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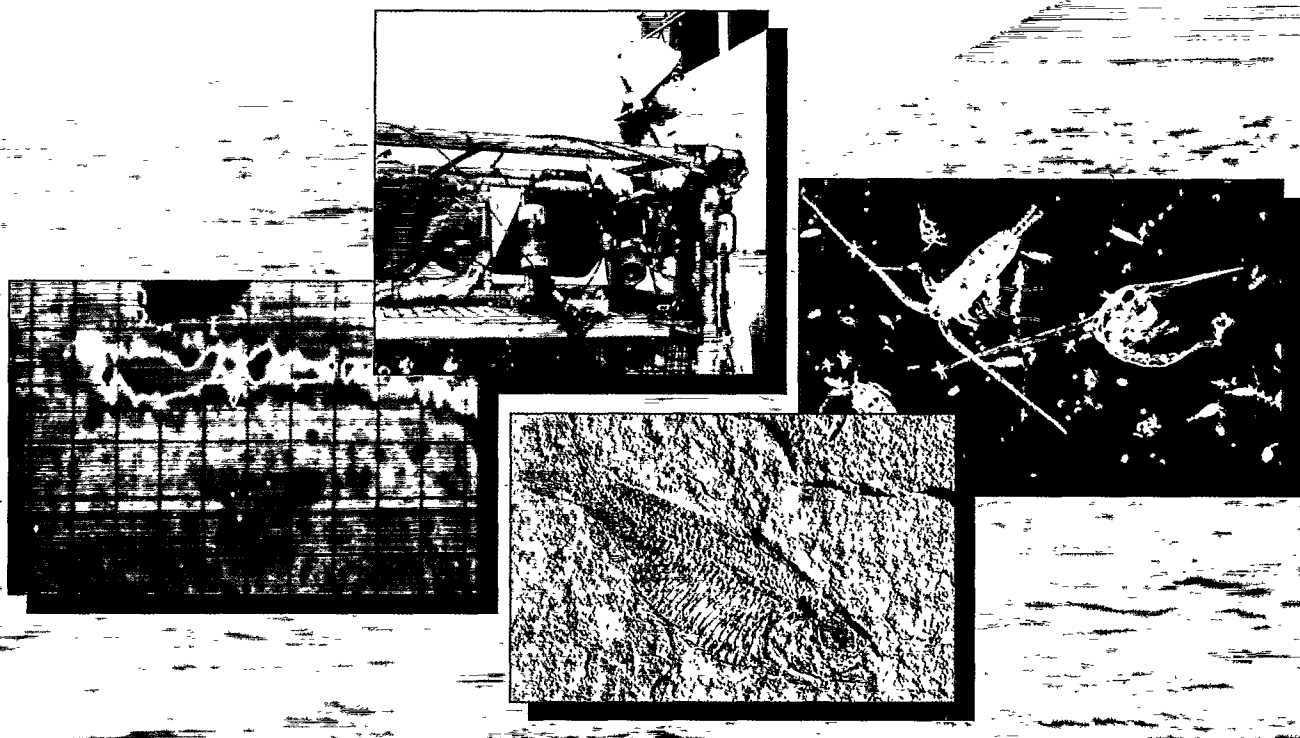

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REPORT No. 7

SONUS:
The SOuthern Nutrients Study 1995-1997

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1999

Final Report to the Department of the Environment Transport and the Regions

on

SOuthern Nutrients Study (SONUS) Fieldwork Programme - PECD 1/9/36
(Contract Period 1/11/94 - 30/10/97)

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ABSTRACT

The SONUS project studied possible links between hypernutrification and potential eutrophication of the Solent and Southampton Water. At present within the terms of the Urban Wastewater Treatment Directive Southampton Water is not a eutrophic environment. Algal blooms when they occur are of short duration, and are not associated with obviously related harmful effects. Two points in particular were addressed:- (1) Are significant UK inputs of nutrients to the English Channel and hence the North Sea not detected by existing monitoring? (2) Can novel monitoring methods using new equipment and instruments improve understanding of the connection between the supply of nutrients and the scale of potential eutrophication processes?

Survey data showed that:- direct sewage discharges of phosphate and ammonia to the estuary are greater than the river water inputs; there is no evidence of any discharge of a form of nutrients that is not detected by present monitoring that would cause a significant under estimation of the loads discharged from the Solent; in the English Channel microbial denitrification of nitrate may significantly reduce the effective flux of nitrate-nitrogen to the North Sea.

The SONUS data buoy monitored the development of algal blooms in-situ with a good definition of changes in concentration with time. It was the first successful application of such instrumentation in UK coastal waters. The data showed that although concentrations of nutrients are high enough to support plankton growth throughout the year, the short duration of blooms when they occur in spring and summer is the result of fluctuations in the intensity of the tidal flows and the degree of associated dispersion and turbulence within the estuary. Blooms develop when periods of neap tides and fine weather are coincident. The higher flows during spring tides tend to flush blooms from the estuary.

KEYWORDS

ACRONYM, ALGAL BLOOMS, AMMONIA, DATABUOY, ENGLISH CHANNEL, ESTUARIES, EUTROPHICATION, HYPERNUTRIFICATION, IN SITU ANALYSER, LOAD ESTIMATES, NITRATE, NUTRIENTS, PHOSPHATE, PHYTOPLANKTON, PROJECT, R ITCHEN, R TEST, RIVER INPUT, SEWAGE DISPOSAL, SOLENT, SONUS, SOUTHAMPTON WATER, SOUTHERN NUTRIENTS STUDY, WATER QUALITY

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Parts of this document have or will be published else where as:-

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CONTENTS

SECTION 1
EXECUTIVE SUMMARY

1.1 Overview

- The SONUS project studied possible links between hypernutrification and potential eutrophication of the Solent and Southampton Water. At present within the terms of the Urban Wastewater Treatment Directive Southampton Water is not a eutrophic environment. Levels of nutrients in the rivers have been elevated by human activity but are moderate for rivers draining populated areas with intensive agriculture. Algal blooms when they occur are of short duration, and are not associated with obviously related harmful effects.
- The SONUS project aimed to set up a field programme to measure nutrient processes and fluxes, movement of associated water and suspended matter from the Solent/Southampton Water into the Channel over at least two annual cycles. Two points in particular were addressed :- (1) Are significant UK inputs of nutrients to the English Channel and hence the North Sea not detected by existing monitoring ? (2) Can novel monitoring methods using new equipment and instruments improve understanding of the connection between the supply of nutrients and the scale of potential eutrophication processes in hypernutrified areas such as Southampton Water ?
- 24 monthly surveys (March 1995 - February 1997) of the nutrient distributions in Southampton Water, were undertaken to assess the annual and inter annual variability of nutrient flows through the system, and the associated variability of plankton biomass. This information was examined in the context of river water data from 1974-1997, and data from the English Channel.
- Concentrations in rivers have increased between 1974 and 1997. In 1995 and 1996 loads were highly dependent on river flow volumes. Direct sewage discharges of phosphate and ammonia to the estuary are greater than the river water inputs. Dilution and dispersion of this ammonia is too rapid for significant de-oxygenation due to the nitrification of this ammonia to occur.
- There is no evidence of discharges of a form of nutrients that are not detected by present monitoring that would cause a significant under estimation of the loads discharged from the Solent.
- In the English Channel microbial denitrification of nitrate may significantly reduce the effective flux of nitrate-nitrogen to the North Sea.
- The SONUS data buoy was developed for in-situ monitoring of the growth of algal blooms providing good definition of changes in concentration with time. The SONUS buoy was the first successful application of buoy based instrumentation to monitor algal growth in UK coastal waters.
- The deployment from April to July 1996, collected a data set which has improved understanding of the occurrence of blooms in Southampton Water.
- Although concentrations of nutrients in Southampton Water are high enough to support plankton growth throughout the year, the short duration of blooms in spring and summer is the result of fluctuations in the intensity of the tidal flows and the degree of associated dispersion and turbulence within the estuary. Blooms develop when periods of neap tides and fine weather are coincident. The higher flows during spring tides tend to flush blooms from the estuary.
- Recommendations for future work are discussed in section 2.6.

1.2 Analysis of SONUS survey and Environment Agency River Data Sets

1.2.1 Water Quality (1974-1997) and impact of the Solent discharge on the English Channel

Analysis of river data 1974-1997

- For the period since the establishment of the Water Authorities in 1974, data for the concentration of nutrients in UK rivers has been collected systematically through the Harmonised Monitoring Scheme and is available from the Environment Agency's Data Centre.
- This provides a valuable resource which can be used to evaluate changes in river borne loads of nutrients entering UK estuaries over the past 25 years.
- Over this period flow in the Test has tended to be higher than in the Itchen.
- When data averaged for the individual decades is compared it appears that the flow in the Itchen has remained constant while the flow in the Test has been more affected by the drought in the 1990s previous to 1998.
- The concentrations of nitrate in both rivers are similar and show similar seasonal variations. Maximum concentrations of nitrate tend to occur in winter during periods of high flow.
- A steady and progressive increase in concentration has taken place over the last 24 years from 340µM and 310µM (1974-1979) to 420µM and 390µM (1990-1997) in the Test and Itchen respectively.
- Concentrations of the two other forms nitrogen assimulatable by algae ammonia and nitrite are similar and low in both rivers with mean concentrations of 7µM and 4µM for ammonia and nitrite respectively.
- Concentrations of phosphate in the Itchen have been consistently higher than those in the Test. The impact of a sewage sources is the probable reason for the higher concentrations in the Itchen relative to the Test.
- Concentrations of phosphate were at a maximum in the late 1980s.
- Concentrations decreased between 1990 and 1994 this may be due to the impact of measures to control discharges of phosphorus.
- Between 1995 and 1997 the concentration of phosphate increased in both rivers. However calculation of the daily discharge load by combining the concentration and flow data suggests that the load of phosphorus has tended to fall overall during the 1990s, and that the increase in the concentration of phosphate is a function of reduced flows in the rivers.

Seasonal cycles and bloom events

- A consistent cycle in nutrient concentrations is induced in Southampton Water by biological production which reduces observed concentrations in the summer months.
- Observed levels of chlorophyll (as a measure of the plankton bio-mass) are variable from year to year.
- The degree to which a bloom can develop in Southampton Water is highly dependent on the tidal energy of the system.

Impact of the Solent discharge on the English Channel

- The plume from Southampton Water may extend to the entrances to all three Harbours (Langstone, Portsmouth and Chichester). This suggests that nutrient enriched water from Southampton Water is a possible source water for the Harbours rather than water from the English Channel.
- The contributions of nutrient inputs from the Test and Itchen is small compared with the Seine river. For nitrate plus nitrite the Seine inputs approximately 30 times more than the Test and Itchen, for silicate inputs are 48 times greater and for phosphate inputs are 100 times greater.
- Reassessment of FLUXMANCHE-1 data for the Dover Strait suggests it contains evidence for loss of nitrate probably due to denitrification. This loss reduces the apparent concentration of nitrate in river inputs influencing these coastal waters by about 30%
- There is no evidence in this data for any significant enrichment in the concentration of biologically available nitrogen in these water from sources that are not usually measured such as the detrital nitrogen load.

1.2.2 Assessment of nutrient fluxes

- Plots of concentrations of nitrate and silicate against the salinity of the samples show that the mass of nutrient is conserved in solution during the mixing of river source waters and sea water.
- Plots of concentrations of ammonia, nitrite and phosphate against the salinity of the samples show patterns influenced by major point source inputs from water treatment works rather than simple mixing of river source waters and sea water.
- Estimates based on the SONUS survey data set suggest that over 3000 tonnes of nitrogen and between 114 and 199 tonnes of phosphorus has moved through the estuary and out into the Solent, during the two years of study.
- The loss of nitrate within the low salinity range, which can be seen when comparing theoretical freshwater fluxes with those calculated from EA data. This is most prevalent during summer, especially during 1995, when river flows were relatively low. Over the two years this nitrate loss accounted for between 22 and 27% of riverine nutrient flux.
- Significant inputs of ammonia, nitrite, and phosphate from point sources along the estuary are detected in the survey data. These inputs are related to inputs of waste water from sewage works along the length of the estuary.
- Flux calculations suggest that additions equivalent of up to 46% of phosphate and 104% of ammonia in the river water inputs were added to the estuary through these point sources.
- The increase in phosphate load is significant and is equivalent to 71% of the river load in 1995 and 26 % in 1996.
- Comparison with the above estimate of the potential load from untreated sewage suggest that sewage treatment is effectively removing a large proportion of the potential nitrogen load but that a third of the potential phosphate load was discharged to the estuary in 1995.
- The removal of phosphate and nitrate from solution occurs within the main body of Southampton Water. It is detectable in some spring and summer surveys. Removal is associated with periods of intense algal growth.

1.2.3 Chemical speciation of dissolved nitrogen and phosphorus within the estuary

- The fraction of dissolved phosphorus present in organic compounds is generally small - of the order of a few percent along most of the estuary.
- Ammonia forms a substantial fraction (up to 30%)of the dissolved nitrogen pool on some occasions.
- There is no evidence for significant oxidation of ammonia on the time scale of the rapid flushing of Southampton Water during spring tide conditions.
- The fraction of dissolved organic nitrogen increases from a few percent in fresh water along the length of the estuary to up to greater than 50% in waters with salinities greater than 34.
- There is no evidence to support the assertion that previous estimates of fluxes of biologically available nutrients to coastal waters and between different coastal seas may have been substantial under estimates because organic and particulate fractions were not included.

1.3 Development the SONUS Data-Buoy and Chemical Analysers and their use to observe plankton blooms

- The collection of data at high temporal resolution, using the automated remote techniques is necessary to observe the occurrence of processes like plankton blooms that often occur too quickly (and at present unpredictably) to be sampled accurately by conventional boat based methods.
- The operation of the SONUS buoy has provided valuable experience in how to do this. Design of the SONUS data buoy began in early 1995. The aim was to produce a reliable system that could be built quickly within the constrictions of the available budget.
- The deployment from April to July 1996, collected a data set which has provided information that has improved understanding of when blooms occur within Southampton Water. On that deployment the buoy carried instrumentation that provided information on (a) the physical conditions in the estuary (b) the amount of light available for plankton growth and (c) a measurement of the biomass of plankton present in the water.
- The initial spring bloom in Southampton Water had in previous years tended to be associated with the period of weak tides in May. The data available from the SONUS buoy shows that this did not occur in 1996 because weather was stormy in May.
- The bloom was delayed until the next period of weaker tides in June. The occurrence of the bloom in Southampton Water is critically dependent on the energy of the system, which is principally determined by the state of the tide in the spring neap cycle,
- Associated with the development of the SONUS buoy has been the development of new instrumentation for mounting on the buoy for the in-situ determination of dissolved nutrients.
- The accuracy and precision of the data returned by the in-situ nutrient analyser compares well with that which can be achieved using conventional laboratory based methods. The data clearly demonstrates the ability of the instrument to detect transient changes in discharge levels associated

with storm events. The instrumentation appears to be less prone to fouling than conductivity sensors, because it is "self calibrating".

1.4 Methods used for the analysis of samples collected during the SONUS-fieldwork project 1995-1997: details of methods and quality control procedures

- Between March 1995 and February 1997, twenty four surveys were carried out along the Rivers Test and Itchen, and Southampton Water.
- Analyses include:
    - * Over 1000 nitrate, nitrite, ammonia, and phosphate analyses.
    - * Over 500 dissolved organic nitrogen and phosphorus
    - * 8 surveys collecting particulate associated nutrients
    - * 400 discrete chlorophyll analyses, in order to calibrate a fluorometer that logs every 5 seconds
    - * 400 discrete suspended particulate matter analyses in order to calibrate a transmissometer that logs every 5 seconds
    - * 200 discrete oxygen samples used to calibrate a oxygen.
- The first part of this report gives the procedures undertaken during the project with respect to sampling and storage, and describes the analytical methods used.
- The second part of the report discusses the quality control (QC) procedures used in order to ensure that reliable data had been collected. The following conclusions were drawn from this study:
    - * The collection of an internal bulk QC sample, showed that the stability of such a sample needs to be investigated further, with mean values for nitrate, silicate, and phosphate being 24.74±2.24μM, 3.31±0.85μM, and 0.64±0.19μM. These variations are in excess of the precision that the methods which are 0.6%, 2.5% and 4%, for nitrate, silicate, and phosphate respectively.
    - * Participation in an international inter-calibration exercise, QUASIMEME, was organised. For the estuarine samples, the lab obtained |Z| scores of less than 2 for all nutrient analyses, except for ammonia in one sample. For seawater samples, the lab obtained |Z| scores of less than 2 for all nutrient analyses, except for nitrite in one sample with relatively low concentrations.
- Previous QUASIMEME rounds suggested that accuracy in silicate analysis was significantly impaired by problems in matching sample and wash salinities. Levels were constantly overestimated by some 4μM. Repeated analysis of the current QUASIMEME samples, using washes of differing salinities shows that high salinity washes give significantly lower silicate levels than lower salinity washes. Also, comparative measurements undertaken using analytical equipment and methods used on WOCE cruises suggest some systematic error related to flowcell geometry.

SECTION 2

BACKGROUND TO SONUS CONTRACT, DETAILS OF ACHIEVEMENT WITH RESPECT TO CONTRACT SPECIFICATIONS AND RECOMMENDATIONS FOR FUTURE WORK

2.1 Introduction

World wide there is much debate about the possible deleterious effects of increased concentrations of nutrients in surface waters. On the south coast of the UK, in the Solent area, the natural "Harbours" of the region (Portsmouth, Langstone and Chichester) have been identified as a sensitive area which may be considered to be eutrophic (EEC 1991a). In the Harbours there are extensive mats of macro algae (*Ulva* and *Enteromorpha*). Southampton Water itself is not considered to be eutrophic, because the large blooms of phytoplankton that have been observed in its waters tend to be short lived (see below) and are not associated with any significant prolonged deterioration in water quality. However there is cause for concern because the relationship between the high inputs of nutrients to the system and the intensity and variability that has been observed in phytoplankton blooms is not understood. An additional question has been raised about the scale of inputs of nitrogen and phosphorus from the English Channel to the southern North Sea. This may be significant in comparison to other fluxes when particulate nutrients are taken into account (Laane et al 1993). At present the relative importance of riverine, direct discharges and atmospheric sources of nutrients to the UK south coast as a component of this load, is unclear (Reid et al 1993). In particular the large direct inputs from sewage discharges are poorly characterised, relative to other sources of nutrients. Similarly knowledge of the processes that link these inputs to the growth of plankton organisms that produce nuisances blooms and bacterial processes that create low oxygen conditions are poorly understood, both along the UK south coast and more generally world wide (Reid et al 1993, Hall et al 1996). The high concentrations of nutrients in the rivers draining into Southampton Water, the extensive sewage discharges into Southampton Water and Solent, and the occurrence of algal blooms and macro algal eutrophication in Langstone and Chichester Harbours makes the Solent and its adjacent estuaries, a suitable area for the study of processes leading to potential excessive algal growth.

In 1994 the Department of the Environment set up the Southern Nutrients Study (SONUS). There have been two parts to the SONUS project. Firstly a data base was established of available river discharge data for UK south coast rivers and of observations of nutrient concentrations and pertinent hydrographic data from the English Channel. This work was carried out at the Plymouth Marine Laboratory. The data base is now available from the British Oceanographic Data Centre. At Southampton Oceanography Centre the study involved regular surveys of Southampton Water and the development of new methods for improving the collection of information. The most significant of these new methods was the development and use of an instrumented mooring deployed within the Southampton Water estuary. This continually sampled the estuary at a high temporal resolution.

Interpretation of the data was planned to consolidate ideas stemming from a number of separate earlier observational studies such as those discussed below. In particular an aim was to improve understanding of why blooms in Southampton Water are only of short duration although light and nutrient levels should be sufficiently high to support growth throughout the summer months.

A wide range of chemical elements ("nutrients") in different forms are required for organisms to grow. In surface waters the growth of plants (biological primary production) tends to be limited by the availability of dissolved phosphorus and nitrogen compounds. Increased inputs of nutrients (N and P) from rivers and atmosphere to the seas of the European shelf are well documented (Howarth et al 1996). Nutrient inputs can originate from both point and non point sources. Point sources include waste water treatment plants (human and industrial waste) non point sources include inputs from the atmosphere and agriculture (both land drainage and animal wastes). Between 1930 and 1980 there was a six fold increase in the use of nitrogen fertilisers in the United Kingdom (Anon 1983). Nitrogen and phosphorus losses from farm land increased both in proportion to the addition of fertiliser and to the intensity of land use (Harper 1992). In the Hampshire region increases in agricultural inputs have followed this general pattern, while inputs from sewage sources have increased in line with the population growth in Hampshire which has been one of the fastest growing areas of the UK in the 1980s and '90s.

Excess plant growth can be a consequence of this nutrient enrichment and problems such as anoxic events and blooms of nuisance algae may result (Lancelot 1990). A fundamental feature of the behaviour of marine phytoplankton in temperate latitudes is a period of rapid population increase, referred to as a "bloom" (Vollenweider, 1992). An increase in nutrient concentrations within a body of water should be termed **hypernutrification**, while the term **eutrophic** has come to be applied to those waters where the increase is considered likely to produce deleterious changes in the ecosystem. Two important pieces of European legislation are now in place, with the purpose of curtailing potential damage from the discharge of excess amounts of biologically available nitrogen and phosphorus. These are the Urban Wastewater Treatment (UWT) Directive (EEC, 1991a) and the Nitrates Directive (EEC, 1991b). These require a better understanding of the problem and that remedial action be taken where necessary. The UWT requires the assessment of areas as being sensitive or less sensitive to anthropogenic discharges of nutrients. The criteria that have been established in the UK for this assessment include :- winter concentrations of nutrients, concentrations of plankton, the duration of large plankton populations, effects on dissolved oxygen concentrations, changes in the fauna, changes in macrophyte growth, occurrence of paralytic shell fish poisoning and the formation of algal scums.

A specific recipe controls the growth of plankton - 3.3kg of plankton requires 95g phosphate, 832g nitrate, 1.6kg water, 4.6 kg carbon dioxide and 310 kJ of sunlight. Silicon is also required by some species particularly diatoms. Plankton growth is limited when any one ingredient is in short supply. In the last decade we have begun to understand some of the complexities that this recipe imposes on the system. It has been known for many years that at the temperate latitude of the UK the limited amount of light energy available in late autumn and winter imposes an annual cycle of growth

and decay on plankton populations. We now recognise that physical conditions in the water which determine the amount of light available to plankton can critically control growth during spring and summer. The result is that simply higher nutrient levels in the water do not mean higher bio-mass unless the physical conditions in the water are correct (Tett & Walne1995). Blooms in surface waters occur when the net rate of biomass production is greater than the loss rates due to respiration, grazing, sinking, horizontal transport by advection and turbulent diffusive processes (Cloern, 1996). Estuaries such as Southampton Water have high nutrient availability, so the initial formation of a bloom tends to be a function of available light and physical processes that control the dispersion of plankton communities (Fichez *et al.*, 1992). Chlorophyll *a* concentrations exceeding $10\mu gl^{-1}$ have often been observed and chlorophyll *a* levels up to $40\mu gl^{-1}$ have been recorded (Purdie, 1996; Crawford *et al.*, 1997). The persistent occurrence of blooms in excess of $10\mu gl^{-1}$ chlorophyll *a* is one definition of a system that has become eutrophic (Anon 1993). This has not been the case in Southampton Water, where blooms usually only exist for about two weeks (Iriarte and Purdie, 1994, Purdie, 1996; Crawford et al., 1997). It has been documented that tidal conditions play a major role in the incidence of blooms within Southampton Water (Crawford et al., 1997; Danieri et al., 1992) and other shallow coastal environments (e.g., Cloern, 1996). Differences in water column stability throughout a spring-neap cycle, can both determine the onset and decline of a bloom. The spring tide within Southampton Water has a relatively high range, up to 4.5m, and the currents associated with this large tidal prism are high enough to decrease water column stability, inhibit growth, and, possibly, flush the estuary of part of the standing biomass. During more stable conditions over neap tides, phytoplankton biomass has been seen to increase (Danieri et al., 1992). There is also evidence to suggest that certain phototrophic ciliates and phytoplankton use their motility to avoid tidal flushing by vertically migrating to areas of lower current velocity (Crawford and Purdie, 1992).

2.2 Contract Specification - Objectives

1. To develop a field work programme to measure nutrient processes and fluxes, movement of associated water and suspended matter from the Solent/Southampton Water system into the Channel over at least two annual cycles.
2. To collaborate with the NRA in the design of enhancements to the water quality model for Southampton Water/Solent so that it can be used as a tool to plan the work and evaluate the results of SONUS. Future model enhancements enabled by this work should include transport of suspended particulate matter, geochemical recycling terms, biological removal and input sources for nutrients.
3. To foster close collaborative links with the JONUS programme. This objective will be facilitated through the work of the "JONUS/SONUS modeller".

2.3 Contract Specification - Programme of work

1. Prepare a plan of work for a three year study of the fluxes of nutrients through Southampton Water and the Solent Region The plan will detail the field work to be carried out, including the methods

to be used and samples to be collected. Preliminary plan to be presented to the SONUS steering group meeting in October 1994. Final plan to be sent to- the DOE by 31st November, 1994.

2. Arrange and hold a series of meetings with the NRA to compare contract (SOC) results for measurements in the Southampton Water/Solent with results from NRA measurements in Langstone and Chichester Harbours.
3. In Spring 1995, start a two year long field study of the flux of dissolved nutrients through Southampton Water and the Solent into the English Channel. This work will be based on quasi-synoptic sampling along the length of the estuary. Twenty four monthly surveys will be conducted using the SOC boat "Bill Conway" and sampling from the shore.
4. (i) Design and construct an instrumented mooring, for deployment in the Southampton Water - Solent area. (ii) Carry out (a) test deployments of the mooring and (b) a study to determines the most suitable position for deployment of a single mooring. (ii) Deploy the mooring at the chosen site, to make continuous observations of sediment transport and biological production. Deployment will be from autumn 1995 until the end of the field work programme, for as long as the equipment is operational.

2.4 Contract Specification - Measurements to be reported

Determinations will be made of the solution and suspended phase concentrations of nutrients. Measurements on the monthly surveys of the following forms of nitrogen, phosphorus and silicon will be made in such a way that they are suitable for the calculation of fluxes of nutrients into the Channel: Dissolved:- Ammonia, Nitrate, Nitrite, Organic Nitrogen (*), Urea (*), Dissolved reactive phosphate, Organic Phosphorus, Silicon. In sediment - biologically available nitrogen (*) and phosphorus (*). (Measurement of analytes marked with an asterisk are not routine and some experimental work will be required to find the optimum method for these determinations.)

2.5 Summary of Progress in relation to Programme of work

1. Initial planning and setting up of the programme was completed on time. Dr. Paul Wright was appointed as the SONUS project research assistant in December 1994. He started work in the Oceanography Department at Southampton University in January 1995. Collection and processing of the SONUS samples was carried out by Dr. Wright in conjunction with a number of students at SOC, Southampton Institute and Reading University. Biological sampling on the surveys was provided by Dr. Duncan Purdie of the Oceanography Department at SOC in support of a NERC PhD student project.
2. A series of meetings were held with the NRA (now the Environment Agency) during the course of the project, and data has been exchanged with the Southern Region office at Waterlooville (Dr David Lowthion). Two SONUS steering group meetings were held in 1995. These enabled a useful dialogue to be opened up with a number of interested groups, including Southern Water. A two day SONUS science meeting was held at the new Southampton Oceanography Centre in April 1996.

3. The first SONUS survey of Southampton Water was in March 1995. A survey was then carried out each month during spring tide conditions until March 1997. A list of the new data sets obtained is contained in the "Table of new SONUS data". The coverage of the data was extended into the English Channel through the work of the EU-MAST-FLUXMANCHE project. Additional off shore data are available from the EA quarterly coastal monitoring surveys.
4. Determinations were made of the solution and suspended phase concentrations of the following forms of the nutrient elements - nitrogen, phosphorus and silicon:- *dissolved*:- ammonia, nitrate, nitrite, organic nitrogen, urea, reactive phosphate, organic phosphorus, and silicon; *sediment bound* - biologically available nitrogen and phosphorus. In addition measurements were made of the salinity, chlorophyll and suspended sediment content of water samples.
5. Design of the SONUS data buoy began in early 1995. The aim was to produce a reliable system that could be built quickly within the constrictions of the available budget. The first version of the buoy went out for a test deployment in September 1995. This version had two major defects. Down-loading the data on site, did not work. When the buoy was recovered in November the frame was found to have suffered severe corrosion damage. The buoy was redesigned and rebuilt during the winter and re-deployed in April 1996. The new design used a cellular phone system for data access and this worked reliably. The frame was protected by a 50kg zinc anode which minimised corrosion damage to the frame. This deployment proved to be successful, and provided new insights into the timing of phytoplankton growth. The logger system was damaged by a severe thunderstorm over the site in July. When the buoy was recovered two weeks later the logger was found to be irreparably damaged due to a water leak caused by corrosion of the casing. To stay within the SONUS project budget, the 1997 deployment was a shared cost arrangement with W.S. Ocean Systems who were the suppliers of the instrumentation. Data was collected for 5 weeks after the buoy was deployed in March 1997. This provided good data on physical processes in the water from all the sensors. But a number of failures in the electrical connections prevented any further data being collected. The buoy was removed from service in August 1997.
6. The collection of data at high temporal resolution, using the auto-mated remote techniques is necessary to observe the occurrence of processes like plankton blooms which often occur too quickly (and at present unpredictably) to be sampled by conventional boat and bucket methods. The SONUS buoy provided such information.

2.6 Recommendations for future work

2.6.1 Monitoring inter-annual variability

The SONUS data set shows that there are large differences between both the loads of nutrients entering Southampton Water in 1995 and 1996 and the response of plankton to the different conditions in the two years. This can be set against a background of a steady rise in concentrations of nitrate and phosphate in the rivers Test and Itchen when viewed over the perspective of 24 years of data from 1974 to 1997. The in-situ chemical analysers for nutrients evaluated during the SONUS project (and

currently being developed at SOC for other analytes in addition to nitrate) offer the possibility for more detailed monitoring of both river and estuarine concentrations of nutrients. A combination of instruments in the fresh water sources and in the estuary would make possible improved estimates of both the river inputs and more importantly the estuarine data would provide reliable estimates of the direct discharges to the estuary.

2.6.2 Monitoring of blooms and their variability

With the exception of the period of the SONUS surveys blooms in the estuary have not been monitored on a consistent basis for any length of time. The SONUS surveys were only done during spring tide conditions, and other SONUS data suggests, this was not adequate to detect maximum bloom conditions. A simpler way of doing this than using a data buoy is to upgrade existing in-situ installation of equipment to monitor the chlorophyll concentrations. As part of the SONUS-II fieldwork programme fluorometers have been fitted to the WS Oceans/SOES test data station on Dockhead in Southampton Water, and to an Aran District Council data station (on piling 5km offshore of Littlehampton). A both sites the chlorophyll data will be collected along with water temperature and salinity, and atmospheric meteorological data. In 1998 we will be have information on the timing and magnitude of any blooms that occur within Southampton Water, and in the open waters of the Channel.

2.6.3 Ferry Box

The SONUS data buoy provided unambiguous evidence of the importance of tidal energy and weather conditions in determining the initiation of the spring bloom in Southampton Water. However a moored instrument array provides continuous data but at one point in space, research cruises can provide spatial coverage but only for limited periods. A different approach is needed to get a better description in both time and space and hence understanding of how the "green curtain" of plankton production which exists in a nutrient enriched estuary waxes and wanes with the cycle in tidal energy and weather during the summer months. In Southampton Water this will be achieved by fitting the same type of instruments that were used on the buoy to a commercial ferry that crosses between Southampton and the Isle of Wight six times a day. Chemical and turbidity measurements will give a much fuller description of the changes in the nutrient and sediment discharge from the estuary throughout the year than has previously been possible. By coupling these measurements to mathematical models which analyse the system our ability to make predictions about these processes in other systems would be improved.

2.6.4 Eutrophication of Langstone Harbour

Clear symptoms of eutrophication are present in the Solent Harbours (Langstone, Chichester and Portsmouth) in the form of the extensive beds of macro algae, overlying anoxic sediments. Past research programmes have focused either on the Harbours or on Southampton Water. Work in the Harbours has not found any significant connection between the extent of algal growth and the direct sewage inputs to the Harbours (Soulsby et al 1985). In contrast in the Arcachon Lagoon (France) the growth of weed beds does appear to be associated with particular river discharges (Rimmelin et al 1998). The small number of samples taken in the eastern Solent for SONUS-FLUXMANCHE studies

suggests that a direct flow of nutrient rich water from Southampton Water to the Harbours may occur. This would suggest that agricultural run off and sewage discharges in Southampton Water may make a more significant contribution to the nutrient status of the Harbours than the relatively small direct discharges in the Harbours. Surveys of the waters in the Harbours and the Solent should be undertaken to better identify the source waters to the Harbours.

2.7 Outline of the structure of this report

The remainder of this report consists of three sections covering :-

1. The analysis of survey data from the SONUS estuarine surveys and Environment Agency river data.
2. The development of the SONUS data buoy and interpretation of the results.
3. A detailed description of all the chemical analytical methods used during the study

The dates of each of the SONUS surveys are listed below, followed by a table indicting which determinations were made on which samples from which survey.

Note: Due to problems with compatibility of the different software packages used to produce the diagrams used in this report, the "Figures" for each section have had to be included at the end of that section rather than within the text; for consistency the tables are also included at the end of sections. The references for all sections are included in a single list at the end of the report.

2.8 TABLES

Table 2.1 Table of Dates of SONUS Surveys

Survey	Date	Survey	Date	Survey	Date	Survey	Date
S1	7/3/95	S7	30/8/95	S13	22/2/96	S19	26/9/96
S2	31/3/95	S8	10/10/95	S14	21/3/96	S20	30/10/96
S3	25/4/95	S9	27/10/95	S15	23/4/96	S21	27/11/96
S4	23/5/95	S10	24/11/95	S16	3/6/96	S22	12/12/96
S5	30/6/95	S11	20/12/95	S17	2/7/96	S23	29/1/97
S6	28/7/95	S12	26/1/96	S18	30/7/96	S24	28/2/97

Table 2.2 Table of new SONUS data

	TON	Si	P	NO2	NH4	DON	DOP	DOC
S1	√	√	√					
S2	√	√	√					
S3	√	√	√					
S4	√	√	√					
S5	√	√	√					
S6	√	√	√					
S7	√	√	√	√	√			
S8	√	√	√					
S9	√	√	√	√	√			
S10	√	√	√	√	√			
S11	√	√	√	√	√	√	√	
S12	√	√	√	√	√	√	√	√
S13	√	√	√	√	√	√	√	√
S14	√	√	√	√	√	√	√	√
S15	√	√	√	√	√			√
S16	√	√	√	√	√			√
S17	√	√	√	√	√	√	√	√
S18	√	√	√	√	√	√	√	√
S19	√	√	√	√	√	√	√	√
S20	√	√	√	√	√	√	√	
S21	√	√	√	√	√	√	√	
S22	√	√	√	√	√	√	√	
S23	√	√	√	√	√			
S24	√	√	√	√	√	√	√	

	Urea	O2	Chl a	SPM	Temp	Sal	Storage Technique
S1							Hg
S2			√	√	√	√	Hg
S3			√	√	√	√	Cool
S4	√	√					Cool
S5	√	√	√	√	√	√	Cool
S6	√	√	√	√	√	√	Cool
S7	√	√	√	√	√	√	Cool
S8	√	√	√	√	√	√	Frozen
S9	√	√	√	√	√	√	Cool
S10	√	√	√	√	√	√	Cool
S11	√	√	√	√	√	√	Cool
S12	√	√	√	√	√	√	Cool
S13		√	√	√	√	√	Frozen
S14		√	√	√	√	√	Cool
S15		√	√	√	√	√	Cool
S16			√	√	√	√	Frozen
S17			√	√	√	√	Cool
S18		√	√	√	√	√	Cool
S19		√	√	√	√	√	Frozen
S20			√	√	√	√	Cool
S21		√	√	√	√	√	Cool
S22		√	√	√	√	√	Frozen
S23			√	√	√	√	Cool
S24		√	√	√	√	√	Cool

Method of storage used:
Hg: Preserved with mercuric chloride
Frozen: Stored in a freezer
Cool: Kept cool in a refrigerator and analysed the next day.

SECTION 3

THE ANALYSIS OF SURVEY DATA FROM THE SONUS ESTUARINE SURVEYS AND ENVIRONMENT AGENCY RIVER DATA.

3.1 Description of study area; river water quality (1974-1998); seasonal cycles in concentrations and associated bloom events; and impact of the Solent discharge on the English Channel

3.1.1 Description of study area

Much pertinent background information which is still relevant for the Solent region was collected in the NERC publication "The Solent Estuarine System: An Assessment of Present Knowledge" edited by Burton (1980). Important general eco-system processes were described by Tubbs (1980), sediment transport by Dyer (1980) and hydrodynamic processes by Webber (1980). Phillips (1980) collated the existing information on nutrients and other contaminants.

Southampton Water is an estuary fed by two main rivers, the Test and the Itchen, which have a combined average annual discharge equivalent to 1.54×10^6 m^3/day. Water flows into the English Channel, to the north of the Isle of Wight through the Solent. The estuary is described as "partially mixed", and "macrotidal" (Dyer, 1970). The maximum tidal range is about 4.5m, and the tidal excursion is 2.5km. It is a roughly linear body of water, which is 2km wide, and extends for 10km. It is highly urbanised, with large industrial complexes along its length. In addition to river flow, Southampton Water receives a consented sewage discharge of about 0.1×10^6 m^3/day. Waste water can contribute up to 25% of the flow during periods of low river discharge. Salinities in the main body of the estuary vary between 30 and 33. Using the approach of Officer (1976) and data from Webber (1980), flushing rates for spring tides of about 26 hours, and 76 hours for neap tides were estimated (Wright et al 1997).

The Solent estuary is one of the major sources of fresh water and suspended particles into the Channel from the English coast. The Itchen, Test, Hamble, and to a lesser extent the Beaulieu Rivers all contribute dissolved nutrients to Southampton Water and into the Solent. At present it is still unclear to what extent Portsmouth Harbour, Langstone Harbour and Chichester Harbour are likely to act as sources of phosphorus and nitrogen to the eastern Solent. The sum of the extensive macroalgal growth and associated denitrification in the sediments of the Harbours may be such that they are a net sink for nitrogen.

The rivers Test and Itchen are predominantly fed by chalk streams from catchment areas of 1260km^2 and 400km^2 respectively. The water is clear, hard and alkaline. On the river Test consumptive use represents 2% of the annual average flow and 80% of water abstracted for domestic use is returned after treatment. The catchment of the Test is predominantly rural with the population spread across towns in the north or concentrated in conurbations along

Southampton Water. Above the tidal limit of the Test there are two substantial discharges of treated sewage Fullerton (Andover) and Romsey with consented discharges of 16,000m^3/d and 6,410m^3/d respectively. Other smaller works are at Chilbolton, Kings Sombourne and Stockbridge with discharges less then 500m^3/d. In addition, there are small works on the rivers Blackwater, Dever and Dun. The largest discharge is to the upper estuary at Millbrook and Slowhill amounting to 55,000m^3/d. For the Itchen, treated water from Winchester is filtered though the chalk back to the river (9000m^3/d) and above Winchester the works at Headbourne Worthy has a discharge of 4100m^3/d. Increases in population in the catchment area of the Itchen have required three large sewage works discharging directly to the lower reaches of the river above the tidal limit at Chicknell (Eastleigh 30,000m^3/d) and into the estuary at Portswood (27,700m^3/d) and Woolston (15,000m^3/d) (NRA 1992a & b).

3.1.2 Supply of nutrients to the Southampton Water from the rivers Test and Itchen from 1974 to 1998

For the period since the establishment of the Water Authorities in 1974, data is available from the Environment Agency's Data Centre. At approximately weekly intervals samples have been taken above the tidal limit of both rivers for the determination of nutrient concentrations. The data from both rivers for concentrations of nitrate and phosphate and the corresponding flow data are summarised in Table 3.1.1 and illustrated in Figure 3.1a,b &c. Over this period when flow in the Test has tended to be higher than in the Itchen. When data averaged for the individual decades is compared it appears that the flow in the Itchen has remained constant while the flow in the Test has been more affected by the drought in the 1990s previous to 1998. The concentrations of nitrate in both rivers are similar and show similar seasonal variations. Maximum concentrations of nitrate tend to occur in winter during periods of high flow. A steady and progressive increase in concentration has taken place over the last 24 years from 342µM and 308µM (1974-1979) to 422µM and 393µM(1990-1997) in the Test and Itchen respectively. Concentrations of the two other nitrogen compounds that may be assimulated by algae, ammonia and nitrite, are similar and low in both rivers with mean concentrations of 7µM and 4µM for ammonia and nitrite respectively. Concentrations of phosphate over the period are plotted in Figure 3.1c. Concentrations in the Itchen have been consistently higher than those in the Test. The pattern of variation in concentration of phosphate with the seasons is, in both rivers, the reverse of the nitrate pattern. High concentrations tend to be associated with periods of low flow in summer. This has two causes:- one is the lower rate of solublisation of phosphorus from soils which results in concentrations tending to be diluted at high discharges, the other reason is that sewage inputs make a higher contribution to river loads than is the case for nitrate and these remain relatively constant through the year while the base river flow changes with the amount of rainfall. The impact of sewage sources is the probable reason for the higher concentrations in the Itchen relative to the Test. Concentrations of phosphate were at a maximum in the late 1980s. Concentrations decreased between 1990 and 1994 this may be due to the impact of measures to

control discharges of phosphorus. Between 1995 and 1997 the concentration of phosphate increased in both rivers. However calculation of the daily discharge load by combining the concentration and flow data suggests that the load of phosphorus has tended to fall overall during the 1990s, and that the increase in the concentration of phosphate is a function of reduced flows in the rivers. This is illustrated in Figure 3.1d.

3.1.3 Seasonal cycles and bloom events

The first phase of the SONUS programme conducted 24 surveys of Southampton Water and the estuarine arms of the rivers Test and Itchen up to their navigable limits between March 1995 and February 1997. These were all done during spring tides to make use of the highest navigable range within the estuary. The impact of plankton growth is to produce an annual cycle in nutrient concentrations in the estuary. Concentrations of both nitrogen and phosphorus are lower in the estuary during summer, although in the case of phosphate (Figure 3.1c and 3.2b) the concentration in the river input waters is higher. The scatter in the data at each time point in Figures 3.2a & b is due to the range of salinity encountered on each cruise. The lowest concentrations in the estuary were observed in July 1995. In Figure 3.3a the data for nitrate and phytoplankton chlorophyll from the July 1995 survey are plotted against the salinity of the samples. This shows an almost complete removal of nitrate into plankton biomass at higher salinities. If the amount of nitrate removed at the salinity of each sample is calculated relative to conservative mixing in the estuary and this nitrate deficit is converted to chlorophyll assuming a carbon to chlorophyll ratio of 100 the shape of the estimated and observed chlorophyll distributions are similar. This suggests that the observed chlorophyll is the product of in-situ production in the estuary. The plot also suggests that although the rivers provide a constant supply of new nutrients to the estuary which are present in sufficient quantities to support growth throughout the estuary significant production only takes place in the outer estuary. This is because light levels and turbulence in the water are such that production is limited to this area of the estuary. In June 1998 the estuary was surveyed during both spring and neap tide conditions (Figure 3.3b). A more intense bloom of 50 µg chlorophyll /l was detected during the less turbulent conditions of a neap tide relative to a spring tide maximum of 15 µg chlorophyll/l. Although Southampton Water is a relatively well sampled estuary, this year is the first that such a comparison has been done. We suspect from the SONUS and other observation that this spring-neap cycle in production may be a regular feature of the Solent system. The rivers provide nutrients year round while the spring neap tidal cycle limits the occurrence of suitable conditions for growth to the neap part of the cycle. Monbet (1992) suggested from an analysis of the available data from estuaries round the world that macrotidal estuaries with mean tidal ranges greater than 2m exhibit a greater tolerance to pollution from nitrogen discharges than estuaries with smaller tidal ranges. Off Roscoff on the other side of the Channel where the tidal range is greater, Sournia et al (1987) saw little evidence for changes in productivity through the spring neap cycle. The Solent system seems to the on the border line in terms of the differentiation of

systems based on their tidal range suggested by Monbet 1992, and crosses over from being a low productivity to a high productivity system with the spring-neap tidal cycle. In some years overall levels of production may be much less than others due to the coincidence of unfavourable weather and hydrodynamic conditions. The observation in 1996 (discussed in Section 4) are a good example of low productivity conditions.

3.1.4 Nutrient distributions and fluxes results from the EU-MAST-FLUXMANCHE research project phase 1 and 2

An aim of the University of Southampton, Department of Oceanography contribution to phase 2 of the EU-MAST-FLUXMANCHE project was to assess the scale of inputs of nutrients from the Solent and how they contribute to the overall fluxes of nutrients through the English Channel. FLUXMANCHE was an interdisciplinary project through which additional data on trace metals, chlorophyll, SPM, water flow using ADCP (Acoustic Doppler Current Profiler) and OSCR (Ocean Current Radar), and plankton are available (Hart and Statham 1998). The work reported here focuses on the distribution and fluxes of dissolved nutrients - nitrate plus nitrite, and phosphate (silicon data is not discussed because we consider the data unreliable at high salinities) from the mouth of Southampton Water along the eastern side of the Solent and to the area east of the Isle of Wight. The fate of these nutrients during mixing with Channel waters is still not fully understood, and the existence of a seasonal tidally-generated gyre (Boxall & Robinson, 1987 and Solomon & Breton 1993) to the east of the Isle of Wight further complicates the distribution and fate of nutrients in this area

A large number of determinations were made of concentrations of nutrient in samples collected during the second phase of FLUXMANCHE on the cross channel sections. However this was a complete waste of time as they are not interpretable due to the salinity of the samples not being measured.

The most interesting results are from a survey of the Solent and adjacent water in October 1995. The significance of this limited data set is the indication that the tidally corrected distribution gives of the likely extent of the Southampton Water plume. The plume from Southampton Water may extend to the entrances to all three Harbours (Langstone, Portsmouth and Chichester). This suggests that nutrient enriched water from Southampton Water is likely to be the source water for the Harbours rather than water from the English Channel.

As part of the FLUXMANCHE final report a budget was drawn up comparing the flux from the Solent based on SONUS data to published data for the River Seine. The relative magnitudes of the contributions of nutrient loads from the Test and Itchen compared with the Seine river are shown in Table 3.1.2. (Hart & Statham 1998). For nitrate plus nitrite the Seine inputs approximately 30 times more than the Test and Itchen, for silicate inputs are 48 times greater and for phosphate inputs are 100 times greater.

Data from the first phase of FLUXMANCHE during which data for nutrients and salinity were collected on sections across the Dover Strait is included in the SONUS database compiled by

the Plymouth Marine Laboratory (Joint & Jordan 1996). This data has previously been considered by Bentley et al 1993, although a trend in the data was noted with increasing concentrations with decreasing salinities, no attempt was made to relate this trend to known source concentrations. In Figure 3.7, measurements of nitrate and salinity made during the winter period cruises between December 1990 and March 1991 are plotted. Data from the different cruises is distinguished. The majority of samples are clustered in a group with salinities greater than 35. In this group it can be seen that concentrations increase over the winter and are then lower in March. This decrease is probably due to removal by the initial stage of spring plankton production. The highest concentration samples in this group contain about 10μM of nitrate. This is equivalent to about a 2μM enrichment in concentration relative to concentrations in water of similar salinity at the source of these waters at the shelf break shelf break (Hydes et al In Press). In the samples collected in December and January samples with salinities less than 35, show an increasing trend in concentration with decreasing salinity. This trend is consistent with the mixing of low concentration water with an oceanic source with high concentration fresh waters. A least squares linear regression fit of a straight line to the January 1991 data suggests a fresh water end member concentration of 191μM (r^2=0.89). Concentrations in the likely fresh water sources the Rhine, Seine and the Solent are all above 300μM. This apparent loss of nitrate is consistent with loss of nitrate due to denitrification being a dominant process in these waters (Hydes et al In Press, Seitzinger & Giblin 1996). There is no evidence in this data for any significant enrichment in the concentration of biologically available nitrogen in these water from sources that are not usually measured such as the detrital nitrogen load as has been suggested might be the case by Laane et al (1993).

3.2 The assessment of nutrient fluxes

3.2.1. Introduction

It has been suggested that inputs of nitrogen and phosphorus from the Channel make a significant contribution to the loads entering the southern North Sea (Laane et al 1993). At present the relative importance of direct riverine discharges from the UK south coast as a component of this flux is unclear. In particular the large direct inputs of sewage are poorly characterised, as are the processes operating within estuaries, which modify these riverine fluxes (e.g. Nedwell & Trimmer 1996). The input through Southampton Water is the largest single contribution of freshwater input from the UK into the Channel (Reid et al 1993). An objective of the SONUS project has been to assess this flux, and to identify the processes which determine the actual loads discharged as opposed to those that can be estimated from a knowledge of regional river water concentrations.

This section of the report attempts to describe the nutrient fluxes from the Test and Itchen rivers into the Solent. The SONUS survey data is used to calculate fluxes based on the observed concentrations in the outer estuary and the results compared to fluxes calculated from

Environment Agency river data. Two methods have been utilised; one looking at gross changes between predicted flux from freshwater data and fluxes calculated by extrapolating the entire data set to ascertain a theoretical end member concentration (Hydes & Liss, 1977); the other looking at changes in mean flux between certain fixed locations in order to ascertain where, if anywhere, flux modification might occur (Lebo & Sharp, 1992).

The difference between the estimates loads based on the river discharge and those based on the survey data allows estimates to be made of:-

1. Any changes that may take place in the river input between the Environment Agency's tidal limit sampling point and sampling on SONUS surveys that went up to the highest navigable points on the rivers Test and Itchen.
2. Any significant additions to the load discharged from the estuary due to point source inputs within the estuary such as sewage works.

3.2.2 Variations in freshwater discharge and nutrient concentrations 1995-1997

Throughout the study the flow in the two rivers ranged from $14m^3s^{-1}$ and 2 m^3s^{-1} in the Itchen and Test respectively, during winter 1995, to as low as $1m^3s^{-1}$ through the dry conditions of summer 1995 (Figure 3.5). The flow is characteristically flashy during the winter, when storms bring periodic high discharge events into the estuary. This has implications for nutrient inputs as short term rainfall events are not captured by normal Environment Agency sampling methods or those used in the SONUS programme surveys.

Nutrient levels and river discharges were measured at the tidal limits as part of the Environment Agency's (EA)- DETR Harmonised Monitoring (HM) programme. The variations of nitrate and phosphate are shown in Figure 3.6. It can be seen that both nitrate and phosphate levels vary in response to flow (Figure 3.7). High flow periods tend to be associated with high concentrations of nitrate. Nitrate salts are easily soluble and wetting of any dried out soil by rain rapidly brings any associated nitrate salts into solution. Generally, the Test shows higher levels than the Itchen, especially during the winter months, probably reflecting a combination of factors; flow, land usage in the catchment area and the associated diffuse inputs. There appears to be no significant increase in nitrate concentration during the two years, apart from that explained through changes in the flow. Concentrations of nitrate (Figure 3.7), show a characteristic increase with flow, but then level off at flows of around $7m^3s^{-1}$ and $10m^3s^{-1}$ in the Test. The data for the Itchen further suggest that concentrations of nitrate decrease above flows of about $9m^3s^{-1}$. Therefore, the relationship between high flows and high nitrate levels only applies to a point. Above this flow, wash out from soils slows down or stops. After this, any extra rainfall and the subsequent increase in river flow will serve to dilute what is present within the stream, and concentrations of nitrate in the water will decrease. The data (Figure 7) shows a peak in the data resulting from the combination of these two processes in the Itchen. In the Test the cross over

to dilution at high discharges is not reached, although total flows in the Test are higher than in the Itchen.

Concentrations of phosphate in the Itchen are between two to three times higher than those in the Test, reflecting the lower flow of the Itchen and differences in the combination of land usage and its point source inputs. The lower flow results in less dilution of sewage works inputs. In contrast to nitrate, concentrations of phosphate levels tend to be lower during periods of high flow in both rivers. There are two similar reasons for this. One is the less ready solubility of phosphate salts in soils relative to nitrate salts. Wetting of dried soils does not lead to an immediate release of phosphate into solution as it does for nitrate. Rain water will dilute the phosphate concentration in run off from land into streams. Secondly an important contribution to the phosphate load is from point source inputs such as from sewage treatment works which have relatively constant discharge loads so that extra water flow from rain storms will dilute the phosphate concentration in the discharge. The phosphate data (Figure 3.7) shows that low flows give high levels. As flows increase dilution increases and concentrations fall markedly, levelling off at about 6µM for the Itchen and 5µM for the Test, at flows above about 10 $m^3 s^{-1}$. The data show that the Test is always at or around this background level regardless of flow, suggesting that the river discharge is always large enough to dilute any waste water inputs down to this level. However, it also shows that the Itchen is more sensitive to variations in flow with regard to its phosphate concentrations, and that a doubling in flow can lead to almost a halving of phosphate concentrations, or perhaps more importantly, a halving of flow can double concentrations of phosphate within the river. There appears to be an increase in phosphate in both rivers over the study period, more so within the Itchen. This probably results from the lower flows experienced in 1996.

3.2.3 Nutrient - Salinity relationships

Figures 3.8 to 3.13 show the data expressed in terms of their relationship to salinity for the surveys undertaken during the SONUS project. The general trends are:-

- Nitrate appears to behave conservatively within the estuary. The concentrations in freshwater fall through spring and summer, as flow decreases, and are re-established during the winter months. Occasional surveys show some small amount of removal during spring or summer (e.g. April 1995 and August 1996. Summer months also show zero concentrations within the outer estuary.
- Phosphate appears to behave conservatively in Southampton Water, except during the summer months, when removal occurs. Large point sources are seen on both rivers, relating to the waste water works at Portswood and Millbrook on the Itchen and Test respectively. Concentrations in the Itchen are always higher than those in the Test.
- Silicate is also generally conservative throughout the estuary, with some removal in the outer estuary during summer.

- Ammonia and nitrite distributions are similar to those of phosphate i.e. peaks in relation to waste water outputs, and removal in the lower estuary during the summer.

3.2.4. Assessing nutrient loadings

Whilst concentrations of nutrient found within freshwater have been seen to vary with regards to fresh water flow, source strength, and season, it is also important to assess the changes that may take place to those concentrations as they enter the estuarine zone. The estuary can act as a large chemical system transforming nutrients from dissolved to particulate phases and back again, and consequently modifying the nutrient inputs brought in by the rivers.

It is useful, therefore, to assess the relative contribution of these processes to the overall nutrient flux to the coastal zone. There are two basic methods used for this calculation:

1. Back extrapolating the bulk nutrient salinity plots to zero salinity to estimate the effective fresh water end member and comparing these fluxes with those calculated from freshwater data (Boyle et al., 1974; Hydes and Liss, 1977; Officer, 1979)
2. Using a series of fixed locations and the nutrient concentrations at that point, along with the seawater end-member to calculate an effective fresh water end member, and then comparing these fluxes with the fluxes expected at that point (Lebo and Sharp, 1992)

3.2.4.1. Method 1.

In this method, regression lines are drawn from the most seaward sample, to the next most saline. This process was iterated for the rest of the data set, each time adding the next most saline point to the regression calculation. The Pearson's Moment correlation coefficient for each iteration was computed and its significance assessed. Once this coefficient became insignificant, the previous regression equation was used to calculate a zero salinity theoretical end member concentration (i.e. the intercept of the line). This method gives an indication of bulk addition or removal processes occurring within the estuary (Boyle et al., 1974; Hydes and Liss, 1977; Officer, 1979). For the nitrate data the r^2 coefficient was never less than 0.985, indicating the highly conservative nature of this nutrient throughout the two years. Due to the highly non conservative behaviour of phosphate and ammonia, the procedure was modified and the calculation was restricted to that portion of the data at higher salinity that showed quasi conservative mixing with a regression coefficient (r^2) of greater than 0.985. Each month's survey was treated in this manner. The calculated effective end member concentration is multiplied by the mean monthly discharge of the relevant river, to obtain a monthly nutrient flux. These were then summed to obtain annual fluxes. It should be noted that all the data was used for this method, i.e. there was no differentiation made between Test and Itchen river data.

Yearly summaries for DIP and DIN species are shown Table 3.2.1. By using this method it appears that the estuary acts as a sink for nitrate, and a source for phosphate and ammonia. The loss of nitrate in the very upper end of the rivers is most pronounced during summer months, and at a maximum during the low flow summer of 1995. In contrast to estuaries like the Humber

which contain high concentrations of suspended sediment (Pratska et al 1997), loss of dissolved phosphate to particulate phases has not been observed below the tidal limits of these rivers. The waste water works along the estuary input large amounts of phosphate and ammonia to the estuary. Freshwater data suggest that Itchen phosphate levels are higher than Test freshwater concentrations, possibly due to the river flowing through a more urban environment. The nutrient salinity relationships show that phosphate levels in the Itchen estuary are generally always higher than those of corresponding salinities in the Test, with the occasional exception of samples taken around the Millbrook outfall. This causes the more seaward data to reflect concentrations in the Itchen rather than the Test, so some detail has been lost in this bulk method, with regard to the relative importance of waste water inputs in both rivers. A similar problem is also observed for the ammonia data in the estuaries.

3.2.4.2. Method 2

For this method the assumption is made that the distribution of a nutrient between the seaward end of the survey and the fixed location is conservative, as is the distribution between that survey point and the fresh water end of the estuary.

The method is based on that employed by Lebo and Sharp (1992), such that a number of fixed survey points were used, along with their salinities and nutrient concentrations. The nutrient concentration and salinity of the most seaward sample was used along with that of the location in question to construct a straight line equation, which allowed extrapolation back to another theoretical end member. Again, this end member was multiplied by the discharge at the location in question to give an average monthly flux at this one point. These were then summed to give an annual flux of nutrient through a given location. This method then allowed for nutrient fluxes to be calculated above and below point sources, as indicated in nutrient salinity plots, and to assess the amount of flux modification that can be accounted for by these inputs. The sites chosen for this method were:-

1. Redbridge and Woodmill Lane, representing the nearest stations to the tidal limit surveyed.
2. Cracknore and Northam Bridge, representing estuarine stations below major sewage works (at Millbrook/Marchwood, and Portswood).
3. Dockhead, where the two rivers join
4. Hound (Buoy), about two thirds along Southampton Water

The flows used were provided by the Environment Agency. Therefore flows along the two rivers were considered to be represented by that entering the river at the head of the energy, and no additional discharges from waste water outlets were added to the flow. This may be an omission, but without better availability of data from Southern Water this was impossible. The flow at Dockhead and Hound, therefore, was taken to be the summed mean flows of the two rivers (shown as "Exp Dkhd" on the figures). The fluxes calculated from HM data and flows in both rivers were summed to give expected fluxes at Dockhead, and are shown as "T+I".

A 1% error was added onto the SONUS data to represent the spread of concentrations associated with the accuracy of the autoanalyser. End-members were calculated and compared as above. The reason for adding these errors was to help ascertain how an error in analysis could be compounded in predicting an end-member. This is especially relevant to those stations further down the estuary. The further the extrapolation to zero salinity (i.e. the higher the salinity of the last point used in the regression), the more magnified the error in predicted freshwater end member will be. River fluxes in the Test do not appear to have changed much over the two years, although the Itchen has discharged a little more phosphate over 1996 (about 10 tonnes). The flux from the Itchen is always higher than that from the Test reflecting the higher end members recorded at Gater's Mill relative to Testwood.

3.2.4.3 Phosphate

Figures 3.14a & b show annual fluxes at each of the five stations during 1995 and 1996. There appears to be no significant process occurring between the Environment Agency Harmonised Monitoring Programme stations (labelled Test and Itchen in Figures 3.16a&b) and the last navigable point on the surveys (labelled Redbridge and Woodmill respectively in Figures. 3.16a &b). Results of Method 2 show, much more clearly, the influence of waste water inputs. There is also a suggestion that some phosphate is lost in the lower estuary, although the errors associated with these calculations are large.

3.2.4.4 Nitrate

Nitrate is the predominant form of dissolved nitrogen throughout the estuary, varying between 97 and 100% of the total oxidised nitrogen measurement. Figures 3.15a and b show nitrate fluxes during the two years under discussion. The Test is the major source of nitrate to the system, as already mentioned, mainly due to the slightly higher freshwater concentrations and a much greater river discharge volume. A loss of nitrate between the Environment Agency Harmonised Monitoring Programme stations and Redbridge and Woodmill is evident in 1995. During 1996, loss of nitrate is only discernible within the Test. There appears to be no impact on nitrate concentrations from the sewage treatment works. Below Dockhead the flux appears to be conserved throughout the estuary in both years.

3.2.4.5 Ammonia

Ammonium fluxes, from the Test and the Itchen, based on Environment Agency data are similar (Figures 3.16a and b). There appears to be little variation over the two years. Between Testwood and Redbridge ammonia is added to the river during 1995 and 1996, whilst there is no evidence of addition within the upper parts of the Itchen estuary. The fluxes calculated between Gater's Mill and Woodmill are similar, and the error on the Woodmill calculation prevents us from inferring anything from such a relatively small change.

Similarly, large errors on calculations for fluxes at Cracknore and Woodmill Lane prevent us from inferring any flux change below the sewage treatment works. This can only be inferred from nutrient salinity plots, and it is impossible to quantify the impact of these outfalls on the ammonium flux. This problem is further experienced towards the sea, where large errors on the Dockhead and Hound calculations prevent any further conclusions to be drawn about modification to the riverine ammonia.

3.2.5 Discussion

3.2.5.1 Comparison of methods for estimating addition and removal in the estuary

Combining the results from Methods 1 and 2 for the riverine output into the estuary we can attempt to summarise the fluxes from the two methods and see how they differ from fluxes calculated from fresh water data. The results are presented in Table 3.2.2, along with the figures from the EA freshwater data. Method 1 shows the flux from end-members extrapolated to zero salinity, and the Method 2 results are derived from summing the expected fluxes calculated for Woodmill Lane and Redbridge.

It can be seen that the two extrapolation methods used here give similar results for TON, some 6% different, suggesting that TON acts conservatively in the surveyed estuary, and that any extrapolation method will, in essence, give the same result. Comparisons, however, with EA data, which show the real flux of nutrients to the upper estuary suggest that between 22 and 27% of TON is lost in the short distance between the HM station and the highest navigable point. This was true for both rivers in 1995, and only clearly detectable in the Test in 1996.

Recent research (Nixon et al., 1996) suggests that an increase in residence time will effect the rate of denitrification occurring within the estuary. This may help to explain why the upper part of the estuary underwent wide scale nitrate loss during the low flow summer of 1995. It is possible, but as yet unproven, that the large reed bed communities within the upper Test estuary act as large "biofilters" and remove the nitrate either by supplying enough organic matter to the sediment to cause denitrification and draw down of water column nitrate, or by placing a biological demand on the water column nitrate during their main growing season. A further source of a denitrification processes may come from microbial communities associated with suspended sediments producing their own denitrifying microenvironments.

In comparison to freshwater data, the two methods both over and underestimate in phosphorus depending on the method used. For method 1, this underestimation is about 46%, suggesting that the gross change we see within the study area is an addition. Nutrient salinity plots point to waste water inputs as being sources of phosphate to the system. In Method 2, which is supposed to examine the influence of these point sources more carefully, the results between theoretical and actual are much closer. In fact, the results from Method 2 are about 15% lower than suggested by the EA data. It is not clear why this discrepancy has occurred. It might be that Method 2 places large emphasis on the seawater end member, which, at certain times of the year is at or very near zero. Also, this table has been calculated with data representing the flux at the

highest navigable point, where nutrient levels are lower than mid estuary. Method 1 relies upon more data points all of which are below the influence of waste water inputs. Weighting the extrapolation in such a way might, arguably, at least lower calculated fluxes in Method 2 over those of Method 1. The second method is only really useful here for gaining extra information about the flux changes above and below possible point sources.

3.2.5.2Estimates of contribution of sewage sources to the load of nutrients exported from Southampton Water

An important question in all estuaries is the extent to which both natural and anthropogenic processes in the estuary modify the load of nutrients that arrives in receiving waters (Nixon 1996). In Southampton water one of the critical tasks is the assessment of the scale of direct sewage discharges into the system. From published maximum flow and population equivalents for the sewage works a maximum likely impact can be calculated and this can be a compared to estimates based on observations. The potential size of the direct discharges into the estuary if the sewage were untreated can be calculated. This is done using:- (i) figures for the per capita estimates of potential human discharges of nitrogen 3.3kg/y and 0.4kg/y of phosphorus, and, (ii) published population equivalent for appropriate sewage works. The totals for the Millbrook, Slowhill Copse, Portswood and Woolston works comes to 1211tonnes N/y and 147 tonnes P/y. The SONUS survey data can be used to assess export loads from the estuary in comparison that which can be calculated from the river input flow and concentration data.

The estimates made using the more appropriate method (Method 1) listed in Table 3.2.1 suggest that the directly discharged sewage load to the estuary was 44 tonnes of phosphate in 1995 and 19 tonnes in 1996, and 3 tonnes of ammonia in 1995 and 18 tonnes in 1996. The increase in total nitrogen discharge is small compared to the river load and appears to be less than the amounts of nitrate lost from the upper estuary. However the increase in phosphate load is significant and is equivalent to 71% of the river load in 1995 and 26 % in 1996. Comparison with the above estimate of the potential load from untreated sewage suggest that treatment is effectively removing a large proportion of the potential nitrogen load but that a third of the potential phosphate load was discharged to the estuary in 1995.

3.2.6. Conclusions

Calculating nutrient fluxes to the coastal zone, through an estuary, is fraught with difficulty, and is more involved than combining EA and freshwater nutrient data. Estuaries act as sources and sinks for all major nutrients, these processes being driven by chemical and biological reactions, and the output of waste waters from industrialised and urbanised areas. Assuming the flux calculated from freshwater end member data from the EA archives arrives at the coastal zone presupposes that these nutrients act conservatively in the estuarine zone, such that their concentration-salinity profiles are determined solely by the mixing of fresh and sea water.

The above estimates based on the SONUS survey data set (Table 3.2.2) suggest that over 3000 tonnes of nitrogen and between 114 and 199 tonnes of phosphorous has moved through the estuary and out into the Solent, during the two years of study. However, by examining theoretical fluxes and nutrient salinity plots, it is clear that all the nutrients undergo some non-conservative behaviour at some time of year. This can be summarised as:

- The loss of nitrate within the low salinity range, which can be seen when comparing theoretical freshwater fluxes with those calculated from EA data. This is most prevalent during summer, especially during 1995, when river flows were relatively low. Over the two years this nitrate loss accounted for between 22 and 27% of riverine nutrient flux.
- Significant inputs of ammonia, nitrite, and phosphate from point sources along the estuary are detected in the survey data. These inputs are related to inputs of waste water from sewage works along the length of the estuary.
- Flux calculations suggest that additions equivalent to up to 46% of phosphate and 104% of ammonia in the river water inputs has been added to the estuary through these point sources.
- The increase in phosphate load is significant and is equivalent to 71% of the river load in 1995 and 26 % in 1996.
- Comparison with the above estimate of the potential load from untreated sewage suggest that sewage treatment is effectively removing a large proportion of the potential nitrogen load but that a third of the potential phosphate load was discharged to the estuary in 1995.
- The removal of nutrients within the main body of Southampton Water occurs for all nutrients, but is only detectable in some spring and summer surveys. Detectable removal is associated with periods of more intense algal bloom conditions.

3.3 Chemical speciation of dissolved nitrogen and phosphorus within the estuary

3.3.1 Introduction

Inorganic forms of nitrogen and phosphorous in waters are taken up into biological material during the growth of micro and macro algae in estuaries when light levels are high enough for photosynthesis to occur. Decay of this plant material or its grazing by higher organisms tends to return the nitrogen and phosphorus back to solution in a range of both organic and inorganic compounds. Bacterial action leads to the return of less refractory organic compounds back to inorganic forms. It has been suggested that as much of the work on the nitrogen and phosphorus flows through estuaries has tended to focus on the more easily determined inorganic forms of nutrients (nitrate-nitrogen and phosphate-phosphorus) that by neglecting the organic and particulate forms, fluxes of nutrients to coastal waters and between different coastal seas may have been substantially under estimated (c.f. Laane et al., 1993).

In this section of the report we present an analysis of the relative sizes of the pools of different forms of biologically available nitrogen and phosphorus compounds in the Southampton Water - Solent system.

3.3.2 Results

3.3.2.1 Nutrient-salinity relationships

Figures 3.8,3.9,3.11,3.12, and 3.13 show the distribution of N and P species through the estuary. Data for representative surveys between November 1995 to February 1997 are shown for DOP and DON (Figure 3.13). Samples from the two arms of the estuary the Test and Itchen and the main body of the estuary Southampton Water are shown distinguished by different symbols in these plots. (*Note*: At times of low river flow events, and adverse tidal conditions, it was not always possible to sample low salinity water along the river Test.) As has already been discussed, the relative influence of direct discharges from sewage treatment works is different in these three areas. This gives rise to some distinct differences in distributions in the three parts of the estuary.

Patterns (Figure 3.9) of distributions of concentrations of dissolved inorganic phosphorus (DIP) are generally controlled by sewage inputs at Portswood and Millbrook/Marchwood. Concentrations within the Test are 2 to 5 times lower than those in the Itchen, reflecting both land usage and the relative contribution of waste water to fresh water in the two rivers. Levels are often higher when river flow is low, reflecting the lack of dilution of the effluent by river water. When the data from each survey is plotted against the salinity of the sample, the general pattern seen in the distribution in the River Itchen is a peak associated with the waste water outfall, followed by conservative behaviour to the mouth of the river at Dockhead. In the Test, conservative behaviour maybe inferred from Redbridge to Dockhead, with a peaks associated with Marchwood and Millbrook discharges. However, in the Test these inputs from sewage treatment works are only measurable close to the discharge point and have less impact on phosphate levels than Portswood does in the Itchen. In Southampton Water phosphate levels are an average of the two inputs, and behaviour appears to be conservative through the year except at times of significant biological production. Concentration levels drop to near zero values in high salinity waters (salinity > 34) during the summer months (Figure 3.2b).

Patterns (Figure 3.13) of distributions of concentration of dissolved organic phosphorus (DOP) are erratic. Concentrations are often low, and rarely exceed 5µM. However, during June 1995, concentrations up to 20µM were recorded in parts of the rivers, and this was equivalent to some 50% of the total dissolved phosphorus load. The location of the peak within the estuary coincides with the peak in DIP input from the Portswood sewage works. Such a large peak was only observed on one survey so the results should be treated with some caution as possible analytical error cannot be ruled out. A check of the associated records found no transcription or arithmetic errors.

Throughout the year nitrate distributions with respect to salinity tend to be conservative. The apparent riverine end member concentrations (Burton 1973) cycle through the year from a winter high (440µM in January 1996 to a summer minimum (330µM in June 1996). There is little difference between nitrate levels within the Test and the Itchen. Conservative behaviour

continues out into the Solent except during the summer, when near zero concentrations of nitrate were found within Southampton Water at high salinities (salinity >34, Figure 3.2a). There appears to be no significant influence from the waste water discharges throughout the estuary.

Distributions of concentrations of nitrite (Figure 3.11) vary throughout the year. A consistent cycle with the season is not evident. Riverine end member concentrations vary between about 3μM in January 1996 to 8μM in September of the same year. Concentrations within the Itchen tend to be higher than those in the Test, except where a distinct point source input is evident on some surveys data sets at around a salinity of 25. These are associated with the water treatment works at Millbrook and Marchwood. It is most marked during the summer and least evident during higher flow conditions. In the Itchen, a peak in the upper part of the estuary is associated with the Portswood waste water treatment works discharge. Distributions downstream of the point sources appear to be conservative. Within Southampton Water distributions are generally controlled by conservative mixing and concentrations of nitrite tend to be low during the summer months. Concentrations of ammonium (Figure 3.12) are substantially higher than those of nitrite at times reach 30% of the nitrate concentration. Patterns of ammonia distributions tends to vary in much the same way as those of nitrite, suggesting that the dominant source of both is the same and is from sewage treatment works. Point sources on the Test and the Itchen are distinguishable, and, as with nitrite, concentrations up and downstream of these point sources are generally conservative. Riverine end member concentrations are lower than those of the waste water. They vary between 3μM in summer, and up to 9μM in the winter. As with nitrite low concentrations of ammonium were found during the summer surveys in Southampton Water.

Distributions of concentrations dissolved organic nitrogen (DON) are plotted in Figure 3.13. Clear indications of point source inputs are not obvious in these plots. With the exception of the Itchen during November 1996 levels rarely exceeded 25 μM. Lowest values were found during the high flow conditions of January 1996, where near zero levels were found within the rivers. In the rivers, there is some relationship between higher levels of DON and proximity to waste water outputs. However, this is not always clear and consistent. There is some suggestion in the plots of an increase in DON levels within Southampton Water, with a tendency to fall back to low levels within the Solent (as in November 1996). This trend is better defined in relation to concentrations of total nitrogen discussed below.

3.3.2.2 Dissolved organic species as proportions of the total dissolved nutrient pool

The pie charts in Figure 3.17, shows the proportion of each of nitrate, nitrite ammonia and dissolved organic nitrogen relative to the total dissolved nitrogen (TDN) measurement in the sample. Four locations have been used to identify the geographical as well as seasonal changes that occur within the estuary. The data is shown in the form of pie charts for these sites.

The data show that nitrate dominates the dissolved nitrogen pool within the rivers at the heads of the estuary (Woodbridge-Itchen and Redbridge-Test), and this is true throughout the year.

Nitrate contributed between 97% and 72% of the TDN. The highest proportion occurring during January 1996. Nitrite never represented more than 3% at any time through the year, being highest in September. Ammonium levels were highest during November 1996 (8%) within both rivers, but generally contributed less than 4% to the TDN pool. DON levels within the rivers were usually small, and sometimes not detectable during periods of high flow. However, during the spring and summer and, occasionally, during the autumn DON made up between 6% and 19% of the TDN pool.

Further down the estuary, at the confluence of the two rivers (Dockhead), the inorganic constituents of the TDN pool were still the greater proportion, however DON was more important than in the rivers themselves. During autumn and the summer, nitrate accounted for between 38% and 42% of the TDN. However, during periods of high flow, during January the proportion of nitrate rose to 78%. This was also true of March 1996, when there was no DON present. Ammonium levels varied through the year from 13% in March to 25% in September 1996, with little evidence of seasonality. Nitrite levels were again a minor component of the TDN pool, compromising between 0.5 to 3.5% of total dissolved nitrogen. DON proportions varied between 0% in March 1996 to over 40% in November 1995 and June 1996. During the autumn of 1996 DON levels were about 30% of the TDN pool, whilst during high flow conditions in January 1996 DON levels were relatively low, at 8%.

At Calshot, towards the Solent and the Channel, the organic fraction of the TDN pool increased further, with exception of March 1996. In the inorganic fraction, nitrate was still dominant, ranging between 10% to 85% of TDN. During winter and autumn nitrate contributed between 15% and 45% of the TDN. During summer, inorganic nitrogen levels were relatively low, so DON was the dominant N species. However, during the spring, no DON was found at Calshot. In general, DON values varied between 31% and 65% of the TDN pool during the autumn and winter, whilst during the summer DON values peaked at 82% of total dissolved N.

As discussed above concentrations of DOP are highly variable, when calculated as a fraction of the total dissolved phosphorus concentration (TDP) values range from zero to 50% (Figure 3.18). The plots are noisy with out consistent patterns suggesting that any detailed analysis of the apparent variations would be unreliable. The noise in the data in probably inherent in the method used to distinguish the two fractions, and relies on the difference between two large numbers, which in them selves may be relatively precisely determined but the relative error in the difference may be large. (DOP is determined as the difference between the amount of phosphate detected in the sample before and after an oxidation reaction is carried out on the samples to release phosphorus from organic compounds.) Taking a broad view of the data in Figure 3.18 it appears that the fraction of DOP in the Solent system is small and not likely to be larger than a few percent of the concentration of phosphate this consistent with observation sin other UK estuaries (Sanders et al 1997).

3.3.3 Discussion and Conclusions

Nitrate concentrations throughout the year were found to be conservative (Liss 1973), suggesting that there were no significant point sources that were releasing nitrate into the estuary. This was confirmed by Southern Water (A. Saunders Pers Comm), who carry out large scale denitrification in their waste water treatment plants that input to estuarine waters. There was little evidence of significant biological uptake of nitrate within the estuary except at high salinities in summer. At high salinities in the open Solent in summer nitrate concentrations are below the detection limit of the method that we use to determine it (<0.5µM). In July 1995 chlorophyll concentrations in excess of 10µg/l were observed in Southampton Water (Figure 3.3a).

Nitrite, ammonia, DIP and DOP distributions highlight the influence of waste water works, showing the inputs at Portswood, on the Itchen, and Millbrook/Marchwood on the Test. There appears to be a difference in the way discharges influence nutrient levels in the two rivers. In the Itchen, the outfall dominates the nutrient concentrations and levels fall from these peaks in a quasi conservative manner, whereas within the Test, the influence of sewage discharge is seen on a much more localised scale. This probably reflects the relative volumes of the two systems at the points of discharge. The Millbrook outfall enters the Test estuary into water of relatively high salinity i.e. into a relatively large volume of water. Hence the noise in data collected around the discharge is result of sampling poorly mixed waters, so that a waters of particular salinity actually contain different relative components of river water and sewage discharge. Concentrations at Dockhead are usually higher than final samples from the Test and lower than final samples in the Itchen, reflecting the mixing of these two sources. Nutrient behaviour in Southampton Water is predominantly conservative, but summer surveys have demonstrated areas of nutrient depletion near the mouth of the estuary due to removal by biological production. There is no evidence in these data sets for significant oxidation of ammonia and nitrite to nitrate occurring in the estuary. This is consistent with the rapid flushing, of the order of a day, of the estuary during spring tide conditions (Wright et al 1997), which is similar to the empirical first order oxidation rate constant (= $1 day^{-1}$) used in water quality models (J. Maskell HR Ltd Pers Comm). A limitation of the SONUS surveys was that they were only conducted during spring tide conditions. At the lower rates of flushing, of the order of 3 days, during neap tides (Wright et al 1997) it is possible that greater conversion of ammonia to nitrate might be seen along with an associated depletion in concentrations of dissolved oxygen. No significant depletions in dissolved oxygen saturation levels greater than 10% were seen on SONUS surveys on which dissolved oxygen concentrations were measured by people working on other projects (D. Purdie, Pers. Comm).

The rivers are dominated by the input of nitrate, from diffuse agricultural sources in the catchment area, and little organic N is measured. High flow periods are associated with an inorganic bias. More often than not, organic N is found within the rivers during low flow conditions, when the influence of river borne nitrate is less. In more open water, inorganic N is transformed to organic N as summer approaches. Biological production and low flows ensure that there is a major proportion of DON in the dissolved pool during the summer and autumn. The

influence of the annual phytoplankton bloom is seen through until about spring, when most of the TDN is inorganic. In terms of the relative contribution of organic forms to the dissolved pool, it is clear that the estuary switches from an inorganic N dominated system at the head, to an area where organic N is as or as almost important than inorganic forms. There is no significant contribution by dissolved organic forms of nitrogen to the load of nitrogen exported from Southampton Water to the English Channel above that which can be estimated from measurements of riverine inorganic nitrogen. Production of significant pool of organic nitrogen compounds takes place in the marine waters themselves. The levels of and seasonal variation in DON we have determined are similar to those that would be expected in comparison to the results of Butler et al (1979). The lack of data sets of measurements of DON in coastal waters is high lighted by the fact than the recent modelling work of Anderson & Williams (1998) had to be solely based on the Butler et al (1979) data set, for want of a larger, better or a more recent study. There is no evidence to support the assertion that by neglecting the organic forms of nutrients, that previous estimates of fluxes of nutrients to coastal waters and between different coastal seas may have been substantially under estimated (c.f. Laane et al., 1993).

3.4 TABLES

Table 3.1.1
Summary of Environment Agency data for the rivers Test and Itchen 1974-1998

	Test	Test	Test	Itchen	Itchen	Itchen
	Flow (m3/s)	NO3 (uM)	PO4 (uM)	Flow (m3/s)	NO3 (uM)	PO4 (uM)
1974-1997						
count	935	1081	1051	819	976	952
average	10.2	385.9	5.3	5.6	362.1	10.7
median	9.5	386.4	5.2	5.4	364.3	9.7
maximum	30.4	578.6	16.1	15.7	695.7	39.7
minimum	1.5	94.3	0.3	1.6	136.4	0.3
stdev	4.6	66.1	1.9	2.2	62.0	5.0
%stdev	44.9	17.1	36.5	39.4	17.1	47.2
1974-1979						
count	255	254	250	249	256	253
average	10.3	342.4	4.1	5.1	308.2	7.4
median	9.3	341.4	3.9	4.4	309.3	7.0
maximum	24.3	568.6	12.6	11.1	445.7	39.7
minimum	3.3	211.4	0.7	2.2	202.9	0.6
stdev	4.1	55.5	1.5	1.9	44.7	3.6
%stdev	39.5	16.2	35.8	38.0	14.5	48.8
1980-1989						
count	420	454	429	290	309	311
average	11.1	380.3	6.1	5.9	365.1	13.1
median	10.7	382.1	5.8	5.8	370.0	12.3
maximum	25.3	578.6	11.9	10.6	695.7	29.4
minimum	5.1	94.3	0.3	2.7	136.4	0.3
stdev	3.7	61.2	2.0	1.8	57.5	5.7
%stdev	33.2	16.1	33.3	31.0	15.7	43.2
1990-1997						
count	260	373	372	280	411	388
average	8.8	422.3	5.3	5.9	393.5	10.9
median	7.4	420.7	5.2	5.4	400.0	10.3
maximum	30.4	557.1	16.1	15.7	685.7	32.6
minimum	1.5	164.3	0.3	1.6	214.3	0.3
stdev	5.9	57.9	1.7	2.7	51.1	4.0
%stdev	67.1	13.7	31.9	46.2	13.0	37.2

Table 3.1.2.
Estimates of dissolved nutrient inputs from the Test and Itchen (combined) and the Seine

	N Flux tonnes/year	Si Flux tonnes/year	P Flux tonnes/year
Test and Itchen	1,829	1,653	66
Inputs from the River Seine	53,400	79,600	6,900

Table 3.2.1.
Comparison of fluxes calculated from extrapolated end members (Method 1) from the SONUS data set, and those from EA fresh water data. All units are tonnes

	1995	1996
Actual TON flux (EA)	2138	1799
Predicted TON Flux (SONUS)	1560	1612
Rem/Add	-579	-186
Rem Add (%)	-27	-10
Actual Ammonia flux (EA)	29	27
Predicted Ammonia Flux (SONUS)	32	46
Rem/Add	3	18
Rem Add (%)	11	67
Actual P flux (EA)	62	74
Predicted P Flux (SONUS)	106	93
Rem/Add	44	19
Rem Add (%)	71	26

Table 3.2.2.
Comparison of three methods of freshwater flux calculations over the SONUS project. (All units are in tonnes.)

	Method 1	Method 2	Environment Agency
TON	3172	2966	4059
Phosphorus	199	114	136
Ammonia	78	114	56

3.5 FIGURES

Figure 3.1a. Environment Agency data for river water flow volume m^3/s in the rivers Test and Itchen.

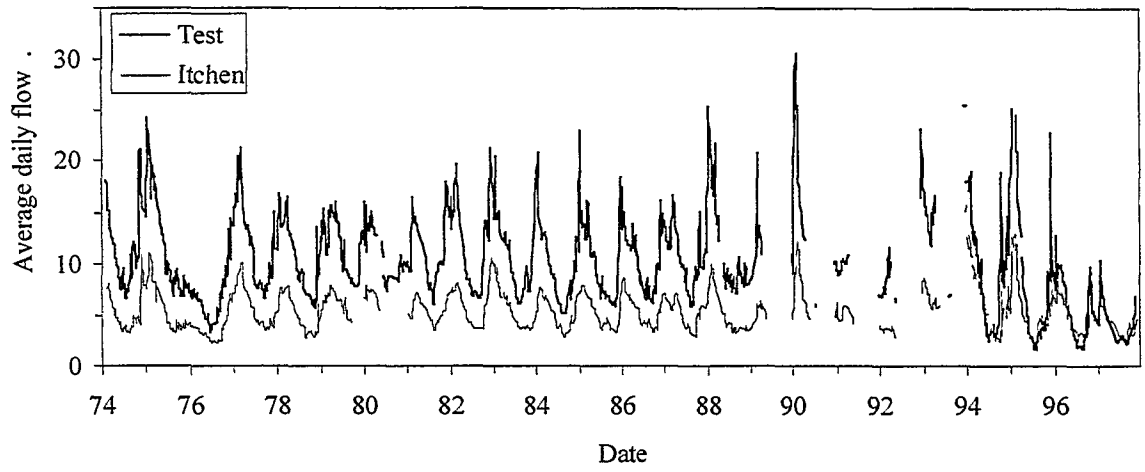


Figure 3.1b Environment Agency data for concentrations of nitrate in the rivers Test and Itchen.

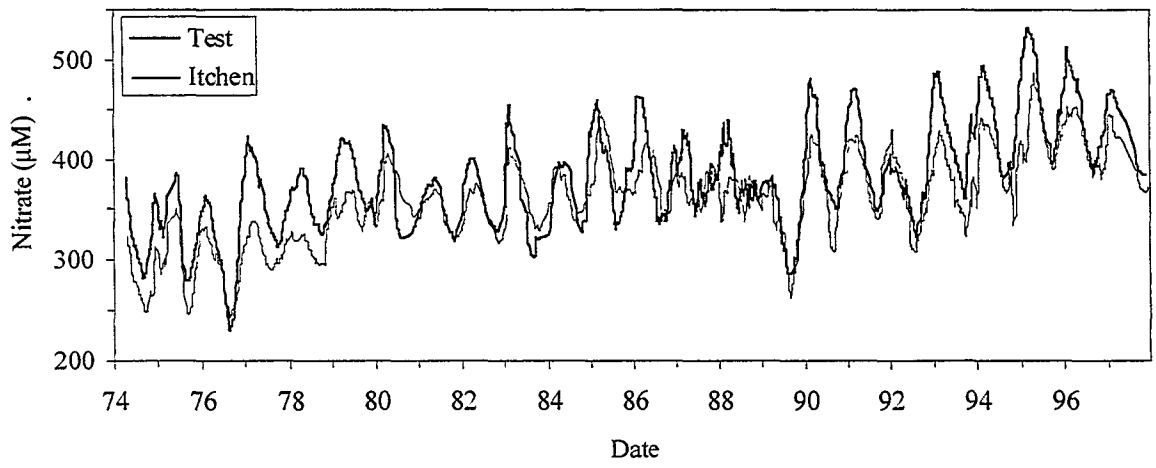


Figure 3.1c Environment Agency data for concentrations of phosphate in the rivers Test and Itchen.

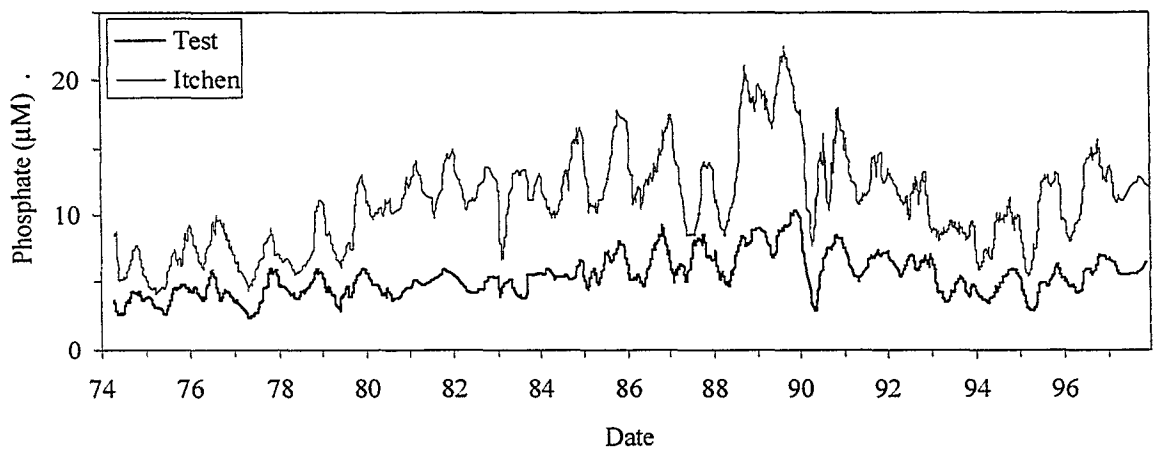


Figure 3.1d Phosphate load in river Itchen estimated from Environment Agency data.(individual daily values).

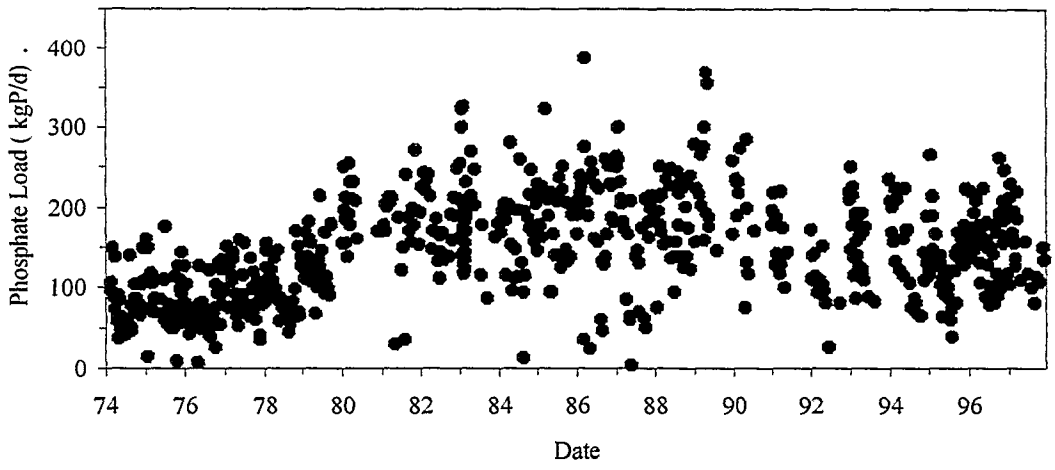


Figure 3.2a SONUS survey data for concentrations of nitrate in Southampton water

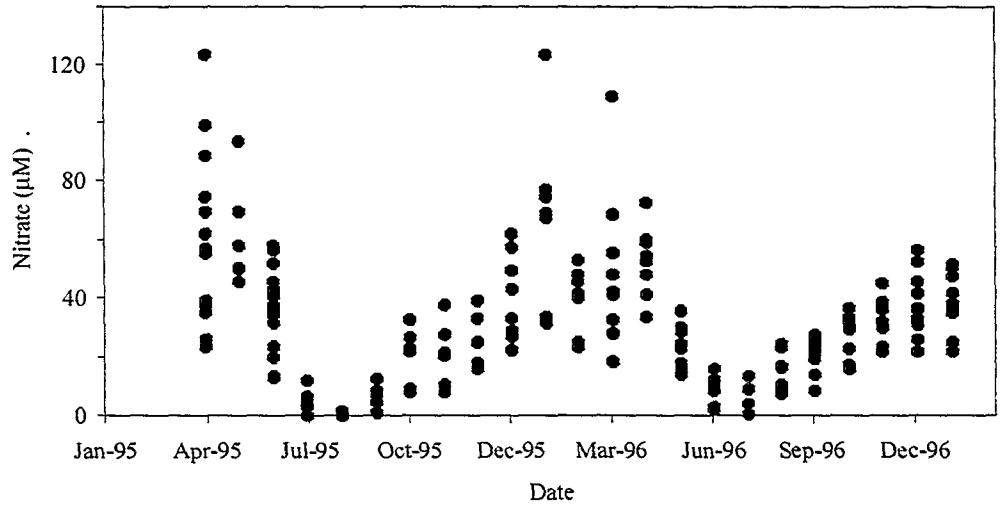


Figure 3.2b SONUS survey data for concentrations of phosphate in Southampton Water

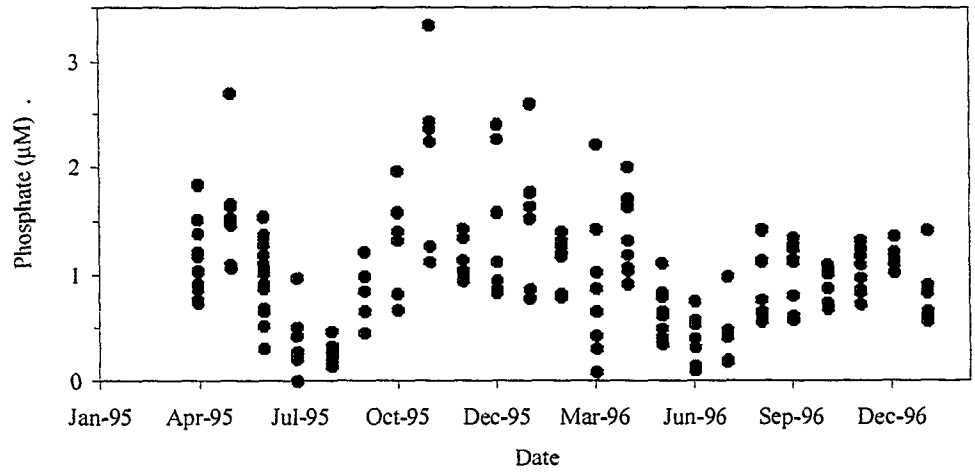


Figure 3.3a SONUS survey data July 1995. Observed and estimated blooms

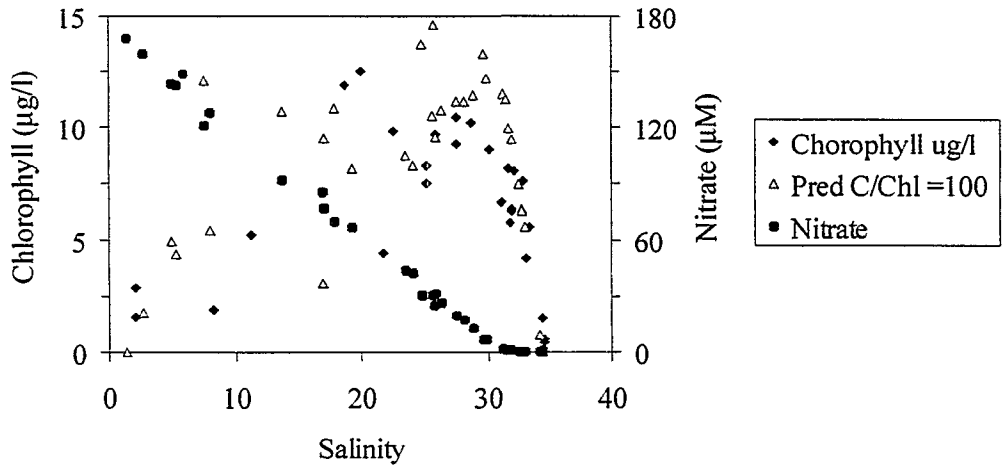


Figure 3.3b SONUS survey data June 1998. Comparison of Neap and Spring tide surveys

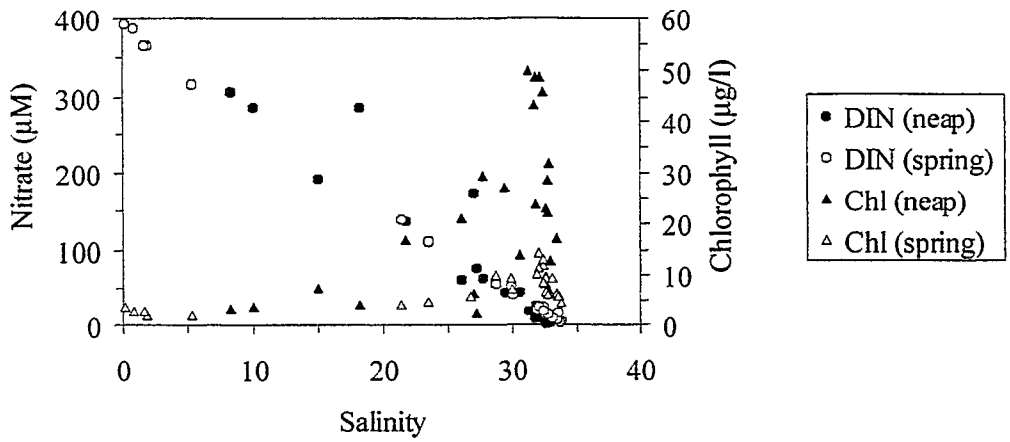
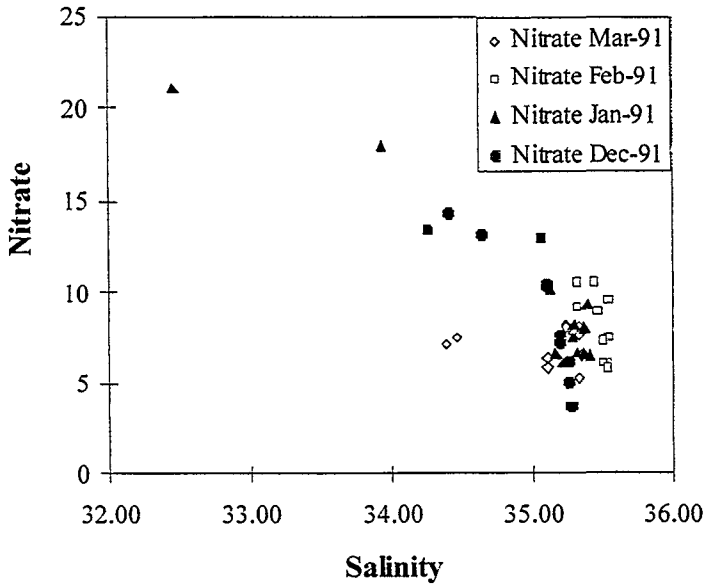


Figure 3.4 FLUXMANCHE-I data from Dover Strait. Winter nitrate concentrations



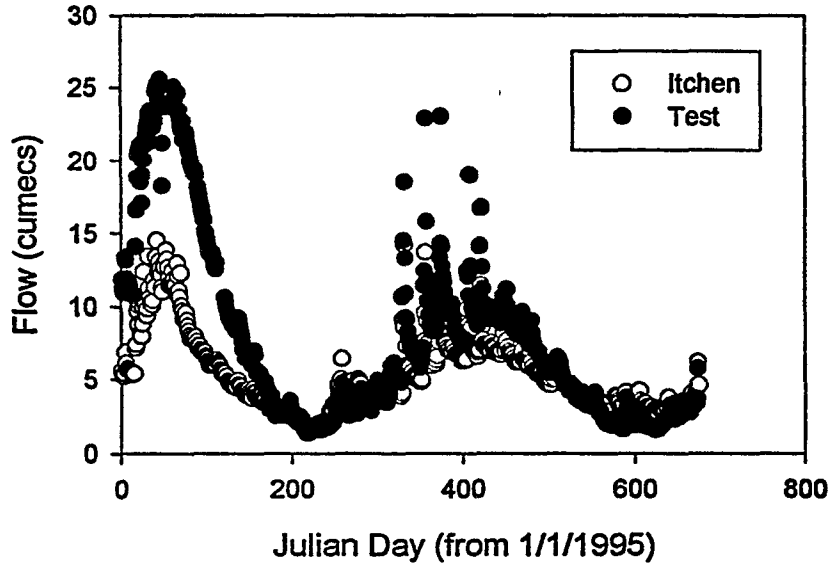


Figure 3.5. Flow data for the Test and the Itchen during 1995 and 1996. Data courtesy of the Environment Agency

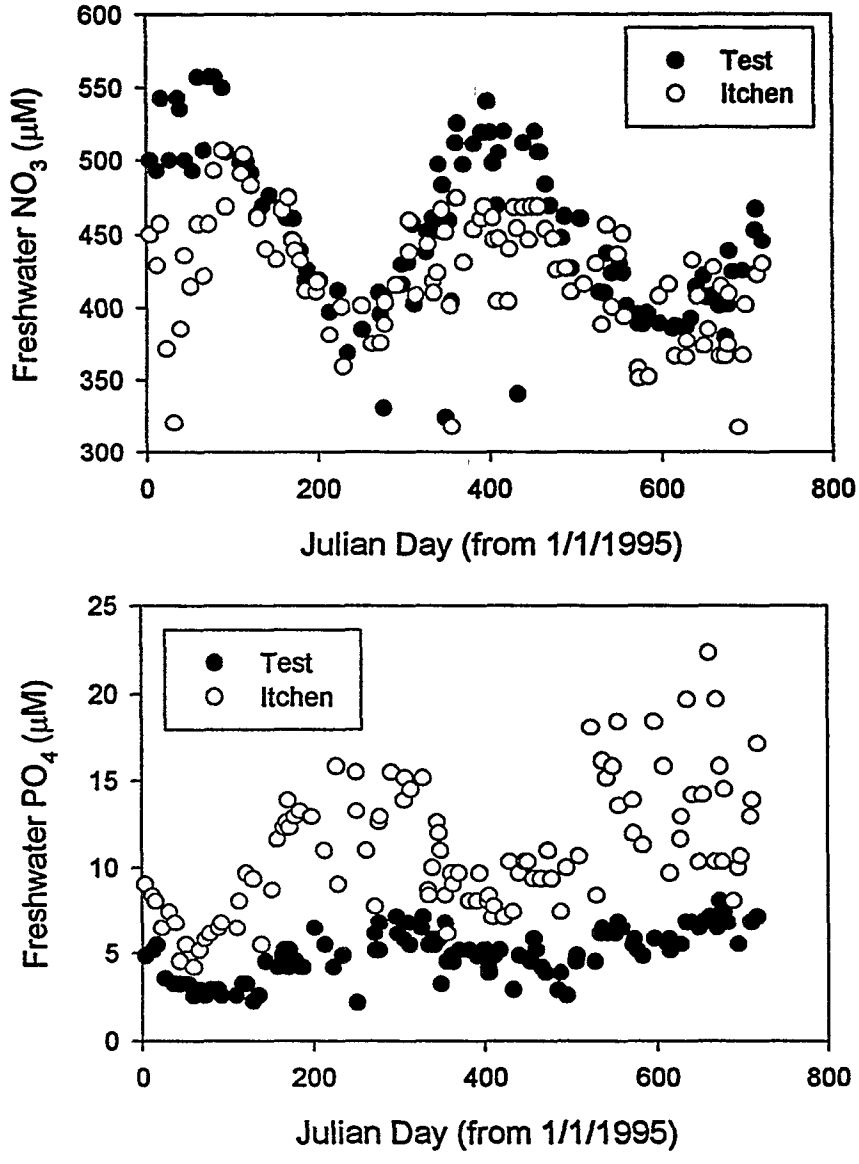
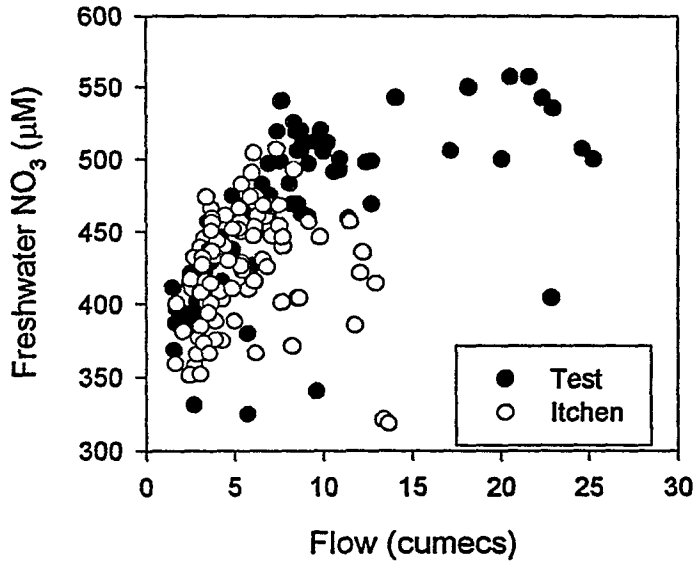


Figure 3.6. Variations in freshwater nitrate and phosphate levels within the Test and the Itchen during 1995 and 1996. Data courtesy of the Environment Agency



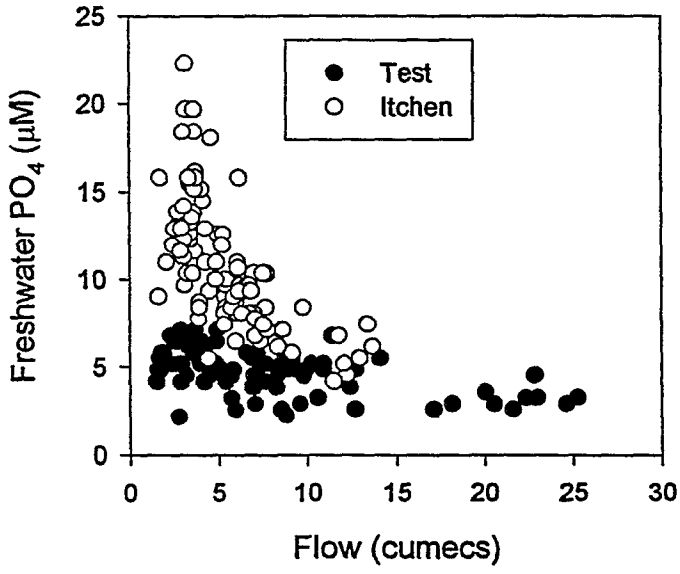


Figure 3.7. Nutrient - Flow relationships for nitrate and phosphate in the Test and Itchen during 1995 and 1996. Data courtesy of the Environment Agency

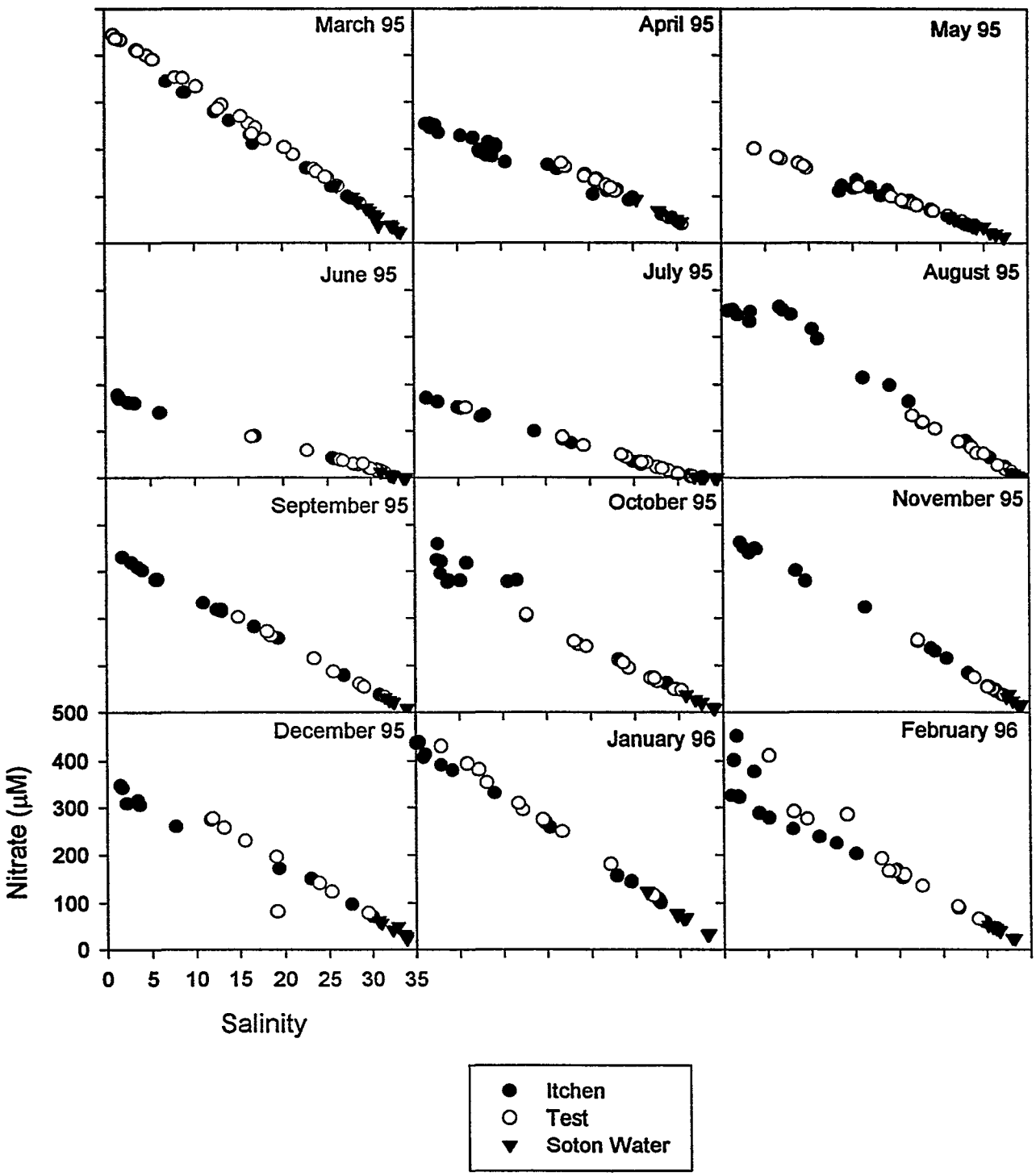


Fig. 3.8 Nitrate salinity relationships for the SONUS surveys

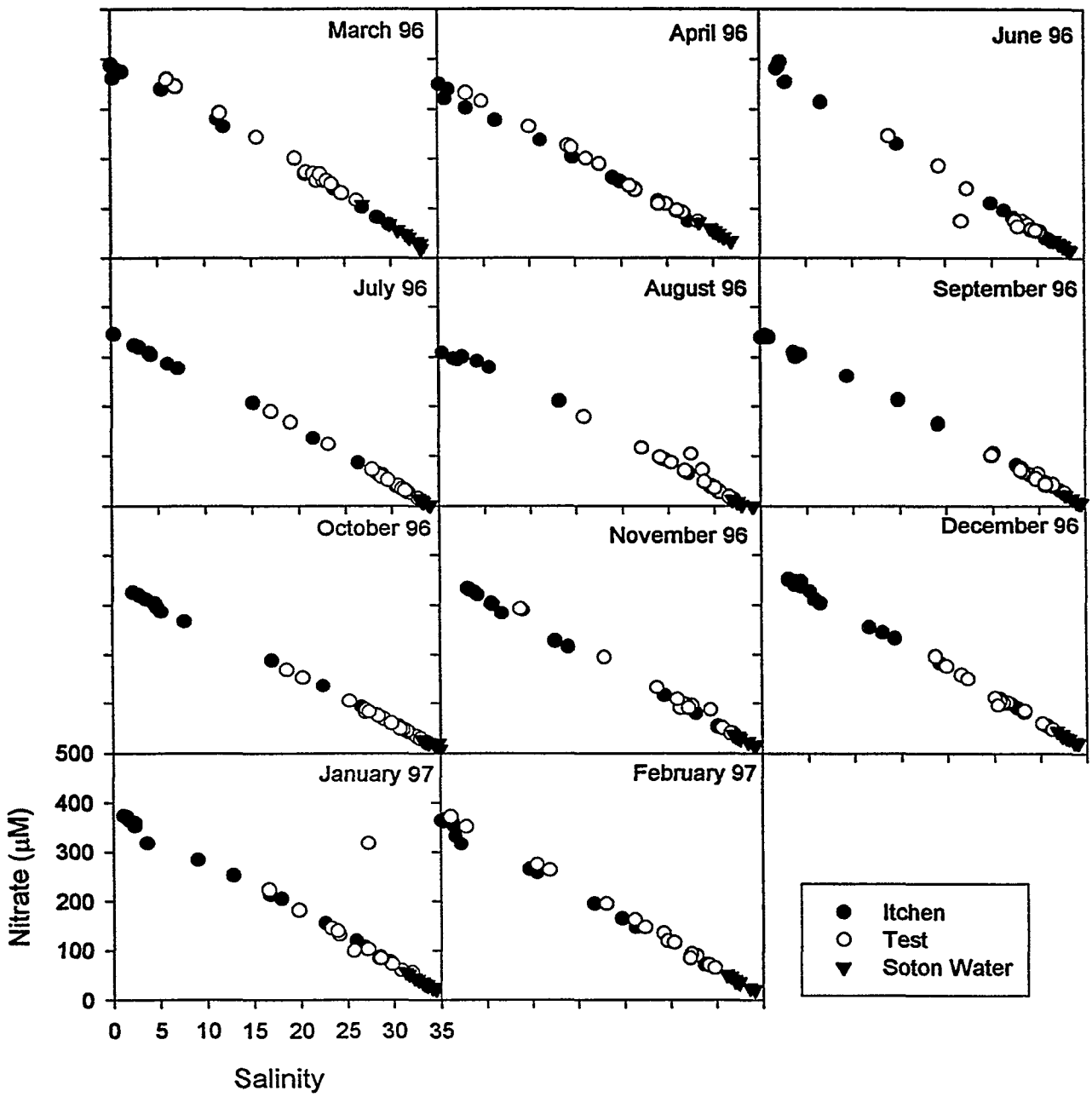

March 96
April 96
June 96
July 96
August 96
September 96
October 96
November 96
December 96
January 97
February 97
Nitrate (µM)
0
100
200
300
400
500
0 5 10 15 20 25 30 35
Salinity
Itchen
Test
Soton Water

Fig. 3.8 Contd.

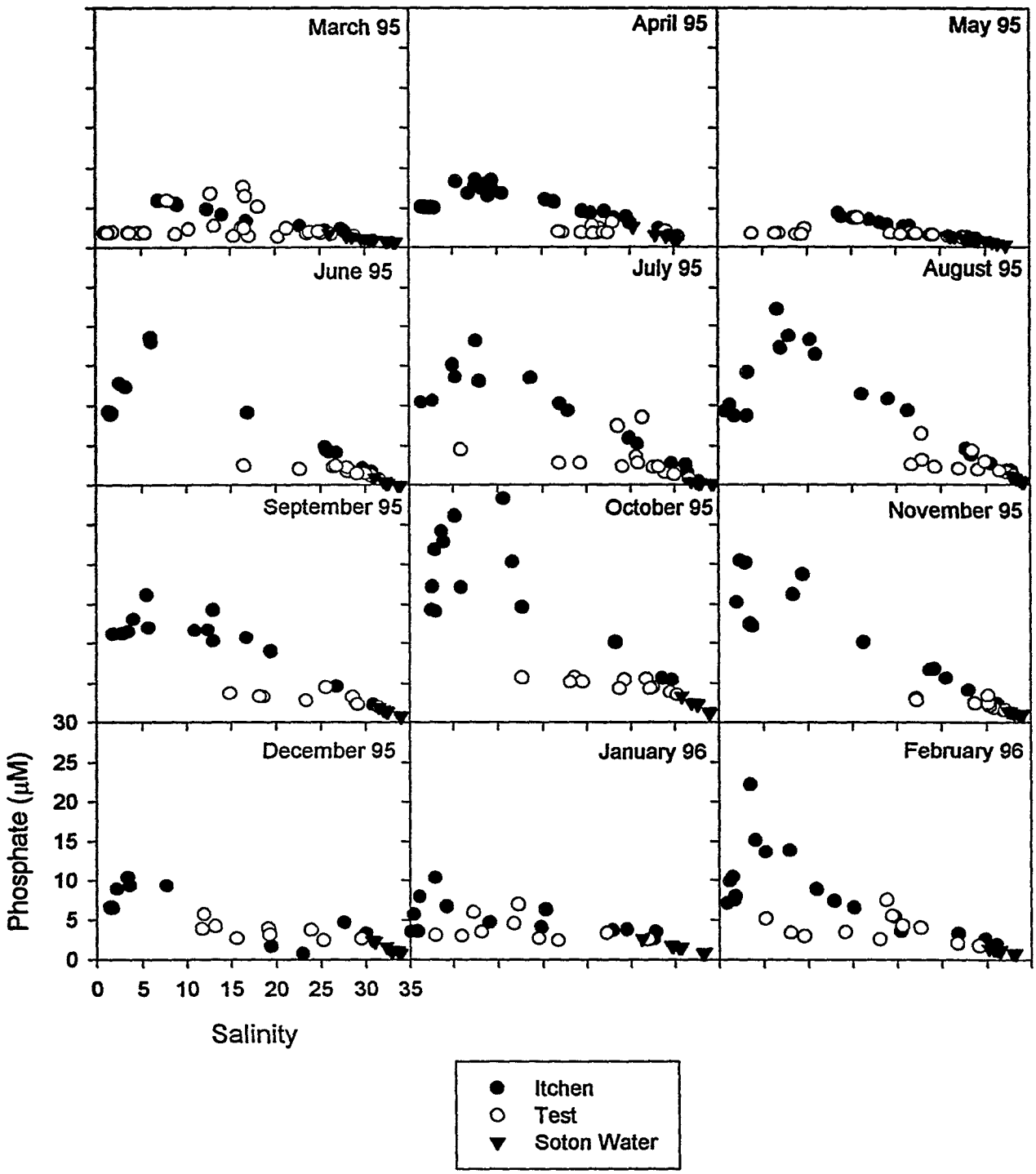


Fig. 3.9 Phosphate salinity relationships for the SONUS surveys

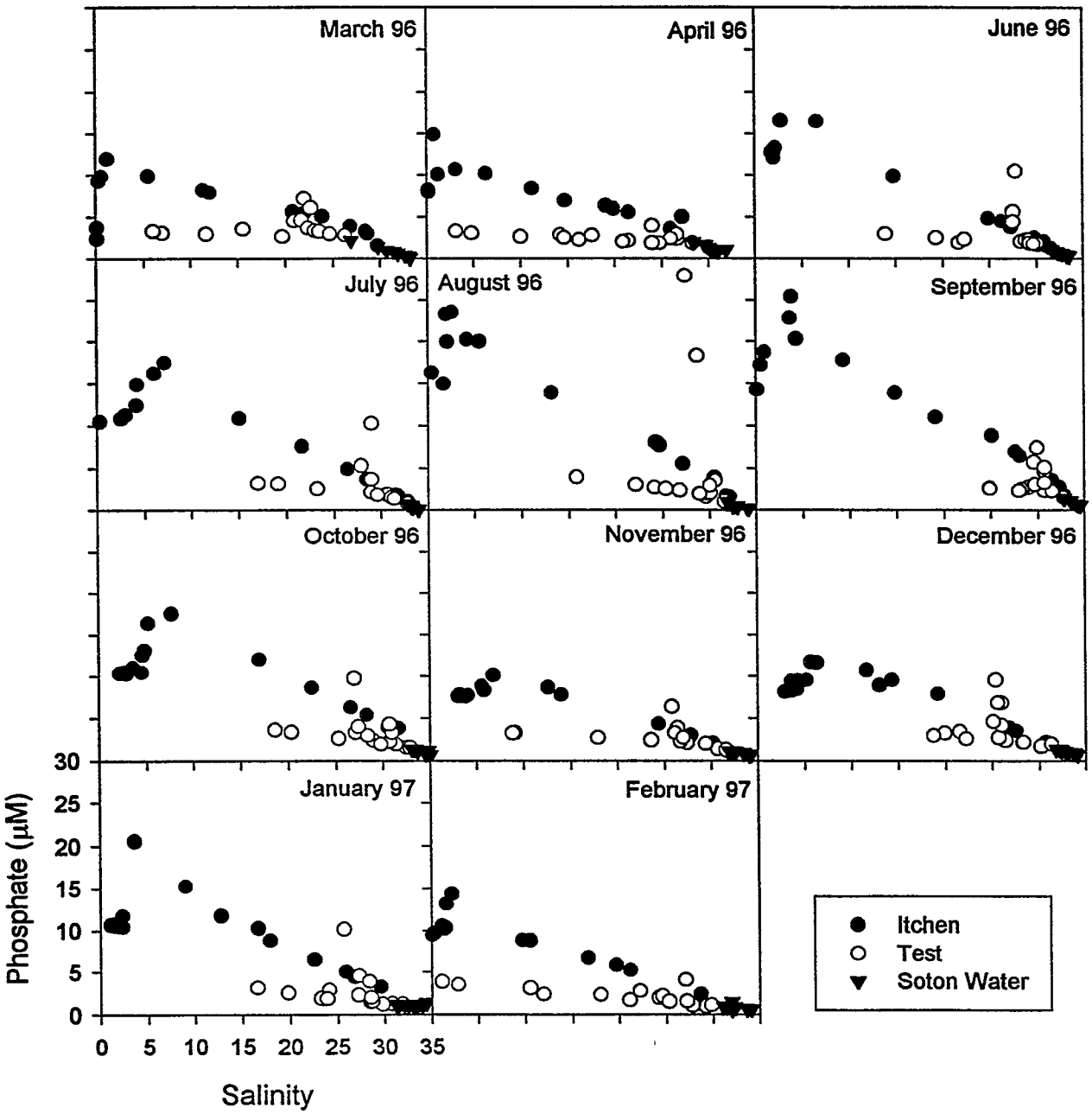

March 96
April 96
June 96
July 96
August 96
September 96
October 96
November 96
December 96
January 97
February 97
Phosphate (µM)
Salinity
0
5
10
15
20
25
30
35
Itchen
Test
Soton Water

Fig. 3.9 Contd.

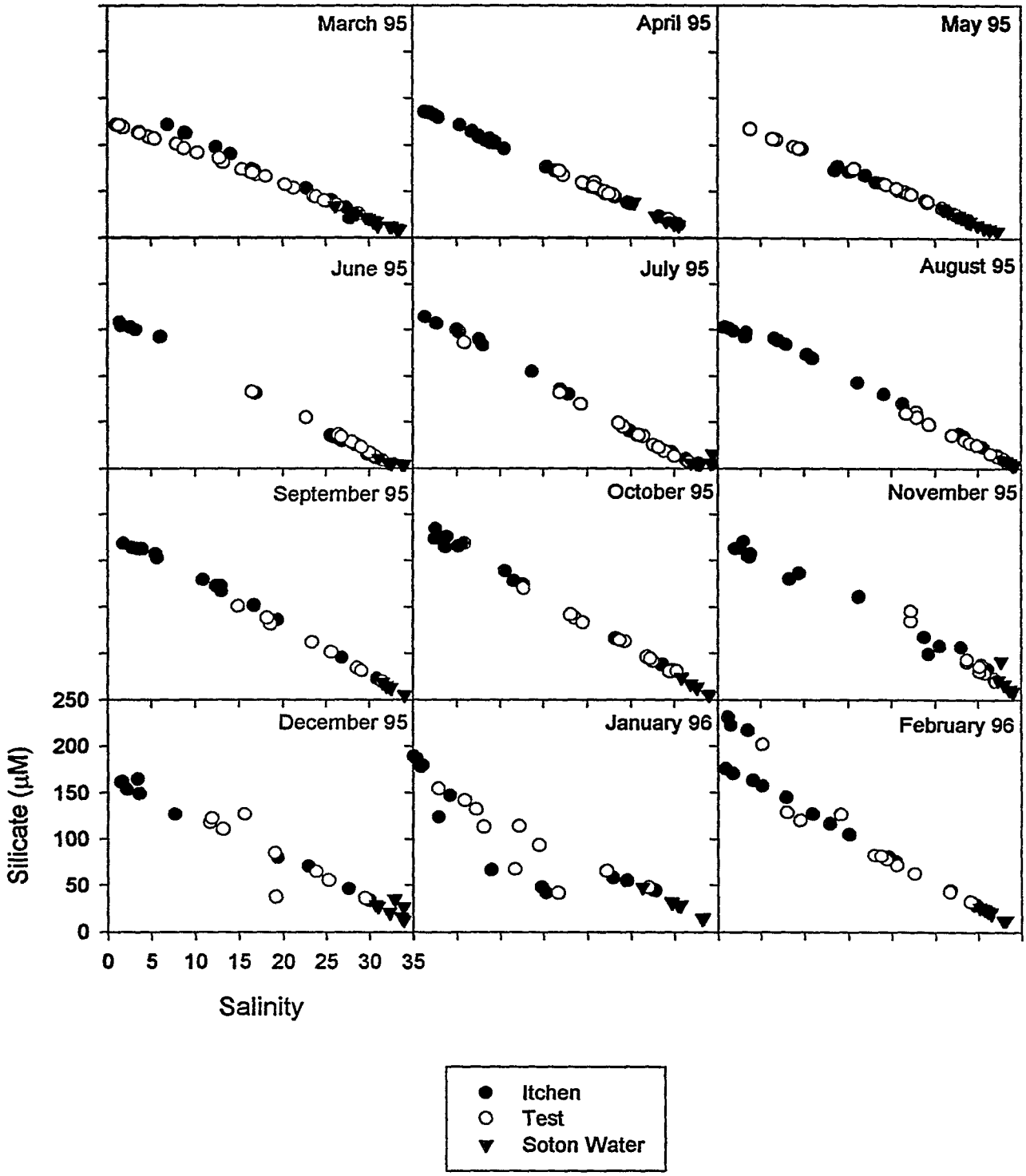


Fig. 3.10 Silicate salinity relationships for the SONUS surveys

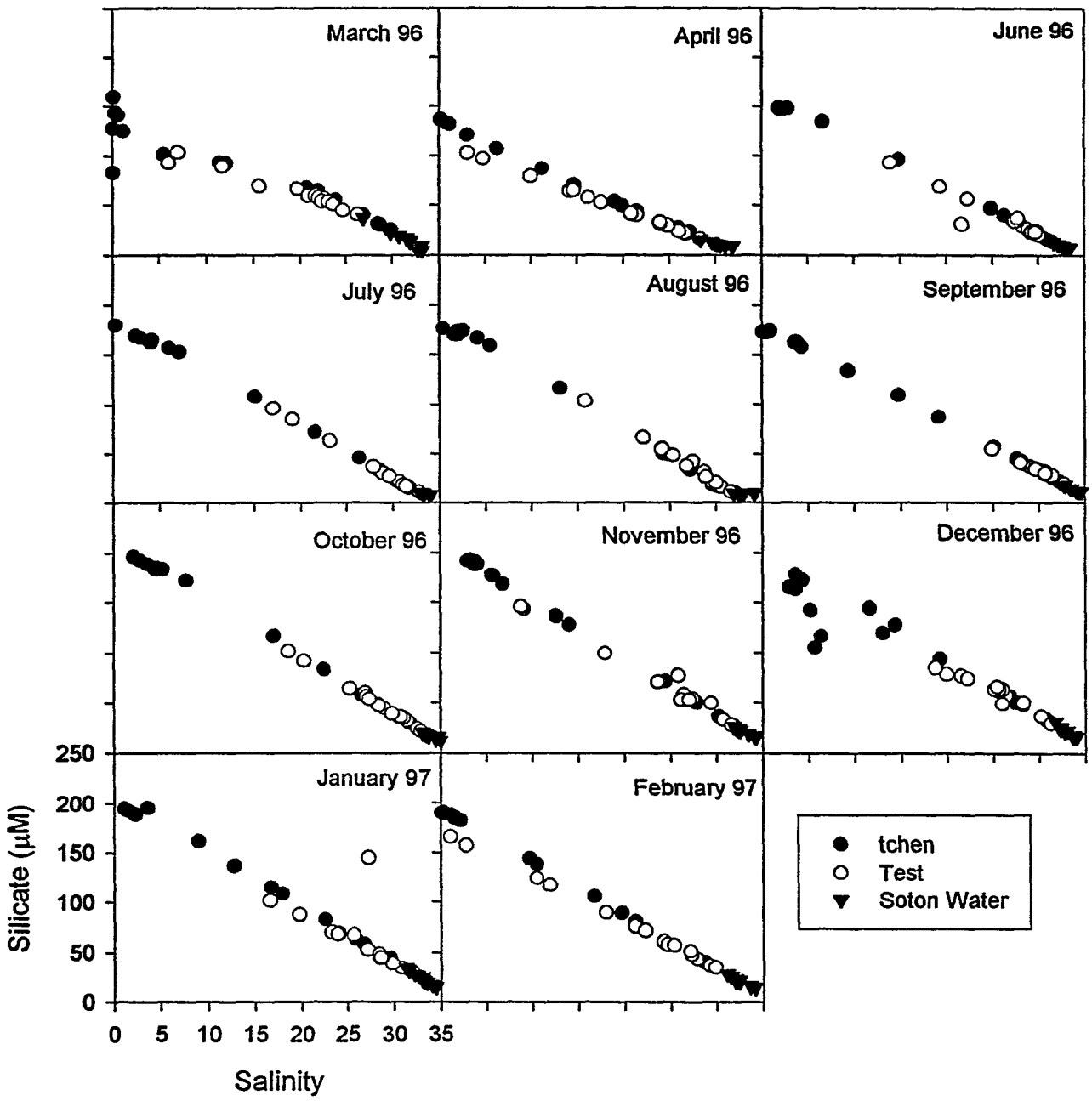


Fig. 3.10 Contd.

Fig. 3.11 Nitrite salinity relationships for the SONUS surveys

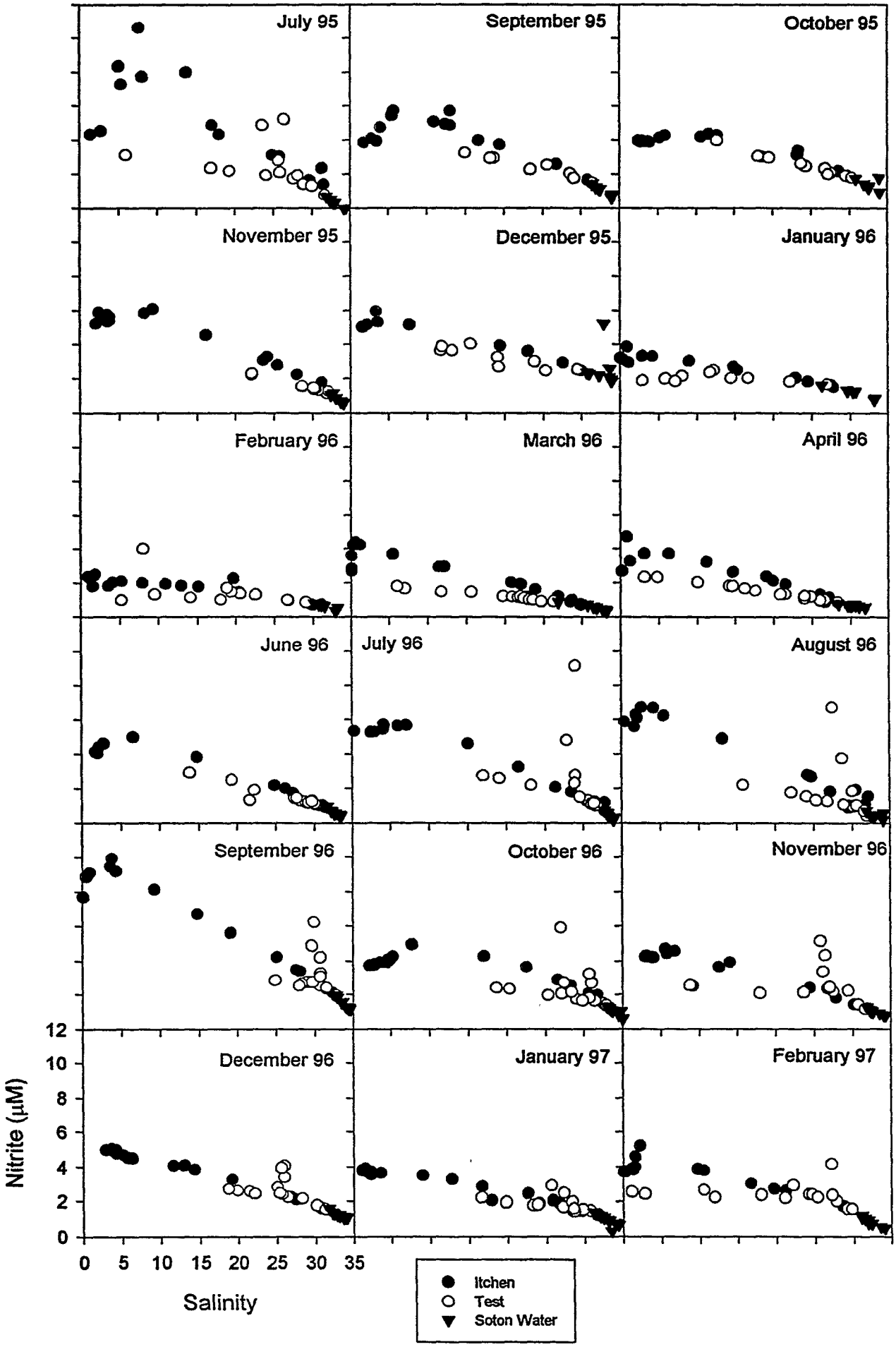
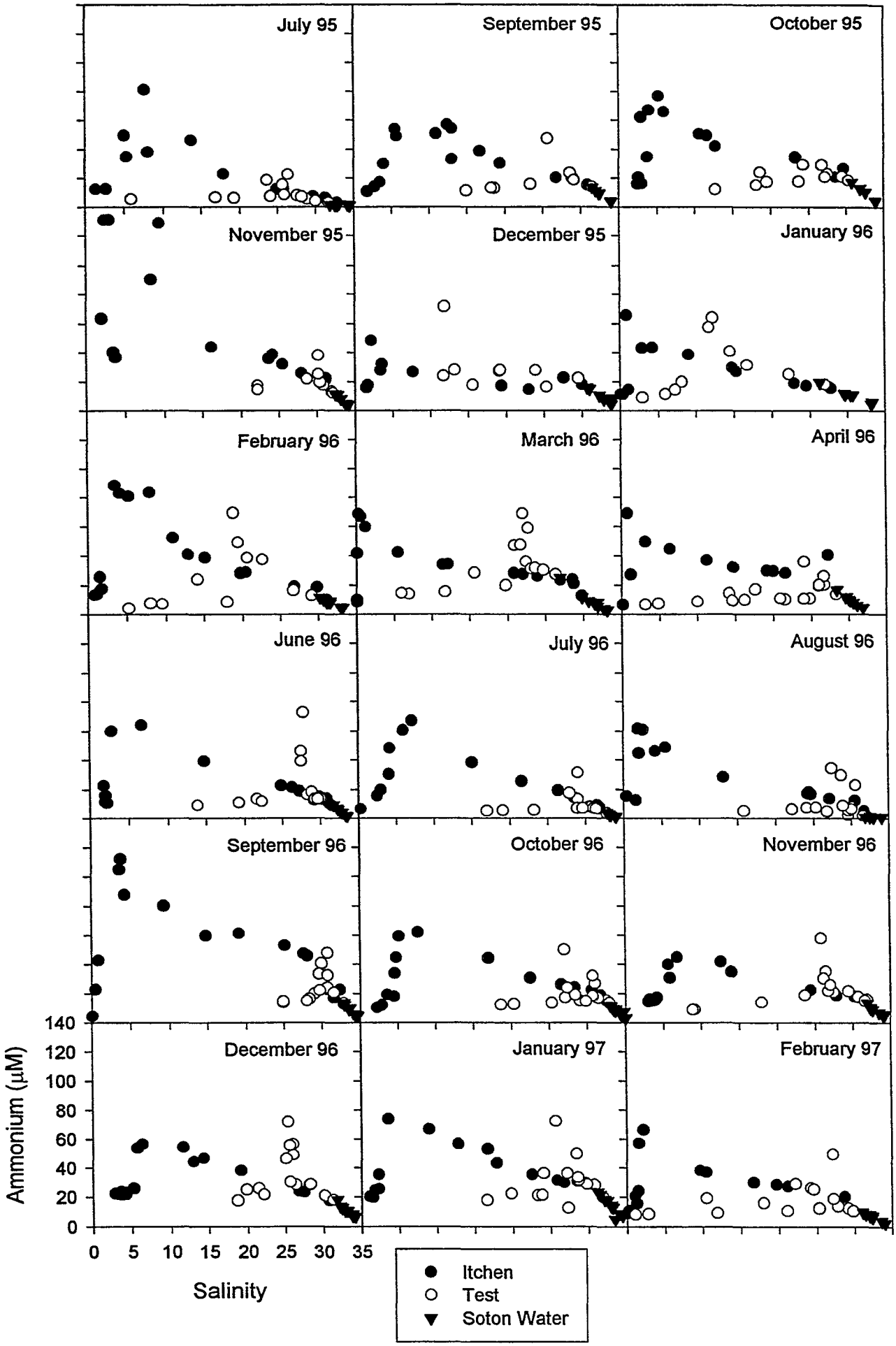


Fig. 3.12 Ammonia salinity relationships for the SONUS surveys



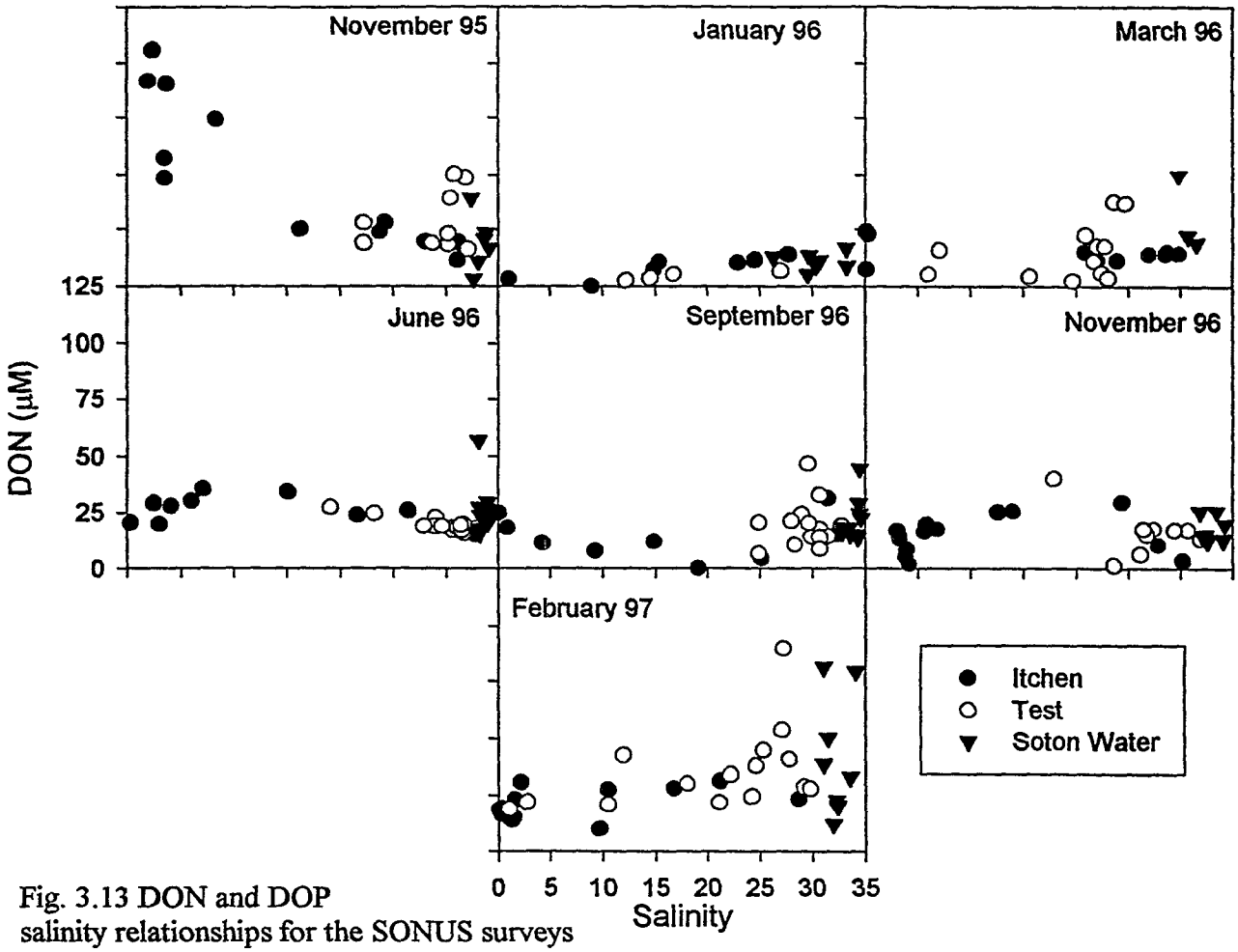
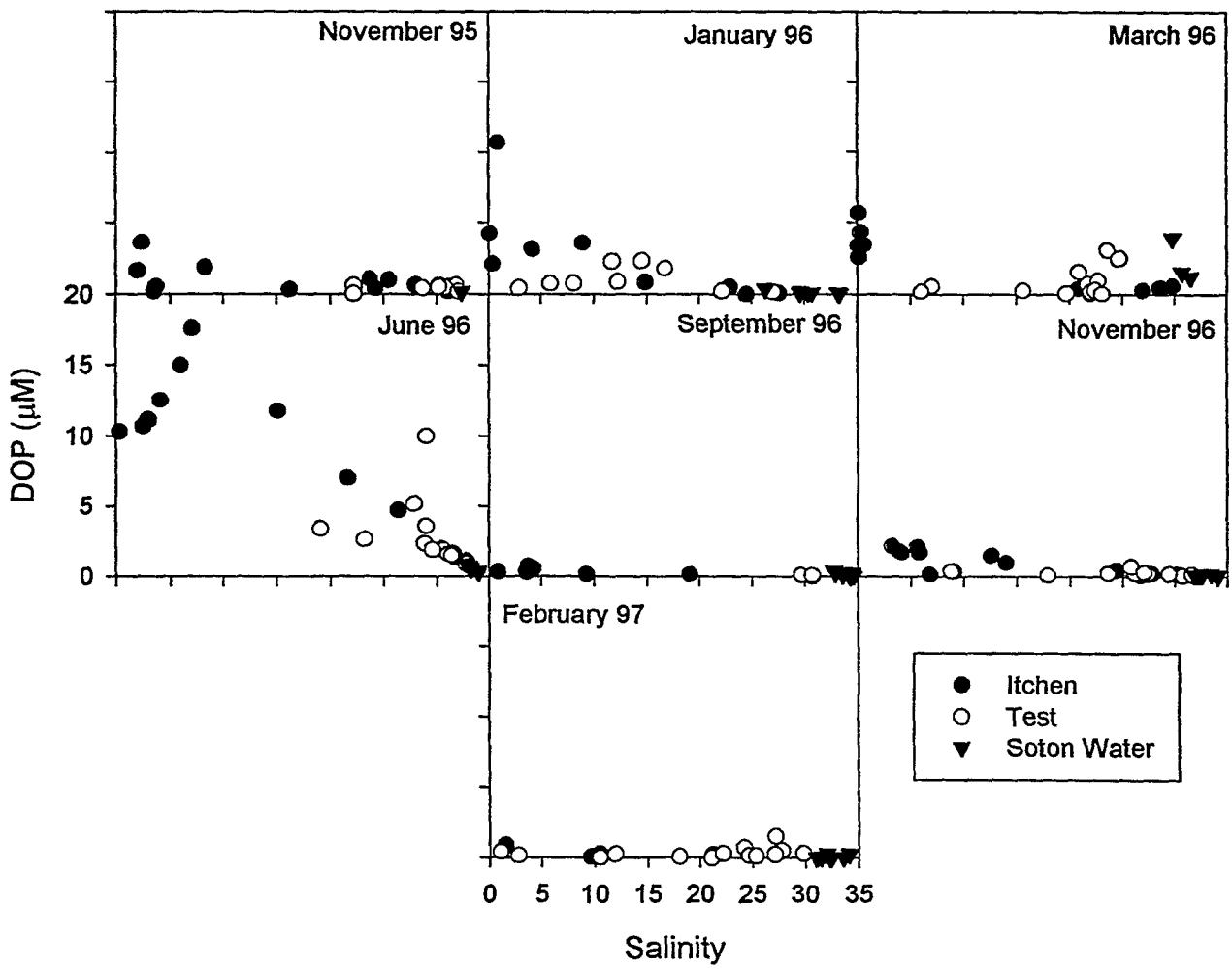


Fig. 3.13 DON and DOP salinity relationships for the SONUS surveys



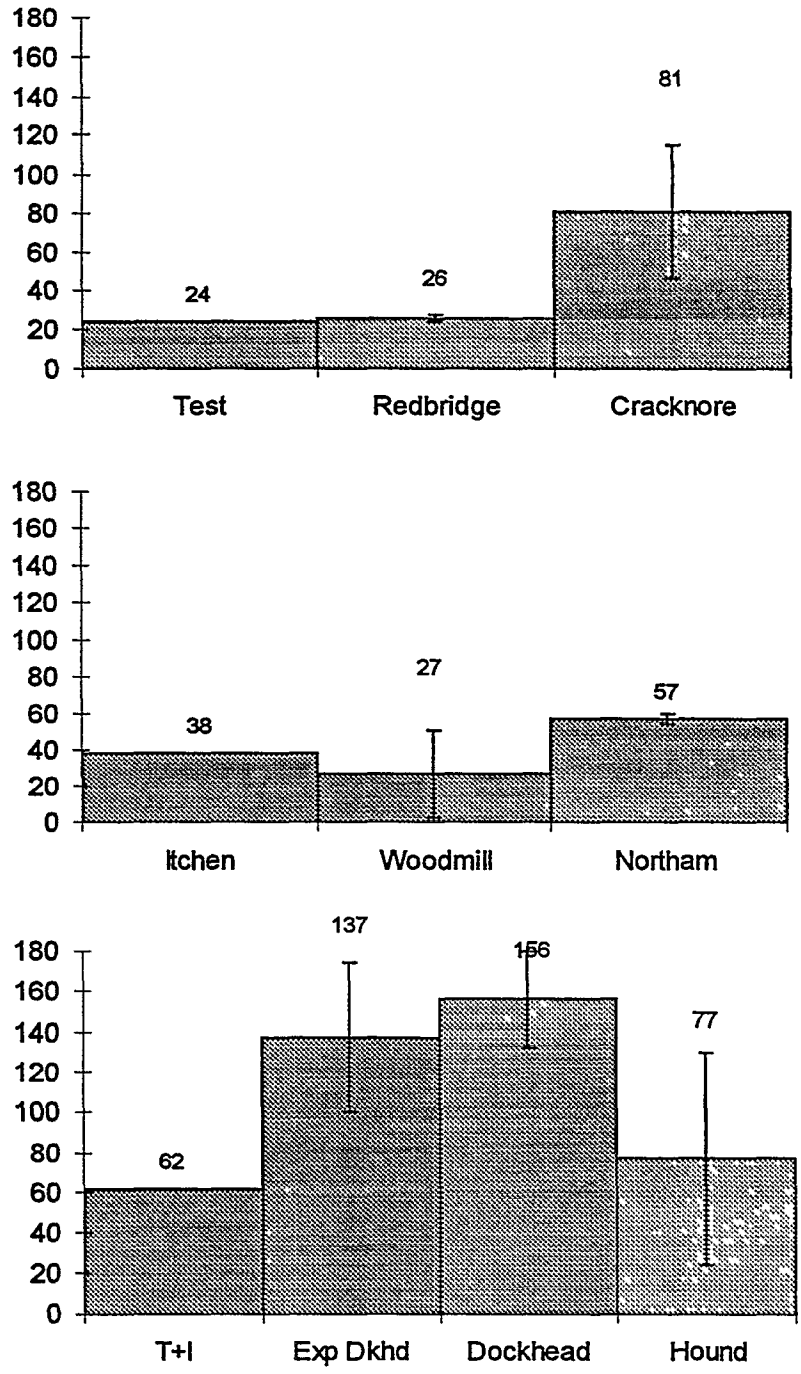


Figure 3.14a. Phosphate fluxes at the five stations during 1995. The Test and Itchen fresh water data are from the EA, and are summed to give "T+I". Cracknore and Northam Bridge fluxes are summed to give an expected flux at Dockhead (Expd Dkhd), independant of that measured at Dockhead.

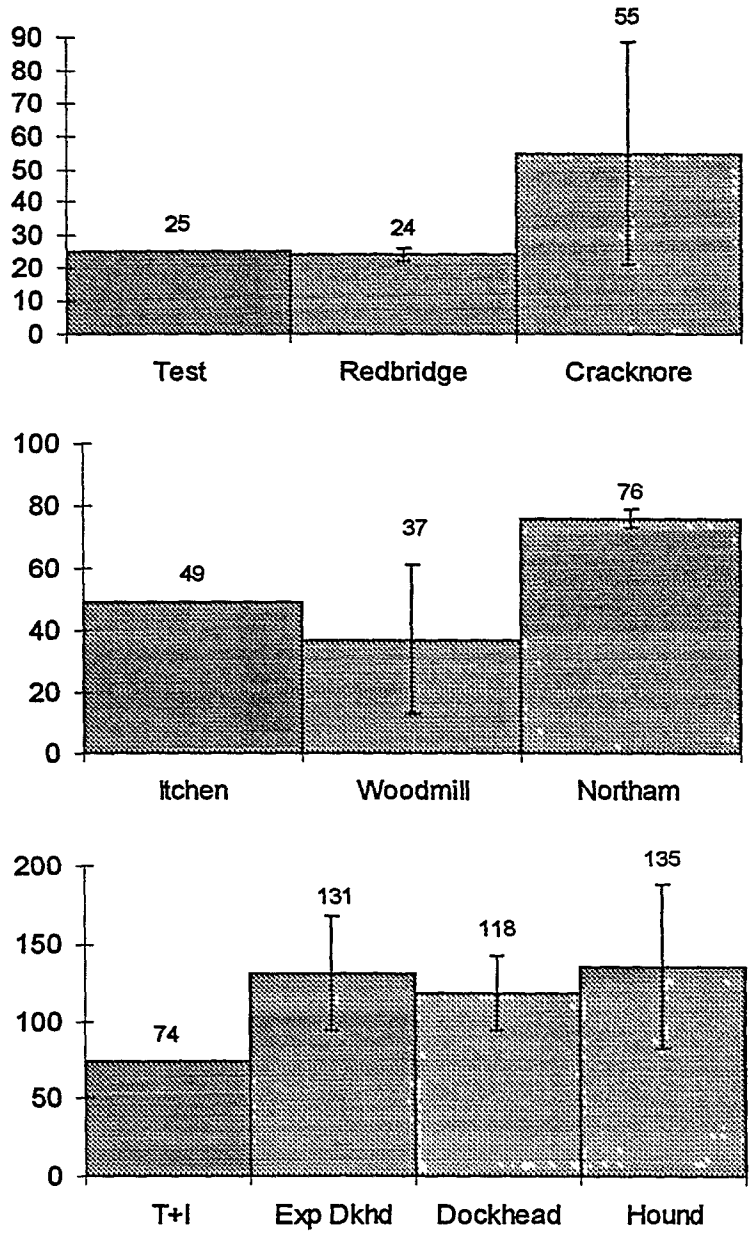


Figure 3.14b. Phosphate fluxes at the five stations during 1996. The Test and Itchen fresh water data are from the EA, and are summed to give "T+I". Cracknore and Northam Bridge fluxes are summed to give an expected flux at Dockhead (Expd Dkhd), independant of that measured at Dockhead.

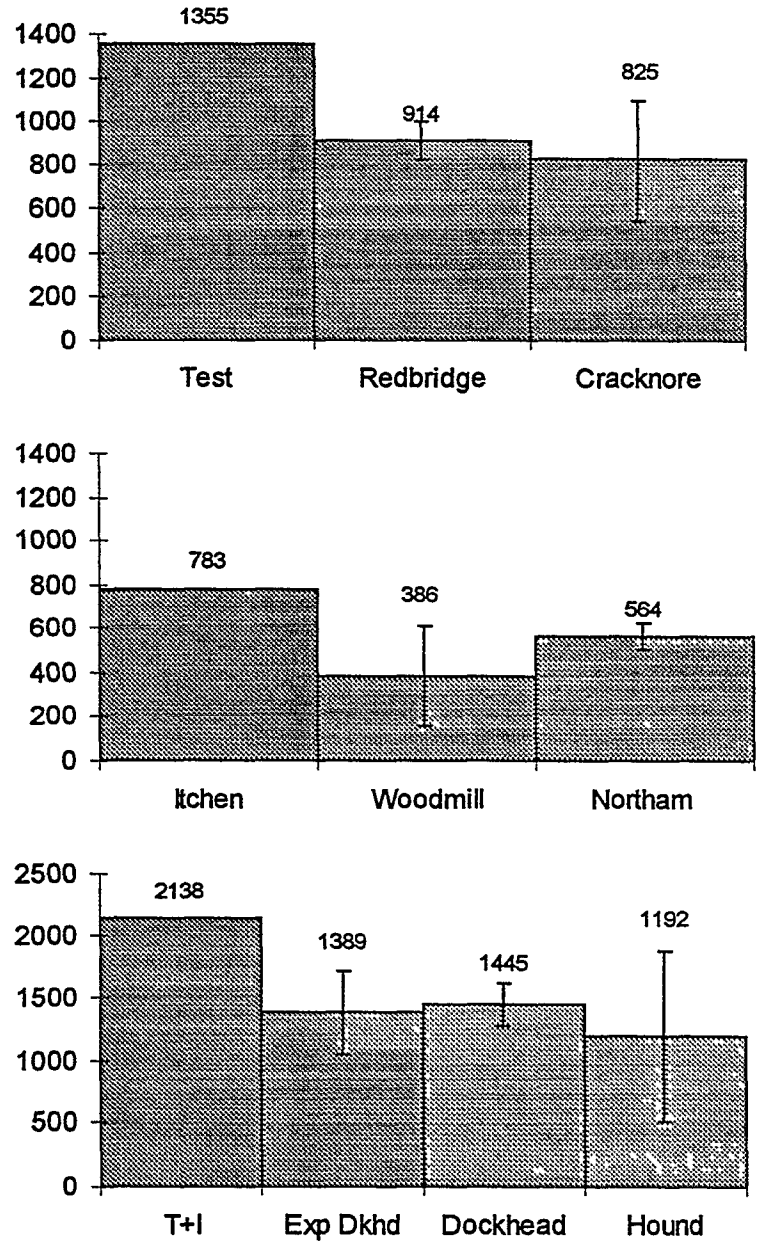


Figure 3.15 a. TON fluxes at the five stations during 1995. The Test and Itchen fresh water data are from the EA, and are summed to give "T+I". Cracknore and Northam Bridge fluxes are summed to give an expected flux at Dockhead (Expd Dkhd), independant of that measured at Dockhead.

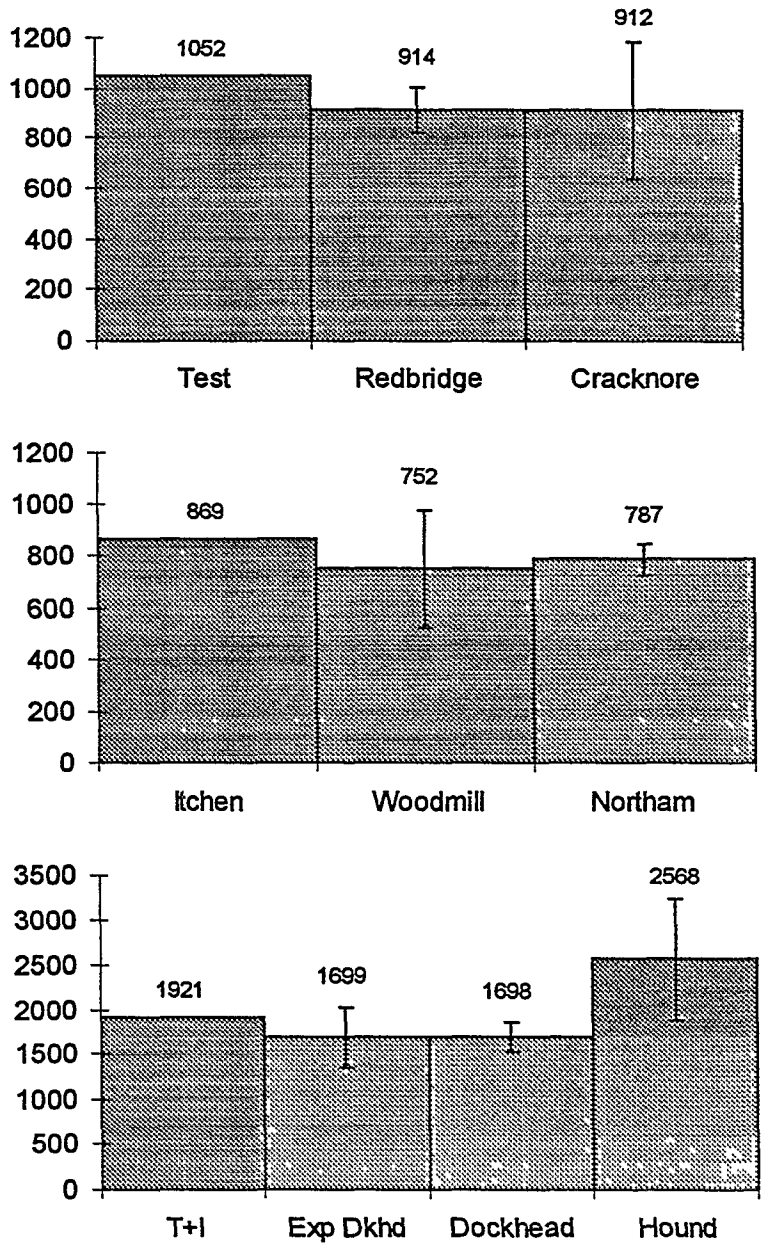


Figure 3.15b. TON fluxes at the five stations during 1996. The Test and Itchen fresh water data are from the EA, and are summed to give "T+I". Cracknore and Northam Bridge fluxes are summed to give an expected flux at Dockhead (Expd Dkhd), independant of that measured at Dockhead.

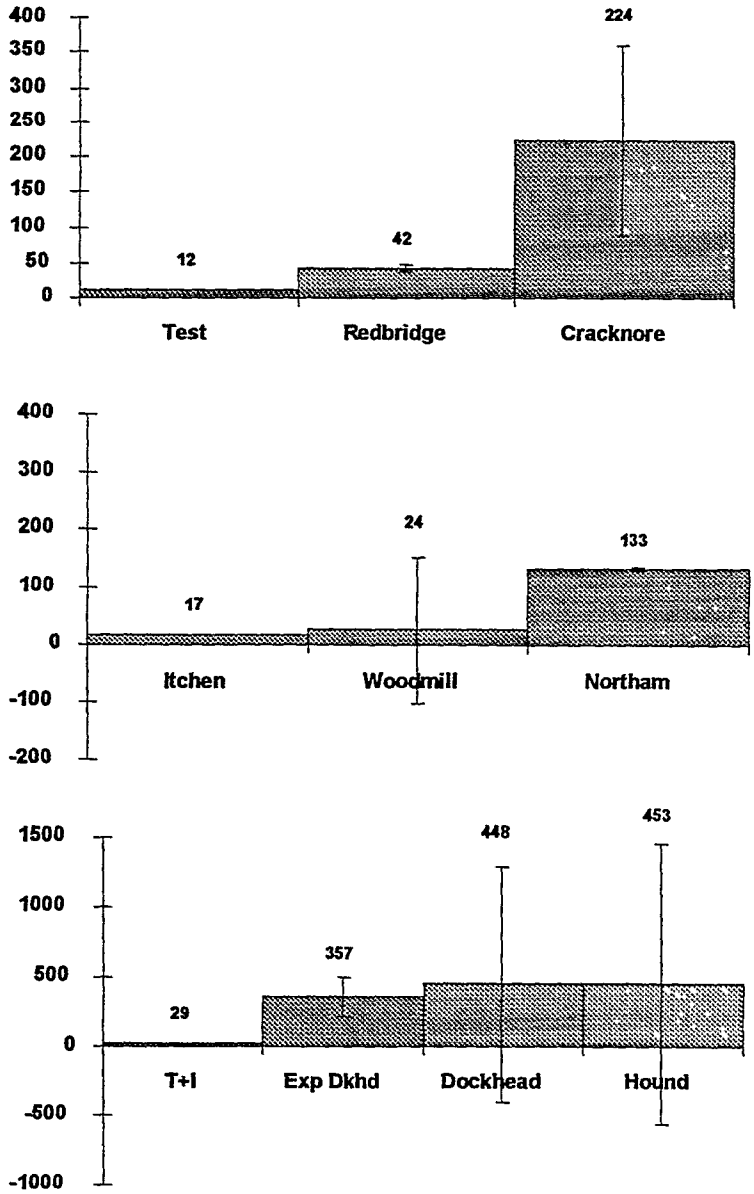


Figure 3.16a. Ammonia fluxes at the five stations during 1995. The Test and Itchen fresh water data are from the EA, and are summed to give "T+I". Cracknore and Northam Bridge fluxes are summed to give an expected flux at Dockhead (Expd Dkhd), independant of that measured at Dockhead.

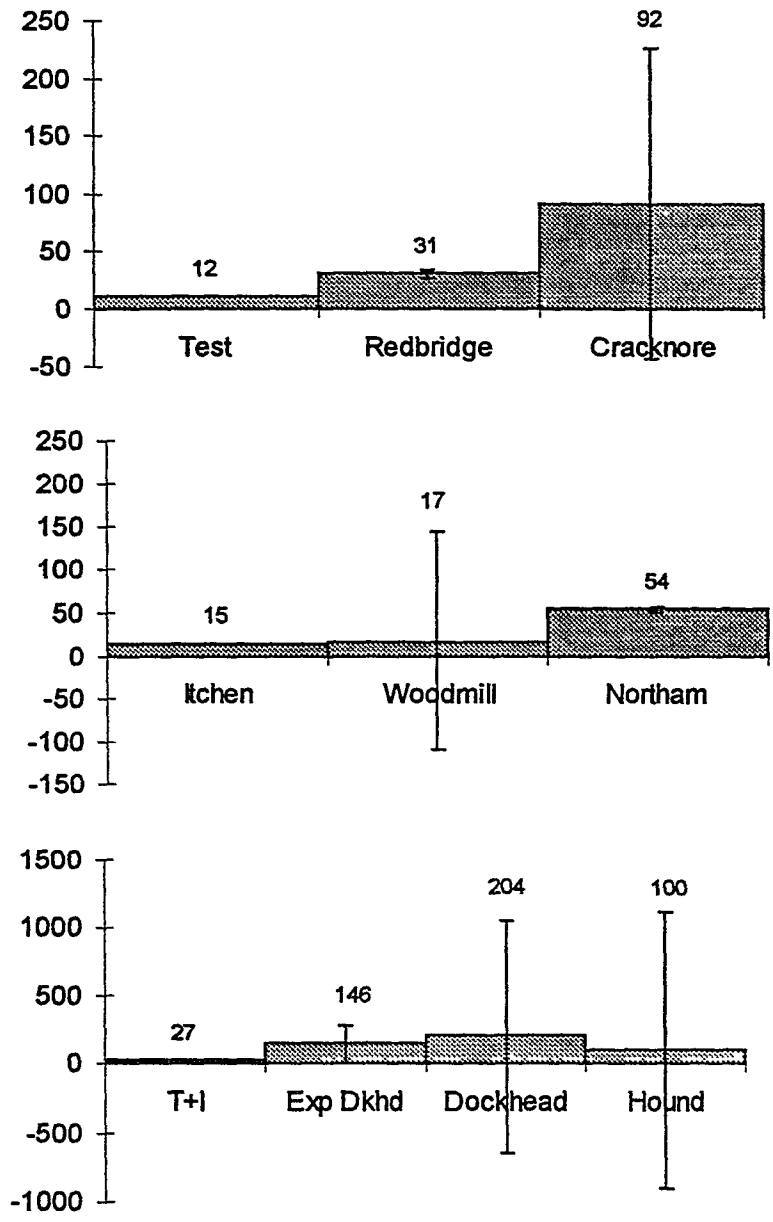


Figure 3.16b. Ammonia fluxes at the five stations during 1996. The Test and Itchen fresh water data are from the EA, and are summed to give "T+I". Cracknore and Northam Bridge fluxes are summed to give an expected flux at Dockhead (Expd Dkhd), independant of that measured at Dockhead.

Figure 3.17 Pie charts showing the relative proportions of nitrate, nitrite, ammonia and dissolved organic nitrogen in the total dissolved nitrogen load at different geographical points in the estuary during the seven SONUS surveys representing the annual cycle.

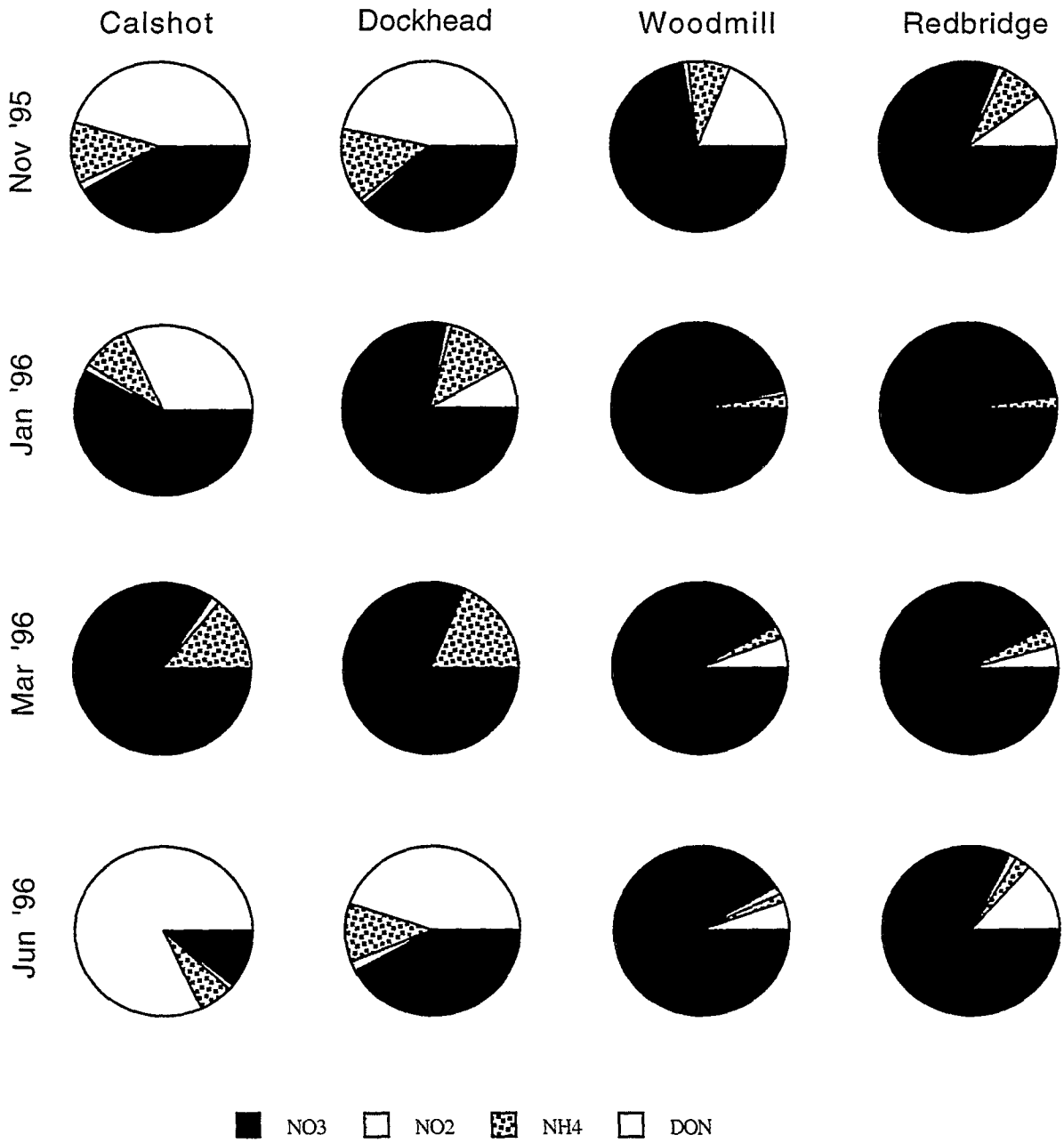


Figure 3.17 (Continued). Pie charts showing the relative proportions of nitrate, nitrite, ammonia and dissolved organic nitrogen in the total dissolved nitrogen load at different geographical points in the estuary during the seven SONUS surveys representing the annual cycle.

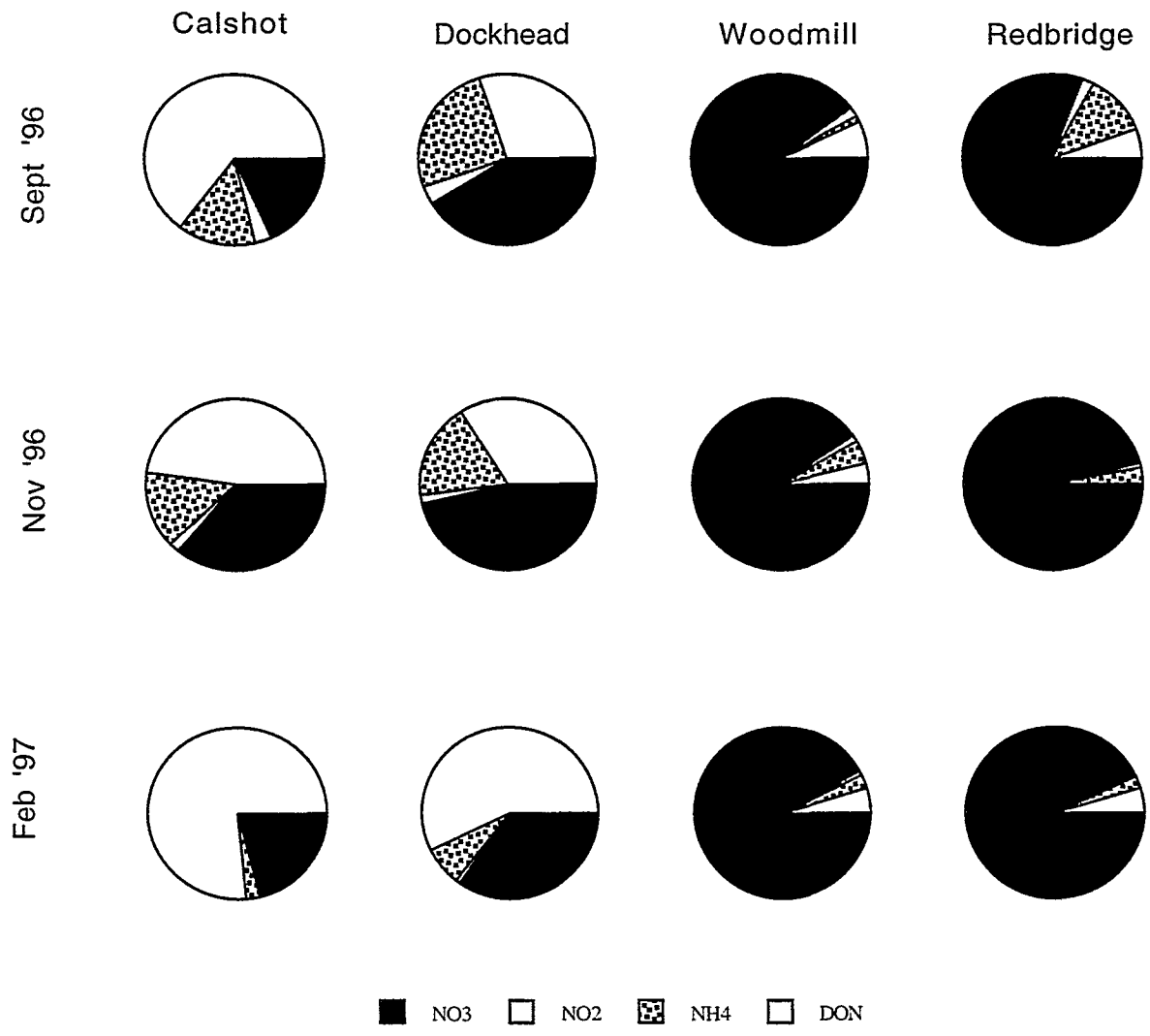
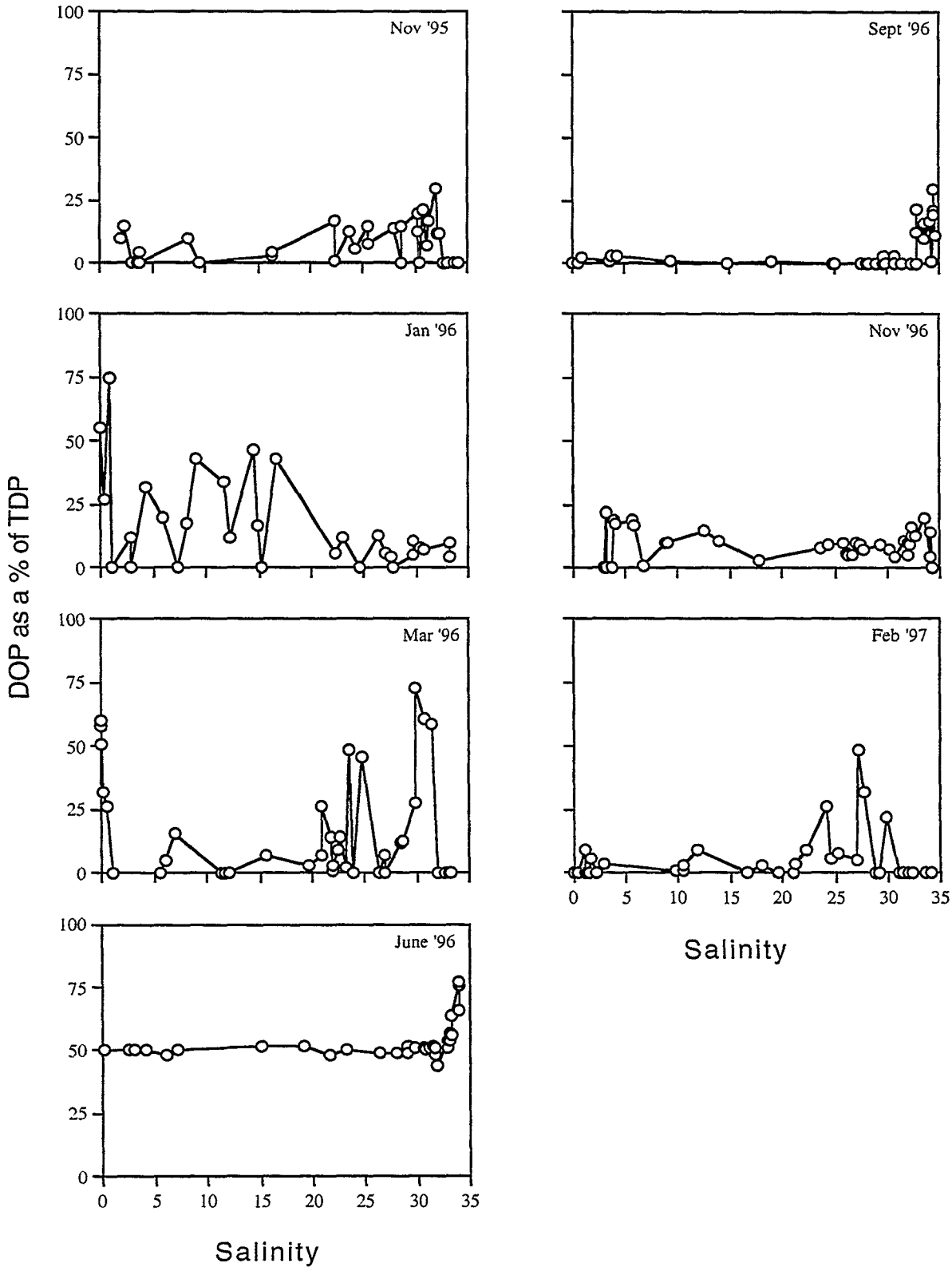


Figure 3.18. Relative percentage distribution of dissolved organic phosphorus (DOP) compared to dissolved inorganic phosphorus (DIP) plotted against salinity - for surveys between November 1995 and February 1997.



SECTION 4

THE SOC-SONUS-DATA-BUOY USED TO STUDY PHYTOPLANKTON GROWTH CONDITIONS IN SOUTHAMPTON WATER: DEVELOPMENT AND RESULTS 1995-1997

4.1 Introduction

4.1.1 Background to biological and chemical studies

A fundamental feature of the behaviour of marine phytoplankton in temperate latitudes is a period of rapid population increase, referred to as a "bloom". The potential intensification of bloom events stemming from eutrophication is of particular concern to the south coast of the UK because the concomitant decrease in water quality has an economic impact if the recreational use of the coastal water is hindered (see discussion in Section 2.1). An objective of the Southern Nutrient Study (SONUS) fieldwork programme was to use an instrumented mooring deployed within the Southampton Water estuary, to continually sample this estuary at a high temporal resolution. Interpretation of the data would consolidate ideas stemming from a number of separate earlier observational studies (Section 2.1). In particular an aim was to improve understanding of why blooms in Southampton Water are only of short duration although light and nutrient levels should be sufficiently high to support growth throughout the summer months.

For this work phytoplankton abundance was monitored using a well established method based on the determination of chlorophyll *a* fluorescence. However at the start of this work no similarly well established methodology was available for the detailed monitoring of nutrient concentrations.

Traditional techniques of nutrient monitoring may involve collection of samples on estuarine surveys, at tidal stations or regular sampling from prearranged locations. Monitoring schemes in which only a single sample per river is collected, often no more frequently than weekly, can fail to identify transients, such as storm events, which can pass in a matter of hours. It has been postulated that the input of nutrient rich storm waters to coastal zones can have a dramatic effect upon primary production (Gallegos et al., 1992). Similarly, if such transient signals are not detected estimates of total discharge load are severely under estimated. Models of nutrient uptake by algae need to be validated against data sets collected at temporal resolutions that are difficult to match using conventional sampling techniques. Additionally, there is still debate as to how well samples can be preserved between collection and analysis in the laboratory (Dore et al., 1996). Whilst the consensus of opinion suggests that nitrate levels are rarely effected by sample freezing, it has been shown that concentrations of other nutrients, particularly silicate, can be altered by freezing. Mercuric chloride is frequently added to samples as a preservative (Kremling & Wenk, 1986). Use of mercuric chloride is both undesirable from a safety aspect, and also gives rise to problems with the subsequent analysis. It may effect the sensitivity of the standard nitrate reduction technique by changing the properties of the cadmium

reduction column (Nydal, 1976), and during the determination of ammonia it can prevent the formation of the coloured complex.

In order to eliminate these problems in monitoring of nutrients, the need existed for autonomous, in situ, techniques to measure nutrients at a high temporal resolution (hourly) and that could be left within the environment for a period of time giving continuous, longer term (weeks to months) data. As part of the SONUS fieldwork project, evaluation and deployments was undertaken of newly developed chemical analysers designed for such in-situ use for the determination of concentrations of nitrate and phosphate. The instrument described is the NAS-2E, manufactured by WS Ocean System Ltd. The original design concept was developed at the Scottish Office Marine Laboratory, Aberdeen.

4.1.2 Description of study area

Southampton Water is located on the south coast of the UK, with the city of Southampton surrounding its upper reaches (Figure. 4.1). It is fed by two main rivers, the Test and the Itchen, which have a combined average annual discharge equivalent to 1.54×10^6 m^3day^{-1}. Water flows into the English Channel, via the passage to the north of the Isle of Wight known as the Solent. It is a partially mixed, macrotidal estuary with a maximum tidal range of about 4.5m, and a tidal excursion of 2.5km. It is a roughly linear body of water, which is 2km wide, and extends for 10km. The estuary is between 6 and 8m deep, except for the dredged shipping channel which is 13m deep. It is highly urbanised, with large industrial complexes along its length. In addition to river flow, Southampton Water receives a consented sewage discharge of about 0.1×10^6 m^3day^{-1}. Waste water can contribute up to 25% of the flow during periods of low river discharge. Historical data shows that subsurface estuarine waters contain between 5 and 40 mgl^{-1} of suspended particulate matter (NRA, 1994; Lauria, unpublished data). Salinities in the main body of the estuary vary between 30 and 33. Using the approach of Officer (1976) and data from Webber (1980), flushing rates for spring tides of about 26 hours, and 76 hours for neap tides are estimated.

4.1.3 Deployment site

A major problem with in-situ deployment of instrumentation is damage by shipping. This was thought likely to be a particular problem in Southampton Water which is a very busy waterway. In co-operation with BP, all the deployments of the SONUS buoy described were done within the confines of the BP Oil terminal jetty in Southampton Water (Figure 4.1) to prevent possible damage by shipping. The shape of BP's jetty at Hamble (Figure. 4.2) provides a protected environment for the buoy, while the jetty is constructed such that the water flowing by the buoy will be fully representative of conditions in more open water.

4.2 Development and technical description of SONUS data buoy

4.2.1 Purpose of system

The original concept of the SONUS buoy was that it could be used to provide information on both the processes of bloom development and the transport of dissolved nutrient loads through the estuary. Specifically:-

(1) For productivity related measurements to achieve measurements of the timing and duration of plankton blooms and of indicators of the processes controlling such blooms. The measurements of processes should be made at a frequency and over a time scale commensurate with the rates of such processes. The degree of detail should be similar or greater than that which can be achieved in mathematical water quality model output, so that it can be used for the validation of such models. At the start of the work measurements that were considered feasible and suitable for water quality model development were:-

- Light (PAR - photosynthetically available radiation), a driving variable.
- Transmission, as a measure of the in-situ limitation on the available light.
- Nitrate, driving variable.
- Fluorescence, - as a measure of primary biological production.
- Oxygen, as a measure of production.
- Salinity, as a water mass identifier and tracer of dispersion processes.
- Temperature, as a water mass identifier.

(2) For the estimation of export loads to monitor dissolved nitrogen flows from the estuary with high temporal resolution, to provide:- (i)measurement of the degree to which the apparent export of nitrogen from the Solent is connected to high sporadic discharges (e.g. storms). (ii)by comparison with routine monthly surveys an assessment of the likely errors in extrapolating the survey data to estimates of export loads from the estuary. This would be achieved by the measurement of nutrient concentrations and salinity. Regression of the nutrient data against salinity would be used to estimate the effective concentration of nutrients in fresh water entering the estuary. This estimate coupled with the appropriate flow data would give an estimate of the load entering the estuary.

4.2.2 History of development

Work on the SONUS buoy began at the Institute of Oceanographic Sciences (IOS), Wormley Laboratories, before the Institute became part of the Southampton Oceanography Centre. In December 1994, Ian Waddington of the IOS moorings group designed a robust mooring which could be serviced on site. This was based on an existing toroid float. Running through the centre of the float was to be cage structure enclosing rails along which the instrument package could be lowered into the water and raised out of the water for servicing (see Figure 4.3). At the same time a consultation and purchasing exercise was begun with the IOS OTD Division for the instrumentation. Pat Gwilliam designed the data capture and power system for the mooring. The main unit of the initial instrumentation was a sonde that combined a data logger

with built-in temperature, conductivity, transmissometer, and pressure sensors. An oxygen probe, fluorometer, and down welling light meter were connected externally to the sonde. All these units were delivered and tested at IOS shortly before the move to SOC in summer 1995. With Duncan Purdie from SUDO possible sites in Southampton Water and the Solent were assessed. For this work a site was needed at which:- (i) the total service visit time would be less than one day including travel time, (ii) that was well protected from other marine activities such as trawling, (iii) that was in enough water for a mooring to be feasible, and (iv) that was in an area where algal blooms were known to be significant. The BP Hamble jetty was considered to be our first choice site. BP were approached and gave permission to place our mooring within the area of their jetty. The proviso being that the mooring met the exacting safety requirements for such a site.

The first deployment was for seven weeks starting in September 1995. No useful data was collected due to problems with down loading the data to a portable computer on site. A major problem which became visible when the buoy was returned to SOC was that the main frame was severely damaged by corrosion.

The buoy was redesigned and rebuilt during the winter. The centre frame was rebuilt and extended in height to make servicing of the instruments easier. To reduce corrosion damage to the frame a 50 kg zinc anode was attached to the base plate. The sonde was modified so that data could be transferred automatically to SOC using the Vodaphone Paknet data transmission system which uses the Vodaphone cellar telephone network. The modified buoy was moored at the BP jetty on the 4 April 1996. This deployment proved to be successful, and provided new insights into the timing of phytoplankton growth. It worked reliably until logger circuitry was damaged by a severe thunderstorm over the site in July. When the sonde was recovered two weeks later it was found to be irreparably damaged due to a water leak caused by corrosion of the casing.

On 22 August 1996 the toroid buoy was recovered from the BP jetty and replaced by a smaller buoy. This buoy was of similar overall design to the SONUS buoy. Its purpose was to test chemical analysers for nitrate and phosphate (W.S. Ocean Systems Ltd "NAS-2E" type in-situ analysers).

To stay within the SONUS project budget, the 1997 deployment was a shared cost arrangement with W.S. Ocean Systems Ltd. No major mechanical changes were required for this deployment. The float and frame were cleaned and painted. The central instrument trolley was rebuilt to take a changed instrument payload, and four solar panels were fitted to keep the batteries charged, so that the batteries did not have to be changed on site. The buoy was deployed in March 1997. Data was collected for 5 weeks before an electrical connector on the body of the sonde failed when it was being serviced. In March and April 1997 measurements were collected from all the sensors. To repair the connector the whole system had to be recovered from the water. Repairs took six weeks to complete. When the buoy was redeployed it again failed due to a problem with the network. No further data was collected. The buoy was removed from service in August 1997.

4.2.3 Description of Buoy

The arrangement of the SONUS buoy is shown in Figure 4.4. The buoy carried an instrument package held at fixed depth below the surface from a surface float. The surface float was a toroid 2m in diameter. Passing through the centre of the float was cage of four vertical bars which contained two rails along which the instrument package could be wound in and out of the water. Extending from the buoy was an arm which held the PAR sensor at 2m depth, and away from shading by the buoy super structure. The scientific equipment fitted on the buoy in 1996 consisted of the (i) main sensor array (temperature, salinity, oxygen, fluorescence, light transmission and pressure) (ii) a light sensor mounted on an arm extending from the buoy under water (iii) a logger unit (iv) four battery boxes (containing 80 amp.hour gel filled lead acid batteries) mounted to the deck of the buoy. All electrical connections between the battery box, sensors and logger were standard marine full-ocean-depth marine connectors to ensure firm connections proof against ingress of water and air. All electrical circuits were protected by fuses to prevent damage to any of the batteries.

4.2.4 Sensor package specification 1996

The initial design specifications of the sensors were:- Light~1watt/m^2/d Transmission ~5%, Nitrate ~1μM, Fluorescence ~5% or 0.1μg chlorophyll/l, Oxygen ~1μM, Salinity.~0.05, Temperature ~0.1°C. The measurement rate was to be one reading every - 15 minute (equivalent to 10^{-3}Hz). The target duration was 3-4 month with the instruments being serviced at a two weekly interval.

4.2.5 Instrumentation fitted in 1996

Logger-Sonde

W.S. Ocean Systems "SV-1, UMI Ocean Monitor". Temperature, conductivity, pressure sensors and transmissometer are built into a single housing. Its specifications are:-

1. Data acquisition: The instrument provides 16 channels with 14 bit resolution plus a single RS 232 input.
2. Data storage: Memory - A 4mbyte PCMCIA SRAM removable card with additional downloading via a serial link. Data down load - (i) Data can be down loaded via the serial link, to a PC with an RS 232 port, in a comma delimited ASCII format. The typical communications protocol is 19.2K baud, 8 data bits, 1 stop bit, no parity. (ii) System software set to automatically transmit data via a cellular radio link after each set of reading is taken, at a programmable time interval.
3. Power source - For this use the UMI powered by external batteries.
4. Sampling - All channels sampled within the active sample period. Sampling performed on a "top of the minute" basis.
5. The sample interval programmable from 1 to 60 minutes in 1 minute intervals. (ii) The data acquisition system gathers 160 samples (from 12 channels) per second. Programmable averaging of 1 to 500 samples provided for all channels.

Integrated Sensors

1. Conductivity: Type: Inductive cell (Aanderaa Instruments, Norway); Range: 0 - 50 mS/cm; Precision: 0.05 mS/cm
2. Temperature: Type: Platinum resistance thermometer; Range: -2 to +30 °C; Precision: ± 0.02 °C
3. Pressure: Type: Pressure transducer model PDCR910 (Druck Ltd): Range: 20 Bar; Precision: 0.02 Bar.
4. Transmissometer: Type: Folded Beam; Path length: 25 cms; Output: 0 -5 v DC; Precision: ± 1 mv

External Sensors

1. Fluorometer: Manufacturer: Chelsea Instruments Ltd; Type: Aquatracker III; Range: 0.01 µg/l
2. Light: Manufacturer: Chelsea Instruments Ltd; Type: PAR Irradiance Meter PR46; Output: 0 - 5 v DC; Approx. Cal.: PAR (ln µW/cm2) = -0.005 * signal(mv); Range: 450 -700 nm; Precision: ± 3%; Range : 400 - 450 nm; Precision: ± 8%

Data Transmission

Data transmission is provided by the Vodaphone-Paknet cellular radio system. This linked the buoy via a base-station to a transceiver at SOC. This two way communication allows external control of onboard devices. The system communicates to the UMI via a communications controller supplied by WS Ocean Systems.

4.2.6 Sensor package modifications 1997

The central sonde used in 1997 was similar to that used in 1996 except that all the power control circuitry was incorporated into the sonde termed - *a multi-parameter oceanographic data acquisition system (DAS)*, - and the folded bean transmissometer was replaced by a turbidity meter. The external sensors were a Seatech fluorometer (an LED excitation instrument) and two NAS-2E nutrient analysers ; one performing nitrate analysis and the other phosphate. The mode of operation for the integrated instrument package was with the DAS acting as the "master" for data acquisition and telemetry for all the other "slave" instruments in the suite. The nitrate and phosphate analysers were connected to the DAS via an RS485 "network". Both the fluorometer and the turbidity sensor have digital control of their analogue gain and this was intelligently manipulated via the DAS. The DAS performed the system timing and stored all data acquired from the other devices for subsequent telemetering. In normal (logging) operation the DAS operated as master on the RS485 network. Each NAS 2E operated in slave mode. The DAS has the facility to interrupt each NAS-2E by toggling the "slave" reset line that is connected to each slave. The DAS used this signal to activate the slave devices prior to communication.

The Paknet radio PAD was connected to the DAS via a further RS232 serial port. The DAS controlled power to the PAD. To establish communication with the base transceiver the DAS powered the buoy PAD and "dialled-out". Once connection was made data was transferred at

4800 baud. After communication was complete the DAS switched off the buoy PAD and re entered "sleep" mode.

4.3 Development and technical description of the NAS-2E Analyser for use on the SONUS data buoy

4.3.1 Introduction

Two variations of the W.S. Ocean Systems Ltd "NAS" in-situ nutrient analyser were evaluated and used during the SONUS fieldwork project. These were designed to determine nitrate and phosphate. The nitrate analyser worked well. Details of the analyser are presented below along with a discussion of results collected both in Southampton Water and in collaboration between W.S. Ocean Systems Ltd and the IFREMER Laboratory, Brest, France. Reliable results were not obtained from the phosphate version of the analyser. Further development of the phosphate analysers forms part of the research work of a PhD student who started work at SOC in October this year (1998).

The data presented here show that the NAS-2E wet chemical analyser, can produce results for the determination of nitrate in-situ which are comparable in quality to those obtainable in a laboratory using more conventional automated systems. This quality of data can be achieved and maintained for periods of over one month. The data suggest that where problems arise from fouling the NAS-2E which is self calibrating may be more reliable than other instruments even well established ones such as conductivity sensors. The instrument works well within coastal areas, identifying both short term and long term variations which are difficult to observe during more traditional surveys.

4.3.2 Main Components

The NAS-2E nitrate sensor has five major components. These are an eight way rotary valve, a motor driven syringe, a colorimeter, reagent housing, and an electronic controller unit. The layout of a NAS-2E is shown in Figure 4.5. The rotary valve and syringe are both driven by stepper motors. The chemicals used in the analysis are stored in plastic "transfusion" bags in an upper housing attached to the top of the unit as it is shown in Figure 4.5. The unit is about 80cm long, 21cm in diameter, and weighs approximately 10kgs. The chemical system is essentially pressure balanced as all the chemical circuitry is at ambient pressure and external to the electronic instrumentation. The depth limitations is 250m, which is the pressure rating of the housing for the electronics. The likelihood of bio-fouling of moving components is minimised as all moving parts are contained within housings. Where the turbidity of the water is high, problems could arise from high blanks which are difficult to measure reproducibly, or particles fouling the valves and contaminating the cadmium reduction column. To combat the introduction of foreign matter into the unit, a filter is fitted at the end of the sampling tube.

Control and retrieval of data can be done by direct connection of a PC-computer through a RS232 communications port on the instrument, or can be done remotely by means of

telemetry. Instructions can be given either by a menu driven program, or by means of a command language. The software allows for control of these protocols by the user. For example, longer periods between the collection of samples can be set up or the details of the procedure can be altered - such as the relative volumes of samples and reagents, or the duration of the reduction step in the copper-cadmium column.

4.3.3 Chemical Method

The chemical method used to determine concentrations of nitrate follows well documented techniques (Wood et al., 1967; Grasshoff, et al., 1983). The method requires the reduction of nitrate to nitrite. Chemical reduction is achieved by passing the sample over a reduction column of copper coated cadmium wire (Stainton, 1974; Nydal, 1976). The nitrite produced is reacted with sulphanilamide and napthylethelynedihydrochloride in an acidified solution to form an azo dye. The intensity of the purple colour of the dye is measured and should be proportional to the original concentration of nitrate in the sampled water.

Reagents

Sulphanilamide: Dissolve 10g in 200ml of 50% HCl, dilute to 1l with distilled water, then add 2ml BRIJ-35 wetting agent (30% solution).

Napthylethelynedihydrochloride: Dissolve 1g in 1l distilled water.

Ammonium chloride: Dissolve 20g and 0.2g copper sulphate in 1l of distilled water.

For marine applications the On Board Standard (OBS) is prepared in Low Nutrient Seawater (LNS). LNS is an aged surface sea water containing less than 0.1 µM of nitrate plus nitrite. It is supplied by Ocean Scientific International Ltd. An amount of a primary standard containing 10.00 mM of nitrate as potassium nitrate in distilled water is added to the LNS to give a nitrate concentration at the upper end of the range expected for the observations to be carried out.

A water sample is taken by aligning the rotary valve to the inlet port then drawing down the syringe plunger. This blank aliquot is then injected into the colorimeter and the value recorded. After expulsion of the blank, another aliquot is taken. The sample is then pushed out of the syringe onto the reduction column. After reduction from nitrate to nitrite has occurred, the sample is drawn back into the syringe. The valve moves around to the next ports and draws in the two reagents in turn. By moving the piston up and down 4 times the sample and reagents are effectively mixed by the vortices set up in the liquid each time it re-enters the syringe cylinder. Two minutes are allowed for colour formation then the solution is pushed into the colorimeter where the extinction of the solution is measured. The colorimeter consists of a narrow linear capillary tube with a light emitting diode (LED) source at one end and a photodiode detector at the other. An additional detector is placed adjacent to the source to monitor LED intensity directly.

The concentration of nitrate is calculated by comparing the absorbance of the sample to the value obtained for an "on board standard" (OBS) after correcting the measured absorbance by the value obtained for the blank. As mentioned above blanks are determined prior to every

sample taken. OBS values are determined at a rate of one per six samples. The repeated analysis of the OBS allows the user to monitor how the unit has drifted over the time. Drift is likely due to changes in the functioning of the colorimeter circuitry and because the amount of colour developed in sample will vary as the temperature of the instrument changes in response to changes in the surrounding water. In the case of the determination of nitrate this temperature drift is likely to be relatively small as the colour forming reaction is rapid and the reaction will be near to its end point before it is introduced into the colorimeter. For the determination of nitrate the major cause of drift in the values obtained for the OBS and samples is likely to be shifts in the efficiency of the cadmium reduction column.

4.4.2 Results

Results from three deployments are summarised in Table 4.1. These deployments were off the French coast in March and April 1995, and in the more turbid waters of Southampton Water, in August-October 1996 (SONUS Buoy deployment 3), and March-April 1997 (SONUS Buoy deployment 4). At both sites the analyser was moored in waters in which the salinity was in the range 30±3. Anthropogenic discharges of nutrients in both areas are relatively high.

In Figure 4.6, the data from the first week of the deployment off the French coast are plotted. During this deployment a boat was used each working day when weather and other conditions permitted to collect a sample using a standard water sampling bottle. This sample was collected to coincide with the sample collected by the NAS-2E close to 1300hours each day. The sample was then returned to the laboratory and its nitrate concentration was determined using a standard auto-analyser method. Figure 4.6 shows that the NAS-2E data is providing a record of the variation in the concentration as the water conditions around the analyser change with the state of the tide. The accuracy of the measurements compared to the bottle samples appears to be good.

In total 18 samples were collected by boat during the first deployment. In Table 4.2 the concentrations of nitrate determined in these samples are compared with the value recorded by the NAS-2E closest to the time of collection of the boat sample. The mean difference over all 18 samples is equivalent to 1.2 μM of nitrate a percentage difference of 6.7 %. This result compares favourably with the degree of accuracy that is usually reported, when different laboratories report determination of nitrate in inter-comparison samples (Aminot and Kirkwood 1994). A potential problem with the determinations carried out on the NAS-2E is that the calibration of the NAS-2E samples is only done relative to a single standard solution and a blank value. For this to give accurate results the instrument must be set up so that all the samples measured will be with in the linear working range of the colorimeter at the wavelength of the analysis. A relatively wide dynamic range of sample concentrations was encountered during the first deployment as it extended into the period of the phytoplankton bloom which reduced observed concentrations of nitrate from 29 μM at the start of the observations to 5μM at the end. The plot of the NAS-2E results against the boat results (Figure 4.7) shows that there

appears to be no significant difference between the linearity of the NAS-2E and auto-analyser determinations over this concentration range.

A critical problem that has to be overcome with all determinations of nitrate in sea water is maintaining a reproducible response from the cadmium reduction column for periods of time of a few months. The design of the reduction column on the NAS-2E follows the suggestion by Stainton (1974) of using cadmium wire coated with precipitated copper. In order to retain the reactivity of the column between sample determinations the column is flushed at the end of each processing cycle with ammonium chloride buffer solution containing copper sulphate.

In Figure 4.8 all absorbance measurements recorded for the On Board Standard are plotted for the deployment off the French coast and SONUS buoy deployment 3. The variation seen in this plot is as noted above probably mostly due to changes in the condition of the cadmium column, but will also be influenced by other factors such as the ambient temperature and the condition of the chemical reagents. In Figure 4.9, for comparison, we present data which records the equivalent change in the calibration coefficient for the determination of nitrate after reduction to nitrite using a Stainton type cadmium wire reduction column on an AA-II type auto-analyser during an oceanographic cruise (RRS Discovery 216). These data were obtained by the analysis of four standard solutions in duplicate at the start of each analytical run before the determination of samples. Omitting the first 3 runs at the start of the cruise the percent standard deviation was 4.1%.

4.3.5 Results in Southampton Water

The third deployment of a SONUS buoy in Southampton Water started on 22 August 1996 and lasted for 56 days. Figure 4.10 shows variations in nitrate levels that occur with respect to the daily tidal signal and on longer time scales. On a daily time scale, higher nitrate concentrations correspond to the presence of a larger component of fresh water rich in nitrate at low water. There is also cyclicity in the data which corresponds to the spring neap tidal cycle. Again this is due to the variation in the fraction of fresh water at the mooring site. The general increase over the whole period is due to the increase in concentrations of nitrate in open sea water in autumn at the end of the phytoplankton production season.

It has been suggested that storm events have an impact on the water quality of coastal waters, since they deliver a pulse of nutrient rich water along the rivers out to the sea (Gallegos *et al.* 1992). Julian Day 236 experienced a large rain storm. Nitrate levels were higher following this storms than they were during the following neap tide (Figure 4.10). No corresponding measurements of salinity are available from this deployment, so it is not possible to know if this higher concentration of nitrate reflects both an increase in the concentration of nitrate in fresh water entering the estuary or just an increase in the fraction of fresh water in the estuary at the observation point following the storm.

During the fourth SONUS deployment, the NAS-2E was deployed in conjunction with a wider array of sensors. From this deployment we have available corresponding data from a conductivity sensor. This data can be used to calculate the salinity of the water. All the nitrate

data and corresponding salinity data are plotted against each other in Figure 4.11. On inspecting this data it can be seen that while the nitrate results stay within similar range through the course of this deployment, the salinity values drift to values which are unreasonably high for Southampton Water. The gradual progression in this drift has been indicted in Figure 4.11 by plotting the data in weekly groups. The cause of the drift in salinity measurements is probably fouling of the sensor by the growth of plant matter around the conductivity sensor head. Logistical difficulties prevented servicing of the mooring during this deployment. This suggests that where problems arise from fouling analysers like the NAS-2E which are self calibrating may be more reliable than other instruments even well established ones such as conductivity sensors.

4.4 Data-buoy measurements of the dynamics of plankton growth

4.4.1 Introduction

The second deployment of a SONUS buoy at the BP jetty started on 4th April 1996 (Julian Day 95). This deployment proved to be successful, and data was recorded from all the sensors except the oxygen sensor up until 8th July when the logger circuitry was damaged by a severe thunderstorm over the sit. This data has provided new insights into the timing of phytoplankton growth and links together the ideas from previous observations in Southampton Water discussed in the main introduction section above. The discussion focuses on the data for plankton bio-mass measured in terms of chlorophyll via the fluorometer. This study represents one of the first attempts to monitor phytoplankton growth related processes, at high temporal resolution in an estuary. A nearly continuous record was achieved over approximately 100 days during the main period of phytoplankton production in spring and summer.

Tidal variation plays a dominant role in governing the growth of phytoplankton within the estuary. Comparison of observations in 1996 with predictions based on earlier years suggests that blooms, in an estuary such as Southampton Water, can only occur during periods of relatively low tidal energy. However periods of low solar radiation and, perhaps, water column instability appear to have coincided with these lows in tidal energy. This may have prevented a bloom occurring in May and limited the extent of the bloom in June.

By monitoring at high temporal resolution it has been possible to see small scale repeating fluctuations in concentrations of chlorophyll. A spring-neap cyclicity is caused by variations in water column stability between these two tidal states. During the relatively stable conditions associated with neap tides phytoplankton production can increase. The resulting populations are then broken up with the increase in dispersion associated with the higher energy of the following spring tide. On a diurnal basis, during a spring tide, a significant amount of variation in chlorophyll seems to be controlled by the re-suspension of bottom sediments, and the associated benthos. During a neap tide, it seems more likely that the increase in chlorophyll levels is a response to the daily cycle in irradiance. This increase could either be due to increased

rates of photosynthesis or due to migration of phytoplankton through a more stable water column.

4.4.2 Results

In Figures 4.12a, & b, all the observed values for temperature and chlorophyll, as measured by the SONUS buoy are plotted, along with and the predicted tidal range (Admiralty Tide Tables, 1996). The data set is, incomplete during the bloom event in summer due to an error in restarting the logger during a service visit carried out in poor weather conditions. Patterns within the data are discernible on three different time scales corresponding to the daily tidal cycle, the spring neap tidal cycle and longer term changes corresponding to changes in the weather and the development of a plankton bloom.. The temperature record proved to be useful "integrator" of weather conditions. Water temperature increased steadily from 6°C on day 94 to 11°C on JD 118, in late April. During this time weather conditions were calm with mostly sunny days. Temperature remained relatively constant up until JD 140 in mid May, during two weeks of stormy and cloudy weather. Weather conditions then improved and water temperatures increased steadily to about 18°C until JD 170 in mid June. Temperatures then levelled off, and after JD 175, water temperature fell to about 16°C, corresponding to another period of un-seasonably stormy weather.

Figure 4.12b shows that between the start of observations on JD 94, through to JD 165 chlorophyll levels ranged between 0.5 and 1μgl^{-1}. After JD 165, chlorophyll values increased to a maximum concentration of about 3.6 μgl^{-1} on JD 179. Values then returned to the 1μgl^{-1} level by day 185. A boat survey carried out on JD 176 showed chlorophyll levels reaching about 8μgl^{-1} within the estuary. Analysis water samples collected on this boat survey observed the species composition of the bloom to be dominated by the diatom *Skeletonema costatum*, and dinoflagellates, *Peridinium spp.*

Figures 4.13a & b, show typical variations that were observed in measurements of attenuation, and chlorophyll over a spring to neap to spring tidal cycle, between Julian Days 94 and 112. The chlorophyll concentrations peak on or just before the spring tide and fall away on the following neap tide. This spring-neap cycle is also seen within the attenuation data. Attenuation and chlorophyll concentrations are greater on spring tides, suggesting that a significant part of the suspended matter contains chlorophyll *a* which is stirred up in the water column, when the stronger ebb and flood flows associated with spring tides disturbs bottom sediment.

Consistent patterns can be discerned in the data which are characteristic of the daily cycle, with the most pronounced difference in the pattern being between days at opposite ends of the spring-neap cycle. Figures 4.14a, b, and c show chlorophyll, PAR values (from 2m depth), attenuation and tidal range data throughout JD 96. The data for this day is typical of the pattern that was observed to occur repeatedly on days at the peak of the spring tide. Figures 4.14d, e, and f show data for the equivalent pattern which was repeated during neap tides. During the spring tide, both chlorophyll and the attenuation data peak twice daily, prior to the "young flood

stand". On neap tides, the pattern shows a peak of chlorophyll, during the afternoon, after the peak readings in PAR. A smaller secondary peak appears during the hours of darkness, at low tide. Concentrations of chlorophyll are lower over the neap tides than over days on spring tides (1.1 μgl^{-1}, as compared to 1.6 μgl^{-1}), as seen in Figures 4.14a and d. Comparing figures 4.14b and 4.14e, attenuation is also lower on neap tides (0.85 m^{-1}, compared to 2.25 m^{-1}). During the neap tides, peaks in the attenuation data are associated only with the ebb flow, which is when current speeds are highest (Webber, 1980). Characteristically, two peaks are associated with both the ebb and flood, during spring tides. These patterns are at their most distinct at the maximum or minimum of tidal ranges, but are also evident two to three days before and after.

The attenuation and chlorophyll data were further examined by Fourier analysis, using the Fast Fourier Transform method (Press *et al.*, 1986). This allows identification of periodicities within the data set. For example, if variations within the data set were due to tidal factors, then, when considering the data in the frequency domain, the results should show a number of clearly defined periods that match those of the tidal regime of Southampton Water. Figures 4.15a and b shows the results of these analysis. In general the data is noisy, reflecting the natural short term fluctuations in the environment. Within the chlorophyll data set (Figure 4.15a), periods are found at one day and 0.5 days. There is also a suggestion of periods at 0.52 and 0.26 days. There are other significant periods at 0.6 and 0.97 days. The attenuation data is noisier than the chlorophyll data, which may be due in part to fouling of transmissometer window. In Figure 4.15b, there is some suggestion of periods at 0.17, 0.26, 0.52 and 0.58 days. Unlike the chlorophyll data, no peak is present at a period of a day.

4.4.3 Discussion

Previous observations for Southampton Water have suggested that a spring bloom, dominated by diatoms, tends to appear in May (Kifle and Purdie, 1993; Iriarte and Purdie, 1994). A later summer bloom can occur and is usually associated with populations of the phototrophic ciliate *Mesodinium rubrum* (Crawford and Purdie, 1992; Leakey *et al.*, 1992; Kifle and Purdie, 1993; Crawford *et al.*, 1997). Data from the preceding ten years suggested that the spring bloom tends to occur in May and that both the spring and summer blooms tend to coincide with periods following spring tides with tidal ranges less than 4 metres. This would suggest that a spring bloom should have occurred around JD 138 in the middle of May in 1996. No bloom occurred at this time. But a bloom was observed around JD 172, and was coincident with a period of lower tidal energy. The magnitude of this bloom was somewhat less than seen in previous years.

For a bloom to occur there must be adequate levels of nutrients and light to support photosynthesis and the water column must be stable enough for the plankton to absorb sufficient light energy (Hobbie *et al.*, 1975; Fichez 1992). Water column stability appears to be important in bloom formation, especially in tidally dynamic areas, like Southampton Water. However, tidal height may not be the best indicator of the turbulence of the system. The pattern of temperature increase may provide a good record of overall weather conditions. Changes in temperature of the

water depend on the balance between heat input from solar radiation and cooling which can be enhanced by increased turbulence.

The levelling off of temperature during the period of the expected spring bloom (JD 125-132) may be due lower levels of total radiation. Meteorological Office total radiation data for the area suggests that this period experienced only three relatively sunny days, reaching a total radiation level of c.7000 $Wm^{-2}day^{-1}$. (Figure 4.16, the shaded area marked A) and then falling rapidly to less than 2000 $Wm^{-2}day^{-1}$. Whether the predicted bloom was inhibited from forming by lack of light, or that this low light period was coupled with stormier weather and, therefore, greater water column mixing, is unclear. When the bloom did occur, around JD 172 (Figure 4.16, the shaded area marked B), the solar radiation levels were not only higher throughout the majority of this period, but there was a sustained level of relatively high radiation, with five consecutive days having a total daily radiation in excess of 8000 $Wm^{-2}day^{-1}$.

Analysis by Fourier transform identifies two periods in the chlorophyll data (Figure 4.15a) which are associated with the astronomical tides M_2 (0.52 days) and S_2 (0.5 days) tides. The coincidence and opposition of these tides gives rise to a spring neap tidal cycle. The corresponding variation in the observed chlorophyll data is evident in Figures 4.14b and 4.14e. The causes of this may be that during neap tides, current speeds drop, to about half those on peak spring tides (Webber, 1980). The concomitant water column stability may slow turbulent diffusive loss of phytoplankton biomass, deepen the photic zone as tidal re-suspension of bottom sediments weakens, and reduce the vertical flux of phytoplankton to the benthic consumer animals (Cloern, 1996). Any of these factors may increase phytoplankton production. The onset of spring tides causes greater tidal mixing and so there will be a dissipation of accumulating phytoplankton. Also, the decrease in retention time associated with the spring tide means that a greater proportion of phytoplankton can be flushed from the estuary (Ketchum, 1954).

The period of 0.26 days is associated with the M_4 tide. This a tidal period caused by the shallowing water and friction with the bed. Along with the higher frequency M_6 tide it may be associated with periods of re-suspension of sediments. The relatively high amplitude signals of the M_4 (and possibly M_6) tides in the attenuation data suggests that their is a significant amount of variation in the suspended matter that is related to the re-suspension of bottom sediment. The suggestion of the M_4 tide in the chlorophyll data set may indicate that some variation in the chlorophyll data could also be caused by the re-suspension of bottom sediment. This is consistent with the double peak in chlorophyll concentrations seen on and around the maximum of spring tide.

The period of one day observed in the analysis of the chlorophyll data is not necessarily induced by tidal flows. During spring tides it appears that this daily signal is controlled by the re-suspension of bottom sediments, as discussed above. However, during the neap tides, the daily chlorophyll maximum is most probably linked to the daily light cycle. Within Southampton Water there may be two explanations for this. It is possible that the diurnal increase in chlorophyll is due to *in situ* growth. Observations of chlorophyll concentrations using a moored

fluorometer in an area of transient stability (Tett and Walne, 1995) have shown similar rapid response of the production to changes in the stability of the water column. A second possible explanation is that we have detected motile phytoplankton responding to the light. Within Southampton Water certain plankton populations have been observed to migrate within the water column, and it has been hypothesised that this behaviour allows them to move into less rapidly moving water so that the population can increase its residence time within the estuary (Crawford and Purdie, 1992; Crawford *et al.*, 1997). Lower energy conditions are exemplified by the poor relationship between chlorophyll and attenuation (Figures 4.14d and 4.14e), as less sediment is mixed into the upper 2m of the water column. Energy conditions were possibly low enough for plankton migration through the water column to take place throughout the day, and this process not to be disturbed by turbulent mixing. Such a process may also be responsible for the rapid decrease in chlorophyll after the peak levels were recorded, as the phytoplankton migrate to deeper waters to avoid the currents on the ebbing tide.

There are other periods identified within the data by this analysis, such as at 0.85 days in the chlorophyll, and at about 0.18 and 0.6 days in the attenuation data. Further work is needed to ascertain whether these have any significance to the processes occurring within the estuary.

4.5 Comments on status of in-situ measurements

- Mooring of fluorometers attached to buoys as part of the NERC-North Sea Programme in 1988/89 clearly demonstrated that data with high temporal resolution from buoys could provide a more accurate description of how plankton blooms developed and decayed than had previously been possible from ship borne studies. Further use of buoys has to improve on this. The instrumentation carried and the positioning of the buoy must be such that pertinent questions can be answered.
- Southampton water is a good location for use of a data buoy in that the area of maximum phytoplankton activity is well defined, and the SONUS project showed that a buoy can be moored successfully in the area.
- The SONUS data-buoy produced a valuable data set describing the conditions and the rates of change of concentration induced by physical and biological changes in a detail not seen before. However a limitation of some of this data and potentially other buoy based data sets is the poor of calibration of some of the sensors at present. Calibrations are needed to convert a *qualitative* picture into a *quantitative* understanding. In section 4.3.5 we have discussed the value of using sensors such as the NAS-Nitrate sensor which are self calibrating, other sensors such as the fluorometers appear to be relatively resistant to fouling. Others such as conductivity sensors show substantial drift.
- More experience needs to be gained of how best to maintain the calibration of sensors over periods of time extending from weeks to months. Some experience will be developed internationally in the coming years within the context of the GOOS Global Observing Systems project. However experience of the effects of local conditions on instrumentation

and supporting structures will always be required, particularly as many of the areas of environmental concern will be in aggressive coastal and estuarine environments.

- An important development that coincided with the building of the SONUS buoy was the development of the Vodaphone PakNet data transmission network. This enabled relatively simple and inexpensive equipment to be used to transfer measurements from the buoy to be to the laboratory for subsequent processing in real time.
- Buoys such as the SONUS buoy are capable of providing large amounts of data. As noted above, this data needs to be calibrated as accurately as possible, it also needs to be handled in such away that important features in the data can be readily identified. The ability to review the 1996 data from the SONUS buoy as it was being collected allowed us to begin analysis of the data at an early stage. As a result we were able to present a paper on our results at a scientific meeting in November 1996 (Wright et al 1997).

4.6 Recommendations with respect to further buoy (or other continuous real time) observations

- A data-buoy should be used if an area of impact is well defined relative to a single point measurement location. Otherwise alternative ways of getting data such as instrumented ships of opportunity should be considered, this may be more cost effective than using a network of buoys.
- Two questions should be addressed (1) whether or not the buoy can be moored in an appropriate location, and (2) can it be serviced at sufficiently frequent intervals for the measurement quality not to be degraded.
- The instrumentation package on the buoy should be appropriate for the processes to be studied . The reliability of the calibration of the instruments should be known.
- Means of rapidly accessing and viewing the data should be found. A good example of what might be done has been developed by IFREMER for the system of three data buoys and a dock-side station they are establishing to monitor the Baie de Seine off Le Havre. Progress with this project and recently acquired data can be inspected through the IFREMER web site (http://www.ifremer.fr/marel/).

4.7 TABLES

Table 4.1

Summary of 3 deployments of the NAS-2E nitrate analyser

SURVEY	BREST	SONUS 3	SONUS 4
Start	21/3/95	22/8/96	5/3/97
End	18/4/95	17/10/96	9/4/97
No. of samples	561	1343	697
No. of OBS	114	224	138
OBS concentration (µM)	47.5	30	50
Conc. ranges samples (µM)	5-30	33-5	10-60
% Std Deviation Blank	0.7	4.0	N/A
% Std Deviation OBS	5.3	8.9	13.4

Table 4.2.

Comparison of results from NAS-2E with those from conventionally collected samples

	Nitrate µM	Nitrate µM		
Day 1995	NAS-2E	Boat	Difference	%Differ.
81	29.4	28.6	0.8	2.7
82	28.0	27.6	0.4	1.3
83	24.8	24.6	0.2	1.0
86	24.8	23.1	1.7	6.9
87	23.8	22.9	0.9	3.6
88	26.2	25.3	0.9	3.3
89	31.0	30.1	0.9	3.0
90	24.4	23.8	0.6	2.6
93	21.9	19.8	2.1	9.5
94	19.4	18.1	1.3	6.6
95	19.1	17.1	2.0	10.6
96	18.3	16.3	2.0	10.8
100	12.9	10.8	2.1	16.2
101	14.7	14.0	0.7	4.6
102	15.2	13.6	1.6	10.6
103	12.7	11.0	1.7	13.3
104	10.8	9.3	1.5	13.5
108	5.6	5.5	0.1	1.2
			mean	mean
			1.2	6.7

4.8 FIGURES

Figure 4.1.
Location map of the Southampton Water estuary, showing the location of the mooring deployment.

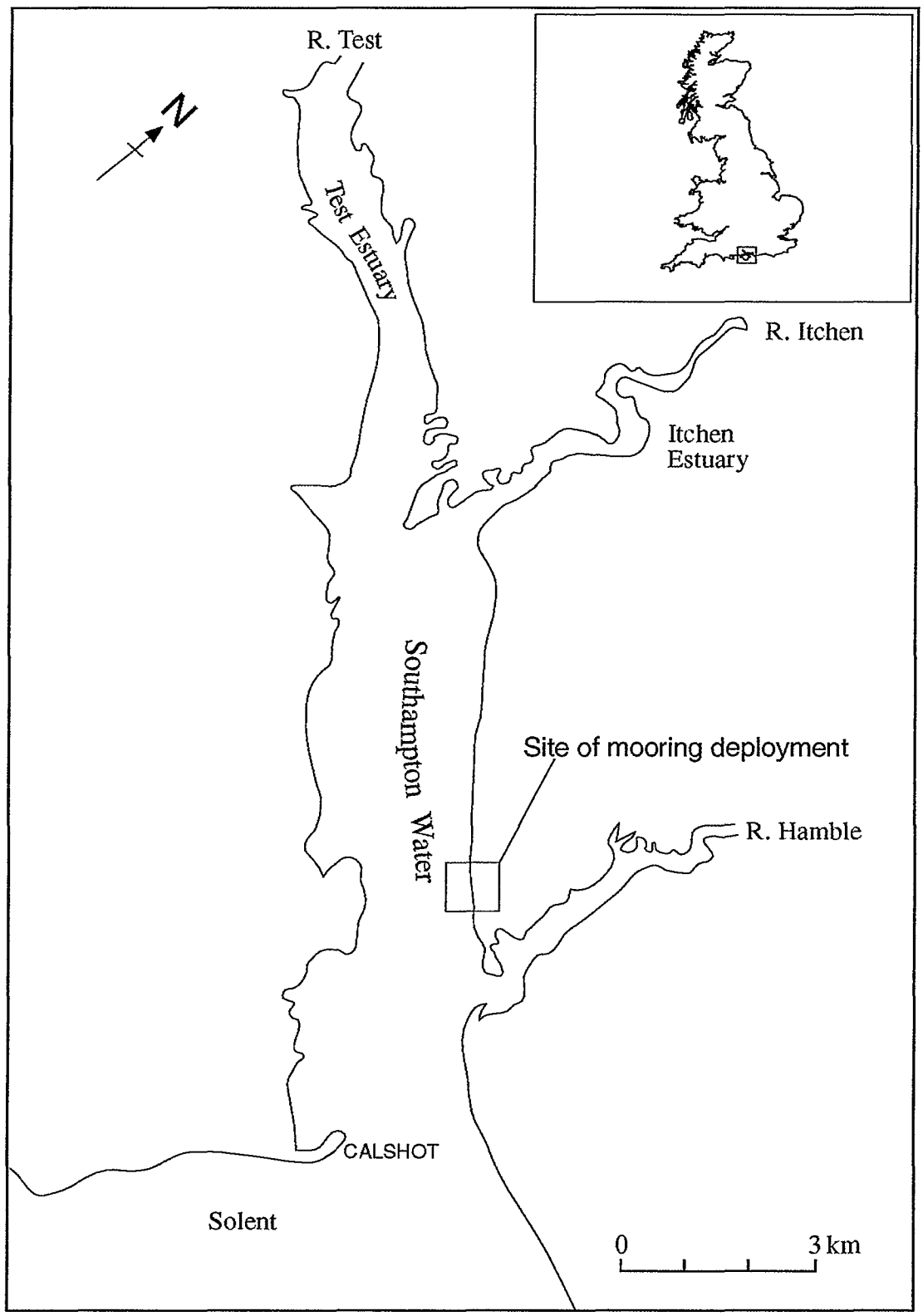


Figure 4.2
Aerial photograph of the BP Oil Terminal at Hamble on Southampton Water.

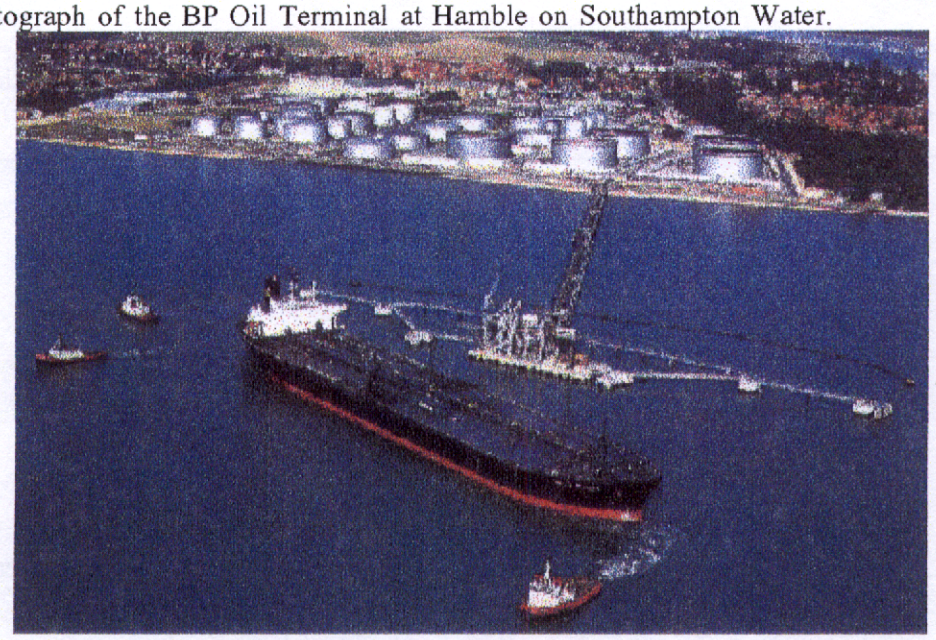


Figure 4.3
Photograph of the SONUS buoy being moved from the rigging shop to the dock side at SOC, 3 April 1996.

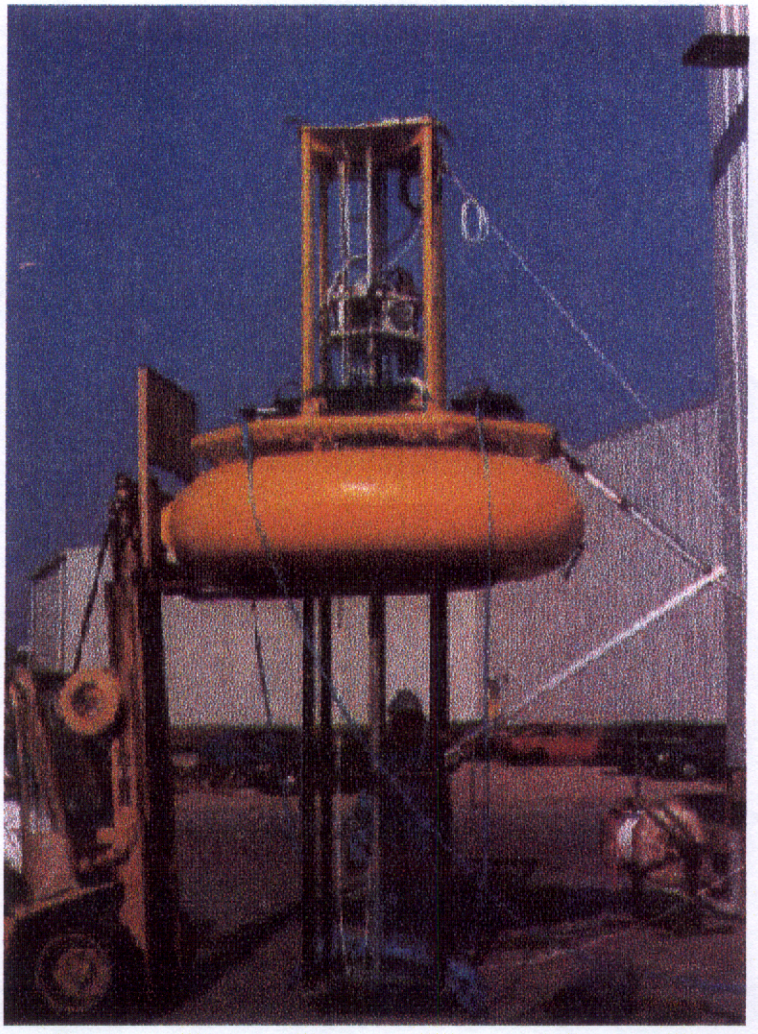
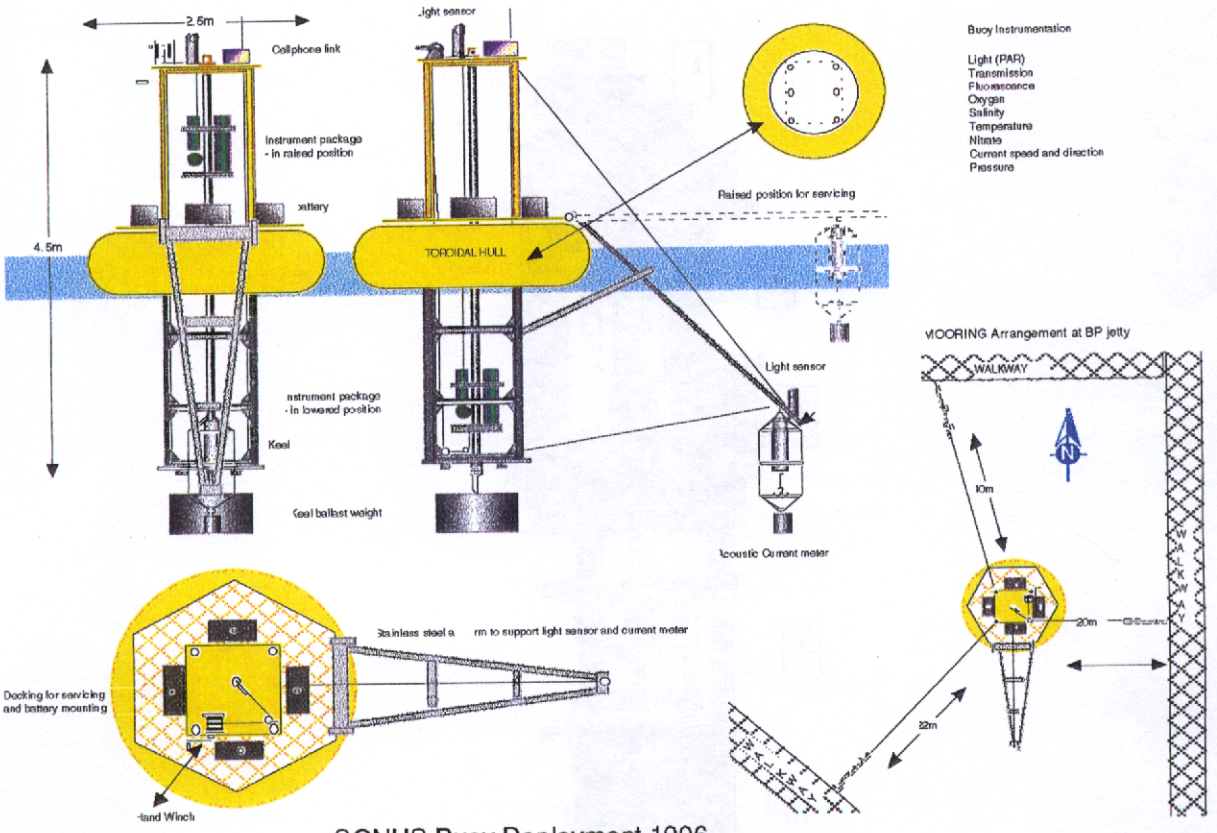


Figure 4.4
Diagram of the configuration of the SONUS Buoy, and the arrangement for mooring at the BP Jetty (see Figure 4.2)



SONUS Buoy Deployment 1996

Figure 4.5
Diagram of mechanical structure of a NAS-2E. 1. Stepper motor. 2. Multi-port valve 3. Syringe 4. Colorimeter 5. Syringe drive motor. 6. Control electronics

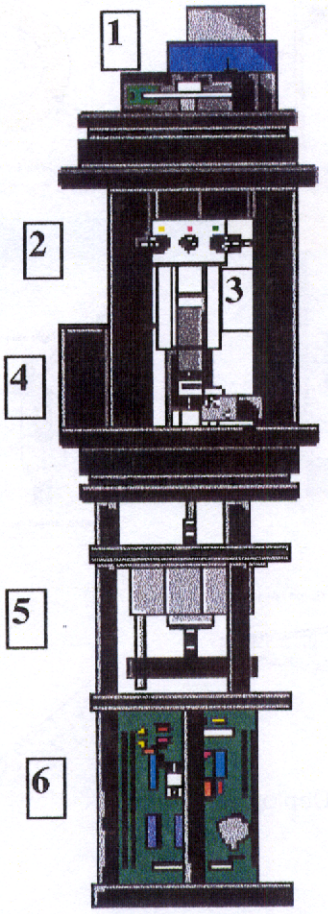


Figure 4.6
Detailed plot of first weeks observations made on the deployment off the French coast

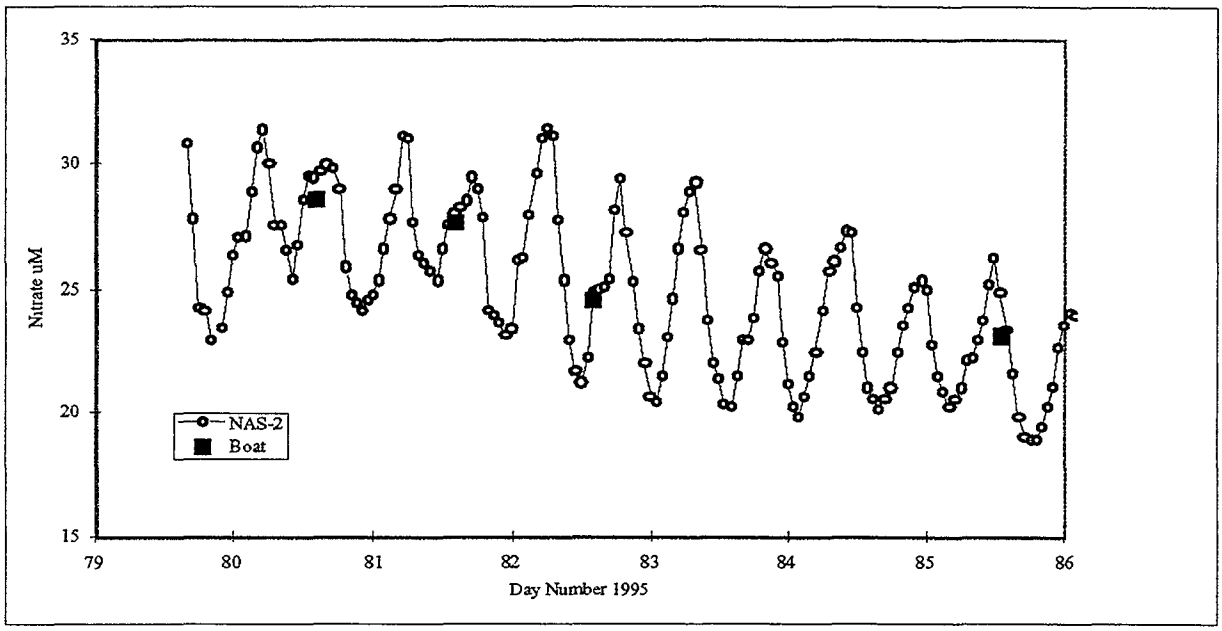


Figure 4.7
Plot of the NAS-2E data against data from laboratory based auto-analyser measurements on samples collected by boat. Results of linear regression analysis of the data are shown.

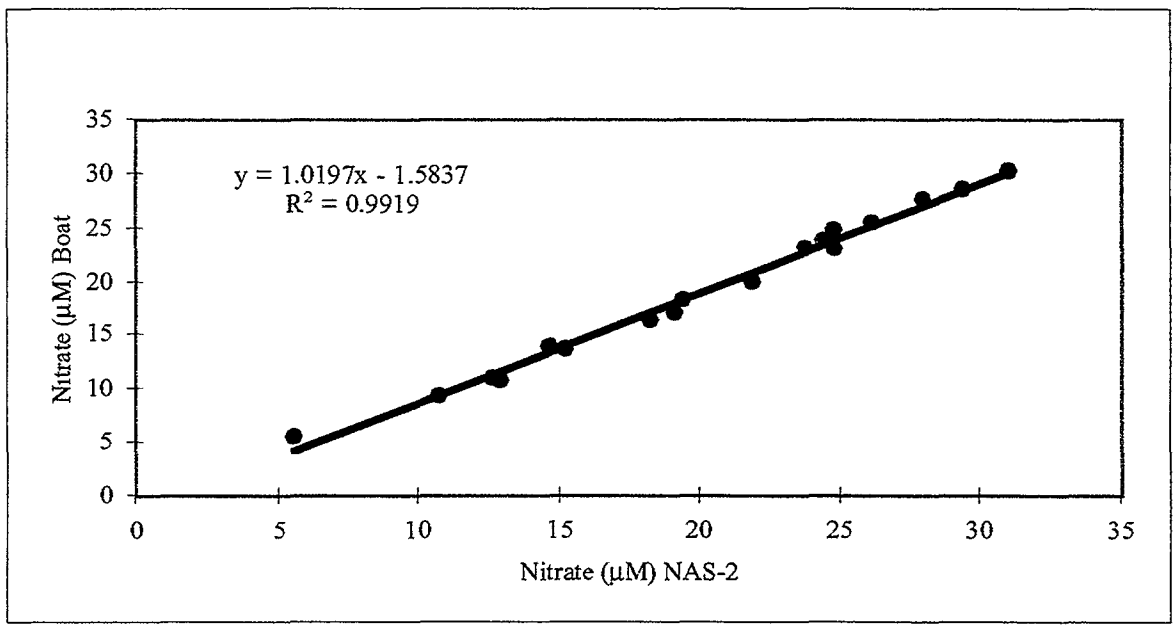


Figure 4.8
Plot of the variation with time of the absorbance measured for the On Board Standard during the deployment off the French coast - OBS-1 and the first SONUS deployment - OBS-2.

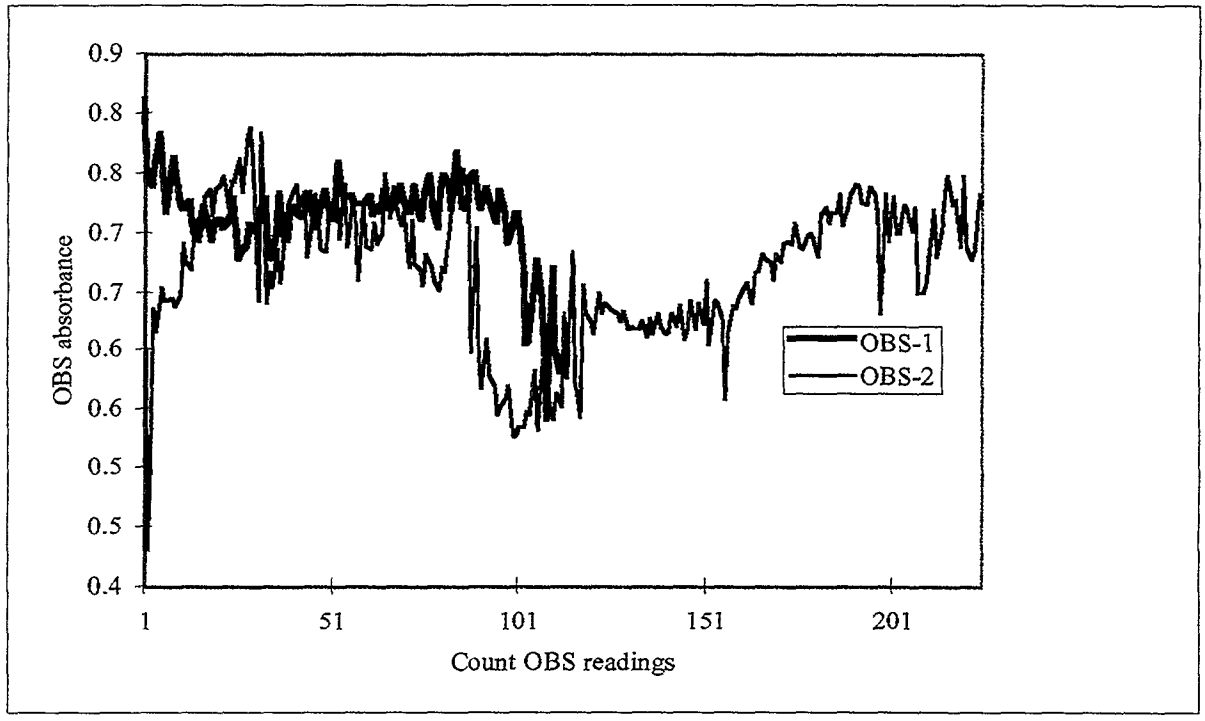


Figure 4.9
Plot of the variation in the calibration coefficient obtained on a AA-II type auto-analyser for nitrate determinations over 20 days on RRS Discovery cruise 216.

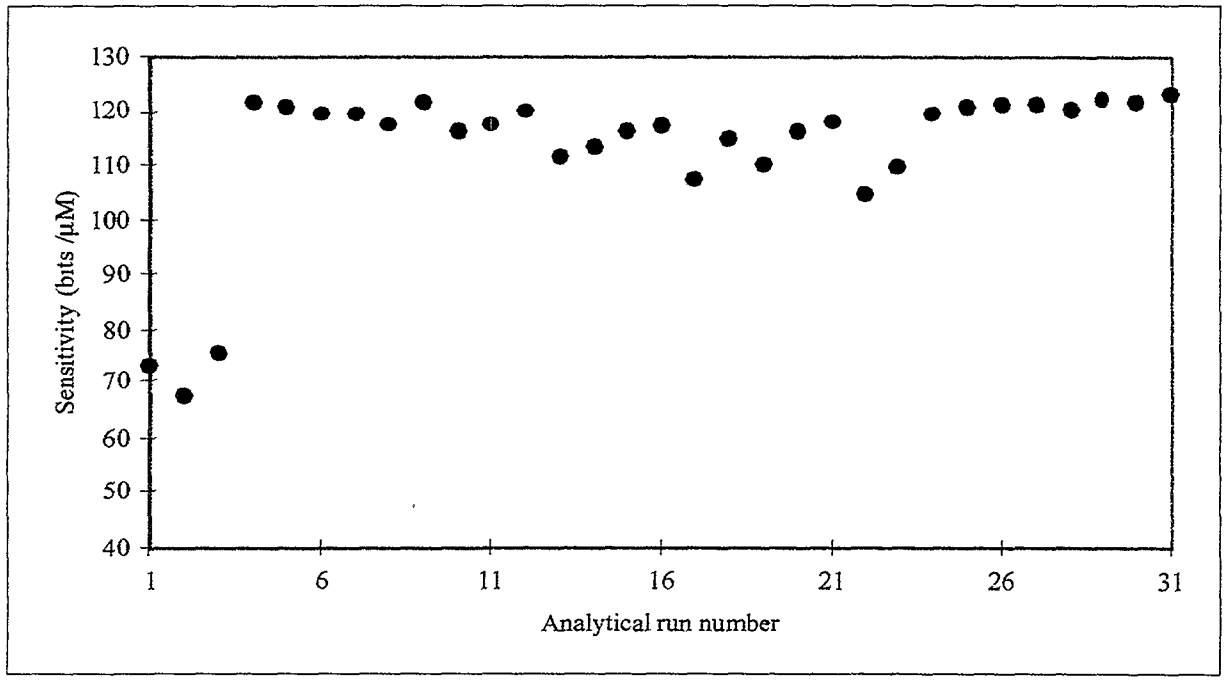


Figure 4.10
Results of NAS-2E determinations of nitrate in Southampton Water between 22 August and 17 October 1996.

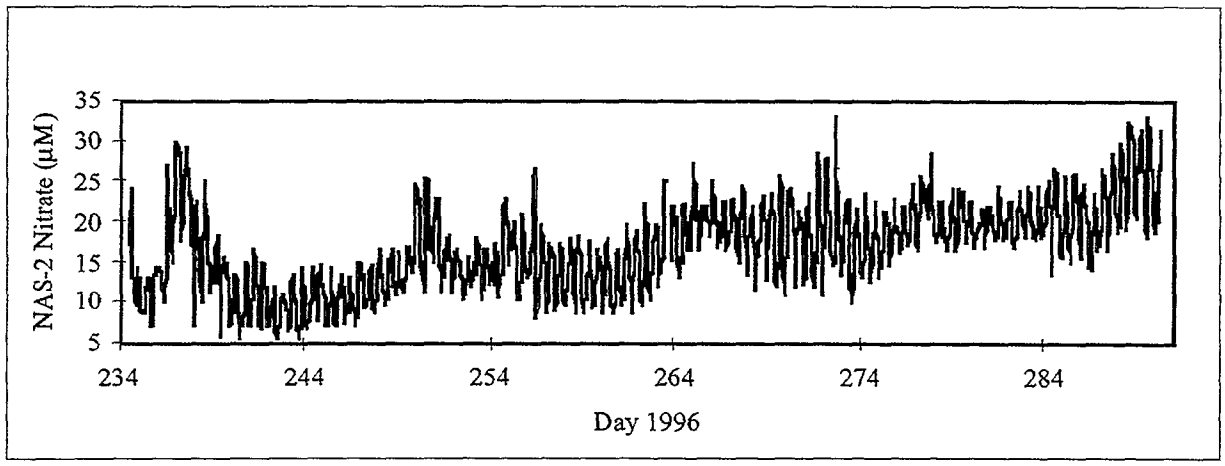


Figure 4.11
Results from the second SONUS deployment starting on the 5 March 1997 (Day 61 1997). Data are grouped into weekly sets starting with days 61 to 67.

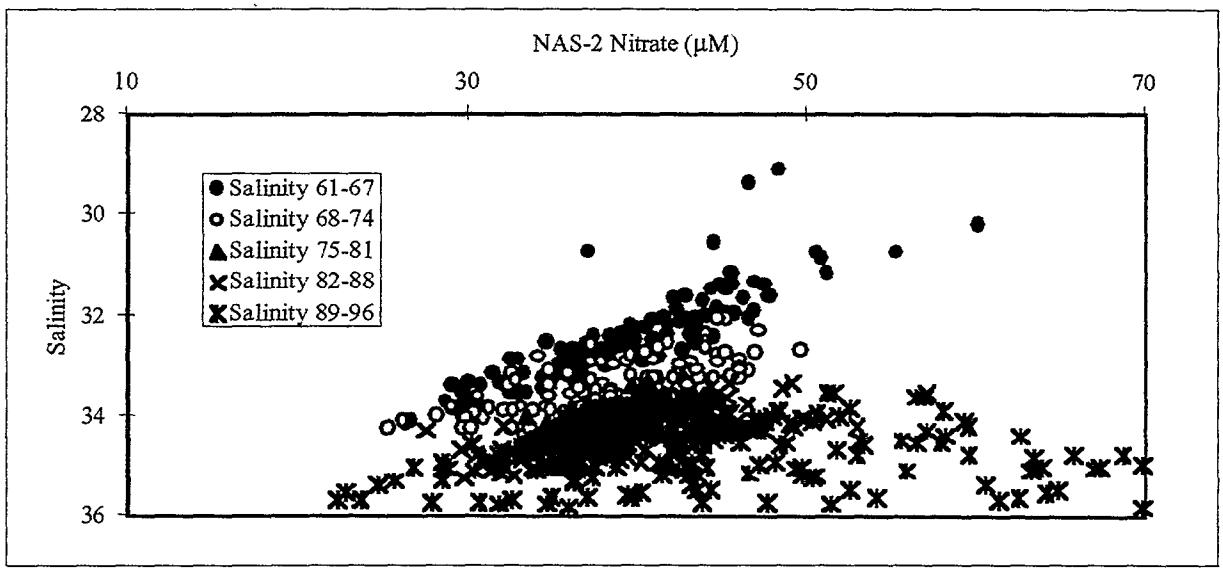
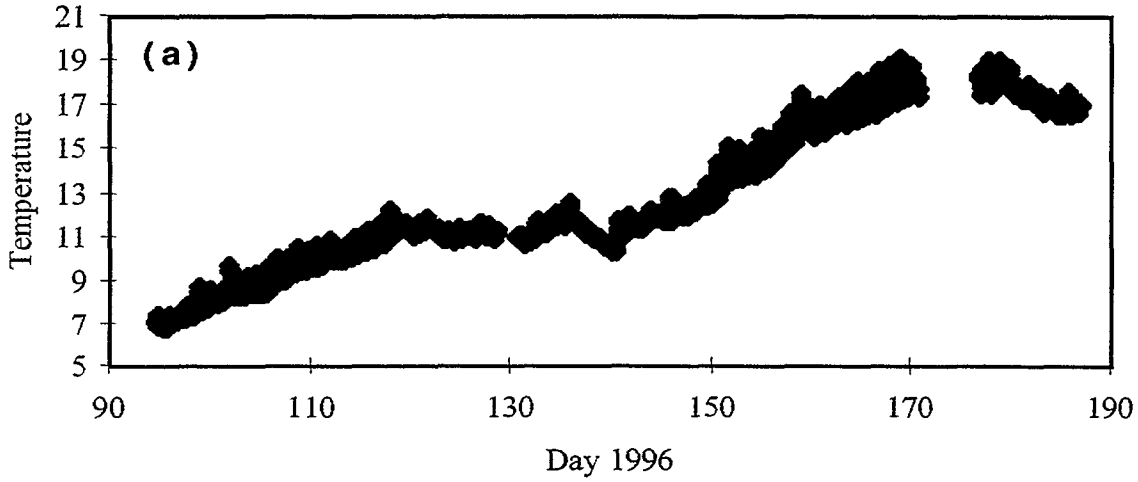
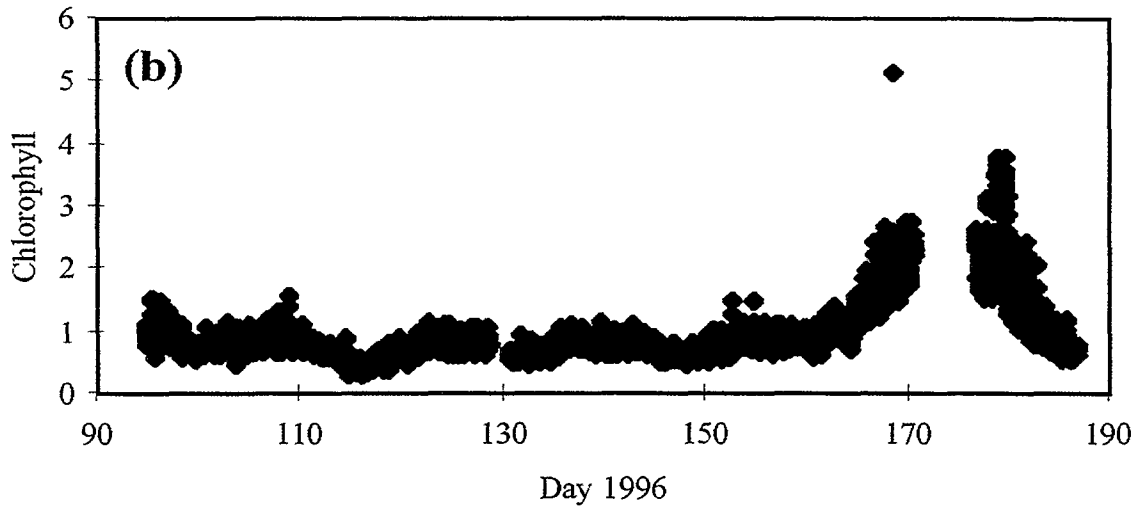


Figure 4.12
Complete data set, from 4th of April to 8th of July, for (a) temperature, (b) chlorophyll a, and (c) tidal range.





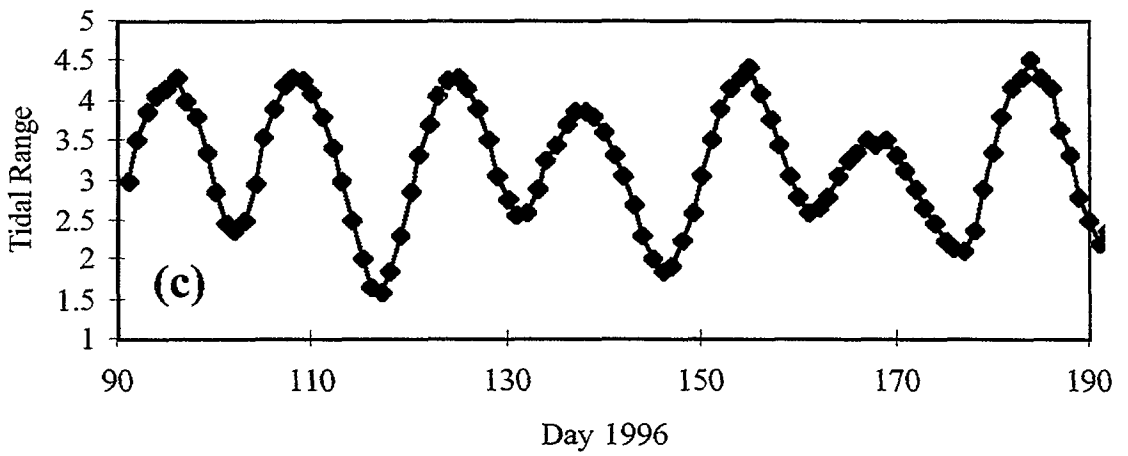


Figure 4.13
(a) Attenuation, (b) chlorophyll, and (c) tidal range for Julian Days 94 to 122, showing a spring-neap cyclicity within the data.

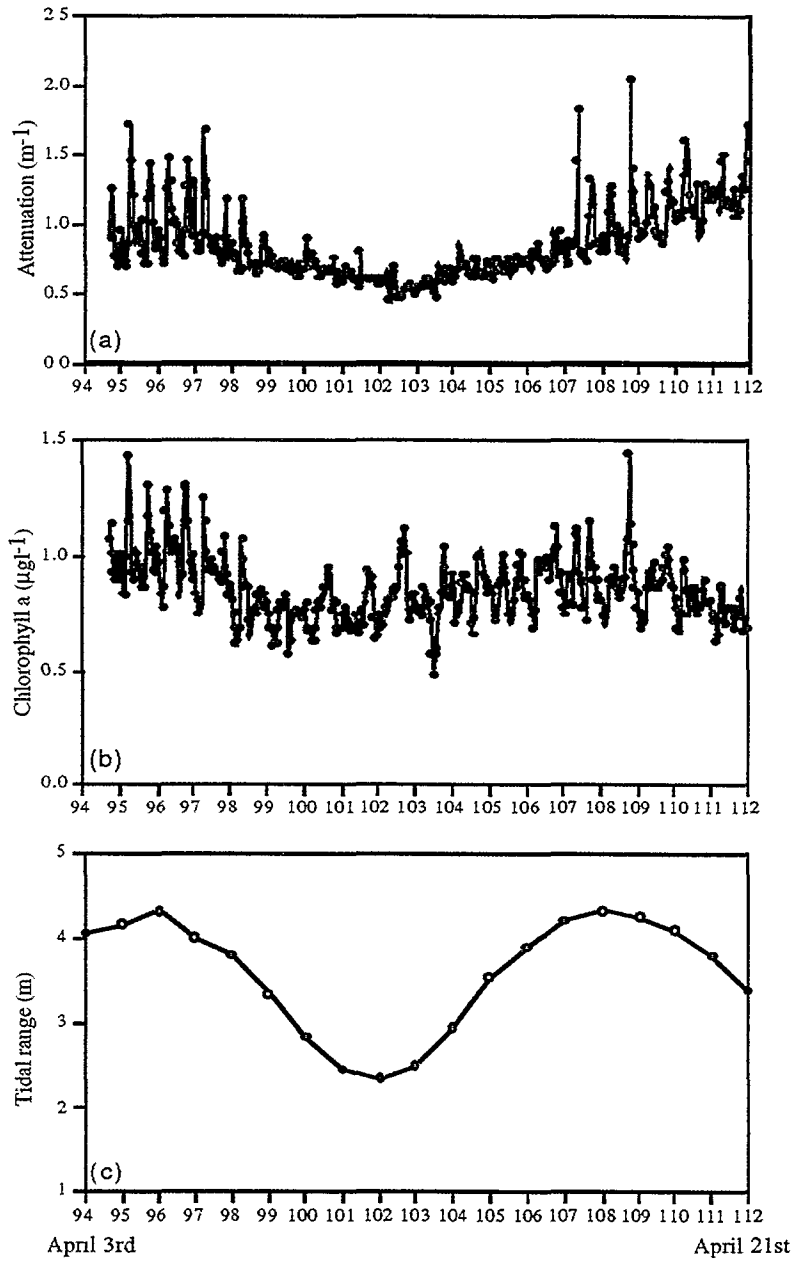
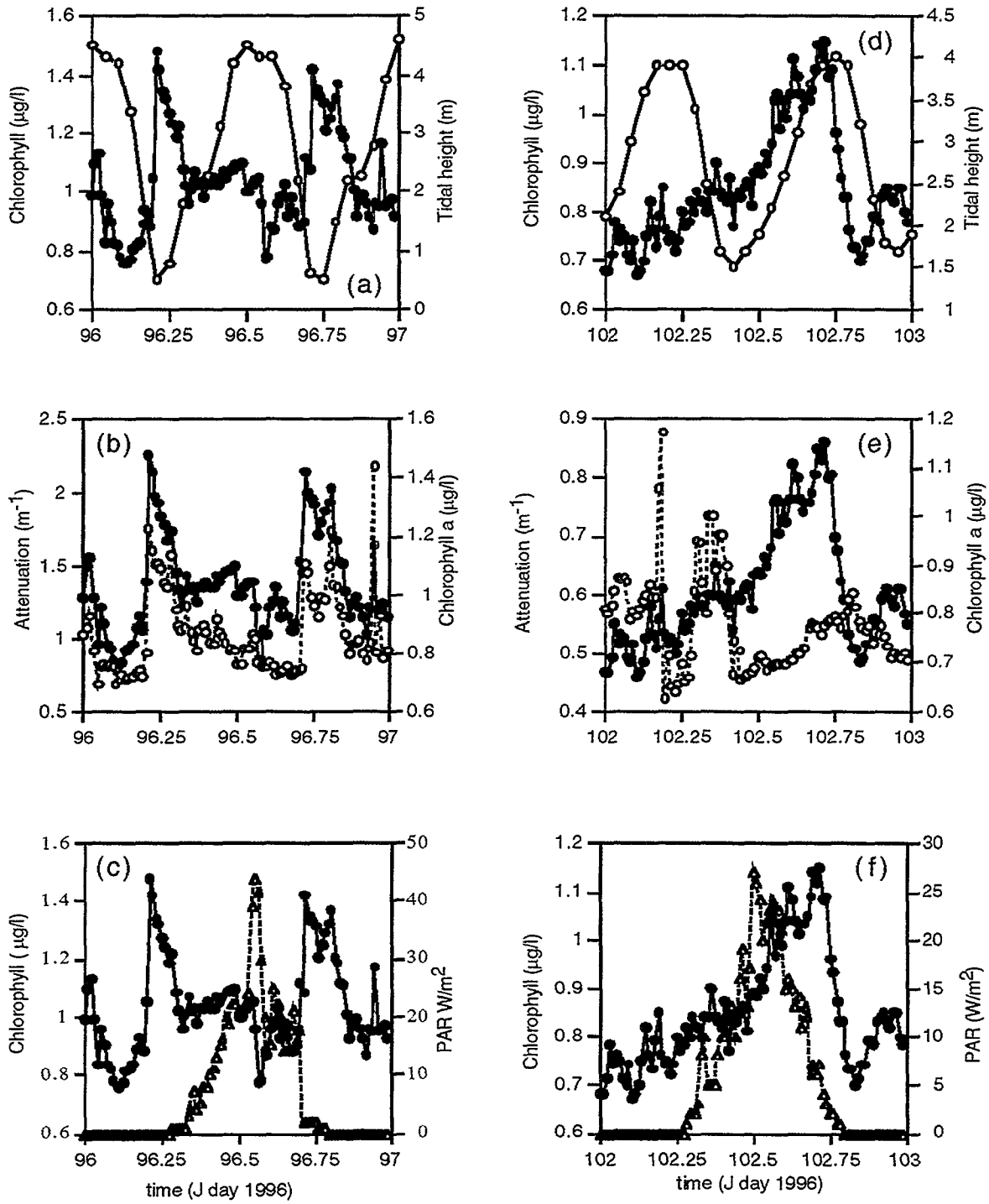


Figure 4.14.
Daily variations in chlorophyll (filled circles with a solid line) and tidal height (open circles with a solid line), attenuation (open circles with a dashed line) and chlorophyll, and PAR (open triangles with a dashed line) and chlorophyll during a spring tide, JD 96 (a, b, and c), and a neap tide JD 102 (d, e, and f).



Spring tide
April 5th

Neap tide
April 11th

Figure 4.15
Harmonic analysis of (a) chlorophyll and (b) attenuation data.

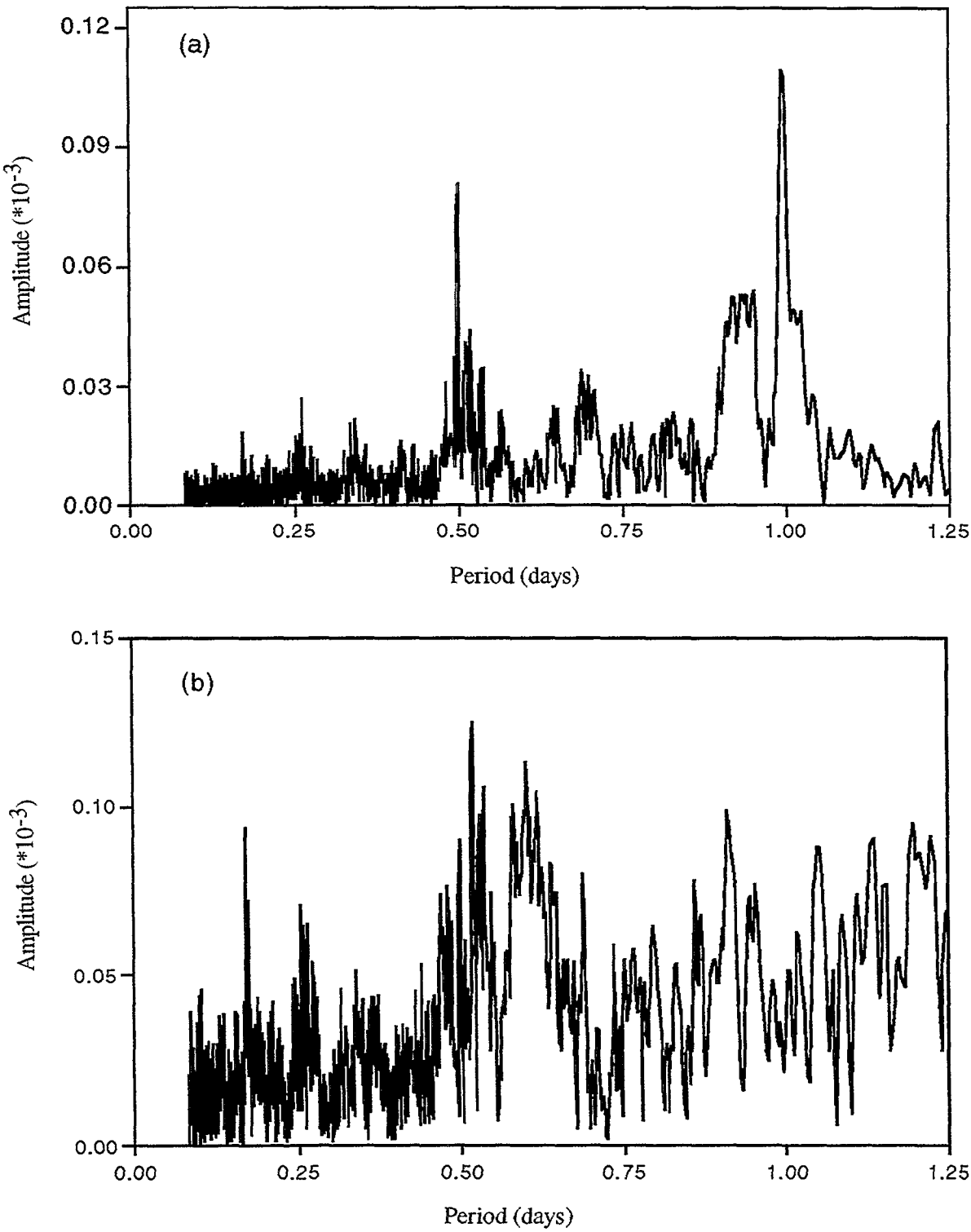
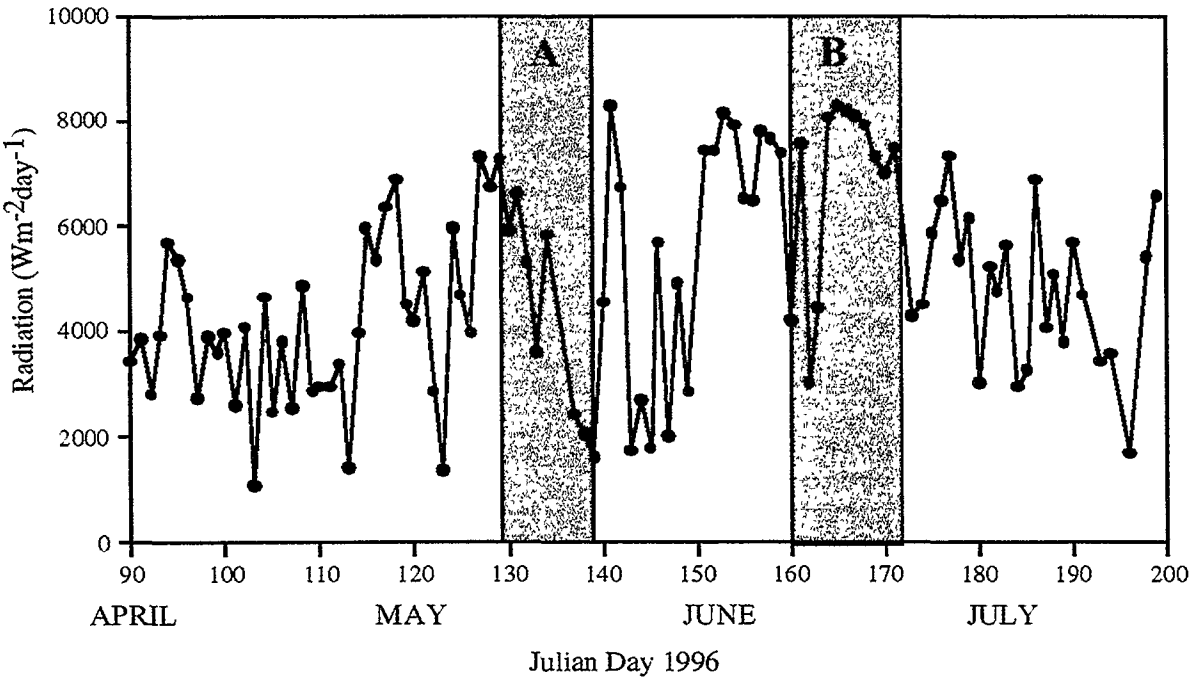


Figure 4.16
Total irradiation data from the period of mooring deployment. The shaded area (A) indicates the period when the first major bloom of the year may have been expected, and the shaded area B indicates the period when the bloom was observed. Data courtesy of the Meteorological Office, and was measured at a mainland weather station to the west of the Hamble site.



SECTION 5

METHODS USED FOR THE ANALYSIS OF SAMPLES COLLECTED DURING THE SONUS-FIELDWORK PROJECT 1995-1997: DETAILS OF METHODS AND QUALITY CONTROL PROCEDURES

5.1 Introduction

The following report contains all details of the various methodologies used throughout the Southern Nutrient Study (SONUS) between March 1995 and August 1997. Water and suspended particulate samples have been collected throughout this period. Details of storage, preparation, and analytical techniques are included. Further studies are advised to follow similar routines so as to ensure as tight a control on data quality as is possible. However, in the light of analytical developments this report is designed to serve as a starting point for such further work. Throughout the project, data quality has been assessed by monitoring analytical performance by analysing an internal standard and several samples provided by an organised intercalibration exercise (QUASIMEME). The conclusions from these tests are contained within this document.

5.2 Methods

5.2.1 Dissolved inorganic nutrients

5.2.1.1 Sampling and storage procedures

Samples from the *Bill Conway* trips were collected via a bucket, and taken from the outflow of an instrument box, which was fed by the launch's deck wash. All the samples collected represented waters from about 1m depth. This water was then measured for salinity using an independent salinometer (WTW L320, see section 2.5) and then filtered via syringe and GF/F filter into a virgin 30ml "diluvial". Each receptacle for water was washed three times with filtered sample before filling. Separate samples were taken for inorganic and total analysis.

At first, filtered and unfiltered samples were poisoned with 2% w/v $HgCl_2$ (300µl per 100ml). On return to Southampton laboratory, the samples were stored in the dark at about 4°C. Analysis usually took place within 48 hours, or, quite often, the following day. Later trips eliminated the use of $HgCl_2$ as it did effected the sensitivity of the cadmium column, prohibited the formation of any colour during ammonium analysis, and it also carries serious health risks. Also, the time between sampling and analysis did not warrant its use. On subsequent trips the samples were stored cold, in a fridge, or if analysis was likely to be longer than a couple of days then freezing was used. Slow thawing is essential in this case to redissolve any silicate that may precipitate during freezing.

Figure 5.1 shows the effects freezing has on nutrient concentrations. It has been reported that freezing can lead to the precipitation of a polymerized form of silicate, which may be recovered by slow thawing (Dole *et al.*, 1996), and it is also thought that plastic surfaces can adsorb phosphate. However, Kremling & Wenk (1986) report that although freezing of seawater

samples has no immediate impact on nutrient concentrations, the storing of frozen sea water can lead to considerable variability between subsamples, which increases with respect to length of storage time. The data show 6 samples taken along a salinity gradient ranging from about 12 to 33. Two subsamples were collected, in duplicate, in glass and plastic. These were analysed immediately upon return to the lab, frozen for a month, and then reanalysed. The time period of a month is in excess of the usual length of storage used in this study. The data indicate that, for phosphate, there is little difference between glass and plastic stored samples, and that storage in plastic does not significantly alter phosphate concentrations over time (as long as they are frozen). The largest differences occur at the high end of the concentration range, where analytical error between duplicates is as large as error between samples that were immediately analysed and those which were frozen. Nitrate concentrations were not significantly altered by freezing, and choice of storage vessel was not significant. Silicate, as would be expected, did show a distinct difference with regard to type of storage vessel. Those stored in glass were much higher than those stored in plastic, which was due to silica dissolving from the bottle walls. Freezing the sample, and storing them in plastic, did not have any significant effect on silicate concentrations.

5.2.1.2 Introduction to the analytical methods

Inorganic nutrient analyses were performed on an automated analytical system linked up to a Digital-Analysis Microstream data capture and reduction system. Nitrate and nitrite, phosphate, and silicate were measured using a Burkard Scientific SFA-2 Auto-analyser, whilst ammonium and nitrite were measured on a ChemLab Auto-analyser. The manifold diagrams for these method are also appended.

All the methods described here are "colorimetric", that is a chemical reaction is carried out with the micronutrient in the seawater sample to produce a coloured solution. The density of the colour is proportional to the concentration of the nutrient present (where the Beer-Lambert law holds). Colour density is measured accurately using a photometer containing filters corresponding to the colour developed in the solution. The Beer-Lambert law

$$I_a = I_o(1 - e^{cx})$$

I_a - light absorbed, I_o - incident light, c - concentration of nutrient, x -constant for particular system) generally holds where the amount of light absorbed is less than about 85% of the incident light. Most spectrophotometers are calibrated in terms of transmittence, i.e.

$$I_o - I_a / I_o$$

and absorbance which is the log of the reciprocal of transmittence and is directly proportional to the concentration. In the auto-analyser colorimeter the output from the photometer is fed through a logarithmic converter to give a signal which is proportional to concentration (where the Beer Lambert law holds). It is not calibrated. This means that the linear working range has to determined empirically for each method. When developing a method the dilution of sample in the analysis stream is adjusted to keep to the maximum concentration likely to be encountered within the linear range of the Beer Lambert law. In operation the gain control on the colorimeter is

adjusted to give full scale deflection on the chart recorder (being used to record the signal from the colorimeter) for the most concentrated sample.

The fundamental feature of continuous flow automated chemistry is segmentation of a flowing stream of sample and reagent with bubbles of air (MEE, 1986). The bubbles serve three purposes. Firstly they cause friction with the tubing, this creates turbulent flow which tends to mix sample and reagents. Secondly they prevent diffusional and turbulent mixing of one sample with the next. Thirdly they continuously scrub the walls of the tubing, again limiting tailing of one sample into the next.

An important concept to grasp is that it is not necessary to have reactions go to completion to gain the increase in precision which is inherent in automated systems. This is because all operational conditions are maintained the same, so that each sample is subjected to exactly the same quantity of reagents, the same temperature, and the same mixing time as every other sample. Therefore each subsample between bubbles is repeatedly measured at some constant percentage of the completed chemical reaction. The precision of determinations is not therefore effected detrimentally although the sensitivity may be slightly lower than if the reactions had gone to completion.

When air and reagents are pumped into an injector fitting the air bubble increases in size until it fills the main tube and breaks away. The size of the bubble depends on the geometry of the injector and the surface tension of the reagent mixture. It is independent of the rate of air input. Increasing air input will increase the frequency of bubbles. The more frequent the bubbles the more effective will be their scrubbing action. The optimum size of bubble is one where the length should be about twice the tube diameter. Resolution is degraded when bubbles are larger or smaller than this.

Bubbles in the flowing stream of reagents and sample, and, coiling of tubing induces mixing of solutions of different viscosities. As the two layers of different viscosity pass along straight tube the more viscous reagent moves to the rear of the segment. As the segments go round a coil because the outer circumference of the coil is greater than the inner, liquid on the outer edge moves relatively more quickly than that on the inner surface. This induces circulation within the individual segments producing mixing. For this effect to work best the segments should not be too long. About two and a half to three segments per turn of coil is optimal.

Inside the colorimeter cell mixing of debubbled solutions occurs. This *carryover* of one sample into the next is seen as overlapping peaks and tailing of peaks on the chart recording. The rate at which one sample is washed out of the cell by the next depends on the geometry of the colorimeter cells and the viscosities of the solutions. As a good approximation the degree of carryover of one peak to the next when expressed as a fraction of the previous peak is fairly constant for a particular set of conditions at a given time after the preceding peak. Hence the degree of carryover depends on the total time between peaks, i.e., sampling time plus wash time, and does <u>not</u> depend on the ratio of sample time to wash time. Measurement of peak heights will be most precise where sampling time is sufficiently long for the peak to reach a plateau. Note:-

Practically speaking the likelihood of possible attainment of the plateau will actually be reduced by long wash relative to sample times. When deciding on sample and wash times a balance must be drawn between the following points. (A ratio of 60 secs to 40 secs is used in this study.)

- The longer the sampling time, the more near will be the approach to steady state in the colorimeter cell and the more precise the measurement.
- The longer the sample and wash time the less will be the necessary correction.
- How much sample is available.
- The overall time for the analytical run.

5.2.1.3 Setting up and Closing Down

Setting up

For the initial setting up.

Place the pump tubing in the peristaltic pump manifolds in the order shown in the method sheets. Connect these to the chemistry manifolds keeping the lengths of tubing to a minimum, trimming the pump tubes.

Lengths of tubing into reagent bottles should be trimmed so they just reach the bottom of the bottles.

Daily

One hour should be allowed for warm-up of the colorimeter and heating baths.

Start the reagents pumping through the lines after 20 minutes switch on the chart recorders and begin to observe the quality of the baselines.

Check that the bubble pattern is steady, and that all the reagents are being pumped.

If the nitrate column is to be used it should be fitted to the manifold after the buffer solution has been pumping for 10 minutes. If possible allow one hour after fitting the column before the start of an analytical run.

Before starting the main run, determine 3 top of the range standards, and check that they are on scale and that the system is giving the expected response.

Closing down

At end of run, remove the nitrate column.

Place all reagent lines into distilled water containing the appropriate wetting agent, and leave pumping for at least 15 minutes.

If nitrate/nitrite line has been used it is recommended to flush this out by pumping 10% "Decon" solution through the lines for five minutes before changing over to distilled water containing Brij-35. The Decon is more effective at removing any adsorbed colour from the flow cell than Brij-35

If the machine is not to be used for several days follow the wetting agent rinse by pumping distilled water through all the lines including the wash line for 15 minutes. Then pump all the lines dry.

Open up the pump plattern and wipe the excess oil from the pump tubes.

Relax the tubes to first peg at each side of plattern. Do not unhook them, because of the danger that if the pump is started before the blocks are hooked up one may jam in the rollers and damage the pump. Such damage is repairable but it takes time (see "Chemlab" manual).

5.2.1.4 Methods

"Anala R" grade chemical should be used throughout for the preparation of reagents. For most methods water of "single distilled quality" is of adequate purity. Throughout the SONUS project, high purity water (HPW) of 18MΩ was used. When ammonia determinations are being made it is important to be aware that initially pure water which is in contact with the atmosphere can in some laboratories absorb relatively large quantities of ammonia in excess of those likely to encountered in even polluted natural waters. Therefore, freshly deionised HPW was used where possible for all solutions used in the determination of ammonia. The theories behind all the methods used here can be found in Grasshoff *et al.* (1983)

5.2.1.4.1 Nitrate-nitrite

The analysis of nitrate requires the reduction of nitrate to nitrite. Nitrite is determined by forming a diazo compound and then an azo dye, which is measured at 540nm. For seawater the most practical way of reducing nitrate to nitrite is heterogeneously using cadmium metal. To simplify compliance with Health and Safety procedures, we now buy in preprepared copperised-cadmium from Skalar.[1]

Reagents:

Ammonium chloride: Dissolve 50g in 2L distilled water.

Sulphanilimide: Dissolve 2.5g in 500ml distilled water containing 25ml concentrated hydrochloric acid. Add lml Brij-35 (25%w/v) when dissolved.

Naphthylethelynedihydrochloride (NED): Dissolve 0.25g in 500ml distilled water. Add lml Brij-35 (25%w/v) when dissolved.

Maintenance of the copper-cadmium column:

The Cu/Cd reductor column supplied by Skalar takes the form of a glass U-tube filled with dry copper coated cadmium granules. The column appears to be fully active when ammonium chloride has been pumped through the tube for about an hour, thoroughly wetting the granules and removing all air which might effect flow through the column. Once the column is wet, care should be taken to prevent air bubbles getting in to the column as these will effect flow pattern and reduce the effective surface area of the cadmium. The cadmium is not a catalyst and is slowly dissolved by the reduction reaction. A nitrite standard should be included in each analytical run on the auto-analyser. The height of this peak should be compared to that of a nitrate standard of the same concentration as a measure of the reducing efficiency of the column. When the efficiency of the column falls below 95%, the column should be repacked.

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[1] Skalar UK Ltd., Murton Way, Osbaldwick, York, YO1 3US
T: (01904) 414956 F: (01904) 430121 http://www.skalar.com

Standard Solutions:

NO_3: Dissolve 0.510g potassium nitrate in 500ml distilled water. Transfer to screw top bottle for storage. This gives a 10mM solution.

NO_2: Dissolve 0.345g sodium nitrite in 500ml distilled water. Transfer to screwtop bottle for storage. This gives a 10mM solution.

Prepare working standards of 150, 100, 50, and 25µM (TON), and 10, 7.5, 5, 2.5µM (NO_2) by further dilution in 100ml of artificial sea water or surface sea water. By using a shorter path length of 15mm the linear portion of the calibration curve was extended up to 400µM.

Lines: (Figure 5.2)

Buffer (Yellow-Blue 1.40ml/min)

Air (Black 0.32ml/min)

Sample (Orange-White 0.23ml/min)

Return (White 0.60ml/min)

Air (Black 0.32ml/min)

Sulphanilamide (Green-Orange 0.1ml/min)

Naphthylethelynedihydrochloride (NED) (Green-Orange 0.1ml/min)

Return (Yellow 1.2ml/min)

5.2.1.4.2 Silicate

Dissolved silicate in seawater reacts rapidly in acidic molybdate solutions to form yellow silicomolybdic acid. This may be reduced using a number of reducing agents to give an intense blue coloured compound. Oxalic acid is added prior to the reduction step to prevent interference from phosphate. Ascorbic acid is recommended here as the reducing agent because it is the simplest and most stable one to use.

Reagents:

Ammonium molybdate: Stock solution - dissolve 30g in 1 litre distilled water.

Sulphuric acid: Dilute 140ml concentrated H_2SO_4 in 900ml distilled water.

Working solution To 80ml stock solution add 10ml dilute sulphuric acid and 25ml stock SDS then dilute to 250ml.

Sodium dodecyl sulphate - SDS (sodium lauryl sulphate): Dissolve 25g in 500ml distilled water.

Oxalic acid: Dissolve 25g in 1 litre distilled water.

Ascorbic acid: Dissolve 18g in 1 litre distilled water.

Standard Solutions:

Dissolve 0.960g sodium silica fluoride in 500ml distilled water. Start dissolution in 100ml plastic beaker by grinding the fluoride powder using a plastic rod to a paste with a few drops of water. Transfer to a screw top bottle for storage. Prepare standards of 150, 100, 50, and 25µM by dilution of the primary standard in 100ml of artificial sea water or silica free surface sea water.

Lines: (Figure 5.3)

Molybdate (Orange 0.42ml/min)

Air (Black 0.32ml/min)

Sample (Black 0.32ml/min)

Oxalic acid (Black 0.32ml/min)

Ascorbic acid (Orange 0.42ml/min)

Return (Yellow 1.2ml/min)

Note: Using a 660nm filter in the colorimeter, along with a shorter 15mm path length gave a linear response with the above conditions up to 200µM.

5.2.1.4.3 Phosphate

Phosphate is reacted with acidified molybdate reagent to give a phosphomolybdate complex which is then reduced to a highly coloured blue compound. Ascorbic acid is used as the reducing agent with potassium antimonyl tartrate in a single solution reagent. The mixed reagent reacts rapidly with phosphate ions to give a blue-purple complex containing antimony and phosphorus in a 1:1 atomic ratio. Measurement is made at 880nm.

Reagents:

Ammonium molybdate: Dissolve 15g in 500ml distilled water.

Ascorbic acid: Dissolve 25g in 500ml distilled water.

Potassium antimonyl tartrate: Dissolve 0.68g in 500ml distilled water.

Sulphuric acid: Dilute 140ml concentrated H_2SO_4 in 900ml distilled water.

Sodium dodecyl sulphate - SDS (Sodium lauryl sulphate): dissolve 25g in 500ml distilled water.

Diluent: Add 12.5ml SDS to 500ml distilled water.

Mixed Reagent:

20ml Ammonium molybdate

50ml Sulphuric Acid dilute (2.5M 140ml conc acid/l)

20ml Ascorbic Acid

10ml Potassium Antimonyl Tartrate

(Prepare and use within 6 hours)

Standard Solutions:

(A) Dissolve 0.681g potassium dihydrogen phosphate in 500ml distilled water.

(B) To prepare working standards dilute the primary standard 10 parts + 90 parts distilled water to make 1 mM solution. Then make up standards of 5, 4, 3, and 2µM.

Lines: (Figure 5.4)

Diluent (White 0.6ml/min)

Air (Black 0.32ml/min)

Sample (Orange 0.42ml/min)

Mixed Reagent (Orange-White 0.23ml/min)

Return (Red 0.80ml/min)

5.2.1.4.4 Ammonium

Ammonia in seawater is determined by a modification of the Bertholet reaction. Phenol and hypochlorite react with ammonia to form chloramine then aminophenol and finally indophenol blue which is measured at 625nm. Dichloroisocyanurate provides a convenient source of hypochlorite. A concentrated citrate buffer is used to prevent interference by magnesium.

Reagents:

Tri sodium citrate: Dissolve 34g in 500ml distilled water, containing 20ml of dilute sodium hydroxide and lml of Brij-35 (25% w/v).

Sodium hydroxide: (dilute) Dissolve 10g in 500ml distilled water.

Phenol: (Stock solution): Dissolve 10g in 500ml distilled water.

Sodium nitroprusside: (stock solution): Dissolve 1g in 500ml distilled water.

Sodium dichloroisocyanurate: Dissolve completely 2.5g Sodium hydroxide in 250ml distilled water. Dissolve 0.4g D.I.C. in this then make up to 500ml (stable 14 days).

Mixed phenol/nitroprusside: 10 volumes of phenol plus 1 volume of nitroprusside (prepare fresh daily).

Standard Solutions:

Dissolve 0.134g ammonium chloride in 500ml distilled water (5mM). Further dilution of this standard gives calibration standards of 25, 18.75, 12.5, and 6.25µM.

Lines: (Figure 5.5)

Citrate Buffer (White 0.6ml/min)

Air (Black 0.32ml/min)

Sample (Black 0.32ml/min)

Phenol. Nitroprusside (Orange 0.42ml/min)

(Black 0.32ml/min)

Return (Yellow 1.2ml/min)

5.2.1.5 Standards

All analytical runs were calibrated upon the basis of four mixed secondary standards run in duplicate at the start of each run. Drift and blanks were also measured at regular intervals during and at the end of each run. Secondary standards were made from stock standards diluted with $20gl^{-1}$ NaCl solution. The "wash" used was also a $20gl^{-1}$ NaCl. Calibration was by the linear fit by least squares regression forced through the origin. The gains were set at the start of the project and not altered throughout each SONUS run.

Standards were prepared from dried salts (110°C for 2 hours and cooled in a dessicator) with a precision of weighing of one part per thousand. The amounts used are shown in the sections above, and the solutions prepared in a 1l calibrated glass volumetric. These solutions were then stored in plastic screw top bottles in the fridge. These primary standards were prepared routinely every 2 or 3 months. The secondary standards for calibration were prepared fresh for every analytical run.

5.2.2 Total dissolved nutrient determinations

Once dissolved inorganic constituents had been determined, a persulphate oxidation technique was used to digest all dissolved organic nitrogen and phosphorous compounds. The method used was that of VALDERRAMA (1981).

Two millilitres of the oxidising reagent was added to the water sample in a screw topped Teflon cup (50mm x i.d. 25mm, BDH). This was then put into a pressure cooker and the water allowed to boil and the plug in the cooker lid to seal. The heat was then turned down (level 4) and the sample left to digest for 30 minutes. Blanks were also treated in the same fashion. Once digested the samples can be stored without degradation and analysed for N and P on an Auto-analyser as in 2.1.

Reagent:

Oxidising Reagent: Dissolve 7.5g of sodium hydroxide, 15g of boric acid, and 25g of di-potassium peroxydisulphate in 500ml. The solution should be made fresh every day.

5.2.3 Determination of Dissolved Organic Carbon - DOC analysis

One litre DOC samples were taken from surface waters using a plastic bucket. The deck wash was not used so as to eliminate any contamination from its rubber hosing. DOC samples were taken first from the bucket before in order to contamination from hands etc. These waters were subsequently filtered as soon as the survey was finished, through a Whatman GF/F, back at SUDO and stored in glass prior to analysis. These bottles had been acid cleaned and rinsed thoroughly with HPW.

DOC analysis consisted of three steps: initial removal of inorganic carbon, oxidation of organic carbon to CO_2, and quantification of the CO_2 produced. The method used is that of Statham & Williams (1983). The manifold diagram is appended.

Reagents and blanks are made from Low Organic Carbon Content (LOCC) water and purged with oxygen. The LOCC is generated by bulk UV photo-oxidation of water in an irradiator for 4 hours. 0.25ml of 30% hydrogen peroxide is added to the water to aid free radical formation.

Prior to analysis, samples of 10 ml are acidified to below pH 4 with 0.25ml 0.1M HCl. This converts all the inorganic carbon to CO_2. The sampler arm of the analyser has been modified to pump samples with oxygen (150 cm^3 min^{-1}) to purge the sample of the resultant "inorganic" carbon dioxide. Before the sample is subsampled by the analyser, and if concentrations are likely to be in excess of 5mgC l^{-1}, potassium persulphate ($2.5gl^{-1}$) and sodium tetraborate buffer ($75gl^{-1}$) are added on the manifold (see Figure 5.6). The resultant solution is then passed through a UV irradiator which liberates CO_2 from DOC in the solution. The sample is then acidified down to pH <2 with 1M HCl and hydroxylamine hydrochloride (1M) is then added to convert any resulting chlorine back to chloride. CO_2 is stripped from the solution by a series of stripping coils, separated from the aqueous phase and dried. The gas is then passed through to an infra-red gas analyser (Analytical Developments Ltd. 225).

Reagents:

Hydrochloric acid: 178 ml in 1l of LOCC. Dilute 20 times to give 0.1M HCl

Hydroxylamine hydrochloride: 17.4g in 250ml LOCC

Potassium persulphate: 25g in 1l of LOCC

Sodium tertraborate: 70g in 1l of LOCC

Standard:

A stock standard solution of 1mgC ml-1 is prepared from 0.7669g of potassium oxalate mono-hydrate in 100ml of LOCC. Stored in the dark, this is stable for up to 8 months.

Lines: (Figure 5.6)

Borate buffer: 0.16 ml/min

Persulphate: 0.16 ml/min

Sample: 1.6 ml/min

Oxygen: 0.32 ml/min

Wash water: 1.6 ml/min

Oxygen: 0.32 ml/min

Return to degassing procedure: 2 ml/min (up to 2.5 if buffer added)

Return to wash: 2 ml/min

HCl: 0.05 ml/min

Hydroxylamine hydrochloride: 0.05 ml/min

Waste: 2.5 ml/min

5.2.4 Suspended Sediment

At various points along the transect water samples were taken for analysis of particulate C, N, and P. A measured aliquot was taken and filtered onto precombusted, preweighed GF/F filters (550°C/6 hrs) 45mm diameter filters were found to be the best to use, as this allows collection of enough sample for analysis. After filtering the samples were washed with a small amount of HPW to remove salt. On return to the lab, the filters were dried to a constant weight in a dessicator.

5.2.4.1 Nitrogen and Carbon

Analysis for particulate carbon and nitrogen was performed on the Carlo Erba CHNS-O EA 1108 Elemental Analyser in the Geology Department. The method followed was that of PROENÇA (1994). The filters were dried for an hour in an oven at 60°C. Subsamples of the filter were taken by quartering the filter. Pre weighed tin cups were used to hold the samples, and these were shaped to enable them to drop into the furnace. These samples were then combusted and the amount of CO_2 and N_2 evolved was measured chromotographically. Calibration was performed using known masses of isothiourea as a standard.

5.2.4.2 Phosphorus

The extraction of phosphorus from the filters was carried out using a method developed by Ormaza-González (1990). The filter was placed at the bottom of a conical flask and 25ml of HPW and 2ml of oxidising reagent were added. The flasks were heated on a hotplate in a fume

cupboard. The flasks were stoppered with glass balls when boiling became violent (at about a volume of 10ml). After dryness was reached the heat was increased and nitrous oxide was released. The stoppers were removed to let all the nitrous oxide escape, and the flasks left to cool. 10ml of 0.4M HCl were added and the flasks stoppered and heated at 80°C for 30-35 minutes. After further cooling 10ml of HPW was added. 10ml of this resulting solution was placed in a centrifuge tube and 1ml of mixed reagent was added. The tubes were centrifuged for 5 minutes and a measurement at 885nm was taken using the method of Parsons *et al.* (1984), which is essentially the same as a manual version of the method described in section 2.1.4.3. Generally, however, the analysis was carried out using the method outlined in 2.1.4.3.

Reagents:

Oxidising reagent: 20g of $Mg(NO_3)_2.6\ H_2O$ dissolved in 95% ethanol.

Hydrochloric acid: 0.1M HCl is made from 89ml of concentrated acid in 1l of HPW, and diluted accordingly (2.5ml in 100ml)

Mixed Reagent: As in section 3.1.3.

20ml Ammonium molybdate: Dissolve 15g in 500ml distilled water

50ml Sulphuric acid: Dilute 140ml concentrated H_2SO_4 in 900ml distilled water.

20ml Ascorbic acid: Dissolve 25g in 500ml distilled water

10ml Potassium antimonyl tartrate: Dissolve 0.68g in 500ml distilled water

(Prepare and used within 6 hours.)

5.2.5 Calibration of underway sensors

The fluorometer (Chelsea Instrument Aquatracker) and transmissometer were housed in the instrument box. The sensors, along with the temperature and salinity, were measured every 5 seconds, and this data was stored in a Chelsea Instruments logger and downloaded at various stages onto a laptop computer, usually when the logger memory was seen to be about 85% full. These sensors give a voltage output and, therefore, need to be calibrated to determine actual chlorophyll and SPM concentrations. 25Mm diameter GF/F filters were precombusted (550°C/6 hrs) for use in the chlorophyll analysis. A known aliquot of water was run through the filter in order to collect chlorophyll. The filter was retained and stored frozen until analysis. The SPM filters were stored in a dessicator until a constant weight was reached, reweighed, and the amount of suspended material collected was calculated.

5.2.5.1 Determination of chlorophyll and SPM from discrete samples

The frozen filters were put into a homogenising tube and 10ml of 90% acetone was added. At this stage, to prevent acidification, a very small amount of magnesium carbonate was added. The sample was ground for about 2 minutes, with the tube in a beaker of water to prevent heating of the sample. This extract was then transferred to a centrifuge tube and spun at 2000rpm for 10 minutes. The supernatant was then removed to a clean tube ready for analysis on an 'Ameco' fluorometer before and also after addition of two drops of 10% HCl. The fluorometer was calibrated against a standard of known concentration, at wavelengths of 665 and 750nm.

Chlorophyll concentrations were calculated using the method of Lorenzen (1967), with the absorbance at 665 corrected by subtracting that at 750nm (to account for turbidity):

Chl a (mgm^{-3}) = (26.7 * (665_0-665_a) * v) / (V_f * l)

665_0-665_a. Difference in absorbance at 665nm before and after addition of acid, v- volume of acetone used in extraction, V_f- volume of water filtered, l- volume of cuvette

Reagents:

Acetone: In a fume cupboard, measure 900ml and make up to 1l.

Hydrochloric acid: 20ml of conc acid added to 180ml of HPW.

Standard:

Using a standard preparation of a SIGMA chlorophyll 'a' pellet (about 1mg dissolved in 90% acetone).

Forty seven millimetre GF/F were preweighed for SPM analysis. Again, a given aliquot was filtered and the samples stored in a dessicator once back in the lab. After dryness was reached the samples were reweighed. Between 15 and 20 such discrete samples were used to calibrate the output of the sensors.

5.2.5.2 Calibration of oxygen probe

The oxygen probe (YSI 6000) is preprogrammed for a 2 minute data interval. It records the detector signal as a voltage, so discrete samples were taken for calibration. These were taken from a small tube leading from the instrument box, which helps reduce bubble formation and, thus, aeration. Triplicate samples were taken in Winkler bottles and 0.5ml of $MnCl_2$ (3M) and 0.5ml of an alkaline iodide solution (see section 2.6.1) were added, and the temperature and salinity were noted. These bottles were stored in a bucket of water until return to shore and analysis.

5.2.5.3 Determination of oxygen from discrete samples.

Oxygen determinations are carried out using an in-house adaptation of the Winkler titration method (Bryan *et al.*, 1976) using a photometric end-point method. 0.5ml of sulphuric acid is added to each BOD bottle and placed in a water filled holder with a clean magnetic stirrer. A titre delivery tube is placed in the bottle and stepwise additions of sodium thiosulphate are added using a Metrohm Dosimeter. This thiosulphate has been previously titrated against a known potassium iodate standard with 0.5ml of sulphuric acid and 0.5ml of alkaline iodide solution added. At end point, as measured from a chart recorder, the dosimeter reading is taken. Dissolved oxygen concentrations are calculated using this titre, thiosulphate normality, salinity, and temperature within a dedicated BASIC program:

O_2 mgl^{-1} = 0.1016 * f *V * 16

V- Titration volume corrected for blanks

f= 5.00 / v, where v is the volume of thiosulphate titrated against 5ml of standard iodate in a distilled water blank until end point is reached.

Reagents:

Manganous chloride: In a 1l beaker weigh 600g of $MnCl_2$ and dissolve in 500ml of HPW. Filter solution through a Whatman No.1 filter and transfer to a 1l flask and make to 1l.

Sodium iodide (alkaline iodide): Dissolve 320g of NaOH in 200ml of HPW in a 1l beaker. Within a fume cupboard place this beaker on a magnetic stirrer and dissolve 500g of sodium iodide gradually. Filter through a Whatman No.1 filter, transfer and make up to 1l in a volumetric flask.

Sulphuric acid: 280ml of conc. sulphuric acid in 720ml of HPW

Sodium thiosulphate: 2.9g in 1l of HPW adding 0.1g sodium carbonate

Standards:

Weigh c.0.5g of potassium iodide into a pyrex beaker. Oven dry at 105°C for 1 hour. Weigh out 0.3567g of the dried salt and disslove in HPW made up to 1l in a calibrated volumetric flask..

5.2.6 Calibration of the WTW salinometer.

The WTW salinometer is calibrated against a standard potassium chloride KCl solution, supplied by the manufacturers. This solution has a known conductivity. It is placed in a beaker, in a water bath, at the specified temperature, usually 20 or 25°C. The cell constant is set by altering the conductivity to the required level using the arrow keys on the hand held unit. Detailed instructions for this are kept with the meter. The salinometer must ALWAYS be run with the "nLF" marker showing in the window. This activates a non-linear algorithm, which enables the full range of estuarine salinities to be calculated.

5.3 Quality control procedures during SONUS

During the project care has been taken to deliver a high standard of data control. This was essential if we were to be confident about any conclusions derived from the data. Two techniques were used to assess the quality of the data obtained form this study. Firstly, a large bulk sample was taken from Calshot Buoy in May 1995. This was stored and frequently reanalysed. Secondly, the lab participated in the sixth and eighth rounds of QUASIMEME, an international laboratory performance study (results from other participating laboratories are not yet available for round 8). Here a variety of samples were repeatedly analysed over a short period of time.

5.3.1 Machine performance

The initial gains were set on the colorimeter with full scale deflection of 200mV on the chart recorder. The instrument was returned to these gain settings for all determinations of SONUS samples. Other users have altered these settings when determining relatively low nutrient waters, and this may have introduced some noise into the observed sensitivities. The gain settings for the TON , silicate, and phosphate, ammonium, and nitrite channels were 0.6, 1.7, 1.75, 6.0, and 1.7, respectively.

Figure 5.7 shows the peak heights of the top standards of nitrate, phosphate, and silicate over the runs where SONUS samples have been analysed. The dotted lines show the first samples where fresh bulk standards were used. The data shows that the peak heights of standards changed markedly after the instrument was resited at the SOC. This coincided with a new bulb being fitted into the colorimeter. It is unclear why this should have changed the peak heights, but it may have been due to how the bulb was aligned with the cells and detectors. Within the two subsets of data, however, the standards and the colorimeter seem to be consistent given that the machine could have been turned off for a month at a time, new reagents were always used, the pump had been retubed several times, and lab conditions could have changed. The top nitrate standard appeared to vary much less after transfer to the SOC, which is marked by the time the bulb was changed, and this is probably partly due to the use of the manufactured reduction columns.

Figure 5.8a shows the calibration coefficients over 40 runs where an internal QC sample was analysed. Outside of the 40 runs shown, the calibration coefficients were consistent with the values shown in this figure TON and silicate usually greater than 0.9999, whilst the phosphate coefficient is usually greater than 0.999. The calibrations on the phosphate channel have not been as good as for TON and silicate, which is mainly due to baseline drift and noise. No carryover was used during the calculation of these coefficients for phosphate. In figure 5.8b, it can be seen that calibration coefficients for ammonia were lower, at around 0.996. Calibration of the ammonia standards was effected by the base line drift on the ammonium line, probably from the reaction between the phenol reagent and the pump tubing. Nitrite calibration coefficients were consistent with those of TON.

Standard errors calculated for runs with the lowest calibration coefficients show errors for TON, silicate, phosphate, ammonium, and nitrite as being 0.82, 1.09, 0.07, 1.28, and 0.15μM respectively.

5.3.2 Use of the Internal Standard

A 5 litre bulk sample was taken at Calshot Buoy on the 31/5/95. Once ashore, this sample was then stored cool for 24 hours and filtered and poisoned with $HgCl_2$. This was then decanted into a number of diluvials and stored for later use.

Two months later, some 20 vials were opened and run all at the same time. This gave an idea of both analytical error and the variability that could be found between samples. The results are shown in figure 5.9. The results indicated that the mean concentrations for TON, silicate, and phosphate were 24.74±2.24μM, 3.31±0.85μM, and 0.64±0.19μM respectively. The data also suggests that there is some variability between samples, especially within the TON levels, where the range of concentrations is between 21.3 and 27μM.

Up to 40 runs were made using this internal QC standard, the practice was stopped on moving to the SOC as safety regulations over the use and disposal of $HgCl_2$ made the use of poisoned samples difficult. Also, many of the diluvials packed for the move came open in transit. Figure 5.10 shows the data from these 40 or so runs. The ranges given are those from the mean and standard deviations obtained from the data included in figure 5.9.

The majority of the phosphate data fall within the ranges established from figure 5.9 i.e. within the error associated with natural and analytical variability between samples. Although this is generally true of the TON and silicate data, both of these have two groups of samples that fall outside these ranges. These are the first seven runs and the last four runs. These jumps did not coincide with the preparation of fresh primary standards, and one would intuitively expect the data to be higher if the standards had deteriorated, which was not always the case. Reagents used in the determination of these species were different, so were remade at differing intervals, and some were common to phosphate and there is no perceivable change in those data.

Clearly, there is no systematic difference between the three groups of runs. Unfortunately, these changes are much more than expected from inter vial variability. However, the calibration coefficients for these runs were acceptable, as was the stability of the standard, as shown by top standard peak heights in figure 5.7. Therefore, it has been impossible to distinguish the reasons behind the changes in concentrations. However, it does indicate that the inclusion of an internal standard into the QC procedure, whilst being of some use, needs to be studied further. The variability between samples needs to be addressed for this QC procedure to be meaningful. By collecting as pristine water and biologically inactive water as possible may help. This would mean taking the bulk sample further from the coast, probably during winter.

5.3.3 Use of the external QUASIMEME intercomparison solutions

Analytical performance was assessed by determining nutrient concentrations in a set of preprepared solutions during the QUASIMEME 6 programme. This was carried out between June and November 1996 and the results are summarised in figures 5.11a-c. The dotted lines signify the permissible range of concentrations as given by the QUASIMEME project office (QPO). There were four samples, two of which were sea water (marked by the suffix SW), and two of which were estuarine (with the suffix EW)

It can be seen that most of the samples run for phosphate (figure 5.11a) were within 200nM of the acceptable range, whilst nearly all samples analysed for TON were within the range permitted by the QPO. There appears to be no systematic reason why the phosphate levels should vary. The greatest variations appear in the estuarine samples, where there is a under estimation of about 0.2μM.

In the silicate and nitrite data (figure 5.11.b), the seawater samples are over the limits set by the QPO. This over estimation is significant in the silicate data, being in the order of about 4μM. Results of analyses performed upon the estuarine water samples were within the limits set by the QPO. The overestimation in the seawater concentrations of silicate may be due to the comparability of optical properties when mixing washes and samples of different densities (Froelich & Pilson, 1978). This was investigated further, and the results shown in section 3.4.

For one of the QUASIMEME solutions, levels of ammonium were below detection. Although the QPO assigned a value to this sample, determination of ammonium on this sample was impossible for a large number of the labs involved in the exercise. Ammonium levels were

consistently underestimated by some 4μM in sample AQ43EW, yet the other samples fell within the limits set by the QPO.

Table 5.1. summarises the Z scores for each nutrient and sample. The Z score is used to give a normalised measure of performance by comparing the participants values with those gained from labs with strict data control. A |Z| score of 2 is deemed satisfactory. This represents a reported value which is within ca.95% of all values obtained by the QUASIMEME reference laboratories, where strict data control is practised.

Overall, the laboratory performed satisfactorily within this round of QUASIMEME. The exercise was also useful to highlight analytical problems that appear to be occurring with certain determinations. By participating in further QUASIMEME rounds, it will be possible to establish if the steps taken to ameliorate these problems have been successful.

5.3.4 Errors from optical aberations caused by differing wash salinities

If there is a mismatch between wash and sample density there can often be an optical effect in the cell, can distrort the observed peaks corresponding to samples in the analyser output (Froelich & Pilson,1978). It was apparent from the use of the QUASIMEME standards that there was a significant error in silicate in seawater samples determined on the instrument used for measuring estuarine samples at the SOC. This error was not present in our instrumentation used for marine nutrient analysis.

To examine the problem, repeated analyses were done using a range of wash solutions of differeing optical densities.Ten samples of each standard were run on the Burkard SFA2, to give some idea of intersample variation. Standards were made up in HPW, and the blanks and intersample wash were also HPW. This analysis was repeated using artificial seawater (ASW) as the wash, blank, and matrix for the standards. Two batches of these analyses were run, with the ASW being made up of 20 and 40gl^{-1} NaCl. Finally, the analytical run was repeated with the wash, blanks and standards made up in Low Nutrient Seawater (LNS) (OSI Ltd.). The means of these data are shown in figure 5.12. The variation between samples for each standard, using any of the 4 matrices, was small. The standard deviations of ten replicates run using each of the four matrices ranged from 0.4 to 2% for nitrate, 0.7 to 5% for silicate, and 3 to 6% for phosphate.

It can be seen that with all 4 matrices nitrate and phosphate concentrations do not significantly vary. However, with silicate there is an obvious problem. Generally, the higher the salinity of the wash, the lower the calculated concentration. At first this was suspected to be a contamination problem in the NaCl used, but the problem persisted when LNS was used. There were two possible reasons for this. Firstly, the peak shape for silicate is severely affected by a mismatch in densities. In one of the estuarine samples, 47EW, the peak shapes were so bad that the computer failed to recognise them. This effect is seen to occur when the situation is reversed and the seawater samples (suffixed SW) are run with low salinity washes. Secondly, regardless of sample density all measurements appear decrease as wash density increases (figure 5.12). This pointed to a problem in the cell itself. A Chemlab AAII was set up to measure silicate and nitrate using a 40gl^{-1} wash, as used for all WOCE cruises. The measurement of silicate on this equipment

has been shown to be reliable (Hydes, 1997). The comparison of these results is shown in figure 5.13.

The nitrate data obtained from the Chemlab are consistent with those obtained from the Burkard. The silicate data obtained from the Chemlab is similar to that from the Burkard, with respect to the estuarine samples. However, the silicate data for seawater show that there is a significant error between the two pieces of equipment, using the same methods and the same washes. In general, concentrations obtained from the Chemlab are around 3-4μM less than the Burkard running a HPW or $20gl^{-1}$ NaCl wash, yet 3-5μM more than the Burkard running $40gl^{-1}$ or a LNS wash. This, in part, explains why the combined Burkard and Chemlab silicate data given to the QPO was much better than those data presented in figure 5.11b and table 5.1, since the lower Chemlab data brought the mean of our results down. It also serve to highlight that there is an important problem with wash and sample salinities that needs to be addressed in the Burkard autoanalyser. Results from QUASIMEME 8 will enable us to ascertain which method is feasible for the analysis of seawater silicate. Figure 5.13 suggests that even using the same wash density, there isan error between equipment, so, until the results are published from this QUASIMEME round, no conclusions as to the accuracy of either piece of equipment can be made.

5.4 TABLE

Table 5.1.

Z scores for nutrient determinations from the QUASIMEME 6 round.

Sample	Nitrate	Phosphate	Silicate	Ammonia	Nitrite
QNU040SW	0.68	1.65	-0.53	0.26	0.29
QNU041SW	-0.91	-3.19	-0.22	n.s.	4.15
QNU042EW	0.40	-1.80	-0.37	-0.72	0.57
QNU043EW	0.48	-1.11	0.10	-5.21	0.47

5.5 FIGURES

Figure 5.1.

Graphs showing the comparison in nitrate, phosphate, and silicate concentrations between samples collected in plastic and glass, and stored frozen for a month.

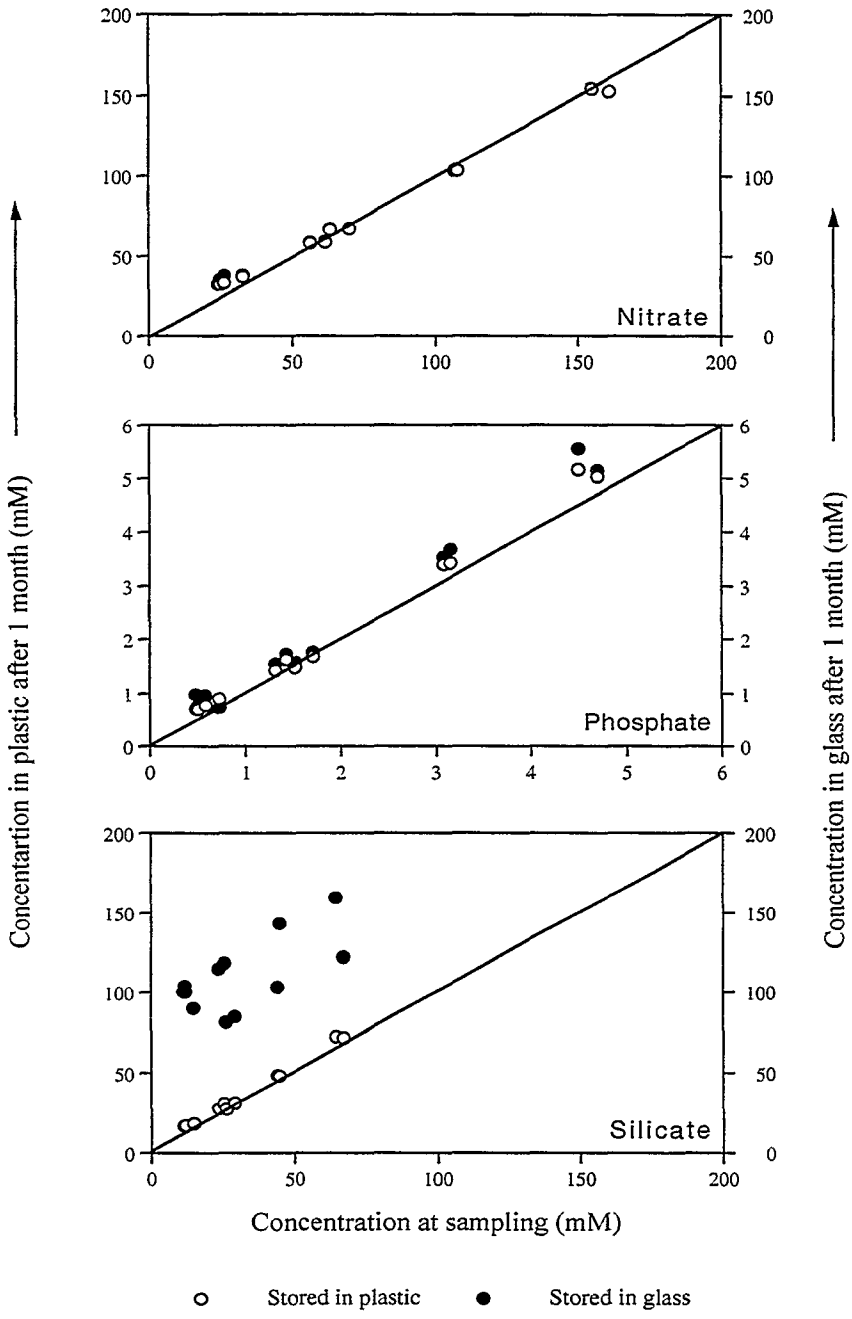


Figure 5.2
Auto-analyser manifold for determinations of Nitrate and Nitrite

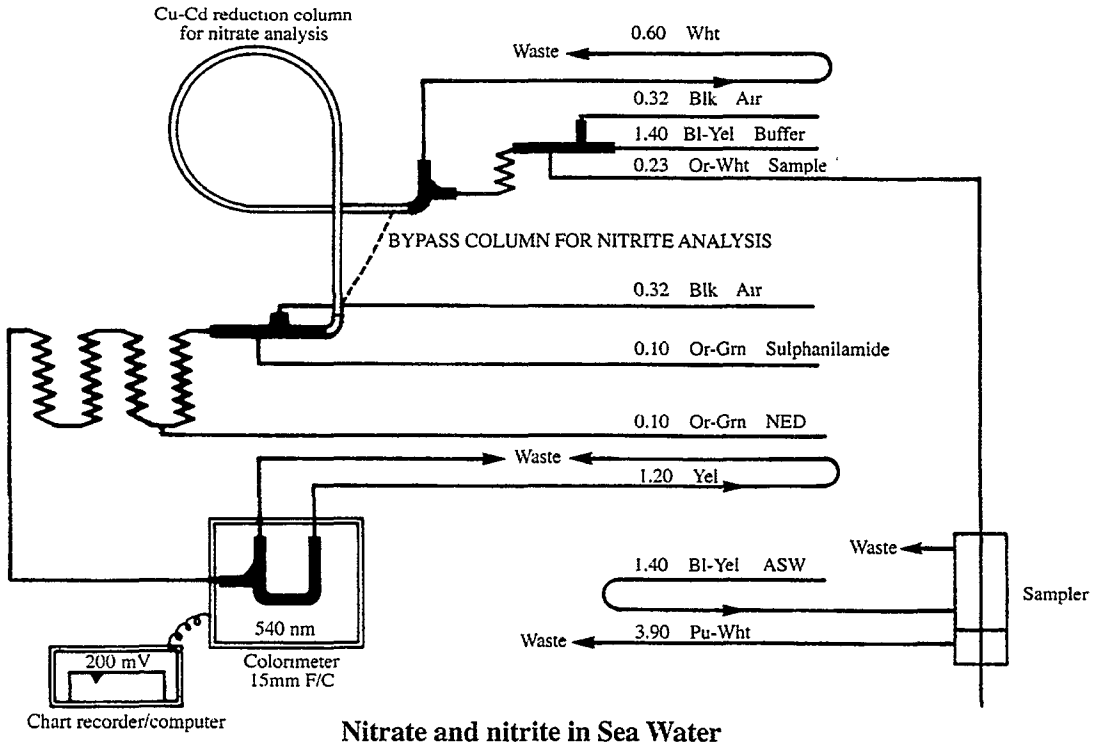


Figure 5.3
Auto-analyser manifold for dtermination of dissolved Silicon (Silicate)

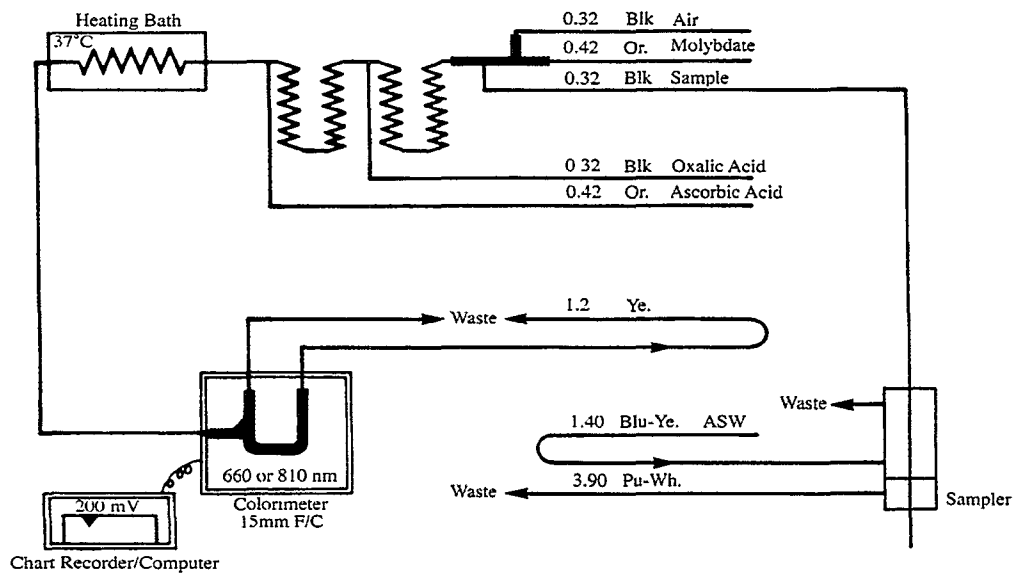


Figure 5.4

Auto-analyser manifold for the determination of Phosphate

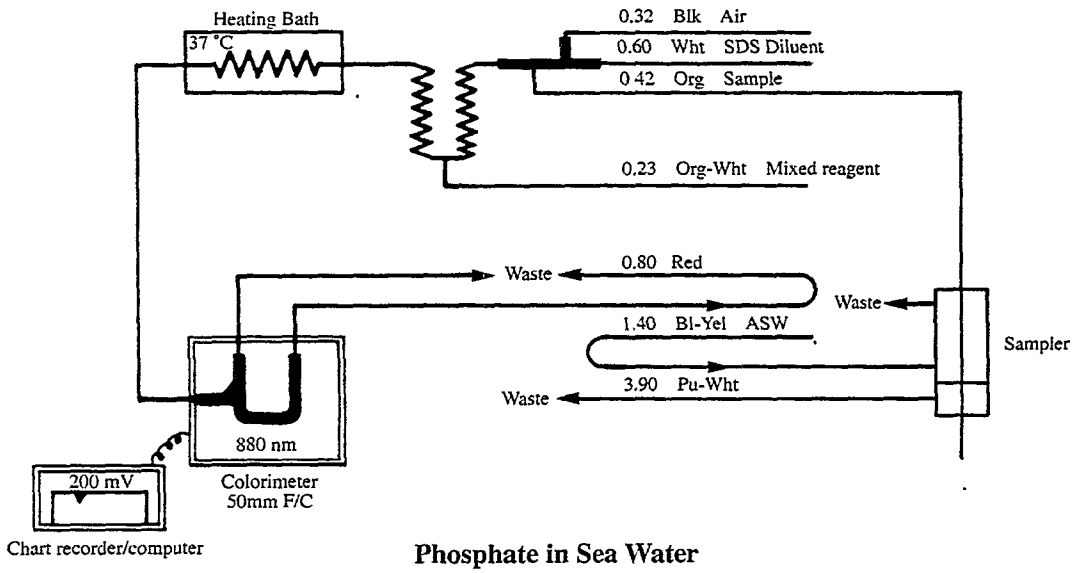


Figure 5.5
Auto-Analyser manifold for determinations of Ammonia

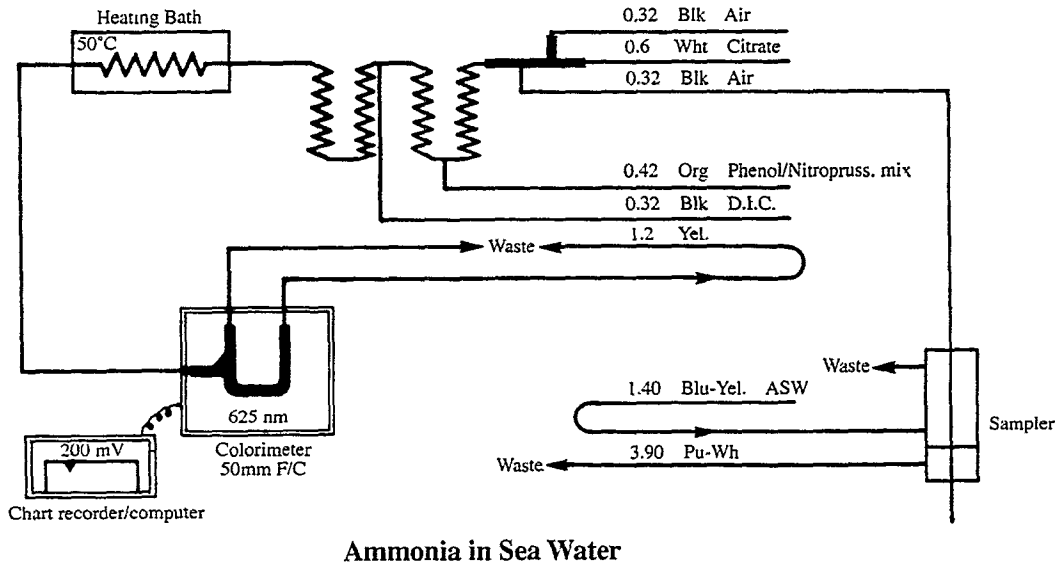
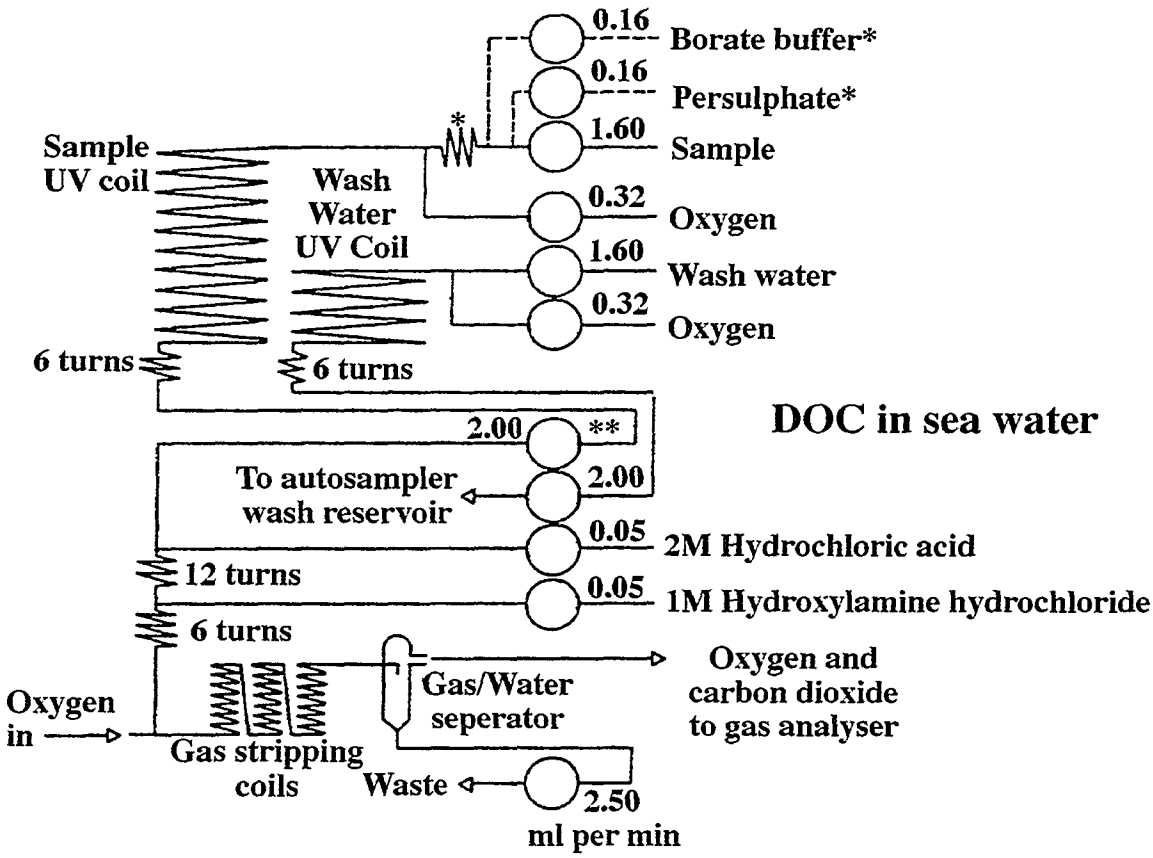


Figure 5.6
Auto-analyser manifold for determinations of dissolved organic carbon



*** high DOC concentrations only**
**** increase to 2.5 ml per min if borate and persulphate are added**

Figure 5.7
Peak heights of the top silicate, phosphate, and nitrate standards during the SONUS analytical runs.

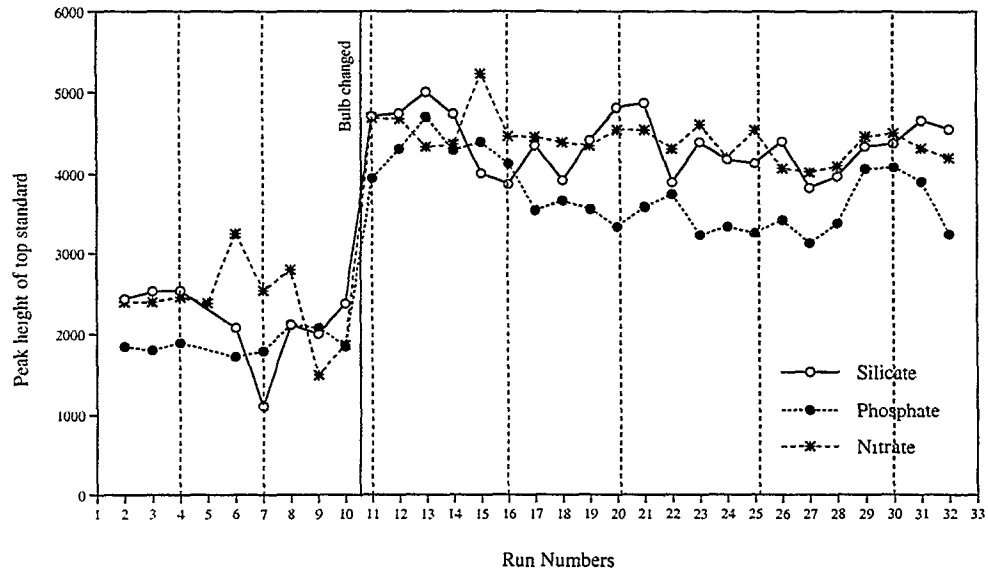


Figure 5.8

Graphs showing variations in calibration coefficients for the 5 nutrients analysed.

Note: the run numbers on the TON/silicate/phosphate graph are not identical to those in the nitrite/ammonium graph, as they were run on two different machines.

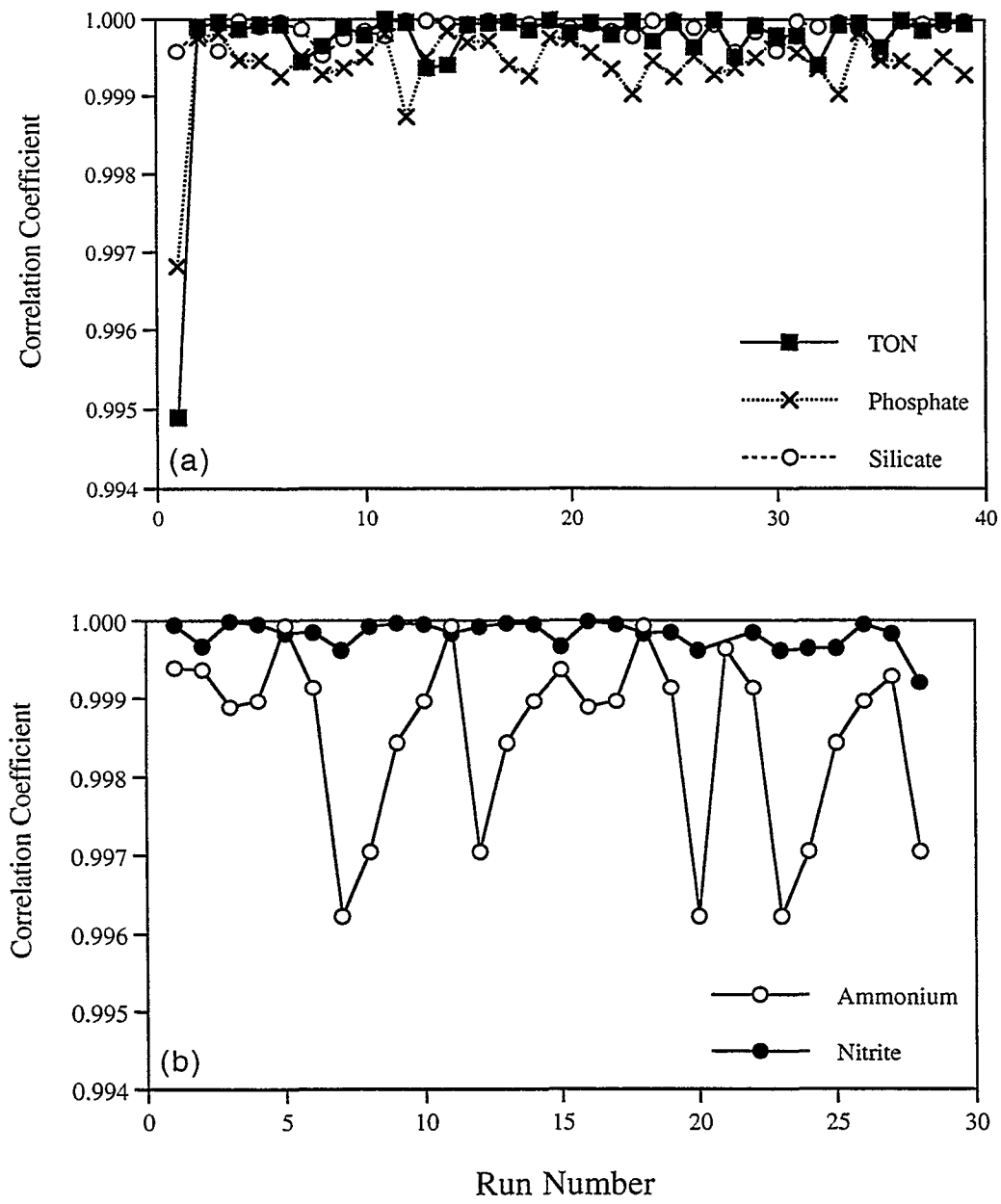


Figure 5.9

Internal QC data from 20 vials, all from the same analytical run.

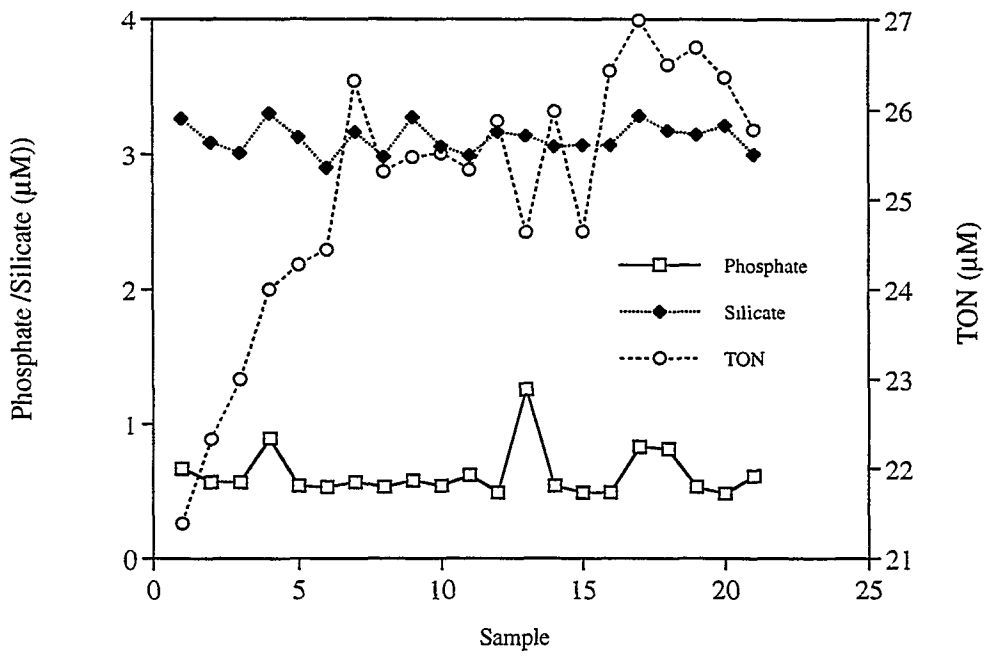
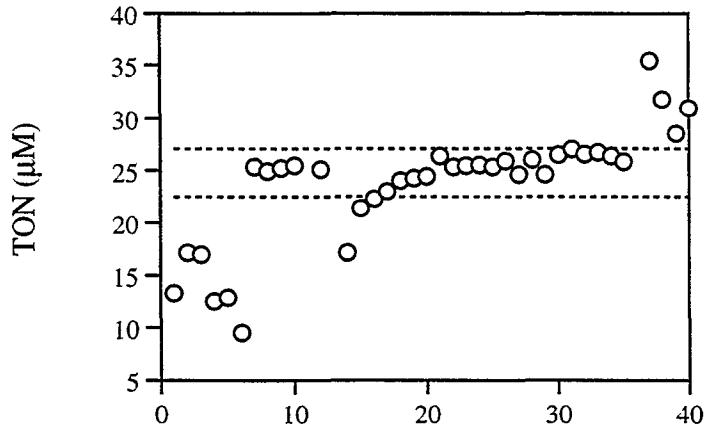
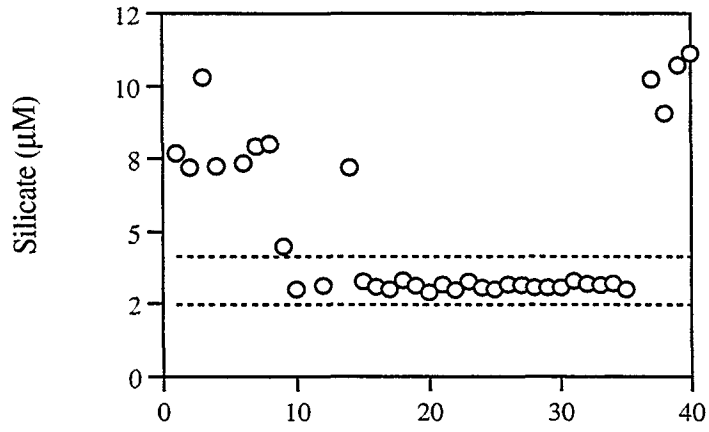


Figure 5.10. Graphs showing the variations in the internal QC standard over a series of 40 analytical runs.





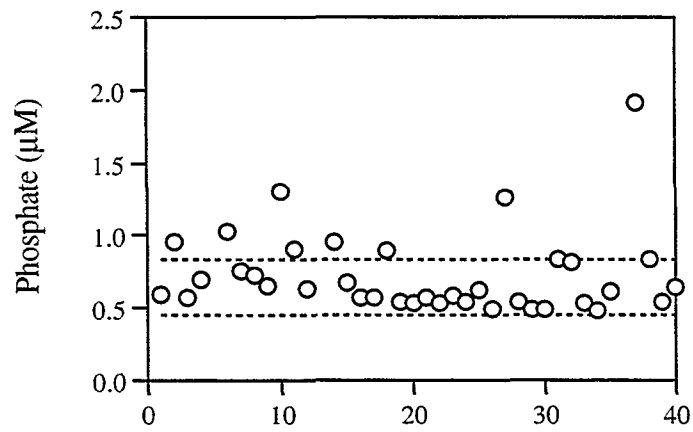


Figure 5.11a

Calculated phosphate and TON levels from four QUASIMEME6 standards. The dotted line show the ranges assigned by the QPO.

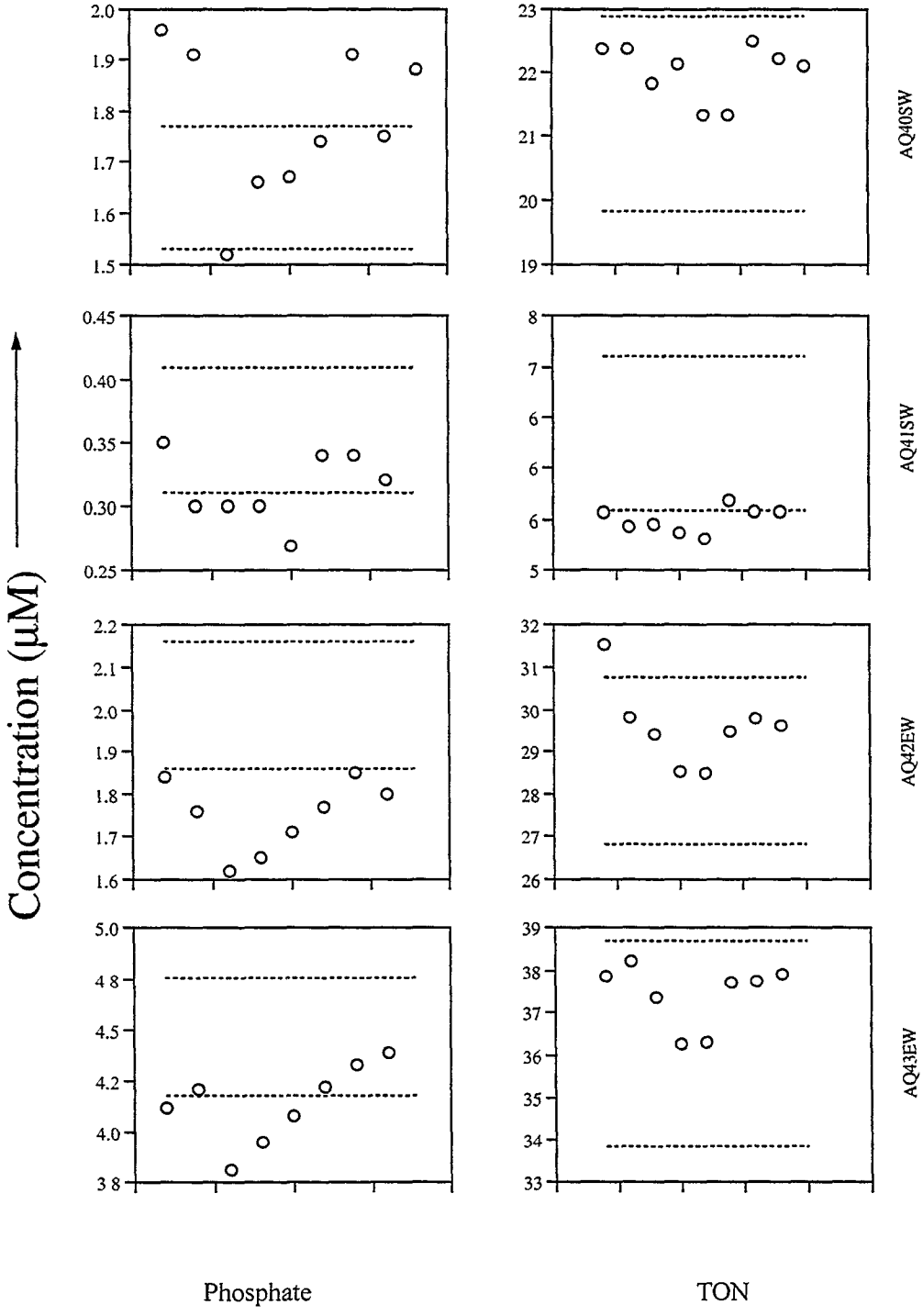


Figure 5.11.b

Calculated levels of silicate and nitrite within four QUASIMEME6 standards. Dotted lines show permissible ranges, as set by the QPO.

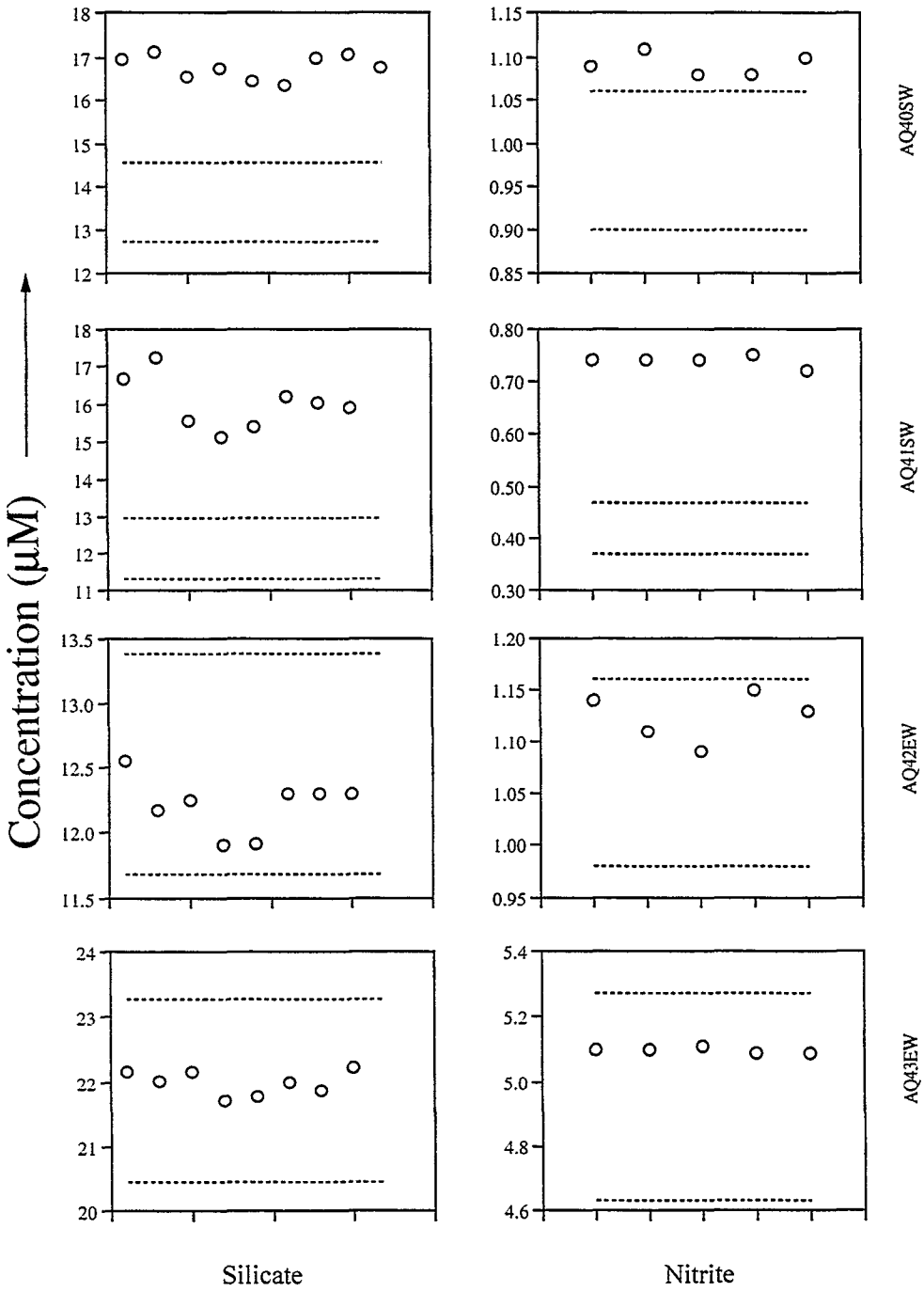


Figure 5.11.c

Calculated levels of ammonium in four QUASIMEME6 standards. Dotted lines show permissible ranges as set by the QPO.

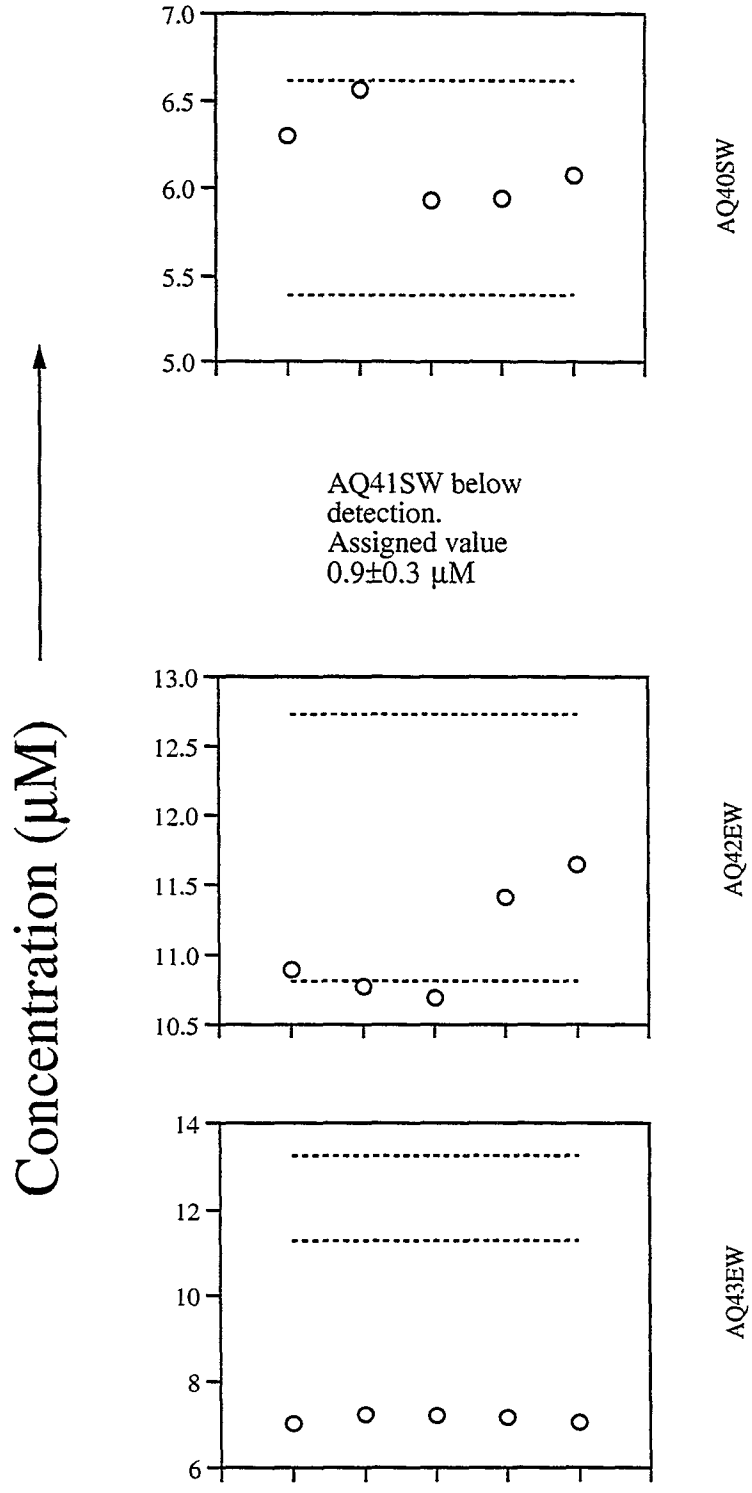


Figure 5.12.

Data from four QUASIMEME 8 standards showing the differences in concentrations obtained by using different washes.

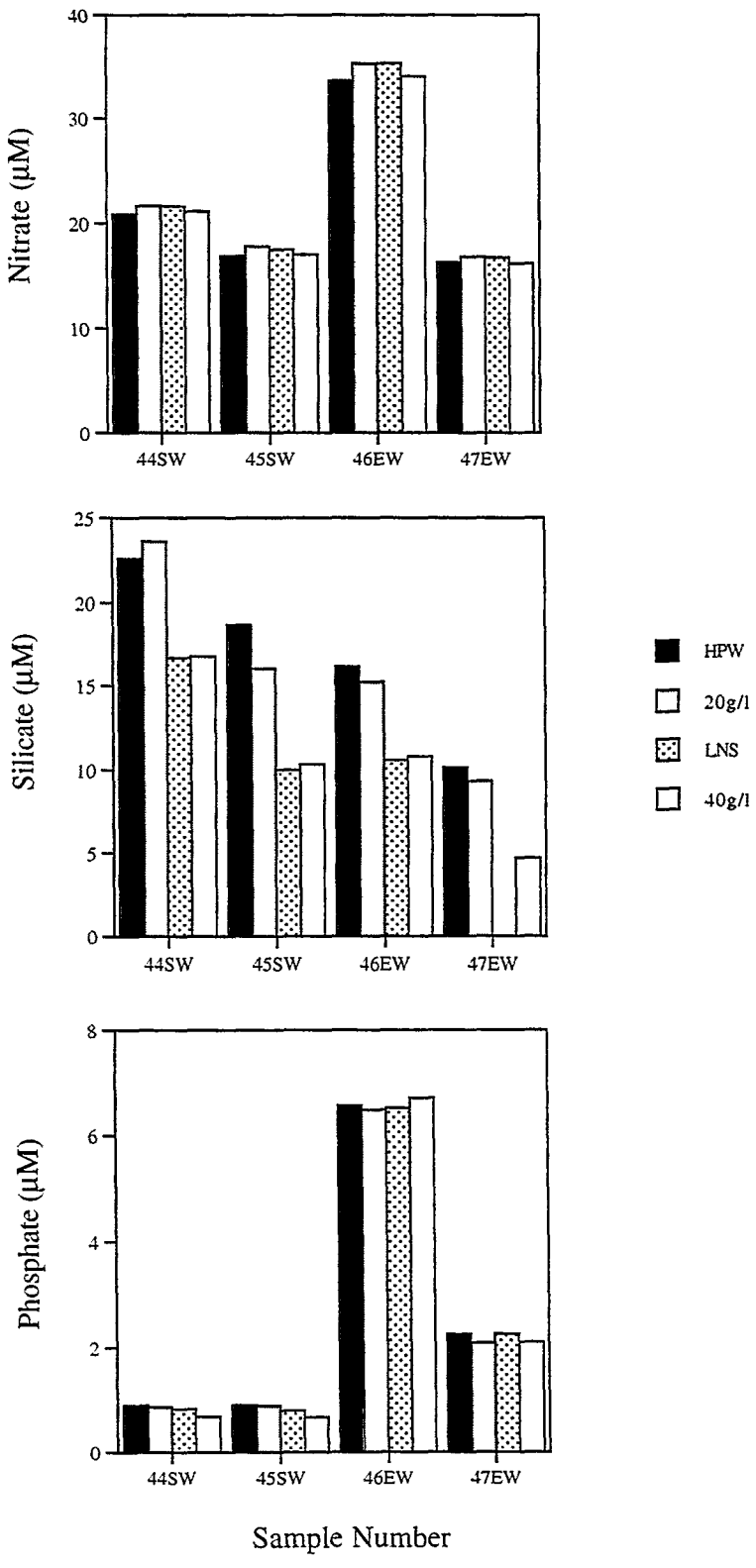
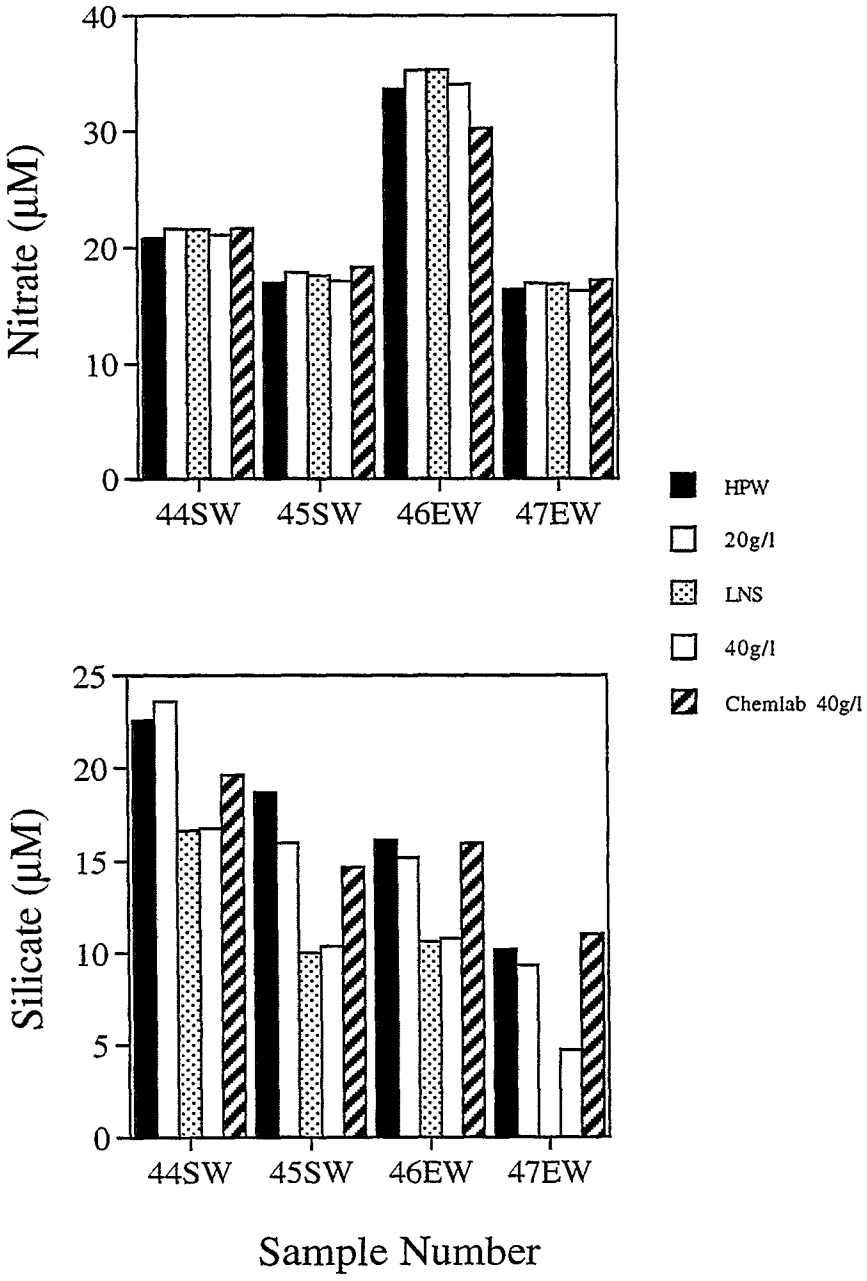


Figure 5.13.

Nutrient concentrations in four QUASIMEME 8 standards using a Burkard SFA 2 autoanalyser, and a number of washes of different densities, and a Chemlab AAII autoanalyser running a 40g/l wash.



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