upper estuary these were located at Newbridge (site 1) at the tidal limit, Little Pill (site 2) where the estuary forms a narrow channel and Barnstaple (site 3) where the estuary widens. The sample sites in the lower estuary were site 4 (close to the outflow of Ashford STW) and site 5 (near RAF Base Chivenor), both surrounded by large intertidal sand flats, and site 6 (Airy Point) which is at the estuary mouth. Data on nutrient concentrations in the effluent of Ashford STW were also collected by the EA. Nutrients loads from the River Taw and other tributaries to the estuary were provided by the NERC Centre for Ecology and Hydrology (Wallingford, UK). They were calculated from Harmonised Monitoring Scheme data following Method 5 from Littlewood *et al.* (1998):

$$L = \left(\frac{K \sum_{i=1}^n (Q_i C_i)}{\sum_{i=1}^n Q_i} \right) \bar{Q}$$

where K is the number of seconds in the N -day year, C_i the sampled concentration, Q_i the corresponding daily mean flow and \bar{Q} is

$$\bar{Q} = \frac{\sum_{i=1}^n Q_k}{N}$$

where Q_t is the daily mean flow for each day N of the year.

The annual loads of nutrients from the STW were estimated by multiplying the average annual concentration of a given constituent in the effluent with the consented dry weather flow⁶ of $15,231 \text{ m}^3 \text{ d}^{-1}$.

3.2.3. Data pre-treatment

The routine monitoring data for the period 1974–2004 were subjected to a structured statistical treatment. The original dataset contained 3536 data rows from samples collected between April 1974 and December 2004 from ten sample sites. Four sample sites were excluded due to insufficient data. Similarly, data prior to 1990 were excluded from the analysis because of temporal patchiness. Algal blooms⁷ largely occurred between April and September (Figure 3.3), and hence only data from these months were used for the correlation and regression analyses. Also, on several occasions, samples were collected along a depth profile. Only samples collected from the surface (0–1 m depth) were included in the analyses.

The remaining data were then amalgamated to give one coherent dataset, which involved scanning the data for errors (*e.g.* obvious typing mistakes), merging of variables with multiple listings into a single column and standardization of nutrient concentrations to micromoles per litre (μM). Concentrations of chemical parameters and chlorophyll *a* which were below the limit of detection (<LoD, 7.7% of the data) were converted into LoD/2 following the approach of Littlewood *et al.* (1998), in order to

⁶ Dry weather flow (DWF): The EA uses the definition from the Institute of Water Pollution Control (IWPC, 1975): The average daily flow to the treatment works during seven consecutive days without rain (excluding a period which includes public holidays) following seven days during which the rainfall did not exceed 0.25mm on any one day.

DWF is used in the setting and enforcement of effluent discharge consents in STW design, and, together with other quality parameters, to define the load that can be assimilated by the receiving (aquatic) environment (Heywood and Bramley, 2005).

⁷ Algal blooms: Chlorophyll *a* concentrations $>100 \mu\text{g L}^{-1}$ (Tett 1987).

include as many data records as possible for graphical and statistical analysis. The STW data were treated in the same way.

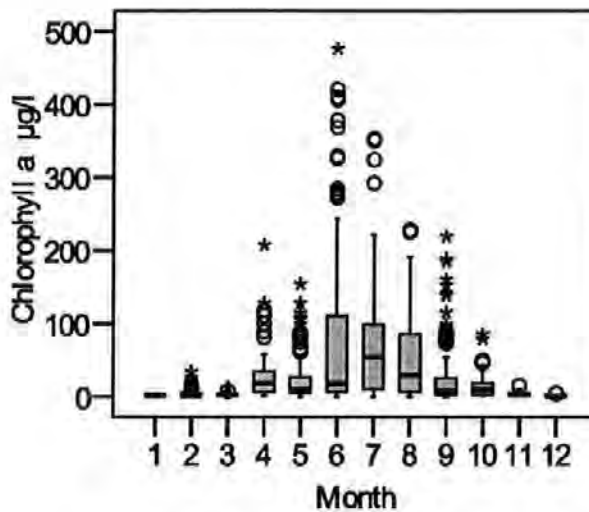


Figure 3.3. Range of chlorophyll *a* concentrations at all sampled sites from the EA dataset for each month throughout the period 1990–2004. For detailed explanation of the box and whisker plots, see caption of Figure 3.2.

The final estuary data matrix based on the EA data, of which subsets were used for graphical and statistical analysis, contained 1793 data rows with 17,789 data points from the six sample sites. The entire dataset was used for the cluster analysis, the subsets for the correlation and regression analyses contained only data from April–September (for rationale see section 3.3.2) with 10,434 data points. The following variables were used: water temperature ($^{\circ}\text{C}$), salinity, ammonium (NH_4 , μM), nitrate (NO_3 , μM), phosphate (PO_4 , μM), silicate (SiO_2 , μM), chlorophyll *a* ($\mu\text{g L}^{-1}$), turbidity (NTU), dissolved oxygen concentration (O_2 , mg L^{-1}) and dissolved oxygen saturation ($\text{O}_2\%$). Additionally, river flow data (from the NRFA) were included. The same variables (except the river flow data) were extracted from the STW dataset. Loads were converted into t a^{-1} .

3.2.4. Statistical analyses

Cluster analysis has been successfully used on environmental datasets (*e.g.* Einax *et al.*, 1998; Panda *et al.*, 2006); its main advantage is that it reduces the amount of data, which helps pattern recognition and the identification of trends in the dataset. This is achieved by grouping objects or data into subsets according to their proximity (based on traits they have in common), which is expressed by a measure of distance. For this study, the similarities between 10 variables of the Taw Estuary dataset have been assessed by performing a cluster analysis based on Euclidean distance, the appropriate distance measure for environmental data (Clarke and Warwick, 2001), using PRIMER 6 (PRIMER-E Ltd., 2006).

Prior to the analysis, data rows with missing values were eliminated. Because the individual variables had different scales, all data were normalized (also called standardized) following Clarke and Gorley (2006), using the following equation:

$$x_{i \text{ norm}} = \frac{x_i - \bar{x}}{s}$$

where x_i is the value to be normalised, \bar{x} the arithmetic mean of all values of a variable and s their standard deviation.

Correlation analysis was undertaken to identify the variables that covaried with chlorophyll *a* concentrations and to aid in the selection of variables suitable for the generation of a multiple regression model (see below). Non-parametric correlation (Spearman's ρ) was used, as none of the variables were normally distributed (Kolmogorov–Smirnov One-Sample Test). Significance of the correlation coefficients was tested at the $p < 0.01$ and $p < 0.05$ levels.

In order to estimate the degree of influence of individual variables on chlorophyll *a* concentrations, stepwise backward elimination multiple regression analysis (or backward elimination in short) was conducted for each sample site. The multiple regression models included all variables at the outset, with the advantage that the imposition of a user defined structure on the data was avoided. Using iteration, variables with the least significance were then eliminated until a linear, heuristic best-fit model, which included the most significant variable(s), was achieved (*i.e.* all remaining variables were significant or only one variable was left). As a normal distribution of the dependent variable (here chlorophyll *a*) is one of the formal requirements for regression analysis, it was $\ln(x+1)$ transformed and normalized prior to the analyses. Also, the transformation and normalisation of the dependent variable helps to approximate linearity in the regression. Normal distribution of the standardized residuals was confirmed using the Kolmogorov–Smirnov One-Sample Test. Both, the non-parametric correlation analysis and the backward elimination regression analysis were conducted using SPSS 15.0 (SPSS Inc., 2006).

3.3.Results

3.3.1. Source contributions to the annual nutrient loads

In order to provide an overview of the importance of the main sources for individual nutrients in the estuary, a summary of inputs of nitrate, ammonia and phosphate over the study period was compiled.

The annual average river input of nitrate to the estuary was $2726 \text{ t a}^{-1} \text{ NO}_3\text{-N}$ during the period 1990–2004 (Figure 3.4a), to which the River Taw contributed on average $1977 \text{ t a}^{-1} \text{ NO}_3\text{-N}$ (*ca.* 73%).

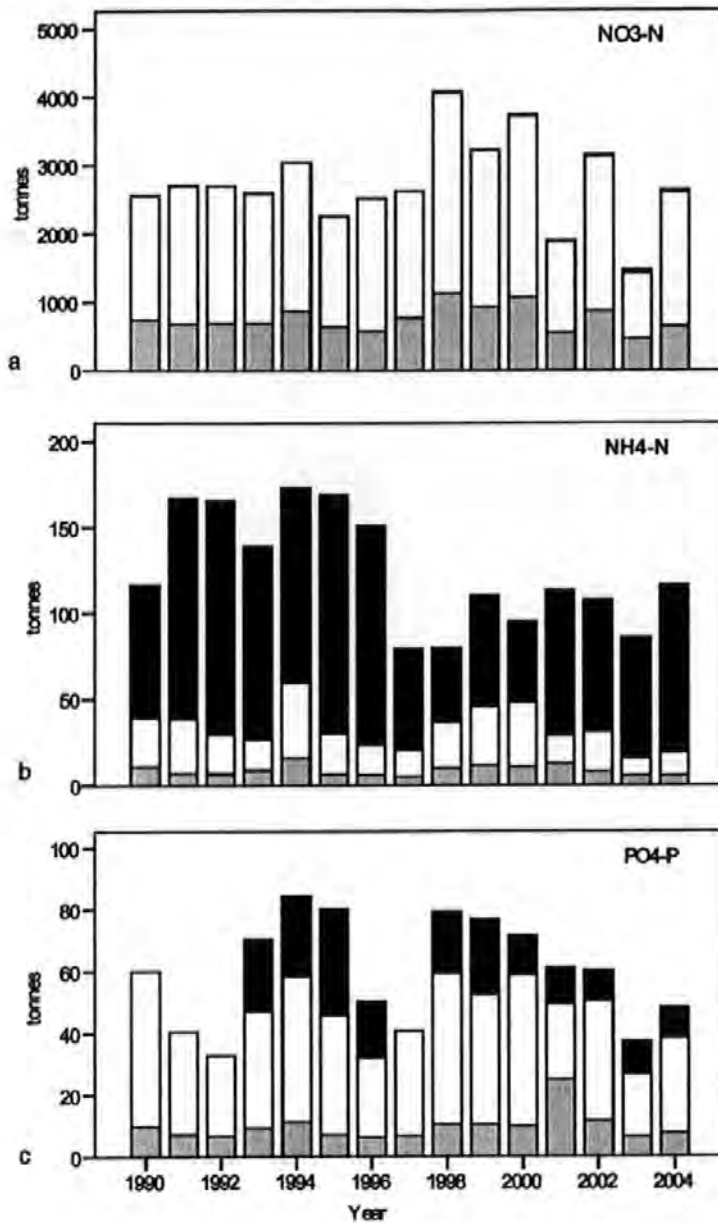


Figure 3.4. Estimates of annual loads in tonnes of nutrients into the estuary: (a) nitrate (no STW data for 1997), (b) ammonium, (c) phosphate (no STW data for 1997 and 1990–1992). Black = STW, white = River Taw, grey = other rivers. River load data were obtained from CEH; STW loads were calculated using EA data (see text).

The annual contribution of nitrate for the same period from the STW was 6–49 t NO₃-N (mean = 16 t NO₃-N) and hence was relatively unimportant, contributing only 1–3% of the total nitrate load.

Mean river inputs of ammonium between 1990 and 2004 were $33 \text{ t a}^{-1} \text{ NH}_4\text{-N}$, of which the River Taw contributed on average $24 \text{ t a}^{-1} \text{ NH}_4\text{-N}$ (Figure 3.4b). The most significant source of ammonium was the Ashford STW, ranging from 42 to $135 \text{ t a}^{-1} \text{ NH}_4\text{-N}$, with a mean of $89 \text{ t a}^{-1} \text{ NH}_4\text{-N}$. On average, the STW contributed 74% of the annual ammonium load to the estuary. Of the total inorganic N (TIN) loading, nitrate was by far the most dominant species, comprising 95% of the total TIN load, followed by ammonium (4.4%) and nitrite (0.6%). On average, the river TIN load into the estuary, normalized to the catchment area, was $2278 \text{ kg km}^{-2} \text{ a}^{-1}$, which is higher than that in a moderately impacted catchment, defined by Hessen (1999) to have an export of $500\text{--}2000 \text{ kg N km}^{-2} \text{ a}^{-1}$. The average annual $\text{PO}_4\text{-P}$ load to the estuary was 65 t a^{-1} (Figure 3.4c), of which 71% was riverine (37 t a^{-1} from the Taw, 10 t a^{-1} from tributaries). Mean annual input of $\text{PO}_4\text{-P}$ from Ashford STW was 18 t (maximum 34 t in 1995), and the STW contributed 18–43% of the total $\text{PO}_4\text{-P}$ loading. The average P load (area normalized) from the Taw catchment was $39 \text{ kg km}^{-2} \text{ a}^{-1}$. This is very low when compared with the average P loads of UK catchments of $152 \text{ kg km}^{-2} \text{ a}^{-1}$ (Nedwell *et al.*, 2002) and North Sea catchments of $117 \text{ kg km}^{-2} \text{ a}^{-1}$ (Howarth *et al.*, 1996). The main pathway of PO_4 into rivers is through soil erosion. The possible reason for the low PO_4 export from the Taw catchment might be the predominant land use as dairy country: soil erosion rates from grass land are much lower than those from certain crop monocultures, *e.g.* maize or wheat. For Si, the estimated average riverine load to the estuary was 1730 t a^{-1} , ranging from 973 t a^{-1} (2003) to 2473 t a^{-1} (1994). These results supported the classification of the Taw Estuary under the ND and UWWTD and helped to identify priorities for nutrient stripping actions. However, when looked at on their own, load data are usually not sufficient to evaluate the drivers of phytoplankton growth in an estuary.

3.3.2. Spatial and temporal distribution of salinity, nutrients and chlorophyll *a*

The highly dynamic character of the estuary is highlighted by the fact that all sites, apart from site 1, experienced the entire range of salinities over the lifetime of this dataset (Figure 3.2a); high salinities at site 2 close to the tidal limit represent intrusions of coastal waters at high tide during times of low freshwater inflow whereas low salinities at site 6 are due to received freshwater input after high rainfall. The estuary was generally well oxygenated (Figure 3.2b and c) with highest dissolved oxygen concentrations in the upper and central parts, decreasing towards the mouth, following reduced solubility of oxygen with increasing salinity. Sites 3, 4 and 5 experienced super-saturation of dissolved oxygen (Figure 3.2c), with values exceeding 150% during periods of high algal biomass.

Nitrate and silicate showed highest concentrations at the freshwater limit, which then decreased with increasing salinity towards the mouth (Figure 3.2d, e). As the main source of nitrate and silicate is the catchment, their estuarine concentrations correlated well with freshwater inflow (0.49 and 0.43 at $p < 0.01$). Ammonium concentrations (Figure 3.5a, b) were highest, and showed greatest variability, at site 4 near the STW outlet. Here, they regularly exceeded 20 μM , strongly indicating the importance of the STW discharge as a source of ammonium. Median phosphate concentrations were highest at the freshwater limit (site 1) and decreased towards the mouth; nevertheless, the highest concentrations were observed at site 4, suggesting significant inputs from the STW (Figure 3.5c, d). Estuarine molar TIN:P ratios showed a high degree of variability between individual sites, with site specific means ranging from 50 at the mouth to 150 in the middle and upper estuary and generally exceeded the Redfield ratio of 16 (Redfield *et al.*, 1963).

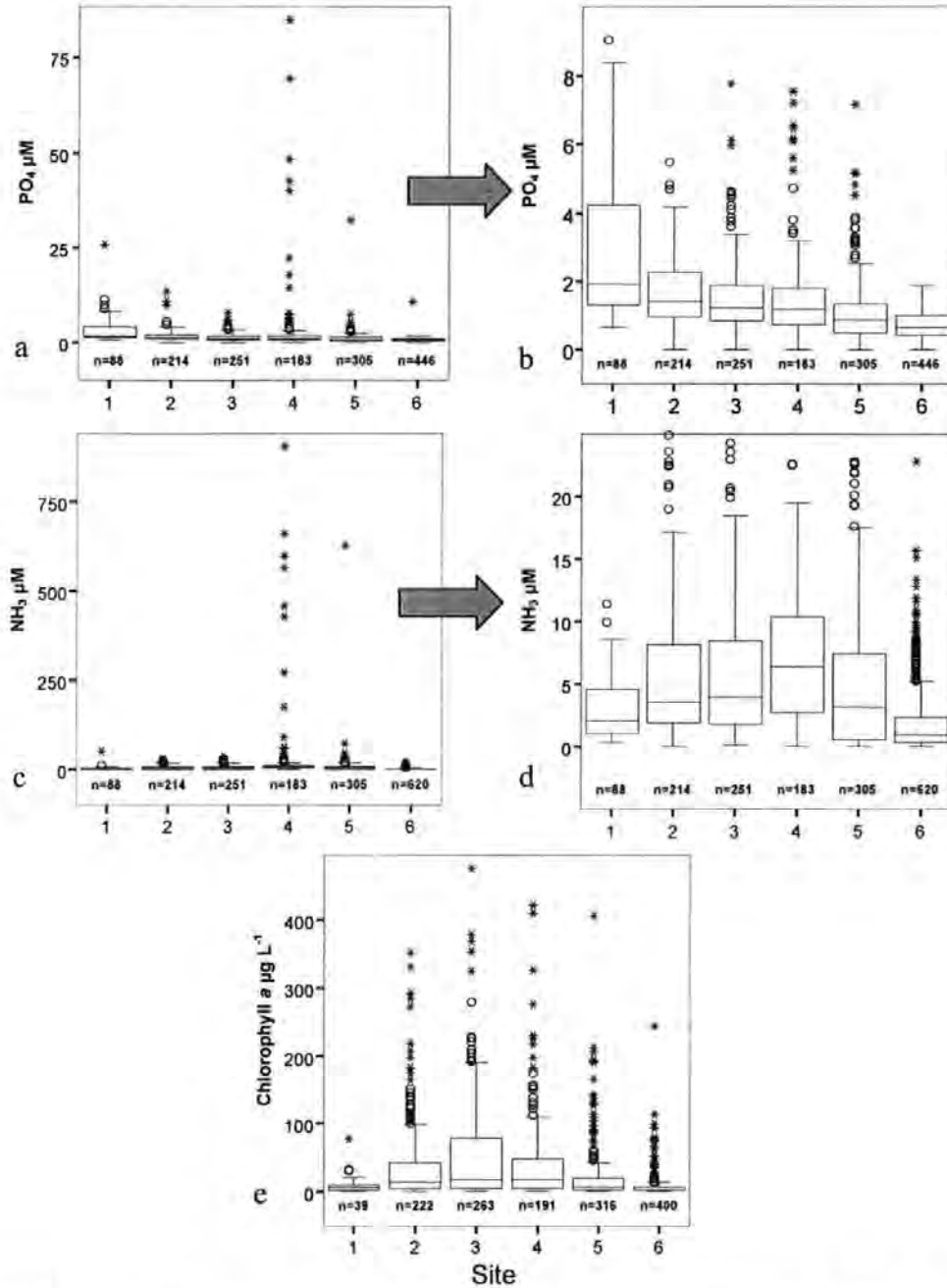


Figure 3.5. For explanations, see caption for Figure 3.2. Concentrations of PO_4 and NH_4 are shown at two different scales because of the high variability of concentrations at site 4.

Similarly, N:Si ratios in the upper estuary, with means between 5 and 7, were considerably higher than the Redfield ratio for N:Si of 1 and much higher than that for pristine estuaries (Justić *et al.*, 1995b). N:Si ratios increased towards the mouth, with means from 10 to 16. Similar ratios have been reported for the Great Ouse Estuary (UK), and these have been attributed to high nitrate inputs from its agriculturally

dominated catchment (Sanders *et al.*, 1997). N:P ratios are usually higher in freshwater than in seawater (Elser and Hassett, 1994; Hecky *et al.*, 1993) and will therefore show a degree of fluctuation in estuaries, but it is known that large deviations from the Redfield ratio under nutrient limiting conditions can change the composition of the phytoplankton community and favour harmful species (Anderson *et al.*, 2002).

In total, 1432 chlorophyll *a* data points were analysed here, of which 916 were from the main growth period (April–September). The highest median concentrations of chlorophyll *a* occurred during summer months (June–August, Figure 3.3 and Figure 3.6a) at sites 3 and 4, and to a lesser extent at site 2 (Figure 3.5e).

Chlorophyll *a* levels were also highest during low and intermediate river flows ($\leq 5 \text{ m}^3 \text{ s}^{-1}$) from the River Taw (Figure 3.6b) and at low to intermediate salinities (0–24 psu; Figure 3.6a and b).

OSPAR assessment criteria (OSPAR Commission, 2003a) listed chlorophyll *a* concentrations above $15 \mu\text{g L}^{-1}$ as undesirable and will lead to the designation of the assessed water body as “Problem Area”. This threshold was exceeded by 49% of the samples during the main growth period and in 34% of the overall dataset. Chlorophyll *a* concentrations in estuaries exceeding $40 \mu\text{g L}^{-1}$ were considered to be high (Bricker *et al.*, 2003) and this value was exceeded in 19% of the all-year dataset. During the period covering May–September, $40 \mu\text{g L}^{-1}$ was exceeded in 28% of the dataset. In 12% of the dataset during the main growth period between 1990 and 2004, chlorophyll *a* concentrations exceeded $100 \mu\text{g L}^{-1}$, a threshold level which Tett (1987) has used to define the presence of phytoplankton blooms. Outside the main growth period, the $100 \mu\text{g L}^{-1}$ threshold was not exceeded.

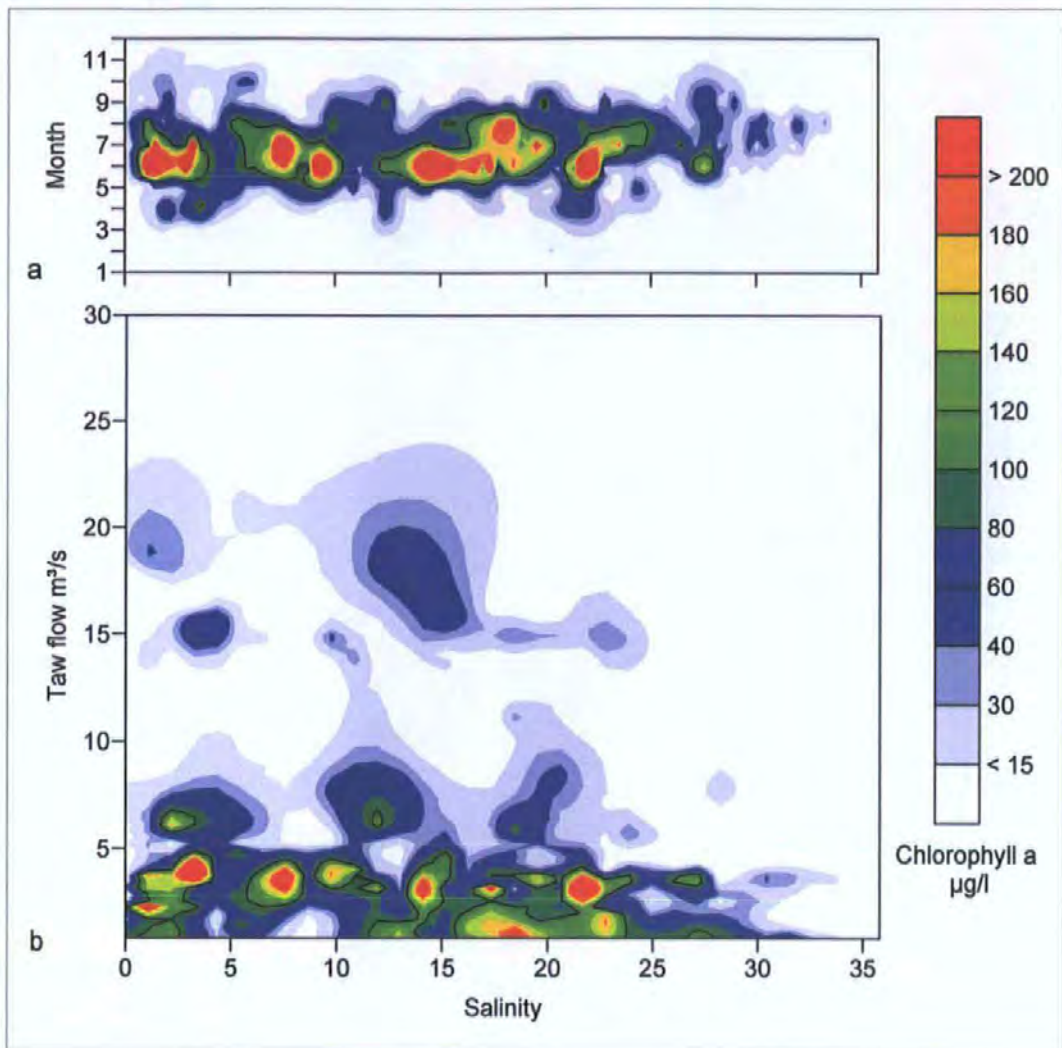


Figure 3.6. Contour plots of chlorophyll a concentration as a function of (a) salinity and month ($n = 725$) and (b) salinity and river flow ($n = 1285$). The solid line indicates $100 \mu\text{g L}^{-1}$ of chlorophyll a.

3.3.3. Cluster analysis

The aim for conducting a cluster analysis was to identify associations between variables and general trends in the data. After elimination of data rows with missing values from the initial 1793 rows, 6900 data points in 460 rows (26%) remained for cluster analysis. In the resulting dendrogram (Figure 3.7), the variables are shown as branches. The position of the node (on the x-axis) where two branches merge indicates their similarity: the lower the distance value is, the more likely is a positive association

between two variables. Oppositely, variables with a negative (or inverse) association show maximum distance. For the assessed EA data, three main branches could be identified:

- (i) The 'catchment branch' with the variables River Taw flow, turbidity, nitrate and silicate.
- (ii) The 'STW branch' with the variables ammonium and phosphate.
- (iii) The 'phytoplankton branch' including the variables chlorophyll *a*, water temperature and dissolved oxygen.

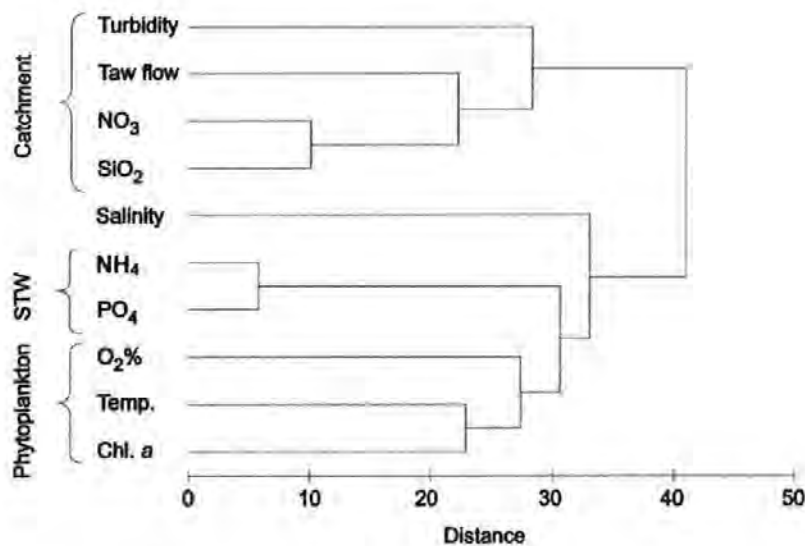


Figure 3.7. Dendrogram showing the Euclidean distance between individual variables ($n = 460$ data rows).

The 'catchment branch' was notably influenced by rainfall and its effects. Turbidity becomes higher as river flow increases, probably following increased sediment remobilisation and increased land erosion. Nitrate and silicate inputs into the estuary are also dependent on rainfall in the catchment. The percolating water dissolves nitrates from the soil and subsoil. Silicate originates from the weathering of minerals containing

silicates, but its concentrations in the receiving waters are relatively independent of land use. Its major pathway into rivers is via terrestrial runoff (e.g. Ittekkot *et al.*, 2006). With increasing rainfall, more nitrate and silicate are exported from the catchment into the river, which resulted in high nitrate and silicate concentrations in the estuary when river flow was high.

Salinity, represented by a fourth branch, showed maximum separation from the variables on the 'catchment branch'. Salinity would be expected to be situated on the 'catchment branch' as it is to an extent dependent on rainfall in the catchment. The numerical association between the other variables from the 'catchment branch' is positive, whereas salinity has a negative association with these variables (*i.e.* high rainfall corresponds with high sediment and nutrient loads but with low salinity in the estuary due to increased dilution by freshwater and *vice versa*), which in turn creates maximum numerical separation.

The 'STW branch' consists of phosphate and ammonium and is located closer to the 'phytoplankton branch' than to the 'catchment branch'. For both of these nutrients the STW was an important source to the estuary.

The 'phytoplankton branch' showed variables that were particularly associated with primary production. High chlorophyll *a* concentrations occurred during the summer months when water temperatures were highest. The proximity of oxygen saturation and chlorophyll *a* is related to photosynthetic oxygen release during periods of high algal biomass.

3.3.4. Non-parametric correlation and stepwise backward elimination regression analysis

Throughout the estuary, various chemical and physical variables experienced strong gradients from the tidal limit to the mouth. The waters in the upper reaches close to the tidal limit were of low salinity, concentrations of catchment borne nutrients were high and water residence times were likely to be short. In the central part of the estuary, water residence times were longer and tidal influences were strong, resulting in large variations in salinity, strong tidal currents and high turbidity. Also, the outflow of the STW discharged into this part of the estuary with resulting high concentrations of ammonium and phosphate. Closer to the mouth, the estuary is wider and the water mass was largely derived from coastal inflow of saline water with comparatively low nutrient concentrations. Due to these gradients, the individual variables (*i.e.* ecological factors) exhibit a different degree of influence on algal growth at each sample site. For these reasons, a single statistical model incorporating all sample sites cannot be expected to describe the actual interrelationship between a variable and algal biomass. Therefore, the data for the correlation and regression analyses were split into six subsets, one for each site.

Due to an insufficient amount of data for site 1, none of the correlations with chlorophyll *a* were significant and therefore site 1 is not discussed further. The negative influence of high river flow on algal growth is evident from the negative correlations between river flow and chlorophyll *a* at the upper and central sites 2–4 (Table 3.1), where high river flow reduced water residence times significantly, resulting in down-estuary flushing of suspended algae after rainfall in the catchment. River flow was less important in the wider outer estuary, where the larger volume of water led to longer residence times and the algae remained *in situ* longer. The negative correlations of

nitrate and silicate with chlorophyll *a* in the upper estuary are consistent with this interpretation, as both of these nutrients were sourced mainly in the catchment and the inflowing freshwater was their main path into the estuary. In the outer estuary, nitrate and silicate correlated positively with chlorophyll *a*. There, water residence times were long enough for the phytoplankton to respond to an increase in concentrations of nutrients by increasing biomass. The correlation of temperature with chlorophyll *a* decreased from site 2 to site 6, again reflecting the influence of the catchment, where the temperature variation during summer was much higher in terrestrial runoff and shallow, semi-enclosed sections of the upper estuary than in coastal waters. The highest chlorophyll concentrations occurred at low to intermediate salinities (Figure 3.6b) where inorganic nutrients were present at higher concentrations than in coastal seawater, which the correlation analysis confirmed: salinity *versus* chlorophyll *a* had a positive ρ at the more freshwater influenced sites 2–4 and became negative at the sites 5 and 6 where marine influence was stronger.

The two variables ammonium and phosphate, both located on the 'STW branch', had similar results in the correlation analysis. The negative correlation coefficients of ammonium with chlorophyll *a* at sites 3 and 4, where ammonium concentrations were highest, suggested that phytoplankton growth was to an extent inhibited by high ammonium concentrations, *i.e.* highest chlorophyll *a* concentrations at sites 3 and 4 only occurred when ammonium concentrations were relatively low. Planktonic algae normally prefer ammonium to nitrate (Cochlan and Harrison, 1991; Conway, 1977) as ammonium is the energetically favourable form of N for amino acid synthesis. However, Dugdale *et al.* (2007) reported for San Francisco Bay that ammonium concentrations $>4 \mu\text{M}$ inhibited nitrate uptake by phytoplankton and that plankton growth rates were also slowed. Only when ammonium concentrations fell below $4 \mu\text{M}$

was nitrate metabolized, resulting in much higher phytoplankton growth rates. A similar relationship between ammonium and nitrate was observed by Dugdale and Hopkins (1978) in the Gulf of Saronikos (Greece), with the elevated concentrations of ammonium resulting from sewage discharges.

Ammonium concentrations were considerably lower at sites 2, 5 and 6 (Figure 3.5d), presumably due to dilution by freshwater from the catchment or inflowing coastal water, coupled with smaller inputs in these regions. At these sites ammonium was positively correlated with chlorophyll *a* and thus did not appear to inhibit nitrate-induced accelerated growth; indeed it would have contributed to the bioavailable N pool. The values of the correlation coefficients for phosphate with chlorophyll *a* and ammonium with chlorophyll *a* were similar (Table 3.1), and were probably an artificially created signal by the inputs from the STW, where phosphate followed the same temporal input pattern as ammonium, rather than the actual interaction of phosphate with phytoplankton. A linear regression of ammonium and phosphate concentrations from site 4 gave an r^2 of 0.68 over the entire range of concentrations and an r^2 of 0.40 (Figure 3.8) after entries with very high values ($\text{NH}_4 > 20 \mu\text{M}$, $\text{PO}_4 > 4 \mu\text{M}$) were removed. The two variables were also closely associated in the cluster analysis.

The correlation analysis also revealed some of the effects from high algal biomass and photosynthetic activity: dissolved oxygen saturation had a positive ρ (0.28-0.66) with chlorophyll *a* throughout the estuary with the exception of site 6 (Table 3.1), where the correlation for dissolved oxygen saturation with chlorophyll *a* was not significant. Light limitation could not be examined with the available data; indeed, turbidity correlated positively with chlorophyll *a* (except at site 4) and turbidity appeared to be following high phytoplankton densities in the water column rather than suspended sediment.

Table 3.1. Correlation coefficients (Spearman's ρ) of individual variables with chlorophyll *a* concentrations. Figures of significant correlations at $p < 0.01$ are bold, and at $p < 0.05$ underlined (Temp. = temperature, Turb. = turbidity).

| Site | | Taw flow | Temp. | Salinity | Turb. | NO ₃ | SiO ₂ | NH ₄ | PO ₄ | O ₂ % |
|------|----------|--------------|-------------|--------------|-------------|-----------------|------------------|-----------------|-----------------|------------------|
| 2 | ρ | -0.65 | 0.52 | 0.68 | 0.51 | -0.63 | -0.53 | 0.35 | <u>0.22</u> | 0.28 |
| | <i>n</i> | 114 | 95 | 96 | 96 | 82 | 71 | 96 | 96 | 92 |
| 3 | ρ | -0.59 | 0.58 | 0.43 | 0.33 | -0.53 | -0.45 | -0.29 | -0.12 | 0.62 |
| | <i>n</i> | 141 | 123 | 123 | 123 | 104 | 93 | 123 | 123 | 119 |
| 4 | ρ | -0.50 | 0.44 | 0.41 | <u>0.24</u> | -0.48 | -0.33 | -0.47 | -0.43 | 0.66 |
| | <i>n</i> | 115 | 97 | 97 | 97 | 76 | 64 | 97 | 97 | 93 |
| 5 | ρ | -0.10 | 0.29 | -0.39 | 0.53 | <u>0.23</u> | 0.19 | 0.23 | 0.23 | 0.44 |
| | <i>n</i> | 150 | 132 | 132 | 132 | 110 | 96 | 132 | 132 | 127 |
| 6 | ρ | 0.00 | -0.02 | -0.64 | 0.43 | 0.45 | 0.43 | <u>0.19</u> | 0.25 | 0.13 |
| | <i>n</i> | 133 | 130 | 128 | 131 | 105 | 78 | 131 | 131 | 130 |

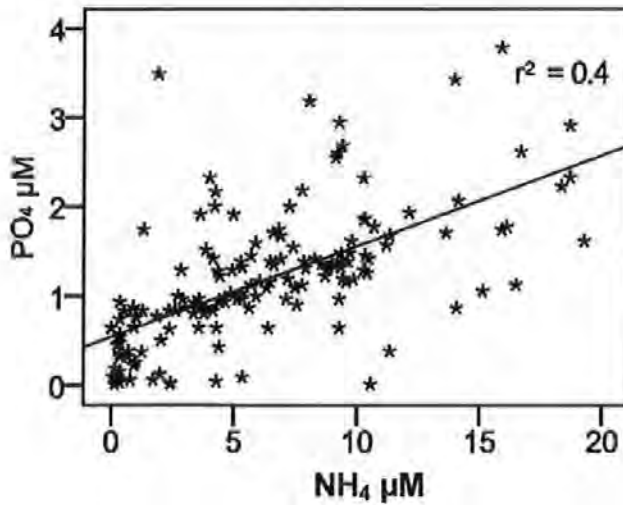


Figure 3.8. Scatter plot of phosphate versus ammonium concentrations at site 4 after outliers ($\text{NH}_4 > 20 \mu\text{M}$, $\text{PO}_4 > 4 \mu\text{M}$) were removed.

Following the results of the correlation analysis, key variables were selected for the stepwise regression analysis. The two prerequisites were that a variable was correlated at one or more sites with chlorophyll *a* and that there was reasonable certainty that a variable determined chlorophyll *a* concentrations and not *vice versa*. This led to the exclusion of two variables, dissolved oxygen saturation and turbidity. The variables then used for generating the regression models were river flow, temperature, salinity, nitrate, silicate, ammonium and phosphate.

The models from the backward elimination regression analysis (Table 3.2) explained 26–49% of the variation in chlorophyll *a*, except the model for site 4, which only explained 13% of the variation. All models contained either freshwater inflow, salinity or both. This underlines the importance of river flow for algal growth throughout the estuary. Freshwater inflow was significant in the models for the sites 2–4. The negative slopes in all cases were consistent with the inverse relationship between river flow and phytoplankton biomass in the upper, narrow channel of the estuary. Under intermediate or high riverine flow, phytoplankton is flushed down-estuary from these sites. The

Table 3.2. Model summaries obtained from backward eliminating multiple linear regression analysis (p = probability, b = slope).

| | p | b | r^2 |
|------------------|-------|--------|-------|
| Site 2 | | | |
| Salinity | 0.012 | 0.051 | 0.49 |
| PO ₄ | 0.067 | 0.081 | |
| SiO ₂ | 0.093 | -0.007 | |
| Flow | 0.001 | -0.092 | |
| Site 3 | | | |
| Flow | 0.000 | -0.134 | 0.38 |
| Site 4 | | | |
| Flow | 0.002 | -0.064 | 0.13 |
| Site 5 | | | |
| Salinity | 0.000 | -0.054 | 0.40 |
| NH ₄ | 0.004 | -0.018 | |
| PO ₄ | 0.006 | 0.350 | |
| SiO ₂ | 0.000 | -0.023 | |
| Temperature | 0.000 | 0.099 | |
| Site 6 | | | |
| Salinity | 0.000 | -0.084 | 0.26 |
| SiO ₂ | 0.013 | -0.025 | |

positive slope of salinity for site 2 confirmed this, as medium and high salinities in this part of the estuary only occurred during low river flow, when water residence times were longest. Salinity also contributed to the models for sites 5 and 6, but had negative slopes in these instances; given sufficient residence times in the outer estuary, phytoplankton biomass is higher in the presence of nutrient-rich estuarine water than in

low nutrient (but euhaline; see Table 4.8) coastal water that advances into the estuary with the incoming tide. Silicate was included in the models for sites 2, 5 and 6; its slopes indicated covariability with freshwater flow. Phosphate was significant in the models for sites 2 and 5 and two other variables were only significant in the model for site 5; ammonium, and water temperature (due to its direct influence on algal growth). Their significance should therefore be treated with caution and interpreted together with the results from the correlation analysis.

The correlation analysis provided insight into the interactions between key variables and chlorophyll *a* and how these interactions changed along the estuary at different sample sites. It also facilitated identification of the appropriate variables for use in the backward elimination regression. However, the results of the correlation analysis did not allow unequivocal conclusions about the importance (*i.e.* the predictive power) of a variable for algal growth. This was done by looking at the best-fit models (*i.e.* the model with the highest predictive power) generated by the backward elimination regression analysis. Throughout the estuary (with the exception of site 4) these were salinity and/or river flow, both variables related to physical, rather than biogeochemical processes.

3.4. Discussion

The monitoring data clearly showed that the Taw Estuary was highly eutrophic during the summer months, with concentrations of chlorophyll *a* regularly exceeding $100 \mu\text{g L}^{-1}$ over the period 1990–2004 (Figure 3.3, Figure 3.5e). The data revealed two important regulators of bloom dynamics in the estuary: ammonium inhibition and the flow regime of the River Taw.

Ammonium inhibited nitrate uptake at site 4, near the outlet of the STW, which prevented algal biomass from reaching the maximum achievable level under ambient nitrate concentrations.

The influence of the River Taw was strongest in the upper reaches of the estuary at sites 2 and 3 and to a lesser extent at site 4; low freshwater inflow resulted in relatively long water residence times, allowing the phytoplankton to reproduce in the mid and upper estuary under nutrient replete conditions. Under intermediate flow, algal growth continued in the outer estuary, whereas with high flows, nutrients were flushed into the adjacent coastal waters. Conceptually, this can be compared to a chemostat bioreactor (e.g. in Sommer, 1986) with the estuary being a reaction vessel that contains a steady state system. This "estuarine chemostat system" is regulated by river inflow, determining dilution and loss rates. Dilution rates below the growth rate of the phytoplankton (*i.e.* under low river inflow) lead to an increase in algal biomass with little loss to the adjacent coastal waters. On the other side, dilution rates were highest under high inflow and lead to a decrease in phytoplankton concentrations when the dilution rate exceeded the growth rate of the phytoplankton: the cells were lost to the coastal sea. The negative correlation coefficients between nitrate and chlorophyll *a* in the upper and central estuary also followed riverine inflow: nitrate availability (or concentrations) was highest under high river inflow when phytoplankton biomass was low. In the outer estuary, where dilution rates were presumed to be lower (due to the larger volume of water that needs to be replaced), increased nitrate concentrations coincided with high phytoplankton biomass. However, whether this phytoplankton originated from *in situ* production, resulted from an upstream population that was flushed down, or both is unclear.

The observed situation in the Taw Estuary with a negative correlation of river flow and nitrate input with phytoplankton biomass is consistent with observations from other small estuaries (*e.g.* the Urdaibai; Orive *et al.*, 1998) and the opposite to what has been observed in large estuaries with relatively long water residence times, such as the Neuse River Estuary, North America, where primary production correlated positively with river flow and nitrate loads (Mallin *et al.*, 1993). This reinforces the fact that conclusions, which are true for one estuary, may not be transferable across different estuarine scales.

The applied approach has demonstrated the value of data mining of historical monitoring datasets and shown that it is possible to use archived estuarine datasets from the EA to good effect, particularly after several datasets have been combined (EA estuarine and STW data, data from the Harmonised Monitoring Scheme and the National River Flow Archive). This is true even when the datasets were originally collected for different purposes than they were used for in this chapter. However, it is evident that substantial data mining and structured data editing of disparate datasets is necessary. The application of easy to use and proven statistical treatments for environmental datasets provided considerable added value to the data: it facilitated a systemic (although not comprehensive) view of eutrophication processes in the Taw Estuary when compared with mere descriptive approaches such as graphical representations.

The insights also outline potential future problems in the Taw with algal blooms and their management. Given the importance of low river flow for phytoplankton growth in the estuary, climate change has a significant potential to severely exacerbate eutrophication events. An increase in the seasonality of the annual river flow for the River Tamar (a catchment adjacent to the Taw catchment) was predicted (Arnell and

Reynard, 1996; Arnell, 2004), together with an average reduction in summer flow of 25% by 2050 with extremes >50% lower under one scenario. The implications of increased chlorophyll concentrations following rising water temperatures, similar to what has been observed in the North Sea (McQuatters-Gollop *et al.*, 2007), could further aggravate the trophic status of the Taw and other nutrient-rich estuaries in the region.

The management of current ammonium inputs to the estuary should be carefully assessed; paradoxically, increased ammonium nitrification capacity in the STW, leading to reduced ammonium concentrations in the vicinity of the effluent outlet, may not improve, but actually worsen the trophic situation in the Taw Estuary if there is no reduction in overall N and P inputs. However, ammonia concentrations at site 4 were repeatedly in the range of acute toxicity for marine animals (6–250 μM , depending on species; Eddy, 2005) and also regularly exceeded the environmental quality standard (EQS) of specific pollutants for salt waters of 1.23 μM (21 $\mu\text{g L}^{-1}$; UK TAG WFD, 2007a). This means that the physico-chemical conditions do not ensure ecosystem functioning and exceeds the EQS's for specific pollutants (UK TAG WFD, 2007b) and the estuary fails to achieve 'good ecological quality' under the EU WFD. These factors clearly need to be reconciled if environmental impact is to be minimised.

The value of current and future monitoring actions would be increased by including data on dissolved organic N (DON), dissolved organic P (DOP) and dissolved organic carbon (DOC) in future surveys and by conducting targeted high temporal resolution studies:

- (i) DON originates mostly from regenerated N within a system (*e.g.* phytoplankton and zooplankton excretion, microbial processes) and it has

been shown that in some instances DON (especially urea) is preferred over dissolved inorganic N (DIN; Twomey *et al.*, 2005) and that it has a significant impact on algal growth (Glibert *et al.*, 1991; Twomey *et al.*, 2005). Also, the ratio of dissolved organic carbon to dissolved organic N (DOC:DON) has been related to HABs (Anderson *et al.*, 2002). However, currently available data for the Taw Estuary do not allow any conclusions to be drawn about the role of dissolved organic nutrients in the system which leads to a considerable gap in the understanding of the quantitative importance of DON as an N source for phytoplankton. Given the importance of nutrient stripping for eutrophication mitigation under the ND and UWWTD, the absence of DON data for the estuary and its tributaries leads to considerable uncertainty about the significance of such measures. Further, in many waters, the DOP fraction is at least as abundant as the dissolved inorganic P (DIP) fraction and represents a potentially bioavailable pool of P but its quantification has been traditionally ignored in favour of DIP (*e.g.* Worsfold *et al.*, 2008; Monbet *et al.*, 2009).

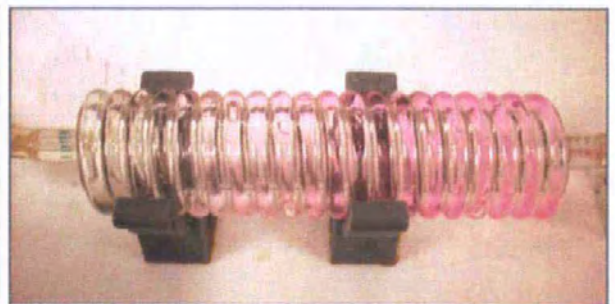
- (ii) The data used for this chapter were collected on a fortnightly to monthly basis and only provided snapshots of the estuary. Monitoring the estuary on a much higher temporal resolution over several weeks in summer would allow gradual changes in nutrient concentrations and phytoplankton successions to be observed and documented over the course of bloom formation. This would help to identify the causes of algal bloom formation and the associated nutrient biogeochemistry with increased certainty, information that is essential for the efficient management of estuarine eutrophication. Such high frequency sampling campaigns have been applied

to other systems, with good success, to elucidate species succession and the regulating processes of algal blooms (*e.g.* Rantajärvi *et al.*, 1998; Wang *et al.*, 2006).

With regard to the ND and the UWWTD (and to a lesser extent also for the WFD) it is clear that following status monitoring only may not always be sufficient to provide the required information to support adequate management decisions for achieving the Directive's goal. It is necessary to have a sound understanding of a particular estuary because the drivers of eutrophic symptoms are complex and often very specific to that estuary.

MATERIAL AND METHODS

*Details from the
Skalar SANplus
flow analyzer*



The journey time from Plymouth to Barnstaple and back (~5 h) set time constraints on the number of sites that could be sampled and samples processed in a day. Hence four sites (A-D, Figure 4.1) were selected for the work described in chapter 5.

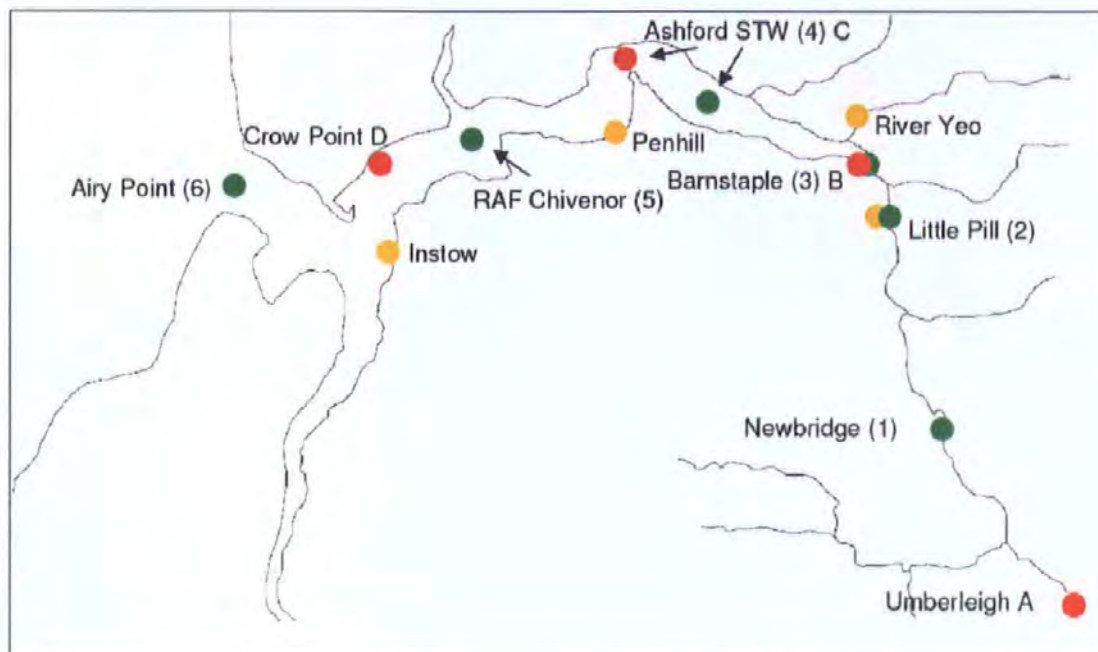


Figure 4.1. Location of sample sites. Green circles: EA sites; red circles: sites sampled during the entire spring/summer 2008 campaign; yellow circles: sites sampled episodically. The numbers in brackets are the EA site numbers used in chapter 3, the letters are the site codes for the spring/summer 2008 campaign.

A graphical compilation of the EA sites and sites for the spring/summer 2008 campaign is provided in Figure 4.1. Because the sampling campaign was land based, the EA sites 6 (Airy Point) and 5 (Royal Air Force Base Chivenor) were excluded as there was no practicable access. Instead, site D was used to represent the lower reach of the estuary. The sample location for EA site 4 (Ashford sewage treatment works) could be closely matched to a terrestrial access point (C). The same was the case for site 3 near Barnstaple town centre. EA site 2 (Little Pill) was only included during the first three days of the spring/summer campaign. Access to this site was difficult, so the collection of water samples and *in situ* measuring of physico-chemical variables proved

impossible at times. As this location is only about 800 m away from site B (EA site 3), it was decided not to continue sampling at EA site 2.

EA site 1 (Newbridge) is located at the tidal limit of the estuary. Access to the site would have involved working from a busy highway bridge, so for safety reasons sampling was moved up-river to Umberleigh (site A), where the EA maintains a flow gauging station.

Water samples were collected episodically from a number of other sites but they were not included in the survey as access to the water was either limited and water had to be collected with a bucket (Penhill), too dangerous (River Yeo) or the suspected influence of other systems distorted the signal from the Taw (Torridge Estuary for Instow, and the River Yeo).

4.2. Sampling dates and times

A summary of sample dates and times including the tidal state is given in Table 4.1. The surveying campaign was split into two parts:

The first part of the campaign covered the period from late winter to early summer (March 15th and June 13th) and consisted of fortnightly monitoring to obtain background values of the system while primary production was still low. Data collected by the EA indicated that phytoplankton biomass was highest during or shortly after neap tides. Therefore, samples were collected 2 to 3 days after the neap tides to cover these potential chlorophyll maxima.

The second part of the campaign (high temporal resolution monitoring) was to document the rise and decline of one or more algal blooms. Therefore, as soon as conditions appeared to be favourable for bloom formation (*i.e.* a period of dry and

Table 4.1. Sample dates and times for the sampling campaign March-August 2008, including time difference to nearest high water (HW).

| Site | Date | Time | HW a.m. | LW a.m. | HW a.m./p.m. | LW p.m. | HW p.m. | Δt to HW* |
|------|-----------|-------|------------|------------|-----------------|------------|--------------|-------------------|
| B | 18/Mar/08 | 14:55 | 3:41 | 8:05 | 16:12 | 20:24 | | 1:17 |
| C | 18/Mar/08 | 13:20 | | | | | | 2:52 |
| D | 18/Mar/08 | 11:18 | | | | | | 4:54 |
| B | 1/Apr/08 | 17:10 | 2:57 | 7:00 | 15:42 | 19:39 | | 1:28 |
| C | 1/Apr/08 | 15:46 | | | | | | 0:04 |
| D | 1/Apr/08 | 14:05 | | | | | | 5:47 |
| B | 14/Apr/08 | 16:35 | 1:36 | 5:46 | 14:30 | 18:24 | | 2:05 |
| C | 14/Apr/08 | 14:55 | | | | | | 0:25 |
| D | 14/Apr/08 | 13:21 | | | | | | 3:51 |
| B | 28/Apr/08 | 13:19 | | 3:22 | 11:48 | 15:39 | | 1:31 |
| C | 28/Apr/08 | 12:49 | | | | | | 1:01 |
| D | 28/Apr/08 | 12:14 | | | | | | 0:26 |
| B | 15/May/08 | 18:05 | 3:32 | 7:44 | 16:05 | 20:05 | | 2:00 |
| C | 15/May/08 | 17:20 | | | | | | 1:15 |
| D | 15/May/08 | 16:30 | | | | | | 0:25 |
| B | 30/May/08 | 19:09 | 2:21 | 6:14 | 14:54 | 18:46 | | 4:15 |
| C | 30/May/08 | 18:39 | | | | | | 3:45 |
| D | 30/May/08 | 18:04 | | | | | | 3:10 |
| B | 13/Jun/08 | 18:52 | 2:42 | 6:40 | 15:15 | 19:06 | | 3:37 |
| C | 13/Jun/08 | 18:21 | | | | | | 3:06 |
| D | 13/Jun/08 | 17:38 | | | | | | 2:23 |
| B | 5/Jul/08 | 12:04 | | 0:39 | 8:27 | 12:52 | 20:47 | 3:37 |
| C | 5/Jul/08 | 11:19 | | | | | | 2:52 |
| D | 5/Jul/08 | 10:34 | | | | | | 2:07 |
| B | 8/Jul/08 | 15:22 | | 2:34 | 10:44 | 14:44 | 23:05 | 4:38 |
| C | 8/Jul/08 | 14:42 | | | | | | 3:58 |
| D | 8/Jul/08 | 13:56 | | | | | | 3:12 |
| B | 11/Jul/08 | 16:34 | 0:39 | 4:29 | 13:11 | 16:48 | | 3:23 |
| C | 11/Jul/08 | 16:01 | | | | | | 2:50 |
| D | 11/Jul/08 | 15:23 | | | | | | 2:12 |
| B | 15/Jul/08 | 20:35 | 4:54 | 9:06 | 17:20 | 21:34 | | 3:15 |
| C | 15/Jul/08 | 19:56 | | | | | | 2:36 |
| D | 15/Jul/08 | 19:00 | | | | | | 1:40 |
| B | 20/Jul/08 | 17:57 | | 0:23 | 8:08 | 12:34 | 20:26 | 2:29 |
| C | 20/Jul/08 | 18:30 | | | | | | 1:56 |
| D | 20/Jul/08 | 19:13 | | | | | | 1:13 |
| B | 23/Jul/08 | 14:25 | | 1:56 | 9:59 | 14:06 | 22:21 | 4:26 |
| C | 23/Jul/08 | 13:45 | | | | | | 3:46 |
| D | 23/Jul/08 | 13:03 | | | | | | 3:04 |
| B | 26/Jul/08 | 16:20 | | 3:46 | 12:21 | 16:06 | | 3:59 |
| C | 26/Jul/08 | 15:46 | | | | | | 3:25 |
| D | 26/Jul/08 | 15:06 | | | | | | 2:45 |
| B | 29/Jul/08 | 19:21 | 3:35 | 7:43 | 16:11 | 20:30 | | 3:10 |
| C | 29/Jul/08 | 18:47 | | | | | | 2:36 |
| D | 29/Jul/08 | 18:10 | | | | | | 1:59 |
| B | 1/Aug/08 | 21:30 | 6:41 | 11:08 | 19:00 | 23:43 | | 2:30 |
| C | 1/Aug/08 | 20:59 | | | | | | 1:59 |
| D | 1/Aug/08 | 20:33 | | | | | | 1:33 |
| B | 6/Aug/08 | 15:39 | | 2:03 | 10:07 | 14:11 | 22:24 | 5:32 |
| C | 6/Aug/08 | 16:09 | | | | | | 6:02 |
| D | 6/Aug/08 | 16:40 | | | | | | 6:33 |

Δt relates to the HW in bold which is in most cases the temporally closest HW to the time of sample collection

settled weather following sufficient rainfall to flush the estuary) the estuary was sampled every 3 to 5 days for one month. To ensure consistency of the data and to avoid the introduction of artefacts, sample collection was timed to represent similar tidal states, *i.e.* during the ebbing tide between the first and fifth hour after high tide.

4.3. Sample sites

4.3.1. Umberleigh, Site A

Umberleigh (Figure 4.2) at the River Taw is 7.16 km south of Newbridge, which is the tidal limit. The sample site is located at 50° 59' 43" N, 3° 59' 06" W at the river flow gauging facility of the EA. The river bed and banks appeared to be in a near pristine condition without any major channelling or construction apart from the adjacent road bridge. The surrounding land was mostly pasture with some woodland.



Figure 4.2. (left) River Taw at Umberleigh with the EA gauging facility in the foreground (25th Sept. 2006); (right) River Taw at Umberleigh with surface algal scum (25th Sept. 2006).

4.3.2. Barnstaple, Site B

Sampling site B is located at 51° 04' 33" N, 4° 03' 26" W near Barnstaple town centre close to the Barnstaple Leisure Centre car park (Figure 4.3). While it is still the upper, channelled section of the estuary, it starts to widen out only a few hundred metres

downstream. The banks are partly heavily modified with stonewalls and urban (transport) structures and partly of marshland character (Figure 4.4). The substrate is silt and mud.

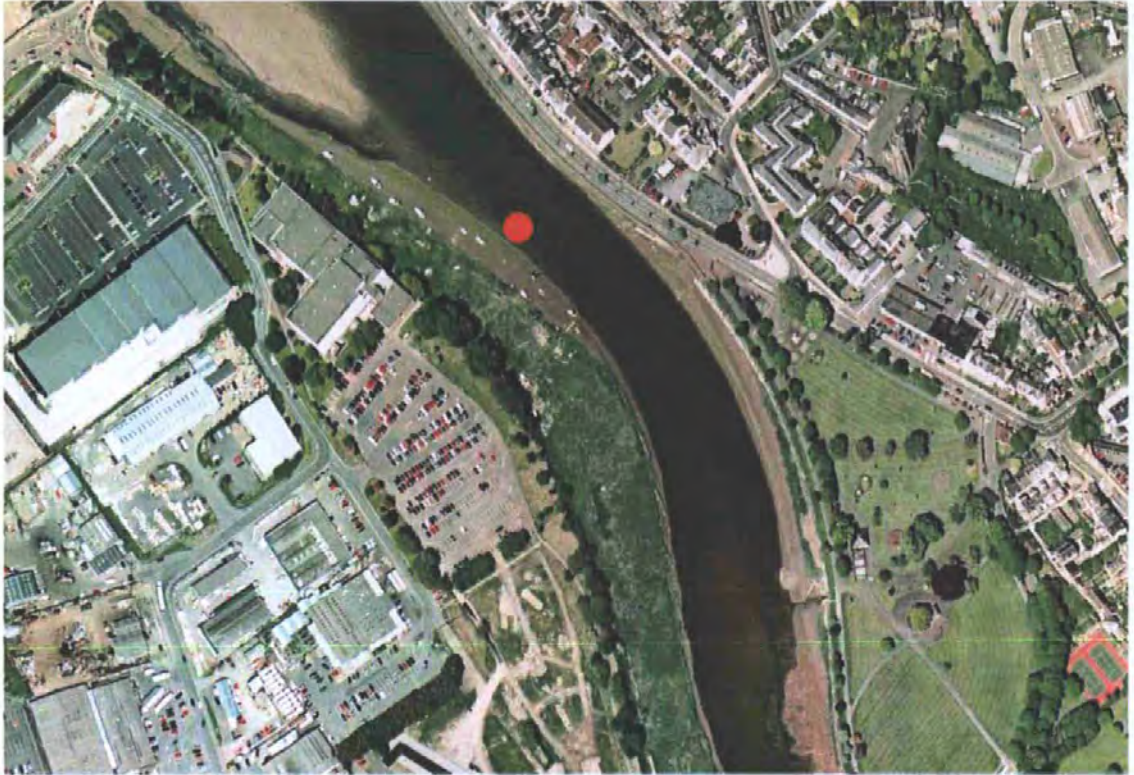


Figure 4.3. Satellite image of the surroundings of site B at the red circle (Google Earth).



Figure 4.4. (left) Stone structures on the northern bank of the Taw Estuary as seen from site B (22nd April 2007); (right) Looking south from site B (22nd April 2007).

4.3.3. Ashford STW, Site C

Site C is located at 51° 05' 38" N, 4° 07' 25" W in the central section of the estuary, 2.09 km linear distance WNW of the outflow of Ashford sewage treatment works (Figure 4.5).



Figure 4.5. Tilted satellite image of the area around site C (red circle), looking WNW. In the foreground are the Ashford STW and the main channel of the Taw Estuary (Google Earth).



Figure 4.6. (left) Looking south-east from site C (23rd Aug. 2007); (right) Looking north-west from site C (23rd Aug. 2007).

Despite the width of the estuary, the sample site is adjacent to the main channel. The bank at the site consists of a concrete enforced dyke (Figure 4.6) and most of the surrounding land is used as farmland. The substratum is mud with rocky debris, covered with fucoid algae, becoming more sandy towards the middle of the estuary.

4.3.4. Crow Point, Site D

Site D is located at 51° 04' 35" N, 4° 10' 54" W, 1.28 km NNE of Crow Point and was the outermost site sampled (Figure 4.7).



Figure 4.7. Satellite image of the area surrounding site D (red circle) at extreme low tide (Google Earth).

The surrounding area consists of transformed marshland that is used for sheep and cattle grazing. To the SW is some salt marsh with abundant *Atriplex portulacoides*, extensive sand dunes and the mouth of the estuary. The north bank at the sample site consists of a dyke and rocky structures against shifting sands and beach erosion (Figure 4.8). The substrate is sand at the upper shore with some silt closer to the low-water line,

interspersed with some *Spartina sp.* and *Salicornia europaea*. In May 2006, vast intertidal areas were covered by dense stands of *Ulva (Enteromorpha) intestinalis* (Figure 4.8).



Figure 4.8. (left) Looking towards Instow from site D (25th Sept. 2006); (right) *Ulva (Enteromorpha) intestinalis* and several *Fucaceae* covering the intertidal flat near site C, view to the east (13th May 2006).

4.4. Field equipment

A YSI 6820 V2 multiprobe (Figure 4.9) was used to measure salinity, conductivity, temperature, pH, turbidity and dissolved oxygen. The data were stored in the system and on paper as a backup. The dissolved oxygen probe was calibrated for every sample day for barometric pressure. The pH, salinity and turbidity probes were calibrated at the beginning of the field campaign in March and again before the start of the intense sampling campaign in June with a 3 point calibration as laid out in the user manual. Accuracy was checked on a regular basis using standard solutions. The results from the calibration checks showed that no recalibration was needed during any campaign.

4.5. Sampling, sample preservation and storage

After measuring physico-chemical parameters with the multiprobe, the samples were collected in acid washed 2.5 L HDPE bottles. Initially, the samples were processed in

the field but this proved to be impractical, particularly in wet and windy conditions, and involved a high potential for sample contamination. Therefore, samples were stored in a portable fridge at 8 °C until arrival at the laboratory facilities in Plymouth.

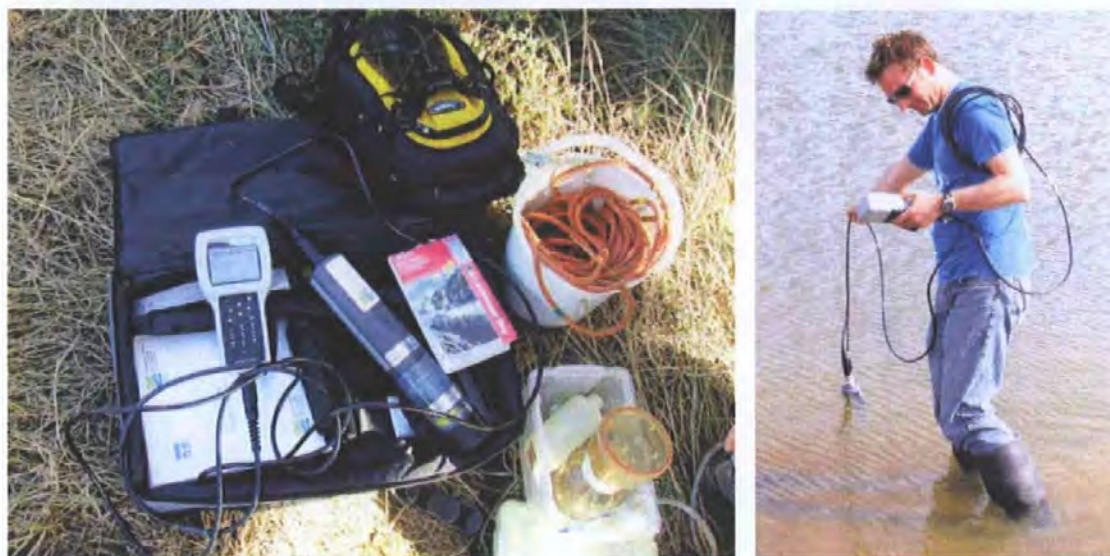


Figure 4.9. (left) Some field equipment including the YSI 6820 V2 multiprobe; (right) The YSI multiprobe in the field.

Upon arrival, each sample for the macronutrient determination was vacuum filtered through a 0.45 μm Whatman cellulose acetate membrane filter (Fisher Scientific, UK; FDC-820-030T), held in a Nalgene polysulfone filtration unit. The filtrate was sub-sampled for PO_4 , NO_2+NO_3 and SiO_2 for subsequent determination on a SKALAR SANplus segmented flow analyser (see section 4.7). Each sub-sample was transferred into an acid washed (see section 4.7.2) 20 mL Wheaton scintillation vial (Fisher Scientific, UK; VGA-875-030C), labelled, transferred into sealable plastic bags and stored at -20 °C until analysis, following the recommendations of Dore (1996) and Gardolinski *et al.* (2001). A separate sub-sample was taken at the same time for ammonium determination. The required volumes for the measurement of fluorescence, matrix effects and background fluorescence (see section 4.8.6) were pipetted into cleaned (see section 4.8.1) 20 mL Wheaton scintillation vials, labelled, transferred into

sealable plastic bags and frozen at -20 °C until analysis (Degobbis, 1973; Avanzino and Kennedy, 1993).

For the determination of dissolved organic carbon and total dissolved nitrogen (DOC-TDN), a sample of known volume was filtered through a clean, precombusted Whatman GF/F filter (Fisher Scientific, UK; FDJ-570-070S) using a vacuum pump and a clean (see section 4.9.2) glass filtration unit. Because the filter membrane with the retained phytoplankton was to be used for pigment analysis, the filtration was performed under subdued light, as chlorophylls are very light sensitive. Each filtered sample was transferred to a clean, precombusted (see section 4.9.2) 30 mL Chromacol glass vial (Fisher Scientific, UK; VGA-080-080S) and acidified with 50% (v/v) hydrochloric acid to pH ~2 and then frozen in sealable plastic bags at -20 °C until analysis (Sharp *et al.*, 1995).

The filter membranes used for chlorophyll extraction were transferred into test tubes with HDPE screw caps filled with 90% acetone (see section 4.10.1) and stored at -20 °C. To protect the extracted pigments from light damage, each test tube was wrapped in aluminium foil.

4.6. River flow

Discharge of the River Taw was measured by the EA at the gauging station #050001 at Umberleigh and reported to the National River Flow Archive (NRFA), maintained by the Centre for Ecology & Hydrology (CEH) in Wallingford, from where the data were obtained. Data were provided as average daily flow in m^3s^{-1} .

4.7. Determination of nitrate + nitrite, phosphate and silicate

4.7.1. Instrumentation

An automated, air segmented continuous flow nutrient analyser (SKALAR SANplus, Breda, NL) was used for the determination of NO_2+NO_3 , PO_4 and SiO_2 . It consists of a computer controlled autosampler (SKALAR series 1074) for up to 300 samples and a peristaltic pump, a SKALAR SA 4000 chemistry unit equipped with two 16 channel peristaltic pumps, an air bubble injector with a separate air compressor, a four channel module holder, on which the manifold is set up for the different chemistries and four flow-through dual-channel single-beam photometer heads. The set up also includes two SKALAR SA 6250 dual-channel single-beam photometers, which are linked to a MS Windows environment through a SKALAR SA 8502 interface, which modulates the analogue voltage signal to digital data. These are quantified by the SKALAR FlowAccess 2.0.11 software package. This software computes the calibration regression according to the set standards and calculates the analyte concentrations, which are corrected for sample drift by measuring a drift standard after every ten samples. A typical first order calibration curve for NO_2+NO_3 is shown in Figure 4.10; the output curves for PO_4 and SiO_2 are similar.

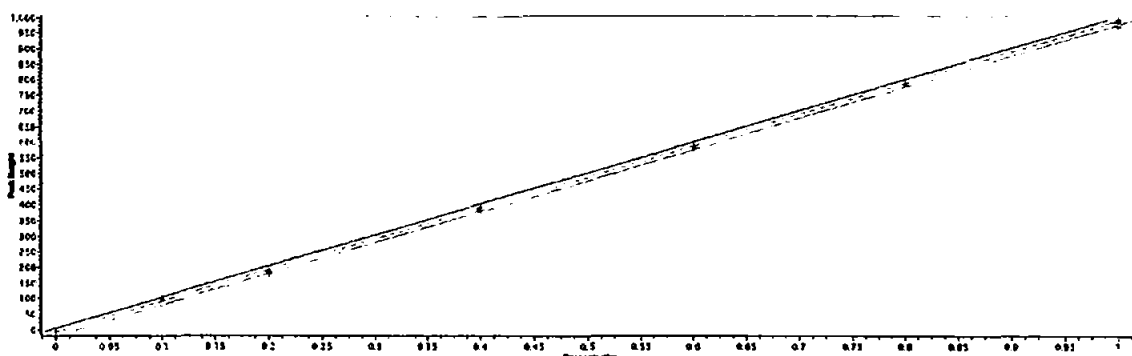


Figure 4.10. Example calibration regression curve for NO_2+NO_3 over the range 0 – 72 μM .

Intercept = -7.20, Slope = 997.71, $r^2 = 0.99976$.

4.7.2. Cleaning protocol

All glass- and plastic-ware, as well as pipette tips and the 20 mL HDPE Wheaton scintillation vials (Fisher Scientific, UK; VGA-875-030C) for water samples were soaked for at least 24 h in a nutrient-free detergent solution (2% v/v, Neutracon, Decon Laboratories, UK), rinsed five times with water obtained from a reverse osmosis system (RO-water) and leached for at least 24 h in 10% (v/v) hydrochloric acid. Afterwards, all containers were rinsed five times with high purity water (HPW; $18.2 \text{ M}\Omega \text{ cm}^{-1}$) and left to dry in a covered plastic container to prevent contamination from dust. The dried apparatus was stored in sealable plastic bags.

4.7.3. Method description for the determination of nitrate plus nitrite

The method is based on the reduction of nitrate in copperised cadmium, followed by the diazotization of nitrite with sulfanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form a pink azo dye with a maximum light absorption at 540 nm.

The following two reagents are used:

- A buffer solution, containing 50 g ammonium chloride (Fisher Scientific, UK; A/3920/53), 1 mL ammonium hydroxide (Fisher Scientific, UK; A/3240/PB17) and 2 mL surfactant (Brij 35, 30%, SKALAR Analytical B.V., 13900), made up to 1000 mL with HPW.
- A colour reagent, containing 150 mL o-phosphoric acid 85% (Fisher Scientific, O/0500/PB17), 10 g sulfanilamide (Sigma Aldrich, S9251-500g), 0.5 g N-(1-naphthyl)ethylenediamine dihydrochloride (Sigma Aldrich, 2222488-25g) and made up to 1000 mL with HPW.

The HPW used for the production of reagents and standards was degassed for 15 min by sparging with helium.

To produce the stock solution for the standards, 0.606 mg of pre-dried sodium nitrate, accurately weighed, was dissolved in 1000 mL of HPW. The working standards were produced on the day of analysis by dilution from the $\text{NO}_3\text{-N}$ stock with degassed HPW and sonicated for 15 min. The method used (Figure 4.11) was described by Tuckwell (2007a) to be suitable for concentrations of $0.02 - 2.0 \text{ mg L}^{-1} \text{ N}$ ($1.42 - 142 \text{ }\mu\text{M}$). However, the calibration standards produced a linear signal up to $5.0 \text{ mg L}^{-1} \text{ N}$ ($357 \text{ }\mu\text{M}$), and hence a single manifold setup was used for all samples from the Taw Estuary.

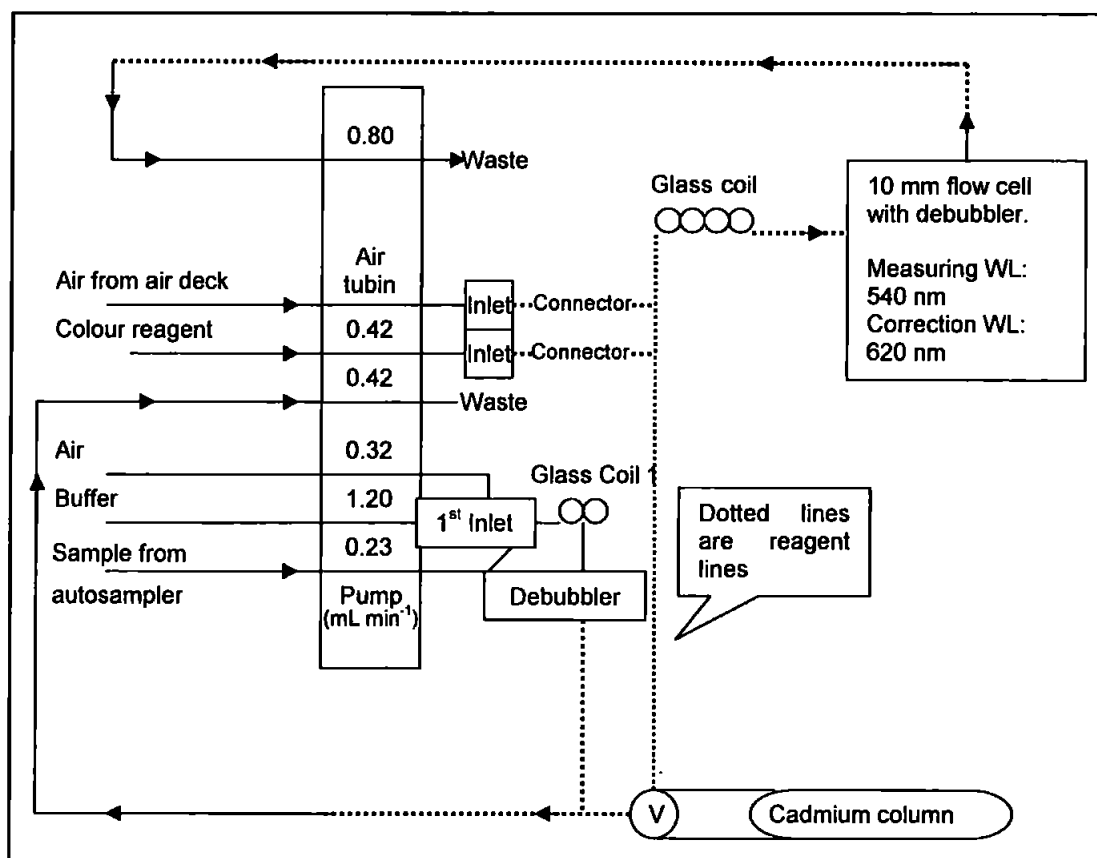


Figure 4.11. Setup of the chemistry manifold for the determination of NO_2+NO_3 . Modified from Tuckwell (2007a).

Typically, the calibration set shown in Table 4.2 was used. Estuarine NO_2+NO_3 concentrations varied over two orders of magnitude between the freshwater end member and the marine end member. Hence two calibration subsets were used: one for low concentration samples and one for high concentration samples. The calibration curve from standards S0–S6 (Table 4.2) have been used for samples with NO_2+NO_3 concentrations $<73 \mu\text{M}$ and the calibration curve from standards S0, S6–S10 (Table 4.2) for concentrations $>73 \mu\text{M}$.

Table 4.2. Typical calibration set for the determination of NO_2+NO_3 .

| Standard | $\text{NO}_2+\text{NO}_3\text{-N mg L}^{-1}$ | μM |
|----------|--|---------------|
| S0 | 0.00 | 0.00 |
| S1 | 0.10 | 7.27 |
| S2 | 0.20 | 14.5 |
| S3 | 0.41 | 29.0 |
| S4 | 0.61 | 43.6 |
| S5 | 0.81 | 58.1 |
| S6 | 1.02 | 72.7 |
| S7 | 2.04 | 145 |
| S8 | 3.05 | 218 |
| S9 | 4.07 | 291 |
| S10 | 5.09 | 363 |

Table 4.3. Parameters of the calibration regression line for NO_2+NO_3 in Figure 4.10 with the intercept (a), the slope (b) and the regression coefficient r^2 .

| Calib. set | a | b | r^2 |
|------------|-------|--------|--------|
| Low range | -7.20 | 997.71 | 0.9998 |
| High range | 99.76 | 878.21 | 0.9975 |

4.7.4. Method description for the determination of phosphate

The basis of this method is the molybdenum blue chemistry: dissolved phosphate reacts at pH ~ 2 with ammonium molybdate and potassium antimony tartrate to form a

heteropoly antimony-phosphomolybdate acid which is reduced by ascorbic acid to molybdenum blue with a maximum light absorbance at 880 nm.

The method on the SKALAR manifold uses two reagents:

- An ammonium molybdate solution, containing 0.230 g potassium antimony tartrate (Acros Organics, 22380-1000), 69.4 mL sulfuric acid (Fisher Scientific, UK, S/9160/PB17), 6 g ammonium molybdate (AnalaR, BDH, 10028), 2 mL of FFD6 surfactant (SKALAR Analytical B.V, 13908) and made up to 1000 mL with degassed HPW.
- An ascorbic acid solution, containing 11 g ascorbic acid (Reagent ACC, Acros Organics, 401475000), 60 mL acetone (Fisher Scientific, UK, A/0600/PC17), 2 mL FFD6 and made up to 1000 mL with degassed HPW.

The manifold setup is shown in Figure 4.12 (Tuckwell, 2007b) and was set up for concentrations ranging from 0.5 – 500 $\mu\text{g L}^{-1}$ P (0.016 – 16.14 μM).

Standards were produced from pre-dried potassium dihydrogen orthophosphate. 0.4394 g of potassium dihydrogen orthophosphate was accurately weighed and dissolved in 1000 mL HPW to obtain a 100 mg L^{-1} $\text{PO}_4\text{-P}$ stock. From this, a 10 mg L^{-1} intermediate stock solution was created. This allowed larger volumes to be transferred by pipette into the working standard volumetric flasks, which helped improve the accuracy of the standard concentrations. The working standards were produced fresh on each day in degassed HPW and sonicated for 15 min. A typical set of calibration standards is shown in Table 4.4.

Typical calibration regression line elements were $a = -3.38$, $b = 13.55$ and $r^2 = 0.9997$ where a is the slope and b the intercept. The sample concentrations were calculated by

the FlowSoft software and corrected for sample drift by measuring a drift after every ten samples.

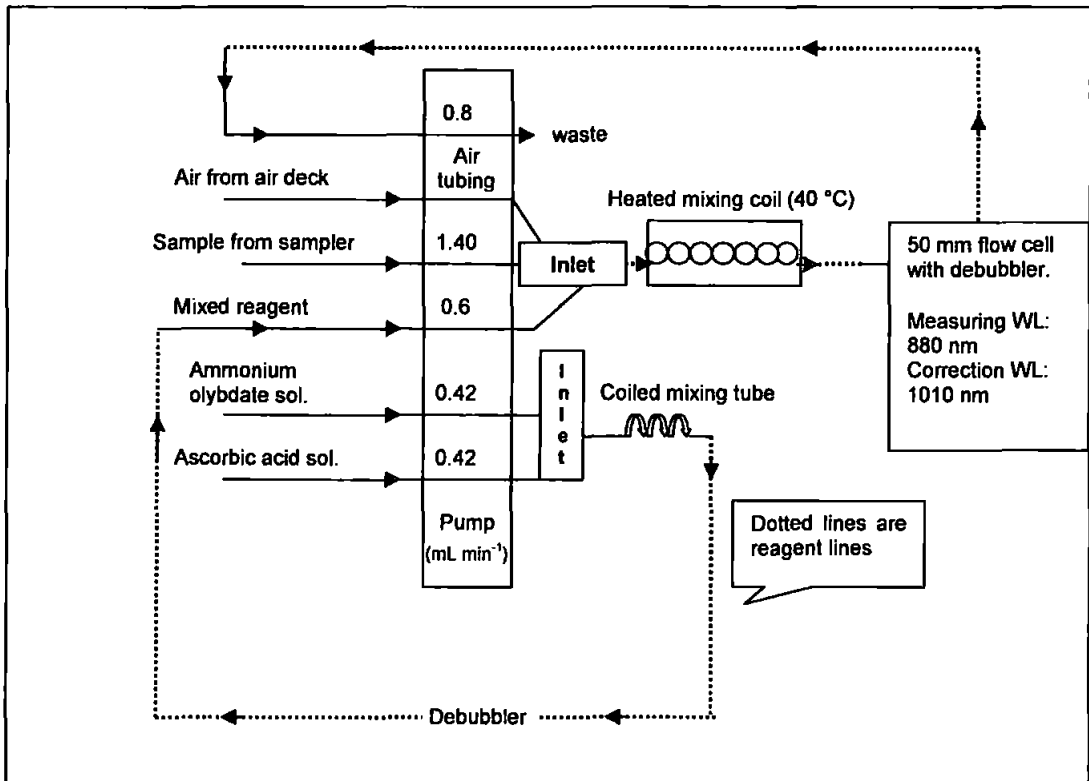


Figure 4.12. Setup of the chemistry manifold for the determination of PO_4 . Modified from Tuckwell (2007b).

Table 4.4. Range of standards used for the determination of PO_4 .

| Standard | $\text{PO}_4\text{-P } \mu\text{g L}^{-1}$ | μM |
|----------|--|---------------|
| Blank | 0 | 0.00 |
| S1 | 2.5 | 0.08 |
| S3 | 5 | 0.16 |
| S4 | 10 | 0.32 |
| S5 | 20 | 0.65 |
| S6 | 40 | 1.29 |
| S7 | 60 | 1.94 |
| S8 | 80 | 2.58 |

4.7.5. Method description for the determination of silicate

In this method, silicate forms molybdosilicic acid in the presence of dilute sulfuric acid and ammonium molybdate. The molybdosilicic acid is reduced with ascorbic acid to form a blue dye with a maximum absorbance wavelength at 810 nm. To avoid interference from phosphate present in the sample, oxalic acid is added.

The method requires four reagents, all of which were prepared using HPW, degassed by sparging for 15 min with helium:

- A sulfuric acid solution with 5 mL of sulfuric acid (Fisher Scientific, UK, S/9160/PB17) plus 2 mL of FFD 6 (SKALAR Analytical B.V, 13908) in 1000 mL of HPW.
- An ammonium molybdate solution of 10 g ammonium molybdate (AnalaR, BDH, 10028) with 2 mL of FFD6 in 1000 mL HPW.
- An oxalic acid solution containing 44 g oxalic acid (AnalaR, BDH, 101744U) in 1000 mL HPW.
- An ascorbic acid solution with 40 g ascorbic acid (Reagent ACC, Acros Organics, 401475000) made up to 1000 mL in HPW.

A 100 mg L⁻¹ SiO₂ stock solution was prepared with 0.473 g sodium metasilicate in 1000 mL of HPW. From this the working standards were prepared fresh with degassed HPW on the day of analysis. Following the method described by Tuckwell (2008), the manifold was set up as shown in Figure 4.13 and is suitable for the determination of silicate ranging from 0.2 – 5 mg Si L⁻¹ (3.3 – 166 μM), covering the concentrations expected in the Taw Estuary.

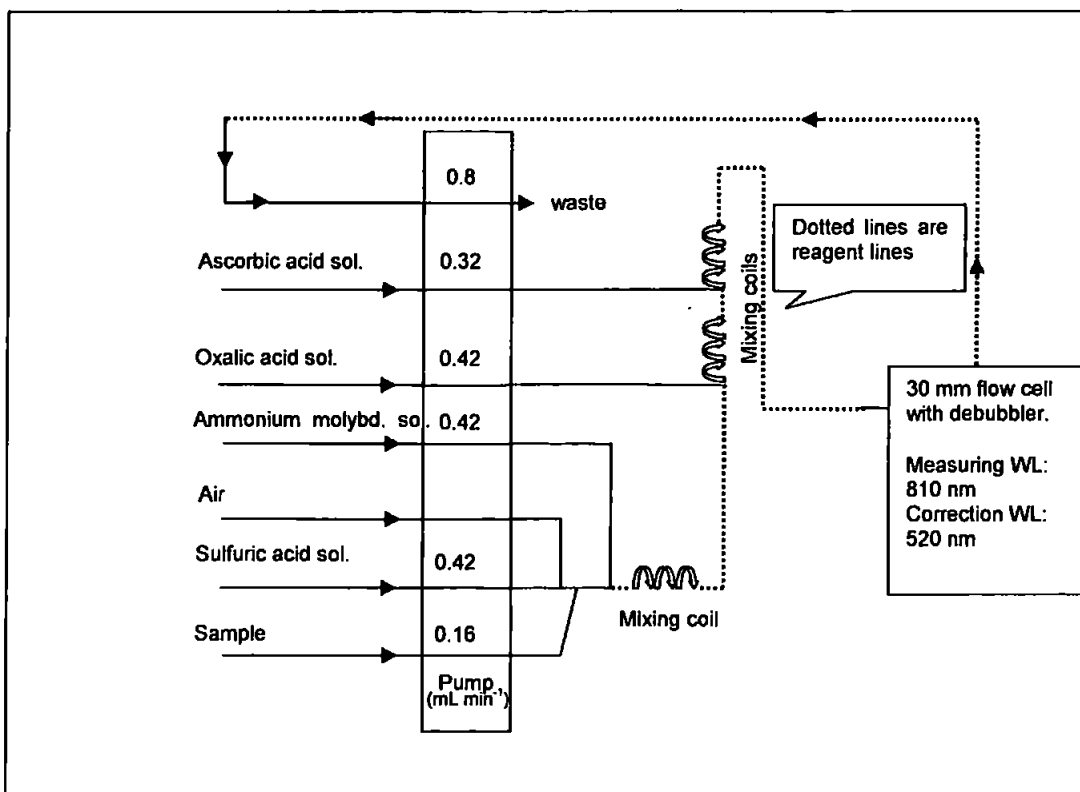


Figure 4.13. Setup of the chemistry manifold for the determination of silicate.

Table 4.5. Typical calibration set for the determination of SiO₂.

| Standard | SiO ₂ mg L ⁻¹ | μM |
|----------|-------------------------------------|------|
| S0 | 0.00 | 0.00 |
| S1 | 0.10 | 1.72 |
| S2 | 0.21 | 3.44 |
| S3 | 0.41 | 6.89 |
| S4 | 0.62 | 10.3 |
| S5 | 0.83 | 13.8 |
| S6 | 1.03 | 17.2 |
| S7 | 2.07 | 34.4 |
| S8 | 3.10 | 51.6 |
| S9 | 4.14 | 68.8 |
| S10 | 5.17 | 86.1 |

For calibration, the set of standards listed in Table 4.5 was used. Because silicate concentrations vary over two orders of magnitude from the river end member to the marine end member, the calibration set was split into two subsets, one with standards

S0S6, covering concentrations below 18 μM Si, and one with standards S0 and S6 – S10 for concentrations >18 μM Si. The calibration data for the regression equations are provided in Table 4.6.

Table 4.6. Parameters of typical calibration regression lines with the intercept (*a*), the slope (*b*) and the regression coefficient r^2 .

| Calib. set | <i>a</i> | <i>b</i> | r^2 |
|------------|----------|----------|--------|
| Low range | 139.48 | 180.94 | 0.9946 |
| High range | 554.22 | 160.21 | 0.9927 |

4.8. Determination of ammonium

For measuring ammonium in seawater a number of methods exist, most based on the indophenol method (Brzezinsky 1987, Catalano 1987, Grasshoff et al 1999). However, the drawbacks of the indophenol blue method, such as high and variable blanks, difficulties with high limits of detection and the use of toxic reagents, led to the decision to use the method of Holmes *et al.* (1999), which is applicable to samples from a wide range of aquatic environments, relatively simple and accurate, even at very low concentrations. Also, none of the reagents used are toxic. The active agent is orthophthaldialdehyde (OPA), which reacts with ammonium and primary amines to form a highly fluorescent product (Roth 1971). In the presence of sodium sulfite (instead of mercaptoethanol) OPA loses its sensitivity to amino acids and becomes essentially specific for ammonium (Kerouel and Aminot, 1997).

4.8.1. Cleaning procedure

The 20 mL HDPE Wheaton scintillation vials (Fisher Scientific, UK; VGA-875-030C) for water samples and standards were soaked for a minimum of 24 h in a nutrient-free detergent solution (2% v/v, Neutracon, Decon Laboratories, UK), rinsed five times with

reverse osmosis water and incubated for at least 24 hours in OPA working reagent (see 4.8.2). After the OPA incubation, all containers were rinsed six times with HPW. To avoid contamination of the inside of the container, the vials were left to dry on the outside only with the caps on. The volumetric flasks for standard preparation and pipette tips were immersed for a minimum of 24 h in nutrient-free detergent (Neutracon, Decon Laboratories, UK), then rinsed five times under RO-water and then transferred for at least 24 h to a 10% (v/v) hydrochloric acid bath. The last step involved rinsing six times under HPW, drying and storage of the items in sealable plastic bags until use.

4.8.2. Reagents

All reagents were prepared using HPW and all chemicals were of analytical reagent grade. The sodium sulfite solution contained 0.4 g sodium sulfite (Fisher Scientific, UK; S/6850/53) in 50 mL of HPW. For the buffer solution, 40 g of sodium tetraborate (Fisher Scientific, UK; S/7040/53) was dissolved in 1 L of HPW, sonicating for 15 min. For the OPA solution, 4 g of orthophthaldialdehyde (98%; Alfa Aesar, UK; A13299) was dissolved in 100 mL of high purity ethanol (Fisher Scientific, UK; E/0650DF/08). Because OPA is light sensitive, this step and the shaking of the 100 mL volumetric flask were conducted under subdued light. To obtain the final working reagent, in a brown Winchester bottle, 2 L of sodium tetraborate solution and 10 mL of sodium sulfite solution were mixed and 100 mL of OPA solution added. The final OPA-working reagent was stored in the dark at room temperature and left to age for at least one day, as its contribution to the blank signal decreased over time. Also, 2 L of borate buffer solution without OPA or sodium sulfite was stored separately in a brown Winchester bottle.

4.8.3. Instrumentation and instrument settings

A Hitachi F-4500 fluorescence spectrophotometer was used for all fluorescence measurements. The excitation and emission slits were set to 5 nm, the PMT voltage was 700 V and the response was set to “auto”. Maximum fluorescence was achieved at an excitation wavelength of ~362 nm and an emission wavelength of ~422 nm. Scans of the spectra obtained are shown in Figure 4.14. Peak height was used for the calculation of background fluorescence, matrix effects and the final ammonium concentrations.

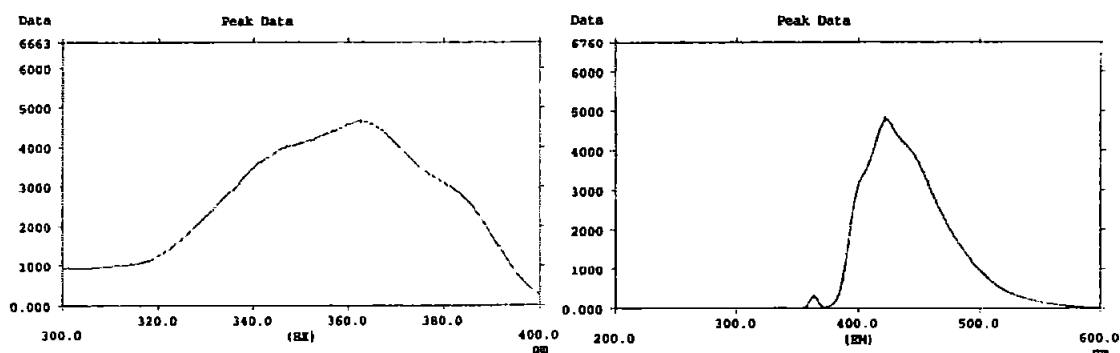


Figure 4.14. Excitation (left) and emission spectra (right) at the applied fluorimeter settings.

4.8.4. Analytical procedure

The samples were defrosted at room temperature for 2 h. Then, 2.5 mL of borate buffer were added to the background fluorescence containers. The matrix effects containers with only 5 mL of sample were spiked with 5 mL of the 1.0 μM ammonium standard. Finally, 2.5 mL of OPA-working reagent (OPA-WR) were added to the standards, the spiked standards, the sample and the spiked samples. Holmes *et al.* (1999) reported that maximum fluorescence was achieved after incubation in the dark for 2 h. Fluorescence then decreased slightly over the next hour and remained stable for another 4 h. For this reason, and to obtain stable fluorescence values during analysis (depending on the number of samples, this could last for up to 3 h), all samples and standards were

incubated in the dark for about 3 h. Also, one standard was used as a drift standard and analysed every 30 minutes to assess for changes in fluorescence.

4.8.5. Preparation of standards and calibration

For the preparation of a 10 mM stock solution, 534.92 mg of ammonium chloride (Fisher Scientific, UK; A/3920/53) was accurately measured and dissolved in 1000 mL HPW.

A 100 μM stock solution was obtained by two 1:10 serial dilutions. From this, 5 ammonium standards were generated: 0.1, 0.5, 1, 5 and 9 μM . All standards and the 100 μM stock solution were prepared in 250 mL volumetric flasks. To minimise the risk of introduced artefacts the zero standard underwent the same treatment. The stock solution was stored in a fridge at 4 °C, the intermediate stocks and working standards were prepared on the day of analysis.

Fluorescence was linear over the required range (0.1 – 9 μM) with very good precision in the lower range between 0.1 and 1 μM (Figure 4.15). The limit of detection (LoD) was calculated as the intercept of the regression curve plus three times the standard deviation of the fluorescence of 5 blanks, resulting in an LoD of this method of 0.075 μM .

4.8.6. Calculation of background fluorescence, matrix effects and ammonium concentrations

Holmes *et al.* (1999) found that background fluorescence or sample auto fluorescence was generally low and pH dependent but there was spectral overlap with the ammonium-OPA fluorescence signal. To correct for this possible error, the fluorescence

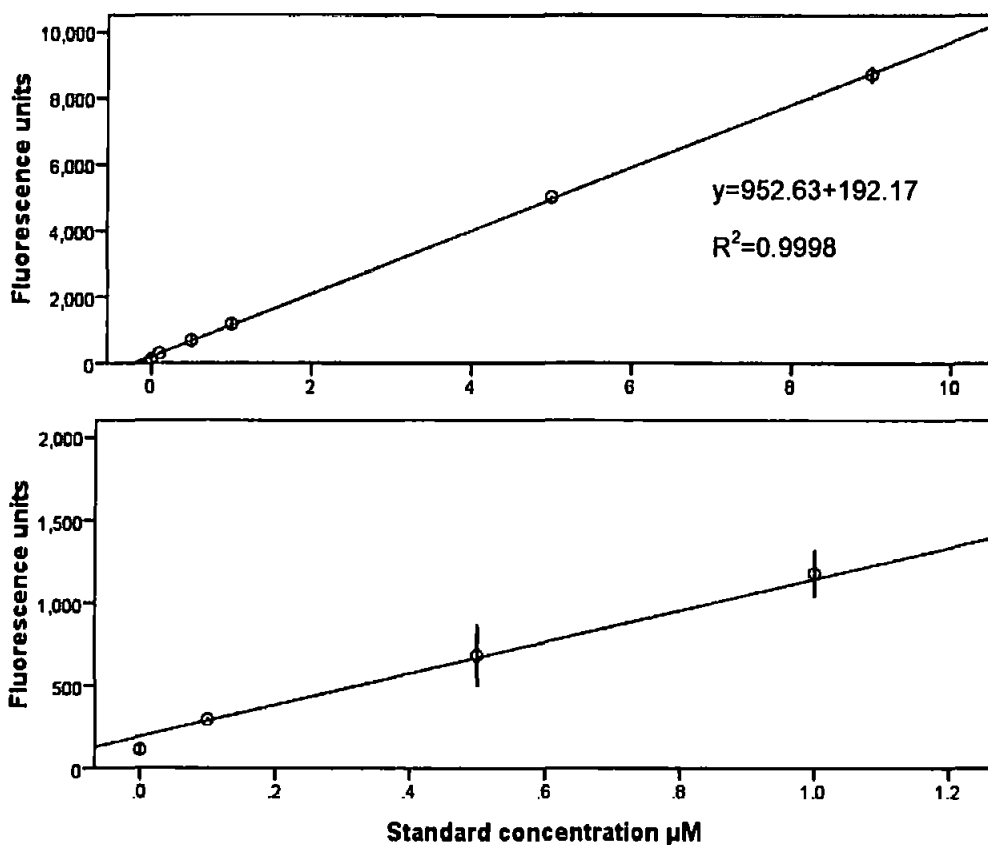


Figure 4.15. (top) Calibration curve for ammonium with the standards 0, 0.1, 0.5, 1, 5 and 9 μM with the equation for the calibration curve and the regression coefficient. (bottom) Detail of the calibration set with the standards 0, 0.1, 0.5 and 1 μM . The error bars depict the 95% confidence interval of the mean.

of the sample incubated with borate buffer ($F_{\text{Sample BF}}$) was subtracted from the fluorescence of the sample incubated in OPA-WR ($F_{\text{Sample (observed)}}$)

$$F_{\text{Sample (NH}_4)} = F_{\text{Sample (observed)}} - F_{\text{Sample BF}}$$

which yields the corrected ammonium fluorescence $F_{\text{Sample (NH}_4)}$.

Matrix effects (ME) were reported by Holmes *et al.* (1999) to originate from sea salts and dissolved organic matter, which makes the sample behave differently than the standards. Following the Holmes' method, samples and standards were treated with the same amount of ammonium and the response was calculated:

$$ME = \left[\frac{F_{Standard (spike)} - F_{Standard (zero)} - (F_{Sample (spike)} - F_{Sample (observed)})}{(F_{Standard (spike)} - F_{Standard (zero)})} \right] \times 100$$

To calculate the sample's ammonium concentration, the value $F_{Sample (corrected)}$ was entered into the standard regression:

$$F_{Sample (corrected)} = F_{Sample (NH_4)} + \left[F_{Sample (NH_4)} \times \left(\frac{ME}{100} \right) \right]$$

4.9. Determination of dissolved organic carbon and dissolved organic nitrogen

4.9.1. Method description and instrumentation

Dissolved organic carbon (DOC) in marine waters is mostly determined using wet chemical oxidation with persulfate (Ogura, 1970), UV oxidation (Armstrong *et al.*, 1966), or high temperature catalytic combustion (HTCC; Suzuki *et al.*, 1985). After oxidising the organic carbon, the CO₂ produced is usually quantified using non-dispersive infrared detection (Pan *et al.*, 2005).

Currently, there is no suitable method for the direct determination of dissolved organic nitrogen (DON; Pan *et al.*, 2005), therefore total dissolved nitrogen (TDN) and the dissolved inorganic nitrogen fraction (DIN; *i.e.* NO₂, NO₃, NH₄) have to be determined first and DON determined by difference:

$$DON = TDN - DIN$$

Methods for the determination of TDN include wet chemical oxidation using persulfate digestion and UV oxidation followed by the spectrophotometric determination of nitrate (Sharp *et al.*, 2004) and high temperature catalytic combustion followed by chemiluminescence detection of nitric oxide (NO; Badr *et al.*, 2003). For this study,

high temperature catalytic combustion of total organic carbon coupled with nitrogen chemiluminescence detection (HTCC TOC-NCD) was used, following the method of Pan *et al.* (2005). The instrumentation consisted of an ASI 5000A autosampler, a Shimadzu TOC 5000A Analyser, a Sievers NCD255 Detector, a vacuum pump and two independent PCs connected to the TOC analyser and the NCD detector, respectively (Figure 4.16).

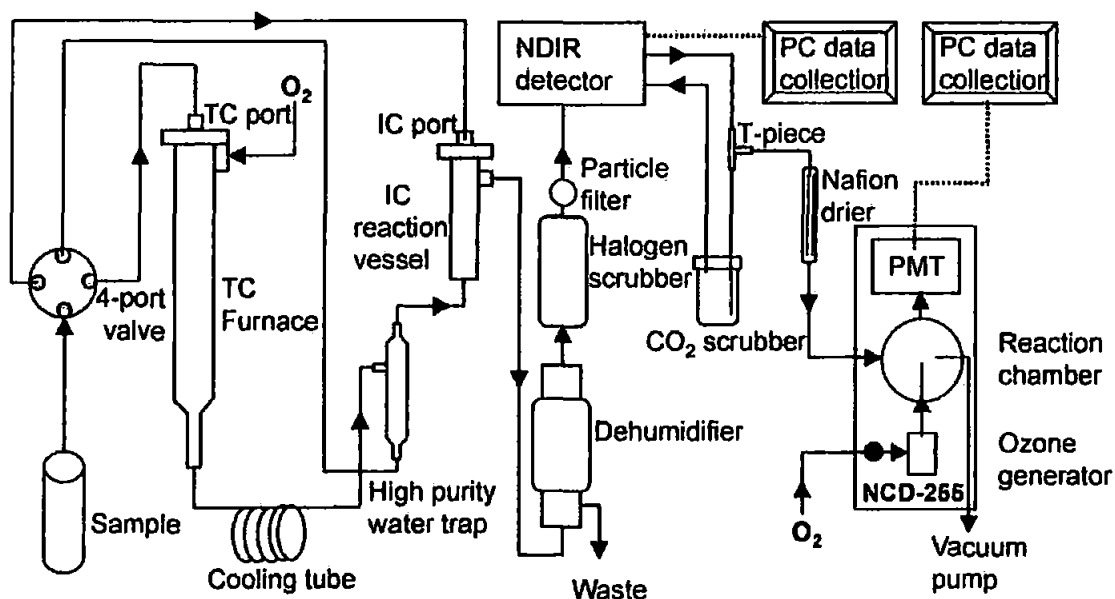


Figure 4.16. Setup of the Shimadzu TOC 5000A total carbon analyser coupled with the Sievers NCD 255 nitrogen chemoluminescence detector (from Badr *et al.*, 2003).

Before the acidified sample was introduced into the TOC analyzer, dissolved inorganic carbon was removed by sparging the sample with high purity oxygen, which was also the sample carrier. 100 μL sample aliquots were injected onto the catalytic column (0.5% platinum on aluminium oxide) and combusted at 680 $^{\circ}\text{C}$. The resulting combustion products (CO_2 , nitric oxide, water, and free radicals) were then passed through a 25% v/v phosphoric acid solution to prevent the absorption of CO_2 by the water vapour, dehumidified and cleaned by a halogen scrubber and membrane filtration. The CO_2 signal (voltage) from the infrared gas analyser was then recorded and reported

as peak area by the Shimadzu TOC software. The peak areas were then used for the calculation of the calibration curve and sample DOC concentrations.

The exhaust gases from the TOC analyzer were then pulled into the NCD by a vacuum pump and passed through another dehumidifier to remove residual water vapour. The nitric oxide (NO) from the combustion process in the TOC analyser was oxidised with O₃ from the ozone generator in the NCD detector to form the NO₂* radical. As it decayed to its ground state, the emitted chemoluminescence was detected by a PMT with the resulting signal (voltage) being recorded. The integrated peak areas were then used to calculate sample concentrations using the standard calibration graph.

4.9.2. Cleaning procedure

All glass- and plastic-ware that came in contact with either samples or standards was soaked for at least 24 h in nutrient-free detergent solution (2% v/v, Neutracon, Decon Laboratories, UK), rinsed five times with RO water and then transferred into 10% (v/v) hydrochloric acid. After a minimum immersion time of 24 h, the items were rinsed five times with HPW. The plastic-ware (*e.g.* pipette tips, caps and lids) were then left to dry, whereas the glassware was wrapped in aluminium foil and combusted for 6 h in a furnace at 450 °C.

4.9.3. Calibration and analytical procedure

All standards were prepared using HPW and all chemicals were of analytical reagent grade. Potassium hydrogen phthalate (KHP; VWR BDH Prolabo; 102075k) and glycine (VWR BDH Prolabo; 284584L) were used as standards. Both were dried in a beaker covered with a watch glass at 110 °C for 24 hours. For the 600 mM C / 100 mM N stock solution 0.51056 g KHP and 0.37535 g glycine were weighed on a high precision balance (readability to 0.01 mg) and dissolved in 50 mL of HPW. Intermediate stock

solution of 60 mM C / 10 mM N and 6 mM C / 1 mM N were obtained by serial dilution. From the 6 mM C / 1 mM N stock, the following standards (including one blank) were generated (Table 4.7).

Table 4.7. Standards for TOC-NCD analysis.

| | C μ M | N μ M |
|-------|-----------|-----------|
| Std 1 | 0 | 0 |
| Std 2 | 60 | 10 |
| Std 3 | 120 | 20 |
| Std 4 | 240 | 40 |
| Std 5 | 360 | 60 |
| Std 6 | 480 | 80 |
| Std 7 | 600 | 100 |

All stock and intermediate stock solutions and all standards were acidified to pH \sim 2 with 6 M hydrochloric acid. The acidified 600 mM C / 100 mM N stock solution was stored in the fridge at 4 °C, the intermediate stocks and working standards were freshly prepared every week. Typical calibration sets for DOC and TDN are shown in Figure 4.17. The observed LoD's of the method were 12 μ M C and 2 μ M N.

Due to the high nitrate concentrations, all samples for TDN determination were diluted three fold with HPW to allow the signal of the NCD analyser to return to the baseline between the samples and avoid carry-over.

Certified deep seawater reference material (CRM; Florida Strait, 700 m, batch nr. 7-2007: DOC 41 – 44 μ M, TDN 33 μ M) from the Hansell Laboratory at the Rosenstiel School of Marine and Atmospheric Science (RSMAS), University of Miami, was analysed after every 12 samples to check the accuracy of the method. The agreement between the CRM concentrations and the observed concentrations was satisfactory for

DOC ($45 \mu\text{M}$, $\pm 4.7 \mu\text{M}$), whereas the TDN results were on average 14% lower than the certified reference value ($28.4 \mu\text{M}$, $\pm 2.4 \mu\text{M}$ (Figure 4.18).

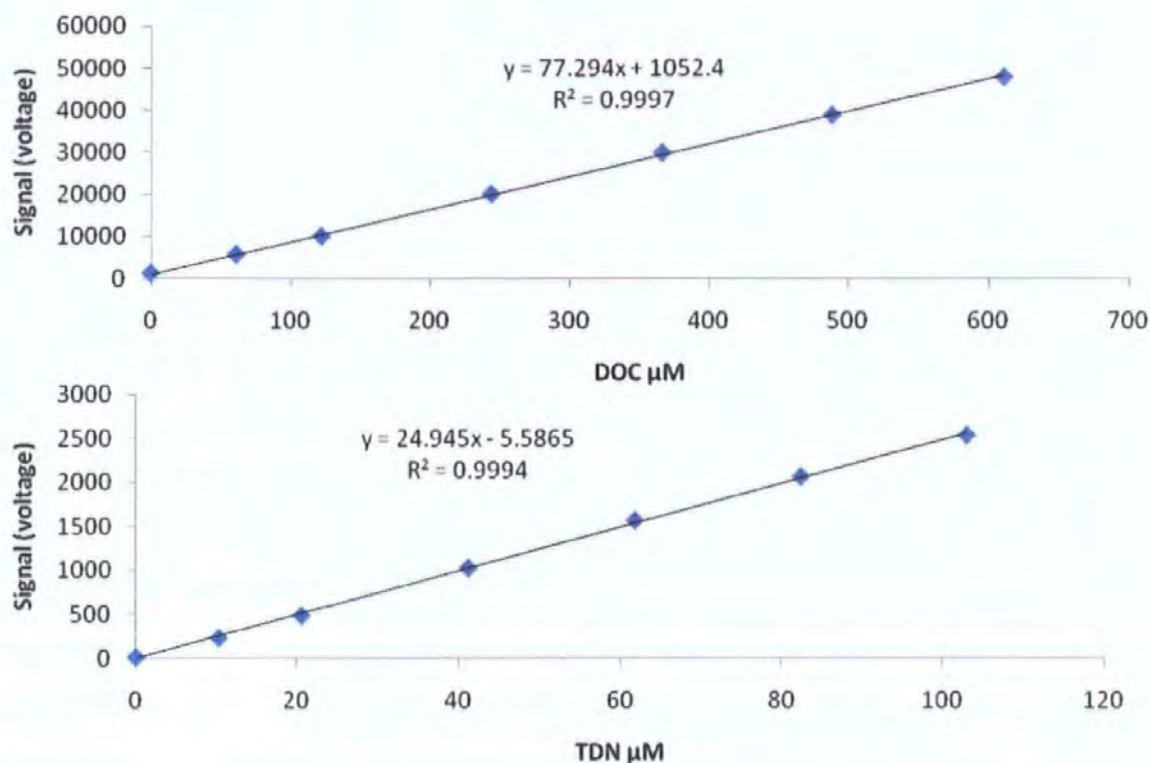


Figure 4.17. Typical calibration curves with regression curve equations and regression coefficient for (top) DOC and (bottom) TDN.

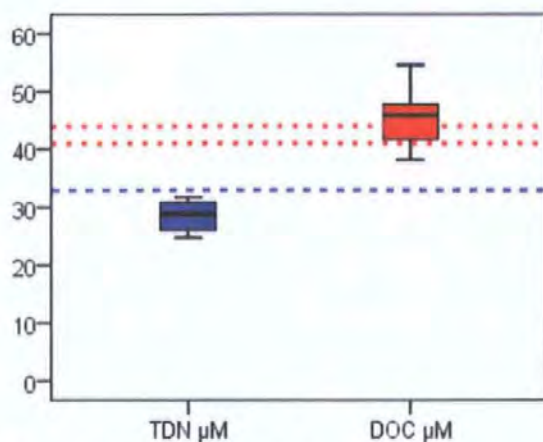


Figure 4.18. Box plots of observed CRM results for TDN and DOC. The dotted lines indicate the reference concentrations: (blue) TDN $33 \mu\text{M}$, (red) DOC in the range of $41 - 44 \mu\text{M}$.

An underestimation of TDN was observed in samples where TIN was $\geq 100 \mu\text{M}$ (Figure 4.19, left). In most of these samples, TIN concentrations were $>\text{TDN}$, which would generate negative values for DON. To correct for this and to minimise mass balance issues later in the calculation of DON, the measured TDN concentration in a given sample was multiplied by a correction factor based on its closest neighbouring CRM value. This correction factor was obtained by calculating the ratio of the observed CRM-TDN concentration to the known concentration reported by the CRM certifying laboratory. The application of this correction factor resulted in most of the DON results being positive (Figure 4.19, right). Values that were negative after correction were set to $\text{LoD}/2$ to be included in the statistical analyses.

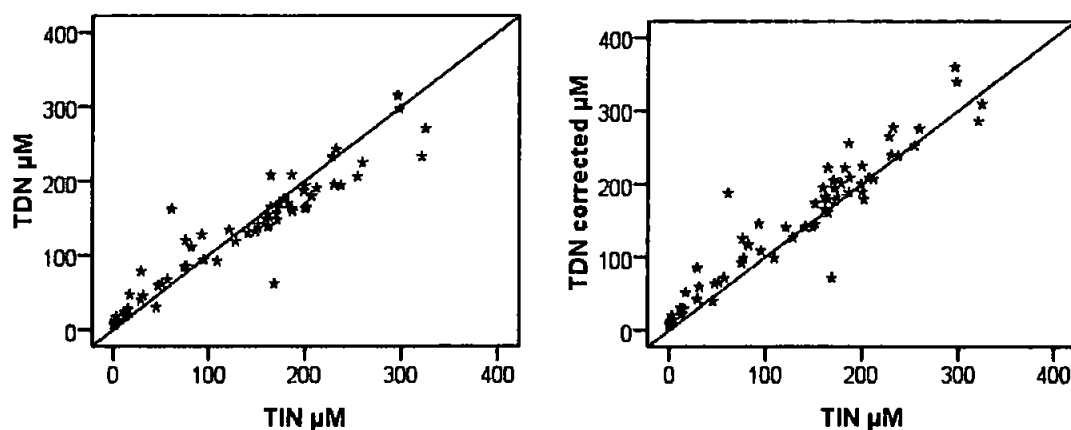


Figure 4.19. Scatter plots of TDN versus TIN concentrations. The reference line is set at $y = x + 0$. TDN values above the reference line are higher than the TIN fraction and were used for the calculation of DON concentrations. TDN values below the reference line are lower than the TIN concentration and were rejected. (left) Untreated results and (right) results after the application of the CRM derived correction factor.

The underestimation of TDN can be attributed to humic substances that were observed to flocculate during the thawing process in some samples, which may have removed nitrogen from the measurable TDN pool. Similar observations have been reported by Tranvik (1990) and Homewood (2005) for freshwater samples. Also, the purging of the sample with oxygen may cause the loss of volatile TDN fractions, equivalent to a loss

of up to 5% that has been observed with DOC measurements (Statham and Williams, 1999).

4.10. Determination of chlorophyll a concentrations

4.10.1. Method description

Chlorophyll *a*, was measured spectrophotometrically, following the method of Parsons *et al.* (1984). The 45 mm GF/F filter from the the DOC/TDN filtration that was conducted under subdued light was transferred into a test tube with 90% acetone and 10% HPW, mixed well by shaking and stored at -20 °C until analysis 3 to 5 days later. The test tubes were wrapped in aluminium foil to avoid pigment degradation by light. On many occasions, the sample was so turbid that only 100 mL of water could be filtered. In such cases, more than one filter was used to collect a sufficient mass of pigment. Depending on sample turbidity and phytoplankton density, 500 to 1000 mL of estuary water was filtered.

Before analysis, the samples were centrifuged at 3000 rpm for 15 min. For the analysis a quartz vial with a path length of 1 cm was used in a Hewlett Packard HP 8453 UV-Visible Spectrophotometer. Absorption was measured at wavelengths of 750, 664, 647 and 630.

Chlorophyll *a* concentrations in the extract were calculated using the following equation (Parsons *et al.* 1984):

$$\text{Chl } a = 11.85 E_{664} - 1.54 E_{647} - 0.08 E_{630}$$

where E_n is the corrected absorption at a given wavelength. The absorptions were corrected by subtracting the absorption value obtained at 750 nm from the 664, 647 and 630 nm absorption values..

The pigment concentration in the water samples was calculated using:

$$\text{Pigment } (\mu\text{g L}^{-1}) = \frac{P \times v}{V}$$

where P is the pigment concentration in the test tube, v is the volume of acetone in the test tube (mL) and V the volume of filtered sample water in litres.

A limit of detection for this method cannot be given, as it depends on the volume of water filtered. Parsons *et al.* (1984) reported that filtering 10 L of seawater would give an LoD of $0.02 \mu\text{g L}^{-1}$ and filtering 1 L of seawater would give $0.2 \mu\text{g L}^{-1}$. The limiting factor is the amount of suspended solids in the water as this clogs the membrane over time. However, the instrument precision, expressed as the relative standard deviation (*i.e.* the absolute value of the coefficient of variation) was less than 10% for 500 – 1000 mL of filtered Taw Estuary water with chlorophyll a concentrations $>2 \mu\text{g L}^{-1}$ (Figure 4.20).

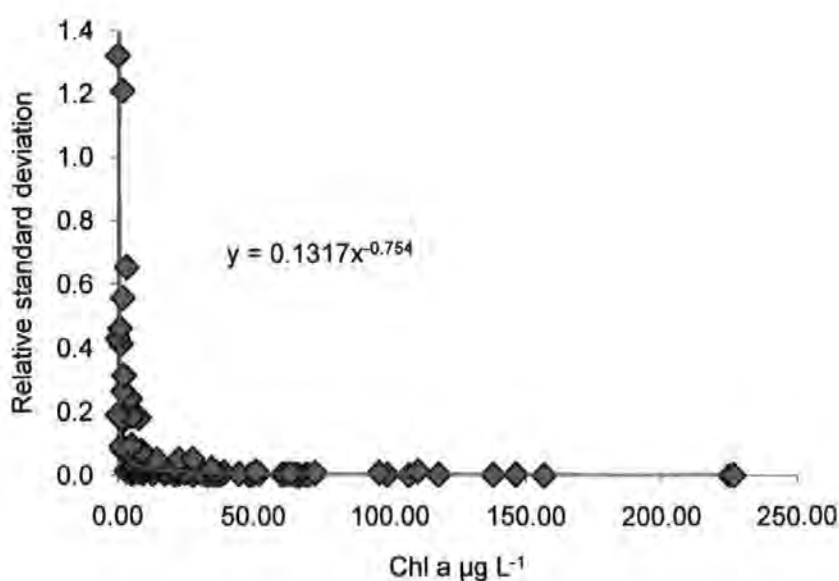


Figure 4.20. Scatter plot of the relative standard deviation against measured chlorophyll a concentrations in 5 instrument readings.

4.11. Treatment of data, visualisation and analysis

In order to compare the EA data with data from the spring/summer 2008 campaign (section 5.2) Mann-Whitney *U* tests using SPSS 16.0 were undertaken. As this test is non-parametric, data did not undergo any pre-treatment such as normalisation or transformation.

X-Y contour maps (section 5.2.1) were generated using SURFER 8.02 (Golden Software, Inc.). The chosen method of interpolation was linear point kriging.

Principal component analysis (PCA) and cluster analyses (section 5.3) were performed using PRIMER 6 software (PRIMER-E Ltd). PCA requires an even, non skewed data distribution. When data of individual variables are skewed or extreme outliers are present, a transformation of the data is necessary. Following Clarke and Warwick (2001) and Clarke and Gorley (2006), the best method of transformation was identified empirically by comparing the distribution of variables in a Draftsman plot. Fourth root transformation gave the best result, *i.e.* an even sample distribution (Figure 4.21). Also, environmental data often incorporate variables of different scales and units (*e.g.* pH 5-9, no unit; ammonium, 0.05-20 μM ; chlorophyll *a*, 1-250 $\mu\text{g L}^{-1}$). This requires the data to be normalised by subtracting the mean from each entry for a single variable and dividing the difference by the standard deviation (see also section 3.2.3).

The appropriate resemblance measure in a cluster analysis for environmental data is Euclidean distance (Clarke and Warwick, 2001). For the same reasons as for the PCA and to avoid the introduction of artefacts, data were fourth root transformed and normalised (see section 3.2.4). Samples were linked by group-averaging.

The salinity classification referred to in chapter 5 followed the Venice System (Anonymous, 1958) as modified by Remane (1971) (Table 4.8).

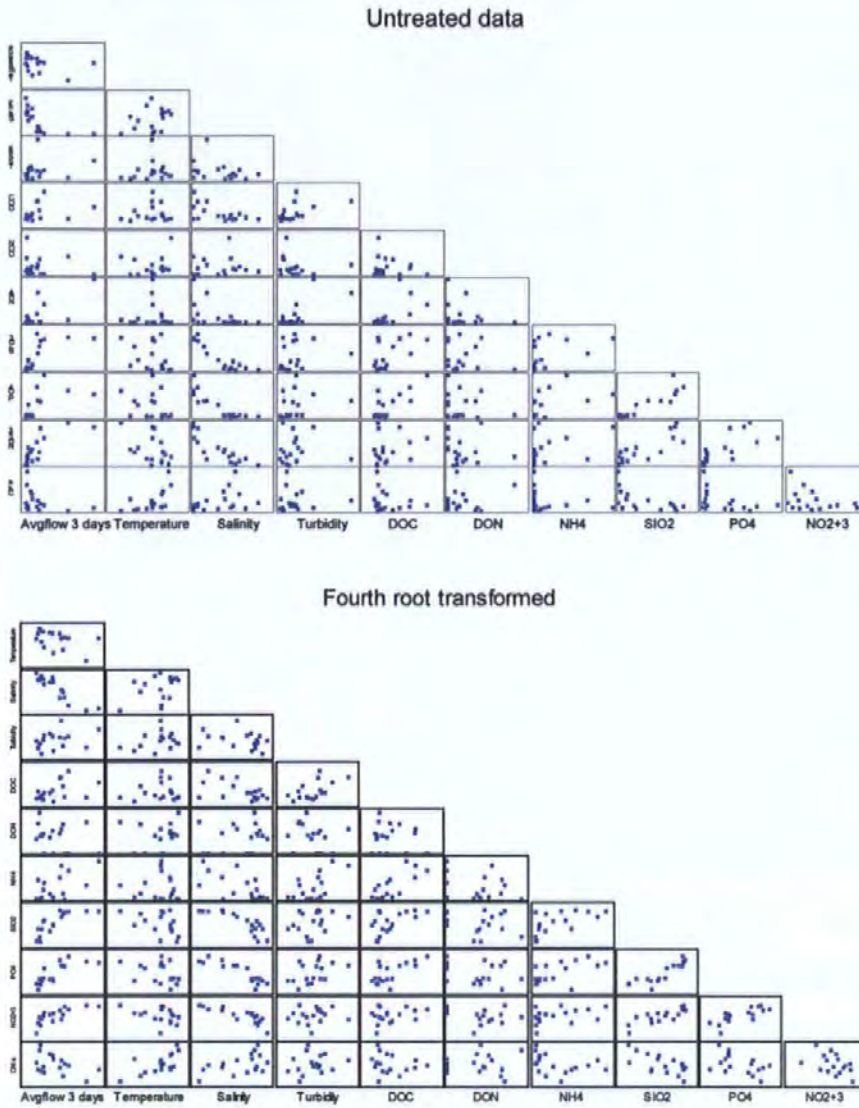


Figure 4.21. Draftsman plot of data from site C. (top) Untreated and (bottom) fourth root transformed data.

Table 4.8. The Venice system for the classification of saline waters (modified from Remane, 1971).

| Class | Subclass | Salinity |
|-----------------------|-----------------------|----------|
| limnetic (freshwater) | | <0.5 |
| oligohaline | | 0.5-5 |
| | β -oligohaline | 0.5-3 |
| mesohaline (brackish) | α -oligohaline | 3-5 |
| | | 5-18 |
| | β -mesohaline | 5-10 |
| polyhaline | α -mesohaline | 10-18 |
| | | 18-30 |
| euhaline (marine) | | 30-40 |

4.12. Summary and conclusions

Samples were collected fortnightly during the background monitoring campaign (March 18th, 2008 – June 13th, 2008) and at intervals between three and five days during the intense sampling campaign, which lasted from July 5th, 2008 – August 6th, 2008. The selected sample sites represent key locations of interest of estuarine biogeochemistry and allow an investigation of the two main sources of nutrients for the estuary: site A at Umberleigh to integrate nutrient loads from the catchment and site C to incorporate nutrient inputs from the STW. Also, the areas with the highest phytoplankton biomass were covered (site B, Barnstaple city centre and site C, Ashford STW) together with the coastal end member at site D, Crow Point.

The analytical ranges of the instruments covered nutrient concentrations throughout the estuary (Table 4.9); after threefold dilution also DON and TDN concentrations were all within instrument range.

Using spectrophotometry for pigment measurements, particularly at chlorophyll *a* concentrations $>5 \mu\text{g L}^{-1}$ proved to be suitable for a high chlorophyll/high turbidity environment such as the Taw.

In summary, the chosen sample locations and analytical methods provided good results for the expected range of individual variables in the Taw with sufficient accuracy and good spatial and temporal coverage.

Table 4.9. Summary of data ranges for dissolved nutrients and organic carbon.

| | NO₂+NO₃ | PO₄ | SiO₂ | NH₄ | DOC | TDN |
|----------------------|--------------------------------------|-----------------------|------------------------|-----------------------|------------------------|------------------------|
| <i>n</i> | 68 | 68 | 68 | 68 | 68 | 68 |
| LoD | 1.42 μM | 0.016 μM | 3.3 μM | 0.075 μM | 12 μM | 2 μM |
| Upper limit of range | 357 μM | 16.14 μM | 166 μM | 9 μM ⁽¹⁾ | >600 μM ⁽²⁾ | ~100 μM ⁽²⁾ |
| <LoD | 5 | 2 | 11 | 0 | 0 | 0 |
| >Range | 0 | 0 | 0 | 1 | 0 | 0 |
| Manipulated | 0 | 0 | 0 | 0 | 0 | 10 ⁽³⁾ |

⁽¹⁾ Upper limit of instrument range in HPW matrix. After the inclusion of matrix effects from natural waters, the range can be considerably higher. ⁽²⁾

Samples were diluted 3x to remain within instrument range. ⁽³⁾ Calculated DON values <0 μM, see section 4.9.3

**HIGH TEMPORAL RESOLUTION STUDY OF BLOOM
DYNAMICS IN THE TAW ESTUARY (MARCH-AUGUST 2008)**



Spring tide near Velator

5. High temporal resolution study of bloom dynamics in the Taw Estuary (March-August 2008)

5.1. Introduction

The detailed analysis of archived data from the Environment Agency for England and Wales (EA) left a number of uncertainties regarding the dynamics of eutrophication events in the Taw Estuary (chapter 3). This was because the EA sample design was primarily targeted at monitoring and documenting the trophic status of the estuary under their national and international monitoring obligations, for which a temporal resolution of fortnightly to monthly data collection was sufficient (*e.g.* the recommended sampling frequency under the WFD is 3 months for most physico-chemical variables and 6 months for phytoplankton). Although it was possible to identify the importance of freshwater inflow for the regulation of primary production in the Taw, some considerable gaps in the understanding of primary production dynamics in the Taw remained. The aim of the study discussed in this chapter was to address the following questions:

1. Are the sampled sites comparable to the EA sample sites?
2. What were the estimated nutrient loads in 2008 from the STW and the River Taw to the estuary?
3. Did nutrient limitation occur and in which order did nutrients become limiting?
4. Does riverine freshwater input determine chlorophyll *a* concentrations?
5. Are multivariate analytical methods suitable to identify discrete environmental states, which are characteristic for eutrophication events in the Taw?

To answer these questions, a two-step monitoring campaign was set up:

1. The first part of the campaign covered the period from late winter to early summer (March 15th and June 13th) and consisted of fortnightly monitoring to obtain background values of the system while primary production was still low.
2. The second part of the campaign (high temporal resolution monitoring) was to document the rise and decline of one or more algal blooms. Therefore, as soon as conditions appeared to be favourable for bloom formation (*i.e.* a period of dry and settled weather following sufficient rainfall to flush the estuary) the estuary was sampled every 3 to 5 days for one month.

The rationale for the selection of sample sites including a map (Figure 4.1) and sample site descriptions are given in chapter 4 (section 4.2), where the sampling procedures (section 4.4) and chemical analyses (sections 4.6-4.9) are also discussed in detail.

The data were analysed using a number of graphical representations (X-Y contour maps, overlay line plots, cluster diagrams and graphical output from the statistical analyses) and several statistical methods, beginning with the methodology used in section 3.2.4 and then extending the analysis using a combined ordination approach, merging principal component analysis (PCA) and cluster analysis. This type of PCA could not be used for the EA data in chapter 3 because of the temporal patchiness, missing variables and because samples were collected at very different tidal states. Hence there were too few data points to construct a coherent dataset with the potential to generate meaningful PCA results. Therefore, the March-August 2008 campaign was specifically designed to generate a dataset that could be analysed with this method by sampling at comparable biweekly (during the background sampling) and daily (during

the high resolution sampling) tidal states and by ensuring that no data points were missing.

5.2. Comparability of data from the March–August 2008 campaign with EA data for March to August (1990-2004).

The EA may have used different methodologies over the span of their entire monitoring activities on the Taw. Also, the sampled sites from the spring/summer 2008 campaign did not all exactly match the EA sites. Therefore, the comparability of data was assessed by performing a number of Mann-Whitney U tests using SPSS 16.0. It is also known as the Wilcoxon-Mann-Whitney test or Wilcoxon rank sum W test.

Many of the sampled variables showed extreme outliers, particularly ammonium and chlorophyll a . Therefore, the Mann-Whitney U test was chosen as a non-parametric alternative over the t -test or one-way ANOVA, as it does not make any assumptions about homogeneity of variances or normal distributions. The Mann-Whitney U test is a typical rank test, where the data are converted into ranks before the test is carried out. This makes this test the preferred option when extreme values make the t -test undesirable. Although the Mann-Whitney U test is less powerful than the t -test or one-way ANOVA, it is also less likely to find a significant result when there is no real difference (Dytham, 2003). A comparison of the entire data set covering March to August 2008 was deemed inappropriate, as data for July and August 2008 would have been overrepresented when compared with the EA data which had a much more even temporal distribution. Therefore, the final data set consisted of a subset of EA data, covering July and August of the years 1990-2004, and a subset of the March-August 2008 campaign, collected between July 5th and August 6th 2008. The H_0 assumed that the two compared groups are different. The null hypothesis (that the two groups had the

same median value) was rejected when p was <0.05 . The results of the Mann-Whitney U test are summarized in Table 5.1.

The data for variables at sites A and 1 (See Fig. 4.1 for sample site codes) showed very little comparability. The reason for this is probably that Umberleigh (site A) represented a riparian environment whereas the EA site 1 (Newbridge), although freshwater dominated, was under tidal influence. For the sites B and 3 (both near the city centre of Barnstaple), more variables were in agreement; only temperature, salinity, nitrate+nitrite and chlorophyll a were different. The majority of the variables at the sites C and 4 (near the Ashford STW) as well as D (Crow Point) and 6 (Airy Point, near the estuary's mouth) matched well; exceptions were turbidity at C and 4 and phosphate, chlorophyll a and oxygen saturation/concentration at D and 6. A large fraction of the EA data was not tidally standardized or was collected at a different tidal state than the July / August 2008 data. It is possible that some of the above discussed differences originated there.

5.1.Loads to the estuary

Load estimates were made using Method 2 of Littlewood *et al.* (1998). The daily river nutrient load was calculated by multiplying the measured nutrient concentration at site A (Umberleigh) with river flow. From this, the average monthly load for the period March-August 2008 was calculated, of which the overall average was used to estimate the annual nutrient loads. The same approach was used to calculate loads from the STW. Concentration data were provided by the EA; the sampling interval was 7-10 days. As an estimate for STW flow, the consented dry weather discharge ($15,231 \text{ m}^3 \text{ d}^{-1}$) was used. The calculated annual loads are shown in Table 5.2 and compared with the average loads over the period 1990-2004 from section 3.3.1.

Table 5.1. Results of a Mann-Whitney *U* test comparing the median values of variables for July and August from the March-August 2008 campaign and the EA dataset.

Values for $p < 0.05$ are underlined and mean that there is a significant difference in the compared subsets.

| Site (M-A 08 ¹ and EA ²) | | Temp. | Salinity | NH ₄ | NO ₂ +NO ₃ | PO ₄ | SiO ₂ | Chl. <i>a</i> ³ | pH | Turbidity ⁴ | O ₂ % | O ₂ conc. |
|---|----------|--------------|--------------|-----------------|----------------------------------|-----------------|------------------|----------------------------|-------|------------------------|------------------|----------------------|
| Umberleigh A / | <i>n</i> | 20 | n/a | 20 | 20 | 20 | 21 | 6 | 20 | 10 | 20 | 20 |
| Newbridge 1 | <i>Z</i> | -1.97 | n/a | -0.38 | -2.50 | -2.72 | -2.32 | - | 0.00 | - | -1.78 | -2.61 |
| | <i>p</i> | <u>0.049</u> | n/a | 0.705 | <u>0.013</u> | <u>0.006</u> | <u>0.020</u> | - | 1.000 | - | 0.075 | <u>0.009</u> |
| Barnstaple B / | <i>n</i> | 27 | 27 | 27 | 21 | 27 | 18 | 31 | 27 | 27 | 23 | 21 |
| Barnstaple 3 | <i>Z</i> | -2.11 | -3.11 | -0.05 | -2.46 | -0.40 | -1.60 | -3.00 | -0.18 | -0.28 | -1.46 | -0.56 |
| | <i>p</i> | <u>0.035</u> | <u>0.002</u> | 0.960 | <u>0.014</u> | 0.688 | 0.110 | <u>0.003</u> | 0.860 | 0.782 | 0.145 | 0.573 |
| Ashford C / | <i>n</i> | 29 | 29 | 29 | 23 | 29 | 19 | 33 | 29 | 29 | 25 | 23 |
| Ashford 4 | <i>Z</i> | -0.37 | -1.38 | -0.96 | -1.55 | -1.61 | -0.24 | -0.35 | -1.04 | -3.81 | -0.22 | -0.43 |
| | <i>p</i> | 0.713 | 0.169 | 0.335 | 0.121 | 0.108 | 0.806 | 0.724 | 0.300 | <u>0.000</u> | 0.824 | 0.664 |
| Crowe Point D / | <i>n</i> | 133 | 133 | 133 | 26 | 32 | 22 | 32 | 129 | 32 | 130 | 128 |
| Airy Point 6 | <i>Z</i> | -0.13 | -1.93 | -1.48 | -0.90 | -3.31 | -0.20 | -2.16 | -0.52 | -0.49 | -2.51 | -3.83 |
| | <i>p</i> | 0.895 | 0.054 | 0.140 | 0.369 | <u>0.001</u> | 0.843 | <u>0.031</u> | 0.600 | 0.625 | <u>0.012</u> | <u>0.000</u> |

¹ July and August data from the March-August 2008 campaign; ² Environment Agency data from July/August 1990 – 2004; ³ no chlorophyll *a* samples were collected during the March-August 2008 campaign for site A; ⁴ insufficient data for site 1. Temp. = water temperature.

The river loads of nitrate, phosphate and ammonium for 2008 compared well with the annual average from the EA data but the 2008 silicate load was only 63% of the 1990-2004 average. The loads from the STW showed an increase in nitrate loads and a strong decrease in ammonium loads. Phosphate loads were halved, which is possibly a sign of successful phosphate stripping after the implementation of the UWWTD.

The major source of N to the estuary during the 2008 campaign was from the River Taw in the form of nitrate. The STW contribution to the total nitrate load in the estuary was negligible (2%). However, despite the observed load reductions for ammonium and phosphate, the STW still accounted for 37% and 28% of the total loads respectively.

Table 5.2. Estimated annual nutrient loads (t a^{-1}) from the River Taw and Ashford STW to the Taw Estuary. The 1990-2004 average annual loads for the river and all STW loads were calculated from EA data.

| | River Taw | | Ashford STW | |
|-----------------------------------|--------------|------|-------------|------|
| | 1990 – 2004* | 2008 | 1990-2004* | 2008 |
| $\text{NO}_3\text{-N t a}^{-1}$ | 1977 | 1416 | 16 | 31 |
| $\text{NO}_2\text{-N t a}^{-1}$ | n/a | n/a | n/a | 10 |
| $\text{PO}_4\text{-P t a}^{-1}$ | 37 | 21 | 18 | 8 |
| $\text{NH}_4\text{-N t a}^{-1}$ | 24 | 29 | 89 | 17 |
| $\text{SiO}_2\text{-Si t a}^{-1}$ | 1418 | 901 | n/a | n/a |

*) average. n/a = not available.

5.2. Phytoplankton bloom dynamics in the Taw Estuary (March – August 2008)

5.2.1. Temporal and spatial variability of the data

To visualise temporal and spatial trends in the data, X-Y contour maps were generated. The data were split into two subsets; the first set covering the fortnightly sampling between March 18th and June 13th and the second set for the high temporal resolution

sampling between July 5th and August 6th. These are given in Figure 5.1/Figure 5.2 and Figure 5.5/Figure 5.6 respectively.

5.2.1.1. Patterns of variables between March 18th and June 13th

River flow showed a transition from the high winter discharge to the low discharge summer regime (Figure 5.1, top left), following precipitation patterns typical for NW Europe. On May 30th flow was very high ($27.1 \text{ m}^3 \text{ s}^{-1}$) after a week of rainfall. Temperatures were low during early spring ($7.1\text{-}10.0 \text{ }^\circ\text{C}$ on March 18th) and increased to $16.5\text{-}18.3 \text{ }^\circ\text{C}$ on June 13th. Within the estuary, the temperature maximum zone moved during late spring from the coastal end to the more central site C. At the start of the campaign (March 18th), the freshwater-saltwater interface (FSI; at salinities of $\sim 0.5\text{-}1$) was located at site C but moved then upwards to site B. The tidal freshwater area usually extended upstream of site B to the tidal limit at Newbridge. During high freshwater inflow on March 18th and May 30th this zone expanded to site C, which was otherwise characterised by mesohaline and polyhaline waters. Euhaline waters were only present at the outermost part of the estuary (site D), but only when the freshwater inflow was $\leq 10 \text{ m}^3 \text{ s}^{-1}$. In partly-mixed and well-mixed estuaries, the FSI is often associated with a turbidity maximum zone (TMZ), where fine, cohesive, suspended particulate matter (SPM) accumulates (Uncles and Stephens, 1993). Although it is feasible to assume that the Taw Estuary is not different in this, the turbidity data collected during this campaign are inconclusive about the existence and location of a TMZ in the estuary. Typically, turbidity was highest in the central part of the estuary. On May 30th, the system experienced unusually high turbidity (with maximum turbidity of 133 NTU at site B) during high river flow. Oxygen saturation was usually in the range of 90-130%, without any clear pattern apart from a drop below 90% on May 30th at site C. As this coincides with high river inflow, high turbidity and high DOC, this

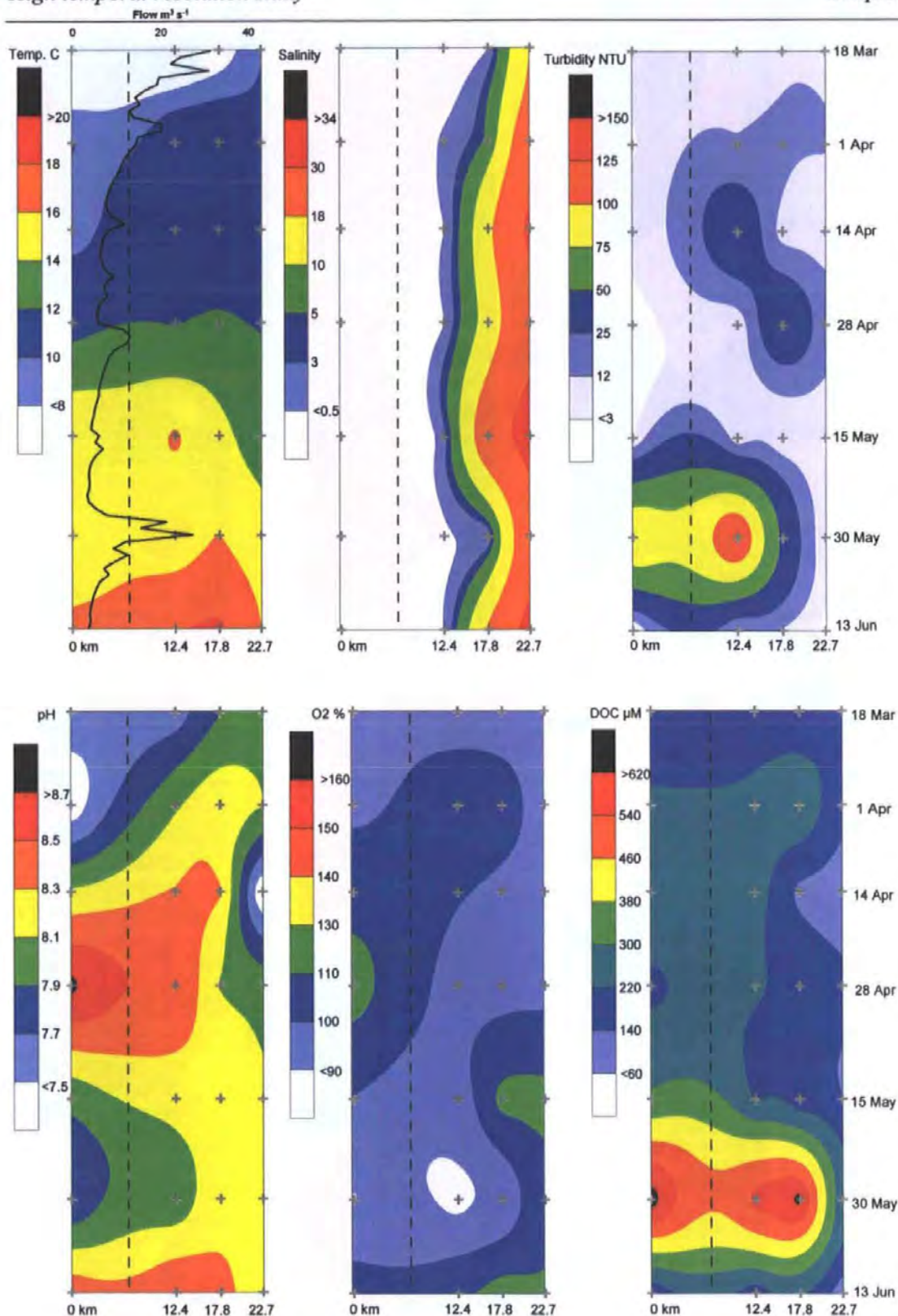


Figure 5.1. Surface contour plots showing the temporal variability of constituents during the period March 18th to June 13th 2008. The numbers along the x-axis indicate the distance from site A, UMBERLEIGH (0 km): site B (12.4 km), site C (17.8 km) and site D (22.7 km). The dashed line indicates the position of the tidal limit, the solid line in the top left figure represents River Taw discharge.

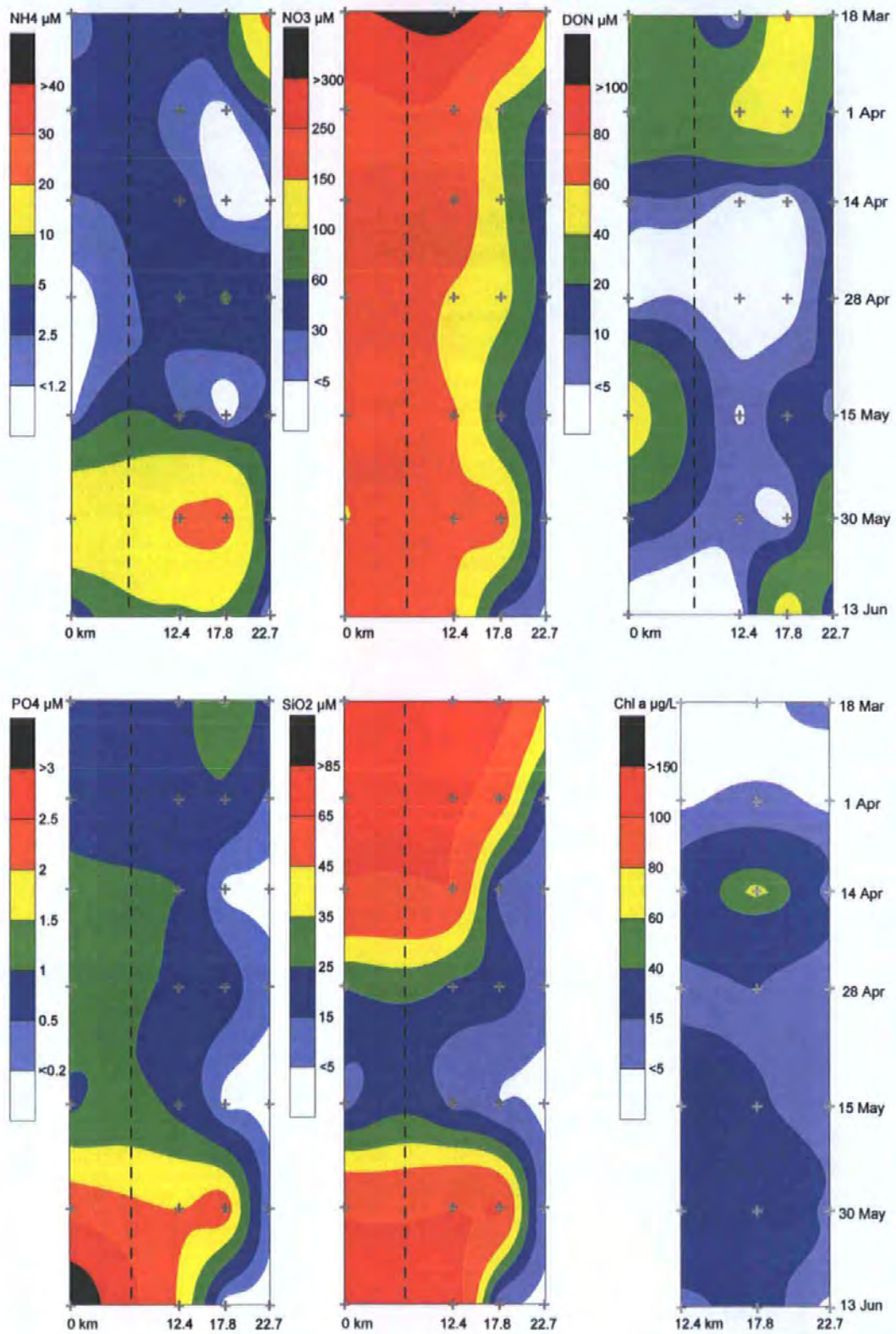


Figure 5.2. March 18th to June 13th 2008, see Figure 5.1 for details. No chlorophyll *a* data were collected for site A. Note the different x-axis scale.

might reflect increased bacterial activity, metabolising easily degradable organic matter from the storm water runoff. Overall, DOC showed a tendency to decrease from the river end at site A (148-659 μM) towards the mouth of the estuary (site D, 91.8-238 μM).

Ammonium (Figure 5.2) showed highest variability at site C with measured concentrations ranging from 0.11 μM to 59 μM . This is also the site located closest to the outflow of the Ashford STW. Concentrations in the estuary were highest on March 30th. Nitrate concentrations in the estuary decreased with increasing distance from the freshwater end and showed an inverse relationship with salinity (Figure 5.3).

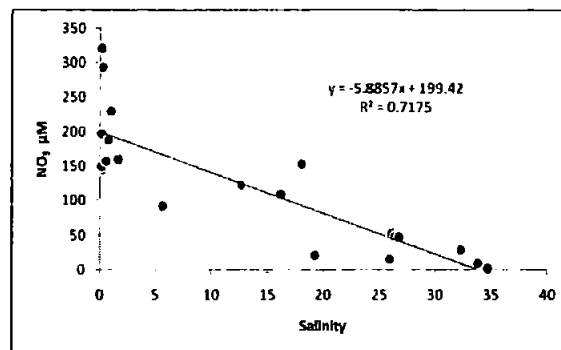


Figure 5.3. Scatter plot of nitrate concentrations versus salinity at estuarine sample sites B-D between March 18th and June 13th 2008.

No patterns could be found for DON. Phosphate concentrations decreased from the freshwater end towards the mouth of the estuary and were highest on May 30th throughout the estuary, ranging from 0.13 μM at site D to 2.40 μM at site C), and on June 13th at site A (3.48 μM). Silicate concentrations were highest in the upper estuary and during high flow (maximum of 78.9 μM , March 18th, site B) and decreased with flow and proximity to the mouth. Both, phosphate and silicate concentrations, had an inverse relationship with salinity (Figure 5.4 a, b). Chlorophyll *a* increased throughout the spring sampling campaign (e.g. at site C from 3.25 $\mu\text{g L}^{-1}$ on March 18th to

22.5 $\mu\text{g L}^{-1}$ on June 13th) but showed signs of a spring bloom at site C on April 14th with 70.2 $\mu\text{g L}^{-1}$.

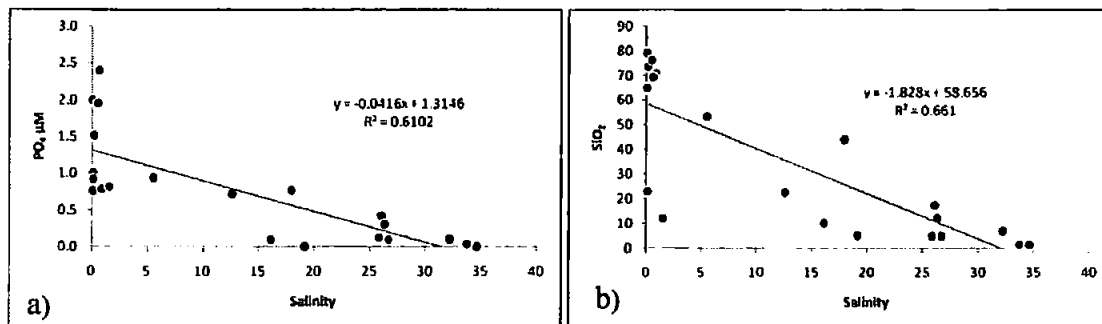


Figure 5.4. Scatter plot of (a) phosphate and (b) silicate concentrations versus salinity at estuarine sample sites B-D between March 18th and June 13th 2008.

5.2.1.2. Patterns of variables between July 5th and August 6th

The results for the period July 5th to August 6th are summarised in Figure 5.5 and Figure 5.6. River discharge was low ($<5 \text{ m}^3 \text{ s}^{-1}$) at the start of the high resolution sampling campaign but increased to $105 \text{ m}^3 \text{ s}^{-1}$ on July 9th. River flow then decreased to $3.8 \text{ m}^3 \text{ s}^{-1}$ and remained low until August 6th when it increased again to $15.3 \text{ m}^3 \text{ s}^{-1}$. Water temperature generally increased over the summer with its maximum ($>20 \text{ }^\circ\text{C}$) at sites B and C on July 26th and 29th respectively, coinciding with the river discharge minimum and the chlorophyll *a* maximum.

The location of the FSI was very variable and depended on river flow. At the beginning of the high resolution monitoring (July 5th), mesohaline waters advanced up-estuary to site B but were replaced by freshwater following the increase in river discharge around July 11th. While river flow was low, mainly β -oligohaline water prevailed at site B until river flow increased again and displaced it with freshwater. Site C can be regarded as brackish, dominated by mesohaline and polyhaline water, with less saline water only present during high river discharge (July 11th, 15th, August 6th). Site D, where euhaline

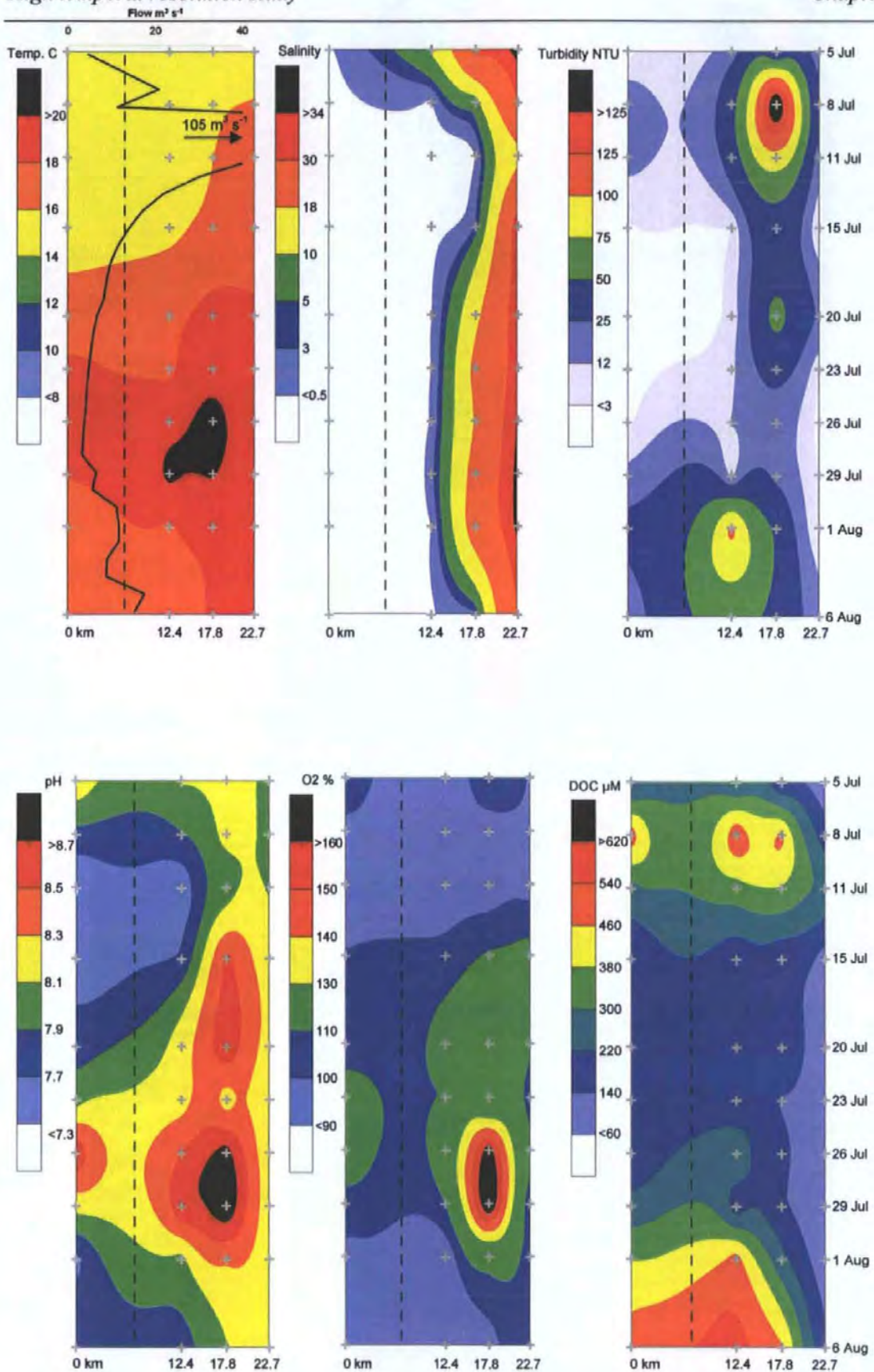


Figure 5.5. Surface contours plots showing temporal variability of constituents during the bloom period of July 5th to August 6th 2008. For explanations see Figure 5.1.

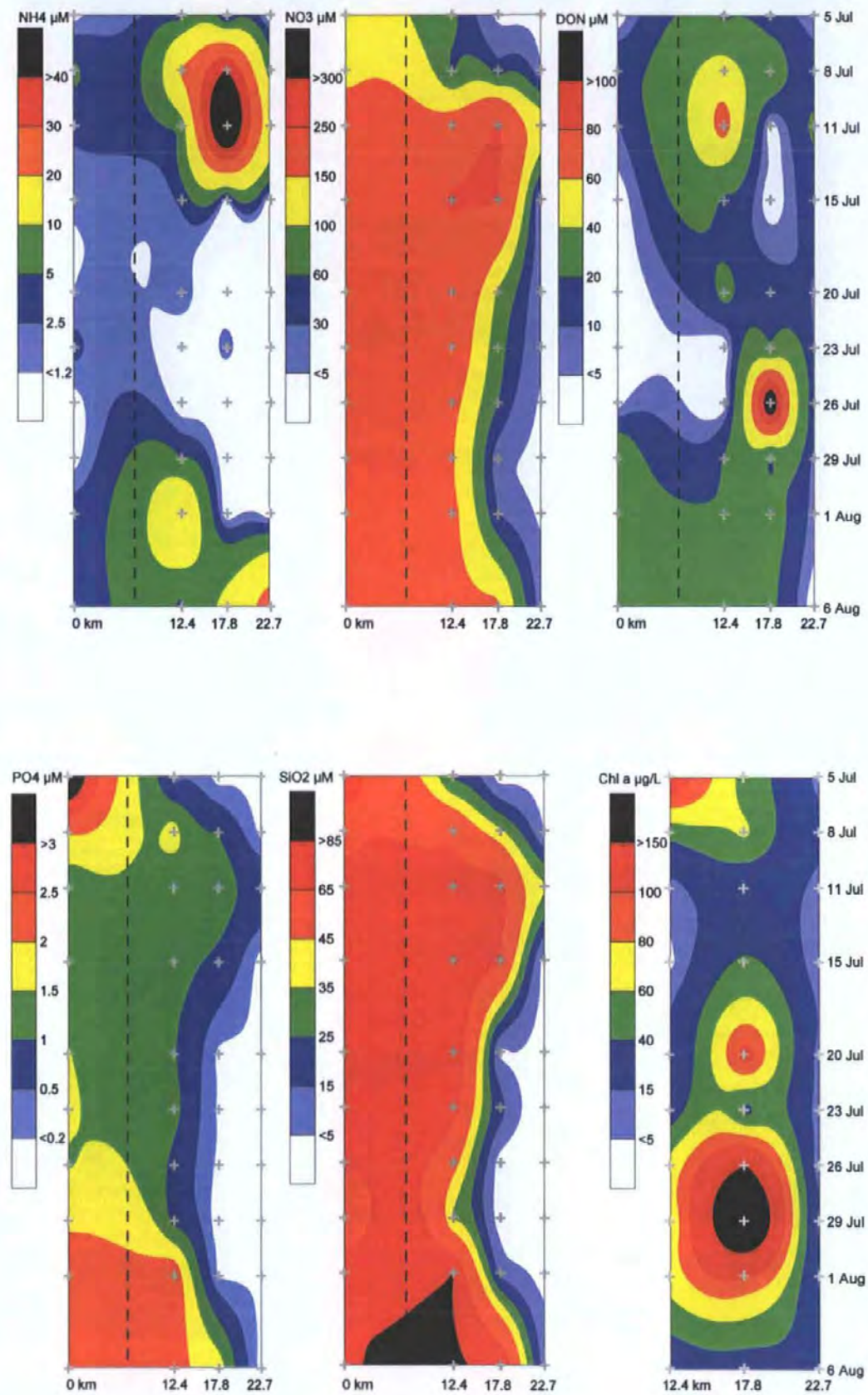


Figure 5.6. July 5th to August 6th 2008, see Figure 5.1 and Figure 5.2 for explanations. Note the different scale of the x-axis for chlorophyll *a*.

waters prevailed for most of the time, showed both coastal and estuarine characteristics because salinity dropped to below 30 (down to 15.6 on July 11th) when river flow was high. Again, no distinct TMZ could be identified. Turbidity was lowest at the freshwater and marine ends of the estuary; high turbidity in the central estuary coincided with high chlorophyll *a* concentrations.

pH values were lowest at the freshwater end and increased down-estuary. The pH maxima coincided with times of maximum chlorophyll *a* concentrations. Dissolved oxygen saturation was continuously >90%, with maxima again coinciding with maxima in chlorophyll *a* concentrations.

DOC concentrations increased with flow and distance from the sea, with the lowest values at site D (84.9 μM on July 5th) and the maximum at site B (567 μM , August 6th). Ammonium concentrations (Figure 5.6) were highest in the central and outer estuary when river discharge was high (e.g. 59.4 μM at site C on July 11th). During low river flow (from July 15th to August 1st) ammonium concentrations were lowest at sites C and D (e.g. on July 26th 0.11 and 0.35 μM respectively) and increased slightly towards sites A and B (0.55 and 0.21 μM). Nitrate concentrations again generally behaved inversely to salinity (Figure 5.7). DON did not show any obvious patterns, although maxima (e.g. Site C on July 26th, 126 μM) occurred with temporal proximity to peaks in chlorophyll *a* concentrations. Phosphate and silicate behaved similarly to nitrate, with both decreasing in concentration with increasing distance from the freshwater end and with increasing salinity (Figure 5.8 a, b).

Chlorophyll *a* showed three distinct peaks, one of a residual phytoplankton bloom on July 5th at site B and two peaks at site C, the first on July 20th, the second on July 29th with 226 $\mu\text{g L}^{-1}$ of chlorophyll *a*.

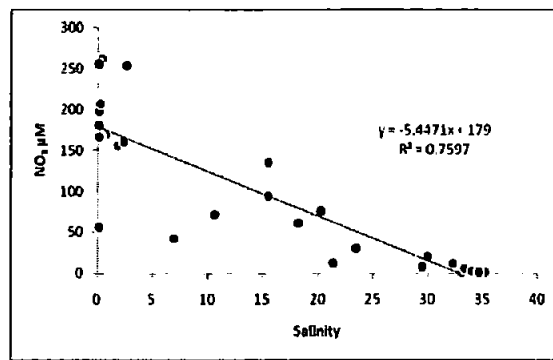


Figure 5.7. Scatter plot of nitrate concentrations versus salinity at estuarine sample sites B-D between July 5th and August 6th 2008.

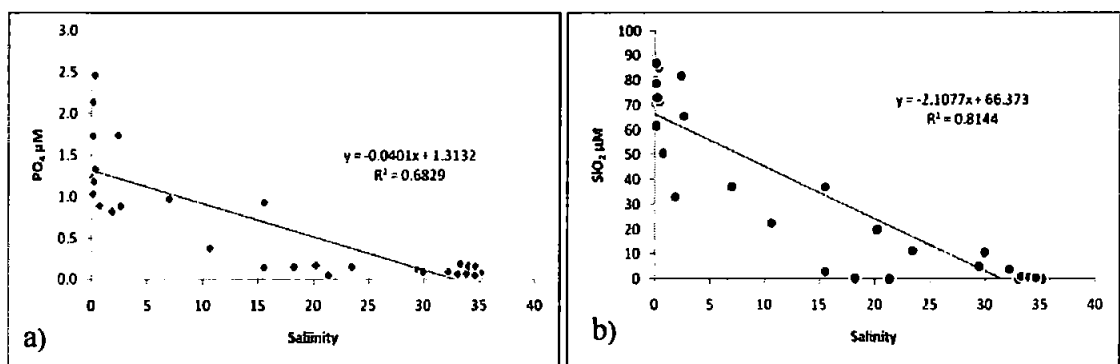


Figure 5.8. Scatter plot of (a) phosphate and (b) silicate concentrations versus salinity at estuarine sample sites B-D between July 5th and August 6th 2008.

5.2.2. Non-parametric correlation and backward eliminating multiple regression analyses

The statistical approach used for the EA long term monitoring data (section 3.2.4) was also applied to the data gathered during the March-August 2008 campaign.

5.2.2.1. Non-parametric correlation analysis

The results of the non-parametric correlation analysis are summarised in Table 5.3. Temperature showed a significant positive correlation with chlorophyll *a* concentrations at sites B and C. Also, salinity correlated positively with chlorophyll *a* at site B. Chlorophyll *a* concentrations and flow did not show any significant correlation, despite

the close coupling between decreasing river flow and enhanced algal growth that was clearly shown with other methods (see sections 5.2.4 and 5.3). The coefficients of chlorophyll *a* with river flow were negative at sites B and C, and positive at site D (compare Table 3.1) but were not significant. The most likely reason for this is the low number of samples for each site ($n = 17$). Also, no significant correlations with chlorophyll *a* were found for turbidity, DOC, DON or phosphate. In none of these cases was p near the examined levels of significance. Tidal amplitude showed positive correlation with chlorophyll *a* at the uppermost and outermost sites, but no correlation at the central site C. It is possible that this was caused by dispersal of phytoplankton from site C during spring tides under increased tidal stirring. The significant negative correlations of nitrate (site B) and silicate (site C) were due to two factors. Firstly, both constituents originated mostly in the catchment (section 5.1) and their concentrations were highest when river flow was high and chlorophyll *a* was low, and secondly, high phytoplankton biomass during the bloom peaks caused a reduction of these nutrients (section 5.2.3). The situation for ammonium was similar at site D, where ammonium depletion was observed during chlorophyll *a* peaks (Figure 5.10). The positive correlation between dissolved oxygen saturation and chlorophyll *a* is due to increased oxygen release by the phytoplankton during the day, which increases to super-saturation levels during a bloom. For site D, with the exception of tidal amplitude, no significant correlations of any variable with chlorophyll *a* were found. This is likely to be due to the less extreme bloom dynamics at this site, the low number of samples and the reduced influence of river flow and associated variables.

Table 5.3. March-August 2008 campaign: Correlation coefficients (Spearman's ρ) of individual variables with chlorophyll a . Figures of significant correlations at $p < 0.01$ are bold, and at $p < 0.05$ are underlined (Temp. = temperature; Turb. = turbidity; amp = amplitude).

| Site | | Flow | Temp. | Salinity | Turb. | Tidal amp. | DOC | DON | NO ₃ +NO ₂ | SiO ₂ | NH ₄ | PO ₄ | O ₂ |
|------|-----|-------|--------------|--------------|-------|--------------|-------|-------|----------------------------------|------------------|-----------------|-----------------|----------------|
| B | rho | -0.45 | <u>0.60</u> | <u>0.56</u> | 0.36 | <u>0.65</u> | 0.29 | 0.06 | -0.64 | -0.40 | 0.07 | 0.07 | -0.27 |
| | p | 0.068 | <u>0.011</u> | <u>0.020</u> | 0.160 | <u>0.042</u> | 0.264 | 0.807 | 0.006 | 0.110 | 0.801 | 0.786 | 0.311 |
| | n | 17 | <u>17</u> | <u>17</u> | 17 | <u>10</u> | 17 | 17 | 17 | 17 | 17 | 17 | 16 |
| C | rho | -0.31 | 0.63 | 0.43 | 0.19 | 0.05 | -0.24 | -0.03 | -0.46 | -0.61 | <u>-0.48</u> | -0.40 | <u>0.55</u> |
| | p | 0.232 | 0.007 | 0.086 | 0.462 | 0.894 | 0.348 | 0.895 | 0.064 | 0.010 | <u>0.050</u> | 0.107 | <u>0.027</u> |
| | n | 17 | 17 | 17 | 17 | 10 | 17 | 17 | 17 | 17 | <u>17</u> | 17 | <u>16</u> |
| D | rho | 0.40 | 0.30 | -0.16 | 0.50 | <u>0.72</u> | 0.15 | -0.24 | -0.07 | -0.05 | 0.19 | 0.10 | -0.19 |
| | p | 0.112 | 0.244 | 0.529 | 0.051 | <u>0.020</u> | 0.573 | 0.348 | 0.786 | 0.844 | 0.468 | 0.708 | 0.487 |
| | n | 17 | 17 | 17 | 16 | <u>10</u> | 17 | 17 | 17 | 17 | 17 | 17 | 15 |

5.2.2.2. Stepwise backward eliminating multiple regression analysis

To generate a stepwise backwards eliminating regression based model, the analysis starts with all the variables used and then removes, with every iteration, the one with the smallest (non-significant) contribution, until only variables are included that constitute a significant (*i.e.* $p < 0.05$) contribution to the model. The aim of this was to identify the variables, which had the biggest impact on algal growth and also to outline connections between the independent variables and chlorophyll *a*. However, this method is not suitable to generate a predictive model, because (1) it is unlikely that the relationships are linear and (2) the necessary normalisation and transformation would make the obtained equation useless for generating predictions.

The results of the regression analysis are summarised in Table 5.4. The variables at the outset were nitrate, ammonium, DON, phosphate, silicate, DOC, temperature, salinity, river flow and turbidity as independent variables and chlorophyll *a* as the dependent variable. For the formal assumptions for regression analyses and an explanation of the normalisation and transformation procedures, see section 3.2.4. For consistency with later analyses (cluster analysis and principal component analysis), the dependent variable was fourth root transformed which was sufficient to achieve near normal distribution.

For site B, increases in temperature, salinity and ammonium could explain 89% of the variation in chlorophyll *a*, showing that the phytoplankton at this site thrived best under a high salinity – high temperature regime. Such conditions (high water temperature and salinity) typically occur during dry and settled weather and usually also include high light levels, conditions favourable for the growth of marine phytoplankton. Also, during

settled weather, water residence times are likely to be high with resulting low dilution rates. In this model was also included phosphate, which had a negative slope. It is possible that this is due to algal consumption of phosphate. The positive slope for ammonium could possibly indicate increased excretion by zooplankton during times of high phytoplankton (and hence chlorophyll) concentrations. Considering these possibilities, it is possible that phosphate and ammonium were not independent variables, but were in fact influenced by the resident phytoplankton population, here expressed as chlorophyll *a* concentrations.

For site C, temperature and turbidity had positive slopes, whereas river flow, ammonium and silicate had negative slopes. The model for site C could explain 82% of chlorophyll *a* variation. This depicts a situation where phytoplankton grew best under high water temperatures, whilst river inflow was low. The positive slope of turbidity would lead to the wrong conclusion that the phytoplankton preferred high turbidity. However, it was the suspended, unicellular phytoplankton that actually generated the high turbidity when chlorophyll concentrations were high. The negative slopes of ammonium and silicate probably indicate nutrient depletion during times of high algal biomass and were (as discussed above) rather influenced by phytoplankton than *vice versa*.

The model for site D incorporated river flow, turbidity, ammonium (with positive slopes) and silicate with a negative slope. This model could predict 78% of all variation in chlorophyll *a* concentrations. The notable difference to sites B and C was the positive slope of river flow. This indicated that more phytoplankton was present under increased flow, suggesting that the plankton was flushed downstream from site C. The results also showed the uptake of silicate (with possible depletion) and also suggested the excretion of ammonium by grazing zooplankton.

The results of these analyses supported the findings from chapter 3 that phytoplankton growth in the Taw Estuary was highest under low river flow, which is a prerequisite for saline, warm waters in the upper estuary and also for long residence times.

Table 5.4. March-August 2008 campaign: Model summaries obtained from backward eliminating linear regression analysis ($n = 17$; p = probability, b = slope)

| | Variable | p | b | r^2 |
|--------|------------------|-------|-------|-------|
| Site B | Temperature | 0.000 | 0.21 | 0.89 |
| | Salinity | 0.024 | 0.14 | |
| | NH ₄ | 0.093 | 0.05 | |
| | PO ₄ | 0.021 | -1.06 | |
| Site C | Temperature | 0.013 | 0.17 | 0.82 |
| | Turbidity | 0.061 | 0.02 | |
| | NH ₄ | 0.057 | -0.06 | |
| | River flow | 0.084 | -0.09 | |
| | SiO ₂ | 0.033 | -0.02 | |
| Site D | River flow | 0.037 | 0.06 | 0.78 |
| | Turbidity | 0.028 | 0.05 | |
| | NH ₄ | 0.002 | 0.11 | |
| | SiO ₂ | 0.002 | -0.11 | |

5.2.3. Nutrient ratios and nutrient depletion

Nutrient limitation was assessed by identifying deviations from the Redfield ratio for N:Si:P of 16:16:1. Terrestrial waters have generally higher N:P ratios than marine waters and are typically P limited. Accordingly, for the majority of data points limitation was in the order P, Si, N (Figure 5.9). During the chlorophyll *a* maxima at site C on July 5th, 26th and 29th, the limiting nutrient switched from P to Si. At site D, Si limitation persisted for much longer than at site C, *i.e.* from July 20th to August 1st when chlorophyll *a* concentrations were high at site C. The change from P to Si limitation

coincided with the depletion of these nutrients during the blooms (Figure 5.10). Extreme ratios (e.g. for site C on June 13th with DIN:P >2000 and April 14th with DIN:P ~1000) can occur when concentrations of one nutrient approach zero, e.g. when P is becoming depleted.

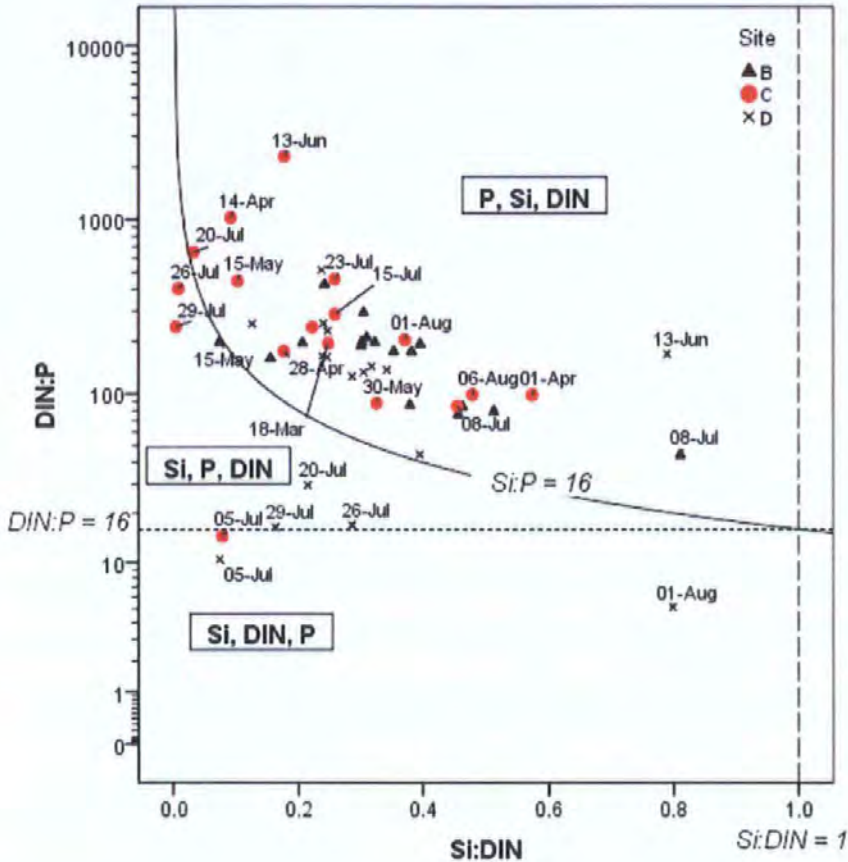


Figure 5.9. Calculated DIN:Si:P ratios during March-August 2008. The graph is divided into six zones with nutrient limitation in the order listed in the boxes. Tax samples were only present in the three zones where Si:N < 1.

Site C was the sample site with the highest chlorophyll *a* concentrations and hence the site where nutrient depletion was the most severe. Depletion of ammonium, phosphate (<0.2 μM) and silicate (<2 μM) was observed at site C during all three chlorophyll *a* maxima (Figure 5.10). Nitrate depletion (<2 μM) was only observed during the first

bloom on July 5th. The second nitrate minimum on July 29th was 12 μM , which, although low, still represented a nutrient replete state.

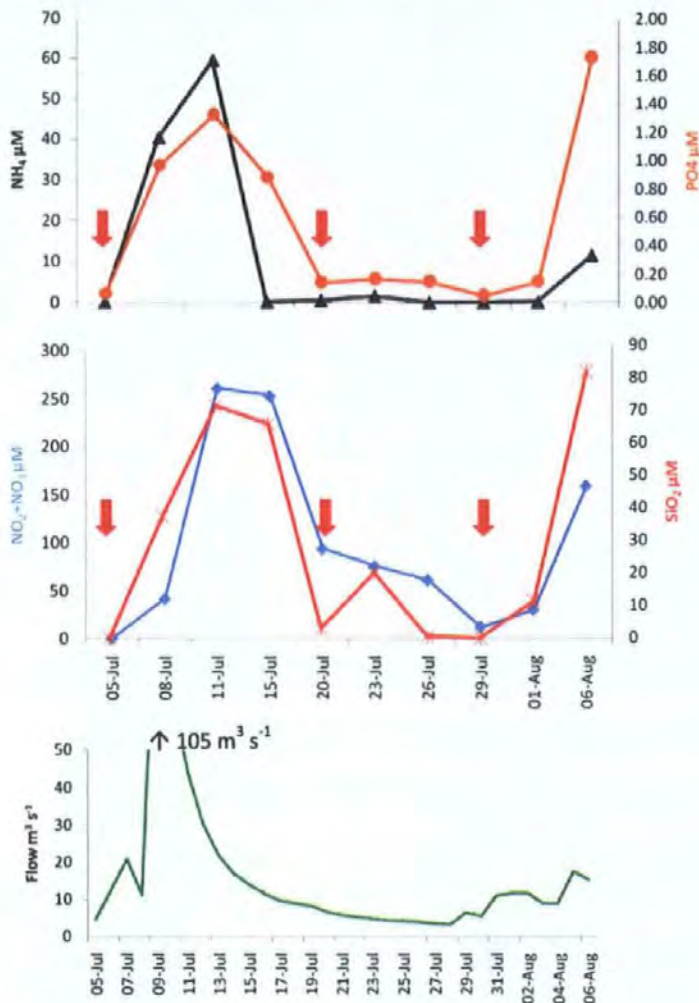


Figure 5.10. Nutrient concentrations and Taw discharge between July 5th and August 6th 2008 during the three blooms at site C. The red arrows indicate times of chlorophyll *a* maxima.

5.2.4. Physical forcing

The strong influence of river discharge on algal biomass in the upper and middle estuary is evident from the results reported in chapter 3 and also suggested by the findings of the correlation and regression analyses in section 5.2.2. Phytoplankton present in these reaches was flushed out under high river discharge to the estuary mouth. Tides also have a strong influence on flushing times in the Taw (Sturley, 1990);

because of the large differences in tidal amplitude between spring and neap tides (Figure 5.11), water residence times are considerably longer during neaps.

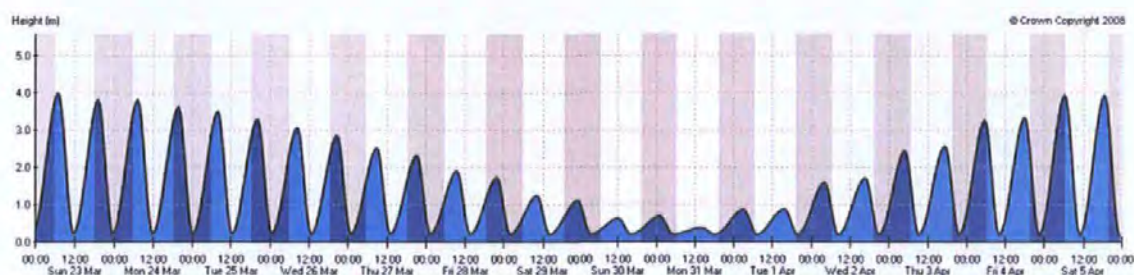


Figure 5.11. Variation in the tidal amplitude (m) at Barnstaple, March 23rd-April 5th, 2008. The boxes indicate day light (white) and night (grey). Generated from Admiralty Easytide™, Crown Copyright 2008.

Chlorophyll *a* concentrations observed during July and August 2008 directly followed river flow and tidal amplitude (Figure 5.12).

At sites B and C river inflow was the variable with the strongest influence on algal biomass. Both sites experienced high biomass at the beginning of the high resolution monitoring on July 5th, when river inflow was very low. Following a sharp increase in river flow, chlorophyll *a* concentrations declined rapidly around July 11th. Over the following days, during reduced river flow and neap tides, phytoplankton biomass at site C increased markedly and then declined abruptly with the onset of spring tides after July 20th, despite the low river flow. At site B phytoplankton recovery was delayed when compared with site C and bloom levels were not achieved before the onset of spring tides. A major algal bloom then occurred at both sites during a period of low river flow and neap tides, resulting in a chlorophyll *a* maximum of 226 $\mu\text{g L}^{-1}$ at Site C on July 29th. Subsequently, the bloom declined at both sites when river flow increased and spring tides became dominant.

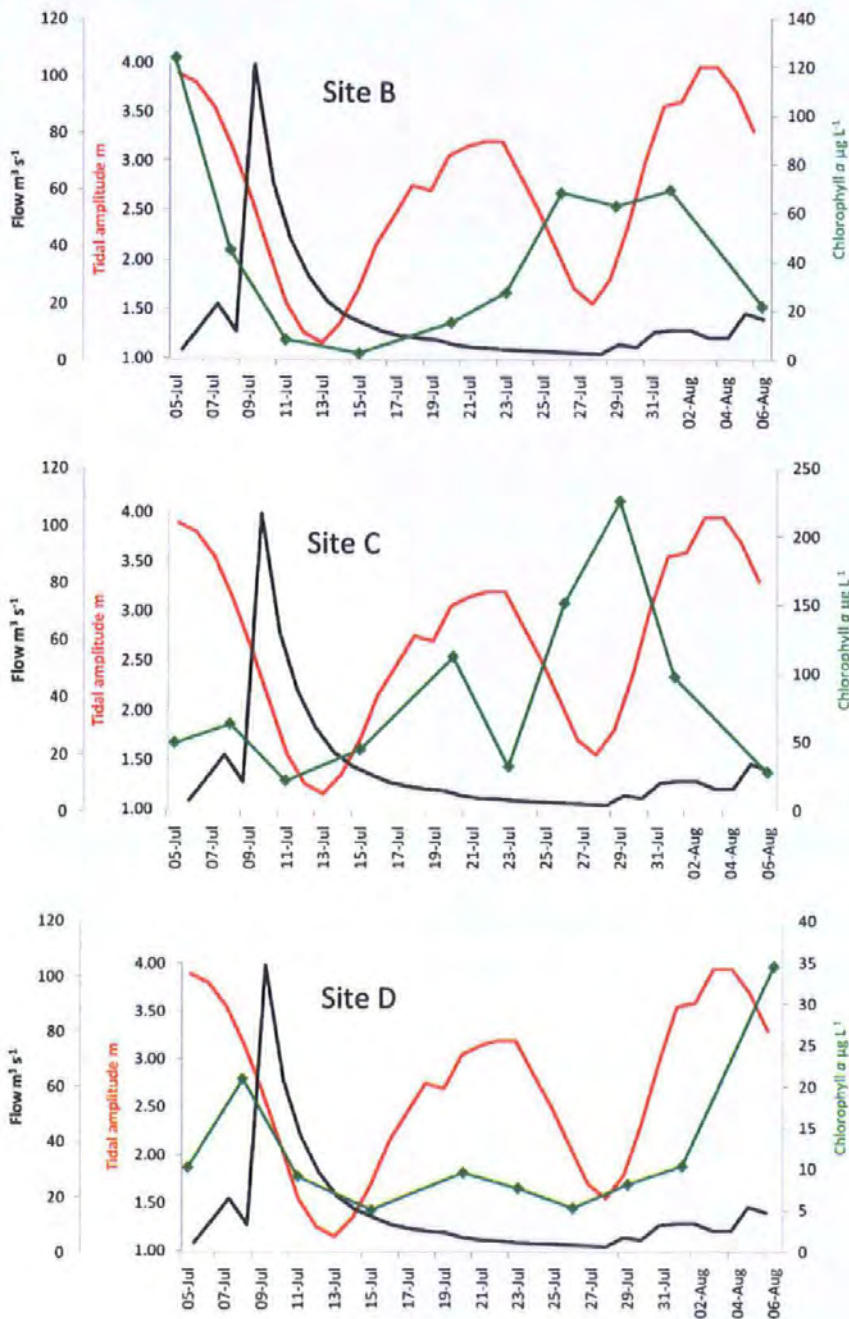


Figure 5.12. Physical forcing through tidal exchange and freshwater inflow at (top) site B, (middle) site C and (bottom) site D between July 5th and August 6th 2008. Diamonds indicate days on which samples were collected. The red line indicates the tidal amplitude at Barnstaple, site B; for sites C and D the tidal amplitudes are expected to be similar, but only the Barnstaple graph is shown to indicate neap and spring tides. Note the different scales of chlorophyll *a* concentrations.

At sites B and C, the flow threshold below which excessive algal growth developed was in the range 5-10 m³ s⁻¹ and varied with tidal influence. Under suitable conditions,

bloom formation took about 3 to 5 days. An average freshwater inflow $>15 \text{ m}^3 \text{ s}^{-1}$ over five days brought a significant reduction in chlorophyll *a* concentrations following the peak at site B on July 5th. The chlorophyll *a* maximum on July 26th ($226 \mu\text{g L}^{-1}$) at site C was reduced to $28 \mu\text{g L}^{-1}$ within seven days by a combination of spring tides and a moderate increase of river flow. However, under (considerably) higher flow rates and/or in combination with spring tides, the same might be achieved in a shorter time.

In contrast to sites B and C, chlorophyll *a* concentrations near the estuary mouth at site D were considerably lower and corresponded to some degree inversely to river flow (also see section 5.2.2.1). A moderate increase in river flow in combination with arriving spring tides led to an increase in algal biomass until July 7th. During the period of very high river discharge around July 10th, algal biomass decreased again but showed a slight increase in response to the arriving spring tides around July 20th. Chlorophyll *a* concentrations then increased considerably, following an increase in river discharge and tidal amplitude.

It can be summarized that in the central estuary, phytoplankton biomass was highest during low river inflow and neap tides, when water exchange with the coastal sea was restricted. Spring tides led to a dispersion of phytoplankton blooms up- and down-estuary. Moderate increases in river flow ($\sim 8\text{-}10 \text{ m}^3 \text{ s}^{-1}$) shifted the chlorophyll maximum to the outer estuary and under high river discharge ($>10\text{-}20 \text{ m}^3 \text{ s}^{-1}$), excessive chlorophyll *a* concentrations were no longer present in the estuary. This process was even more pronounced when high river flow coincided with spring tides.

Although the system lag to nutrient inputs was not specifically tested, the data suggested that response time was very short. Once conditions were favourable for algal growth (*i.e.* low flow), biomass doubled in less than four days, *e.g.* at site C, from

45 $\mu\text{g L}^{-1}$ of chlorophyll *a* on July 15th to 113 $\mu\text{g L}^{-1}$ on July 20th and from 32 $\mu\text{g L}^{-1}$ on July 23rd to 152 $\mu\text{g L}^{-1}$ on July 26th (Figure 5.12). Bloom termination following increased river flow appeared to be within the same time frame.

5.3. Combined ordination analysis of Taw datasets

Ordination is an option frequently used to analyse large, multivariate datasets (Clarke and Warwick, 2001). The two most popular ordination methods are non-metric multidimensional scaling (NMDS) and principal component analysis (PCA). NMDS is typically employed when few (if any) assumptions about the data have to be made, *e.g.* abundance counts for phytoplankton or other faunal or floral assemblages (Clarke and Warwick, 2006). For environmental data (concentrations of chemicals, salinity, temperature, *etc...*), correlation based PCA is usually preferred over NMDS because of the form of the data: unlike in biological assemblage data (abundance counts of organisms), there are generally no large blocks of zero counts that need to be dealt with in a special way (Clarke and Warwick, 2006).

PCA is designed to reduce data complexity, which aids pattern recognition in the data and allows for a visual representation of “similarity” between samples. Here, it provides a way of identifying distinct environmental conditions (or biogeochemical states) in the estuary. For this, two cluster analyses were performed for each set of PCA data. The first cluster analysis was to detect similarities between variables, *i.e.* similar behaviour or covariability (see the approach for EA data, section 3.2.4). The second cluster analysis generated groups of samples, which were based on the similarity of environmental conditions (in these samples). These were then combined with the PCA plots to identify distinct biogeochemical states in the Taw during the development and

decline of algal blooms. The individual steps in the statistical analysis are shown in Figure 5.13.

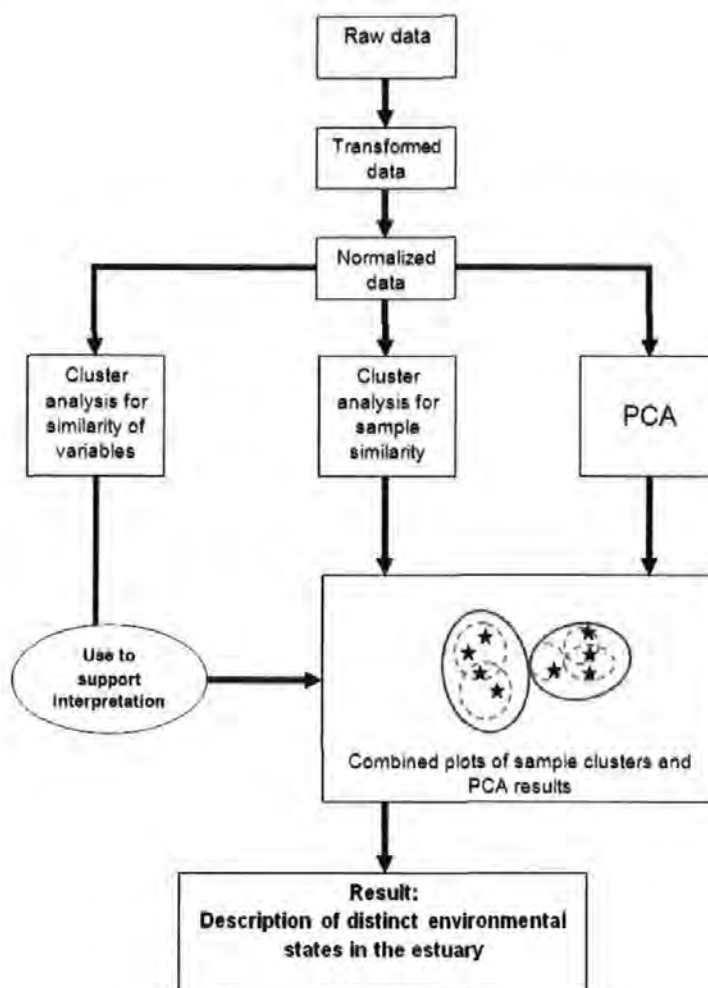


Figure 5.13. Flow diagram, showing the different analytical steps in the combined cluster analysis and PCA.

The aims of this approach were to:

1. Identify similarities in variable behaviour.
2. Identify conditions that favoured excessive algal growth or resulted in the termination of algal blooms.
3. Link distinct environmental states in the estuary to physical forcing through river flow.

5.3.1. Cluster analysis for variable similarity

The cluster analysis for variable similarity revealed three distinct groups of variables, situated on two branches of the dendrogram (Figure 5.14):

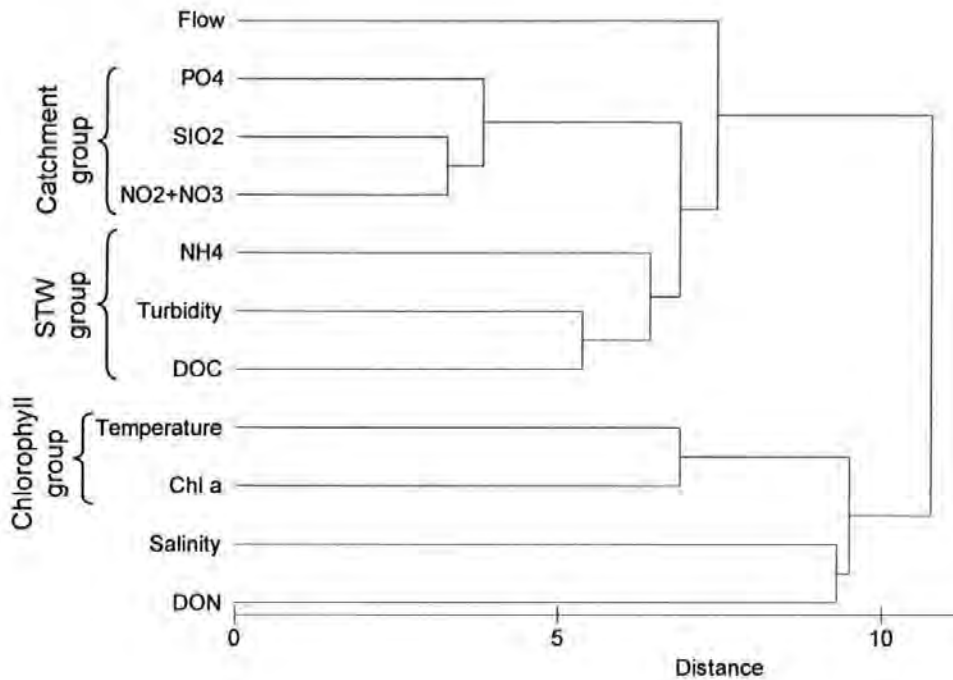


Figure 5.14. March–August 2008 campaign, entire estuary: Dendrogram showing the Euclidean distance between individual variables, integrating data from the entire estuary.

- The top branch of flow associated variables could be divided into two well defined groups, the first one incorporating phosphate, silicate and nitrite+nitrate. This group was named the ‘catchment group’, as the variables mostly originated from the catchment. The second group consisted of ammonium, and DOC, variables often associated with the chemical signal of a of STW outflow, hence it was labelled the ‘STW group’.
- The bottom branch, containing the ‘chlorophyll group’ (chlorophyll *a* and temperature).

Salinity and DON, although situated on the same branch as the 'chlorophyll group', could not be justified to be assigned to that group, and, with a distance of 9.3, did not form an independent group either. However, salinity showed maximum distance from the variables in the 'catchment group', which suggested an inverse relationship (see also section 3.3.3).

5.3.2. Introduction to principal component analysis

The underlying assumption is that the amount of information in a given set of data is equivalent to its variance. The samples are points in an n -dimensional space where n is the number of variables used to characterise each sample. Through this cloud of samples, a principal component is laid along the axis of maximum variance. The samples are then projected perpendicularly onto this axis, which forms the first principal component (PC1) and contains the information of the samples along their axis of maximum variance. Perpendicular to this axis of maximum variance extends the second principal component, PC2, onto which the samples are also projected. Because PC2 is perpendicular to the axis of maximum variance- (*i.e.* PC1), it contains by definition less information.

As this takes place in an n -dimensional space, these projections can be continued ($n-1$) times to generate PC3, PC4, ... PC $_{n-1}$, each orthogonal to the PC from which it extended and each explaining a lower percentage of the initial variance or "information" of the dataset. The first two PCs (PC1xPC2) then form a plane of best fit and represent the maximum percentage of variance that can be encompassed with 2 PCs. Typically this is between 60 and 80%. Clarke and Warwick (2001) suggested as an empirical rule of thumb that a picture that represented 70-75% of the original variation was likely to describe the overall structure rather well. When PC1xPC2 fail to explain more than 40-

50%, a two dimensional PCA ordination may lead to an inadequate or misleading picture. In such cases, a 3 dimensional sample ordination invoking PC3 would yield a more complete picture. If PC1xPC2xPC3 fall short to represent at least 50% of the variation, higher PCs should be included in the analysis.

Additional information and details about the performed data transformations are discussed in section 4.11.

5.3.3. Principal component analysis of the March–August 2008

campaign data

The PCA generated an ordination plane formed by PC1xPC2 which explained 65.2% of the total variation in the data (Table 5.5). PC3 represented 11.2% of the total variation, similar to PC4 and PC5 combined (12.9%).

Table 5.5. March–August 2008 campaign: Percentage of variation explained by each PC and cumulative percentage of variation.

| PC | %Variation | Cum.%Variation |
|----|------------|----------------|
| 1 | 47.1 | 47.1 |
| 2 | 18.2 | 65.2 |
| 3 | 11.2 | 76.4 |
| 4 | 7.7 | 84.1 |
| 5 | 5.2 | 89.3 |

The variable coefficients (Table 5.6) suggested that with the exception of DON the variances of all variables were well represented on the PC1xPC2 plane. DON had its highest variability in PC3.

Table 5.6. March–August 2008 campaign: Coefficients of variables (eigenvectors) that constitute the PCs. The further a coefficient deviates from 0 and approximates either 1 or -1, the more of its variance is explained on the respective PC.

| Variable | PC1 | PC2 | PC3 | PC4 | PC5 |
|----------------------------------|------------|------------|------------|------------|------------|
| Flow | 0.269 | -0.179 | 0.483 | 0.172 | 0.014 |
| Temperature | -0.118 | 0.529 | -0.144 | -0.099 | -0.703 |
| Salinity | -0.375 | 0.065 | 0.292 | 0.261 | 0.099 |
| Turbidity | 0.265 | 0.414 | 0.123 | 0.301 | 0.365 |
| DOC | 0.361 | 0.269 | 0.166 | 0.044 | -0.062 |
| DON | -0.022 | 0.170 | 0.625 | -0.720 | 0.043 |
| NH ₄ | 0.313 | 0.042 | 0.306 | 0.430 | -0.356 |
| SiO ₂ | 0.408 | -0.115 | -0.133 | -0.157 | -0.088 |
| PO ₄ | 0.407 | -0.024 | -0.149 | -0.132 | -0.147 |
| NO ₂ +NO ₃ | 0.377 | -0.093 | -0.249 | -0.233 | 0.206 |
| Chl <i>a</i> | 0.016 | 0.622 | -0.181 | -0.015 | 0.398 |

Interpretation of the results is often facilitated by looking at the variable coefficients (= eigenvectors) and the eigenvector plot. The eigenvectors give the linear combinations that define the PCs. Two examples for which the eigenvectors from (Table 5.6) were used are:

$$PC1 = 0.269(\text{Flow}) - 0.118(\text{Temperature}) - 0.375(\text{Salinity}) + 0.265 (\text{Turbidity}) + \dots$$

$$PC2 = -0.179(\text{Flow}) + 0.529(\text{Temperature}) + 0.065(\text{Salinity}) + 0.414(\text{Turbidity}) + \dots$$

The eigenvector plot (Figure 5.15) is a graphical representation of these coefficients. For example, salinity has the coefficients -0.375 and 0.065. Its main contribution is therefore to PC1, where it increases from right to left because of its negative sign, and has only a slight increase in the positive PC2 direction. If the vector reaches the circle in the eigenvector plot, then all of the variable's other coefficients in the eigenvector table will be 0. In other words, the closer the vector extends to the circle, the more of that variable's information is represented on that plane (here PC1xPC2). The variable groups of the cluster analysis are partly visible in the eigenvector plot (Figure 5.15), but

whereas the cluster analysis showed the similarity of variables based on Euclidean distance, the eigenvector plot elucidated “how much” of the variation of a variable is shown in the PC1xPC2 plane and in which direction this variation extended.

With the exception of DON and, to a lesser extent, ammonium, all the eigenvectors were of comparable length. Figure 5.15 also shows the negative correlation of salinity with flow and that very little of the DON was represented on the PC1xPC2 plane. The eigenvector plot supported the variable groups from the cluster analysis and showed that salinity and flow had an inverse relationship. The vector of DON mostly extended in the direction of PC3 and hence showed very little connection to the other variables on the PC1xPC2 plane.

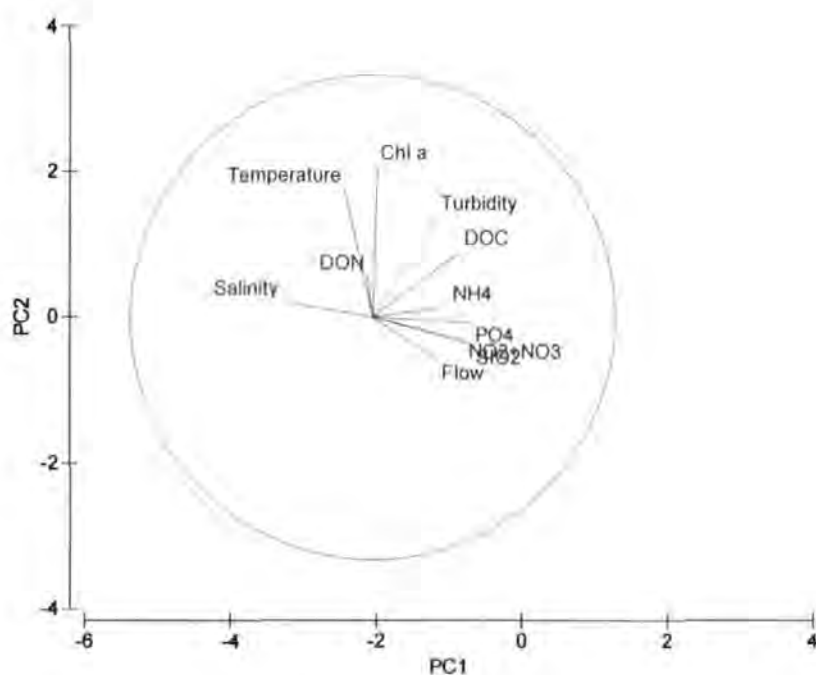


Figure 5.15. March – August 2008 campaign, entire estuary: Projections of eigenvectors onto the PC1xPC2 ordination plane.

- B₃ was the cluster with the lowest chlorophyll *a* concentrations (Figure 5.18, Figure 5.19) and freshwater to mesohaline (polyhaline) characteristics (Figure 5.20). Variables of the 'catchment-group' were present at intermediate to high concentrations (Figure 5.21), concentrations of the 'STW group' were low (Figure 5.22). Turbidity was lowest in this cluster. B₃ was the cluster with the lowest temperatures (Figure 5.23) and the highest river discharges (Figure 5.24). DON concentrations were also highest in this cluster (Figure 5.25). All sample sites were represented in this cluster. From Figure 5.26 it is clear that the conditions represented by this cluster are typical for a high discharge regime, which exists during the winter months and after high rainfall.
- A₂ had very low chlorophyll *a* concentrations but was the cluster with the highest salinities (polyhaline to euhaline). Variables of the 'catchment group' and the 'STW group' had their lowest concentrations in this cluster. Temperatures showed a wide range; flow and DON were low. Most samples in this cluster were from site D, with three from site C. Cluster A₂ represented conditions typical for waters under strong coastal influence.
- B₂ had low to intermediate chlorophyll *a* concentrations and very low salinity. 'Catchment group' variables were present in high concentrations whereas the 'STW group' variables showed low concentrations. Temperatures were relatively high; flows were very low and DON concentrations were low. Only sites B and C were included in this cluster. B₂ indicated transitional conditions between B₃ (high discharge) and A₁ (high chlorophyll *a*) and a freshwater dominated environment with increasing phytoplankton biomass, either in spring, before the onset of a bloom or up-estuary of a bloom.

5.3.3.1. Cluster analysis for sample similarity

The second cluster analysis identified two main clusters (A and B; Figure 5.16) at a Euclidean distance of 5. These two groups could be further divided into 5 sub-clusters, A₁, A₂, B₁, B₂ and B₃ at a distance of 3.6.

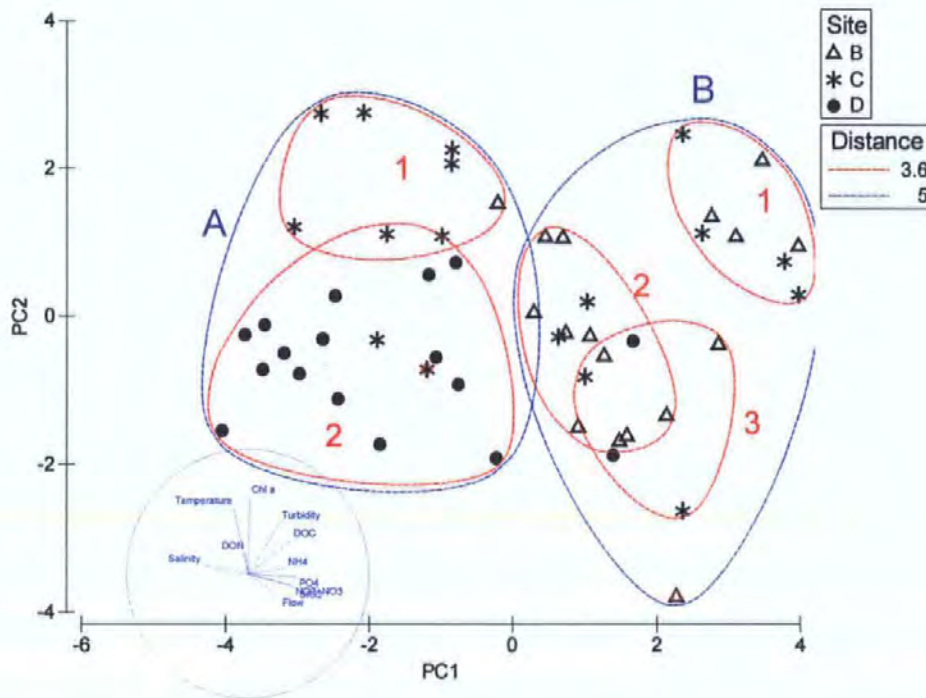


Figure 5.16. March–August 2008 campaign, entire estuary: sample clusters at a Euclidean distance of 3.6 and 5. The main cluster were named A and B, the subclusters received numbers 1, 2, 3.

Variability of salinity and chlorophyll *a* concentrations are shown in Figure 5.17 and Figure 5.18. Additional plots of variables used in this PCA are shown in Appendix A. The main clusters A and B were defined by salinity, with cluster A being more saline than cluster B. The properties of the 5 sub-clusters were further defined by the other variables used in the PCA and are discussed in relation to increasing chlorophyll concentrations, *i.e.* B₃, A₂ ... during the development of a phytoplankton bloom rather than in alphanumeric order. However, the different clusters or stages do not represent

a strict, unidirectional temporal succession; the system can also return to a previous stage, or oscillate for some time between two stages (see trajectory in Figure 5.29).

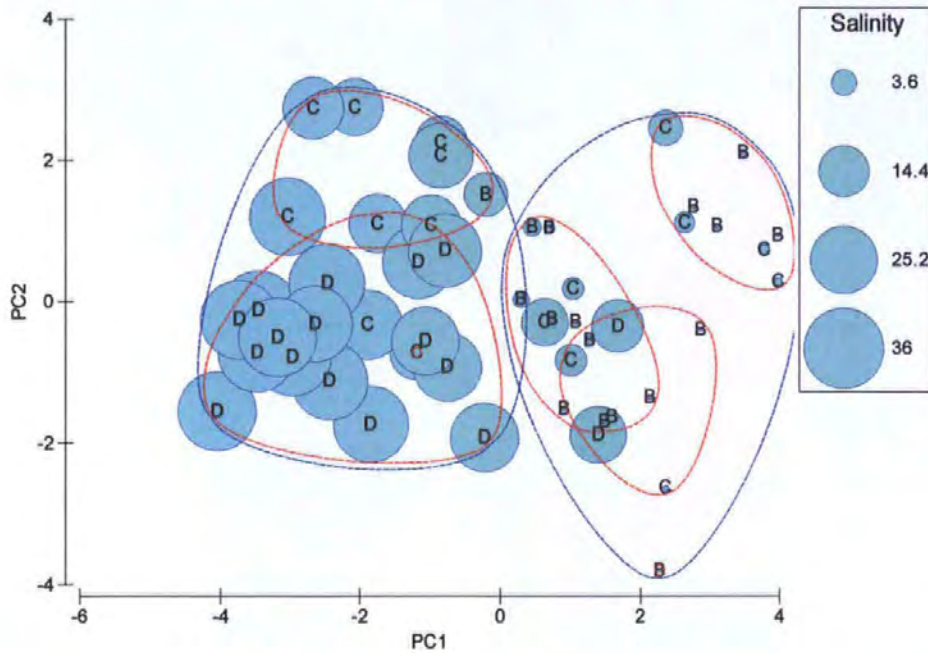


Figure 5.17. March–August 2008 campaign, entire estuary:–Bubble plot of salinity. Bubble size represents ranges in salinity; the letters in the bubbles are site codes.

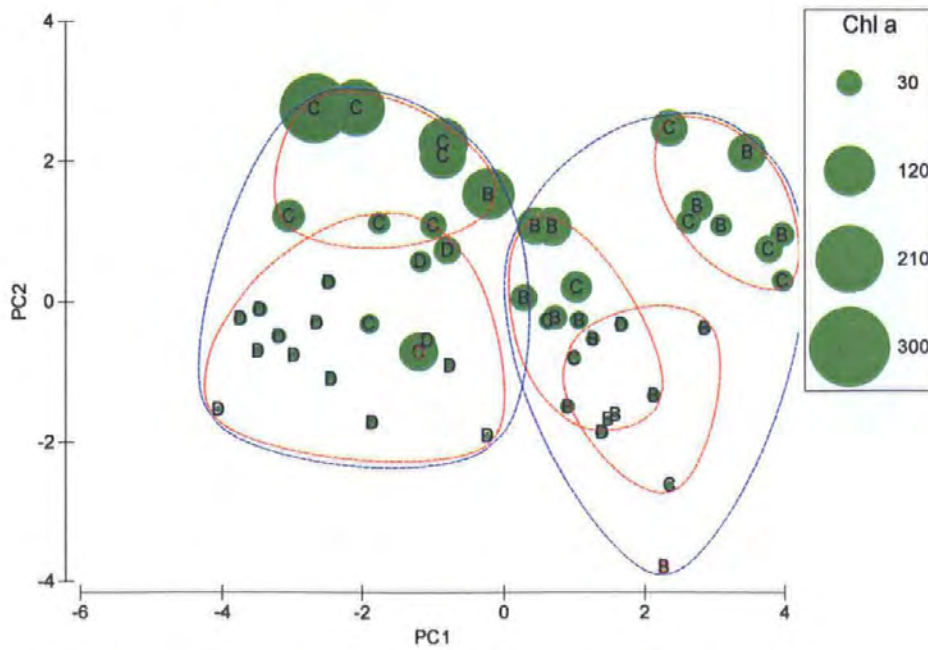


Figure 5.18. March–August 2008 campaign: Bubble plot of chlorophyll *a* concentrations ($\mu\text{g L}^{-1}$).

- B₃ was the cluster with the lowest chlorophyll *a* concentrations (Figure 5.18, Figure 5.19) and freshwater to mesohaline (polyhaline) characteristics (Figure 5.20). Variables of the ‘catchment-group’ were present at intermediate to high concentrations (Figure 5.21), concentrations of the ‘STW group’ were low (Figure 5.22). Turbidity was lowest in this cluster. B₃ was the cluster with the lowest temperatures (Figure 5.23) and the highest river discharges (Figure 5.24). DON concentrations were also highest in this cluster (Figure 5.25). All sample sites were represented in this cluster. From Figure 5.26 it is clear that the conditions represented by this cluster are typical for a high discharge regime, which exists during the winter months and after high rainfall.
- A₂ had very low chlorophyll *a* concentrations but was the cluster with the highest salinities (polyhaline to euhaline). Variables of the ‘catchment group’ and the ‘STW group’ had their lowest concentrations in this cluster. Temperatures showed a wide range; flow and DON were low. Most samples in this cluster were from site D, with three from site C. Cluster A₂ represented conditions typical for waters under strong coastal influence.
- B₂ had low to intermediate chlorophyll *a* concentrations and very low salinity. ‘Catchment group’ variables were present in high concentrations whereas the ‘STW group’ variables showed low concentrations. Temperatures were relatively high; flows were very low and DON concentrations were low. Only sites B and C were included in this cluster. B₂ indicated transitional conditions between B₃ (high discharge) and A₁ (high chlorophyll *a*) and a freshwater dominated environment with increasing phytoplankton biomass, either in spring, before the onset of a bloom or up-estuary of a bloom.

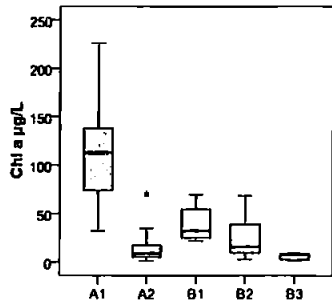


Figure 5.19. Chlorophyll *a*

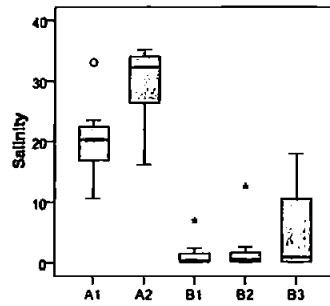


Figure 5.20. Salinity

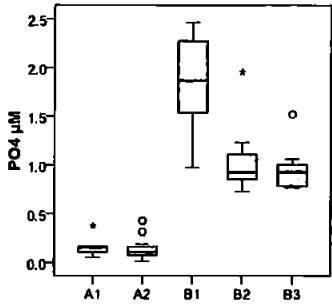


Figure 5.21. 'Catchment group' of variables.

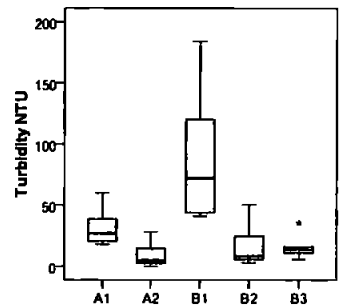
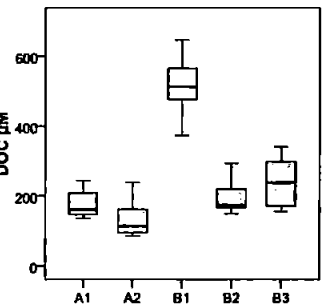
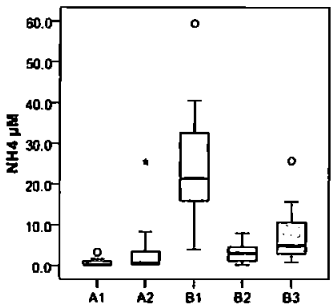
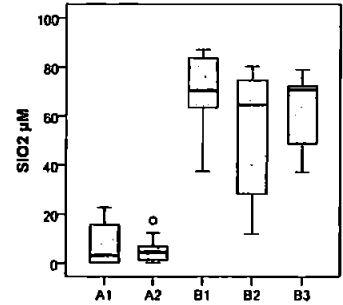
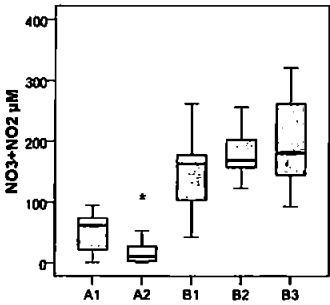


Figure 5.22. 'STW group' of variables'.

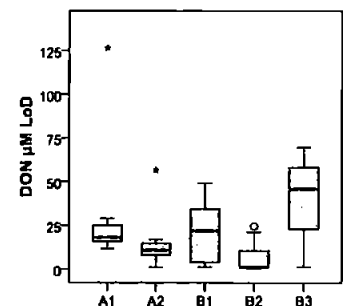
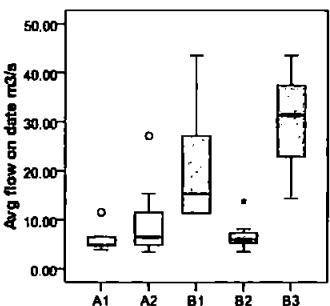
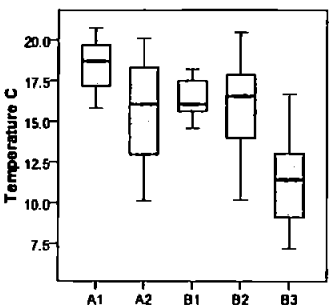


Figure 5.23. Temperature

Figure 5.24. Flow

Figure 5.25. DON

- A₁ was the cluster with the highest chlorophyll *a* concentrations. Salinity was in the mesohaline (brackish) to low polyhaline range. Variables from the

'catchment branch' had low (silicate, nitrite+nitrate) to very low (phosphate) concentrations, similar to the variables of the 'STW group' (very low ammonium, low DOC and turbidity). A₁ was the cluster with the highest temperatures and the lowest river inflows. DON concentrations were intermediate. Most of the samples in this cluster were from site C and one from site B. In summary, cluster A₁ represented conditions present during a phytoplankton bloom with long water residence times, high temperatures and signs of nutrient depletion.

- B₁: Chlorophyll *a* concentrations were low to intermediate whereas salinity was very low. 'Catchment group' variables were present at high concentrations (very high for phosphate) in this cluster. Characteristic features of B₁ were the high concentrations of 'STW group' variables which indicated (together with high phosphate) very high loads from the STW. Temperatures were lower than those of the previous cluster, A₁. Flows were intermediate to high and DON showed high variability. Samples of this cluster were from sites B and C. Conditions represented by B₁ were indicative of a decline of algal biomass with increasing river flow.

Two samples (March 18th, site B and April 14th, site C; Figure 5.16, Figure 5.26) were not part of any cluster at the measured distance of 3.6 but were assigned to cluster B₃ and A₂, respectively, as these were the clusters with the least distance to these two samples.

The combined ordination analysis enabled the identification of five distinct biogeochemical states, which formed a succession of conditions or states (in the order B₃, A₂/B₂, A₁, B₁) that were closely linked to river discharge and (ultimately) changes in

precipitation (Figure 5.26). In late winter when river flow was high, all 3 sites were categorized as cluster B₃, with relatively cold, non-turbid water of low salinity and very low chlorophyll *a* concentrations. This water was high in nitrite+nitrate, phosphate and silicate but with low ammonium and DOC concentrations.

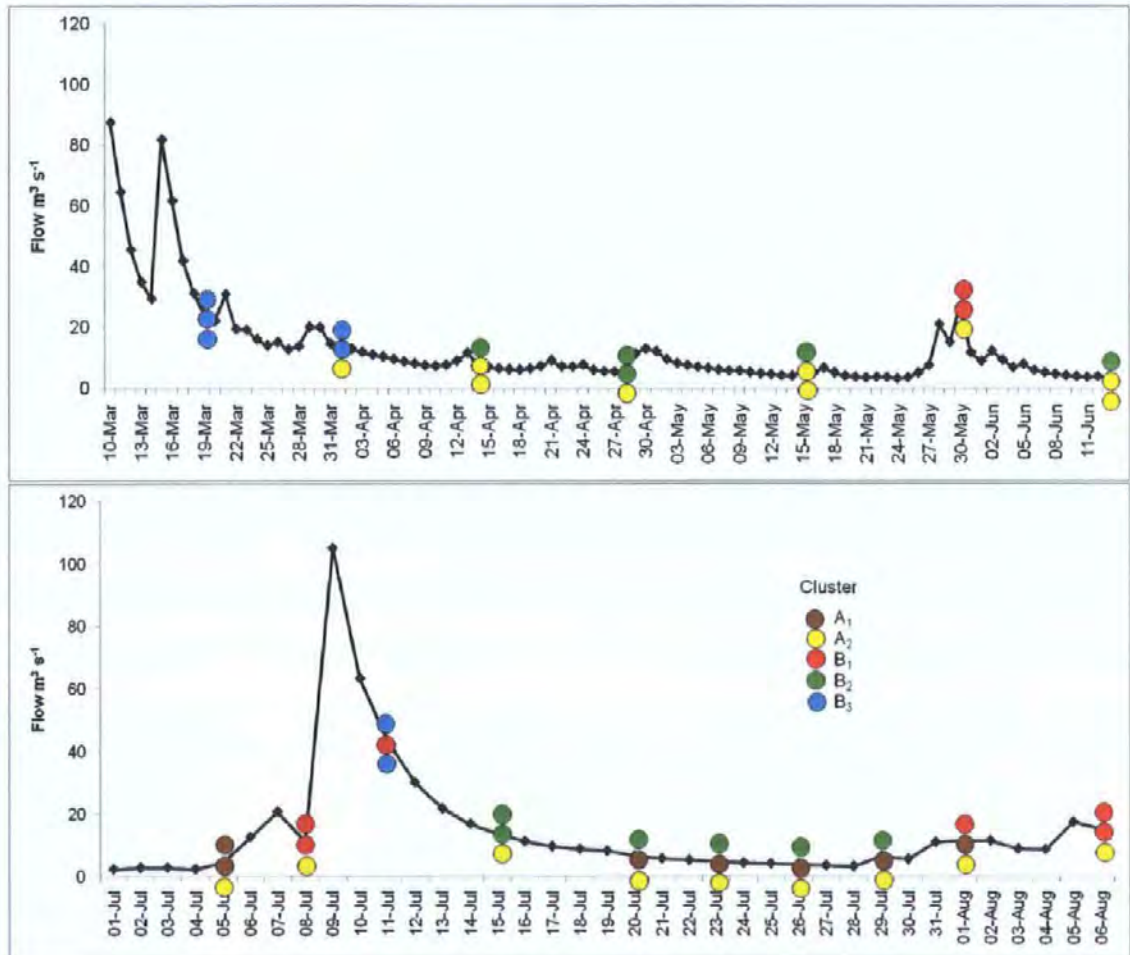


Figure 5.26. March–August 2008 campaign: colour coded distribution of sample clusters and river discharge over time. (top) Background monitoring between March 18th and June 13th, (bottom) temporal high resolution monitoring, July 5th to August 6th. The top circles represent site B, the middle circles site C and the bottom circles are for site D. Samples from March 18th, site B and April 14th, site C were assigned to the respective clusters by empirical judgement (see text).

Under reduced river flow following the onset of spring, saline coastal waters (A₂) intruded from the sea into the outer estuary (site D). These conditions prevailed there

throughout the sample period and advanced up-estuary to site C only occasionally in spring. Beginning with April 14th, waters representative of the cluster B₂ appeared in the estuary, particularly in the upper (and periodically) central reaches. These waters had similar characteristics to B₃ but higher temperatures and higher chlorophyll *a* concentrations and occurred only during very low flow and showed signs of the onset of algal growth.

During summer, when low river flow prevailed for some time, conditions represented by A₁ succeeded B₂ and algal blooms developed in temporal or spatial proximity to the latter (see Figure 5.26). The bloom peaks occurred in relatively warm brackish water with low nutrient concentrations, signifying nutrient depletion from excessive algal growth. The blooms were terminated by increasing river flows and the intrusion of water, classified by cluster B₁, into the upper and central part of the estuary. The properties from this cluster were very different to the former clusters, mostly due to the excessively high concentrations of ammonium, phosphate and DOC and high turbidity. From Figure 5.26 it is evident that B₁ represented an early flushing state of the system following the initial storm water discharge after a period of low river flow and high primary production. The high concentrations of nutrients and DOC are characteristic of such events during which STW's can experience overflows and discharge untreated sewage into the receiving water. It is hypothesized, and suggested by Figure 5.26 (data point for July 11th), that under continued high precipitation, cluster B₁ water would be succeeded by waters with lower nutrient concentrations, particularly of the variables in the 'STW group'.

5.3.4. Principal component analysis for site C

With chlorophyll *a* concentrations as high as 226 $\mu\text{g L}^{-1}$, site C experienced the most severe symptoms of eutrophication *sensu* Nixon (1995). Therefore, the above approach was tested with samples from site C only to assess if site specific conclusions were similar to those for the entire estuary. The PCA generated an ordination plane formed by PC1xPC2 which explained 72.5% of the total variation in the data (Table 5.7). PC3 represented 9.2% of the total variation, similar to PC4 and PC5 together (9.7%). The variable coefficients (Table 5.8) suggested that with the exception of DON all variables' variances were well represented on the PC1xPC2 plane. DON had its highest variability on PC3.

Table 5.7. Eigenvalues, percentage of variation explained by each PC and cumulative percentage of variation.

| PC | %Variation | Cum.%Variation |
|----|------------|----------------|
| 1 | 53.4 | 53.4 |
| 2 | 19.1 | 72.5 |
| 3 | 9.2 | 81.6 |
| 4 | 6.1 | 87.8 |
| 5 | 3.6 | 91.4 |

Generally, the results from the PCA and the cluster analyses showed very similar patterns as before, but were much more pronounced (Figure 5.27). Additional plots are shown in Appendix B.

The cluster analysis for variables generated the same three groups, but with some significant differences. The groups were better defined, which means the variables within one group were closer to each other. The 'catchment group' incorporated phosphate, silicate and nitrate as before, and now also included river flow. The 'STW group' remained the same as in the previous section, but its signal was much better

Table 5.8. Coefficients in the linear combinations of variables making up PCs. The further a coefficient deviates from 0 and approximates either 1 or -1, the more of its variance is explained by the respective PC.

| Variable | PC1 | PC2 | PC3 | PC4 | PC5 |
|-------------------|--------|--------|--------|--------|--------|
| Flow | -0.367 | 0.025 | 0.065 | -0.216 | 0.387 |
| Temperature | 0.171 | -0.528 | -0.013 | -0.293 | -0.595 |
| Salinity | 0.386 | -0.054 | 0.014 | 0.278 | -0.117 |
| Turbidity | -0.168 | -0.542 | 0.090 | 0.085 | 0.337 |
| DOC | -0.280 | -0.379 | -0.257 | 0.174 | -0.106 |
| DON | 0.140 | 0.033 | -0.859 | -0.413 | 0.147 |
| NH ₄ | -0.306 | -0.292 | -0.205 | 0.405 | -0.064 |
| SiO ₂ | -0.385 | 0.077 | -0.038 | -0.041 | -0.300 |
| PO ₄ | -0.388 | -0.029 | -0.011 | -0.154 | 0.096 |
| NO ₂₊₃ | -0.332 | 0.170 | 0.215 | -0.430 | -0.373 |
| Chl <i>a</i> | 0.242 | -0.397 | 0.306 | -0.456 | 0.306 |

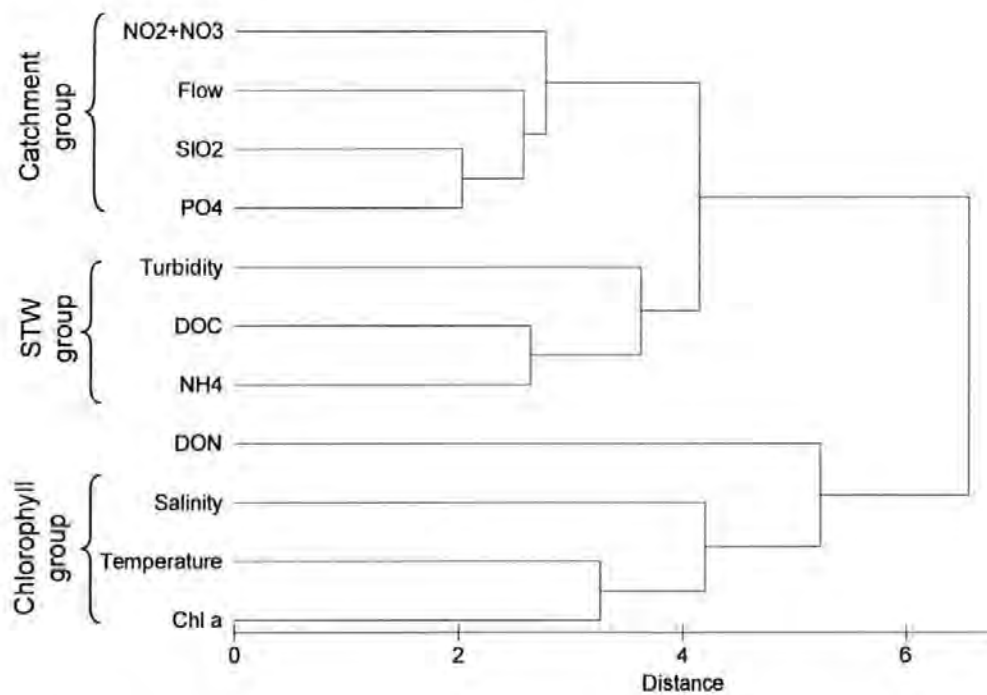


Figure 5.27. March – August 2008 campaign, site C: dendrogram showing the Euclidean distance between individual variables.

defined. It was composed of ammonium, DOC and turbidity. The 'chlorophyll group' consisted of chlorophyll *a* and temperature and (unlike in the whole estuary analysis) salinity. Again, DON did not show close resemblance to any other variable or group, so any close connection to the other variables was deemed unlikely. The combined cluster analysis for sample similarity and PCA showed that the clusters from site C all had a counterpart with similar characteristics to the clusters generated for the entire estuary and were hence named accordingly (Figure 5.28). One sub-cluster of the A main cluster contained samples that were distributed over two clusters, namely A₂ and B₂ in section 5.3.3. It is here referred to as A₂/B₂. The cluster characteristics are summarised in Table 5.9.

Table 5.9. March – August 2008 campaign, site C: summary of variable group characteristics and sample clusters. + high; ± intermediate; - low values.

| Variable group | | Cluster | | | |
|-------------------|---|---------|---|--------------------------------|---|
| | | B | | A | |
| | | 3 | 1 | A ₂ /B ₂ | 1 |
| Catchment group | + | + | ± | - | |
| STW group | - | + | - | - | |
| Chlorophyll group | - | ± | ± | + | |

With data from site C only, it was possible to plot a trajectory over the PCA plot, which showed how the samples shifted over time between almost discrete environmental states at site C (Figure 5.29). Following that trajectory, site C started in late winter/early spring with cluster B₃, characterised by high flow and nutrient concentrations but low temperatures and very little chlorophyll *a*. Site C then moved on to cluster A₂B₂, a cluster intermediate in terms of river flow, temperature and chlorophyll *a* but also, with regard to its position on the plot, embedded between the winter/high flow cluster B₃ and the 'summer bloom cluster' A₁.

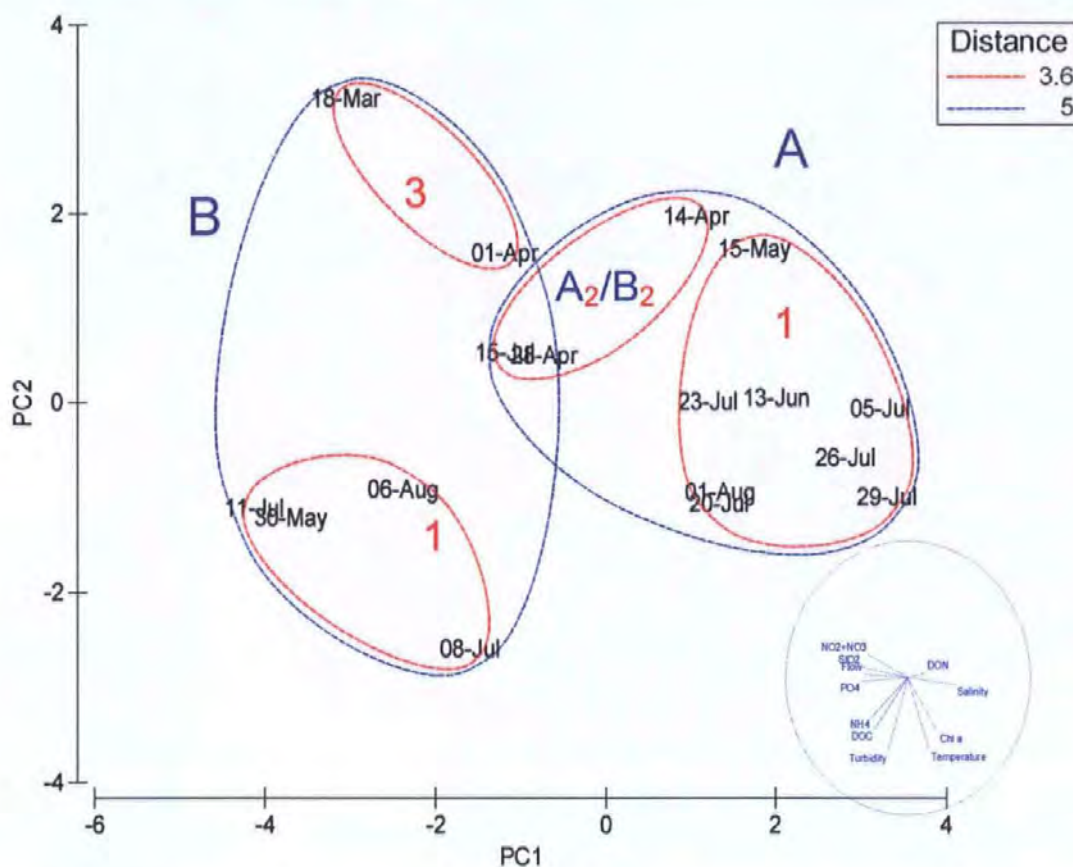


Figure 5.28. March – August 2008 campaign, site C: clusters at a Euclidean distance of 3.6 and 5. On the bottom right is an eigenvector plot.

Beginning with the sample from May 15th the trajectory moved into the ‘summer bloom cluster’, A_1 . Whereas to this point the movement through the clusters was unidirectional, following the seasonal gradients of temperature and river inflow from B_3 via A_2B_2 to A_1 , the trajectory then started to alternate between B_1 , the ‘high DOC cluster’ and A_1 , the ‘summer bloom cluster’ with one return to A_2B_2 . The data showed that the Taw Estuary at site C during late spring/summer shifted repeatedly between two very distinct states: one with conditions favourable for excessive algal growth, such as warm temperatures and low river discharge, summarised in cluster A_1 , and an alternative state, represented by the samples of cluster B_1 , when chlorophyll *a* concentrations were lower but DOC and ammonium were very high.

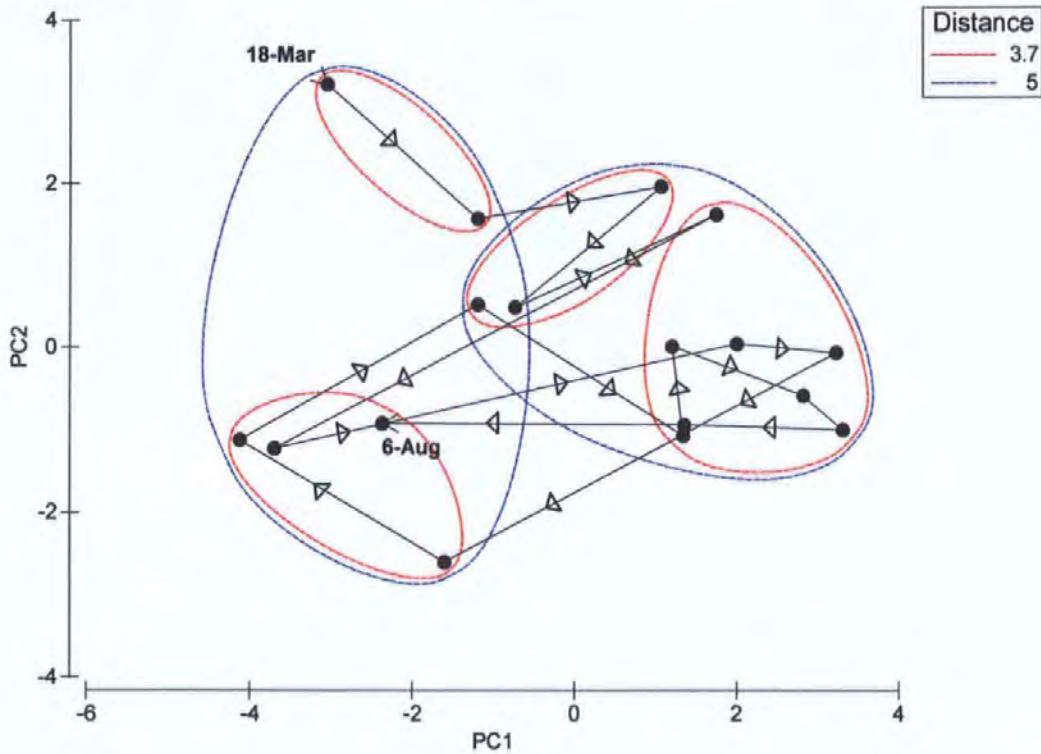


Figure 5.29. March – August 2008 campaign, site C: trajectory of samples on the PC1xPC2 ordination plane.

5.4. Predicting eutrophication in the Taw Estuary: a simple, non-linear, flow based model of eutrophication

River flow was shown to be the central variable to determine phytoplankton biomass in the Taw Estuary. Based on the data collected in July / August 2008, it was attempted to build flow based regression models which were then tested against historic chlorophyll *a* data collected by the EA. The aim of this was to reinforce the findings from the sections above, which already outlined the importance of river flow for the trophic status of the estuary, but also to lay the foundation for a conceptual model of eutrophication in the Taw, which is discussed in chapter 6.

As a starting point, chlorophyll *a* concentrations from each site were plotted against daily river flow. Then, the nature of the relationship between the two variables was

identified. Linear models were not suitable, the best fit curve was described by an exponential function of the form $f(x) = b_1 e^{(b_2 x)}$. However, it was not only the flow on the day of measurement that determined algal biomass, but also the flow during the days before the sample was collected. For example, river flow could be very low on the day of sampling, but 3 days earlier, heavy rainfall and high flow had terminated an algal bloom and algal biomass has not had time yet to reach its maximum, despite the low flow conditions. Therefore, in a second step, this flow variability had to be taken into account. It was used to optimise the model by maximising the coefficient of determination, R^2 . In order to do so, flow averages were calculated, e.g. the average flow for the past 1, 2, 3, 4,... 13 days before, plus the day of sample collection. Then, fit curves were generated, plotting chlorophyll concentrations against the various flows. For each site, the flow data that produced the highest R^2 (the coefficient of determination) were then chosen to generate a non-linear regression model using SPSS, the calibration model.

To test the validity of the models, subsets from the EA dataset analysed in chapter 3 were used. For each EA site with an equivalent site in the summer 2008 campaign (*i.e.* EA site 3 and summer 2008 campaign site B, sites 4 and C, sites 6 and D; Figure 4.1), a subset of summer data (June-September) was selected. The data were filtered for samples that were collected at similar tidal states as the summer 2009 data (2-5 h after high tide) to ensure maximum comparability to the (summer 2008) data which were used to generate the model. Then, the flow data of the EA subsets were used to calculate or “predict” chlorophyll *a* concentrations. The “predicted” chlorophyll concentrations were then plotted against the measured *in situ* EA chlorophyll concentrations and Pearson’s correlation coefficient r was calculated to assess the accuracy of the model.

5.4.1. Site B

The calibration model for site B is shown in Figure 5.30. River flow, averaged over 9 days before, plus the day of sample collection (= 10 days average flow), could explain 94% of all variation in chlorophyll *a* concentrations. Algal biomass showed a very steep decline with increasing river flow.

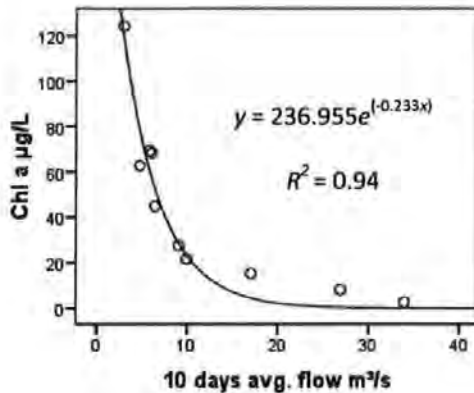


Figure 5.30. Non-linear regression between the average river discharge over 9 days before and the day of sample collection (= 10 days average flow) and chlorophyll *a* concentrations at site B.

Samples were collected between July 5th and August 6th 2008.

When this model was applied to the EA data subset for site 3, the Pearson correlation coefficient (r) between the predicted and the *in situ* concentrations was 0.83 and significant at $p < 0.01$ (Figure 5.31).

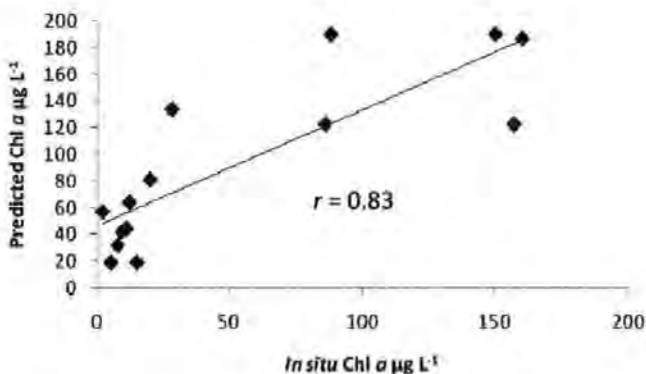


Figure 5.31. Comparison of *in situ* chlorophyll *a* concentrations near site B measured by the EA (June-September, 1995-2004) with flow based chlorophyll *a* predictions from the model shown in Figure 5.30.

5.4.2. Site C

The most accurate calibration model for site C is shown in Figure 5.32. The 3 days before plus the sampling date average river discharge (= 4 days average flow) could predict 30% of the variation in chlorophyll *a* concentrations.

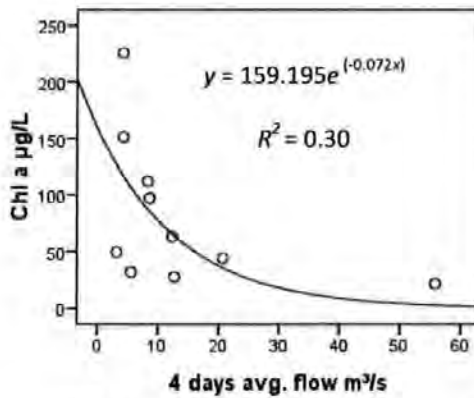


Figure 5.32. Non-linear regression between the average river discharge over 3 days before plus the sampling date average river flow (= 4 days average flow) and chlorophyll *a* concentrations at site C. Samples were collected between July 5th and August 6th 2008.

The correlation coefficient between the predicted chlorophyll *a* and the *in situ* chlorophyll *a* concentrations from the EA subset for site 4 was 0.45 and was significant at $p < 0.05$ (Figure 5.32).

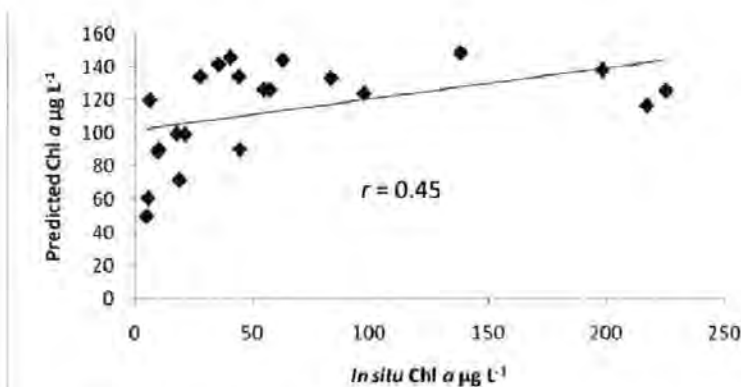


Figure 5.33. Comparison of *in situ* chlorophyll *a* concentrations near site C (at EA sample site 4) measured by the EA (June-September, 1995-2004) with flow based chlorophyll *a* predictions from the model shown in Figure 5.32.

5.4.3. Site D

The best fit curve for site D data had coefficient of determination of only 0.11 with flow averaged over 14 days (Figure 5.34). When the model was applied with a subset of EA data from site D (Figure 5.35), the correlation coefficient was 0.095 and not significant.

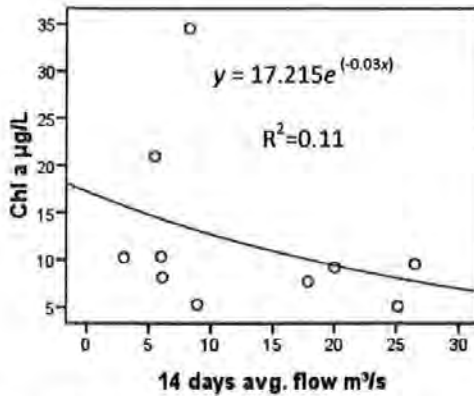


Figure 5.34. Non-linear regression between the average river discharge over 13 days before plus the day of sample collection (= 14 days average flow) and chlorophyll *a* concentrations at site D.

Samples were collected between July 5th and August 6th 2008.

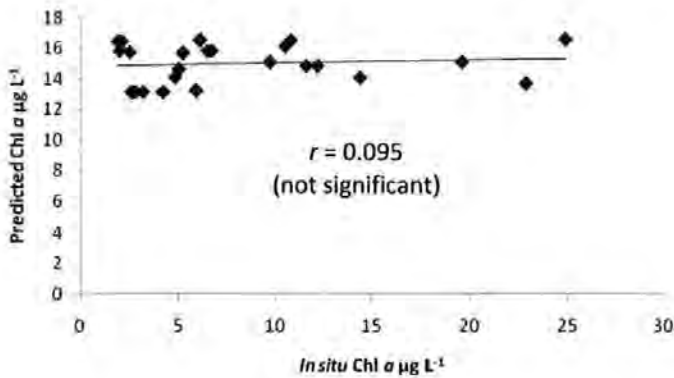


Figure 5.35. Comparison of *in situ* chlorophyll *a* concentrations near site D (at EA sample site 6) measured by the EA (June-September, 1995-2004) with flow based chlorophyll *a* predictions from the model shown in Figure 5.34.

The generated models were very reductionistic and assumed river flow to be the only variable to determine algal biomass. For the upper and central estuary (sites B and C), this was a successful proof of concept: it could be shown that the models were capable

of predicting trends in algal growth, even more so, as the data base for the calibration models was very small ($n = 10$). Although the error margins were very wide, they could be employed to good success.

However, for site D, this approach was not successful. The calibration set showed a wide data spread and a low regression coefficient ($R^2 = 0.11$), and the predicted EA chlorophyll concentrations did not correlate with the measured concentrations. The results discussed in the sections above already demonstrated that the influence of the river significantly decreased towards the estuary mouth, but it also needs to be mentioned that the site D and the EA sample site 6 may have different characteristics due to the distance (~4 km) between them.

Whereas this exercise was rather to demonstrate the general direction into which predictive models for the Taw (and other small estuaries) could develop, some suggestions for further improvements can already be made: A broader database would be desirable, both for calibration and verification, *i.e.* at least 20 data points per site over 3 months would be a minimum requirement. The EA data were the only data available for verification, but future data collection should emphasize tidal standardisation between the calibration and the verification sets. Further, instead of averaging flow over several days, weighting factors could be introduced, emphasizing discharge in the nearer past or taking extreme flow events more into account.

5.5.Summary

Under the present nutrient conditions, phytoplankton biomass (for which chlorophyll *a* was used as a proxy) depended on a combination of freshwater inflow and possibly tidal exchange. In the upper reaches of the estuary, low river inflow enabled the development of algal blooms independently of spring or neap tides. In the middle reaches, the

precondition for the development of severe symptoms of eutrophication *sensu* Nixon (1995) was a combination of low river flow and neap tides. All blooms in the upper estuary were terminated by either spring tides, increased river flow or both. This in turn led to elevated chlorophyll *a* concentrations in the outer estuary, which were, however, well below the levels experienced up-estuary.

All blooms led to nutrient depletion and, in the central and outer estuary, to a switch from P limitation to Si limitation. The findings from the combined cluster and principal component analyses not only represent a way of describing environmental conditions in an estuary, but also showed that in the Taw Estuary very distinct water bodies of different trophic states were present during the study period and that it was possible to differentiate between the environmental conditions that were beneficial and those that were detrimental for algal growth. Further, the importance of river flow for shaping the environmental conditions in the Taw became even more evident.

**OVERALL DISCUSSION AND CONCLUSIONS,
CRITIQUE AND FUTURE WORK**

*Sunset over
Lundy Island*



6. Overall discussion and conclusions, critique and future work

The key finding of this study was that planktonic primary production in the Taw Estuary is primarily governed by freshwater inflow. This was shown by the analysis of archived data from the Environment Agency and from a follow-up, temporal high resolution surveying campaign during spring / summer 2008.

6.1. Analysis of historic EA data

EA monitoring data similar to those analysed in chapter 3 have been used before in riverine and estuarine assessments: Littlewood *et al.* (1998) employed Harmonised Monitoring Scheme (HMS) data for nutrients and dissolved metals and data from the National River Flow Archive (NRFA) to estimate UK river mass loads and Nedwell *et al.* (2002) performed a similar task, but focused on N and P in the context of estuarine eutrophication; they also used HMS and NRFA data to calculate loads to UK estuaries. The novelty of the work presented in chapter 3 is that such data (in this case estuarine water quality monitoring data) were used to identify cause-effect relationships. In combination with load data, it was possible to characterise the drivers of primary production in the Taw Estuary, to identify points of action in eutrophication management and to obtain valuable information on how to design future eutrophication surveys in that system. Also, the sources of nutrients and their relative importance were successfully quantified.

The significance of such data mining and the structured statistical analysis for policy makers and environmental managers, and also for environmental scientists, is obvious: the approach from chapter 3 represents a cost effective and rapid methodology to use

archived EA data from decades of monitoring UK estuaries for trophic assessments and to assist decision making on eutrophication management options.

6.1.A conceptual model of eutrophication in the Taw Estuary

Following the results from the EA data analysis and the follow-up campaign in spring / summer 2008, a conceptual model of primary production and eutrophication in the Taw Estuary was devised (Figure 6.1). It is primarily based on cluster analysis for sample similarity (section 5.3.3.1) but also integrates findings from other sections of the thesis. This conceptual model is capable of describing how river flow affects phytoplankton biomass and, concomitantly, a wide range of variables. It is valid for the upper and central estuary; from just above the town of Barnstaple (between EA sites 2 and 3, Figure 4.1) to about EA sample site 5, near RAF base Chivenor, where algal blooms were predominantly located.

The model represents a succession of trophic states of the estuary, which can be linked directly to the degree of catchment influence. It is valid over several temporal scales, *i.e.* from yearly to tens of days, and represents either the trophic successions in the Taw Estuary over an annual cycle or, alternatively, the different states the idealized system experiences from the development of an algal bloom to its decline and termination. Each of the four states have their predominant occurrence during a particular time of the year (see labels in Figure 6.1), but they also occur in the succession from a well flushed system via a chlorophyll maximum back to a freshwater dominated system.

The starting point for the model was set to when river flow is high, *i.e.* $>>15\text{-}20\text{ m}^3\text{ s}^{-1}$ and has remained high for at least one week. In Figure 6.2 and the combined cluster analysis / PCA in section 5.3.3, this state is named B₃ and colour coded with blue. Such conditions are typical for winter, when discharge rarely falls below $30\text{ m}^3\text{ s}^{-1}$

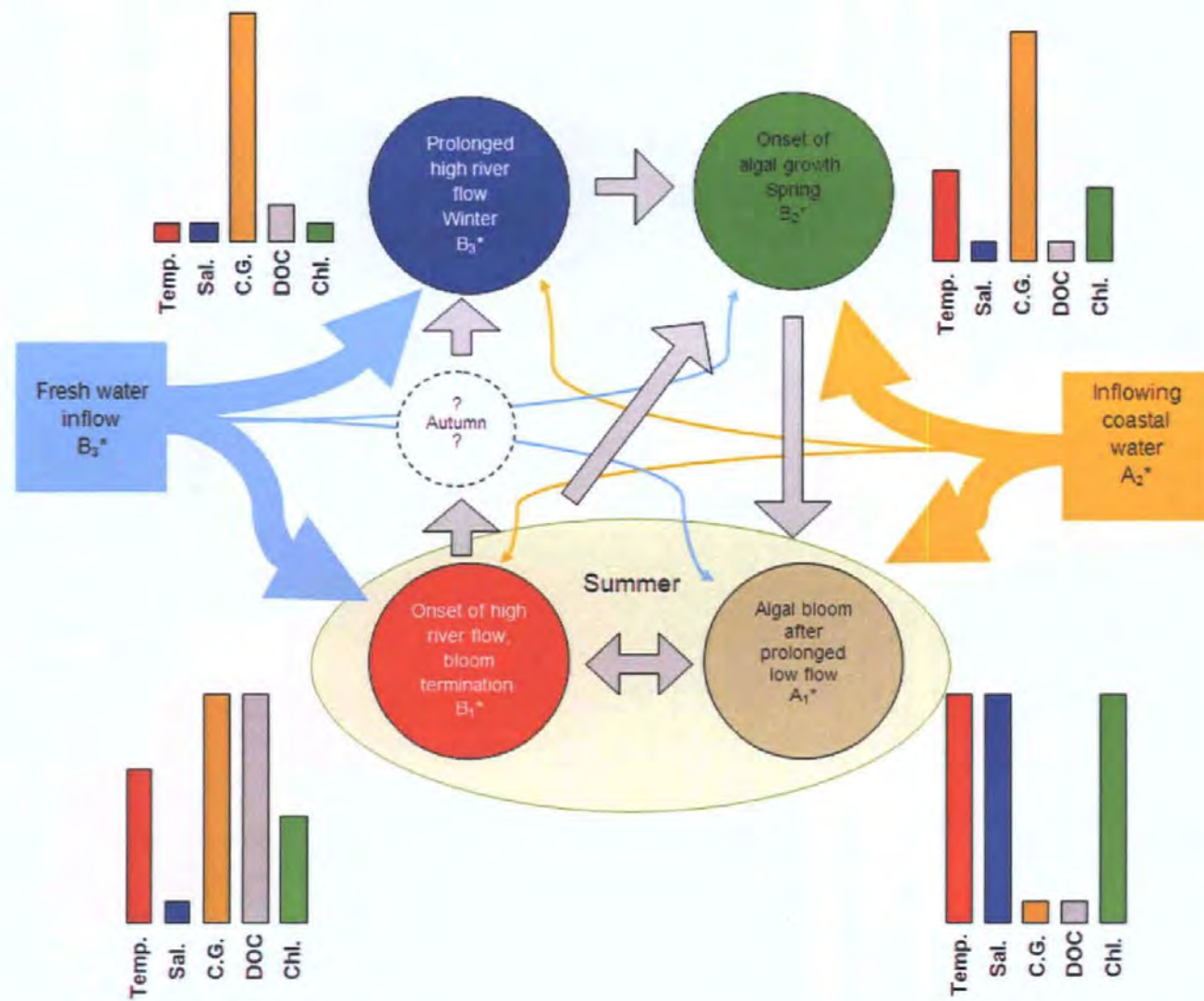


Figure 6.1. Conceptual model of eutrophication in the central and upper Taw Estuary. The graph shows the succession (grey arrows) and consecutive trophic states (coloured circles) during the development and decline of algal blooms. The bar charts show trends of variables at each trophic state. The bar height is proportional to the numerical value of the represented variable. Temp. = temperature. Sal. = salinity, C.G. = variables of the catchment group (i.e. NO₃, SiO₂, PO₄), DOC = dissolved organic carbon, Chl. = chlorophyll.

*) B₃, B₂, B₁ and A₁ refer to the clusters discussed in section 5.3, which were used to define the trophic states.

(Figure 6.2), but can also occur during the summer months, when winds with a westerly component bring extended periods of rainfall.

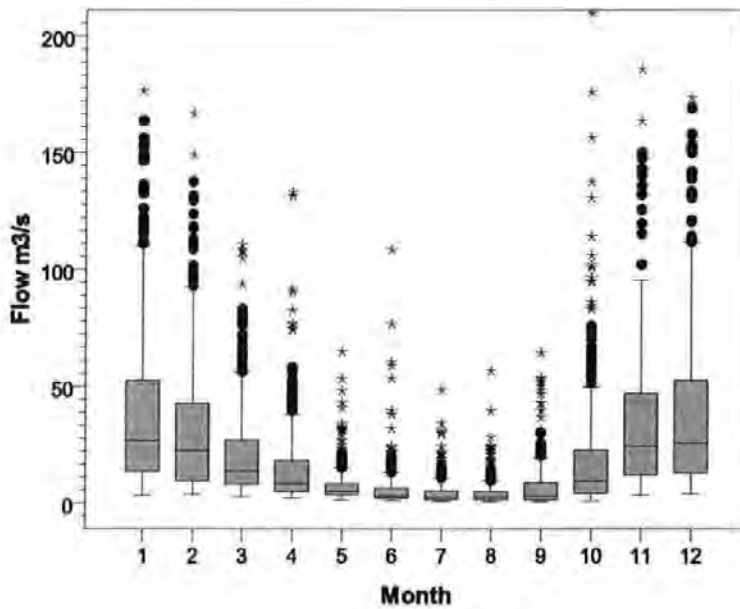


Figure 6.2. Box and whisker plot of the daily averaged freshwater discharge of the River Taw between Jan 1st, 1990 and Dec 31st, 2004. Data were obtained from the NRFA. For explanation of the plots see caption of Figure 3.2. $n = 457 \pm 15$ for each month.

During such periods, the freshwater plume in the Taw Estuary can extend beyond EA site 5 (Figure 3.2a). Water residence times in the estuary are short, temperature and salinity are low. Concentrations of catchment-borne nutrients (particularly NO_3 and SiO_2 , but also PO_4) are very high due to erosion processes in the catchment's soil and subsoil. However, because DOC concentrations are low to intermediate and chlorophyll *a* concentrations are very low ($<5 \mu\text{g L}^{-1}$), the system is oligotrophic and dominated by heterotrophic processes, although on a very low level. With the advancing spring and/or reduced flow levels to $\leq 5 \text{ m}^3 \text{ s}^{-1}$, the system moves to the next state (B_2 , green): Water exchange rates in the estuary decrease and water temperatures rise. The temperature rise is accelerated by the increased irradiance during dry and settled weather. Also, due to the reduced freshwater input, coastal water (A_2 , yellow) advances further upstream. This

marks the onset of algal growth: increasing salinity favours the establishment of estuarine phytoplankton species while nutrient availability is still very high. Low river flow leads to increased water residence times, phytoplankton cell loss rates from dilution decrease below reproduction rates while nutrient uptake by the cells continues, due to the high ambient nutrient concentrations, at very high rates⁸. DOC and NH₄ concentrations are low, but chlorophyll concentrations show a sharp increase. The system is then undergoing eutrophication and shifts from being dominated by heterotrophic processes towards becoming autotrophic. If the settled weather with low precipitation continues, the system will shift to the next state (A₁, brown), characterised by excessive algal growth and very high phytoplankton biomass. Following low freshwater discharge and low water exchange rates, water temperatures are high (~20 °C) and coastal water has advanced considerably upstream, causing relatively high salinities. Nutrient concentrations (NO₃, NH₄, SiO₂ and PO₄) are very low and signs of nutrient depletion occur (see 5.2.3). Because the phytoplankton blooms in the Taw consist mostly of diatoms (during the spring / summer 2008 campaign these were *Thalassiosira guillardii* and *Asterionellopsis glacialis*), the order of the limiting nutrient

⁸ This state is a transition between the previous oligotrophic conditions (B₃, blue) and the next state, which represents eutrophic conditions (A₁, brown). Such transitional conditions can prevail for extended periods of time in the upper estuary around Barnstaple, whilst the central estuary has already moved to the next, fully eutrophic state (compare with Figure 5.26, between July 15th and 29th). The speculated reason for this lies in the different channel width of the upper and the central estuary and different water volumes held by these sections. The central estuary is much wider (~500-800m) than the upper reaches at Barnstaple (<100 m). At freshwater flow rates of <5 m³ s⁻¹ for more than one week, water residence time in the central estuary is long enough for the phytoplankton to develop high biomass, exceeding 100 µg L⁻¹ of chlorophyll *a*. In the upper, more channelled reaches of the estuary, water exchange rates (at riverine freshwater input rates between 5 and 3 m³ s⁻¹) are still too high to develop excessive phytoplankton cell concentrations.

will change from P, Si, N to Si, P, N or even to Si, N, P downstream of a bloom or if eutrophic conditions prevail for longer. This is when the system is most vulnerable to HABs, particularly when such conditions prevail over tens of days. Blooms are typically terminated when river discharge increases to about $10\text{-}15\text{ m}^3\text{ s}^{-1}$ for several days, following the arrival of continued wet weather, and the system moves to the next state (B₁, red), characterised by decreasing temperature, salinity and chlorophyll concentrations. The characteristic features of this state are the very high DOC, NH₄ and PO₄ concentrations. The very high DOC concentrations are likely to originate from organic matter (*e.g.* plant debris, animal faeces), which has accumulated in the catchment during the dry period, but also from the overflowing STW, which is indicated by the high NH₄ concentrations. Depending on the duration and intensity of precipitation, the system will then shift to either B₃ (blue), B₂ (green) or A₁ (brown). During summer, when rainfall events are only of low to intermediate duration and intensity, the central Taw Estuary can oscillate between this high flow/high DOC state and the previous high chlorophyll state (Figure 5.28, Figure 5.29). In this case, it is possible that very high phytoplankton biomasses occur, because of the strong diatom seed population that is still present in the estuary in combination with a good supply of inorganic nutrients. In such a scenario, the role of the high NH₄ concentrations in relation to NO₃ uptake inhibition, as discussed in chapter 3, is not clear and would require further investigation.

6.2. Physical properties and climate change

Water residence time is an important regulator of planktonic primary production in estuaries (*e.g.* Nedwell *et al.* 1999; Scott *et al.* 1999) and this parameter has been suggested as a proxy to assess estuaries for their susceptibility to eutrophication (Painting *et al.* 2007). The observed close inverse coupling of primary production with

freshwater flushing is characteristic of small, temperate estuaries, and has been documented for other small systems such as the Urdaibai Estuary in Spain (Orive *et al.* 1997) and the Solent in the south of England (Iriarte and Purdie, 2004). Such estuaries contrast with large North American systems, such as the Neuse River Estuary, where rainfall in the catchment triggers algal growth in the estuary (Mallin *et al.*, 1993) or estuaries adjacent to upwelling regions, where shelf waters constitute the major source of nutrients (*e.g.* Ria de Ferrol, Spain; Bode *et al.*, 2005a,b).

Because primary production in the Taw is so dependent on river flow, climate change effects, such as changes in precipitation patterns and intensity, might considerably aggravate the trophic situation in the system. Arnell and Reynard (1996) modelled an average 25% reduction in summer flow of the Tamar (a catchment adjacent to the Taw) by 2050 with extremes >50% lower. Updated scenarios produced for the UK Climate Impacts Programme (UKCIP) predicted that by 2020 mean summer river flows will be about 30% lower than the 1961-1990 mean. For Q95 (the flow which is exceeded 95% of the time) the UKCIP02 scenarios predicted a reduction of 20-25% by 2020, 30-50% by 2050 and 50-80% by 2080 (Arnell, 2004). Under these scenarios it is predicted that (with the current availability of nutrients) eutrophication problems in the Taw will become much worse. Low freshwater inflow will result in extended flushing times and increased primary production in the estuary.

The present data for the Taw suggest that under river flow rates of around $5 \text{ m}^3 \text{ s}^{-1}$, spring tides are capable of flushing a large fraction of the phytoplankton out of the estuary and (to some extent) “reset” the system. However, it is not known if (spring) tidal flushing is sufficient to clear the system when freshwater flushing decreases because of the changing climate. Further, the role of future sea level rise in these scenarios and how it would affect tidal exchange in the Taw with the coastal sea is

poorly constrained and no estimates can be made. Therefore, and because there is evidence that in the Taw Estuary deleterious blooms have already occurred (Peter Jonas, EA, personal communication; Clark and Bateman, 1997), further research into the impacts of sea level rise and changing precipitation patterns on primary production and eutrophication patterns in the Taw estuary is imperative.

6.3. Nutrient ratios and potential limitation

Generally, well mixed, turbulent and nutrient rich environments like the Taw naturally favour diatoms over dinoflagellates (Smayda and Reynolds, 2001; Margalef, 1978). Qualitative assessments during summer 2008 of the Taw phytoplankton community showed that these blooms were formed by two diatom species, notably *Asterionellopsis glacialis* and *Thalassiosira guillardii*. In the Taw Estuary, during the spring / summer 2008 campaign, Si depletion (Figure 5.10) and subsequent limitation was observed in the central estuary and lasted for a minimum of 5 days. Because most of the Si was consumed at site C during the chlorophyll *a* peaks, site D near the mouth of the estuary received waters of low Si concentrations. As a consequence of this and because phytoplankton at site D consumed the remaining Si, Si limitation lasted for at least 13 days (Figure 5.6 and Figure 5.9). This depletion, together with increased light availability, poses a higher risk of the occurrence of spring *Phaeocystis* blooms (Peperzak *et al.*, 1998) or, together with high summer temperatures, potentially toxic dinoflagellate blooms. Further, in enclosure experiments using North Sea water, Egge and Aksnes (1992) showed that silicate concentrations of $<2 \mu\text{M}$ changed the phytoplankton community from diatom dominated to flagellate dominated and harmful algae of the genus *Phaeocystis* became dominant when Si concentrations fell below this threshold. With regard to climate change, high N:Si ratios may, in combination with reduced summer discharge, cause the adjacent coastal waters to experience longer

periods of Si depletion. This would channel the available N and P into non-siliceous phytoplankton and further fuel the development of harmful blooms

6.4. The trophic status of the Taw Estuary

It has been shown that during summer, the Taw Estuary can be eutrophic. However, depending on the applied assessment system, different conclusions can be reached about the severity of eutrophication and the required (if any) remediative action. Tett's (1987) chlorophyll *a* threshold of $100 \mu\text{g L}^{-1}$ for the definition of algal blooms was regularly exceeded in the analysed data. However, undesirable disturbances *sensu* Tett *et al.* (2007) were only documented episodically by the EA (*e.g.* Clark and Bateman, 1997), *e.g.* surface scum and odour release. However, there is no indication for the occurrence of more severe disturbances such as anoxic events or mass fish kills. Following the trophic levels compiled by Smith *et al.* (1999; Table 6.1) for lakes, streams and coastal waters, the Taw would be in the category "hypertrophic", although no specific estuarine classification was provided by the authors. By the chlorophyll *a* standards of OSPAR (2003a; $15 \mu\text{g L}^{-1}$), the Taw clearly falls in the category "Problem Area", although this threshold appears to be more suitable for application with coastal waters, rather than (naturally more productive) estuarine waters. For the Basque estuaries, Borja *et al.* (2004) suggested $10 \mu\text{g L}^{-1}$ of chlorophyll *a* as the threshold between "good" and "moderate ecological status" under the WFD, and $>30 \mu\text{g L}^{-1}$ to indicate "bad ecological status".

Under such a classification regime, the Taw would fall clearly into the "bad" category. However, this would imply large anoxic benthic zones, the absence of (most) multicellular life forms (*e.g.* Rosenberg *et al.*, 2004) and the presence of mats of sulphuric bacteria (*e.g.* *Beggiatoa*), all summarized as undesirable disturbance, of

Table 6.1. Average characteristics of lakes (Nürnberg, 1996), streams (Dodds, *et al.* 1998), and coastal marine waters (Håkanson, 1994) of different trophic states. Modified from Smith *et al.* (1999).

| | Trophic state | TN μM | TP μM | Chl <i>a</i> $\mu\text{g L}^{-1}$ |
|---------|----------------------|------------------------------------|------------------------------------|---|
| Lakes | Oligotrophic | <25 | <0.3 | <3.5 |
| | Mesotrophic | 25-46 | 0.3-1 | 3.5-9 |
| | Eutrophic | 46-86 | 1-3.2 | 9-25 |
| | Hypertrophic | >86 | >3.2 | >25 |
| Streams | Oligotrophic | <50 | <0.8 | <10 |
| | Mesotrophic | 50-107 | 0.8-2.4 | 10-30 |
| | Eutrophic | >107 | >2.4 | >30 |
| Marine | Oligotrophic | <19 | <0.3 | <1 |
| | Mesotrophic | 19-25 | 0.3-1 | 1-3 |
| | Eutrophic | 25-29 | 1-1.3 | 3-5 |
| | Hypertrophic | >29 | >1.3 | >5 |

Hypertrophic is the term used for systems receiving greatly excessive nutrient inputs. TN, total nitrogen; TP, total phosphorus.

which neither was documented in the Taw. Following the assessment systems of Devlin *et al.* (2007a, b), the Taw Estuary was preliminarily classified by the EA to be of “moderate ecological status” (EA, 2009), but final classifications will be published in the finalized River Basin Plans in December 2009. The assessment method of Devlin *et al.* (2007a) is based on three hierarchic indices (Figure 6.3), representing driver (nutrient enrichment), state (primary production) and impact (undesirable disturbance). Compliance with index 1 (nutrient enrichment) will lead to classification of the system as either “high” or “good ecological status”. Non-compliance with index 1 will lead to an assessment under index 2 (primary production). In case of compliance the estuary will be classed as “good”, otherwise an assessment of undesirable disturbances, using index 3 will follow. If there are no symptoms of oxygen deficiency, the system will be classed as “moderate ecological status”.

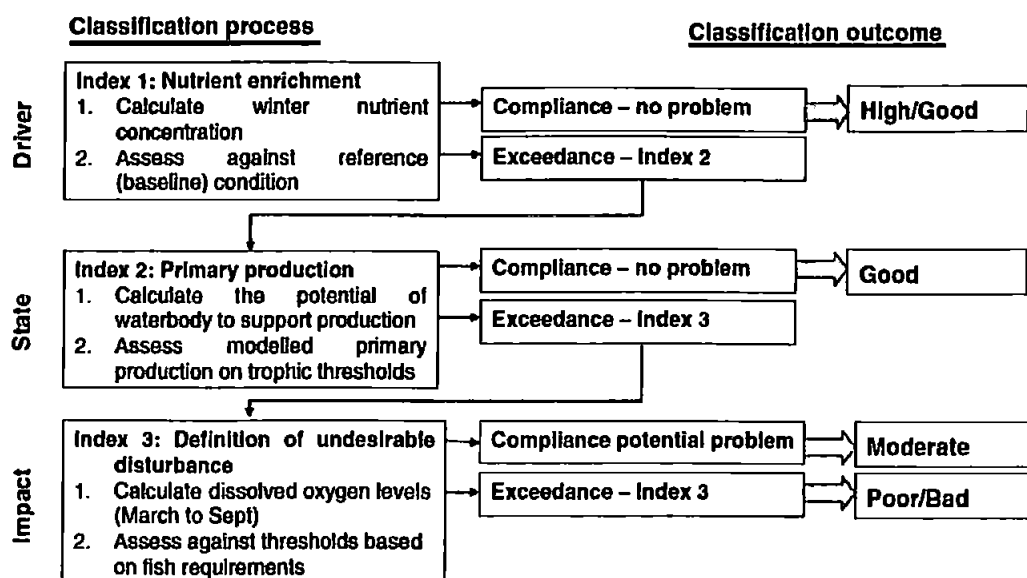


Figure 6.3. Representation of classification process, linking WFD classification boundaries with OSPAR assessment categories. Wide arrows represent a final outcome, with thin arrows moving classification into next index (from Devlin *et al.*, 2007a).

The data analysed for this work in chapters 3 and 5 support the EA classification, particularly with regard to (potential) oxygen deficiency. The EA classification also reflects the spirit of the WFD for phytoplankton as a biological element in the definition of moderate status for transitional water, where it is stated that “*Biomass is moderately disturbed and may be such as to produce a significant undesirable disturbance in the condition of other biological quality elements. A moderate increase in the frequency and intensity of planktonic blooms may occur. Persistent blooms may occur during summer months.*”.

This classification as “moderate” under the WFD, where all surface waters should achieve at least “good” status, is a call for action. Such action has (in part) already been taken by designating the Taw under the ND and the UWWTD. However, although the implementation of actions under the UWWTD have already shown reductions in P loads to the system (Figure 3.4), and ADAS models postulated that the implementation

of NVZ action programme measures in the catchment will lead to a reduction of N inputs into the estuary of *ca.* 10% between September and May and a reduction from June to August of *ca.* 2% (Lord *et al.*, 2007), these actions are unlikely to be sufficient to generate the desired success. Further measures for the reduction of nutrient inputs into the Taw should be evaluated, including an upgrade of Ashford STW for enhanced biological phosphorus removal and/or precipitation treatment, introduction of vegetated buffer strips along waterways in the catchment, and taking some areas out of agricultural production altogether, with afforestation as an alternative option.

This work has shown that the drivers of eutrophic symptoms are complex and very specific to an individual estuary. As a result it is suggested that eutrophic transitional waters (because of their highly individual and dynamic nature) should undergo an individual initial assessment with a specifically targeted research strategy to identify the drivers for algal growth, before any (potentially expensive) remediative actions are set. A good understanding of system specific drivers for excessive algal growth is imperative to set appropriate and (cost) effective management measures. The prescribed monitoring frequencies under the WFD or the OSPAR comprehensive procedure are insufficiently sensitive to identify the causes of eutrophication in a given system although they may be used for monitoring progress once the management actions have been identified.

6.5. Critique and suggested future research

6.5.1. Physical forcing of algal growth

The data available from the EA and those collected during the spring / summer 2008 campaign did not allow the calculation of water exchange rates and residence times in the Taw Estuary at different freshwater inputs and tidal states. Therefore, literature data

had to be employed (Sturley, 1990), which were collected at times of high riverine discharge and did not represent conditions favourable for algal growth.

In order to calculate flushing times following the methods outlined in Dyer (1997), a (temporally and spatially) tight grid of salinity measurements at different river discharge levels would be required. Together with a bathymetric model of the Taw Estuary, the data could be merged into a hydraulic model (and might be coupled with a hydrological model of the Taw catchment) which would form the basis for accurate predictions of algal growth in the Taw. This could also be used to estimate the effects of climate change on algal growth. Such a long term physical model could then be expanded to take into account the effects of sea level rise on water exchange between the Taw Estuary with Barnstaple / Bideford Bay.

6.5.2. Stepwise eliminating backward regression analysis

The linear multiple regression analysis performed in section 5.2.2.2 for a number of variables *versus* chlorophyll might not be an appropriate approach. The results from the predictive model in section 5.4 suggested that the relationships are not linear, especially between flow and chlorophyll *a*.

The results of the regression analyses and general considerations from the results in section 5.2.3 on nutrient ratios and nutrient depletion also suggested that nutrient concentrations were partly influenced by the algae (uptake, excretion) and were hence not independent variables. Therefore, a (curvilinear) regression model without the nutrient data, *e.g.* with only salinity, temperature, river flow, residence times. may be more suitable for describing and predicting phytoplankton dynamics in the Taw Estuary.

6.5.3. Chemical analyses

Dissolved organic nitrogen. For some samples with high nitrate concentrations mass balance issues were encountered for the determination of DON: after DIN was subtracted from TDN, the results were negative. To investigate the reasons for the underestimation of DON in some of the samples (section 4.8.3), the following approaches are suggested:

1. It is possible that volatile nitrogenous compounds evaporated during the sparging process. Therefore, it is recommended to compare sparged and unsparged standards and samples.
2. Cross validation with other methods for the determination of TDN/DON.
3. Compare sets of analytical standards with different nitrogenous analytes, *e.g.* glycine only, urea only, glycine and urea, a combination of ammonium, nitrate and glycine, a combination of ammonium, nitrate and urea, and other amino acids.

6.5.4. Dissolved oxygen monitoring.

During the chlorophyll *a* peaks in August 2008, daytime dissolved oxygen concentrations were 13.7 mg L⁻¹ (170% saturation). It would be important to monitor the diurnal DO fluctuations and night-time concentrations under such conditions, particularly when neap tides, low river flow and calm conditions lead to temporary stratification. For this, a number of automated probes could be deployed at critical sites in the estuary to log DO concentrations at half hourly intervals over several months during spring / summer. Although a macro tidal system like the Taw is unlikely to experience anoxia, it is possible that oxygen concentrations at night decrease sufficiently to harm sensitive fish like juvenile Atlantic salmon.

6.5.5. Biology / ecology

Phytoplankton community structure. A detailed survey of the phytoplankton community structure at different times of the year would help to assess the risks for harmful blooms, not only in the estuary, but particularly in the adjacent coastal waters. It would be important to attempt relating the observed switches from P to Si limitation to changes in phytoplankton community composition.

Incubation experiments with natural Taw phytoplankton. A series of batch culture / nutrient addition experiments with natural phytoplankton communities from the Taw would be useful in order to quantify the role of ammonium inhibition influence on bloom dynamics and also to estimate how changes in the relative and absolute availability of N, P and Si influence phytoplankton community structure and total biomass.

By using chemostat cultures instead of batch cultures, changes in water residence time can be simulated and its effects on (harmful) bloom formation could be assessed.

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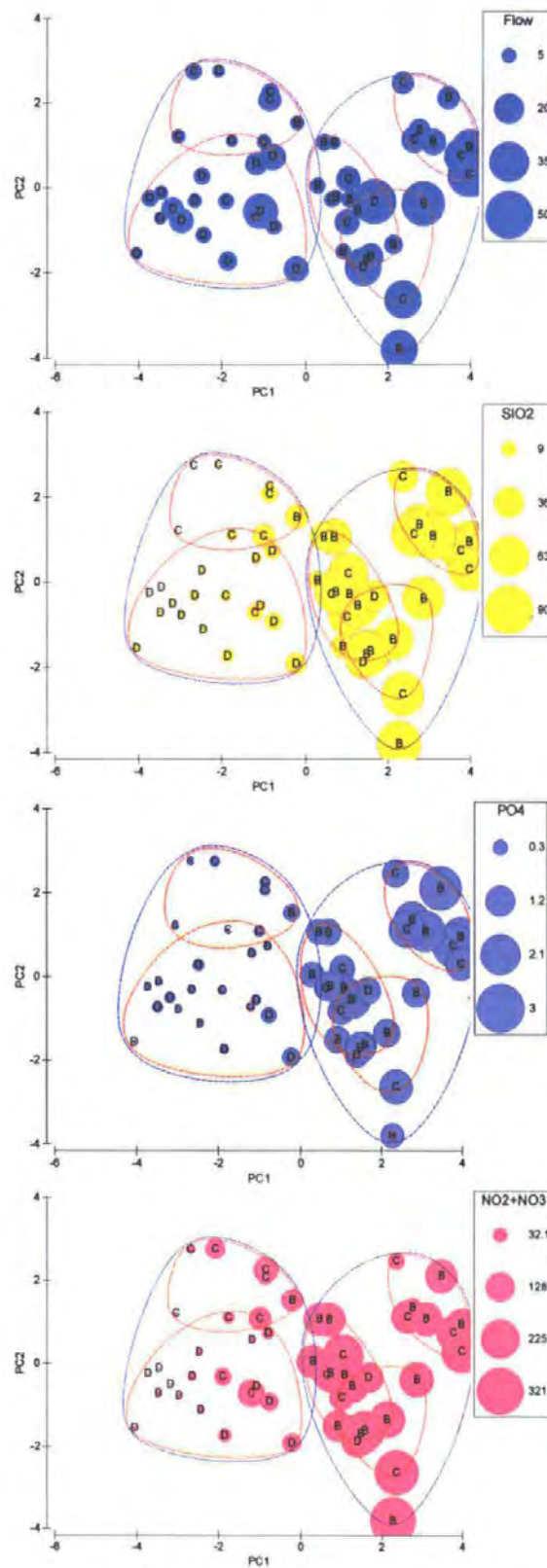
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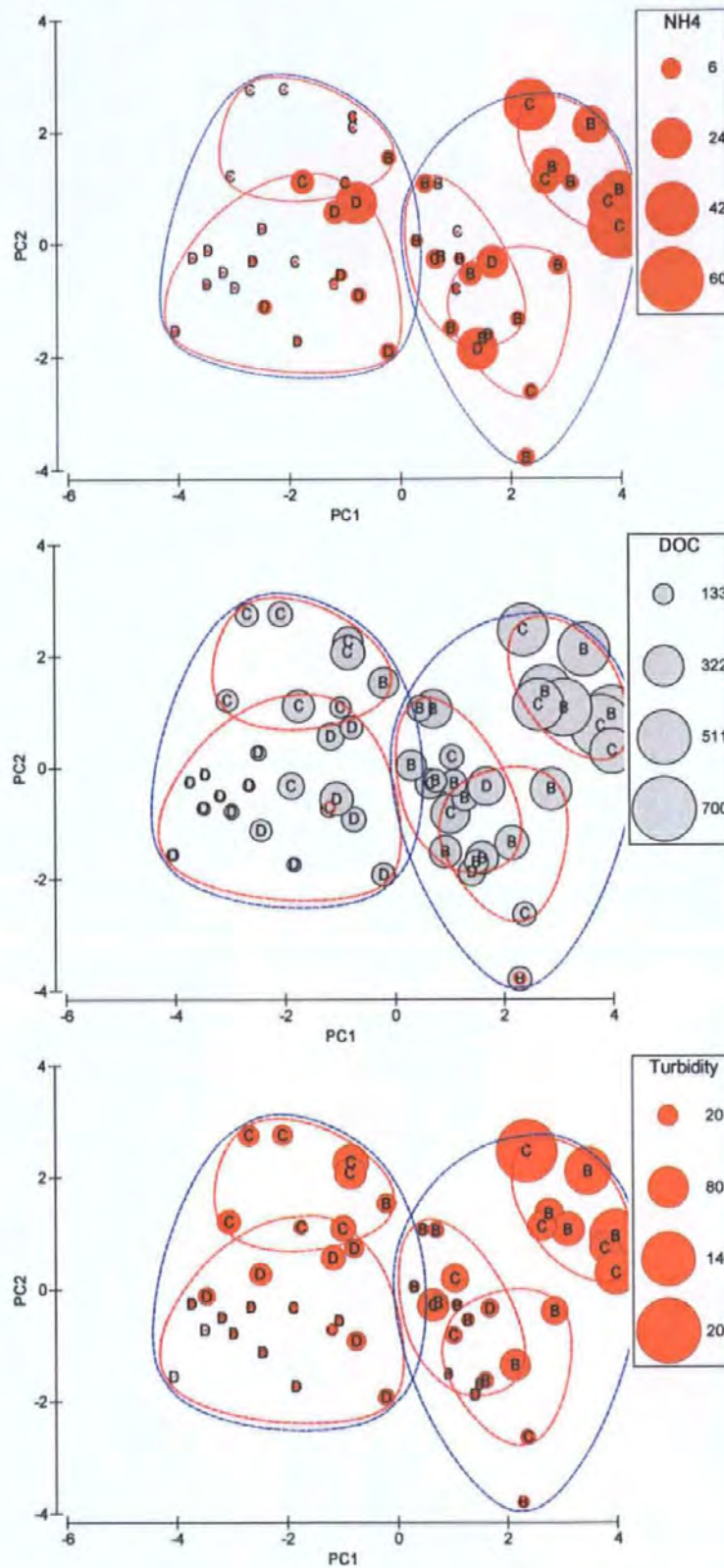
APPENDICES

APPENDICES

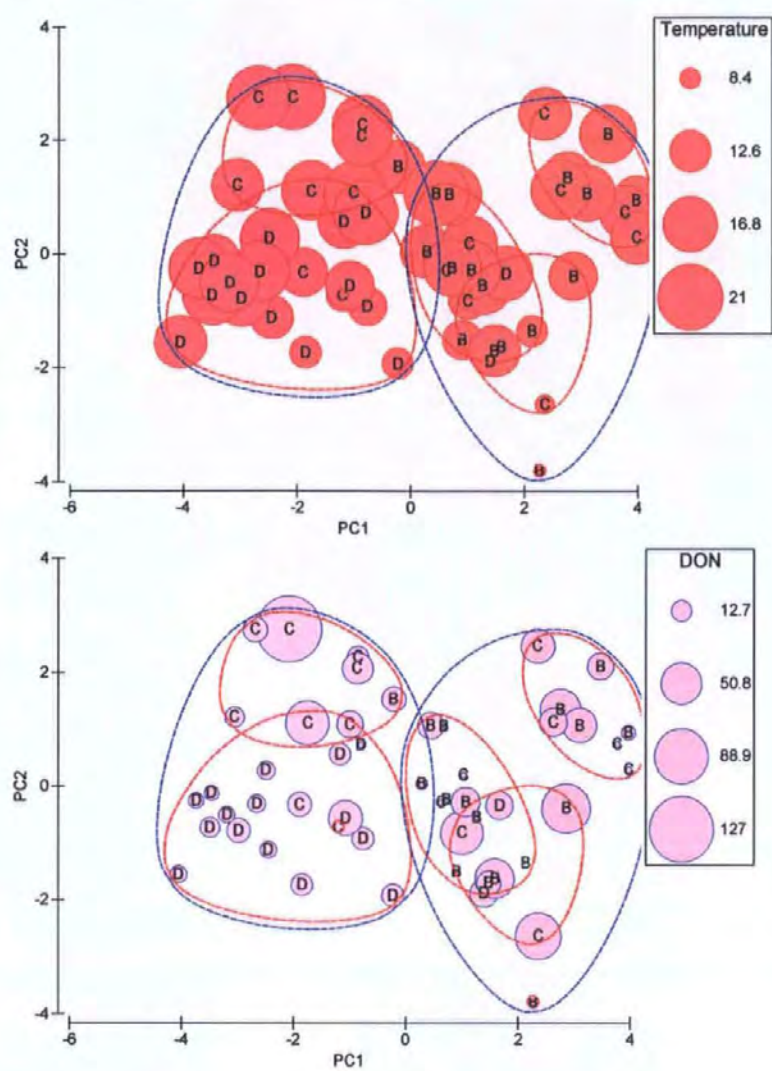
Appendix A: Variable plots for the PCA of the entire estuary



March–August 2008 campaign, entire estuary: Bubble plot and clusters representing variables of the ‘catchment group’. Flow is given in $\text{m}^3 \text{s}^{-1}$, concentrations are in μM .

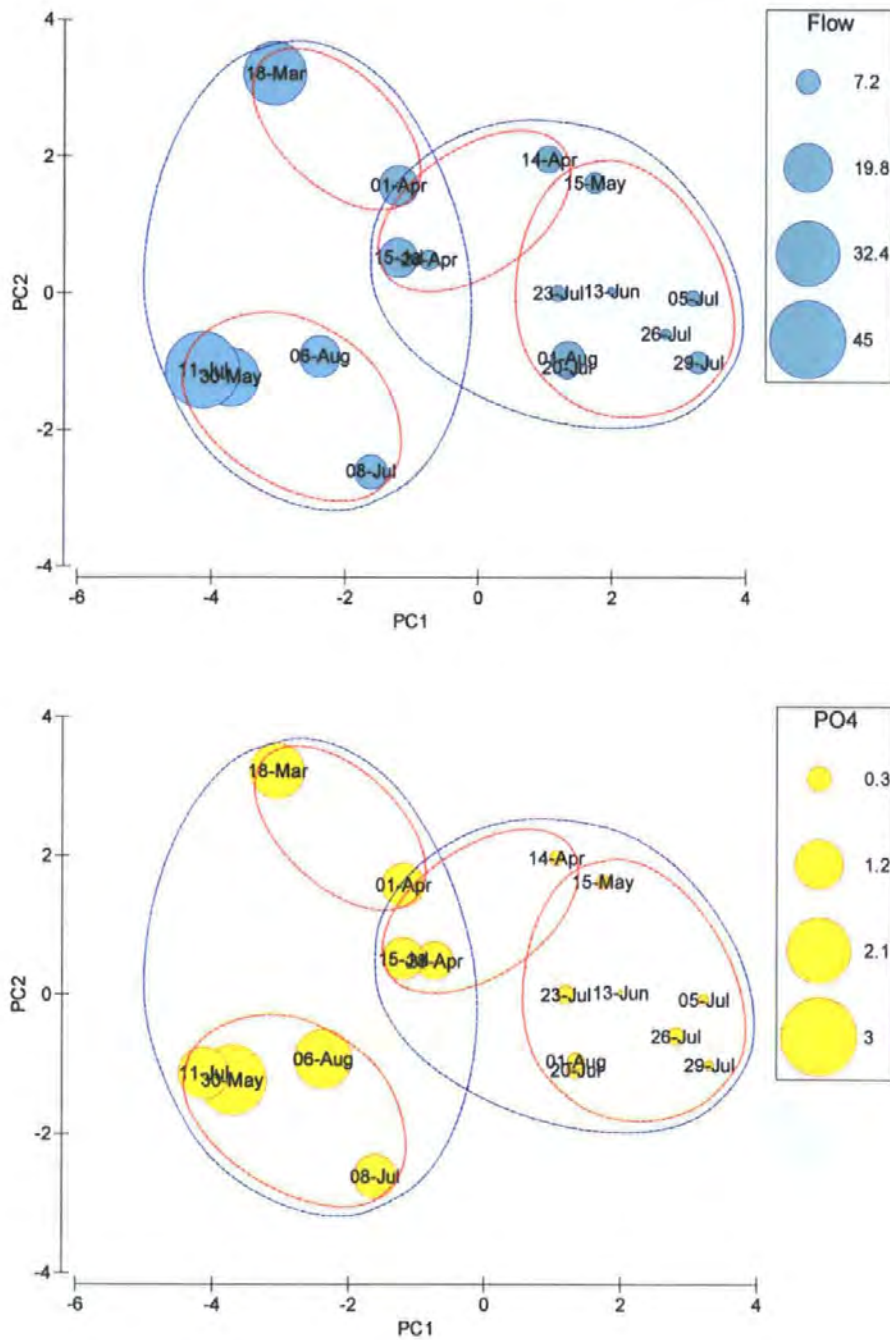


March–August 2008 campaign, entire estuary: Bubble plot and clusters representing variables of the ‘STW group’. Flow is given in $\text{m}^3 \text{s}^{-1}$, Ammonium and DOC concentrations are in μM , turbidity is given in NTU.

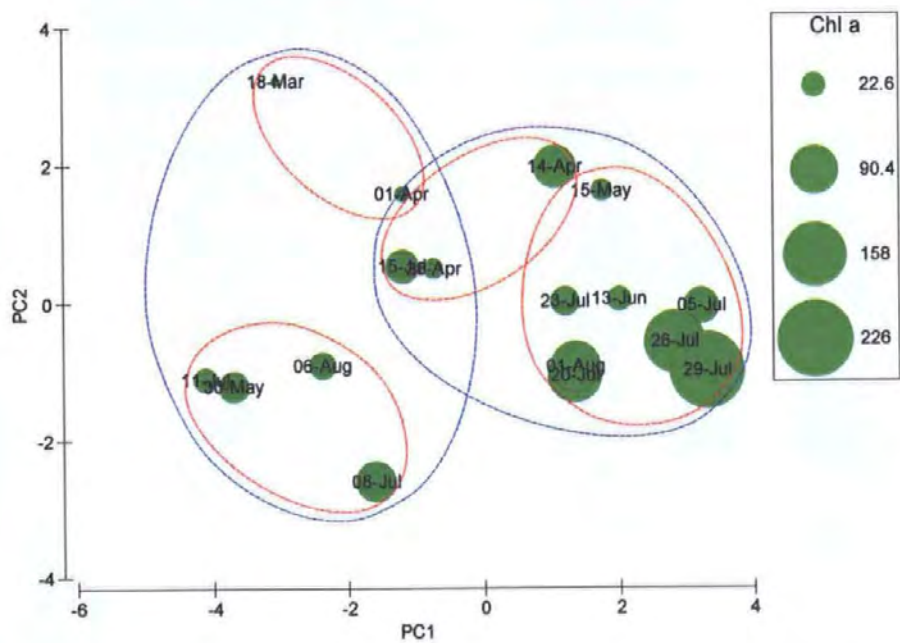
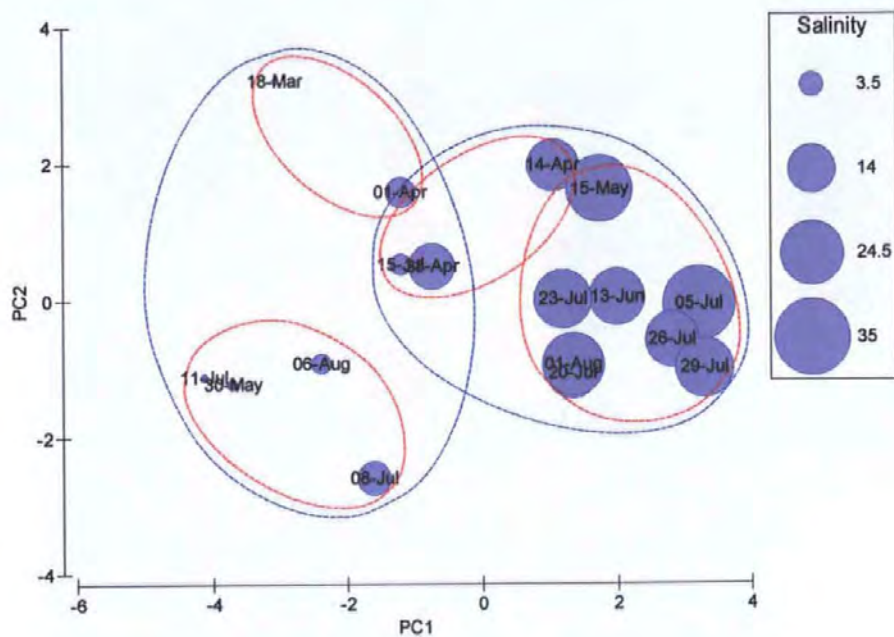


March–August 2008 campaign, entire estuary: Bubble plot and clusters for water temperature ($^{\circ}\text{C}$) and DON (μM).

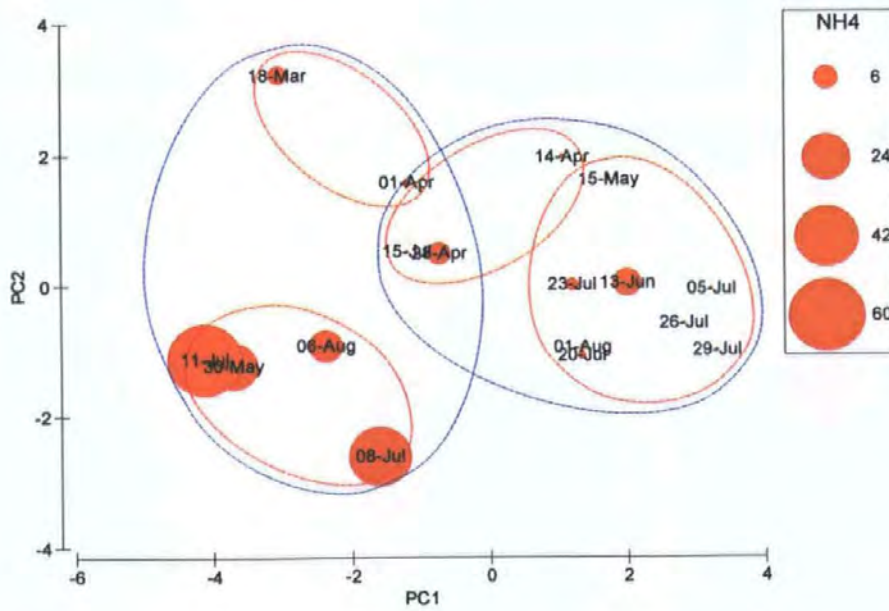
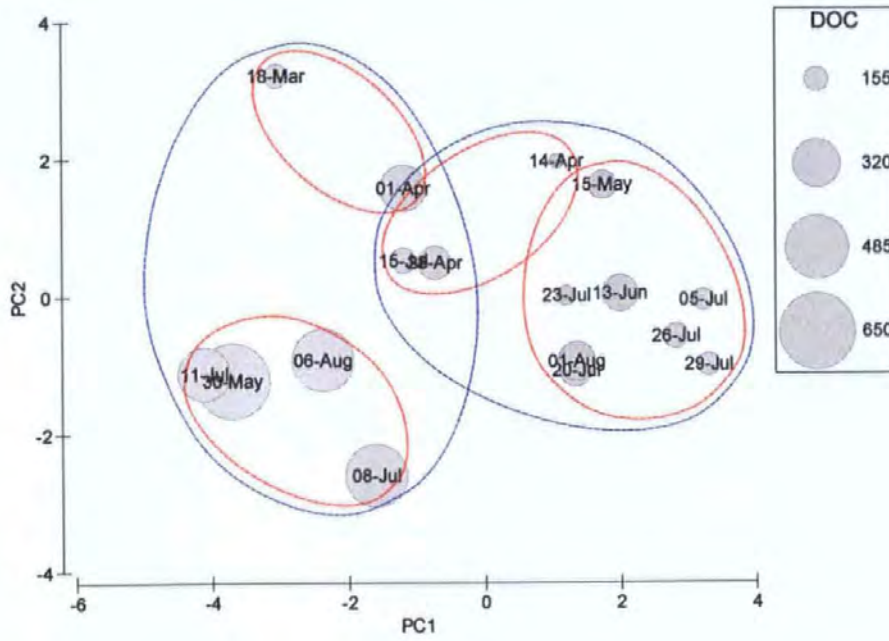
Appendix B: Additional results for the PCA of site C



March – August 2008 campaign, site C: Bubble plot and clusters representing two variables of the ‘catchment group’:(top) river flow ($\text{m}^3 \text{s}^{-1}$) and (bottom) phosphate (μM).



March – August 2008 campaign, site C: Bubble plot of (top) salinity (psu) and (bottom) chlorophyll *a* ($\mu\text{g L}^{-1}$), two representatives of the ‘chlorophyll group’.



March – August 2008 campaign, site C: Bubble plot of (top) DOC (μM) and (bottom) ammonium concentrations (μM), both from the 'STW group' of variables.

PUBLICATIONS

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**ESTUARINE EUTROPHICATION IN THE UK:
CURRENT INCIDENCE AND FUTURE TRENDS**

Estuarine eutrophication in the UK: current incidence and future trends

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ABSTRACT

1. Increased inputs of nutrients to estuaries can lead to undesirable effects associated with eutrophication, including algal blooms, changes in species composition and bottom anoxia. Several estuaries and coastal areas around the UK have increased nitrogen (N) and phosphorus (P) concentrations, elevated concentrations of chlorophyll *a* and changes in algal community composition and abundance. This paper reviews the pressures that lead to high nutrient concentrations in estuaries and considers the likely effectiveness of current and proposed regulatory actions.

2. The main sources of nutrients to estuaries are river runoff, sewage discharges, atmospheric inputs and possibly submarine groundwater discharges, although little is known about the latter. Significant reductions in N and P inputs have been realized following application of the EU's Urban Waste Water Treatment Directive. Atmospheric NO_x and NH_x emissions have also decreased and are expected to decrease further in the next decade as implementation of existing legislation continues, and new controls are introduced for activities such as shipping.

3. Agricultural inputs reach estuaries principally through diffuse sources, either in surface water (and in some areas possibly groundwater) or, for N, via the atmosphere. Over 10 years ago the Nitrates Directive was introduced to tackle the problem of N discharges from agriculture but little change in N loads to estuaries has been recorded.

4. To meet the aims of the EU Water Framework Directive, for at least 'good' ecological status, more rigorous application and implementation of the Nitrates Directive, together with changes in the Common Agriculture Policy and farming practice are likely to be needed. Even then, the slow response of the natural environment to change and the inherent variability of estuaries means that their responses may not be as predicted. Research is needed into the relationship between policy drivers and environmental responses to ensure actions taken will achieve the planned results.

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INTRODUCTION

Eutrophication has been defined by OSPAR (2003) as 'the enrichment of water by nutrients causing an accelerated growth of algae and higher forms of plant life to produce an undesirable disturbance to the balance of organisms and to the water quality concerned...'. Tett *et al.* (2007) define an undesirable disturbance as 'a perturbation of a marine ecosystem that appreciably degrades the health or threatens the sustainable human use of that ecosystem', noting that the

source of the problems arising from eutrophication is the uncoupling of production and use of organic matter in aquatic systems. This definition, like that of de Jonge and Elliott (2001), encompasses not simply the presence of excess nutrients but also adverse effects on the ecosystem such as enhanced algae growth, changing species composition, abundance and mass. This facilitates discrimination between eutrophication and hypereutrophication in which excess nutrient inputs may not cause observable detrimental impacts within the estuary. This may often be the case in estuaries where, for

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example, high turbidity or rapid flushing times might limit primary production. However, estuarine environments are naturally stressed systems with an ecological assemblage reflecting the high degree of variability in physico-chemical characteristics, such as salinity, temperature and oxygen, as well as high organic productivity and inputs (Elliott and Quintino, 2007). This makes detecting the presence and extent of eutrophication resulting from anthropogenic stressors in estuarine systems an important and challenging area of scientific debate (Dauvin, 2007; Tett *et al.*, 2007).

Eutrophication has been described as one of the greatest contemporary threats to the integrity of coastal ecosystems (Vitousek *et al.*, 1997; Vidal *et al.*, 1999) and it is widely accepted that the increased availability of nutrients (generally N and P) is a major factor that drives eutrophication in estuaries (Nixon, 1995; Nedwell *et al.*, 1999; Scott *et al.*, 1999; de Jonge and Elliott, 2001). Estuaries are among the marine systems most at risk, as they only have limited interaction with adjoining pelagic waters (Vollenweider, 1992). Rising global population and its associated activity has caused a substantial increase in fluxes of N and P to estuarine and coastal waters. Although N and P fluxes may decrease in industrialized countries, resulting from the implementation of new environmental legislation, this can be very slow and predictions for less industrialized countries are the reverse (Nixon 1995; Carstensen *et al.*, 2006; Gray *et al.*, 2006).

In the European Union (EU), eutrophication has been identified as a priority issue for fresh water protection for some years but only recently has concern grown about transitional, coastal and marine waters (CIS, 2005). Two key policy instruments were introduced in the early 1990s to address the most significant pressures leading to eutrophication: the Nitrates Directive (ND, 91/676/EEC), which considers the agricultural contribution and the Urban Waste Water Treatment Directive (UWWTD, 91/271/EEC), which focuses on urban sewage discharges. The importance of atmospheric deposition has also been recognized and addressed most recently through the Thematic Strategy on Air Pollution which notes the importance of agricultural sources of atmospheric nitrogen as well as combustion sources (principally energy and transport) to the eutrophication of surface waters (CEC, 2005). Now the Water Framework Directive (WFD, 2000/60/EC) has been introduced with new definitions of good ecological status and new goals for 2015. A Common Implementation Strategy for the EU is being developed for the WFD (CIS, 2005), and it seems an appropriate time to assess the current status of eutrophication in the UK, 20 years after the problem was first addressed, and to consider what progress has been made. The aims of this paper are to summarize the occurrence of undesirable disturbance within UK estuaries and coastal waters, to identify the main drivers and pressures contributing to these occurrences, and to examine how the incidence of eutrophication may change in response to the application of the legislative framework outlined above.

NUTRIENT ENRICHMENT AND THE OCCURRENCE OF EUTROPHIC CONDITIONS IN UK WATERS

The UK was required by both the EU and OSPAR to review its approach to eutrophication and its monitoring in the late

1990s/early 2000s, and this process has provided the rich source of data concerning the status of UK waters that has been distilled in this discussion. The occurrence of eutrophic waters within the OSPAR maritime area was reported in 2003, and was based on the first application of the Comprehensive Procedure (OSPAR, 2003). The UK focused on offshore areas as part of this Procedure (all of which were classified as non-problem areas), but also included assessments of 16 estuaries and near-shore waters made under the UWWTD and the ND (Figure 1). Twelve sites were classified as problem areas and four as potential problem areas (Table 1). The OSPAR Comprehensive Procedure generally covered the years 1990 to 2001 and results for the UK can be summarized as (OSPAR, 2003):

- (i) Several estuarine and coastal areas showed increased riverine N and P inputs.
- (ii) Several estuarine and coastal areas showed elevated concentrations of dissolved inorganic nitrogen (DIN, i.e. $\text{NO}_3 + \text{NO}_2 + \text{NH}_4$) and dissolved inorganic phosphorus (DIP i.e. PO_4) in winter. Elevated concentrations (defined as >50% above salinity related and/or region specific background concentrations) of winter DIN are $> 10 \mu\text{mol N L}^{-1}$ and winter DIP are $> 0.8 \mu\text{mol P L}^{-1}$ for the UK.
- (iii) Many areas experienced elevated winter DIN:DIP ratios.
- (iv) Several areas showed elevated levels of chlorophyll *a*. Concentrations of chlorophyll *a* considered elevated (>50% above salinity related and/or region specific background concentrations) are $> 10 \mu\text{g L}^{-1}$ for UK offshore waters (>34 salinity) and $> 15 \mu\text{g L}^{-1}$ for UK coastal waters (<34 salinity). Region specific levels were used to assess elevated levels of chlorophyll *a*, but it was not specified whether reference values were defined for means or maxima. The UK did not derive its chlorophyll *a* definitions from background concentrations but from chlorophyll *a* concentrations expected based on nutrient concentrations found in adjacent Atlantic waters.
- (v) Available data on phytoplankton communities were examined in relation to perturbations of the balance of organisms resulting from nutrient enrichment. All areas were classified as non-problem areas i.e. no evidence of impacts on the balance of organisms, despite the occurrence of elevated nutrient concentrations and/or DIN:DIP ratios. In the offshore southern North Sea, Continuous Plankton Recorder (CPR) data provided evidence of a changing diatom to flagellate index, but this was explained by climate variability (Edwards *et al.*, 2001).
- (vi) Some areas showed shifts in macrophyte (including macroalgae) species and abundance, from long-lived species like eelgrass to nuisance short-lived species like *Ulva*.
- (vii) Dissolved oxygen concentrations were generally good, although a degree of oxygen deficiency occurred in one local case.

Considering the nutrient loading to coastal waters, the UK's National Marine Monitoring Programme (NMMP) identified that, from 1985–2001, annual inputs of DIP (river and direct discharges) to UK coastal waters fell by 40–50%, but there was no reduction in DIN inputs (MEMG, 2004). In



Figure 1. Locations of coastal and estuarine waters assessed for their eutrophic status as part of national and international monitoring programmes. UK regional seas: I—Northern North Sea, II—Southern North Sea, III—Eastern English Channel, IV—Western English Channel, Celtic Seas and South-West Approaches, V—Irish Sea and North Channel, VI—West Scotland including the Minch, VII—Scottish Continental Shelf, VIII—Atlantic North-West Approaches, Rockall Trough and Faroe/Shetland Channel. Estuarine waters: 1, Ythan Estuary; 2, Montrose Bay; 3, Tay Estuary; 4, Eden Estuary; 5, Forth Estuary; 6, Lindsfarne; 7, Tyne Estuary; 8, Seals Sands (Tees Estuary); 9, Humber Estuary; 10, Wash; 11, Deben Estuary; 12, Orwell Estuary; 13, Stour Estuary; 14, Colne Estuary; 15, Crouch Estuary; 16, Blackwater Estuary; 17, Pagham Harbour; 18, Selsey Bill; 19, Chichester Harbour; 20, Langstone Harbour; 21, Portsmouth Harbour; 22, Southampton Water; 23, Holes Bay; 24, Poole Harbour; 25, Fleet Lagoon; 26, Exe Estuary; 27, Erme Estuary; 28, Tamer Estuary; 29, Fal complex; 30, Taw Estuary; 31, Tawe Estuary; 32, Loughor Estuary; 33, Cardigan Bay (R. Teifi); 34, Mersey Estuary/Liverpool Bay; 35, Solway Estuary; 36, Clyde Estuary; 37, Belfast Lough; 38, Strangford Lough. From Nedwell *et al.* (2002), OSPAR (2003), DEFRA (2004).

relation to direct discharges, from 1990–2001, annual inputs of DIN and DIP have declined by 30–40%, reflecting the effectiveness of measures taken to control point source discharges direct to marine waters. It was added that the recent extension of Nitrate Vulnerable Zones (NVZ) and DIP stripping at inland sewage treatment works (STW) is expected to decrease diffuse inputs of N and direct inputs of DIP to rivers (MEMG, 2004). Monitoring the nutrient status of UK coastal waters is restricted to winter months, aiming to estimate maximum DIN and DIP concentrations, and hence indicate the concentration of nutrients available to support spring algal growth (MEMG, 2004). However, concentrations

continue to rise during late winter and early spring until conditions are suitable for algal growth, and also vary considerably on a short-term basis. Annual winter nutrient samples for 37 sites around the UK, from 1999–2001, revealed the following (MEMG, 2004):

- (i) Median total oxidized nitrogen (TO_xN , i.e. $\text{NO}_3 + \text{NO}_2$) exceeded OSPAR assessment criteria in the inshore waters of the Wash, Clyde, Belfast Lough, Liverpool Bay, Cardigan Bay, Southampton Water and Thames (Figure 1).
- (ii) Median DIP concentrations exceeded OSPAR assessment criteria in the inshore waters of the Thames, Clyde, Belfast Lough, Liverpool Bay, Cardigan Bay, Forth and Humber.
- (iii) It is assumed that N is the limiting nutrient in coastal waters, but it was in excess when compared with DIP at 17 of the 37 sites sampled, and at almost all the sites when compared with Si. The Wash and Selsey Bill exhibited the greatest excess of N.
- (iv) The DIN:DIP ratio was greater than 25:1 in the Wash, Selsey Bill, Cardigan Bay, Celtic Deep and close to the Thames at South Varne. The NMMP did not collect data on the biological effects of nutrient inputs, but the report advised that future monitoring should include routine measurements of chlorophyll *a* and assessment of phytoplankton species composition.

DEFRA, reviewing the state of the UK's seas in 2005, identified the following for estuarine and coastal waters (DEFRA, 2005):

- (i) Since 1990 there has been a 35–50% reduction in direct inputs of N and P (similar to the 30–40% reduction stated in MEMG (2004)), although riverine inputs, which are in part dependent on river flows, have not shown any significant change.
- (ii) UK marine waters with significant freshwater influence, which are confined to estuaries and coastal waters close to large rivers, tend to have elevated levels of nutrients but are often turbid, and so less susceptible to the risk of excessive growth of phytoplankton. This demonstrates the difference between hypernutrified and eutrophic waters since a secondary factor, turbidity, may limit primary productivity in these waters. DEFRA consider that waters beyond these areas are dominated by the movement of Atlantic waters and generally unaffected by direct anthropogenic nutrient inputs.
- (iii) The threat posed by anthropogenic nutrient inputs to the ecological status of marine waters varies by region in the UK. The highest concentrations of nutrients occur in coastal areas off the south-east coast of England in Region II (Figure 1) but the indicative effects are generally below the OSPAR assessment criteria (OSPAR, 2005b). It is probable that tidal mixing, shallow water depth and turbidity prevent undesirable disturbance in this region. Riverine inputs from Region II account for about 40% of total UK nutrient inputs. These are affected significantly by flow variability and only marginal reductions in N inputs have been achieved in this area. In contrast on the north-eastern coast of the UK (Region I) inputs of N have been reduced by 60% while in the north-west of Scotland (Regions VI, VII and VIII) no problems were evident and

Table 1. Classification of UK estuarine and coastal waters and estuaries under the OSPAR Comprehensive Procedure, the Nitrates Directive (ND) and the Urban Waste Water Treatment Directive (UWWTD)

| No. | Water body | OSPAR | ND | UWWTD |
|-----|--|------------------------|---|----------------------------|
| 19 | Chichester Harbour (England) | Problem area | | Sensitive Area (Eutrophic) |
| 24 | Holes Bay—a small part of Poole Harbour embayment (England) | Problem area | Part of the Poole Harbour Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 37 | Inner Belfast Lough and Tidal Lagan Impoundment (Northern Ireland) | Problem area | NVZ | Sensitive Area (Eutrophic) |
| 20 | Langstone Harbour (England) | Problem area | | Sensitive Area (Eutrophic) |
| 6 | Lindisfarne NNR Area (England) | Problem area | Eutrophic Water NVZ | |
| 32 | Loughor Estuary (Wales) | Potential problem area | | Sensitive Area (Eutrophic) |
| 17 | Pagham Harbour (England) | Problem area | | Sensitive Area (Eutrophic) |
| 24 | Poole Harbour (England) | Potential problem area | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 21 | Portsmouth Harbour (England) | Potential problem area | | Sensitive Area (Eutrophic) |
| 38 | Quoile Pondage—in Strangford Lough (Northern Ireland) | Problem area | NVZ | Sensitive Area (Eutrophic) |
| 8 | Seal Sands, Tees Estuary (England) | Problem area | | Sensitive Area (Eutrophic) |
| 30 | Taw Estuary (England) | Problem area | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 31 | Tawe Estuary Impoundment (Wales) | Problem area | | Sensitive Area (Eutrophic) |
| 25 | The Fleet (England) | Potential problem area | Eutrophic Water NVZ | |
| 29 | Truro, Tresillian and Fal Estuaries (England) | Problem area | Eutrophic Water NVZ | Sensitive Area (Eutrophic) |
| 1 | Ythan Estuary (Scotland) | Problem area | NVZ | Sensitive Area (Eutrophic) |

Numbers indicate position of sites as shown on map in Figure 1. From OSPAR (2003).

nutrient concentrations were low in the south-west (Region IV). The Irish Sea (Region V) and the Channel (Region III) both have enhanced nutrient inputs influenced by human activities. In terms of effects, the highest concentrations of chlorophyll occur in Region V (the north-eastern Irish Sea) where concentrations occasionally exceed the OSPAR assessment criteria. DEFRA noted that records from the CPR suggest that UK offshore waters are not generally affected by nutrient inputs from land based sources and effects are limited to localized inshore areas such as the Ythan Estuary, Chichester, Langstone and Portsmouth Harbours and inner Belfast Lough.

In view of the WFD it will be necessary to standardize the definitions used to describe the boundaries between good and moderate ecological status to give clarity and ensure agreement throughout appropriate ecoregions in the EU. Multimetric indices are being developed for eutrophication that incorporate the causes and effects within estuaries and coastal waters. For example, Devlin *et al.* (2007) propose incorporation of indices of pressure (nutrient concentrations), state (potential primary productivity) and impact (oxygen depletion) into a hierarchy such that high nutrient inputs alone, without evidence of excessive primary production, will define water as good rather than high quality, while if there is also elevated primary production the water body will be defined as moderate or poorer quality. This enables the susceptibility of waters to respond to high nutrient inputs, identified by Painting *et al.* (2007), and linked to light availability and water residence times, to be taken into consideration. Similar indices are being developed with respect to a range of parameters that may be affected by excessive nutrient inputs including benthos and attached macroalgae (Borja *et al.*, 2007; Wilkinson *et al.*, 2007).

PRESSURES LEADING TO NUTRIENT ENRICHMENT

Estuaries receive nutrient inputs from river and other runoff, from the atmosphere, from submarine groundwater discharges (SGD), waste discharges, mariculture and from adjacent coastal waters. Nutrient inputs to an estuary, either directly or via riverine inputs, can originate from either point (e.g. waste discharges) or diffuse sources (e.g. atmospheric, leaching from surrounding land). Point sources are localized and they are easier to monitor and control (Smith *et al.*, 1999), while diffuse sources are much more difficult to regulate (Scott *et al.*, 1999). The relative contribution of diffuse and point inputs to an estuary's nutrient load varies spatially, depending primarily upon local human population densities and land use. A significant correlation between urbanization and area-normalized nutrient load has been seen for P but no correlation was apparent for N (Nedwell *et al.*, 2002).

Riverine inputs and direct discharges to estuaries

DEFRA reported estimates of the riverine and direct inputs of DIN, NH_x (separately) and DIP to UK estuaries and coastal waters for the period 1990–2003 as part of the OSPAR Comprehensive Study on Riverine Inputs and Direct Discharges (DEFRA, 2005; OSPAR, 2005a). Littlewood *et al.* (1998) also calculated river loads of these nutrient fractions to UK estuaries for the longer period of 1975–1994 using the National River Flow Archive and the Harmonised Monitoring Scheme databases. These time series are shown in Figure 2. The river loads of DIN are in the region of 250 000 t yr⁻¹, with NO₃ the dominant measured fraction.

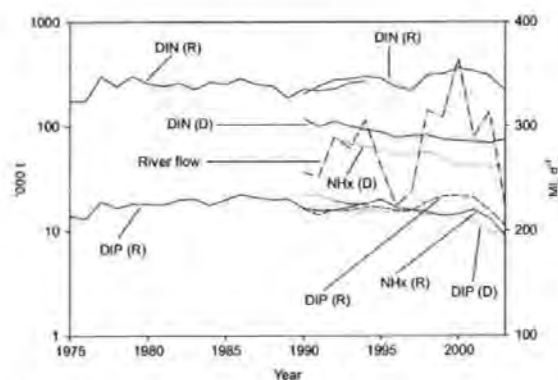


Figure 2. Annual estimates of river and direct discharges of DIN, DIP and ammonium (NH_x) and river flow (right hand axis) to UK coastal waters between 1975 and 2003. Data from 1975–1994 are from Littlewood *et al.* (1998); data from 1990–2003 are from DEFRA e-Digest Environmental Statistics, coastal and marine waters (accessed 25/5/06). R = river, D = direct.



Figure 3. Total N deposition to the UK for 1997, calculated as the average deposition accounting for different land cover types. Grey = 20–25 kg N ha⁻¹ yr⁻¹; black = > 25 kg N ha⁻¹ yr⁻¹. Redrawn from NEG-TAP (2001).

The largest inputs occurred in the high flow years, reflecting the importance of diffuse, agriculturally derived, sources of NO₃. Overall, however, there has been no underlying change in the magnitude of the loads (Littlewood *et al.*, 1998; DEFRA, 2005). In contrast, direct inputs of DIN decreased from 115 000 t in 1990 to 75 000 t in 2003, largely because of a reduction in NH₃ discharges from 78 000 t to 43 000 t over the same period. River inputs of DIP showed no clear trends, with loads of ca. 15 000–20 000 t yr⁻¹. Direct inputs of DIP have halved, however, from 22 000 t in 1990 to 10 000 t in 2003 (Figure 2), reflecting the change in sewage treatment works discharges to estuarine waters. On a regional basis increasing loads of river DIN and DIP have been identified (OSPAR, 2005a). Nedwell *et al.* (2002) conducted an assessment of river nutrient inputs on a catchment basis and calculated that the average catchment area normalized river DIN load to UK estuaries was 1570 kg N km⁻² yr⁻¹. This was of the same order of magnitude found for other European catchments draining into the North Sea. Normalized loads were highest in areas draining high nitrate soils, which were often within Nitrate Vulnerable Zones (NVZs) (i.e. the Severn, Mersey, Clyde, Humber, Thames and around the Solent). The majority of the UK's catchment-normalized N loads were in the 'moderately influenced by human activity' category of Hessen (1999). In contrast, the average catchment-normalized river DIP load of 152 kg P km⁻² yr⁻¹ was above the average load of 117 kg P km⁻² yr⁻¹ for catchments around the North Sea, and was highest for the Mersey and Thames catchments. Nedwell *et al.* (2002) also estimated estuary area-normalized loads based on the general assumption that a large estuary may be better buffered than a small estuary for a given nutrient loading. They found that there were large differences in the nutrient impact on UK estuaries, with two orders of magnitude variation in the estuary area-normalized loads for the nutrients. Particularly high estuary area-normalized loads of TO₄N and DIP were found from the Tweed to the Humber and around the Solent. In contrast, most of the Welsh and north Scottish estuaries had much lower loads.

Aeolian inputs

Aeolian N is deposited via dry fallout of aerosols or wet fallout of rain, mist and cloud. Deposition can be from natural and anthropogenic sources, and will include the oxidized species nitric oxide, nitrous oxide, nitrogen dioxide and nitrate, and the reduced species ammonia and ammonium. The two main sources are nitrogen oxides from fossil fuel combustion and ammonia/ammonium and nitrate from agriculture (particularly N fertilizers and intensive livestock farming). The most recent estimate, from 1997, of N deposition in the UK is 380 000 t yr⁻¹, of which 43% is oxidized N and 57% is reduced N (NEG-TAP, 2001). Areas of highest deposition include the uplands of northern England, Wales, regions of western Scotland, south-west England and East Anglia (Figure 3), and is linked to ammonia emissions from cattle, pig and poultry farming in these regions. The deposition patterns indicate that many catchments in the UK are receiving aeolian N inputs that are similar in size to the area-normalized river inputs of N to estuaries (1570 kg N km⁻² yr⁻¹). Resolving the proportion of the riverine N load which originates from aeolian input in any one estuary is difficult and it may vary

significantly geographically. A modelling study of N sources to river loads in the Great Ouse, Nene, Welland and Witham catchments in East Anglia reported by DEFRA (2004) estimated that aeolian inputs contributed 5% of the total N river load, while agriculture accounted for 71% and point sources 24%. Reduced N is more reactive than oxidized N and its atmospheric residence time is much shorter (5 h compared with 30 h), and most reduced N is deposited within 150 km of its source (NEG-TAP, 2001). However, it is likely that most of the major effects from ammonia occur in a very large number of small area deposition hot spots within a few hundred metres of intensive livestock units (Sutton *et al.*, 1998). Further afield, it has been reported that aeolian N accounts for 29–43% of terrestrial N inputs to the North Sea (OSPAR, 2005b). Atmospheric inputs of P to surface waters are generally small, except perhaps in environments influenced by soil erosion (Sharpley *et al.*, 1995). However, there appear to be few, if any, data for the UK.

Submarine groundwater discharges (SGD)

Anthropogenic nutrient enrichment of groundwaters arises primarily from agriculture and urbanization. There is a paucity of data on SGD and their nutrient loads to near shore waters globally. Fluxes of N from SGD can vary over orders of magnitude, and in some regions can rival river N inputs (Slomp and van Cappellen, 2004). The range in fluxes of P appears smaller, but the highest fluxes occur where the groundwater is anoxic (Krest *et al.*, 2000). DIN:DIP ratios in groundwaters are generally above the Redfield ratio, and therefore may have disproportionate impacts on N-limited receiving waters. Within the UK the influence of SGD on estuarine nutrient biogeochemistry is likely to be regionally variable (Nedwell *et al.*, 1999) although there appear to be no published data (Slomp and van Cappellen, 2004). It is likely that the largest SGD inputs of nutrients to estuaries and near shore waters will occur in regions of aquifer bearing strata outcropping at the coast and occurring within NVZs. These conditions are found in north-east England, north and south of the Humber Estuary, north Norfolk, east Kent and along parts of the Channel coast, as shown in Figure 4.

Mariculture

Scotland contributes *ca.* 90% of all UK mariculture production (DEFRA, 2005), and the predominant farmed species is Atlantic salmon. The farms are mainly located in sea lochs of the west coast and Western Isles, Orkney and the voes of Shetland. Production increased from 80 000 t in 1996 to 150 000 t in 2002, with concomitant N inputs to coastal waters rising from 3200 t yr^{-1} to 6000 t yr^{-1} (Islam, 2005; SEPA, 2005). These estimates are based on 35–45 kg N t^{-1} of fish produced, lower than the UK limit for salmon of 123 kg N t^{-1} (Islam, 2005). In general, the impact of nutrients from aquaculture in the UK is localized and where flushing is high the impact may be minimal, although the state of the marine environment around the islands is being studied for the OSPAR Comprehensive Review (SEPA, 2005).



Figure 4. Regions of aquifer bearing strata outcropping at the coast and occurring within Nitrate Vulnerable Zones. Grey = aquifer; black = groundwater NVZ. Reproduced with permission from UK Natural Environment Research Council and British Geological Survey.

Nutrient speciation and ratios

N and P fractions can be inorganic or organic and operationally defined as dissolved ($<0.45 \mu\text{m}$) or particulate ($>0.45 \mu\text{m}$). The inorganic species (e.g. NO_3 , NO_2 , NH_4 , PO_4) are readily utilized by primary producers and appear to have more potential to limit plant growth. Dissolved and particulate organic N may be significant fractions of the total N load to estuaries (Bronk, 2002), and the extent of their bioavailability is only now beginning to be realized. In relation to P, the quantity, composition and role of dissolved organic P requires further investigation (Nedwell *et al.*, 1999).

The concept of nutrient limitation is a keystone of eutrophication research (Smith *et al.*, 1999; Turner, 2002) and as important as element loading rates and concentrations. The average N:P atomic ratio of phytoplankton is 15.5:1 (Redfield *et al.*, 1963) and combined with the N:P ratio of 16.5:1 for zooplankton gives the Redfield ratio for marine seston of 16:1. It has often been postulated that this nutrient ratio is required for optimum growth of marine algae and biomass production would be limited by the nutrient that is first depleted (i.e. if ambient N:P ratios deviate widely from Redfield's ratio) and there is no other limiting factor (e.g. light or temperature). *In situ* growth rates are usually not affected

by ambient nutrient ratios, as long as the absolute concentrations are high enough to sustain optimal growth. It is only after growth rates start to be limited by lowered nutrient concentrations that limitation of ultimate biomass production begins (Kocum *et al.*, 2002). Hecky and Kilham (1988) pointed out, however, that in order to determine which nutrient is possibly limiting, information on intracellular concentrations should be favoured over nutrient concentrations in the water column, as it is often difficult to relate external concentrations to growth rates. For example, under conditions of ammonium-limited growth, *Thalassiosira pseudonana* (3H) and probably other small algae can grow at about 80% of their maximum growth rates while ammonium concentrations in the water column remain immeasurable (Kilham and Hecky, 1988). Biochemical composition of nutrient replete algae and cyanobacteria suggests that the critical N:P ratio that marks the transition between N- and P-limitation is likely to lie in the range between 15 and 30 (Geider and La Roche, 2002). Kamer *et al.* (2004) showed experimentally that *Enteromorpha intestinalis* (a ubiquitous nuisance species) from a southern Californian estuary with N:P tissue ratios of <26 was N limited, but they also raised the question that N:P ratios indicative of nutrient limitation may vary over regional and local scales and may be site- or species-specific. However, the general theory of nutrient limitation of algal growth has been demonstrated or inferred in many estuarine and marine ecosystems (Hecky and Kilham, 1988; Howarth, 1988; Vitousek and Howarth, 1991). In experiments, ambient nutrient limitation has been shown to have the potential to shape phytoplankton communities in fresh water (Tilman, 1977; Sommer, 1986) and estuarine environments (Piehler *et al.*, 2002) and it is known that the relative availability of Si determines the competitive success of diatoms (Hecky and Kilham, 1988 and literature cited therein).

Generally N is the limiting nutrient in many coastal waters, P may limit the production in some estuarine systems, and nutrient limitation may switch seasonally in others (Howarth, 1988; Vollenweider, 1992; Vitousek *et al.*, 1997; Conley, 2000; Rabalais, 2002). However, this natural variation may be overridden by anthropogenic inputs and, for example, might be masked by inputs of STW effluents with relatively high P content (low N:P). In this case, the estuary might become N limited all year (e.g. the Thames Estuary, Nedwell *et al.*, 2002). Seasonal switching has been related to sediment regeneration of P (Conley, 2000) and lack of N fixation by cyanobacteria in estuaries, combined with N loss by denitrification (Howarth, 1988). Nutrient limitation in UK estuaries is probably in the order $P > Si > N$ (Nedwell *et al.*, 2002). However, the potentially limiting nutrient indicated by nutrient ratios during the active growing season in the spring and summer may be quite different to that indicated by the mean annual nutrient ratio, as the peak fluvial loads of NO_2 and NO_3 occur in the winter when growth is light limited (Nedwell *et al.*, 2002).

Estuaries are not only transitional waters in terms of salinity, but also by the decreasing degree of terrestrial influence towards the adjacent coastal waters. Terrestrial plants have high N:P ratios (up to 110; Hedin, 2004 and literature cited therein) which is reflected in the relative concentrations of N and P in the receiving rivers, where input of terrestrial plant debris plays an important role (Vannote *et al.*, 1980), while ocean water has N:P ratios approaching Redfield's. Consequently, estuaries exhibit steep gradients in nutrient concentrations and ratios between

their fresh water head and their mouth. When the adjacent coastal water is potentially N limited (which is not always the case), a shift from potential P limitation to potential N limitation down estuary will probably occur. These inherent properties of estuarine environments naturally favour opportunistic, bloom-forming phytoplankton species.

The terrestrial influence on estuaries is also reflected in nutrient pulses, following precipitation events in the catchment, which may account for 80–90% of the nutrient load delivered (Tappin, 2002). Experimental research on (temporal) nutrient patchiness (Sommer, 1986) has shown that individual species of algae respond quite differently to low, homogenous nutrient levels and to nutrient pulses. In an experiment with natural phytoplankton populations from Lake Constance, Sommer (1986) identified that in populations exposed to static (i.e. unpulsed) Si and P inputs, only two species persisted, but in those with pulsed P and Si inputs between six and nine species survived. Kilham and Hecky (1988) assumed that both marine and freshwater algae respond to nutrient pulses in a similar manner. These findings may be important for the understanding of the processes behind algal blooms in UK estuaries, where nutrient inputs are often pulsed, following precipitation events in the catchment. During summer, when precipitation and consequently nutrient pulses are low or absent for weeks, these conditions, along with increased irradiation and temperature, might competitively enable one or two bloom-forming species whereas under pulsed conditions a more diverse assemblage would persist.

Physical estuarine characteristics

In addition to the various forms of nutrient input to an estuary or coastal system, the physical characteristics of an estuary will influence its productivity and the likelihood that eutrophication as opposed to hypernutrification will occur (de Jonge and Elliott, 2001). High nutrient loads do not necessarily lead to undesirable disturbance in all estuaries, indicating the need for a comprehensive assessment to identify the risk of eutrophication in individual estuaries and coastal waters adjacent to hypernutrified estuaries.

Key variables affecting trophic status include the fresh water flushing time for the estuary, which dictates the residence time of the dissolved nutrients (Nedwell *et al.*, 1999; Scott *et al.*, 1999), the morphology of an estuary (including water depth) and its turbidity, which both have a controlling influence on light availability (de Jonge *et al.*, 2002), and the stratification of the estuary, which may support plankton in the surface layers while also facilitating the formation of bottom anoxia (Scott *et al.*, 1999). High turbidity leading to a low light regime within estuarine waters frequently limits primary productivity in UK estuaries (Painting *et al.*, 2007). The estuaries in the UK identified as eutrophic (Table 1) are typically muddy systems, with a large tidal range and an open expanse of mudflats.

Nutrients delivered to an estuary which are not used for primary production can accumulate in the sediments or be transported into the coastal waters but the relative importance of the roles played by these processes in individual estuaries is not well understood (Tappin, 2002). Estuaries are regions of sediment accumulation and both N and P can be retained within sediments although it is more significant for P than for N. Depending on the nature of the estuary a significant proportion of the retained N may be removed from the system

by denitrification within the sediments while the P may be temporarily stored and re-released in the future as conditions change (Tappin, 2002). Nutrients transported through hypereutrophic estuaries may produce eutrophic symptoms in coastal waters. The WFD includes coastal waters to 1 nautical mile offshore and hence these waters will also have to meet the required standard of good ecological status.

POTENTIAL FUTURE TRENDS IN EUTROPHICATION STATUS

Impacts of existing legislation

OSPAR led activities

International agreements under the auspices of the EU and OSPAR have been crucial to the development of UK policy with regard to nutrient discharges and eutrophication. Three principal sources of nutrients to estuaries have been identified each of which have separate control requirements: those discharged with urban wastes, those from agriculture and, for N discharges only, those entering via the atmosphere.

OSPAR adopted three recommendations concerning the reduction of nutrient (or nitrogen) inputs to estuaries and coastal waters in 1988, 1989 and 1992 (OSPAR, 2003). However, it was not until the 'Strategy to Combat Eutrophication' adopted in 1997 and implemented through the Common Procedure, that the UK recognized a need to reduce nutrient discharges to coastal waters and eutrophication around its coasts. The Common Procedure identified those areas which clearly do not have a problem with respect to eutrophication and then required a comprehensive assessment of the remaining areas to categorize regions into problem, non-problem and potential problem areas as shown in Table 1.

Following the implementation of the Common Procedure OSPAR is piloting an integrated set of Ecological Quality Objectives (EcoQOs) for eutrophication as part of an adaptive management approach to tackling the problem alongside its recommendations for reduction of pollution at source (OSPAR, 2005a). Based on the same classification process, these EcoQOs consider cause and effect criteria including winter nutrient concentrations (causes), phytoplankton indicator species and chlorophyll *a* concentrations (direct effects) and oxygen depletion and changes in zoobenthos (indirect effects).

Atmospheric emissions of N are also recognized by OSPAR as a key input to marine waters which must be reduced if the aims of the Eutrophication Strategy are to be met. In their 2005 report they note the activities of the EU and other international fora, and point to their role in improving data collection and assessment (OSPAR, 2005b).

Urban Waste Water Treatment Directive (UWWTD)

The EU has adopted a multi-sectoral approach (Elliott and de Jonge, 2002) towards the control of anthropogenic nutrient enrichment that aims to combat both point source discharges, specifically sewage discharges under the UWWTD, and diffuse pollution, including agricultural pollution under the ND, and atmospheric discharges. To fulfil the requirements of the UWWTD it was necessary to assess the condition of water

with respect to eutrophication to determine whether action should be taken under the Directive to reduce inputs to a given water body. The selection methodology used to identify 'sensitive areas', with regard to nutrients, under the UWWTD is based on a water body being classed sensitive if it is, or is likely to become, eutrophic in the near future. There is also the possibility under the UWWTD of classifying areas such as estuarial or coastal waters as 'less sensitive areas' in which secondary treatment of sewage is not required.

From an initial selection of 38 sensitive areas in the UK under the UWWTD in 1995, there are now 347 across the UK, classified for reasons of eutrophication and as bathing waters (CEC, 2004). A number of areas not designated, including the Thames, Humber, Wash and some coastal waters, were subject to infringement proceedings (CEC, 2004). The designation of less sensitive areas (under the UWWTD), which allowed sewage treated to primary standard only to be discharged into areas classified as having 'High Natural Dispersion', was proposed when the UWWTD was introduced for the UK, but is no longer being applied (DEFRA, 2003). Therefore the application of the UWWTD with the Bathing Waters Directive (76/160/EEC) has been instrumental in improving the treatment of sewage effluent discharged to estuaries and coastal waters round the UK and has led to a reduction of NH_x and DIP as already reported. However, while there has been a significant upgrading of sewage treatment works around the UK, to improve bathing waters, eliminate sewage sludge dumping at sea and tackle nutrient inputs, the European Commission is of the opinion that further upgrading the level of sewage treatment and the performance of the facilities in sensitive areas is still necessary (CEC, 2004).

Nitrates Directive (ND)

As for OSPAR and the UWWTD, the Nitrates Directive requires water bodies to be classified according to current and likely future status. In the first instance the UK classified water bodies only for their impact on drinking waters and hence the emphasis was on classifying waters with a NO_x concentration at or above 50 mg L^{-1} , the limit set by the World Health Organisation to protect human health. This led to 8% of England being classified as an NVZ. Following a judgement by the European Court of Justice that it was necessary to protect all surface and groundwaters, and not just those used for drinking, the UK Government broadened its classification to include surface waters which were, or were likely to become, eutrophic (EC, 2002). In October 2002 the UK Government classified 55% of the land area of England as an NVZ (DEFRA, 2006) including five estuarine and coastal waters (see Table 1 and Figure 5). This land will now be subject to action programme measures to reduce the losses of N and P compounds from agricultural land.

Policy on atmospheric inputs of nitrogen

The EU has recognized atmospheric inputs of nitrogen to ecosystems as a serious concern and in its Thematic Strategy on Air Pollution notes the scope for improvements in shipping, as a source of NO_x , and of farming, as a source of ammonia, to the atmosphere (CEC, 2005). The UK has met the emissions reductions for NO_x laid out in the UN CLRTAP (Convention on Long Range Transboundary Air Pollution) Nitrogen Oxide

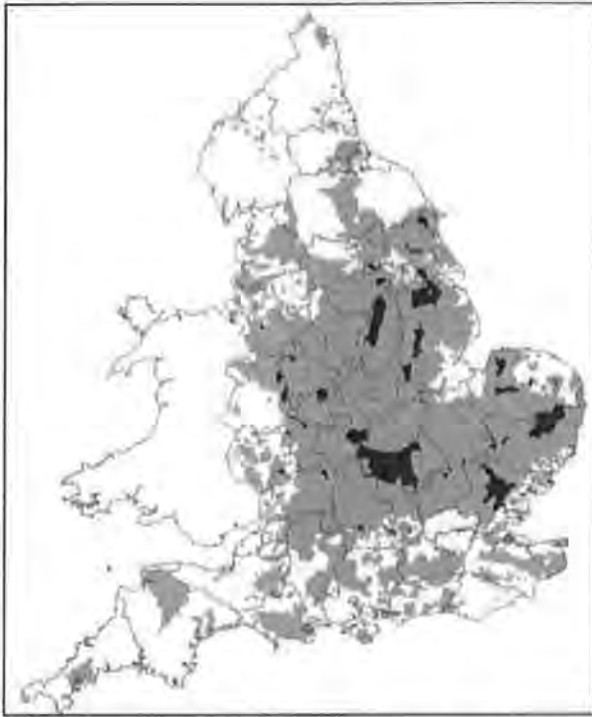


Figure 5. Nitrates Vulnerable Zones in England and Wales as designated in 1996 (dark grey) and 2002 (light grey). From DEFRA (2006).

Protocol Target and the Fifth Environmental Action Programme, and NO_x emissions have decreased by *ca* 45% since 1990. This trend has also satisfied the target of a 56% reduction in NO_x emissions over the period 1990–2010 under the UNECE Gothenburg Protocol (Cunha *et al.*, 2002). However, because only 20% of NO_x emissions are deposited in the UK, the wet and dry deposition of NO_x has shown only a small decrease since 1986 (NEG-TAP, 2001). Additional emissions policies for ammonia are found in the EC National Emission Ceiling Directive. The target of an 11% reduction in emissions between 1990 and 2010 is expected to be met (NEG-TAP, 2001). However, the strategy notes that even if existing legislation were fully implemented across Europe it is likely there would be only a 14% reduction on 2000 figures in the area affected by eutrophication. The strategy (CEC, 2005) calls for reductions of 60% in NO_x emissions and 27% in NH_3 relative to 2000 emissions and believes this can be achieved in part at least through streamlining and better managing existing legal instruments, including the Common Agricultural Policy (CAP), and also through introduction of new controls, such as those on shipping. In terms of the UK's estuarine and coastal waters the key is likely to lie with farming and the impact of the CAP is uncertain. It is proposed in the CAP strategy that additional controls on the N content in feedstuffs and action to prevent excessive use of nitrogen fertilizers may be appropriate (CEC, 2005).

The possible implications of future actions

NVZ Action Programme measures

The Nitrates Directive seeks to reduce and further prevent nitrate inputs from diffuse sources (*i.e.* agriculture) through

the regulation of agricultural practices in 'vulnerable zones'. These (nitrate) vulnerable zones are areas which drain into waters (including estuaries, coastal waters and marine waters) that are found to be eutrophic, or may become eutrophic in the near future if no action is taken. The objectives of the ND are to be achieved through the implementation of Action Programme measures for the NVZs. These include rules concerning (i) seasonal periods considered suitable for application of organic fertilizer to sandy and shallow soils, (ii) the capacity of storage vessels for livestock manure in order to bridge closed periods (*i.e.* when manure must not be applied to land) and (iii) limitation on the quantity of fertilizers applied to land, taking into account (among other features) soil type and slope, N demand of the planted crop, and climate conditions. Appropriate record keeping detailing land use and management is also a requirement. The UK was slow to implement controls on nutrients but now the Directive is being implemented over 55% of England (Figure 5).

Closed periods, when fertilizers may not be applied to land, may potentially have an impact during September in England and Wales, when light and temperature conditions are suitable for primary production. Reduction of N loads may limit the possibility of autumn phytoplankton blooms. However, this would depend on the residence time and losses of N within the estuary's catchment, which will vary spatially (*e.g.* according to soil type and topography) and temporally (*e.g.* weather/climate variability). In relation to manure specifically, the closed period would be most effective if applicable to all soil types (rather than just sandy or shallow soils) so that groundwater and surface water inputs to estuaries are protected from nitrate leaching. For example, in an arable or grassland area where clay soils dominate, the application of slurry during August or September prior to a high rainfall event is a potential source of nutrient enrichment.

Restricting the application of N fertilizer and organic manure when the soil is waterlogged, flooded, frozen or snow covered may reduce winter nitrate losses from the land to the estuary. This could potentially reduce spring N concentrations in the estuary as less N will have been buried during the preceding winter. This would be important in estuaries that are not P limited in spring. However, our understanding of the temporary burial of organic N and its release is limited. Inhibiting the application of N fertilizer and organic manure on steep slopes will reduce N loss via runoff in certain catchments, and potentially reduce N inputs to estuaries in those catchments. During the summer and early autumn, a reduction in N loads to estuaries is likely to diminish the occurrence of nutrient enrichment. Spreading fertilizer or manure evenly and accurately, which is dependent on machinery being calibrated regularly, has the potential to reduce N loss as has the regulation specifying that water courses should be protected from contamination by N fertilizer and organic manure by, for example, the use of buffer strips alongside streams. The NVZ measure on waste storage capacity will ensure that farmers can comply with the closed period regulations, which may contribute towards a reduction in nitrate leaching to ground and surface waters during the winter months when precipitation is highest.

Capping the total amount of N which can be applied to agricultural land also has the potential to reduce the amount lost to surface water. However, the limits set in England are high and for inorganic fertilizer application rates are based on

crop requirements that relate to an economic optimum. This is likely to lead to high losses as the residual soil N concentrations will be high and available for leaching. It has been noted that this implementation of the ND will require little change in practice for farmers in NVZs (Nimmo-Smith *et al.*, 2007).

It is possible that annual N loads to estuaries may be reduced as a result of NVZ Action Programme measures but there is concern that this reduction may be too small to have any significant effect (ADAS, 2007; Nimmo-Smith *et al.*, 2007). The operation and interactions of environmental processes over a range of temporal and spatial scales may mask anticipated beneficial changes in water quality. These measures are fundamentally designed to impact on groundwater concentrations of N to protect drinking water quality and so they should, eventually, also lead to a reduction in submarine inputs but the timescale for this is unknown. DEFRA is currently consulting on revisions to the Action Programme measures (and will report early 2008) which may reduce the total load of N that can be applied to agricultural land (DEFRA, 2007).

Water Framework Directive (WFD)

Two key policy drivers can be expected to steer the change in the nutrient status of the UK's estuarine waters in the first decade of the 21st century: the first is the Water Framework Directive and the second is the Common Agricultural Policy. The WFD clearly addresses the status of transitional waters (such as estuaries, rias and coastal lagoons), integrating these with groundwater and inland surface water management. It requires member states to achieve 'high' or 'good ecological status' in all surface waters by 2015 (Table 2) and to ensure that there is no deterioration in water quality—a far higher aspiration than has been the case in the past. It bases its assessment on ecological quality status, requiring evidence of impacts on biological quality elements as well as supporting physico-chemical data to confirm the likely cause of the impacts.

Currently the European Commission is developing the Common Implementation Strategy for the WFD and in this

it considers the implications of other initiatives and directives (CIS, 2005) to ensure the classifications are compatible. The WFD classification scheme for water quality is compared in Table 2 with those developed for the ND, the UWWTD and by OSPAR. This shows that all water bodies that are classified as 'sensitive' under the UWWTD, 'vulnerable' under the ND or a 'problem area' under OSPAR will need to be considered in a programme of measures alongside those which, even though they are currently classified as of 'good' or 'high' ecological status, may become eutrophic in the near future (CIS, 2005). The WFD specifically mandates the control and mitigation of diffuse pollution impacts (Haygarth *et al.*, 2003), and it is likely that the drive to achieve 'good ecological status' may over-ride the implementation of the Nitrates Directive in many locations. Ensuring clarity concerning these action levels and harmonizing the quality indices used will be key to ensuring efficient and effective management.

Common Agricultural Policy reform

The Common Agricultural Policy has been in existence for 40 years and during that time subsidies from the EU encouraged increased production partly by excessive use of fertilizers (de Clercq *et al.*, 2001). Now, recognition that supporting such intensive systems is expensive in terms of economic, social and environmental costs, the CAP is being revised. Some of the key elements of the CAP reform are (i) the decoupling of subsidies for farms from production, (ii) linking the payment to respect for environmental, food safety, animal and plant health and animal welfare standards, as well as the requirements to keep all farmland in good agricultural and environmental condition ('cross-compliance'), (iii) a reduction in direct payments for bigger farms, and (iv) asymmetric price cuts in the milk sector (CEC, 2003). The aim of these reforms is, in part, to reduce the pressure on the environment.

GFA-RACE Partners Ltd (2004) investigated the potential impacts of the CAP reform on N and P losses in the UK and concluded that the losses to ground and surface waters are likely to be reduced. For example, farmers may be more focused on reducing input costs and targeting N and P use to crop requirements in the future. However, N and P losses will

Table 2. Comparison of assessment results under various policies for waters responding to nutrient enrichment (based on the assumption that the WFD classification is the starting point and that the different sources of pollution are relevant)

| Ecological status | Assessment of current status | | | |
|-------------------|---|---|---|------------------|
| | WFD normative definition | UWWTD Directive | Nitrate Directive | OSPAR |
| High | Nearly undisturbed conditions | Non-eutrophic, designation of sensitive area is not required | Non-eutrophic, not a polluted water, designation of NVZ not required | Non-problem area |
| Good | Slight change in composition, biomass | Non-eutrophic, designation of sensitive area is not required | Non-eutrophic, not a polluted water, designation of NVZ not required | Non-problem area |
| Moderate | Moderate change in composition, biomass | Eutrophic or may become eutrophic in the near future, designation of sensitive area is required | Eutrophic, or may become eutrophic in the near future, polluted water, designation of NVZ is required | Problem area |
| Poor | Major change in biological communities | Eutrophic, designation of sensitive area is required | Polluted water, designation of NVZ is required | Problem area |
| Bad | Severe change in biological communities | Eutrophic, designation of sensitive area is required | Polluted water, designation of NVZ is required | Problem area |

From CIS (2006).

increase in certain regions where further specialization will occur, such as concentration of dairy production in the south-west, north-west and west Midlands. The study (GFA-RACE Partners Ltd, 2004) also considered how organic wastes will be affected by the reforms, suggesting that livestock numbers will decline overall, leading to a reduction in organic wastes in areas where livestock farming is predominant, although consolidation within the dairy sector may present specific problems in some catchments as farm size and herds increase. Furthermore, investment in infrastructure on larger farms may help to reduce problems from organic wastes but nutrient loading will remain a problem.

Therefore, at a national level, it would appear that CAP reforms will reduce N and P losses to the aquatic environment, but in relation to estuarine eutrophication, the picture is less clear. The location of the eutrophic estuaries is critical; if they are located in regions where dairy production concentrates for example, then it is possible that nutrient enrichment will increase. The Taw Estuary in Devon is one such example: it is classified as being eutrophic under the ND and UWWTD and the predominant land use in the catchment is dairy and livestock farming. Thus, the impact of CAP reforms on estuarine eutrophication in England and Wales is uncertain at present.

The UK's DEFRA recognizes diffuse water pollution from agriculture to be the greatest threat to the successful implementation of the WFD (DEFRA, 2007) and sees the implementation of the CAP reform as an important opportunity to reduce this threat. A modelling exercise by Haygarth *et al.* (2003) undertaken for DEFRA, considered the likely interaction between the CAP and WFD requirements and identified that substantial changes in agricultural land use and management will be required to achieve 'good ecological status' in all waters by 2015. They propose for example, that to meet this goal it may be necessary to reduce stocking densities and to take certain sensitive areas out of production altogether (Haygarth *et al.*, 2003). Therefore, it is suggested that implementation of the WFD may require significant changes in agricultural practice if it is to achieve its potential to reduce nutrient enrichment and possibly estuarine eutrophication.

DO NUTRIENT CONTROL MEASURES WORK?

There is conflicting evidence on the ability of nutrient load control measures to reduce nutrient enrichment and the impact of eutrophication. Following a marked decrease in the use of commercial fertilizers in Eastern Europe in the late 1980s European rivers responded only slowly and to a limited degree (Grimvall *et al.*, 2000). This could reflect residence time in the system or the importance of other nutrient sources (Grimvall *et al.*, 2000). The narrow, coastal inlets of the Bodden (Baltic Sea) have not shown recovery, despite decreases in nutrient inputs during the 1990s (Meyer-Reil and Köster, 2000). De Jonge (1997) concluded that there was no evidence that reduced loads of DIP from the River Rhine or Lake IJssel had proportionally reduced primary production in the western part of the Dutch Wadden Sea. In contrast, a clear relationship between partial recovery of the Black Sea's pelagic and benthic communities, seriously damaged by eutrophication, and reduced nutrient inputs has been reported (Rabalais, 2002). Tampa Bay (USA) experienced symptoms of over-fertilization

in the 1970s, and remedial action included the installation of sewage treatment works and a decreased P loading from fertilizer applications. By 1980 the annual wastewater loading of N had decreased 10-fold and by 1990 the mean annual chlorophyll *a* biomass had decreased by more than half (Cloern, 2001). It appears that the use of nutrient load control measures is not straightforward in terms of reducing nutrient enrichment down-estuary. It is likely that effective water quality management requires both a multi-dimensional approach to controlling nutrient discharge within catchments, and also a general multi-sectoral management strategy towards N and P, as demonstrated in the following examples.

Denmark's control of agriculturally-derived nutrient inputs to estuarine and coastal waters has been in development since 1987, when its first Action Plan for the Aquatic Environment was devised, and can be described as a multi-dimensional approach. The Danish Action Plan measures go beyond the requirements of the Nitrates Directive, and include the re-establishment of wetlands, afforestation, improved feed utilization, and optimized livestock density requirements (Iversen *et al.*, 1998). These measures have led to farms' utilization of 65–75% of the N content in their organic manure (Winther, 2002), which has subsequently contributed towards a 37% decrease in the use of manufactured N fertilizer between 1985 and 2000 (Grant and Blicher-Mathiesen, 2004). Nitrate leaching from agricultural fields (the root zone) has been modelled for seven agricultural catchments in Denmark and the results showed a reduction of 32% over the period 1990–2000 (Grant and Blicher-Mathiesen, 2004). In addition, Andersen *et al.* (2004) stated that the 30% reduction of annual mean nitrate concentrations in streams within cultivated areas, over the period 1989–2002, was mainly due to reduced leaching from cultivated fields. Recently, it has been reported that total N concentrations in Danish estuaries and coastal waters have decreased by up to 44% over the period 1998–2003 (climate variability taken out), primarily in response to reduced diffuse inputs of nutrients (Carstensen *et al.*, 2006). The response time of Denmark's estuarine and coastal waters to controls on nutrient inputs has been longer than 10 years, reflecting the historical legacy of increased nutrient inputs, and the subsequent storage of nutrients in sediments and their long-term recycling to the water column.

Efforts to manage nutrient inputs from agriculture to the Chesapeake Bay have focused on Best Management Practices (Soil and Water Conservation Plans, Nutrient Management Plans, and state agricultural cost-share programmes) that aimed to prevent soil erosion, reduce nutrient application and control nutrient movement (Boesch *et al.*, 2001). Reduction of nutrient inputs by 40% was required to improve water quality in the Chesapeake Bay, yet reductions of non-point inputs of P and N, under the Chesapeake Bay's soil conservation-based management strategies, were projected by models to achieve only 19% and 15% reduction (Boesch *et al.*, 2001). Strategies were successful in reducing P transport in areas of the Bay catchment predisposed to high erosion rates but less effective in addressing dissolved nutrient transport in surface runoff or leaching to groundwater. Subsequently, there has been a lack of reduction in nutrient concentrations in streams and tidal waters in some areas of the Chesapeake Bay. It is suggested that a multi-sector approach is required to control nutrient inputs to the Chesapeake Bay in the future, including the

development of more effective agricultural practices, reduction of atmospheric sources of N, enhancement of nutrient sinks, and control of suburban development (Boesch *et al.*, 2001). This perspective is also advocated by Whitall *et al.* (2004) who evaluated a variety of management strategies for reducing N to four east coast US estuaries, concluding that comprehensive, multi-sector management is critical to effective N reduction and can result in 35–58% reductions in N loads to coastal ecosystems. In comparison, specifically in less urban catchments, reductions in agricultural loading alone can result in 5–56% reductions.

SCOPE FOR IMPROVEMENT IN THE UK

Some UK estuaries undoubtedly do suffer from eutrophication, as defined by de Jonge and Elliott (2001) (Table 1), while many have elevated nutrient inputs but do not present symptoms of eutrophication, largely owing to high tidal range, large fresh water flows and high estuarine turbidity. These characteristics result in a hypernutrified estuary which, while it does not present ecological symptoms of eutrophication, such as excessive algal growth or speciation changes, will export the high nutrient load to the coastal waters where such symptoms may be encountered. The UK has only slowly come to accept the need to implement strategies to protect estuaries from eutrophication but under the WFD, as the definitions for the new ecological status classifications are refined, the requirement for improved protection is likely to become increasingly apparent.

The UWWTD has been highly significant in reducing P and NH₄ inputs to estuaries but there is limited scope for further reductions. Current implementation of the Nitrates Directive may have some impact on the nutrient status of estuaries, as the Action Programme measures are introduced across the catchments designated as NVZs following the European Court of Justice judgement in 2000, but on their own they are unlikely to enable estuaries to meet the WFD classification of 'good' or better (ADAS, 2007). Significant improvements could be made through the current revision of the Action Programme measures by DEFRA following the examples of countries such as Denmark but this will require a significant change in attitudes towards farming activities (Nimmo-Smith *et al.*, 2007). There is an opportunity now to make that change through the implementation of the CAP single payment scheme. Waterborne and atmospheric inputs from agriculture are the most significant pressure on eutrophication in transitional waters in the UK and the CAP is a key policy driver which could be addressed in association with the WFD to modify this pressure.

However, research is needed to observe the impacts of changes in policy and legislation on nutrient loads and estuarine eutrophication. Not only is the impact of changes to the Action Programme measures and the Single Farm Payment on farm practices uncertain but also the effect of changes in practice on actual concentrations in surface water and their export to coastal waters is not easily predicted. The significance of submarine groundwater discharges to eutrophication of estuarine and coastal waters is relatively unknown whilst the importance of aeolian inputs of N to estuaries is poorly quantified. Responses to a change in emissions of nutrients from agriculture may be slow and

natural characteristics of estuaries may result in complex responses to this change. For example, nutrient storage in sediments, seasonal changes in primary production and responses to flash flood events all complicate our view of the impact of changes in the drivers and pressures acting on the estuary. The ability to make these connections between the policy drivers and the environmental impacts is critical to successful environmental management and, given the economic (and environmental) importance of sectors such as agriculture, fishing and tourism, the need for more research is very clear.

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**THE USE OF MONITORING DATA FOR IDENTIFYING
FACTORS INFLUENCING PHYTOPLANKTON BLOOM
DYNAMICS IN THE EUTROPHIC TAW ESTUARY**



The use of monitoring data for identifying factors influencing phytoplankton bloom dynamics in the eutrophic Taw Estuary, SW England

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ABSTRACT

Using the Taw Estuary as an example, data routinely collected by the Environment Agency for England and Wales over the period 1990–2004 were interrogated to identify the drivers of excessive algal growth. The estuary was highly productive with chlorophyll concentrations regularly exceeding $100 \mu\text{g L}^{-1}$, mostly during periods of low freshwater input from the River Taw when estuarine water residence times were longest. However, algal growth in mid estuary was often inhibited by ammonia inputs from the adjacent sewage treatment works. The reported approach demonstrates the value of applying conventional statistical analyses in a structured way to existing monitoring data and is recommended as a useful tool for the rapid assessment of eutrophication. However, future estuarine monitoring should include the collection of dissolved organic nutrient data and targeted high temporal resolution data because the drivers of eutrophication are complex and often very specific to a particular estuary.

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1. Introduction

Eutrophication is one of the greatest contemporary threats to the integrity of coastal ecosystems (Gray et al., 2006; Vitousek et al., 1997) and has been defined as an increase in the rate of supply of organic matter to an aquatic ecosystem (Nixon, 1995), mostly via increased primary production by benthic and suspended algae, following elevated inputs of nitrogen (N) and phosphorus (P). This can give rise to undesirable effects (De Jonge and Elliott, 2001), including nuisance and toxic algal blooms, changes in taxonomic composition towards opportunistic species, hypoxia resulting in mass kills of fish and invertebrates, and odour release. On a global scale, the quantitatively most important pathways of N and P to estuarine and coastal systems are surface water inputs (Tappin, 2002), usually originating from either diffuse sources (e.g. fertilizer and manure from agricultural activities for N, land erosion for P) or point sources (e.g. storm water and sewage outfalls). However for estuaries, which are highly dynamic environments, the links between nutrient inputs and organism response are not straightforward. Although N and P can be related to an increase in chlorophyll *a* concentrations in coastal and estuarine waters on a general basis (Smith, 2006), estuarine eutrophication is regulated through a range of 'filters' (Cloern, 2001). The relative contribution of each filter is system specific, which makes it difficult to relate biological responses linearly to nutrient inputs (Cloern, 2001). The two most important filters are probably light

availability as a function of turbidity and freshwater flushing time. In light-limited estuaries, symptoms of eutrophication may not develop at all and the estuary is termed hypernutrified (De Jonge and Elliott, 2001). Flushing time strongly controls primary production in an estuary (Painting et al., 2007) and also shapes phytoplankton biodiversity (Ferreira et al., 2005), simply by determining how long the cells remain in the estuary to reproduce before being flushed out to the sea.

Despite the launch of the European Union's (EU) Water Framework Directive (WFD; 2000/60/EC) in 2000, two other EU Directives are still in place to target explicitly the control and mitigation of eutrophication in EU coastal, transitional (i.e. estuarine) and inland waters and provide a framework of management options. The Nitrates Directive (ND; 91/676/EEC), specifically addresses diffuse N pollution from agriculture, whilst the Urban Waste Water Treatment Directive (UWWTD; 91/271/EEC), aims to protect water bodies where urban waste water discharges are understood to be the drivers of increased primary production.

For the UK, the occurrence and extent of estuarine eutrophication has repeatedly been acknowledged (e.g. Maier et al., 2009; MEMG, 2004; OSPAR Commission, 2003). The Taw Estuary was selected for this study as it is one of the few UK estuaries to be designated under both the UWWTD and the ND. In 1996 the Environment Agency for England and Wales (EA) during an assessment under the UWWTD found evidence for eutrophication in the Taw including surface algal scum, concentrations of suspended chlorophyll *a* exceeding the OSPAR threshold of $15 \mu\text{g L}^{-1}$ (OSPAR Commission, 2003), and diurnal fluctuations in concentrations of dissolved oxygen. Subsequently (1998) the estuary was designated

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a Sensitive Area (Eutrophic), with the requirement that inputs of nutrients from the main sewage treatment works (STW), at Ashford (Fig. 1) be reduced by the end of 2004. In 2005 the EA estimated that diffuse sources of inorganic N to the estuary were significant throughout the year, contributing 99% of the N loading in the winter and up to 40% during the summer. On the basis of this assessment, the EA recommended that the Taw Estuary be classified as a Polluted Water (Eutrophic) under the ND. However, nutrient stripping following Action Plans under either Directive can be very expensive and for small catchments such as the Taw costs can quickly approach several million Euros (Atkins and Burdon, 2006; Gren, 2000). It is therefore clear that a sound understanding of the drivers that trigger algal blooms in an estuary is required to justify investment of public funds, particularly because the support of the local community for eutrophication management measures is imperative (Atkins et al., 2007).

The main aims of this paper were to assess the potential of the large monitoring datasets, developed by the EA as a result of its statutory sampling obligations, to identify the drivers of excessive algal growth in the Taw Estuary, and to provide a template for further eutrophication assessments of UK estuaries using existing water quality monitoring data. To achieve these aims, the specific objectives of the study were to (i) optimize data pre-treatment in order that the maximum amount of good quality information could be extracted, (ii) enhance information recovery from the dataset using appropriate statistical methods, and (iii) based on (i) and (ii), highlight where monitoring-type data collection under the ND and UWWTD can be improved in order to provide more robust eutrophication assessments of UK estuaries.

2. Materials and methods

2.1. Site description

The Taw Estuary is located in the south west of England, draining an area of 1211 km² (Environment Agency, 2000) and forms, together with the Torridge Estuary, a twin estuarine system that discharges into the Bristol Channel (Fig. 1).

The Taw Estuary is 23 km in length, extending from its tidal limit at Newbridge to its mouth. The estuary is macro-tidal (tidal range >4 m) with a tidal range at the mouth during spring tides of ca. 7 m and ≤5 m during neaps. Further up-estuary, at Barnstaple, the tidal range is ca. 4 m during springs and can be <1 m during neaps. The approximate flushing time of the system is 2–3 days (Sturley, 1990) but may be considerably longer during neap tides and dry weather or shorter during spring tides and heavy rain.

There are extensive intertidal sand and gravel beds (with some mud) at the mouth, and mud flats in the upper reaches. Above Barnstaple the estuary is dominated by freshwater, whilst the mid and lower reaches are usually influenced by coastal water, as shown in Fig. 2a. However, at low tide during high river flows, the freshwater plume can extend as far as site 5. The main freshwater inflow to the estuary is from the River Taw. Average annual rainfall in the Taw catchment is highest near the source on Dartmoor (~2200 mm) and below 940 mm at the river mouth (Haygarth et al., 2005). Precipitation is strongly seasonal and hence the River Taw has a distinct annual flow pattern with maximum mean flow in December (~40 m³ s⁻¹) and minimum flow in August (5 m³ s⁻¹). The type of soil and subsoil, and the low groundwater storage in the catchment, means that the river responds quickly to rainfall, with rapid rises in river levels (Environment Agency, 2000); over 95% of the catchment is covered by clay and clay loam soils (Lord et al., 2007). Although groundwater reserves are generally low, they do contribute to river base flows during dry periods (Haygarth et al., 2005).

About 75% of the catchment area is used for agriculture (59% grassland, 14% arable), 12% woodland and forest and 9% rough grassland (Williams and Newman, 2006). An estimated 77% of the grassland is used for beef cattle and sheep, whilst the remainder is used for dairy cattle (Lord et al., 2007). Given the low population density in the catchment, it can be assumed that most of the inorganic nutrient inputs originate from diffuse agricultural sources. The main point source of nutrients to the estuary is the sewage treatment works at Ashford, processing the sewage from the town of Barnstaple (pop. 46,000).

2.2. Data sources

Physical, chemical and biological water quality data for the Taw Estuary were collected by the EA for routine monitoring purposes and later adapted to the monitoring required under the ND and UWWTD. Sampling was undertaken from the six sites shown in Fig. 1 on a fortnightly to monthly basis over the period 1974–2004. In the upper estuary these were located at Newbridge (site 1) at the tidal limit, Little Pill (site 2) where the estuary forms a narrow channel and Barnstaple (site 3) where the estuary widens. The sample sites in the lower estuary were site 4 (Ashford STW) and site 5 (near RAF Base Chivenor), both surrounded by large intertidal sand flats, and site 6 (Airy Point) which is at the estuary mouth. Data on nutrient concentrations in the effluent of Ashford STW were also collected by the EA. Additional information on the annual loads of nutrients from the River Taw (calculated from Har-

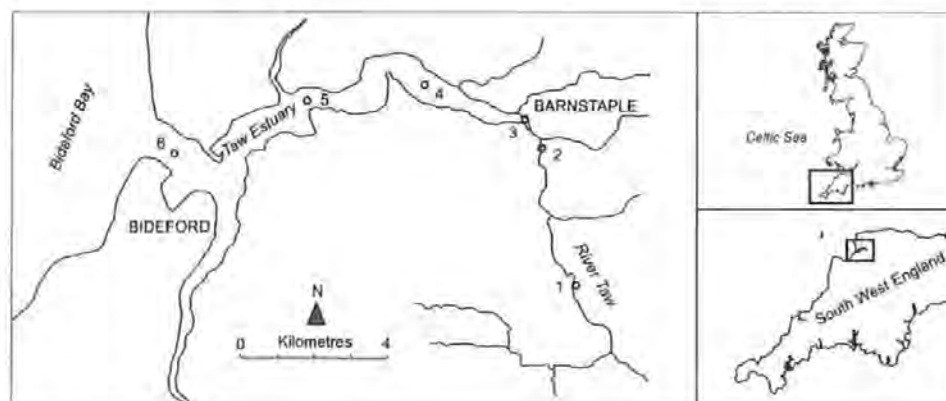


Fig. 1. Location map of the Taw Estuary. Circles represent Environment Agency water quality monitoring sites. (1) Newbridge; (2) Little Pill; (3) Barnstaple; (4) Ashford STW; (5) RAF Chivenor; (6) Airy Point.

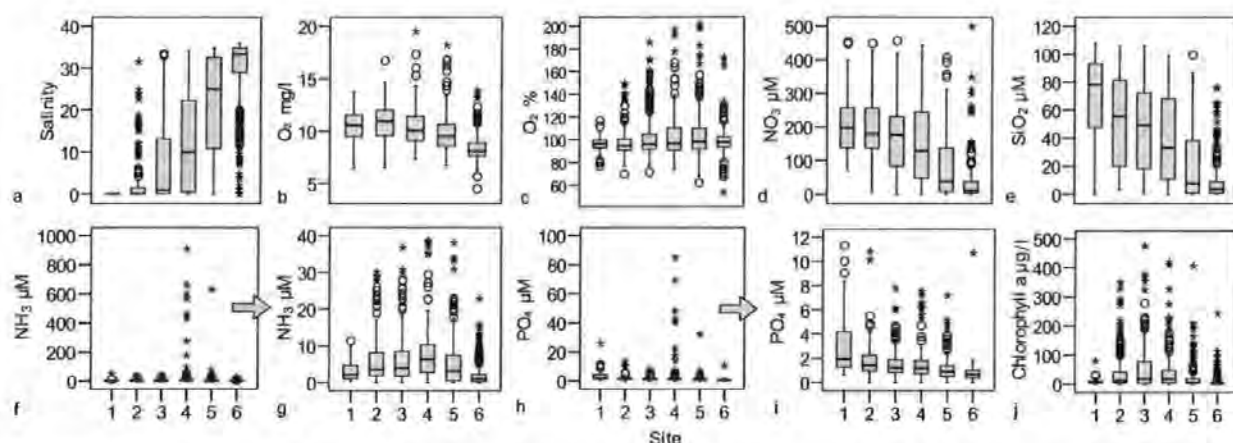


Fig. 2. Box plots of assessed estuarine variables at individual sample sites. Within the box are all observations between the first and third quartile (50% of total observations), the solid line inside each box is the second quartile (median). The whiskers represent $1.5 \times$ the interquartile range (IQR) from the box or, in the absence of values at the $1.5 \times$ IQR, the maximum and minimum value. Outliers are shown in open circles and are outside the $1.5 \times$ IQR, extremes are depicted as stars and are outside the $3 \times$ IQR.

monised Monitoring Scheme data) and other tributaries to the estuary were provided by the NERC Centre for Ecology and Hydrology (Wallingford, UK). The annual loads of nutrients from the STW were estimated by multiplying the average annual concentration of a given constituent in the effluent with the consented dry weather flow of $15,231 \text{ m}^3 \text{ d}^{-1}$.

2.3. Data pre-treatment

The routine monitoring data for the period 1974–2004 were subjected to a structured statistical treatment. The original dataset contained 3536 data rows from samples collected between April 1974 and December 2004 from ten sample sites. Four sample sites were excluded due to insufficient data. Similarly, data prior to 1990 were excluded from the analysis because of temporal patchiness. Algae blooms largely occurred between April and September (Fig. 3), and hence only data from these months were used for the correlation and regression analyses. Also, on several occasions, samples were collected along a depth profile. Only samples collected from the surface (0–1 m depth) were included in the analyses.

The remaining data were then amalgamated to give one coherent dataset which involved scanning the data for errors (e.g. obvious typing mistakes), merging of variables with multiple listings

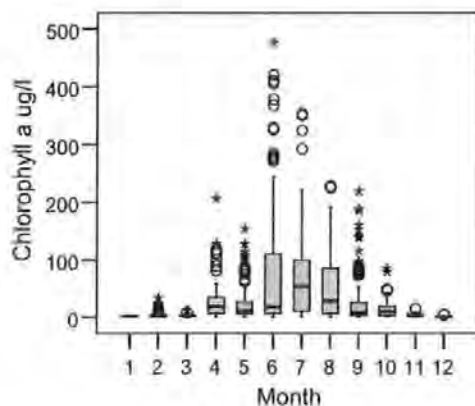


Fig. 3. Range of chlorophyll *a* concentrations for each month throughout the period 1990–2004. For detailed explanation of the box and whisker plots, see caption of Fig. 2.

into a single column and standardization of nutrient concentrations to micromoles per litre (μM). Concentrations of chemical parameters and chlorophyll *a* which were below the limit of detection ($< \text{LoD}$, 7.7% of the data) were converted into $\text{LoD}/2$ following the approach of Littlewood et al. (1998) in order to include as many data records as possible for graphical and statistical analysis. The STW data were treated in the same way. The final estuary data matrix, of which subsets were used for graphical and statistical analysis, contained 1793 data rows with 17,789 data points from the six sample sites. The following variables were used: water temperature ($^{\circ}\text{C}$), salinity (psu), ammonia ($\text{NH}_3 \mu\text{M}$), nitrate ($\text{NO}_3 \mu\text{M}$), phosphate ($\text{PO}_4 \mu\text{M}$), silicate ($\text{SiO}_2 \mu\text{M}$), chlorophyll *a* ($\mu\text{g L}^{-1}$), turbidity (NTU), dissolved oxygen concentration ($\text{O}_2 \text{ mg L}^{-1}$) and dissolved oxygen saturation ($\text{O}_2\%$). The same variables were extracted from the STW dataset. Loads were converted into t a^{-1} .

2.4. Statistical analyses

Cluster analysis has been successfully used on environmental datasets (e.g. Einax et al., 1998; Panda et al., 2006); its main advantage is that it reduces the amount of data which helps pattern recognition and the identification of trends in the dataset. This is achieved by grouping objects or data into subsets according to traits they have in common (i.e. their proximity) which are expressed by a measure of distance. For this study, the similarities between 10 variables of the Taw Estuary dataset have been assessed by performing a cluster analysis based on Euclidean distance, the appropriate distance measure for environmental data (Clarke and Warwick, 2001), using PRIMER 6 (PRIMER-E Ltd., 2006). Prior to the analysis, data rows with missing values were eliminated. Because the individual variables had different scales, all data were normalized by subtracting the mean from each entry for a single variable and dividing the difference by the standard deviation, following Clarke and Gorley (2006).

Correlation analysis was undertaken to identify the variables that covaried with chlorophyll *a* concentrations and to aid in the selection of variables suitable for the generation of a multiple regression model (see below). Non-parametric correlation (Spearman's ρ) was used, as none of the variables were normally distributed (Kolmogorov–Smirnov One-Sample Test). Significance of the correlation coefficients was tested at the $p < 0.01$ and $p < 0.05$ levels.

In order to estimate the degree of influence of individual variables on chlorophyll *a* concentrations, backward elimination mul-

multiple regression analysis was conducted for each sample site. The multiple regression models included all variables at the outset, with the advantage that the imposition of a user defined structure on the data was avoided. Using iteration, variables with the least significance were then eliminated until a heuristic best-fit model, which included the most significant variable(s), was achieved (i.e. all remaining variables were significant or only one variable was left). As a normal distribution of the dependent variable (here chlorophyll *a*) is one of the formal requirements for regression analysis, it was $\ln(x+1)$ transformed and normalized prior to the analyses. Normal distribution of the standardized residuals was confirmed using the Kolmogorov–Smirnov One-Sample Test. Both the non-parametric correlation analysis and the backward elimination regression analysis were conducted using SPSS 15.0 (SPSS Inc., 2006).

3. Results and discussion

3.1. Source contributions to the annual nutrient loads

In order to provide an overview of the importance of the main sources for individual nutrients in the estuary, a summary of inputs of nitrate, ammonia and phosphate over the study period

was compiled. The annual average river input of nitrate to the estuary was $2726 \text{ t a}^{-1} \text{ NO}_3\text{-N}$ during the period 1990–2004 (Fig. 4a), to which the River Taw contributed on average $1977 \text{ t a}^{-1} \text{ NO}_3\text{-N}$ (ca. 73%). The annual contribution of nitrate for the same period from the STW was $6\text{--}49 \text{ t NO}_3\text{-N}$ (mean = $16 \text{ t NO}_3\text{-N}$) and hence was relatively unimportant, contributing only 1–3% of the total nitrate load. Mean river inputs of ammonia between 1990 and 2004 were $33 \text{ t a}^{-1} \text{ NH}_3\text{-N}$, of which the River Taw contributed on average $24 \text{ t a}^{-1} \text{ NH}_3\text{-N}$ (Fig. 4b). The most significant source of ammonia was the Ashford STW, ranging from 42 to $135 \text{ t a}^{-1} \text{ NH}_3\text{-N}$, with a mean of $89 \text{ t a}^{-1} \text{ NH}_3\text{-N}$. On average, the STW contributed 74% of the annual ammonia load to the estuary. Of the total inorganic N (TIN) loading, nitrate is by far the most dominant species, comprising 95% of the total TIN load, followed by ammonia (4.4%) and nitrite (0.6%). On average, the river TIN load into the estuary, normalized to the catchment area, was $2278 \text{ kg km}^{-2} \text{ a}^{-1}$ which is higher than that in a moderately impacted catchment, defined by Hessen (1999) to have an export of $500\text{--}2000 \text{ kg N km}^{-2} \text{ a}^{-1}$.

The average annual $\text{PO}_4\text{-P}$ load to the estuary was 65 t a^{-1} (Fig. 4c), of which 71% was riverine (37 t a^{-1} from the Taw, 10 t a^{-1} from tributaries). Mean annual input of $\text{PO}_4\text{-P}$ from Ashford STW was 18 t (maximum 34 t in 1995), and the STW contributed 18–43% of the total $\text{PO}_4\text{-P}$ loading. The average P load (area normalized) from the Taw catchment was $39 \text{ kg km}^{-2} \text{ a}^{-1}$. This is very low when compared with the average P loads of UK catchments of $152 \text{ kg km}^{-2} \text{ a}^{-1}$ (Nedwell et al., 2002) and North Sea catchments of $117 \text{ kg km}^{-2} \text{ a}^{-1}$ (Howarth et al., 1996). For Si, the estimated average riverine load to the estuary was 1730 t a^{-1} , ranging from 973 t a^{-1} (2003) to 2473 t a^{-1} (1994), depending on river flow. These results supported the classification of the Taw Estuary under the ND and UWWTD and helped to identify priorities for nutrient stripping actions. However, when looked at on their own, the load data were not sufficiently resolved to evaluate the drivers of phytoplankton growth in the Taw Estuary.

3.2. Spatial and temporal distribution of salinity, nutrients and chlorophyll *a*

The highly dynamic character of the estuary is highlighted by the fact that all sites, apart from site 1, experienced the entire range of salinities over the lifetime of this dataset (Fig. 2a); high salinities at site 2 close to the tidal limit represent intrusions of coastal waters at high tide during times of low freshwater inflow whereas low salinities at site 6 are due to received freshwater input after high rainfall. The estuary was generally well oxygenated (Fig. 2b and c) with highest dissolved oxygen concentrations in the upper and central parts, decreasing towards the mouth, following reduced solubility of oxygen with increasing salinity. Sites 3, 4 and 5 experienced super-saturation of dissolved oxygen (Fig. 2c), with values exceeding 150% during periods of high algal biomass.

Nitrate and silicate showed highest concentrations at the freshwater limit, which then decreased with increasing salinity towards the mouth (Fig. 2d and e), i.e. these constituents exhibited conservative behaviour. As the main source of nitrate and silicate is the catchment, their estuarine concentrations correlated well with freshwater inflow (0.49 and 0.43 at $p < 0.01$). Ammonia concentrations (Fig. 2f and g) were highest, and showed greatest variability, at site 4 near the STW outlet. Here they regularly exceeded $20 \mu\text{M}$, strongly indicating the importance of the STW discharge as a source of ammonia. Median phosphate concentrations were highest at the freshwater limit (site 1) and decreased towards the mouth; nevertheless, the highest concentrations were observed at site 4, suggesting significant inputs from the STW (Fig. 2h and i). Estuarine molar TIN:P ratios showed a high degree of variability between individual sites with means ranging from 50 at the mouth to 150 in the middle and upper estuary and generally exceeded the

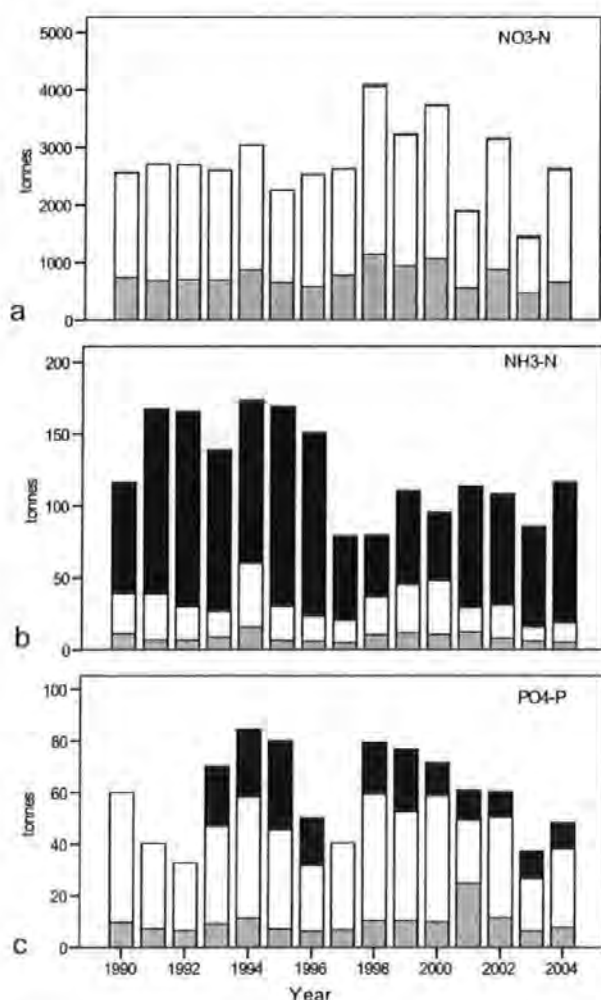


Fig. 4. Estimates of annual loads in tonnes of nutrients into the estuary: (a) nitrate (no STW data for 1997), (b) ammonia, (c) phosphate (no STW data for 1997 and 1990–1992). Black = STW, white = River Taw, grey = other rivers.

Redfield ratio of 16 (Redfield et al., 1963). Similarly, N:Si ratios in the upper estuary, with means between 5 and 7, were considerably higher than the Redfield ratio for N:Si of 1 and much higher than that for pristine estuaries (Justić et al., 1995). N:Si ratios increased towards the mouth, with means from 10 to 16. Similar ratios have been reported for the Great Ouse Estuary (UK), and these have been attributed to high nitrate inputs from its agriculturally dominated catchment (Sanders et al., 1997). N:P ratios are usually higher in freshwater than in seawater (Elser and Hassett, 1994; Hecky et al., 1993) and will therefore show a degree of fluctuation in estuaries, but it is known that large deviations from the Redfield ratio under nutrient limiting conditions can change the composition of the phytoplankton community and favour harmful species (Anderson et al., 2002).

In total, 1432 chlorophyll *a* measurements were made, of which 916 were from the main growth period (April–September). The highest median concentrations of chlorophyll *a* occurred during summer months (June–August, Figs. 3 and 5a) at sites 3 and 4, and to a lesser extent at site 2 (Fig. 2j). Chlorophyll *a* levels were also highest during low and intermediate river flows ($<5 \text{ m}^3 \text{ s}^{-1}$) from the River Taw (Fig. 5b) and at low to intermediate salinities (Fig. 5a and b). OSPAR assessment criteria (OSPAR Commission, 2003) listed chlorophyll *a* concentrations above $15 \mu\text{g L}^{-1}$ as undesirable and this threshold was exceeded by 49% of the samples during the main growth period and in 34% of the overall dataset. Chlorophyll *a* concentrations in estuaries exceeding $40 \mu\text{g L}^{-1}$ were considered to be high (Bricker et al., 2003) and this value was exceeded in 19% of the all-year dataset. During the period covering May–September, $40 \mu\text{g L}^{-1}$ was exceeded in 28% of the dataset. In 12% of the dataset during the main growth period between

1990 and 2004, chlorophyll *a* concentrations exceeded $100 \mu\text{g L}^{-1}$, a threshold level which Tett (1987) has used to define the presence of phytoplankton blooms. Outside the main growth period, the $100 \mu\text{g L}^{-1}$ threshold was not exceeded.

3.3. Cluster analysis

After elimination of data rows with missing values from the initial 1793 rows, 6900 data points in 460 rows (26%) remained for cluster analysis. In the dendrogram (Fig. 6) three main branches could be identified:

- (i) The 'catchment branch' with the variables River Taw flow, turbidity, nitrate and silicate.
- (ii) The 'STW branch' with the variables ammonia and phosphate.
- (iii) The 'phytoplankton branch' including the variables chlorophyll *a*, water temperature and dissolved oxygen.

The 'catchment branch' was notably influenced by rainfall and its effects. Turbidity becomes higher as river flow increases, probably following increased sediment remobilisation. Nitrate and silicate inputs into the estuary are also dependent on rainfall (and therefore flow) in the catchment (Section 3.1).

Salinity, represented by a fourth branch, showed maximum separation from the variables on the 'catchment branch'. Salinity would be expected to be situated on the 'catchment branch' as it is to an extent dependent on rainfall in the catchment. The numerical association between the other variables from the 'catchment branch' is positive, whereas salinity has a negative association with

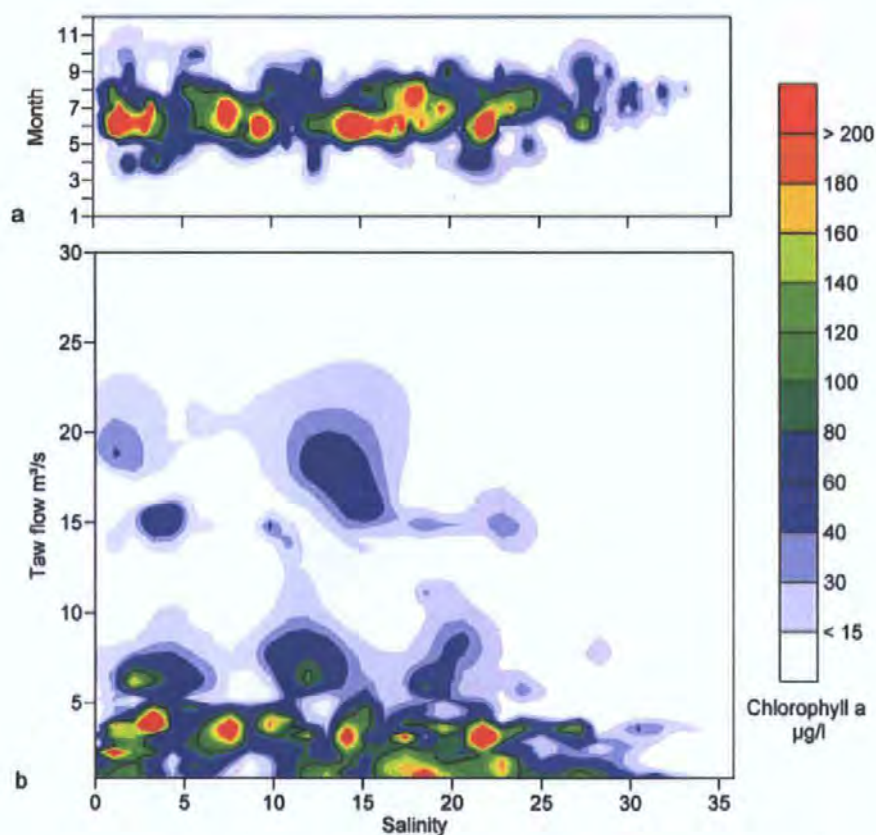


Fig. 5. Contour plots of chlorophyll *a* concentration as a function of (a) salinity and month ($n = 725$) and (b) salinity and river flow ($n = 1285$). The solid line indicates $100 \mu\text{g L}^{-1}$ of chlorophyll *a*.

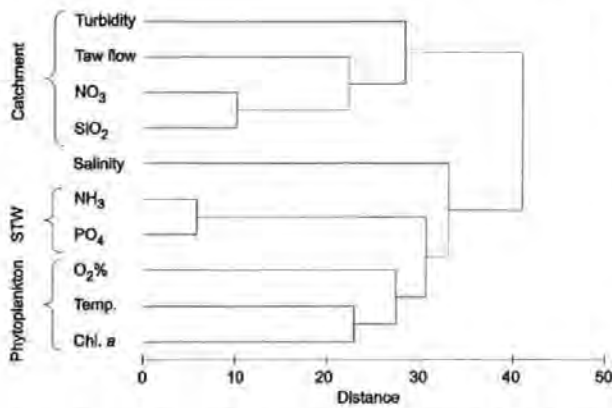


Fig. 6. Dendrogram showing the Euclidean distance between individual variables ($n = 460$ data rows).

these variables (i.e. high rainfall corresponds with high sediment and nutrient loads but with low salinity in the estuary due to increased dilution by freshwater and *vice versa*) which in turn creates maximum numerical separation.

The 'STW branch' consists of phosphate and ammonia and is located closer to the 'phytoplankton branch' than to the 'catchment branch'. For both of these nutrients the STW was an important source to the estuary.

The 'phytoplankton branch' showed variables that were particularly associated with primary production. High chlorophyll *a* concentrations occurred during the summer months when water temperatures were highest. The proximity of oxygen saturation and chlorophyll *a* is related to photosynthetic oxygen release during periods of high algal biomass.

3.4. Non-parametric correlation and backward elimination regression analysis

Throughout the estuary, various chemical and physical variables experience strong gradients from the tidal limit to the mouth. The waters in the upper reaches close to the tidal limit were of low salinity, concentrations of catchment borne nutrients were high and water residence times were likely to be short. In the central part of the estuary, water residence times were longer and tidal influences were strong, resulting in large variations in salinity, strong tidal currents and high turbidity. Also, the outflow of the STW discharged into this part of the estuary with resulting high concentrations of ammonia and phosphate. Closer to the mouth, the estuary is wider and the water mass was largely derived from coastal inflow of saline water with comparatively low nutrient concentrations. Due to these gradients, the individual variables (i.e. ecological factors) exhibit a different degree of influence on algal growth at each sample site. For these reasons, a single statistical model incorporating all sample sites cannot be expected to describe the actual interrelationship between a variable and algal biomass. Therefore, the data for the correlation and regression analyses were split into six subsets, one for each site. Due to an insufficient amount of data for site 1 (Table 1), none of the correlations with chlorophyll *a* were significant and therefore site 1 is not discussed further. The negative influence of high river flow on algal growth is evident from the negative correlations between river flow and chlorophyll *a* at the upper and central sites 2–4, where high river flow reduced water residence times significantly, resulting in down-estuary flushing of suspended algae after rainfall in the catchment. River flow was less important in the wider outer estuary, where the larger volume of water led to longer residence

times and the algae remained *in situ* longer. The negative correlations of nitrate and silicate with chlorophyll *a* in the upper estuary are consistent with this interpretation, as both of these nutrients were sourced mainly in the catchment and the inflowing freshwater was their main path into the estuary. In the outer estuary, nitrate and silicate correlated positively with chlorophyll *a*. There, water residence times were long enough for the phytoplankton to respond to an increase in concentrations of nutrients by increasing biomass. The correlation of temperature with chlorophyll *a* decreased from site 2 to site 6, again reflecting the influence of the catchment, where the temperature variation during summer was much higher in terrestrial runoff and shallow, semi-enclosed sections of the upper estuary than in coastal waters. The highest chlorophyll concentrations occurred at low to intermediate salinities (Fig. 5b) where inorganic nutrients were present at higher concentrations than in coastal seawater, which the correlation analysis confirmed; salinity *versus* chlorophyll *a* had a positive *rho* at the more freshwater influenced sites 2–4 and became negative at the sites 5 and 6 where marine influence was stronger.

The two variables ammonia and phosphate, both located on the 'STW branch', had similar results in the correlation analysis. The negative correlation coefficients of ammonia with chlorophyll *a* at sites 3 and 4, where ammonia concentrations were highest, suggested that phytoplankton growth was to an extent inhibited by high ammonia concentrations, i.e. highest chlorophyll *a* concentrations at sites 3 and 4 only occurred when ammonia concentrations were relatively low. Planktonic algae normally prefer ammonia to nitrate (Cochlan and Harrison, 1991; Conway, 1977) as ammonia is the energetically favourable form of N for amino acid synthesis. However, Dugdale et al. (2007) reported for San Francisco Bay that ammonia concentrations $>4 \mu\text{M}$ inhibited nitrate uptake by phytoplankton and that plankton growth rates were also slowed. Only when ammonia concentrations fell below $4 \mu\text{M}$ was nitrate metabolized, resulting in much higher phytoplankton growth rates. A similar relationship between ammonia and nitrate was observed by Dugdale and Hopkins (1978) in the Gulf of Saronikos (Greece), with the elevated concentrations of ammonia resulting from sewage discharges. Ammonia concentrations were considerably lower at sites 2, 5 and 6 (Fig. 2g), presumably due to dilution by freshwater from the catchment or inflowing coastal water, coupled with smaller inputs in these regions. At these sites ammonia was positively correlated with chlorophyll *a* and thus did not appear to inhibit nitrate-induced accelerated growth; indeed it would have contributed to the bioavailable N pool. The values of the correlation coefficients for phosphate with chlorophyll *a* and ammonia with chlorophyll *a* were similar, and were probably an artificially created signal by the inputs from the STW where phosphate followed the same temporal input pattern as ammonia, rather than the actual interaction of phosphate with phytoplankton. A linear regression of ammonia and phosphate concentrations from site 4 gave an r^2 of 0.68 over the entire range of concentrations and an r^2 of 0.40 (Fig. 7) after outliers ($\text{NH}_3 > 20 \mu\text{M}$, $\text{PO}_4 > 4 \mu\text{M}$) were removed. The two variables were also closely associated in the cluster analysis. The correlation analysis also revealed some of the effects from high algal biomass and photosynthetic activity: dissolved oxygen saturation had a positive *rho* with chlorophyll *a* throughout the estuary with the exception of site 6, where the correlation for dissolved oxygen saturation with chlorophyll *a* was not significant. Light limitation could not be examined with the available data; indeed, turbidity correlated positively with chlorophyll *a* (except at site 4) and turbidity appeared to be following high phytoplankton densities in the water column rather than suspended sediment.

Following the results of the correlation analysis, key variables were selected for the stepwise regression analysis. The two prerequisites were that a variable was correlated at one or more sites

Table 1
Correlation coefficients (Spearman's ρ) of individual variables with chlorophyll *a* concentrations. Figures of significant correlations at $p < 0.01$ are bold, and at $p < 0.05$ underlined (Temp. = temperature, Turb. = turbidity).

| Site | | Taw flow | Temp. | Salinity | Turb. | NO ₃ | SiO ₂ | NH ₃ | PO ₄ | O ₂ % |
|------|----------|--------------|--------------|--------------|-------------|-----------------|------------------|-----------------|-----------------|------------------|
| 2 | ρ | -0.65 | 0.52 | 0.68 | 0.51 | -0.63 | -0.53 | 0.35 | 0.22 | 0.28 |
| | <i>n</i> | 114 | 95 | 96 | 96 | 82 | 71 | 96 | 96 | 92 |
| 3 | ρ | -0.59 | 0.58 | 0.43 | 0.33 | -0.53 | -0.45 | -0.29 | -0.12 | 0.62 |
| | <i>n</i> | 141 | 123 | 123 | 123 | 104 | 93 | 123 | 123 | 119 |
| 4 | ρ | -0.50 | 0.44 | 0.41 | 0.24 | -0.48 | -0.33 | -0.47 | -0.43 | 0.66 |
| | <i>n</i> | 115 | 97 | 97 | 97 | 76 | 64 | 97 | 97 | 93 |
| 5 | ρ | -0.10 | 0.29 | -0.39 | 0.53 | 0.23 | 0.19 | 0.23 | 0.23 | 0.44 |
| | <i>n</i> | 150 | 132 | 132 | 132 | 110 | 96 | 132 | 132 | 127 |
| 6 | ρ | 0.00 | -0.02 | -0.64 | 0.43 | 0.45 | 0.43 | 0.19 | 0.25 | 0.13 |
| | <i>n</i> | 133 | 130 | 128 | 131 | 105 | 78 | 131 | 131 | 130 |

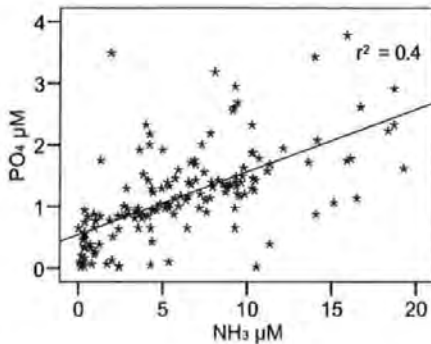


Fig. 7. Scatter plot of ammonia versus phosphate concentrations at site 4 after outliers ($\text{NH}_3 > 20 \mu\text{M}$, $\text{PO}_4 > 4 \mu\text{M}$) were removed.

with chlorophyll *a* and that there was reasonable certainty that a variable determined chlorophyll *a* concentrations and not vice versa. This led to the exclusion of two variables, dissolved oxygen saturation and turbidity. The variables then used for generating the regression models were river flow, temperature, salinity, nitrate, silicate, ammonia and phosphate. The models from the backward elimination regression analysis (Table 2) explained 26–49% of the variation in chlorophyll *a*, except the model for site 4, which only explained 13% of the variation. All models contained either freshwater inflow, salinity or both. This underlines the importance of

Table 2
Model summaries obtained from backward eliminating multiple linear regression analysis (p = probability, b = slope).

| | p | b | r^2 |
|------------------|-------|--------|-------|
| Site 2 | | | |
| Salinity | 0.012 | 0.051 | 0.49 |
| PO ₄ | 0.067 | 0.081 | |
| SiO ₂ | 0.093 | -0.007 | |
| Flow | 0.001 | -0.092 | |
| Site 3 | | | |
| Flow | 0.000 | -0.134 | 0.38 |
| Site 4 | | | |
| Flow | 0.002 | -0.064 | 0.13 |
| Site 5 | | | |
| Salinity | 0.000 | -0.054 | 0.40 |
| NH ₃ | 0.004 | -0.018 | |
| PO ₄ | 0.006 | 0.350 | |
| SiO ₂ | 0.000 | -0.023 | |
| Temperature | 0.000 | 0.099 | |
| Site 6 | | | |
| Salinity | 0.000 | -0.084 | 0.26 |
| SiO ₂ | 0.013 | -0.025 | |

river flow for algal growth throughout the estuary. Freshwater inflow was significant in the models for the sites 2–4. The negative slopes in all cases were consistent with the inverse relationship between river flow and phytoplankton biomass in the upper, narrow channel of the estuary. Under intermediate or high riverine flow, phytoplankton is flushed down-estuary from these sites. The positive slope of salinity for site 2 confirmed this, as medium and high salinities in this part of the estuary only occurred during low river flow when water residence times were longest. Salinity also contributed to the models for sites 5 and 6 but had negative slopes in these instances; given sufficient residence times in the outer estuary, phytoplankton biomass is higher in the presence of nutrient rich estuarine water than in low nutrient (but euryhaline) coastal water that advances into the estuary with the incoming tide. Silicate was included in the models for sites 2, 5 and 6; its slopes indicated covariability with freshwater flow. Phosphate was significant in the models for sites 2 and 5 and two other variables were only significant in the model for site 5; ammonia, and water temperature (due to its direct influence on algal growth). Their significance should therefore be treated with caution and interpreted together with the results from the correlation analysis.

The correlation analysis provided insight into the interactions between key variables and chlorophyll *a* and how these interactions changed along the estuary at different sample sites. It also facilitated identification of the appropriate variables for use in the backward elimination regression. However, the results of the correlation analysis did not allow unequivocal conclusions about the importance (i.e. the predictive power) of a variable for algal growth. This was done by looking at the best-fit models (i.e. the model with the highest predictive power) generated by the backward elimination regression analysis. Throughout the estuary (with the exception of site 4) these were salinity and/or river flow, both variables related to physical rather than biogeochemical processes.

4. Conclusions

The monitoring data clearly showed that the Taw Estuary was highly eutrophic during the summer months with concentrations of chlorophyll *a* regularly exceeding $100 \mu\text{g L}^{-1}$ over the period 1990–2004. The data revealed two important regulators of bloom dynamics in the estuary; ammonia inhibition and the flow regime of the River Taw. Ammonia inhibited nitrate uptake at site 4, near the outlet of the STW, which prevented algal biomass from reaching the maximum achievable level under ambient nitrate concentrations. The influence of the River Taw was strongest in the upper reaches of the estuary at sites 2 and 3 and to a lesser extent at site 4; low freshwater inflow resulted in relatively long water residence times, allowing the phytoplankton to reproduce in the mid and upper estuary under nutrient replete conditions. Under intermediate flow, algal growth continued in the outer estuary,

whereas with high flows, nutrients were flushed into the adjacent coastal waters. This negative correlation of river flow and nitrate input with phytoplankton biomass is the opposite to what has been observed in large estuaries with relatively long water residence times, such as the Neuse River Estuary, North America, where primary production correlated positively with river flow and nitrate loads (Mallin et al., 1993). Therefore conclusions that are true for one estuary may not be applicable or correct in a different system.

The applied approach has demonstrated the value of data mining of historical monitoring datasets and shown that it is possible to use archived estuarine datasets from the EA to good effect, particularly after several datasets have been combined (EA estuarine and STW data, data from the Harmonised Monitoring Scheme and the National River Flow Archive). This is true even when the datasets were originally collected for different purposes than they were used for in this paper. However, it is evident that substantial data mining and structured data editing of disparate datasets is necessary. The application of easy to use and proven statistical treatments for environmental datasets provided considerable added value to the data: it facilitated a systemic (although not comprehensive) view of eutrophication processes in the Taw Estuary when compared with mere descriptive approaches such as graphical representations.

The insights also outline potential future problems in the Taw with algal blooms and their management. Given the importance of low river flow for phytoplankton growth in the estuary, climate change has a significant potential to severely exacerbate eutrophication events; e.g. Arnell and Reynard (1996) predicted an increase in the seasonality of the annual river flow for the River Tamar (a catchment adjacent to the Taw catchment) together with an average reduction in summer flow of 25% by 2050 with extremes >50% lower under one scenario. The implications of increased chlorophyll concentrations following rising water temperatures, similar to what has been observed in the North Sea (McQuatters-Gollop et al., 2007), could further aggravate the trophic status of the Taw and other nutrient rich estuaries in the region.

The management of current ammonia inputs to the estuary should be carefully assessed; paradoxically, increased ammonia nitrification capacity in the STW, leading to reduced ammonia concentrations in the vicinity of the effluent outlet, may not improve, but actually worsen the trophic situation in the Taw Estuary if there is no reduction in overall N and P inputs. However, ammonia concentrations at site 4 were repeatedly in the range of acute toxicity for marine animals (6–250 µM, depending on species; Eddy, 2005) which is not in line with the requirements for 'good ecological quality' under the EU WFD. These factors clearly need to be reconciled if environmental impact is to be minimised.

The value of current and future monitoring actions would be increased by including data on (i) dissolved organic N (DON), dissolved organic P (DOP) and dissolved organic carbon (DOC) in future surveys and (ii) by conducting targeted high temporal resolution studies.

- (i) DON originates mostly from regenerated N within a system (e.g. phytoplankton and zooplankton excretion, microbial processes) and it has been shown that in some instances DON (especially urea) is preferred over dissolved inorganic N (DIN; Twomey et al., 2005) and that it has a significant impact on algal growth (Glibert et al., 1991; Twomey et al., 2005). Also, the ratio of dissolved organic carbon to dissolved organic N (DOC:DON) has been related to HABs (Anderson et al., 2002). However, currently available data for the Taw Estuary do not allow any conclusions to be drawn about the role of dissolved organic nutrients in the

system which leads to a considerable gap in the understanding of the quantitative importance of DON as a N source for phytoplankton. Given the importance of nutrient stripping for eutrophication mitigation under the ND and UWWTD, the absence of DON data for the estuary and its tributaries leads to considerable uncertainty about the significance of such measures. Further, in many waters, the DOP fraction is at least as abundant as the dissolved inorganic P (DP) fraction and represents a potentially bioavailable pool of P but its quantification has been traditionally ignored in favour of DP (e.g. Worsfold et al., 2008; Monbet et al., 2009).

- (ii) The data used for this paper were collected on a fortnightly to monthly basis and only provided snapshots of the estuary. Monitoring the estuary on a much higher temporal resolution over several weeks in summer would allow gradual changes in nutrient concentrations and phytoplankton successions to be observed and documented over the course of bloom formation. This would help to identify the causes of algal bloom formation and the associated nutrient biogeochemistry with increased certainty, information that is essential for the efficient management of estuarine eutrophication. Such high frequency sampling campaigns have been applied to other systems, with good success, to elucidate species succession and the regulating processes of algal blooms (e.g. Rantajärvi et al., 1998; Wang et al., 2006).

With regard to the ND and the UWWTD (and to a lesser extent also for the WFD) it is clear that following status monitoring only may not always be sufficient to provide the required information to support adequate management decisions for achieving the Directive's goal. It is necessary to have a sound understanding of a particular estuary because the drivers of eutrophic symptoms are complex and often very specific to that estuary.

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**THE TAW RIVER CATCHMENT AND ESTUARY:
A CASE STUDY FOR THE EFFECTS OF NVZ MEASURES**

Investigating the Effectiveness of NVZ Action
Programme Measures: Development of a Strategy for
England

Defra contract NIT 18

ADAS reference DWC3400

Report by CEH and University of Plymouth

**The Taw River Catchment and Estuary: A case study
for the effects of NVZ measures**

Part 2 – The Estuary

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13th February 2007

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Executive Summary

The estuary of the River Taw (North Devon) and its freshwater catchment has been designated as an NVZ on the basis that its estuary is eutrophic. The Taw Estuary is 23 km in length, extending from its tidal limit at Newbridge to its mouth at Crow Point. The estuary is macro-tidal, with a flushing time of 2-3 days, depending on river flows. There are extensive inter-tidal sand and gravel beds (with some mud) at the mouth, and mud flats in the upper reaches. Above Barnstaple the estuary is freshwater dominated, whilst the mid and lower reaches are dominated by coastal water. The largest tributary to the estuary is the River Taw, as outlined in Part 1 of this report. The type of soil and subsoil, and the low groundwater storage in the catchment, means that the river responds quickly to rainfall, with rapid rises in river levels i.e. it is flashy in nature. Although groundwater reserves are generally low, they do contribute to river base flows during dry periods.

The aim of this work was to examine how the current trophic status of the Taw Estuary may change in response to the implementation of NVZ Action Programme Measures in the catchment of its main freshwater source, the River Taw. Details of these measures have been described in Part 1 of this report.

The assessment for the estuary was undertaken by interrogating two datasets;

1. Estimates of inputs of the nutrients nitrogen and phosphorus to the estuary from river inflow and direct discharges (see Part 1 of this report).
2. Estuarine water quality measurements undertaken from 1990-2005 by the Environment Agency (EA) within the Harmonised Monitoring Scheme (HMS).

These data were used for several analyses which were designed firstly to estimate the trophic status of the Estuary from 1990 – 2004 at six sites from Newbridge (freshwater) to Airy Point at the mouth of the estuary and, secondly, to assess the factors influencing the trophic status of the estuary. The analyses were:

- An assessment of the spatial and temporal (monthly) distribution of chlorophyll a concentrations across the six sites.
- An estimation of the annual inputs (expressed as $t a^{-1}$ and %) of nitrate, ammonium and phosphate to the Taw Estuary from the River Taw, other rivers and the Ashford sewage treatment works (STW).
- Comparison of the average annual concentrations ($\mu mol/l$) of ammonia, phosphate and nitrate in the effluent of Ashford STW.
- Calculation of the molar ratio of nitrogen to phosphorus for the complete temporal dataset at each of the six sites.
- An assessment of the effect of river flow (high, medium and low) on the chlorophyll a concentrations at each of the six sites.
- Principal component analysis of the data to investigate interactions between key variables (chlorophyll a, nitrate, ammonium, phosphate, N:P ratio, ammonium:nitrate ratio and salinity).

Little is known about how small, well-mixed estuaries with short residence times, such as the Taw, respond to variations in nutrient loading. In particular, how do physical and biological processes control nutrient concentrations, and how do such systems respond to changes in catchment run-off and inputs?

Inputs of TIN to the Taw Estuary are dominated by rivers (90 %), with the River Taw the largest contributor (65-70 %). Modelling studies under current NVZ APM (see part 1 of this report) predict decreases in inputs from the River Taw of ca 10 % between September and May, but only 1.9 % from June to August.

The high ($> 100 \mu\text{g L}^{-1}$) concentrations of chlorophyll *a* observed during June to August and the high TIN:P ratios in the River Taw and the estuary strongly suggest that reductions in N export from the catchment due to NVZ APM will have little impact on the trophic status of the estuary. Furthermore, under low river flow conditions, concentrations of chlorophyll *a* in the estuary are mainly governed by inputs of ammonium and phosphate from the Ashford STW.

Any reduction in nitrate loads is unlikely to have a significant impact on algal growth in the upper and middle estuary as nitrate concentrations in the water column are still high enough to allow maximum uptake rates by phytoplankton for most of the spring and summer period.

It is important to emphasise that any legislative drivers may require a significant period before having a positive, observable effect. For example, the Danish Action Plan measures, which went beyond the requirements of the Nitrates Directive, appear to show that the response time of Denmark's estuarine and coastal waters is longer than 10 years and they may be experiencing the historical legacy of past nutrient inputs (stored in sediments).

Any assessment of estuarine eutrophication should take account of all potentially bioavailable nutrients, including organic forms of N and P. This study suggests that ammonia mostly overrides nitrate, particularly under low flow conditions and in the upper estuary. Nitrate appears to play only a certain role under intermediate flow conditions in the lower reaches of the estuary when ammonia concentrations drop due to dilution effects. However, the dataset did not contain information on DON which leaves some uncertainties about the role of regenerated nitrogen within the studied system. For nitrogen, actions required to reduce fluxes from the catchment should also consider atmospheric deposition.

In summary, the Taw Estuary system has the potential to respond relatively quickly to reductions in nutrient inputs. Reduced inputs of nutrients from the catchment would, if sufficient, lead to an improved trophic status within the estuary. The NVZ APM would not appear to be sufficiently stringent to bring such a change about. Beneficial changes to the trophic status of the estuary are also likely to be impeded if other nutrient inputs, particularly from Ashford STW, but also possibly from the atmospheric deposition of nitrogen to the catchment, are not controlled. In terms of management decisions, it should be emphasised that point sources are easier to control than diffuse inputs.

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**SURFACE NUTRIENT CONCENTRATIONS AND
PHYTOPLANKTON BIOMASS IN THE BALTIC SEA:
A SUMMARY OF THE BFU 2006/7 CRUISES**

BFU RESEARCH BULLETIN



№ 10, 2008



A facility of the UNESCO/IOC



Surface nutrient concentrations and phytoplankton biomass: a summary of the BFU 2006/7 cruises

Ekaterina Kochetkova¹, Gerald Maier²

Introduction

The Baltic Sea is a semi-enclosed water body currently under intense pressure from the human activities on the water and in the catchment. Among the most significant of these pressures is eutrophication, in which high nutrient loads lead to excessive algal growth and imbalanced functioning of the ecosystem. Around 75% of nitrogen and 95% of phosphorus is reported to enter the Baltic Sea through riverine or direct waterborne. The aim of this cruise report is to summarize and relate data on surface nutrient concentrations and phytoplankton biomass obtained during the Baltic Floating University (BFU) cruise on the Baltic Sea during July and August 2007. Also, the current dataset will be compared to data obtained along the same transect during the BFU cruise in July 2006.

For this summary, a subset of nutrient and phytoplankton data from 11 stations (Figure 1), sampled during summer 2006 and 2007 were used. For details about the methods for nutrient and phytoplankton analysis, see the appropriate chapters in this volume.

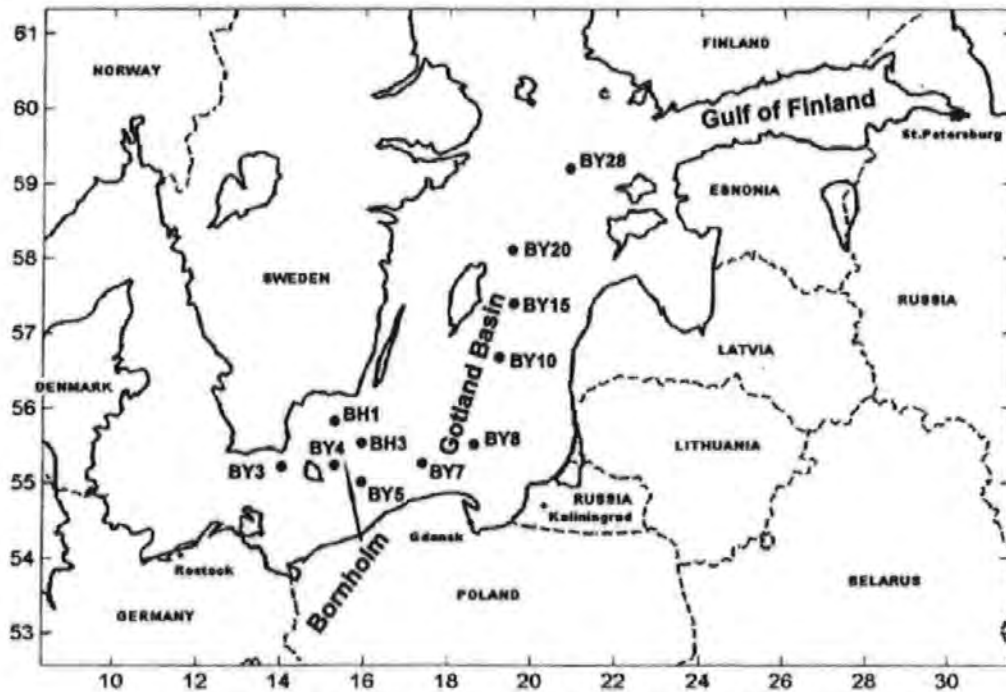


Figure 1. Baltic Sea: position of the stations sampled during the BFU 2006 and 2007 cruises.

Results

Sea surface temperature and salinity

Sea surface temperatures for 2007 (Figure 2) were in the order of about 15 °C for most of the western and central stations and increased to above 16 °C at the north-eastern stations (BY15, BY20, BY28). When 2007 temperature data were compared to 2006, it can be seen that sea surface temperatures were considerably higher in 2006 (on average by 4.2 °C) but showed a drop after station BY10, approaching 2007 levels at site BY20 where the difference was only 0.3 °C. The salinity in the Baltic is low due to limited exchange with the North Sea. During the 2007 survey it was highest at station BH3 (7.57), and decreased gradually to 6.63 at station BY28. In summer 2006, the recorded salinity was highest at station BY4 (7.52) and lowest at BY28 with 5.92.

Nutrient concentrations

Surface concentrations of Nitrate (NO_3) during summer 2007 (Figure 3) were generally below $0.1 \mu\text{M}$ with an average of $0.5 \mu\text{M}$. Concentrations were highest in the western and central parts of the transect between

the stations BY5 and BY8 and dropped considerably further north. Nitrite (NO_2) concentrations in the western part of the transects were mostly below the limit of detection; at station BY10 and the further northern stations, NO_2 was in the magnitude of around $0.05 \mu\text{M}$. Surface phosphate (PO_4) concentrations ranged between $0.07 \mu\text{M}$ (BY4) and $0.18 \mu\text{M}$ (BH1). PO_4 concentrations did not show a clear pattern along the transect. The average atomic N:P ratio ($[\text{NO}_3 + \text{NO}_2] : \text{PO}_4$) was 0.7, ranging from 1.1 (BY8) to <0.1 (BH1), indicating that the system was strongly N limited during Summer 2007. Silicon (Si) concentrations were considerably higher than those of the other inorganic macronutrients. No data were obtained for the stations BY3, BH1 and BY4, but at the other stations, Si concentrations exceeded $11 \mu\text{M}$: they were highest at the western (BH3, BY5) and easternmost stations (BY20, BY28) and showed decreasing values towards BY8 and BY10 in the southern Gotland Basin.

2006 concentrations of PO_4 and Si (Figure 3) were generally lower than in 2007. Whereas there appeared to be little similarity for Si between the two years, PO_4 showed in both years a peak at BH1 and a dip at BY4. NO_3 showed for both years maximum concentrations at station BY8 in the southern Gotland Basin and minimum concentrations at station BH1 in the Bornholm Basin. NO_2 concentrations in 2006 were for most stations above those of 2007 with the exception of stations BY20 and BY28. For the 2006 dataset, the average N:P ratio was 1.6, ranging from 0.2 to 3.7, again indicating strong N limitation.

Phytoplankton biomass

In 2007, the averaged total phytoplankton biomass was 315 mg m^{-3} , ranging from 82 mg m^{-3} at station BH1 to 953 mg m^{-3} at station BY15. Phytoplankton biomass (Figure 4) was strongly dominated by cyanobacteria (cyanophyta), particularly at the stations BY3, BY8, BY15 and BY20. At 7 out of 11 stations, cyanobacteria contributed to more than 50% of the total biomass. The second most important group where the cryptomonads (cryptophyta), which on average contributed 9% to the total biomass, followed by dinoflagellates (dinophyta) with 8%, chlorophyta with 6% and diatoms (bacillariophyta) with 3%. The average proportion of "other", not identified phytoplankton of the total biomass was 14%. None of the groups showed an evident pattern of distribution along our transect. For the 2006 survey, the average phytoplankton biomass was 330 mg m^{-3} , ranging from 130 mg m^{-3} at station BY5 to 776 mg m^{-3} at station BY4. When 2007 data of relative biomass were compared to 2006 data, cyanobacteria were still the dominant group (59% of total biomass) at all stations except BY4, where diatoms were with 49% the most abundant group. In the 2006 dataset, diatoms were the second largest contributor to total biomass, averaging 16%. Their maximum was at stations around Bornholm, declining towards the more north-eastern stations. Dinoflagellates contributed on average 10%, cryptomonads 6% and chlorophytes 3% to the total biomass at each station. None of these groups showed a distinct distribution pattern but their relative contributions to the total biomass in 2006 compared well with the 2007 data. 6% of the total biomass consisted of "other" phytoplankton.

Non-parametric correlation

When data on phytoplankton biomass were related to temperature, salinity and nutrient concentrations using non parametric statistics (Spearman's c), the 2007 data (Table 1) showed only 7 significant correlations in total of which only 2 related phytoplankton biomass to physicochemical parameters: the correlation coefficient between diatom biomass and NO_3 was 0.57 ($p < 0.1$) and -0.65 ($p < 0.05$) between chlorophytes and PO_4 . The 2006 dataset showed more significant correlation coefficients (16) of which 7 could relate phytoplankton biomass to physicochemical parameters (Table 2). Salinity correlated with diatom biomass (0.73, $p < 0.05$), chlorophyte biomass (-0.78 , $p < 0.05$) and biomass of other groups (-0.84 , $p < 0.05$). Of the inorganic nutrients, Si correlated positively with the biomass of chlorophytes and "other" phytoplankton (0.58 and 0.55, for both $p < 0.1$) and PO_4 had a negative c with cyanobacterial biomass (-0.59 , $p < 0.1$). NO_2 had a

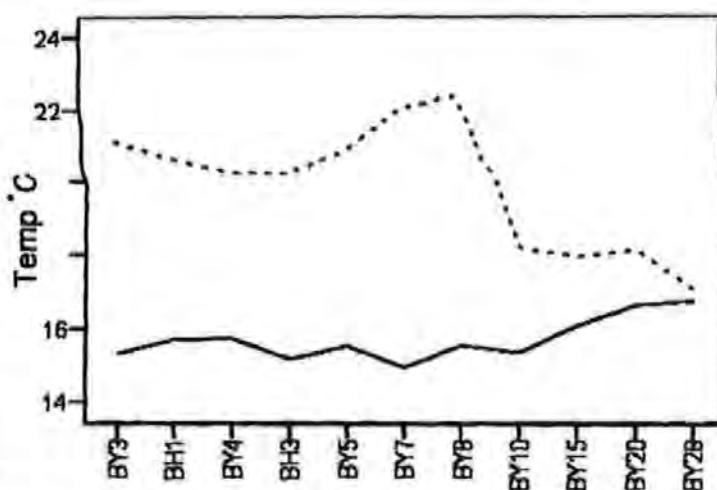


Figure 2. Measured sea surface temperatures along the sampled transect in Summer 2006 (dashed) and Summer 2007 (solid).

Table 1. Correlation matrix, showing Spearman's ρ for the 2007 transect. Bold figures: significant at $p < 0.05$. Italic figures: significant at $p > 0.1$.

| | Temp. | Salinity | PO4 | NO2 | NO3 | Si | Cyanophyta | Cryptophyta | Dinophyta | Diatoms | Chlorophyta | Others |
|-------------|--------------|--------------|--------------|--------------|-------|-------|-------------|-------------|-----------|---------|-------------|--------|
| Salinity | -0.90 | | | | | | | | | | | |
| PO4 | -0.02 | -0.08 | | | | | | | | | | |
| NO2 | <i>0.59</i> | -0.91 | -0.01 | | | | | | | | | |
| NO3 | -0.30 | 0.43 | -0.07 | -0.49 | | | | | | | | |
| Si | 0.24 | -0.10 | 0.24 | 0.25 | -0.07 | | | | | | | |
| Cyanophyta | 0.17 | -0.14 | -0.22 | 0.28 | 0.12 | -0.31 | | | | | | |
| Cryptophyta | 0.12 | 0.00 | -0.47 | -0.13 | 0.09 | 0.24 | 0.27 | | | | | |
| Dinophyta | 0.42 | -0.43 | -0.18 | 0.25 | 0.29 | 0.64 | 0.19 | 0.40 | | | | |
| Diatoms | -0.14 | 0.38 | -0.22 | -0.52 | 0.57 | -0.25 | -0.08 | 0.26 | 0.38 | | | |
| Chlorophyta | -0.19 | 0.20 | -0.65 | 0.04 | 0.18 | -0.59 | 0.41 | 0.43 | 0.21 | 0.44 | | |
| Others | 0.37 | -0.33 | 0.47 | 0.48 | -0.19 | 0.40 | 0.13 | -0.03 | 0.56 | 0.12 | -0.10 | |
| Total | 0.29 | -0.14 | -0.16 | 0.26 | 0.21 | -0.05 | 0.95 | 0.35 | 0.40 | 0.13 | 0.36 | 0.34 |

Table 2. Correlation matrix, showing Spearman's ρ for the 2006 transect. Bold figures: significant at $p < 0.05$. Italic figures: significant at $p > 0.1$.

| | Temp. | Salinity | PO4 | NO2 | NO3 | Si | Cyanophyta | Cryptophyta | Dinophyta | Diatoms | Chlorophyta | Others |
|-------------|--------------|--------------|-------|--------------|--------------|-------|-------------|-------------|-----------|--------------|-------------|--------|
| Salinity | <i>0.55</i> | | | | | | | | | | | |
| PO4 | -0.62 | -0.15 | | | | | | | | | | |
| NO2 | -0.39 | -0.28 | -0.18 | | | | | | | | | |
| NO3 | 0.53 | 0.39 | -0.28 | -0.53 | | | | | | | | |
| Si | -0.60 | -0.81 | 0.26 | 0.44 | -0.70 | | | | | | | |
| Cyanophyta | 0.36 | 0.25 | -0.59 | -0.35 | 0.17 | -0.29 | | | | | | |
| Cryptophyta | -0.07 | -0.11 | -0.24 | -0.36 | 0.01 | 0.02 | 0.39 | | | | | |
| Dinophyta | -0.29 | 0.01 | 0.13 | -0.20 | -0.10 | 0.02 | 0.12 | 0.32 | | | | |
| Diatoms | 0.04 | 0.73 | 0.39 | -0.26 | 0.25 | -0.62 | -0.15 | 0.00 | 0.18 | | | |
| Chlorophyta | -0.26 | -0.78 | -0.12 | -0.05 | -0.21 | 0.58 | 0.19 | 0.18 | 0.09 | -0.86 | | |
| Others | -0.14 | -0.84 | -0.16 | -0.02 | 0.05 | 0.55 | -0.01 | 0.12 | -0.22 | -0.85 | 0.82 | |
| Total | 0.35 | 0.44 | -0.32 | -0.64 | 0.21 | -0.41 | 0.92 | 0.39 | 0.24 | 0.13 | 0.03 | -0.23 |

negative c with total biomass ($-0.64, p < 0.05$).

Discussion and conclusion

- Sea surface temperatures were higher in 2006 than in 2007 which might be reflected in the higher total phytoplankton biomass in 2006 at 7 out of 11 stations. Salinity was similar for both surveys.

- In the western part of the studied area, diatoms showed considerably higher biomass in 2006 than in 2007. The lower Si concentrations in this part of the transect when compared to 2007 could be interpreted as a result of high Si fixation in diatom biomass, although this suggested interpretation of the graphical data (Figure 3, Figure 4) could not be confirmed by the results of the correlation analysis (Table 2). However, the fact that Si correlated positively with the 2006 biomass of chlorophytes and "other" phytoplankton could indicate that in the absence of diatoms (and therefore high Si concentrations), chlorophytes and "other" phytoplankton are competitively more successful in the incorporation of nutrients and the production of biomass.

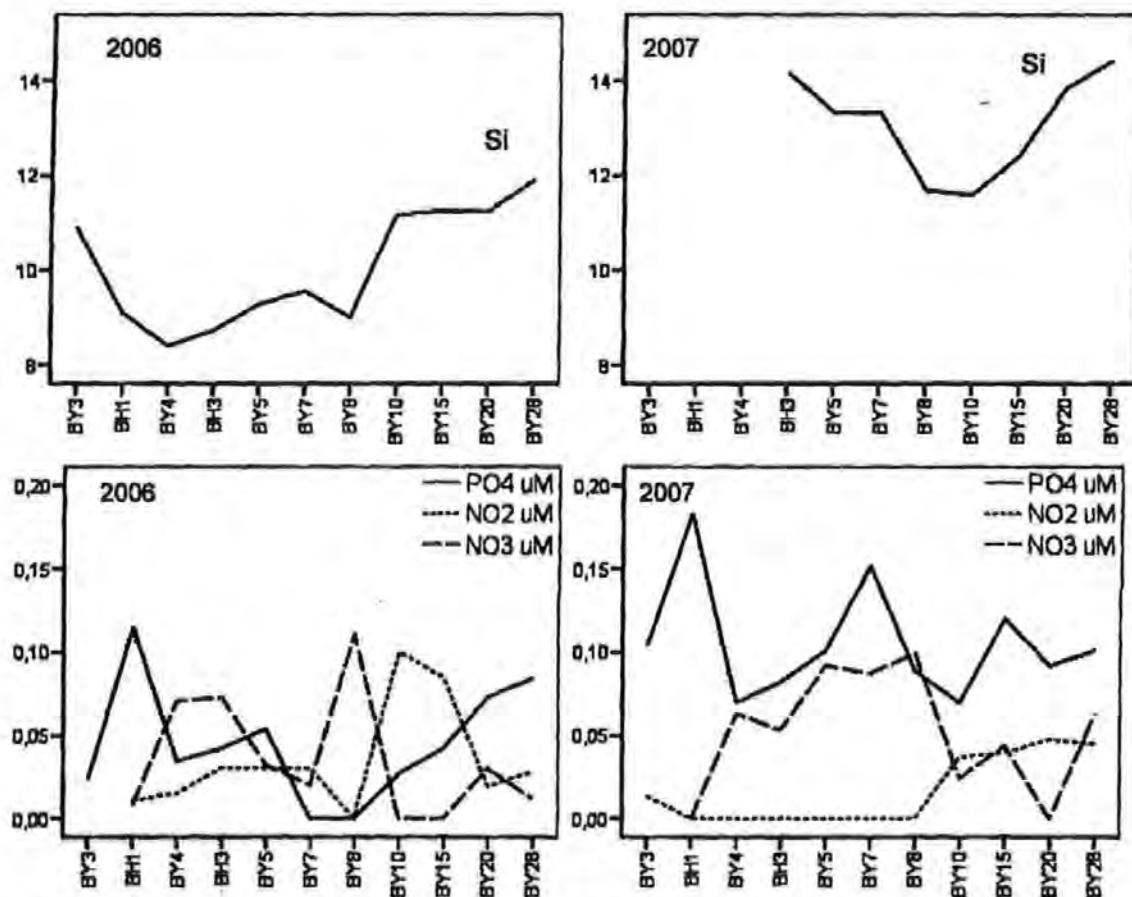


Figure 3. Nutrient concentrations at individual station. Top: Si. Bottom: PO_4 (solid line), NO_3 (dashed line) and NO_2 (dotted line); all concentrations in μM .

- A similar possible relationship between PO_4 and biomass of cyanobacteria could be detected in the 2006 dataset: PO_4 concentrations were lowest at stations with high cyanobacterial biomass, probably following increased uptake of PO_4 . Again, this trend could not be confirmed by the 2007 correlation results, but graphical analysis reveals that the highest PO_4 concentrations were at the stations BH1 and BY7, coinciding with very low cyanobacterial biomass.

- Generally, the results of the correlation analysis showed little accordance of results between the two assessed years. One possible reason may be the differences in water temperature and the following differenced in biomass and taxonomic composition of the phytoplankton community, resulting in different nutrient requirements. A more probable explanation, however, would be the limited spatial, and more importantly, temporal resolution of our data. The data represent a "snapshot" of the ecological and environmental situation, which may not allow a final conclusion about causes and effects for phytoplankton biomass production.

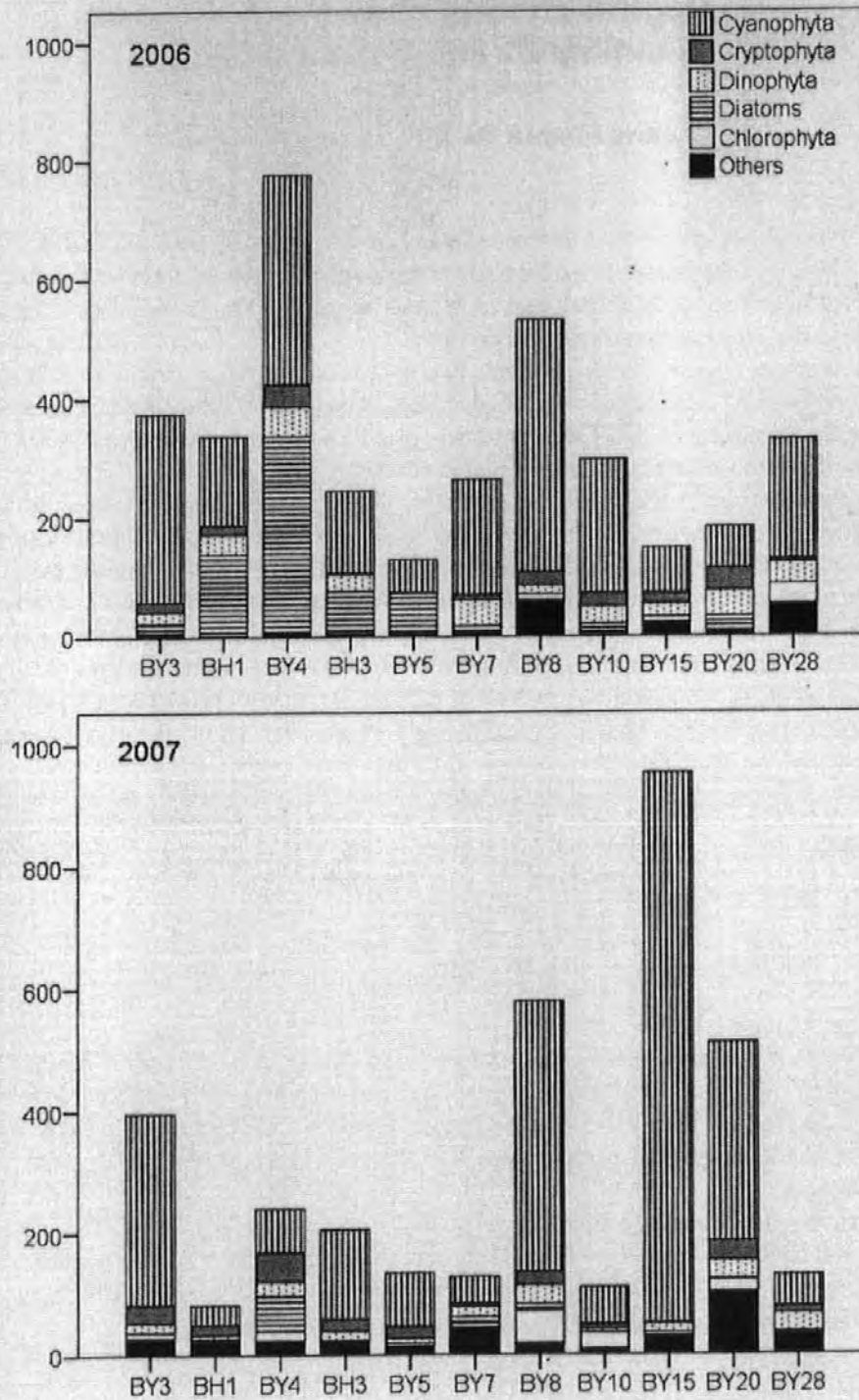


Figure 4. Biomass (mg m^{-3}) of phytoplankton groups at individual stations: cyanophyta (vertical cross bar), cryptophyta (grey), dinophyta (dotted), diatoms (horizontal cross bar), chlorophyta (white), others (black).

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