COCKBURN SOUND ENVIRONMENTAL STUDY

TECHNICAL REPORT ON NUTRIENT ENRICHMENT AND PHYTOPLANKTON

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Department of Conservation & Environment

REPORT No. 3

CONSERVATION CONSERVATION ADDITION AUSTRALIA



TECHNICAL REPORT ON NUTRIENT ENRICHMENT $\ensuremath{\xi_{\text{.}}}$ PHYTOP LANKTON

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FOREWORD

Cockburn Sound began its development as the outer harbour for the Perth-Fremantle area in the 1950's. Since then a major industrial complex has been built up on the eastern shores. Wastewater from several industries and from a major sewage treatment plant is discharged directly into the Sound's waters. A naval facility has been established on Garden Island, which is now linked with the mainland by a causeway, whose construction was completed in 1973.

The industrial area has continued to expand and the Sound's waters are used increasingly for recreation and fishing by both commercial and amateur fishermen.

Concern for deterioration of the marine environment and the building of the causeway led to a series of baseline studies carried out between 1970 and 1975 on the ecology, hydrology and beach morphology of Cockburn Sound. Early in 1975 the Environmental Protection Authority let a contract to a consultant to make a comprehensive review of these studies to identify problems, to propose approaches to solutions and to point out aspects requiring further research. After the review had been considered by the Environmental Protection Authority and the Conservation and Environment Council, the Western Australian Government allocated \$500,000 for a three year (1976-1979) environmental study.

As approved by Cabinet, the objective of the environmental study of Cockburn Sound was to obtain the information necessary to manage the Sound for multipurpose use, accommodating recreational and fishing activities as well as use for port and industry.

The Cockburn Sound Study Group, a core group of professional and technical personnel, was established in November, 1976. The major aspects requiring investigation were identified and designated as segments of the overall study. Work on the segments was carried out by members of the Study Group and by consultants, government departments and universities.

This report covers the work of one of these segments. The conclusions and recommendations presented here relate specifically to the work of this segment. They do not necessarily reflect the conclusions or management proposals detailed in the overview Cockburn Sound Study Report, which has drawn from all segment reports.

COLIN PORTER CHAIRMAN COCKBURN SOUND STUDY STEERING COMMITTEE

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SUMMARY OF RESULTS AND CONCLUSIONS

The Problem

Eutrophication is the nutrient enrichment (natural or otherwise) of lakes, rivers, estuaries and nearshore coastal areas. This nutrient enrichment leads to large increases in growth of both macrophytic and microphytic algae (phytoplankton).

The diverse effects of eutrophication are always associated with extensive changes in water quality. All to often this means a loss of amenity to some or all of the people who use these waterbodies.

At times during the four years which preceded the start of the Cockburn Sound Study in 1976 the waters of the Sound had shown signs of well-developed eutrophication. That is, recent marked colour changes in the waters of the Sound had been shown to be associated with high concentrations of phytoplankton. In addition, much of the near-shore area along the Kwinana-Rockingham foreshore had developed extensive growths of micro and small macro algae on the sandy beaches denuded of seagrass. On occasions, the quality of the water in the Kwinana-Rockingham area had deteriorated to the extent that these areas were no longer attractive to swimmers and beach users.

The following conclusions were drawn from the data obtained during the 16 months of this study.

The Phytoplankton

- . The phytoplankton flora of Cockburn Sound and Owen Anchorage have species diversities comparable with those of near-shore coastal waters.
- . The patterns of species succession in Cockburn Sound and Owen Anchorage were also similar to those described for other marine systems.
- . The frequency of successional changes in Cockburn Sound was very much higher than expected and did not proceed beyond the point where large diatoms dominated. In Owen Anchorage the frequency of successional changes was more comparable with near-shore coastal changes and also proceded further, with dinoflagellates dominating for a much greater proportion of the time.
- . The initiation of a new species succession was associated with an increase in phytoplankton biomass.
- The initiation of a succession and the subsequent pattern of changes in species is thought to be controlled by nutrient availability. Changes in ambient nutrient concentrations in Cockburn Sound are more frequent and extensive than in Owen Anchorage and this is consistent with the observed changes in phytoplankton successions and biomass.
- It is concluded that changes in phytoplankton biomass are, to some degree, the result of successional changes and these changes are associated with changes in nutrients.

Nutrient Inputs

- . Four sources provide almost all of the nutrients to Cockburn Sound. These are: industrial and sewage effluents, groundwater, air emissions and coastal waters.
- . It has been estimated that industrial effluents, air emissions and groundwater now contribute 30 times more nitrogen and 25 times more phosphorus as would have normally entered the Sound through exchange with the open ocean prior to the industrial development of the area.
- . Industrial effluents account for 79 per cent of the total-nitrogen load to the Sound and 96 per cent of the total-phosphorus load.
- . Of the industrial inputs two outfalls contribute 91 per cent of the total-nitrogen (62 per cent from the CSBP/KNC* outfall and 29 per cent from the WPTP[†] outfall), and one outfall contributes 87 per cent of the total-phosphorus (CSBP/KNC).
- . KNC is responsible for almost all of the nitrogen in the CSBP/KNC outfall. Seventy six per cent of this is in the form of ammonium ions and 22 per cent as nitrate plus nitrite ions.
- . The WPTP has 70 per cent of its nitrogen discharged as ammonium ions and the rest is in the organic form.
- . Thirty six per cent of the CSBP's phosphorus is contributed in the inorganic form (orthophosphate).
- . No assessment has been made of recycling of nutrients within the water column or from the sediments. Levels of both nitrogen and phosphorus in the sediments are very much higher in the vicinity of the CSBP/KNC outfall and the WPTP outfall than anywhere else in the Sound.
- . Recycling of nutrients from the sediments is not thought to be important at the moment in Cockburn Sound but this may change if the very high loads from industrial effluents and sewage are diverted from the Sound.
 - It is thought that the most important source of nutrients to Owen Anchorage is the nutrient-rich waters of the Sound.

Seasonal Changes in Nutrients and Chlorophyll a

- . Ambient levels of phosphorus in Cockburn Sound, and to a lesser degree Owen Anchorage, are considerably higher than either Warnbro Sound or the near-shore coastal waters.
- . Cockburn Sound has persistently high levels of phosphorus whereas Owen Anchorage shows a drop in phosphorus over the winter period. This is taken as evidence for the comparatively poor flushing of Cockburn Sound with respect to Owen Anchorage.
- * CSBP & Farmers Ltd. and Kwinana Nitrogen Company
- * Woodman Point Sewage Treatment Plant

Seasonal Changes in Nutrients and Chlorophyll a (Cont'd)

- Nitrogen levels over the body of the Sound and Owen Anchorage are uniformly low. However, there is some evidence in the weekly data of nitrogen build up over the winter in the Sound. It is thought that levels are generally low (despite the very large loads entering the Sound) because nitrogen is limiting to the growth of phytoplankton within the Sound and is therefore rapidly consumed. The build up of nitrogen over the winter period is consistent with reduced rates of phytoplankton productivity due to reduced temperatures or amount of available light.
- Maximum pnytoplankton biomass (measured as chlorophyll <u>a</u>) occurred in Cockburn Sound with values as high as 110 mg m⁻³ being recorded at the peak of a bloom. Values in Owen Anchorage were only 1 to 10 mg m⁻³, in Warnbro Sound 1 to 3 mg m⁻³, and the coastal station were always less than 1 mg m⁻³.

Water Movement and Nutrient Distribution

- . The effects of internal circulation and water exchange on the distribution and loss of nutrients from the Sound was assessed by using the ambient concentrations of orthophosphate as an indicator of nutrient dispersion.
- . The distribution of $\mathrm{PO}_4-\mathrm{P}$ in Cockburn Sound fits into three basic categories.

There is a winter pattern which is a product of the passage of low pressure systems and these result in the most exchange ("flushing") with the ocean.

The other dominant pattern is characterised by the distribution of maximum PO_4 -P values along the east side of the Sound, extending both north and south of CSBP. This pattern is a result of the water movement within the Sound being dominated by a single large gyre moving anti-clockwise in the body of the Sound and frequently a series of additional smaller gyres under low energy conditions.

The third category covers periods when no consistent pattern is readily distinguishable and it was discovered that during these cruises CSBP was not discharging.

- . The data confirm the prediction by the Steedman model that most exchange takes place across the northern opening during the passage of low pressure systems. At other times exchange still seems to occur predominantly across the northern opening.
- . Three of the cruises took place during a period when the CSBP outfall was not operating. The results indicate that, should this discharge be diverted then a rapid improvement in water quality can be expected, i.e. over a period of one or two years, depending on seasonal weather patterns.

. It is concluded that:

Nutrient distribution within the Sound is dominated by the internal circulation pattern. Exchange with the open ocean is a direct product of prevailing meteorological conditions, with most exchange occurring over the winter period as a result of strong low pressure systems.

The residence period of nutrients is a product of the hydrology and this in turn may be a major factor in the net increases in phytoplankton biomass which takes place over the summer period.

Nutrients and Phytoplankton

Simple linear regression showed a strong correlation between the level of phosphorus and high phytoplankton biomass. However, no difinitive cause and effect relationship between nitrogen concentrations (the limiting nutrient) and chlorophyll <u>a</u> could be resolved.

A series of algal assays confirmed that nitrogen is the nutrient limiting increases in phytoplankton biomass in Cockburn Sound. This is consistent with studies done in marine coastal waters elsewhere.

A comparsion of Cockburn Sound with other coastal areas and estuaries clearly demonstrates that the Sound is definitely eutrophic and has very high levels of phytoplankton under bloom conditions.

The following consequences are of prime concern:

- 1. For some of the time over the summer period conditions were clearly unsuitable for most forms of water contact recreation.
- 2. Dissolved oxygen levels have been observed to reach the minimum required to sustain fish life.
- 3. Two incidences of blooms of "red-tide" organisms have been observed. Certain of these species are well documented in other parts of the world as being the agent for a form of paralytic shellfish poisoning.

MANAGEMENT CONSIDERATIONS

A reduction of phytoplankton biomass can only be achieved by reducing the amount of available nitrogen.

If no changes are made to present nitrogen loads or if they are increased then conditions in the Sound can be expected to deteriorate.

Initial improvement could be achieved by the reduction of the input of nitrogen from KNC.

Even if KNC do make a 90-100 per cent reduction, by the year 2000 nitrogen loads will be back to what they are at present as a result of the increased input expected from the WPTP outfall.

The effects of the expected increased input from the WPTP outfall needs to be assessed further. However, it is certain that phytoplankton biomass will increase in Owen Anchorage as well as in Cockburn Sound over the summer period.

The importance of recycling of nutrients from the sediments also needs to be assessed.

1. INTRODUCTION

1.1 The Problem

At the start of this segment of the study in June 1977 it was known that on occasions the water quality in the Kwinana-Rockingham area of Cockburn Sound (Figure 1.1) deteriorated to the extent that this area was no longer attractive to swimmers and other beach users. On these occasions the water became highly turbid and coloured, greasy to feel and unpleasant to swim in. In addition the sandy near-shore regions of the beaches in the area had developed extensive growths of algae (Meagher and LeProvost, (1), (2)). This deterioration in water quality was shown to be associated with extensive "blooms" of planktonic algae (phytoplankton). These blooms are a recent phenomena in the Sound and are reported as occurring only since 1974 (Fremantle Port Authority, pers. comm.).

In reports prepared for the Fremantle Port Authority (FPA) and Commonwealth Department of Housing and Construction (CDC) it was assumed that Nutrient enrichment has been the basic cause leading to the sudden appearance of high phytoplankton concentrations in the Sound (Environmental Resources of Australia Pty. Ltd. (ERA) (3), Meagher and LeProvost (1). This is a reasonable hypothesis as research elsewhere has shown that:-

- Algal blooms are common in many lakes, where they are often associated with increased availability of nutrients (Lund, 1969 (4)).
- Increased phytoplankton productivity in estuaries and nearshore coastal areas has been found to be associated with increases in nutrient concentrations (Ryther and Dunstan (5); Hardy and Jubayli (6)).
- . The nutrients, nitrogen and phosphorus, have frequently been demonstrated to limit the growth of algae. That is, increased availability of these nutrients in culture and in field experiments has lead to increases in algal production (Thayer, 1974 (8); Goldman (9)).

1.2 Previous Data

At the start of this study no comprehensive data were available on the nutrient regimes of Cockburn Sound. A similar situation existed for the phytoplankton of the Sound.

A single set of values for pH, nitrogen, phosphorus and suspended solids, was given for six locations in and around Cockburn Sound on 15 December 1972 by ERA in a report to the FPA and CDC (3). The nutrient values obtained were all unrealistically high. Neither the molecular forms nor the analytical methods used were specified. Even so this single set of values was interpreted by the authors as indicating phosphorus enrichment of the Sound. Because of this, and the observation that "waterbodies" in Cockburn Sound quite often showed distinct colour differences, *in situ* measurements were made of fluorescence for a number of locations in the Sound in October 1973. The data obtained were reported as microvolts. The authors concluded that there was "virtually no phytoplankton in water entering the Sound", and there was "a marked increase in phytoplankton abundance on the eastern side of Cockburn Sound" (3). 1.2 (Cont'd)

In a subsequent report substantial descriptive and photographic documentation was given of algal blooms which occurred in the Sound during the spring and summer of 1973-1974 (ERA (10)). This was accompanied by field measurements of fluorescence (expressed as μ V's) obtained in the last week of February, 1974. From these findings it was concluded by the consultants that phytoplankton biomass was consistently high throughout the summer period of 1973-74 over the eastern side and Mangles Bay areas of the Sound, at times the levels intensified to the point of forming visible, short-lived "blooms".

After reviewing the amounts of principal raw materials imported into the Outer Harbour (Cockburn Sound) from 1969-70 to 1972-73, the consultants concluded that CSBP had had a significant increase in production in the 1972-73 period, and as a result their nutrient loads would also have increased markedly.

Over the period, November 1974 to April 1975, a detailed investigation of chlorophyll <u>a</u> levels was made in the Sound by a consultant using the same technique <u>as</u> used previously (Meagher and LeProvost (1)). An unknown number of grab samples were also taken, and chlorophyll <u>a</u> concentrations determined. These data were used to convert all the fluorescence values to chlorophyll <u>a</u> concentrations.

Values were consistently in the region of 5-10 mg/m³ chlorophyll <u>a</u> throughout the period of the survey.

Although these reports give substantial descriptive and photographic documentation of high algal productivity, much more quantitative data were needed before management recommendations could be made. As a result the present study undertook the collection of considerable ambient data on the nutrient and phytoplankton status of the Sound.

1.3 Study Aims

It was considered important that the nutrient status of Cockburn Sound should be determined, and the effect of man-made wastes and other nutrient sources on the nutrient cycle assessed. The information was to be related to the phytoplankton ecology of the Sound, particular attention being given to changes in levels of phytoplankton and the effects of nutrients on these levels. With this information it was then possible to consider the importance of nutrient discharges on the occurrence of algal blooms, and the possibility of controlling such blooms through the reduction or elimination of nutrient rich wastes from the waters of the Sound.

Four aims were set at the start of this study. These were:

- . To describe the phytoplankton communities of Cockburn Sound, to quantify seasonal changes in diversity and abundance, and to assess the factors limiting phytoplankton production.
- . To quantify the main sources of nutrients in the Sound, to develop an understanding of the effects of the Sound's hydrological behaviour on the accumulation and dispersal of nutrients, and of the effects of biological processes in the cycling of nutrients.

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1.3 (Cont'd)

To derive an understanding of the relationship between nutrient cycling in the Sound and changes in phytoplankton abundance, then consider the effects of any reduction in nutrient levels as a result of the control of point sources to the Sound.

To consider the impact of blooms upon the ecosystem of the Sound, and also upon recreation and industry.

1.4 Description of the Area

Cockburn Sound is a large, deep and well sheltered marine embayment on the western coast of Western Australia, almost immediately south of Fremantle (Figure 1.1). It was originally an interdunal lake which lay close to the coast and was inundated by the sea approximately 4 000 years ago (Churchill(11)). It has a surface area of approximately 103 km². The body of the Sound is a basin 20 m deep, surrounded by narrow, marginal shelves which were the dune shores of the original lake. The northern and south-western openings of the Shore are bounded by shallow sand banks 3-5 m below the surface. Both of these banks and the marginal sills were once covered with extensive growths of seagrass. The seagrass beds have disappeared along the eastern margins of the Sound in the last 25 years and this depletion is continuing within the Sound (Cambridge (12)).

The Sound is being developed as the Outer Harbour of the Port of Fremantle. Since 1955 much of the eastern shore has been developed for industrial use with adjacent port facilities. A number of the larger industries use water from Cockburn Sound for cooling purposes, and a number of industries discharge wastes to the Sound.

The south-western corner of Cockburn Sound is dominated by the township of Rockingham, once important as a timber export port, and now the focus for one of Perths key recreational areas, that is, the southern sector of Cockburn Sound and Cape Peron.

To the north of Cockburn Sound is Owen Anchorage (Figure 1.1). The Anchorage has the same geological origins as Cockburn Sound but is much smaller in size. It is less sheltered than the Sound with the western margin north of Carnac Island being some 7 m deep but is still enclosed by a shallow extensive sand bank to the north (Success Bank, 0-4 m).

The actual deep basin occupies the western half of the Anchorage and is 12-16 m deep (c.f. Cockburn Sound, 16-20 m deep). The eastern side of the Anchorage is a shallow (6-7 m) shelf similar to that found in Cockburn Sound. The mainland shore of Owen Anchorage is the heavily industrialised. A "noxious industries" zone it has a number a abattoirs, food processing plants and tanneries. Some of their discharge wastes go directly to the Anchorage or to the groundwater (Murphy (13)).

To the south of Cockburn Sound is Warnbro Sound (Figure 1.1). It has been used as a control site throughout this study.

Geologically, Warnbro Sound is throught to have once been a southern extension of Cockburn Sound (Carrigy (14)). It has a relatively flat, central basin, 13-16 m deep (c.f. Cockburn Sound, 16-20 m deep). It has been cut off from the sea by two sand bars extending from the

- 7 -

1.4 (Cont'd)

northern and southern ends but separated by a narrow channel 10 m deep. The sand banks are between 2-7 m below the surface. The shores of Warnbro Sound are virtually untouched apart from some urban development on the northern side.

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THE STUDY AREA



2. THE PHYTOPLANKTON

2.1 Introduction

The growth of marine plants (primary production) forms the basis of most food chains within the sea. Solar energy is used by these plants to construct complex organic compounds of high potential energy from carbon dioxide and nutrients. These plants are grazed upon by herbivorous animals (secondary production) and the herbivorous animals are fed upon in turn by carnivorous animals (tertiary production). All three trophic levels contribute to the detritus of the sea floor. Detritus is used directly by some life forms as a source of energy and such biological processes lead to the release of nutrients and carbon for re-use in life processes.

Marine plants fall into three major groups - aquatic angiosperms (seagrasses), macro algae (seaweeds) and micro algae (phytoplankton). Quantitatively, the phytoplankton are thought to account for the greatest production in the sea (Riley and Chester (15)). Phytoplankton are now thought to be the dominant primary producers in Cockburn Sound.

Phytoplankton are single-celled plants which vary in size from less than five micrometres up to two millimetres (Boney (16)). The marine phytoplankton flora is dominated by two classes - the diatoms (Bacillariophyceae) and the dinoflagellates (Dinophyceae). The green algae (Chlorophycaea) and the blue-green algae (Cyanophyceae) are less well represented, both in species number and in biomass. Species of silicoflagellates (Chrysophyceae) also occur in the plankton on occasions.

Species of phytoplankton are found in coastal and oceanic waters both spatial and temporal changes occur in the assemblages of three species. At any one site it is usual to find a characteristic succession of different species throughout the year. Characteristic changes in species usually occur seasonally and this is attributed to changes in light, temperature, availability of nutrients, turbulence and grazing by animals. Fluctuations in environmental factors and varying tolerances of different species to such changes lead to successions of phytoplankton species. r

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Changes in phytoplankton species were monitored weekly for the first 12 months of this study at two locations. One location (station 214) was in Cockburn Sound and the other (station 238) was in Owen Anchorage (Figure 4.1).

The Cockburn Sound site was at the northern end of the CBH jetty and was chosen because it allowed sampling of the deeper water of the Sound in the region where phytoplankton biomass had been observed to be highest (Meagher and LeProvost (1)).

The Owen Anchorage site was at the end of the Mines Department Explosives Reserve jetty. This site was chosen because it is the only structure which extends any distance out into the Anchorage.

Phytoplankton identification and enumeration was undertaken by Miss J.A. Chaney, initially for the Study Group and subsequently as part of an Honours dissertation in Botany at the University of Western Australia.

2.2 Methods

Phytoplankton samples were collected from the two sites at weekly intervals for a total of 51 weeks over the period July, 1977 to August, 1978. At the same time data on nutrient concentrations and chlorophyll a levels were obtained (Section 4).

Discrete water samples were collected using Niskin bottles at three depths at station 214 (1.0 m, 8.0 m, 15.0 m; total depth = 16.0 m) and two depths at station 238 (1.0 m and 7.0 m; total depth = 8.0 m). Samples were preserved on-site and later counted using a membrane filter technique (Ref. Appendix I).

2.3 Results

Over the period of the investigation a total of 32 species of phytoplankton were found at station 214 in Cockburn Sound, and a total of 37 at station 238 in Owen Anchorage. At each station the diatoms were numerically dominant with 23 genera at station 214 and 27 genera at station 238. The remaining species were either dinoflagellates, silicoflagellates or greens. A listing of the species found at each station, their time of occurrence and the dominant species found at each time of sampling is given in Figures 2.1 and 2.2 for station 214 and station 238 respectively.

There are considerable differences between the two locations in the species which are dominant as well as the diversity of species which occurred at any one time throughout the study period. Station 238 shows a dominance of either greens or dinoflagellates with only five instances where diatoms were prolific. However, at station 214, greens and diatoms dominated. Individual species of greens and diatoms once they had become dominant persisted for much longer periods of time at station 214.

The seasonal, successional changes in the four major groups found are better illustrated in Figure 2.3. It is clear from this figure that station 238 is characterised by a higher incidence of dinoflagellates than station 214 which in the first part of the study was dominated by greens and in the latter part by diatoms.

Figure 2.4 shows the changes in phytoplankton biomass which occurred at both stations over the study period measured as chlorophyll a and as cell numbers (counts). For station 214, there is a significant linear correlation (p < 0.01) between cell counts and chlorophyll a. This was not the case at station 238. The latter result is probably a product of low cell numbers and high detrital content which made identification and counting difficult (Chaney (17)). Fewer samples were counted at station 238. The chlorophyll a data are therefore a better indicator of biomass changes at this station.

For station 214, changes in biomass over the study period are characterised by a large spring bloom and then a series of blooms throughout the summer period and well into the winter period. Station 238 has lower concentrations of phytoplankton overall. There is a spring bloom and also small peaks in the late summer and autumn. These peaks are not as extensive nor as frequent at station 238 as those seen at station 214. 2.3 (Cont'd)

At station 214, the spring 1977 peak was dominated by an unknown species (species 2). This species and another, similar, unknown, dominated the phytoplankton throughout November and into December. The series of "blooms" which then occurred from the mid-summer period onwards (January) were initiated by a small chain-forming diatom (*Chaetoceras*), and followed by another diatom (*Asterionella*). Another succession was then initiated by a green (species 4) and dominated by three diatoms (*Asterionella*, *Chaetoceras* and *Thalassiosira*). In May species 4 (a green) again became dominant and similarly in August, otherwise the flora was dominated by the diatoms and occasionally dinoflagellates (*Peridinium* and *Prorocentrum*). The dinoflagellates occurred during periods of low biomass, i.e. at the end of one succession and the commencement of the next, as did the greens. However, the greens were more prevalent than the dinoflagellates.

At station 238, the spring bloom was dominated by two dinoflagellates (*Prorocentrum* and *Peridinium*). *Peridinium* also dominated during the late summer peak. Only on a few occasions did diatoms become dominant and these were in the autumn and winter periods.

2.4 Discussion

2.4.1 Total Diversity

An assessment of long-term changes in the diversity of phytoplankton of Cockburn Sound and Owen Anchorage is not possible as no other data are available. A direct comparison with other studies done in the Indian Ocean is unrealistic in that Cockburn Sound is not only a coastal embayment, but also is part of a biogeographic region which is distinct from the rest of the Indian Ocean. Wood (18), based on his observations of the dinoflagellates, proposed that the nearshoreregion between Shark Bay and Cape Naturaliste was a warm temperature area separate from the rest of the Indian Ocean and Australian coastal regions. Further evidence in support of Wood's proposal, has recently been published by Golding and Symonds (19). They have described well defined eddies with diameters of about 140 km which dominated the surface circulation during the summers of 1973-1976. In summarising his work on the dinoflagellates in the Australian region Wood concluded that this group, in the area between Shark Bay and Fremantle, had an abundant growth of a few species, making specific mention of only three species. None of these three species were recorded in Cockburn Sound.

However, it is reasonable to compare the total numbers of species in different phytoplankton classes in Cockburn Sound with those of other marine systems. Subrahmanyan and Sarma cited in Krey (20), compiled a list of 37 phytoplankton taxa (29 diatoms, seven dinoflagellates and one blue-green) which they calculated contributed to 70-80 per cent of the total biological processes in the Indian Ocean. Tranter and Newell (21), list a total of 11 taxa (eight diatoms and three dinoflagellates) collected from a series of stations due west of Fremantle, but beyond the biogeographic area of the study.

Jeffrey and Carpenter (23) list a total of 28 species of diatoms, and nine species of dinoflagellates, for a nine month study of the phytoplankton at the CSIRO Port Hacking 100 m station.

2.4.1 (Cont'd)

At the Cockburn Sound station a total of 32 species were observed (23 diatoms and four dinoflagellates) while in Owen Anchorage a total of 37 species were identified (27 diatoms and five dinoflagellates). It is therefore reasonable to conclude that Cockburn Sound and Owen Anchorage flora have as high a species diversity, if not a higher diversity, as would be expected from the associated nearshore coastal waters.

2.4.2 Successional Changes

Studies of seasonal, successional changes in Australian waters are limited and have been undertaken only on the eastern Australian coast.

Dakin (22) first described a seasonal succession on the Australian coast, 4-5 miles off-shore from Sydney Harbour, where he found a spring diatom maximum commencing with *Chaetoceras* and *Thalassiosira* in September followed by the diatom species of *Rhizosolenia* in October. A less dominant autumn maximum occurred in February and March.

More recently Jeffrey and Carpenter (23) have described in quantitative terms a definite succession pattern at the CSIRO 100 m station off Port Hacking, eastern Australia. They observed a spring bloom (September) which began with small chain-forming diatoms, mainly of the genera Asterionella, Thalassiosira, Skeletonema, Nitzschia and Chaetoceras. These were succeeded by larger centric diatoms, the most abundant of which were species of Ditylum, Leptocylindrus, Eucampia, Rhizosolenia and Melosira, together with the pennate genus Thalassiothrix. Coccolithophorids, micro flagellates and dinoflagellates showed a first minor pulse in September, and became established in October and November. During late summer and early autumn, diatom numbers were low and the phytoplankton consisted mainly of the first three named groups. A pulse of cryptomonads and silicoflagellates occurred in March and April respectively. A second diatom flowering took place in the autumn (May) dominated by species of Leptocylindrus, Thalassiothrix, etc., which were different from those which initiated the spring (September) bloom.

In general terms, the pattern of phytoplankton successions in Cockburn Sound at station 214 is similar to that described by Jeffrey and Carpenter. However, the number of large and rapid changes in abundance at the Cockburn Sound station were certainly not typical of marine phytoplankton in any way.

The well documented spring and autumn blooms which usually occur in coastal marine phytoplankton are the result of nutrient-rich upwellings (Chapman and Chapman (24); Carpenter and Carpenter (45)). However, Jeffrey and Carpenter (23) have pointed out species specific vitamin requirements and other biochemical factors, involving conditioning of the water by the algae, will most likely dictate the detailed pattern of any observed succession of species.

Margalef (25) has described the general pattern of nutrientstimulated succession as a sequential process based on nutritional requirements, i.e. the process starts with small-celled diatoms capable of a high photosynthetic rate and rapid cell division and hence requiring high nutrient levels. These are followed by slower-growing diatoms of medium size, and then by motile forms (dinoflagellates) and

2.4.2 (Cont'd)

other organisms with more complex nutritional requirements, (e.g. species of the dinoflagellate genera *Gymnodinium* and *Gonyaulax* which cause the "red tides" most commonly found in the temperate and tropical waters of California, Florida, South America and South West Africa (Chapman and Chapman (24)).

It can be seen from Figure 2.3 that the relatively large number of successions at the Cockburn Sound station were dominated by diatoms followed for short periods by dinoflagellates. Between each succession greens and other flagellates also occur.

At station 238 (Owen Anchorage) at most only three successions of species are evident over the study period with dinoflagellates being present for a much greater period of time than at station 214 (i.e., at station 214 there is a high frequency of short-lived and incomplete successions whereas at station 238 there are fewer successions but these proceed much further).

If the general pattern of phytoplankton successions as observed in this study and by others elsewhere (loc. cit.) are controlled by the availability of nutrients as Margalef suggests, then it can be expected that station 214 will be characterised by frequent changes in nutrient concentrations whereas station 238 will be more stable. As is shown in section 4, this is exactly that case. Station 214 has large and frequent changes in nutrients, whereas at station 238 changes in nutrient concentrations are small and less frequent.

If successional changes as illustrated in Figure 2.3 are compared with the changes in chlorophyll <u>a</u> shown in Figure 2.4 it is seen that each succession is associated with an increase in biomass. In section 5, increases in phytoplankton biomass (measured as chlorophyll <u>a</u>) are shown to be strongly correlated with increased concentrations of nutrients. The frequency and extent of successional patterns in the phytoplankton at both of the study sites are consistent.

It is concluded therefore that the changes in phytoplankton biomass in the Sound are, to some degree, the result of successional changes and these successional changes are associated with changes of nutrients.

SPECIES	July August Septemi	ber October November D	lecember January February M	arch April May	June July Aug
	5		20 25 3		0 45
DIATOMS	<u> </u>		er den en e		
Amphiprorg	•		•		
Asterionella					
Biddulphia					
Chastocaros					
Cocconeis					
Coscinodiscus		••••			·•
Dipionals	· · · · · · · · · · · · · · · · · · ·				
Enithamia	•	F			
Fragilaria	•				
Cramatophora		•			
Licmorphora				· · · · · · · · · · · · · · · · · · ·	
Melosira					60
Navicula			+ +		0
Nitzschia		· · ·			
Pleurosigma	•				
Rhizosolenia			• • • •		
Skeletonema		• •			•• •••••
Thalassionema				· · · · · · · · · · · · · · · · · · ·	•
Tholossioslro		•		· · • • • • • · · ·	
Tholassiothrix			•		
Guinardia					
Striatella		•		•	
Amphoro		• •		• •	
DINOFLAGELLATES					
Cerotium			• • • • •	• • • •	• • • • •
Exuviaella			ş		
Peridinlum			• • • • • • • • •	•	
Prorocentrum			• • • • • •	· • • • • •	1 0 1 0
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COMPOSITION & ABUNDANCE OF PHYTOPLANKTON SPECIES AT STATION 214 (COCKBURN SOUND)

>15% OF TOTAL NO.

• SPECIES PRESENT

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	SPECIES		1977	WEEK	NUMBER				197	8		
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	DIATOMS			· · ·								
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q	Bacillaria		1						1		•	
0	Amphora	•	* * *	* *	•		•	*	* •	•	•	
51	Eplthemia			•							¢	
Ξ	Triceratium		۴				·			•	•	
0	Dipioneis							,			•	
~	Thalasslosira		*	* *	•		••	¥	• •	• •	•	
τ. Ω	Grammatophora		•	•							¢	
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ι ^B	Gyrosigma				•				•			
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D D	Licmophora			•	•				•			•
	Rhizosolenia		•					¢				
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Zm	Thalassiothrix		• • •	** *					•			
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σσ	Coscinodiscus	• •	• •	* •			۲	4				4
SE	Amphiprora	٠		Ŷ				° ¢				
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mo	Melosira						•					
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DD	Cymbella		•	-			*	8 .				
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<u> 0</u> <u>7</u>	Skeletonema	,	e							•		
70	Biddulphia			•							١	
n z	Cocconeis	•	•• •									
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, v	Dinophysis			•	•	•		•				
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€>15% OF TOTAL NO.

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0 SPECIES PRESENT

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CHANGES IN THE COMPOSITION OF THE PHYTOPLANKTON OVER THE STUDY PERIOD (from Chaney, 1978)



3. NUTRIENT INPUTS

3.1 Nutrient Cycling in the Ocean

The sea naturally contains small amounts of phosphorus and nitrogen. These can be present in both inorganic and organic soluble forms, or physically and chemically bound to particulate material. They are essential components of plant material, the synthesis of which is termed photosynthesis, and their availability may affect the rates at which photosynthesis and plant growth proceed.

Within the marine ecosystem nitrogen and phosphorus can be made available for plant growth by two means. The first is by the introduction of these nutrients from an external source, and the second is by the recycling of nutrients already within the ecosystem.

3.1.1 The Nitrogen Cycle

Figure 3.1 is a schematic representation of the nitrogen cycle. At the outset it should be noted that in any body of water the concentrations of the different forms of nitrogen result from a dynamic equilibrium between the physical, chemical and biological factors controlling the introduction, recycling and loss of these forms. In the main the concentrations of the various organic and inorganic nitrogen forms in the sea are controlled by biological factors (Riley and Chester (15)).

Inorganic nitrogen exists in the sea as dissolved N_2 and NH_4 ⁺, NO_2^{-2} and NO_3^{-3} ions. Nitrogen is introduced to the oceans in the inorganic forms as run-off from the land in rivers, in groundwater and in rain. Atmospheric nitrogen may also be fixed by certain bacteria and blue-green algae. In most recent times the introduction of nitrogen to the sea has been accelerated by the disposal of man-made wastes such as sewage and industrial effluents, as well as the fall-out of nitrous oxides (NO_v 's).

In marine systems recycling is the source of nitrogen for primary productivity. Bacteria dominate the regenerative processes in which organic nitrogen compounds are converted to inorganic forms. This regeneration takes place within the sediments or the water column. Release to the overlying water from the sediment is accomplished by diffusion, bioturbation and mixing by waves and currents. Phytoplankton normally synthesise their proteins from nitrate, nitrite and ammonia. Living animals contribute by the excretion of ammonia, and to a lesser extent precursers such as urea.

Removal from the system may be by sedimentation at a rate higher than regeneration, by the exchange of water containing dissolved and bound forms of nitrogen, e.g. the movement of suspended material. Under anoxic conditions some denitriphication takes place (Riley and Chester (15)).

3.1.2 Phosphorus Cycle

Phosphorus exists in the sea in both dissolved and particulate form. Inorganic phosphorus is usually present only as the orthophosphate ion (PO_4^{-3}) . Organic phosphorus compounds constitute a significant proportion of the dissolved phosphorus found in the sea. A schematic diagram of the phosphorus cycle is shown in Figure 3.2.

3.1.2 (Cont'd)

Phosphorus is introduced to the oceans by the simple weathering of rocks as well as in the bound organic form. In more recent times in coastal areas its regional availability has been enhanced by increased run-off and weathering through man's activities as well as through the direct discharge of industrial effluents, sewage and detergents to rivers and the oceans.

Phytoplankton usually utilise orthophosphate although some species of phytoplankton can use dissolved organic phosphate. The importance of the latter is not thought to be high. In zooplankton some phosphate is lost in the urine and that lost in the faecal pellets is rapidly hydrolysed back to orthophosphate. The regeneration of phosphate on death of the organism is rapid as most organic phosphate is converted back to orthophosphate by the action of its own enzymes (Riley and Chester (15)). Phosphate is lost from the system by the same transport processes as described for nitrogen, and may also be lost to the sediments by burial and its conversion to phosphate minerals such as apatite.

3.2 Nutrient Inputs to Cockburn Sound

3.2.1 Riverine Input

There is no natural, surface input of freshwater to the Sound or Owen Anchorage. The nearest possible input along the coast is from the Swan-Avon system 3.5 km north of Success Bank (Figure 1.1). This system only flows in the winter months, with flow being dependent on the amount of rain. A small number of observations have been published on the direction of movement of outflow from the estuary mouth (Finucane and Forman (26); Ives (27)). From these observations as well as those made by the author outflow is generally considered to move out to sea and then north or south along the coast but rarely into Owen Anchorage or Cockburn Sound.

Ives (27) records riverine water crossing Parmelia Bank into the top of Cockburn Sound in 1960. Ives reports unpublished data collected by Wilson in 1958 which showed a salinity of 32.5 parts per thousand in the top 7 m in the middle of Cockburn Sound. This value is comparable with values obtained in July, 1978 at stations in Owen Anchorage when river water was observed to have crossed Success Bank into the Anchorage. However, it is thought that such influxes of riverine water into Owen Anchorage occur infrequently and even less frequently into Cockburn Sound. Although the input of nutrients on such occasions may be quite high they occur so rarely that they are not considered a source of nutrients which is critical to the present eutrophication of Cockburn Sound.

3.2.2 Groundwater

The boundary for the groundwater catchment for Owen Anchorage and Cockburn Sound is approximately parallel to the coast and runs 12-15 km inland (Mines Department, W.A.). The water table slopes from east to west and the base of the surface (unconfined) aquifer is 25 to 30 m below sea level (Layton Groundwater Consultants, 1979 (28)).

3.2.2 (Cont'd)

The Mines Department, Western Australia, has made estimates of discharge from the unconfined aquifer for the area between Fremantle and Cape Peron. These volumes have been used to obtain an estimate of the nutrient loads to Owen Anchorage and Cockburn Sound using nutrient concentration data for a number of bores in close proximity to the coast (Layton Groundwater Consultants). Only single sets of analyses have been done on these bores and usually from only one depth. Where samples were taken from more than one depth the concentrations obtained have been averaged. An average concentration was then calculated for all of the bores which occurred between the same flow-lines in the flow net (provided by the Mines Department, Western Australia) (Figure 3.3). This final average of groundwater concentration was multiplied by the discharge volume for each of the segments in the flow net. The individual loads were summated to give total loads for Cockburn Sound and Owen Anchorage.

In the Kwinana/Rockingham area concentrations from the Rockingham Sands aquifer only were used for the calculations and not those determined for the Coastal limestone. This was done as it was considered that only the water from the Rockingham Sands would be important in discharges of groundwater to the Sound.

A daily load of 87 kg of inorganic nitrogen $(NH_4-N + NO - N_2 + NO_3-N)$ and of 0.05 kg of soluble phosphorus (PO_4-P) was estimated for Owen Anchorage. The Cockburn Sound loads were 447 kg per day of inorganic nitrogen and 1.3 kg per day of soluble phosphorus.

The groundwater discharges were calculated for a end-of-year condition. Flows may be slightly higher over the winter period due to increases in recharge and a decrease in evaporation from lake surfaces within the catchment. Many of the bores for which nutrient data were used in the calculations were deliberately sampled because of their close proximity to areas of possible groundwater contamination. As a result, the mean concentrations obtained from the calculations were probably much higher than the actual values for individual segments of the flow net.

3.2.3 Input from Near-Shore Coastal Waters

Steedman (29) has made estimates of exchange between Cockburn Sound and the open ocean under different meteorological conditions. He has also calculated an average annual frequency of occurrence for these conditions (refer Section 5.5 for a more detailed description).

Only three of the described conditions are important to exchange between the ocean and the Sound. Using the maximum daily exchange rates given for these conditions and their percentage frequency occurrence estimates for the total volume exchanged between the ocean and Cockburn Sound have been made. Loads of inorganic nitrogen and phosphorus have been calculated from these volumes using mean annual concentration figures for NO_3-N and PO_4-P from the CSIRO 50 m station for 1977 (unpublished data).

A total of 218 kg per day of inorganic nitrogen and 145 kg per day of phosphorus was estimated to be contributed from entry of oceanic water to the total load in Cockburn Sound.

3.2.4 Effluent Inputs

Very detailed studies of the concentrations and loads of chemicals in effluent discharges to the Sound have been made as part of the Cockburn Sound Study (refer Murphy (13)). A summary of mean annual loads discharged to the Sound in industrial and sewage effluents is given in Table 3.1. It should be noted that the BP Refinery contribution has now been reduced by greater than 90 per cent (Murphy (13)).

The CSBP/KNC outfall contributes the largest loads of both inorganic nitrogen (68 per cent) and phosphorus (87 per cent) to the Sound. In fact, this outfall is the major source of both phosphorus and nitrogen to the Sound. The Woodman Point Treatment Plant contributes an additional 25 per cent of the nitrogen (as NH_4-N). It is not possible to tell what percentage of the phosphorus loads is in the organic form from Table 3.1, but Table 3.2 gives daily loads for both PO_4-P and total phosphorus for CSBP/KNC and Woodman Point Treatment Plant. These data were obtained from a daily sampling programme of both effluents for a month in the summer of 1978. The total loads obtained are very similar to the values given in Table 3.1 It is clear that of the two outfalls the CSBP/KNC outfall not only contributes the majority of the total phosphorus (95 per cent) but also the majority of the inorganic phosphorus (91 per cent).

3.2.5 Air Emissions

Calculations done by the Kwinana Air Modelling Study (pers. comm.), have indicated that, at most, some 667 kg per day of nitrogen (as NO_2) could enter the Sound from stack emissions. This calculation was based on an estimation of the loads from the different stacks in the air-shed, the proportion of time the prevailing winds blow across the Sound and the proportion of NO_X in contact with the water surface from the plumes.

3.2.6 Rainfall

Data on the amount of nutrients in rainfall is sparse. O'Connell, CSIRO, (pers. comm.), recorded 0.7 kg N ha⁻¹y⁻¹ and 0.15 kg P ha⁻¹y⁻¹ in rainfall at Dwellingup some 30 km inland from Cockburn Sound. This location would have a similar rainfall regime to Cockburn Sound. Cockburn Sound has an approximate surface area of 103 km² (Steedman (29)). Using O'Connell's figures this would mean approximate loads of 2 kg-N/ day and 0.5 kg-P/day. As can be seen from Table 3.3 these amounts are of no significance to the overall nutrient loads to Cockburn Sound.

3.2.7 Nitrogen Fixation

Another possible source of nitrogen to Cockburn Sound is through bluegreen algal nitrogen fixation. Throughout this study very few bluegreen algae were found. Some species have been isolated from the Sound but it is not known if they are "fixers" (Huber, pers. comm.). Even if they were, they occur in such small numbers that their contribution of nitrogen would be very small. A single incidence of a small bloom of *Trichodesmium* sp. was noted in the Sound in April, 1972 (Cambridge, pers. comm.). *Trichodesmium* is capable of fixing its own nitrogen (Riley and Chester (15)) but is very slow and inefficient (Ryther and Dunstan (5)), and blooms are a regular occurrence each autumn along the coast (Smith (30). However, blooms have not been seen within the Sound during the course of this study.

3.3 Recycling of Nutrients

No previous assessment has been made of the recycling of nutrients in Cockburn Sound. Time has not allowed estimates to be made of nutrient flux rates to and from the sediments of the Sound. Exchange from the sediment to the overlying waters was thought to be comparatively small as a nutrient source. However, the results from Cruise 7 indicated that the sediments of the Sound may contain high concentrations of inorganic nutrients (Section 4.3) This cruise took place immediately after a period of intense storm activity (Figure 4.16). A measure was, therefore, made of the extent to which the sediments of the Sound contained nutrients which were readily exchangeable with the overlying waters under high energy conditions. A number of sediment cores were collected in Cockburn Sound, Owen Anchorage and Warnbro Sound (Figure 3.3). The top two centimetres were shaken with the overlying seawater and this was then analysed for $PO_{4}-P$, $NH_{4}-N$, and $NO_2 + NO_3 - N$. A correction was made for ambient levels in the overlying seawater (ref AppendixI). The results are shown in Figure 3.4.

Each of these figures show uniformly low levels over much of the Sound but an area of high values in close proximity to the CSBP outfall. Slightly elevated levels of NH_4 -N were also evident in close proximity to the Woodman Point Sewage Treatment outfall. High concentrations of NO_2 + NO_3 -N were also found in the Alcoa turning basin and in Jervoise Bay as well as an area of elevated concentrations in close proximity to the Woodman Point Sewage Treatment outfall. The elevated values along the east coast of the Sound have also been reported by Winch (45).

It seems reasonable to attribute the highly elevated levels of nitrogen and phosphorus to the CSBP effluent. Phosphorus is often readily adsorbed from water on particulate material and sedimentation of a portion of it in close proximity to the outfall is expected.

The areas of high levels of NH₄-N and NO₂ + NO₃-N to the south of the CSBP/KNC outfall were identical. The area of high concentrations of NH₄-N in proximity to the Woodman Point Treatment Plant coincides with that for PO₄-P but not for NO₂ + NO₃-N. High concentrations of NO₂ + NO₃-N were found in Jervoise Bay and the Alcoa turning basis, but high concentrations of NH₄-N were not.

These observations indicate that the areas of high concentrations of NH₄-N in the sediments are directly related to the two discharges, whereas the areas of high levels of $NO_2 + NO_3$ -N are the result of a more indirect process. The highest concentrations of chlorophyll a in the Sound have been observed around the CBH jetty (station 214) and the next highest concentrations along the eastern margin of the Sound north of Woodman Point. As the Jervoise Bay area and the Alcoa basin area are natural sediment traps it is possible that the high $NO_2 + NO_3$ -N values are the result of the accumulation of organic material and the subsequent recycling of the nitrogen.

Recycling of nutrients from the sediments and in the water column of the Sound over the summer period is thought to be secondary to industrial inputs in contributing significantly to the present standing crop (biomass) of phytoplankton. With the cessation of industrial discharges at some time in the future the importance of recycling in the nutrient cycles will have to be assessed.

3.4 Conclusions

From the foregoing assessment of the nutrient loads of the Sound it is apparent that only four sources are of any consequence, i.e. industry and sewage, groundwater, coastal waters and air emissions. The estimated daily loads for these four sources are given in Table 3.3.

The majority of both the nitrogen and phosphorus entering the Sound does so in industrial effluents and in sewage. Air emissions from the industries in the regions add, at maximum, an additional 10 per cent of the nitrogen. The figure for groundwater for nitrogen is a high figure as severe contamination of groundwater has occurred from industries in close proximity to the Sound and Owen Anchorage but even so only adds a total of seven per cent. In Section 4 it is shown that the nutrient levels in Warnbro Sound are comparable with those for the coastal waters. It therefore seems reasonable to conclude that the figure for coastal waters (three per cent of the total-N and four per cent of the total-P), is, in fact, a realistic estimate of the pre-industrial base load to the Sound. This being the case then the present loads represent an increase of approximately 32 times as much nitrogen and 24 times as much phosphorus.

It has not been possible to prepare a complete inventory of nutrient loads to Owen Anchorage. A daily load of 87 kg inorganic nitrogen in the groundwater and 620 kg per day from industrial effluents was calculated. A value of 108 kg per day of total-P was estimated to enter Owen Anchorage from industrial effluents and almost none in the groundwater. It is shown later in this report (Section 5.4, 7.4) that the passage of nutrient rich waters from Cockburn Sound to Owen Anchorage also occurs. It is possible that this is the most important source of nutrients to Owen Anchorage.

The contribution of sediments to the nutrients in the water column under flux conditions is unknown but it can be considerable under persistent high energy conditions (i.e. frequent storms). There is evidence of the accumulation of both N and P in the surface sediments from both the Woodman Point Treatment Plant and CSBP/KNC outfalls. Recycling may become very important should the loads from point sources be diverted or curtailed.

TABLE 3.1

1

LOADS OF NITROGEN AND PHOSPHORUS (kg/d) IN INDUSTRIAL OUTFALLS AND SEWAGE DISCHARGED TO COCKBURN SOUND

	NH₄-N kg/d (%)	NO₂+NO₃-N kg/d (%)	TOTAL INORGANIC NITROGEN kg/d (%)	TOTAL NITROGEN kg/d (%)	TOTAL PHOSPHORUS kg/d (%)
AIS	51 (1)	-	51 (1)	49 (1)	2 <1
BHP	0.2 (<1)	0.6 (<1)	0.8 (<1)	0.9 (<1)	<1 <1
BP	271 (7)	4.2 (<1)	275,2 (6)	322 (6)	8 <1
CSBP/ KNC	2350 (62)	665 (99)	3015 (68)	3075 (62)	3275 (87)
WPTP	1114 (29)	10 (1)	1124 (25)	1422 (29)	261 (7)
SEC	-	-	-	110 (2)	220 (6)
TOTALS	3786	670	4456	4979	3766

TABLE 3.2

MEAN DAILY LOAD OF N & P FROM CSBP/KNC AND WPTP CALCULATED FROM SAMPLES COLLECTED DAILY FROM 12.01.78 TO 14.02.78

	NH4-N kg/d (%)	NO2+NO3-N kg/d (%)	T.I.N. kg/d (%)	PO4-P kg/d (%)	TOT-P kg/d (%)
CSBP/KNC	1769 (64)	501 (100)	2270 (69)	1681 (91)	4663 (95)
WPTP	1011 (36)	-	1011 (31)	176 (9)	250 (5)
TOTALS	2780	501	3281	1857	4913

TABLE 3.3

ESTIMATES OF NUTRIENT LOADS TO COCKBURN SOUND WATERS FROM EXTERNAL SOURCES

	TOTAL-N kg/d (%)	TOTAL-P kg/d (%)
GROUNDWATER	447 (7)	1 (<1)
COASTAL WATERS	218 (3)	145 (4)
INDUSTRIAL EFFLUENTS AND SEWAGE	4979 (79)	3766 (96)
AIR EMISSIONS	667 (10)	1 (<1)







PO₄-P (پوپ/L)





(∟/وע) NO₃-N



KEY

• Sample Station



DISTRIBUTION OF INORGANIC NUTRIENT IN THE SEDIMENTS AS µg/L DRY WT SEDIMENT FOR TOP 2 cm (HIGH ENERG CONDITIONS)

NH₄- N (پو/L)

4. SEASONAL CHANGES IN NUTRIENTS AND CHLOROPHYLL A

4.1 Introduction

The results obtained by Meagher and LeProvost (1) indicated that high algal biomass was generally restricted to the eastern side of the Sound. However, there was no quantitative data on the associated levels of nutrients nor their spacial or temporal changes within the Sound. Nine cruises were, therefore, run during the study to allow an assessment of both spacial and temporal changes in nutrients and phytoplankton biomass.

4.2 Methods

Cruises: To assess the nutrient status of Cockburn Sound on a seasonal basis, nine surveys or cruises were undertaken over the 16 month study period (Table 4.4). The same stations were sampled on each cruise and these were located in four well defined geographic areas. The areas involved are Owen Anchorage (5 stations), Cockburn Sound (22 stations), Warnbro Sound (1 station) and a coastal station 5 km east of the highlevel bridge on the causeway (Figure 4.1). Three replicate sets of samples were collected on each occasion at the coastal station and Warnbro Sound station.

Water samples were collected at two or three depths using 10 litre Niskin bottles (General Oceanics); the bottles were lowered on the same wire and triggered consecutively. Samples were collected 1 m below the surface and 1 m above the bottom. If the total depth exceeded 8 m a middle-depth sample was also collected. Depths were measured with a Kahlsico meter wheel through which the hydro-wire ran.

Water collected from each depth was poured into Whirlpacks (Namco), stored on either wet or dry ice while on board ship, and frozen at the University at the end of the day. The samples were subsequently analysed for orthophosphate phosphorus (PO₄-P), total phosphorus (TOT-P), ammonium nitrogen (NH₄-N), nitrite plus nitrate nitrogen (NO₂ + NO₃-N) and total Kjeldahl nitrogen (TKJN) (Appendix I).

Two-litre samples were filtered on site using GFC papers, which were retained for chlorophyll a and phaeophytin analysis (ref. to Appendix I for details of preservation and analytical methods). In addition, *in situ* readings of temperature, dissolved oxygen, and light (as PAR) were made at each station at 1 or 2 m intervals. Sampling at all 29 stations was usually completed for each cruise over twothree consecutive days.

Immediately after each cruise water samples were collected and *in* situ readings taken at five locations over seagrass beds. One of these locations was on Parmelia Bank, east of Carnac Island; one in Buchanan Bay, on the east side of Garden Island; one in Mangles Bay adjacent to and east of the southern end of the causeway; one in Shoalwater Bay and one in Warnbro Sound (Figure 4.1).
4.2 (Cont'd)

Weekly sampling: To allow a closer surveillance of nutrient and phytoplankton changes at a site in the southern part of Cockburn Sound (the CBH jetty - station 214) and also at a site in Owen Anchorage (the end of the Woodman Point explosives jetty - station 238) (Figure 4.1). The same set of parameters were measured at these sites as described above for the cruises (the rational for choosing these sites is given in Section 2.2).

4.3 Results - Cruises

Uniformity with depth in the data indicated that vertical stratification did not occur, therefore, the results from each station have been depth averaged. The average value for each geographic area was then calculated for each cruise. These averaged values have been plotted against time (Figure 4.2.). The average, standard error and range obtained for each area on each cruise are given in Appendix II. A summary of meteorological conditions, etc., prior to and during each of the cruises is given in Table 5.1.

Orthophosphate Phosphorus (PO4-P) -

Values at the coastal station (station 234) and Warnbro Sound (station 235) are uniformly low compared with those in both Cockburn Sound and Owen Anchorage. Data collected over 16 months show that the variation in the PO_4 -P values in Owen Anchorage has the same pattern as temperature (see below). During May through August values were similar to those in Warnbro Sound and at the coastal station, but increase towards a peak in January which is 20 times higher than at the coastal station. This seasonal pattern is also evident in the Cockburn Sound data but the variation in concentration is much less, and the actual concentrations are much higher.

At the coastal station individual values ranged between 1 and 17 μ g/l whereas in Cockburn Sound values ranged between 5 and 239 μ g/l. The range of concentrations in Owen Anchorage was between 1 and 73 μ g/l, i.e., the maximum was not as great as in Cockburn Sound. The range in Warnbro Sound was 12 μ g/l, i.e., less than that at the coastal station.

Total Phosphorus -

Total phosphorus values differ between Cockburn Sound and Owen Anchorage in much the same pattern as that seen for PO_4 -P. Any suggestion of a seasonal pattern is strongly disrupted by the increased values of Cruise 7 (July 1978). The value at the Warnbro Sound station was equal to that of the Cockburn Sound area on this occasion.

Total phosphorus values in Cockburn Sound ranged between 8 and 576 μ g/l, in Owen Anchorage between 14 and 300 μ g/l, in Warnbro Sound between 1 and 50 μ g/l (with the exception of Cruise 7, when the value was 241 μ g/l) and at the coastal station between 1 and 136 μ g/l. Variability was consistently highest in Cockburn Sound and lowest in Warnbro Sound and at the coastal station.

Ammonium-nitrogen (NH₄-N) -

Mean ammonia nitrogen values of all areas ranged between 2 and 14 μ g/1 with the exception of a four fold increase over the value for Cruise 6 in Cockburn Sound at the end of March 1978 (C.5) and at the end of July 1978 (C.7) in Cockburn Sound (five fold increase), Owen Anchorage (two fold increase) and at the coastal station (two fold increase).

Excluding Cruise 7, station values ranged between 1 and 95 μ g/l in Cockburn Sound, 2 and 30 μ g/l in Owen Anchorage, 2 and 29 μ g/l and 2 to 20 μ g/l at the coastal station.

4.3 (Cont'd)

Nitrite-Nitrate Nitrogen (NO₂-N + NO₃-N) -

As with NH_4-N , mean values in all areas were uniformly low and ranged between 2 and 11 µg/l except for Cruise 7 again. At this time all areas showed a very marked increase in $NO_2 + NO_3-N$. An eight fold increase over the previous cruise was seen in Cockburn Sound, a 32 fold increase in Owen Anchorage, a five fold increase in Warnbro Sound and a three fold increase at the coastal station.

Chlorophyll a -

Values at the coastal station were always less than 1 μ g/l whereas mean values in Cockburn Sound ranged between 1 and 5 μ g/l with an individual mean station value as high as 14 μ g/l being recorded. Values in Owen Anchorage reflected those in Cockburn Sound but were more uniformly high through the winter period. There is the suggestion of a seasonal pattern in the Cockburn Sound values with a drop in concentrations over the winter of 1978.

N:P Ratio -

Marine phytoplankton populations usually contain nitrogen and phosphorus in the ratio of 10:1 - 20:1 (Goldman (9)). Should ambient concentrations of N and P be equal to or less than these ratios then there is a scarcity of nitrogen relative to phosphorus and the availability of nitrogen will be limiting to further increases in phytoplankton biomass. Should ambient concentrations exceed a ratio of 20:1 then phosphorus may become limiting.

N:P ratios (calculated per gram-atom for inorganic totals) were always lowest in Cockburn Sound where the mean cruise values never exceeded 3 (excluding Cruise 7 which had an eight fold increase in $NO_2 + NO_3$ -N over that for Cruise 6). Values in Owen Anchorage closely followed those in Cockburn Sound with the exception of Cruise 7 again, where a mean value of 45 was calculated. A value of 45 was also found at the coastal station during Cruise 2 and this was a product of very low phosphorus values, i.e. less than 1. Conversely a value of 23 at the coastal station during Cruise 6 (March 1978) was due to elevated $NO_2 + NO_3$ -N, as was the case during Cruise 7, when a mean of 17 was calculated. Mean values in Warnbro Sound were usually less than 5 and never exceeded 12.

Attenuation Coefficient (i.e. extinction coefficients) -Attenuation coefficients (calculated using log_{10}) in Cockburn Sound were consistently a factor of 3 higher than the coastal station. Mean cruise values ranging between .10-.16 m⁻¹ in the prior area and 0.05-.06 m⁻¹ in the latter.

Mean cruise values in Owen Anchorage showed much more variation between cruises than occurred in Cockburn Sound with values ranging between .11-.31 m⁻¹ (the value of .31 occurred during Cruise 7).

Warnbro Sound values tended to be similar to those at the coastal station, except during the winter months in 1978 when the Warnbro Sound values were slightly higher.

Temperature -

Temperatures in all areas followed the same seasonal pattern. However, temperatures at the coastal station were usually 2° C higher than at the other locations. The seasonal range of 15-22°C is 4.3 (Cont'd)

comparable with that reported by Rochford (44) for the CSIRO 50 m Rottnest Island station, where the long term average ranged between 18.8° C and 22.2° C.

4.4 Results

Weekly sampling -

The depth averaged results from this programme are shown in Figures 4.3 to 4.13. These two stations are the same as used for sampling phytoplankton (Chapter 2). Their location is shown in Figure 4.1.

Orthophosphate (PO₄-P) Figure 4.3 -

Station 238: Values ranged between 2 - 60 μ g/l with a definite seasonal pattern of high values in summer and low values in winter. Very large changes in values occur over short time periods throughout the year, i.e. 1-3 weeks.

Station 214: Values in Cockburn Sound are much higher, ranging between $20 - 275 \ \mu g/l$. There is no seasonal pattern, but some suggestion of a net increase in concentrations with time. This station is also characterised by large and rapid changes in concentrations.

Total Phosphorus, Figure 4.4 - Station 238: Values ranged between 20 - 240 μ g/l, with a series of very high peaks between 154 - 240 μ g/l from late January through to July, 1978.

Station 214: Values range between 32 - 627 μ g/l with no obvious seasonal pattern. The data are characterised by large and frequent changes in concentrations.

Ammonium Nitrogen (NH₄-N) Figure 4.5 - Station 238: Values range between 6 and 80 μ g/l with a series of very high peaks from March 1978 onwards.

Station 214: Values range between 2 - 194 μ g/l. Again changes in concentration are large and rapid. There is some suggestion of a net increase in concentration over the winter period (May-September).

Nitrite and Nitrate Nitrogens (NO₂ + NO₃-N) Figure 4.6 -Station 238: Values ranged between 2 - 35 μ g/l with the exception of very high values of 132 μ g/l in August 1978. A net increase in concentration occurred over the winter period.

Station 214: Values ranged between 2 - 79 μ g/l with the exception of a very high value of 148 μ g/l in January, 1978. The net increase in concentrations over the winter period is again evident.

Total Inorganic Nitrogen (NH₄-N + NO₂-N + NO₃-N) Figure 4.7 - Station 238: Values ranged between 9 and 196 μ g/l and reflect the ammonium and nitrite/nitrate pattern. The regular (monthly) occurrence of peak values in late 1978 is readily seen.

Station 214: Values ranged between $6 - 273 \mu g/l$. There is a net increase in concentrations over the winter 1978 period in comparison with the preceding summer. The large and rapid changes in concentrations which occur throughout the year are still evident.

Total Kjeldahl Nitrogen, Figure 4.8 - Values below 200 μ g/l have been deleted in the graphs as this is the limit of detection of the analytical method used.

4.4 (Cont'd)

Station 238: Values ranged between <200 - 1087 μ g/l. Three definite peaks occurred over the February to May period and at the same time there was a net increase in concentrations.

Station 214: Values ranged between $<200 - 623 \mu g/1$. Again a series of peaks are evident as is a seasonal pattern with a peak in late summer (February - March) and a trough mid winter (June-July).

N to P Ratio (Atomic units) Figure 4.9 -

Station 238: Values ranged between 0.5 - 26.5. A seasonal pattern is evident with values less than 2 throughout the summer and then a progressive build up from late February through to August. A number of large peaks occurred throughout the period.

Station 214: Values were consistently low, ranging between 0.1 - 3.4

Chlorophyll a, Figure 4.10 -Station 238: Values ranged between 0.4 - 9.5 μ g/l. No seasonal pattern is evident but there is a series of peaks and declines which are variable in both duration and maximum concentrations reached.

Station 214: Values ranged between $1.2 - 18.0 \mu g/1$. No seasonal changes are evident but similar to station 238, a series of peaks and declines are characterised by rather rapid changes in concentrations.

Note: There is some discrepancy between these graphs and those shown in Figure 2.4. This is because values plotted in Figure 2.4 were the same depths as those at which phytoplankton counts had been made. Phytoplankton counts were not always done at all the depths sampled. Data for Figure 4.10 is a mean value of all three depths sampled.

Station 214: The same strong seasonal trend is evident as at station 238. The winter maximum is a little lower with a seasonal range of $13.5 - 25.8^{\circ}$ C. Again a series of short term rises and falls are evident.

Attenuation Coefficients, Figure 4.11 -Station 238: Values range between 0.09 - .30 m⁻¹. No seasonal trend is evident. Changes are also large and rapid within this range.

Station 214: Values ranged between $0.6 - 0.24 \text{ m}^{-1}$. No seasonal trend is evident and changes are large and rapid.

Temperature, Figure 4.12 -Station 238: A strong seasonal trend is evident with values ranging between $15.0 - 26.0^{\circ}$ C. Within the seasonal trend there are a series of short term rises and falls.

Photosynthetic Active Radiation, Figure 4.13 -Values plotted are at 1.0 m depth measured at the time of sampling. Strong diurnal variations does occur and this will account for most of the short term variation in these data. At both stations though a strong seasonal change is evident. A range of 110 to 2000 $\mu \text{Em}^{-2} \text{s}^{-1}$ was measured. Summer values in air are usually around 2400 $\mu \text{Em}^{-2} \text{s}^{-1}$ at midday.

4.5 Coastal Station Data

The coastal station (Garden Island) was included in the cruise sampling programmes to provide reference data against which to compare data from the other three areas. The validity of using the data from the Garden Island station in this way has been assessed by comparing the orthophosphate and nitrate results with values determined for the same time for the CSIRO 50 m station off Rottnest, and the nearshore water used in supplying the State Fisheries aquarium at Watermans Bay (Figure 4.14). Both these sets of data are unpublished and were provided by curtesy of CSIRO.

Plots of the three sets of values are shown in Figure 4.15. It can be seen that, except for mid-May, 1978 (C.6), PO_4 -P values at the Garden Island station are comparable with those at the CSIRO 50 m station. Similarly, the NO_3 -N values are comparable, except in late July (C.7).

The PO₄-P value in mid-May (C.6) at the Garden Island station is similar to that obtained for the nearshore water at Watermans Bay. The Watermans Bay determinations were done on the water entering the aquarium, but before it had passed through the filter beds. The intake for this laboratory is located some 50 m offshore and is anchored on the bottom on a kelp covered, limestone substrate in 3 m depth of water. The PO₄-P and NO₃-N at this location are usually very much higher than at either of the other coastal stations.

However, both PO_4 -P and NO_3 -N at Watermans Bay show large and rapid fluctuations which do not correlate with changes at either of the coastal stations. It is not possible to say at this stage whether the observed range of values at Watermans Bay is typical of the nearshore waters north of Perth. It is, therefore, not possible to affirm that the high value which occurred at the Garden Island station was due to the passage of nearshore coastal waters.

Apart from the two exceptions discussed above it is reasonable to conclude that the water sampled at the Garden Island station is typical of the coastal waters in the Cockburn Sound region.

4.6 Discussion

For most cruises and most parameters the Warnbro Sound station had very similar values to those obtained at the coastal station (station 234). Based on his understanding of the sedimentology and geomorphology Carrigy (31) assumed that Warnbro Sound had limited water exchange with the open ocean. Our understanding of water circulation and exchange in Cockburn Sound, a much larger, more open embayment, would support such a conclusion. It is, therefore, interesting to note that the general nutrient status of Warnbro Sound is more in line with the coastal station than either Cockburn Sound or Owen Anchorage.

The waters of Cockburn Sound and to a lesser degree, Owen Anchorage have very much higher values of phosphorus than either of the other two areas under discussion. Cockburn Sound is the only area receiving large loads of phosphorus (Section 3.4). It is evident that these loads are being at least partly accumulated within the Sound. Similar accumulation is also evident in Owen Anchorage. This accumulation of phosphorus in Cockburn Sound and Owen Anchorage shows a seasonal pattern with the highest levels occurring in summer. It is most likely that the low levels in winter are a result of increased water exchange with the ocean. The importance of water movement to the nutrient status of Cockburn Sound is discussed below in greater detail (Section 5). Nitrogen levels in the Sound and Owen Anchorage are uniformly low and have a comparable range to that observed for the open coastal water and Warnbro Sound. Considering the large loads entering the Sound, (Section 3.2.9) the very low N:P ratios and the evidence from algal assays (Section 5.2) that nitrogen is limiting, it can be assumed that concentrations are maintained in the Sound at low levels because of the utilisation by phytoplankton. A similar conclusion was reached by Ryther and Dunston (5) for Moriches Bay, Long Island, and for the New York bight, and by Smith (32) for Kaneohe Bay, Oahu. For both NO_3 -N and NO_4 -N there is a suggestion of a winter build up. Chaney (7) measured phytoplankton productivities in Cockburn Sound at station 214 at monthly intervals from March 1978 to October 1978. She found that production rates over the winter period were a third of what they were at the end of summer. It is concluded that either light or temperature may limit phytoplankton production rates over the winter period and the build up in available nitrogen is consistent with this conclusion.

The very high levels of NO_3 -N in July, 1979 in Owen Anchorage may well have been due to the southward flow of riverine water from the Swan estuary, but this does not readily explain the high levels in Cockburn Sound, Warnbro Sound and at the coastal station. During this cruise a shallow layer of river water was observed to enter Owen Anchorage, but no evidence was obtained that it crossed Parmelia Bank into Cockburn Sound.

The cruise in July was preceded by a series of five very strong storms of between two and 12 hours duration over a total period of less than two weeks (Figure 4.16). It is, therefore, suggested that the high values of nitrate nitrogen in the southern end of the Sound at this time, resulted from sediment suspension under persistent high energy conditions and the release of nitrate to the water column. This would also explain the high value in Warnbro Sound. It is also likely that the high value of the coastal station is the result of Sound water being moved out through the north passage then southwards down the east coast of Garden Island. The weekly data for station 214 in Cockburn Sound (Figure 4.6) showed persistent high levels of nitrate over the later half of July and this is also consistent with this hypothesis. The importance of sediments to nutrient concentrations in the water is discussed in greater detail in Section 3.2.7.

The high peak of NH4-N in Cockburn Sound at the end of March 1978 (C.5) is considered to be a result of exactly the opposite phenomenon. That is, this very high value is the result of the accumulation of NH4-N due to very poor water movement. Cockburn Sound is the only place showing this sharp peak. The principal form of nitrogen discharged to Cockburn Sound is ammonia (Table 3.2). The high values of NH₄-N occurred in the south-eastern part of the Sound (as did_NO2-N) whereas chlorophyll a levels only reached a maximum value of 5 μ g/l and this occurred in the north-eastern part of the Sound arround Woodman Point. KNC were not discharging from 16 February through to 25 March, i.e., they started discharging only three days before the start of Cruise 5. As can be seen in Figure 4.16 the March cruise was preceded by almost two months of very quiet conditions. This and the Woodman Point Treatment Plant being the only source of nitrogen explains why the maximum chlorophyll a values occur in the vicinity of Woodman Point. For the three days preceding the cruise when KNC had been discharging

4.6 (Cont'd)

wind speeds were very low (Figure 5.5) and the accumulation of NH_4 -N in Mangles Bay is consistent with the expectation that at low wind speeds a separate gyre develops in the southern part of the Sound which would carry effluent from the CSBP/KNC outfall into Mangles Bay.

The only other data which show a strong seasonal pattern are the temperature data. Hodgkin and Phillips (33) found that surface water temperatures in Cockburn Sound follow the same seasonal cycle as air temperatures but with a more restricted range. As a result, the annual range varies slightly from year to year. The range and pattern of temperatures in Cockburn Sound during this study are within the range given by Hodgkin and Phillips for a period of eight years. They also found a slight lag in temperatures and a smaller range at the CSIRO 50 m station in comparsion with values in-shore. A lag was not evident at the Garden Island station but the overall range was less than that for Cockburn Sound, with temperatures being $1.5-2.0^{\circ}$ C higher than inside the Sound over the winter period.

The data obtained weekly from the station in Cockburn Sound and the one in Owen Anchorage show very clearly the same seasonal trends which were evident in the cruise data. These trends are evident at the two weekly stations despite the large and rapid fluctuations which occur in almost all parameters at both stations. The large and rapid fluctuations in concentration seen at both stations is thought to be a result of the combined effects of water movement, variation in nutrient concentrations in the water through chemical and biological interactions as well as variation in the loads discharged.

The other notable feature is the marked differences in the range of concentrations at each station, e.g. the range of PO_4 -P values at station 238 is comparable with that seen for Owen Anchorage and Cockburn Sound for the cruise data, whereas the range at station 214 is almost a magnitude of concentration higher. This can be ascribed to the close proximity of station 214 to the CSBP outfall (2.2 km) (Figure 4.1). The NH₄-N data shows a similar disparity in concentrations.

The chlorophyll a data show that at station 214 phytoplankton biomass is often very much higher than the maximum value for Cockburn Sound observed during the cruises (they are also higher than the individual station values obtained during the cruises). The highest value observed during the study was from a dinoflagellate bloom with a maximum value of 110 mg m⁻³ chlorophyll a in February, 1979. In is evident from the rapid fluctuations that take \overline{p} lace in the chlorophyll a data that periods of very high biomass are very short. There does appear to be a regular pattern of 30-60 day cycles where there is a gradual build up of chlorophyll a and then a sudden drop to a low level again. These cyclic patterns are also evident at station 238, although the range of values is much less. It is most likely that these changes in phytoplankton biomass, as observed at these two stations is the result of phytoplankton successions (section 2). The short term variation is a result of the movement of water past the sampling sites which have phytoplankton at slightly different stages of succession. Physical factors affecting dispersion and aggregation may also be important (Margalef (25)). This would also help to explain some of the rapid fluctuations seen in the concentrations of N and P. However, much more detailed study needs to be done if the reasons for these fluctuations are to be properly understood.

4.7 Conclusions

The observations and conclusions made above from the cruise data compare favourably with the weekly data collected at station 214 (Cockburn Sound) and station 238 (Owen Anchorage). This is important because under certain conditions, very rapid changes can take place in the overall concentrations of nutrients within the Sound (Section 5.4) as well as at specific locations. Both sets of data, one with a high temporal component (weekly sampling) and the other with a spacial component (cruises), show the same seasonal patterns.

Although there is a consistently high nitrogen load to Cockburn Sound from industrial effects ambient concentrations were low throughout the summer. An increase in concentration was seen over the winter period. The low summer values are thought to be due to continual uptake of nitrogen by phytoplankton. Over the winter period phytoplankton production rates drop with a subsequent drop in nitrogen uptake and an observed increase in ambient concentrations in the water. The build up in Cockburn Sound, but not in Owen Anchorage, is a result of poor exchange with the ocean (Section 5).

There are differences in phytoplankton biomass (measured as chlorophyll a) between the open ocean and Warnbro Sound, Owen Anchorage and Cockburn Sound. Maximum values are seen in Cockburn Sound. In Cockburn Sound at station 214 changes were large and rapid when measured on a weekly basis. Changes in Owen Anchorage at station 238 were more regular and the range of values much less. Both stations showed regular patterns of change which are thought to be a product of phytoplankton succession and water movement.





MEAN VALUES FROM FOUR DIFFERENT AREAS FOR EACH CRUISE



PO4-P AT STATIONS 238 & 214 SAMPLED WEEKLY



Figure 4.4



NH4 -N AT STATIONS 238 & 214 SAMPLED WEEKLY



NO_ + NO_ - N STATIONS 238 8 214 SAMPLED WEEKLY





DAY NUMBER

TOTAL INORGANIC NITROGEN AT STATIONS 238 & 214 SAMPLED WEEKLY



OTAL KIELDALL NITROGEN AT STATIONS 238 & 214 SAMPLED WEEKLY



DAY NUMBER

N:P RATIO AT STATIONS 238 8 214 SAMPLED WEEKLY





CHLOROPHYLL 9 AT STATION 238 & 214 SAMPLED WEEKLY



ATTENUATION COEFFICIENT AT STATIONS 238 & 214 SAMPLED WEEKLY



L.





PAR JE " AT STATIONS 238 & 214 SAMPLED WEEKLY





INORGANIC NUTRIENT CONCENTRATIONS AT COASTAL STATIONS OVER THE STUDY PERIOD



5. WATER MOVEMENT AND NUTRIENT DISTRIBUTION

5.1 Introduction

It has been shown that the nutrient and chlorophyll a levels in Cockburn Sound and Owen Anchorage are much greater than those in Warnbro Sound and nearshore, coastal waters (Section 4). It is suggested that there is a build up of nutrients in Cockburn Sound and to a lesser degree in Owen Anchorage. This build up is a result of the large nutrient additions being made to the Sound from two point sources and poor exchange of Cockburn Sound water with the open ocean.

The effects of internal circulation and water exchange on the levels of nutrients in the Sound and Owen Anchorage was assessed using maps of distribution of PO_{4} -P. It has been suggested above that nitrogen is limiting to phytoplankton in Cockburn Sound and is therefore rapidly taken up by phytoplankton. Orthophosphate, on the other hand, is discharged in large amounts and is used by phytoplankton in much smaller amounts than nitrogen. As a result it is available in excess and may therefore be used as an indicator of the distribution of nutrients from the CSBP outfall and the WPTP outfall, Ryther and Dunstan (5) have also used PO_4 -P as a tracer of pollution from duck farms in Moriches Bay, Long Island, and for sewage sludge dumped in the New York bight and its subsequent movement along the eastern seaboard. Maps of PO4-P distribution in Cockburn Sound and Owen Anchorage for each of the cruises have been assessed and the distribution patterns compared with predicted water circulation patterns for the period of each cruise by a numerical model.

5.2 Methods

Mapping -Mapping of the PO₄-P concentrations was done using a computer programme, SYMAP, Version 5.20 developed by the Laboratory for Computer Graphics and Spatial Analysis, Graduate School of Design, Harvard University.

The programme is provided with details of the map outline, the co-ordinates of data-points (sampling stations) and the value for each data point. In this case the mean of the values at each of the three depths sampled at each station was used. SYMAP uses these data to interpolate the values at intervening locations, basing these interpolated values upon the values of and the distances to the other data points. A contour line is then "drawn" by differential shading of the areas between the contour lines using different symbols and overtyping. The contour lines connect all locations having the same value. The contour lines shown on the map are for specified values and values are assumed to smoothly vary over the interval between any two adjacent contour lines forming a continuous surface.

The maps show five evenly distributed contour intervals between the minimum and maximum data values.

Circulation Model -

The internal circulation of Cockburn Sound has been described in terms of a numerical model by Steedman and Associates (29). The model was developed as part of the Cockburn Sound Study. The model is depth integrated and wind-driven. For wind speeds greater than 5 m s⁻¹ it

5.5 (Cont'd)

The second group is characterised by the highest PO_4 -P concentrations occurring along the eastern coast of the Sound, extending well north of the CSBP outfall, and sometimes also south into Mangles Bay. Cruises 2, 4 and 5 fit into this group.

The third group is made up of cruises 1, 3 and 9. Cruises 3 and 9 took place during periods when CSBP was not discharging, and Cruise 1 less than 24 hours after discharge recommenced. No specific pattern is evident.

The consistency of patterns for the first two groups of cruises is readily explained by the water circulation within the Sound as predicted by the Steedman model. The first group (Cruises 6, 7 and 8 took place during the winter of 1978 when the weather was dominated by low pressure systems and the passage of cold fronts. The second group of cruises (Numbers 2, 4 and 5) took place when summer weather conditions prevailed, i.e. seabreezes or persistent easterlies occurred daily as a result of high pressure systems located in the Bight. The third group is for cruises which took place when CSBP was not discharging. No consistent pattern could be seen.

It is clear that the changes in phosphorus distribution that took place over the period of 18-22 September 1978/Cruise 8a, 8 and 8b can be explained by the water circulation within the Sound as predicted by the Steedman model. This is also apparent for all of the cruises which took place when CSBP were discharging effluent. In fact the three sets of samples taken over the duration of Cruise 8 show that the pattern of phosphorus distribution is quite sensitive to even small increases in wind-stress (i.e. water movement). The results for Cruises 6 and 7 are also consistent with this conclusion.

The pattern for Cruise 7 is very similar to that already seen for Cruise 8, i.e. the movement of the highest concentrations presumably from around CSBP down into Mangles Bay with the development of a separate gyre in that region. The intrusion of low concentration marine water into the Sound along the eastern side of Garden 1sland, and the extension of slightly higher concentration water up along the east coast of the Sound in accord with the movement of the main gyre.

In the case of Cruise 6 it appears that the hydrological events which took place on the 15th are critical in explaining the observed pattern of phosphorus distribution even though sampling took place on the 16th-18th.

Cruise 6 is somewhat different in pattern with the highest concentrations of phosphorus being immediately south of CSBP but a band of medium concentration stretching out from the outfall across the Sound along the northern edge of Southern Flats. This pattern can be explained by the development of an anti-clockwise gyre on the morning of the 15th and its subsequent reversal on the 17th when sampling took place. The low values across the top of the Sound and down along the east side accounted for by the reversal of the normally anti-clockwise movement of the main gyre on the morning of the 15th. 5.4 Results

The depth averaged PO_4 -P concentrations for each of the nine cruises have been mapped and are shown in Figures 5.1 to 5.9. In addition Table 5.1 gives the dates of the cruises and relevant meteorological information both prior to and over the duration of each cruise. Each cruise took two, three or four days to complete. The station locations in the diagrams are marked by a set of symbols. All stations sampled on the same day have the same symbol with the relevant date indicated in a legend.

An important consideration when assessing the effects of the hydrology on the PO_4 -P concentration patterns is the possible difference between the sequence of instantaneous predictions made by the model and the composite picture of the PO_4 -P concentrations obtained over the two, three or four day sampling period.

During the September, 1978 cruise (NO. 8, Figure 5.8) an opportunity arose to test the response of the Sound to an increase in wind stress and the resultant effects on the distribution of PO_4-P .

This cruise commenced on 18 September and a number of stations were sampled at the southern end of the Sound. However, on the night of the 18th and during the 19th the passage of a low pressure system and a small front led to poor weather that made it impossible to sample on the 19th. On the 20th sampling resumed and the stations sampled on the 18th were re-sampled. Sampling of the other stations was completed on the 21st. On the 22nd the stations sampled on the 18th and 20th were re-sampled. The resultant PO_4 -P concentrations for each of these days are shown in Figure 5.10.

First of all, it should be noted that the strong winds on the 19th were not high enough to be recorded as a storm event (Figure 4.16), although they did prevent safe sampling at sea. Even so a marked change in the distribution of PO_4 -P concentration did result. On the 18th the pattern was as expected with highest concentrations being located around the CSBP outfall and extending outwards radially. This is in accord with the prediction by the hydrological model that there was no significant water movement. Subsequent to the passage of the front on the 19th the model predicted the development of a small gyre reaching up into Careening Bay from Mangles Bay. The phosphorus distribution from the sampling on the 20th shows a distribution which fits this pattern, with highest concentrations in Careening Bay.

Two other interesting changes in the phosphorus distribution also took place between the 18th and 20th and can be explained by the model. Firstly, values along the inside (east side) of Garden Island on the 20th have dropped to those seen for the waters north of the Sound. This is explained by the intrusion of marine waters from across Parmelia Bank with the development of a gyre down along the east coast of Garden Island. Secondly, there is the extension of water up and around Woodman Point. This is consistent with the predicted development of the main gyre out into Owen Anchorage around Woodman Point.

By the 22nd when sampling again took place a pattern almost exactly the same as that seen on the 18th was evident. This is also consistent with the predicted decay of wind-driven water movement within the body of the Sound.

5.5 (Cont'd)

However, there is evidence of an extensive northwards intrusion of marine water along the east coast of Garden Island from the southern openings during both Cruises 2 and 5. This supports Steedman's suggestion that, factors other than wind forcing are important components in the patterns of exchange and circulation under low energy conditions (but not necessarily to the magnitude of exchange).

Despite Steedman's caution with respect to the possible role exchange across the southern opening could play in terms of total exchange under low energy conditions the evidence from the PO_4 -P distribution data considered here is that most exchange under low energy conditions takes place across the northern opening.

The net exchange during low energy conditions is not very great. Exchange of any magnitude only occurs during the passage of winter low pressure systems which have an estimated annual occurrence of only 28 per cent. The exchange effects of winter low pressure systems are clearly demonstrated by the orthophosphate data from Cruise 1, 3 and 9 (Figure 5.1, 3 and 9). For 24 days before the start of Cruise 1, 12 days before the start of Cruise 3, and 10 days before the start of Cruise 9 the CSBP plant had not been discharging. Although very low values of phosphorus were observed during Cruise 1 (August, 1977) only a small drop in values was evident for Cruise 3 and 9 (December 1977 and November 1978 respectively). As can be seen in Figure 4.16, there was a much higher incidence of storm events preceding the August 1977 cruise than the other two cruises. Cruise 1 is particularly important as it shows the almost complete removal of high levels of PO4-P from the Sound once the CSBP discharge had been stopped. Weekly sampling at station 214 (Figure 4.3) shows a high value for PO_4 -P at the end of July but a progressive drop throughout August. This is consistent with the extensive storm activity in August (Figure 4.16) and the termination of CSBP's discharge at the end of July. The termination of CSBP's discharge during the other two cruises (C3 and C9) did not have as dramatic an effect as that seen in Cruise 1 and this is due to the weather patterns having been dominated by high pressure systems in the Bight on both occasions. As a result, water circulation was slow and exchange very poor.

The occurrence of maximum PO₄-P values in the southern part of the Sound, i.e. Mangles Bay, is a characteristic feature of the winter pattern (Cruises 6, 7 and 8). This would indicate that the Mangles Bay area is the least affected ("flushed") and that almost all exchange takes place across the northern opening.

It can be seen that the factors affecting exchange rates between Cockburn Sound and open ocean are critical to the build up of nutrients in these waters. It was shown in Section 4. that there was a net accumulation of phosphorus and nitrogen in the Sound over the 1978 winter period. It may be that the number and frequency of storm events in any one winter period affects the extent of nitrogen accumulated in the body of the Sound. As N limits phytoplankton growth the overall level of biomass production during the subsequent summer maybe affected. 5.2 (Cont'd)

shows good correlation with current speed and water level records. At low wind speeds ($<5 \text{ m sec}^{-1}$) observations and model calculations would not correlate and this is attributed to density currents which are not included in the model (Steedman (29)).

The model was run by Steedman and Associates using real-time data for a number of days preceding each cruise as well as over the period of each cruise. The results from the model were expressed as stream lines where the distance between each stream line represents the passage of $200 \text{ m}^3 \text{s}^{-1}$ of water, i.e. the closer the stream lines are together the greater the volume of water being displaced.

In the streamline plots the direction of water movement is indicated by the arrows. The size of the arrows is incidental to the rate of water movement. The wind data presented in the same diagrams was recorded at the FPA tower, Fremantle.

5.3 The Oceanography of Cockburn Sound

Before discussing the predicted water circulation during the cruises and the observed patterns of nutrient distribution a number of features need to be noted about the oceanography of Cockburn Sound. These features were derived from the analysis of current metering data and dye studies, as well as the construction and proving of the model and are discussed in greater detail in Steedman (29).

- (1) Wind is the major factor influencing water movement within the Sound and exchange with the sea. Even so, the Steedman study showed that the total volume exchange between Cockburn Sound and the sea is very small. Only under strong wind conditions does the exchange rate increase, but even this it is relatively low. For an estimated 80 per cent of the time the volume transport is less than 1000 m³s⁻¹. Almost all exchange takes place across the northern opening.
- (2) Under low wind speeds (< ms⁻¹) which occur for up to 20 per cent of the time, density currents appear to dominate internal circulation, particularly along the eastern margin of the Sound. At wind speeds between 3-5 ms⁻¹ (occurring for about 27 per cent of the time) the water movement is in a transitional stage between density and wind driven motion.
- (3) The internal circulation pattern is dominated by a large, anticlockwise gyre in the main basin. Under storm conditions the gyre may reverse direction and flow clockwise. During calmer conditions the large gyre breaks up into a series of smaller gyres.
- (4) The Mangles Bay area often appears to have a closed circulation pattern with limited flow to the sea.
- (5) Another important gyre develops in the north-west of the Sound. The flow in this gyre is in the opposite direction to that developed in the main part of the Sound.
- (6) At low wind speeds, closed circulation patterns develop in the Owen Anchorage area. At higher wind speeds (<5 ms⁻¹) a current develops parallel to the coast in Owen Anchorage. The direction of water movement is dependent on wind direction. These parallel currents flow across the north of the Sound through Challenger Passage.

5.4 (Cont'd)

Cruise 6 (Figure 5.6), 7 (Figure 5.7) and 8 (Figure 5.8) all show similar patterns with the area of highest concentration to the south of the CSBP outfall in Mangles Bay. These cruises took place over the winter period and were all immediately preceded by storms producing strong movements of water in the Sound (Figures 4.21-4.23).

Cruise 7 was preceded by the passage of a very strong front on 24 July 1978, Cruise 8 by a milder front on 19 September 1978, Cruise 6 by a passage of a low pressure system over 14-15 May, 1979.

Cruise 2 (Figure 5.2), Cruise 4 (Figure 5.4) and Cruise 5 (Figure 5.5) all show the highest concentrations of PO_4 -P along the east side of the Sound. This pattern occurred during summer months when wind driven circulation is dominated by diurnal changes in wind direction, i.e. land/seabreeze system.

Cruise 2 and Cruise 5 (October 1977 and March 1978 respectively) show almost exactly the same pattern. Water movement is much slower, and overall concentrations much higher than during Cruise 4 (January 1978). This would suggest that exchange with the ocean across Parmelia Bank is minimal and concentrations within the Sound have increased. The effect of the Woodman Point sewage outfall can also be seen. There is an indication of the intrusion of marine water through the high level bridge of the Causeway into the south-western sector of the Sound. Overall values for Cruise 4 are much lower. This is consistent with the higher predicted rates of movement and subsequent higher exchange across the northern opening.

For two of the cruises, Cruise 3 (Figure 5.3) and Cruise 9 (Figure 5.9), CSBP had not been discharged for a number of days (14 and ten days, respectively). On a third cruise, sampling in the southern end of the Sound took place less than a day after effluent disposal resumed.

The Cruise 1 pattern clearly shows the highest concentration of PO_{4} -P located around the CSBP outfall and extending outwards radially. This is consistent with the models prediction of minimal water movement in the body of the Sound. This pattern is very similar to that seen for Cruise 8a (Figure 5.10).

No pattern is readily distinguishable for Cruise 3 (Figure 5.3) although for Cruise 9 (Figure 5.9) the pattern is similar to that seen for Cruise 6, 7 and 8 (Figure 5.6 to 5.8) and most closely resumbles that for Cruise 7.

 PO_4 -P distributions in Owen Anchorage for all cruises is characterised by much lower values than those seen in Cockburn Sound. A consistent feature for cruises 3, 4 and 8 is the movement of water around Woodman Point from Cockburn Sound into Owen Anchorage.

5.5 Discussion

The distribution of PO_4-P for the nine cruises can be placed into three groups. The first group is characterised by the highest PO_4-P concentrations occurring well south of the CSBP outfall in Mangles Bay. Some extension of intermediate concentrations up to the east coast can be seen. Cruises 6, 7 and 8 fit into this group. 5.5 (Cont'd)

When the duration of high speed winds is compared with Cruise 7 it is seen that the lower pressure system which passed over immediately prior to Cruise 6 had a duration of nearly 48 hours whereas the front which passed over prior to Cruise 7 was much shorter in duration.

The difference in wind patterns led to differences in hydrological patterns. Prior to Cruise 6 the low pressure system led to a well sustained movement of water whereas the front prior to Cruise 7 caused a more intense but short lived movement of water. In addition the patterns of water movement on each occasion were slightly different.

It would, therefore, appear that the sensitivity of the Sound's waters to wind stress is a product of both the intensity and duration of high energy conditions, and as a result so to is the pattern of distribution of the effluents from the different outfalls. It is also evident that internal circulation and the resultant patterns of effluent distribution is important to the extent to which nutrients are lost from the Sound and Owen Anchorage during periods of exchange.

Steedman and Associates (29) have classified the winds into a number of categories. For each wind pattern the exchange across the northern opening has been assessed using the model. Model-predicted exchange rates across the northern opening due to wind driven currents, excluding the influence of flows through the southern opening are shown in Figure 5.11, and summarised in Table 5.2, both of which are taken from Steedman (29).

It can be seen that low pressure systems, dissipating tropical cyclones and seabreezes have the largest effects on exchange in that order and that these have an estimated annual occurrence holding 64 per cent. Dissipating tropical cyclones have an estimated annual occurrence of less than one per cent and in this analysis can be ignored. Seabreezes have a predicted exchange rate of 0-300 m^3s^{-1} and this is of the same order of mangitude as the measured exchange through the southern opening.

However, Steedman points out that a total mass flux of 1000 m^3s^{-1} distributed across the opening between Garden Island and Woodman Point would require only a velocity of 1.5 cm s⁻¹. This velocity is well within the range of tidal currents, density currents, and the flow-through currents introduced by the southern opening. He concludes that under most circumstances the exchange through the northern opening due to windforcing may be expected to be comparable with but in no way to dominate that due to either forcing effects such as tide, density currents or flow through the southern opening. The phosphorus data for Cruises 2 and 5 took place when wind conditions were dominated by summer high-low pressure systems and the seabreeze/land breeze pattern had not established itself or been broken down. Circulation was slow. In contrast Cruise 4 took place in January 1978 when a strong seabreeze/land breeze system was operating, and as the flow paths show circulation was rapid. Not only was circulation fast but exchange across the northern end of the Sound was clearly taking place (as indicated by movement around Woodman Point into Owen Anchorage), with the resultant effect that maximum values of P were lower even in close proximity to the CSBP outfall. During Cruises 2 and 5, maximum values in the Sound were much higher, the WPTP outfall was visible (due to poor dispersion) and medium concentration values were even seen along the inside of Garden Island. The suggestion is that exchange across the northern opening is critical to nutrient build up in the Sound even though the total mass flux is of the same order of magnitude as that expected across the southern openings and that this exchange is wind driven.

5.6 Conclusions

The distribution of PO₄-P in Cockburn Sound fits into three basic categories.

There is a winter pattern which is a product of the passage of low pressure systems and these result in the most exchange ("flushing") with the ocean. The area least affected is the southern part of the Sound, i.e. Mangles Bay. As a result, maximum PO_4 -P values occur in Mangles Bay and decrease progressively northwards.

The other dominant pattern is characterised by the distribution of maximum PO_4 -P values along the east side of the Sound, extending both north and south of CSBP. This pattern is a result of the slow water movement within the Sound being dominated by a single large gyre moving anti-clockwise in the body of the Sound and frequently a series of additional smaller gyres.

The third category covers periods when no consistent pattern is readily distinguishable and it was discovered that during these cruises CSBP was not discharging.

The data confirms the prediction by the Steedman model that most exchange takes place across the northern opening during the passage of low pressure systems. At other times exchange still seems to occur predominantly across the northern opening.

It is possible that the annual frequency and duration of low pressure systems, because of their importance to exchange, is critical to the build up of nutrients in the Sound, particularly nitrogen, and the extent of the algal blooms over the next summer.

TABLE 5.1. CRUISE DATES & SUMMARY OF PROCEEDING AND PREVAILING WEATHER CONDITIONS.

NUMBER	CRUISE DATES	SYNOPTIC CONDITIONS* PROCEEDING CRUISE	NOPTIC CONDITIONS* SYNOPTIC CONDITION* OCEEDING CRUISE DURING CRUISE		
1	22-24 August 1977	Series ot cold fronts generated by passage of low pressure systems.	SW winds (5-10m 5 ⁻¹) occasional squalls.	KNC off for preceding 43 days; CSBP for 24 days.	
2	17-20 October 1977	High pressure system in Bight,above normal temperature.	Weak sea breeze pattern.		
3	5-7 December 1977	High pressure system in Bight.	Weak sea breeze pattern.	KNC off for 12 days preceding,CSBP off for 14 days.	
4	23-25 January 1978	Strong front on 14th, other- wise high pressure system in Bight.	Normal sea breeze pattern.	Bloom boundaries visible.	
5	29-30 March 1978	Stationary high in Bight, cold front on 27th.	Light easterly, less 5m 5-1.	KNC discharging only 3 days prior to 29th,off for 38 days.	
6	15-18 May 1978	Low pressure system and weak front, strong NW winds.	High pressure ridge, light easterly winds.		
7	26-27 July 1978	Series of low pressure systems & strong fronts.	High pressure ridge, light easterly winds.		
8a -	18 September 1978	High pressure ridge.	Light north-easterly winds.		
8b	22 September 1978	High pressure system.	Light north-easterly winds.	-	
9	14-16 November 1978	Stationary HP system in Bight, light NE winds.	HP system in Bight seabreeze developing.	CSBP/KNC off for preceding 10 days	

TABLE 5.2.

SUMMARY OF WIND-DRIVEN MODEL EXCHANGE RATES THROUGH NORTHERN COCKBURN SOUND, EXCLUDING THE INFLUENCE OF FLOW THROUGH THE SOUTHERN OPENING (from R.K. Steedman & Associates, 1979)

:

Cate- gory	Wind Pattern	Wind Speeds	Mai Speeds	n Gyre Direction	Month	Estimated Annual	Exchange Rate
		(ms ⁻¹)	(cms ⁻¹)			(%)	(m ³ s ⁻¹)
1	Sea breeze	0-15	<5-20	Anti-clockwise well developed	Oct-May	35	0-300
2	Winter high pressure system	∿5	<5-10	Anti-clockwise poorly developed	Apr-Oct	18	<
3	Low pressure system	5-20	<5-40	Poorly developed otherwise clockwise under storm conditions	A11	28	0-1800
4	Summer high-low pressure system	∿5	<5-10	Anti-clockwise poorly developed	Oct-May	5	250
5	Dissipating tropical cyclone	10-30	10-30	Clockwise well developed	Dec-Apr	<<1	0-700
6	Calms	<1-5	-	Model fails (cf. sections 6.2 and 8.2) density currents important	A11	4	
7	Other (Unclassified)	2-15	<5-15	Anti-clockwise most of time clockwise if north to north east wind	A11	10	

Ton 4

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Figure 5-4

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Figure 5.5



Figure 5-6











MODEL-PREDICTED EXCHANGE RATES ACROSS THE NORTHERN OPENING DUE TO WIND-DRIVEN CURRENTS, EXCLUDING THE INFLUENCE OF FLOW THROUGH THE SOUTHERN OPENING. Only 6-hourly values are plotted. (from Steedman & Assoc., 1979)

6. NUTRIENTS AND PHYTOPLANKTON

6.1 Introduction

It has been shown that Cockburn Sound, and to some degree Owen Anchorage, have high concentrations of phytoplankton in comparison with Warnbro Sound and the nearshore coastal waters. Cockburn Sound receives large loads of inorganic N and P from industrial effluents and sewerage. Restricted exchange of Cockburn Sound water, and to a lesser degree Owen Anchorage, has lead to the nutrient enrichment (eutrophication) of the Sound.

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The concentration of inorganic P is always high, yet the concentration of inorganic N is consistently low. N and P are utilised by phytoplankton at a ratio of between 10:1 and 20:1 and the ratio in the water of Cockburn Sound is always very much less than this. It is therefore concluded that phosphorus is available in excess and it is the availability of nitrogen which controls the amount of phytoplankton in the Sound and Owen Anchorage.

The relationship between phytoplankton and nutrient concentrations may be clearly demonstrated by looking at the distribution of chlorophyll <u>a</u> and inorganic N and P, for each of the cruises. Correlation coefficients between chlorophyll <u>a</u> and the nutrients for each of the cruises as well as the weekly data collected at stations 214 and 238 were calculated as a means of validating the above relationships.

A number of algal assays were run to test the hypothesis that nitrogen was the limiting nutrient.

6.2 Methods

The maps of chlorophyll a and inorganic N concentrations were obtained in the same way as those for inorganic P (Section 5.2).

The correlation coefficients were derived using the techniques of Nie et al (34) on The University of Western Australia Dec 10 computer.

The first two algal assays were run using additions of nitrogen and phosphorus, a combination of both, and a total enrichment media (Table 1, Appendix I). Water containing the natural phytoplankton assemblage from the two weekly sampling locations was used.

Two later assays were done using a number of combined levels of nitrogen and phosphorus only (Table 2, Appendix I). The first such assay was carried out with water from station 214, during a bloom, and the second with water from station 236, which was low in chlorophyll a.

These assays were done as bottle tests following the United States EPA method (Appendix I). Flasks were incubated in a glasshouse under the natural light regime, and submerged in water-baths which were maintained at the ambient temperature of the Sound at the time of sample collection.

6.3 Results

Maps illustrating the distribution of PO_4-P , NH_4-N , $NO_2 + NO_3-N$ and chlorophyll <u>a</u> for a summer cruise (C4), a winter cruise (C6) and during a period of no discharge by KNC or CSBP (C3) are shown in Figures 6.1-6.3 respectively.

6.3 (Cont'd)

The distribution of PO_4-P and chlorophyll <u>a</u> is identical in the summer cruise (Figure 6.1) but with the chlorophyll <u>a</u> being more patchy. The NH₄-N and NO₂ + NO₃-N are exactly the same and the highest concentrations coincide with one of the areas of highest PO_4-P and chlorophyll <u>a</u> concentration (above James Point).

The winter pattern (Figure 6.2) shows an almost identical distribution for all four parameters. The highest concentrations occurred at the southern end of the Sound on the east coast.

The summer pattern after CSBP and KNC had both not been discharging for a period of 10 days still shows maximum chlorophyll <u>a</u> concentrations along the east coast and in Mangles Bay, but peak concentrations of NH₄-N and PO₄-P occur in the vicinity of the WPTP outfall. A high concentration of PO₄-P and NO₂ + NO₃-N also occurs in Mangles Bay.

Significant correlations of nutrients with chlorophyll a for each of the cruises and the data collected weekly at stations 214 and 238 are given in Table 6.1. For all the cruises a very strong correlation (p < 0.001) was found between chlorophyll a and PO₄-P with one exception, Cruise 1 (the correlation here was still significant; p < 0.05).

For NH_4 -N and NO_2 + NO_3 , no consistent pattern was evident. Sometimes one or both are highly significant and sometimes neither.

For the weekly sampling no significant correlations were found at either station for any of the three inorganic nutrient parameters measured.

Results from the algal assays run in April 1978 and August 1978 are shown in Figure 6.4. Mean values for maximum biomass are given for each treatment. Porcella *et al* (35) considers that maximum biomass is a better indicator of limiting nutrients than maximum daily growth rates in batch assays. Maximum biomass has, therefore, been used in assessment of the results from this study. Significant differences between treatments were tested for using a one-way ANOVA. In each case significant differences were found and the Student-Newman-Kenlo procedure (Sokal and Rohlf (36)) was used to determine where the differences occurred. In the figures treatments which are not considered to be different are joined by the underlying bars.

In all cases the addition of P on its own had no significant affect. For station 214 water in April 1978 the addition of nitrogen did have a significant effect, and the addition of N and P, as well as the complete enrichment media had no greater effect, i.e. in this assay nitrogen is considered to be limiting. At station 238 in April, 1979, P on its own had no significant effect whereas N did. The addition of N plus P had an evengreater effect and this was the same as the result with the complete enrichment media.

In August for water from station 214, N and N plus P had a significant effect and the complete enrichment media had an even greater effect. At station 238, the addition of N and P on their own had no significant effect, whereas the addition of the two together did. The effect of the complete enrichment media was no greater than that of N plus P.

6.3 (Cont'd)

To obtain further information about the effects of different concentrations of nitrogen and phosphorus on the phytoplankton of Cockburn Sound, two assays were carried out at the temperature of the Sound using five levels of nitrogen and three of phosphorus. One of these was run in August 1978 (the same time as the second assay discussed above), the other in January 1979. The August 1978 assay used surface water from station 214 and the January 1979 assay used surface water from station 236 (Palm Beach jetty). Results are presented in Figure 6.5.

Two-way ANOVA tests (Sokal and Rohlf (36)) showed that on neither occasions was there a significant difference between phosphorus treatments, nor was there a significant interaction between phosphorus and nitrogen. However, highly significant differences (p <0.001 level) were found between nitrogen treatments on both occasions.

6.4 Discussion

The distribution of chlorophyll a over the summer period along the eastern side of the Sound and in Mangles Bay is the same as that found by Meagher and LeProvost (1).

From the maps of chlorophyll a and nutrient concentrations it can be seen that during both the summer and the winter patterns there is a close association between chlorophyll a and phosphorus and to a much lesser degree chlorophyll a and the two nitrogen parameters. The statistical analysis confirms this. However, there was no significant correlation of chlorophyll a with any nutrient parameter for the weekly sampling data. It has been seen that the phytoplankton at the two weekly stations are continuously undergoing some sort of species succession and as a result quite rapid changes are occurring in phytoplankton biomass and nutrient uptake rates (Section 2). At the same time, mixing and transport of the phytoplankton population are taking place. As a result no direct correlation can be obtained between changes in nutrients and changes in phytoplankton biomass. This is a well recognised problem in the sampling of phytoplankton (Margalef (25)).

However, the strong correlations found between chlorophyll <u>a</u> and nutrients in the cruise data demonstrates clearly the strong spacial relationships between the source of the nutrients and their use by phytoplankton to increase biomass.

From the algal assay results it is concluded that nitrogen was limiting at station 214 in April and also in August, but an unknown component in the enrichment media was secondarily limiting in August. On neither occasion was phosphorus limiting.

At station 238, nitrogen was primarily limiting in April, with phosphorus secondarily limiting. In August an interesting situation occurred where nitrogen and phosphorus on their own had no effect, yet when combined a significant effect was obtained. Consideration of the initial concentrations of nutrients showed that the initial nitrogen levels in all treatments was extremely high. This may be due to nitric acid contamination of the glassware or sample container. The initial N:P ratios for the control, +P, and +N treatment were 64:1, 2.4:1 and 378:1 respectively. Even so, no significant difference in the growth response of these treatments was seen. In the control and the +N treatment phosphorus can be considered limiting 6.4 (Cont'd)

(by default) whereas in the +P treatment nitrogen can be considered limiting. In the +N +P treatment a significant growth response was seen. The initial N:P ratio was still only 8.1 but nitrogen was now available as NH₄-N and not just as NO₃-N. The preferential uptake by plants of NH₄⁺ in preference to NO₃⁻² is generally recognised, for example, it has been shown by McCarthy *et al* (37) for phytoplankton in Chesapeake Bay that NH₄⁺ is used in preference to NO₃⁻².

The results obtained from these assays are similar to those obtained by Smith (32), Ryther and Dunstan (5), Thayer (8), and Axelrad and Bulthuis (38), i.e. that in coastal environments nitrogen is always limiting.

In the assays run using different concentrations of N and P only the nitrogen treatments had any significant effect. The initial N:P ratio within these assays ranged between 1 and 39.

Goldman (9) using continuous culture algal assays has shown that over the entire range of N:P ratios from 3.1:1 to 20:1 nitrogen is always limiting, and not phosphorus.

In the August assay a linear response to increasing concentrations of nitrogen is seen whereas in January this was not the case. The only difference between these two assays was that the August 1978 assay used water from an area with very high initial levels of chlorophyll <u>a</u>, i.e. during a bloom, whereas the January, 1979 assay used water from <u>an</u> area of low initial biomass.

It is possible that the type and extent of phytoplankton succession taking place at the time in the waters used for the assays accounts for this difference. Even so, the basic conclusion remains the same, nitrogen is always limiting regardless of the amount of phosphorus available.

6.5 Conclusions

The results discussed in this section do not allow the fine scale relationships between increases in phytoplankton biomass (measured as chlorophyll a) and ambient concentrations of nutrients to be determined. However, it is clear that high levels of chlorophyll a are strongly associated with high levels of phosphorus and to some degree the other nutrients. This has been illustrated by comparing spacial distribution of these parameters and confirming their association using correlation coefficients. It is therefore concluded that the occurrence of algal blooms in Cockburn Sound may be directly attributed to the discharge of nutrients by CSBP/KNC. The algal assays demonstrate that nitrogen is always limiting and this is consistent with the conclusions drawn from both the cruise data and the weekly sampling data (Section 3) as well as observations made elsewhere for coastal systems.

TABLE 6.1

SIGNIFICANT CORRELATIONS OF NUTRIENTS WITH CHLOROPHYLL <u>a</u> FOR EACH CRUISE AND THE WEEKLY DATA FROM STATIONS 214 & 238

CRUISE NO	DATES	CATEGORY	P04-P	NH4-N	NO3-N
C2	17-20.10.77	Summer	***	N.S.	***
C4	23-25,01,78	Pattern	***	**	*
C5	29-30.03.78		***	N.S.	***
	· · · · · · · · · · · · · · · · · · ·				
C6	15-18.05.78	Winter	***	N.S.	N.S.
C7	26-27.07.78	Pattern	***	***	N.S.
C8a	18.09.78		***	***	***
C8	20-21.09.78		***	N.S.	N.S.
C8b	22.09.78		***	N.S.	*
Cl	22-24.08.77	No Discharge	*	N.S.	*
C3	5-7.12.77	By KNC or	***	N.S.	*
C9	14-16.11.77	CSBP	***	N.S.	N.S.
1					

STATION	DATES	PO4-P	NH4-N	NO3-N
214	19.07.77 to 07.12.78	N.S.	N.S.	N.S.
238	19.07.77 to 07.12.78	N.S.	N.S.	N.S.

Levels of Significance

* = 0.01 ** = 0.001 *** = p ≤ 0.001 N.S. = Not Significant



Figure



NH_-N (µg/L)



CHLOROPHYLL <u>م</u> (المراح)





 $NO_3 - N (\mu g/L)$

DISTRIBUTION OF NUTRIENTS DURING CRUISE 6, DATE 15-18.5.78





RESULTS FROM ALGAL ASSAYS No 1 & 2

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Figure 6.4

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RESULTS OF ALGAL ASSAYS USING 3 ADDITIONAL LEVELS OF NITROGEN AND 2 ADDITIONAL LEVELS OF PHOSPHORUS

7. MANAGING THE PROBLEM

7.1 A Comparison of Cockburn Sound with Other Places

Table 7.1 allows a comparison of Cockburn Sound with other coastal areas and estuaries on the basis of ambient levels of chlorophyll a and nutrient concentrations. It is evident that Cockburn Sound is comparatively highly nutrient enriched and has high levels of phytoplankton standing crop under bloom conditions. A chlorophyll a value of 110 + mg m⁻³ was obtained during a dinoflagellate bloom in February 1979.

7.2 Public Usage of the Sound and the Effects of Eutrophication The use of fertilisers to enhance the fish productivity of natural or artificial poinds is a clear example that nutrient enrichment to some degree can have definite beneficial effects for man. In many water bodies, particularly lakes, eutrophication is a natural process, brought about by the shallowing of the water body as sediments accumulate and the available nutrients are more rapidly recycled (US EPA, (39)). This eutrophication phenomenon has been accelerated in man's recent history by his direct disposal of culturally generated wastes to such water bodies or an acceleration of natural sedimentation and nutrient adding process through clearing of land, fertilising crops, etc. The term eutrophication now has common usage to imply the nutrient enrichment (natural or otherwise) in lakes, rivers, estuaries and nearshore coastal areas.

The effects of cultural eutrophication are many and varied but are always associated with extensive changes in water quality. All to often this means a loss of amenity to some parts or all of the communities which use these waterbodies. There is both government and public concern as to the degree to which Cockburn Sound has become eutrophic. However, even in the light of our present understanding of the extent to which, and the reasons why, such high phytoplankton productivity is now occurring in the Sound, the question needs to be asked: "How much is too much?" The answer to this question lies not only in scientific assessment of the problem but the formation of opinions and value judgements by government, industry and the public at large.

The Cockburn Sound Recreation Survey (40), has shown that the Sound is not only an important recreation area for the most proximal of urban areas but is also an important recreational resource for other areas of the Perth metropolis, as well as being used by both country and city dwellers as a vacation area. In terms of actual usage the Survey showed that the available areas of the Sound were used for picnicing and sightseeing, swimming and sun-bathing, diving, fishing and boating. These uses may be categorised in the following way with respect to water quality as influenced by eutrophication.

- (1) Aesthetics picnicing, sight-seeing, sunbathing.
- (2) Primary Contact Recreation swimming and diving.
- (3) Secondary Contact Recreation fishing, boating and water-skiing.

In addition, the following other uses of the waters of the Sound may also be affected:-

- (4) Fishing both commercial and amateur
- (5) Maintenance of Wildlife both for scientific reasons as well as well as ensuring such activities as fishing.

7.2 (Cont'd)

The effects of excessive primary production as phytoplankton on these uses may be summarised as follows:-

- (1) <u>Aesthetics</u> -The production of objectionable colours, odours, or turbidity, an obvious lack of natural wildlife, i.e. birds, aquatic species, plant life; or an excess of clearly "unnatural" life forms.
- (2) Primary Contact Recreation -Poor clarity or visibility, strong colours, odours or taste. Greasy or oily feel, drying of plant material on the skin once out of the water, irritation of mucous membranes.
- (3) Secondary Contact Recreation -Aesthetic factors, poor clarity, poor "feel".
- (4) Fishing -Fish kills resulting from reduction of dissolved oxygen levels during the decline of a bloom, toxicity of shellfish feeding on dinoflagellate blooms or spores from the same thereby making them unfit for human consumption.
- (5) <u>Maintenance of Wildlife</u> -<u>Poor species diversity and rapid changes in dominant species, low</u> dissolved oxygen due to high BOD leading to suffocation, smothering of invertebrate filter feeders.

Those aspects of high algal productivity which directly influence passive and active recreational usage of marine waters cannot be easily quantified. Such factors as colour, odour, and feel are highly individualistic and may have emotive overtones based on people's general expectations with respect to how a place "should" be, e.g. high colour or turbidity are assumed to be "natural" properties of river water and, therefore, acceptable to swim in whereas the same high levels in seawater are not acceptable.

Even so, such quantifiable parameters as water clarity have been used in legislation as water quality criteria. For example, the Victorian State Environment Protection policy for the waters of Port Phillip Bay requires that "a secchi disk shall be visible to a depth of 2 m except in "learn to swim" areas where a secchi disk shall be visible on the bottom" in segments where primary contact recreation is considered a beneficial use to be protected. Hart (41) makes a similar recommendation.

The relationship between high levels of algal biomass and subsequent drops in dissolved oxygen, as yet, has not been quantified for the Sound. Such a relationship would be highly variable and very much dependent on local conditions at the time. Even so, during this study, dissolved oyxgen levels of 4.0 mg/l were recorded in conjunction with chlorophyll <u>a</u> levels of 35 μ g/l. The level of 5 mg/l is generally accepted as being the lower limit for aquatic species such as fish (Hart (41)).

In February and March this year (1979) dinoflagellate blooms were recorded in the Sound. These organisms cause the "red tides" characteristic of the Alaskan and Florida coasts as well as other regions in the world and may lead to paralytic shellfish poisoning. Not all species of the dinoflagellates that lead to "red tides" produce shellfish poisoning in humans. However, species identification is difficult and the problem is further compounded by the fact that maximum toxicity develops in the resting cysts and not in the mobile plants. The resting cysts not only form a source of further blooms under suitable conditions, but may also be accumulated in shellfish without any visual warning from the "red tide" phenomenon (Dale and Yentsch (42)). Clearly the possible occurrence if such toxic dinoflagellates requires further investigation in Cockburn Sound.

It may be said that Cockburn Sound is eutrophic to such a point that during the summer water quality may be seriously impaired with respect to primary and secondary contact recreation as well as passive recreation (aesthetics). This was clearly demonstrated in December 1975 by Meagher and LeProvost (in unpublished submission to the Cockburn Sound Study Group). Data collected during the present study showed that dissolved oxygen in the water may drop as a result of high algal productivity to marginal levels for the maintenance of species of fish. "Red tides" have also been noted in the Sound, however, their capacity to produce paralytic shellfish poisoning remains unknown.

No single level of phytoplankton biomass, as chlorophyll <u>a</u> can be given as an acceptable maximum for the above designated uses. A figure between 2-10 mg m⁻³ is suggested based on levels normally seen in nearshore coastal waters (Table 6.1).

7.3 Management Options

The results from this study show that Cockburn Sound is nutrient enriched. Two recent man-made changes in the Cockburn Sound environment could have contributed to nutrient enrichment.

- The effluent discharged jointly from the two industries on the eastern side of the Sound which contains high concentrations of nitrogen and phosphorus (CSBP fertiliser works and the Kwinana Nitrogen Company) were both established in 1968.
- In addition the discharge of primary treated sewage off Woodman Point, in the northern part of the Sound, commenced in 1966.
- Construction of a predominantly solid-fill causeway across the southern opening of the Sound, between the mainland and Garden Island, was commenced in January 1971 and completed in April, 1974 (Figure 1.2).

Any contribution the causeway may have made must now be accepted as a *fait accompli*. The only likely option open for the future control of algal blooms in the Sound will be the reduction of the nutrients introduced in waste discharges.

The CSBP/KNC and WPTP outfalls introduce to the Sound a total of 93 per cent of the inorganic nitrogen and 94 per cent of the total phosphorus load from point sources. Of these totals the CSBP/KNC outfall introduces 69 per cent of the inorganic nitrogen and 95 per cent of the total phosphorus. Nitrogen is always limiting to further phytoplankton growth in Cockburn Sound and the curtailment of the CSBP/KNC input of nitrogen would lead to a rapid reduction in the overall phytoplankton concentration of the Sound; as a result the frequency of occurrence and extent of visible algal "blooms" would be reduced. Almost all of the entire nitrogen load from the KNC/CSBP outfall comes from KNCs operations (Murphy (13)).

TABLE 7.1

COMPARISON OF NUTRIENTS AND CHLOROPHYLL A IN MARINE EMBAYMENTS AND ESTUARIES

<i>й</i>			T	•			
Estuary	PO ₄ - P (mg m ⁻³)	Total - P (mg m ⁻³)	NO ₃ -N (mg m ⁻³)	NO ₂ -N (mg m ⁻³)	NH4 -N (mg m ⁻³)	Chlorophyll <u>a</u> (mg m ⁻³)	Source
Port Phillip Bay (Aust.)	52 - 72	69 - 95	2 - 21(6)	- 1 - 4	20 - 80	0.14 - 4.36	46
San Francisco Bay	33 - 262		~0 - 800		<i>≓</i> °0 - 400	<1 - 100	. 49
Chesapeake Bay - Upper Bay (US coast)	13 - 59	26 - 65 31 - 62	50 - 1000			2 - 60 0.9 - 22.7	49
Coastal Waters: Australia South Africa California	1 - 60	<87				<1 - 7 1 - 4.5 0.4 - 11.3	49
Ocean Waters: South-west Pacific South-east Indian Atlantic	0 - 640 typically 32 - 96					$\begin{array}{r} 0 & - & 1.57 \\ 0.01 & - & 0.50 \\ 0.02 & - & 1.09 \end{array}$	49
Westernport Bay	2.5 - 12	10 - 29	1.4 - 32	.56 - 5.1	7.27	0.03 - 55	47
Parramatta River Inner Estuary	6.2 - 86.8		29.4	- 2016		17	48
Cockburn Sound	275 5 - 239	627 8 - 576	2 - 230		1 - 172	110+ 0.1 - 13.8	This Study
Owen Anchorage	60 1 - 73	240 14 - 300	2 - 360		2 - 43	8.5 0.3 - 5.9	This Study
Coastal Stn, (This Study)	1 - 17	1 - 136	2 - 34		2 - 20	0.1 - 1.3	This Study
Warnbro Sound	1 - 12	1 - 24	2 - 37		2 - 33	0.1 - 3.5	This Study

It is possible that should the KNC nitrogen load be diverted from the Sound then a substantial "recovery" could take place within a year, depending on winter weather conditions. A quantitative statement cannot be made at this point in time as to the precise extent of improvement until long term factors such as "flushing", as well as nutrient recycling, can be assessed.

The continuation of the CSBP/KNC discharge will lead to progressive deterioration as it is almost certainly leading to the build up of nutrients in the sediments in the southern part of the Sound as a result, nutrient recycling will play an increasingly more important role in the build up of phytoplankton.

A second consideration in the future management of the Sound is the increased load from the WPTP outfall. At present, any effect this outfall has is secondary to that from the CSBP/KNC outfall. The total point source nitrogen load to the Sound since 1955 and future projected loads are shown in Figure 7.1.

However, it is estimated that by 1982 when a new sewage outfall is commissioned that the daily nitrogen load (as NH_4 -N) will have risen from a present load of 1114 kg to 1420 kg per day. This is an eight per cent increase of the total load and should all other loads remain as they are now it will mean that the WPTP will be contributing 34 per cent of the total load. By 1991 the ammonium load is estimated to have increased to 3690 kg per day. This represents a 39 per cent increase on the total load and will mean that the WPTP will be contributing 58 per cent of the total. Increases are also expected in total phosphorus. The estimates for these and the NH_4 -N increases are shown in Table 7.1.

Even if the KNC discharge is diverted from the Sound, the total input load to Cockburn Sound by the year 2000, because of the increased load from the WPTP, will be approximately the same as it is now (Figure 7.1).

In either case the increase in WPTP loads will not only contribute to the degradation of Cockburn Sound but also Owen Anchorage.

Dispersion trials using PO_4 -P as a totally conservative parameter by the Steedman model indicate that both the CSBP and WPTP effluents move into Owen Anchorage. Examples of some of these predictions are shown in Figure 7.2. The data collected from both the weekly sampling and cruises indicate that there is a build up of phosphorus in Owen Anchorage, i.e. these data support the model's predictions that the water quality in Owen Anchorage is being affected by the WPTP. Further consideration needs to be given to the implications of the increased nutrient load from this source as well as the future placement of any substitute or additional outfalls.

TABLE 7.2

PREDICTED INCREASES IN N AND P LOADS TO COCKBURN SOUND FROM WOODMAN POINT TREATMENT PLANT.

	N	H ₄ -N (kg/d)	TOTAL P (kg/d)			
	1978	1982	1991	1978	1982	1991	
Load Woodman Point Treatment Plant (WPTP)	1 114	1 420	3 690	261	410	960	
Percent Total Load	29%	34%	58%	7%	10%	21%	
Total Load	3 786	4 092	6 362	3 766	3 915	4 465	
Increase on Present Load	-	306	2 576	-	149	699	
Percent Increase on Present Load from plant	-	8%	39%	-	4%	12%	





Figure 74



PRELIMINARY PREDICTIONS OF PO4-P DISPERSION, BY STEEDMAN MODEL FROM CSBP/KNC & WPTP OUTFALL USING A RATIO

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APPENDIX I. METHODS USED DURING THE NUTRIENT ENRICHMENT AND PHYTOPLANKTON SEGMENT OF THE COCKBURN SOUND STUDY

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1. INTRODUCTION

This Appendix gives details of the sampling and analytical methods used during the nutrient enrichment and phytoplankton segment of the Cockburn Sound Study. All of the laboratory sample preparation and analysis done during this segment of the Study are carried out in the Wetlands Study Group Laboratory at the Botany Department, The University of Western Australia. This group is led by Associate Professor A.J. McComb.

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2. SAMPLE COLLECTION

All water samples, whether for nutrient, chlorophyll <u>a</u> and phytoplankton analysis, are collected using plastic, 10 litre Niskin bottles made by General Oceanics.

Water samples for nutrient analysis are decanted into Whirlpacks (Namco) and stored on wet or dry ice and kept frozen on return to the laboratory until analysis are to be carried out.

Chlorophyll a samples are filtered on site. Approximately two litres of water is filtered under low vacuum pressure through a 7 mm GFC filter. The filter is air dried by increasing the vacuum, removed with forceps and folded into quarters. The filter is then wrapped in another GFC filter and stored in manilla seed envelopes. The exact volume filtered is noted and all envelopes stored in air tight plastic bags on ice in the dark. On return to the laboratory, a dissicant is usually added and the filters stored frozen until required for analysis.

Water samples for phytoplankton analysis are collected in 1000 or 500 ml plastic bottles to which a known volume of Lugols-methiolate preservative is added (36 ml/1000 ml - Anon, 1971). These samples are kept stored in the dark.

Details of sample collection for the algal assays and sediments analysis are given in the relative sections below.

3. ANALYTICAL METHODS AND QUALITY CONTROL

This section deals briefly with each of the main techniques used, attention being given to reliability.

3.1 Sample Handling

On return to the laboratory samples are deep-frozen until analysed. Ammonia and reactive phosphate are determined within one or two days of collection, the remainder within two or three weeks. Total nitrogen analyses have been delayed for longer periods early in the year because of the limitation in rate of distillation of digests.

Samples are thawed in a warm water bath just prior to analysis. The Whirl Paks are then shaken vigorously several times, slit open, and two aliquots transferred directly to reaction vessels.

3.2 Capability of Methods

3.2.1 Introduction

Here we consider the capabilities of some of the methods routinely in use in the laboratory. They are ammonium nitrogen, nitrate and nitrite nitrogen, kjeldahl nitrogen, phosphate phosphorus, total phosphorus, and chlorophyll a. Each method is discussed under the following headings: 3.2.2 Determination of Ammonia

Ammonia reacts with cyanurate and phenol, catalysed by sodium nitroprusside, to form the indophenol blue compound, which is then detected colorimetrically. Sample size 100 ml, providing two replicates of 50 ml each (Dal Pont *et al*, 1974.).

Working Range 7.0 - 960.0 μ gL⁻¹ - N

 $\frac{\text{Recovery}}{\text{at } 16.0 \text{ } \mu\text{gL}^{-1}\text{, } 114 \text{ per cent}}$ at 80.0 $\mu\text{gL}^{-1}\text{, } 120 \text{ per cent}$

McGlynn (1974) reports 97 per cent recovery at 12.0 μ gL⁻¹ and 95 per cent recovery at 28 μ gL⁻¹ using the slightly different Solorzano method (Major *et al*, 1972).

<u>Precision</u> At 12.0 μ gL⁻¹ the precision (2 σ) was 7.8 L⁻¹, over a range of 50 to 300 μ gL⁻¹ the precision was 10.4 μ gL⁻¹. McGlynn (1974) reported on the Solorzano method at 18.0 μ gL⁻¹.

Direction Limit 2σ 4.6 μ gL⁻¹

3σ 6.9 µgL⁻¹

3.2.3 Determination of Phosphorus

This method relies on the formation of a phosphomolybdate complex and its subsequent reduction to a highly coloured molybdenum blue by ascorbic acid. The blue colour is then detected colorimetrically (Major *et al*, 1972).

Sample size 40 ml, providing two replicates of 20 ml each.

Working Range 2.4 μ gL⁻¹ - 1000 μ gL⁻¹ PO₄ - P Strickland and Parsons (1972) and Anon (1971) report 1.0 to 1300 μ gL⁻¹.

Recovery For a range of concentrations from 6 to 150 μ gL⁻¹ the recovery was between 95 and 99 per cent.

Precision For a range 1 to $150 \ \mu g L^{-1}$ the precision (2 σ) was $1.6 \ \mu g L^{-1}$. Strickland and Parsons (1972) report a precision of 0.6 $\mu g L^{-1}$ at 9.3 $\mu g L^{-1}$ and 0.9 $\mu g L^{-1}$ at 93 $\mu g L^{-1}$.

3.2.4 Determination of Nitrate and Nitrite

Nitrate is reduced to nitrite by a copper-cadmium reduction column. The nitrite then reacts with sulphanilamide under acidic conditions to form a diazo compound, which then couples with n-1 naphthylethylene-diamine dihydrochloride to form a reddishpurple azo dye which can be detected colorimetrically. This method has been adopted for the autoanalyser (Technicon method No. 158 -71 W).

Sample size 10 ml providing two replicates of 5 ml each.

Working Range

 $2.7 \ \mu g L^{-1} - 500 \ \mu g L^{-1}$

- 1. Brief description of the principles of the technique.
- 2. Working range of the method without dilution of the sample. This is the range over which standards and absorbances are related linearly.
- 3. Recovery. A "spike" of known concentration is added to a sample and the amount "recovered", as determined by the method, noted. The recovery provides a qualitative estimate of the presence or absence of interfering substances. It does not enable the analyst to apply a correction factor to results of an analysis but it does give a basis for judging the applicability of the particular method to the samples being analysed. The parameters required are a blank, a range of standards, duplicate samples, and samples spiked with known amounts of the substance being measured. The spike should be added in sufficient quantity to overcome the limits or error of the method, but not allow the total in the sample to exceed the range of the standards. The blank absorbance should be subtracted from each of the determined values. A standard curve is then drawn, and from this the amount of substance present is calculated -

percent recovery = $\frac{SK - S}{K} \times 100$ where K = known spike, S = unknown sample, and

SK = sample plus spike.

4. Precision. This is the reproducibility of a result with the method is repeated on a homogeneous sample under controlled conditions, regardless of whether or not the observed values are displaced from the true value as a result of a systematic or constant error present throughout the measurement. Assuming a normal distribution the standard deviation (σ) is a measure of precision.

 $\pm \sigma$ = 68.27 per cent confidence

 $\pm 2\sigma$ = 95.45 per cent confidence

 \pm 3 σ = 99.7 per cent confidence

Precision can be expressed as $\pm 2\sigma$ of the mean of n replicates, but is sometimes as $x \pm 2\sigma \div \sqrt{n}$ (i.e. the standard error of the mean), or as per cent.

5. Detection Limit. The lower limit is governed by the precision of the method. The limit of detection should be taken as 3σ where σ is measured for amounts near to the detection limit itself. That is, the amount present should be just significantly different from a blank determination. However, both 2σ and σ are quoted in the literature (Anon. 1971; Strickland and Parsons, 1972), and so both are given here.

The following points should be borne in mind:

- 1. Our laboratory uses 1 cm path length cells.
- 2. Recoveries were done on duplicates of samples with standard deviations averaged over 6-10 samples.
- 3. Detection limits were done on three replicate samples taken from Station 234 in Cockburn Sound.

3.2.4 (Cont'd)

Technicon quote $1.4 - 2000 \ \mu g L^{-1}$, and the USA EPA (anon, 1974) 50 - 10,000 $\mu g L^{-1}$. The higher levels can be achieved by changing pump tubes and using shorter pathlength flow cells, but have not been required in our present work.

Recoveries

 $0 - 50 \ \mu g L^{-1} - 101 \ per \ cent$

 $50 - 500 \,\mu g L^{-1} - 96 \, per \, cent$

Precision

 $0 - 10 \ \mu g L^{-1} - (2\sigma) \ 1.8 \ \mu g L^{-1}$

Detection Limit

2σ - 1.8 μgL⁻¹ 3σ - 2.7 μgL⁻¹

Technical quote $1.4 \ \mu g L^{-1}$

Column efficiency The ability of the reduction column to reduce all the NO_3^- to NO_2^-

Reduced $NO_3 - N$ Reduced $NO_2 - N$ 0 - 50 $\mu g L^{-1}$ - 95 per cent 50 - 500 $\mu g L^{-1}$ - 99 per cent

3.2.5 Determination of Total Phosphorus

Organic phosphorus is mineralised with concentrated perchloric acid, then a total orthophosphate determination is done. The digestion is carried out in 25 x 200 mm test tubes heated in a block digestor (Anon, 1971; McGlynn, 1974) manufactured by Prototype Equipment, Murray Road, Welshpool.

Sample Size 40 ml, providing two replicates of 20 ml each.

Working Range 15.6 μ gL⁻¹ - 1000 μ gL⁻¹ PO₄-P

Recovery at 50 μ gL⁻¹ - 90 per cent

at 50 - 250 $\mu g L^{-1}$ - 98 per cent

Precision $2\sigma - 10.4 \ \mu g L^{-1}$

Detection Limit $2\sigma - 10.4 \ \mu g L^{-1}$

 $3\sigma - 15.6 \,\mu g L^{-1}$
3.2.5 (Cont'd)

The digestion step has increased the level of variability and accordingly the detection limit. Problems with variable heating in the block digestor lead to a range of normalities in the final digest, which sometimes exceeded the required range for optimal colour development resulting in inaccurate determinations.

3.2.6 Determination of Kjeldahl Nitrogen

Organic nitrogen is converted to NH_4^+ by digestion in concentrated H_2SO_4 in the presence of a mercury catalyst, using a block digestor. Prior to June 1978 the ammonia was recovered from an aliquot of digestate by distillation, and determined colorimetrically using the cyanurate method (anon, 1971; Atkins, 1978).

The precision of this method was poor for the low levels of nitrogen encountered in the majority of samples handled by the laboratory. Since June 1978 the following Technicon Auto Analyser method has been adopted. An aliquot of digestate is put through the autoanalyser and the ammonia determined by a colorimetric method in which an emerald-green colour is formed by the reaction of ammonia, solium salicylate, and sodium hypochlorite, catalysed by sodium nitroprusside (Technicon method No. 329 - 74 W/B). The reaction pH is critical and some problems have been encountered in balancing the acidity of the digests with the buffer used in the analyser. The problem is aggravated if the acidity of the digests varies too much because of uneven heating on the block digestor.

Sample size 40 ml, providing two replicates of 20 ml each.

There is no information for recoveries and precision to date. However, some preliminary detection limits have been worked out by digesting a range of standards from 0 to $1800 \ \mu g L^{-1} \ NH_4-N$. This showed the lower end of the working range to be somewhere near $200 \ \mu g L^{-1}$; the overriding problem is that the blank absorbance is too high in relation to the sample absorbance, so that at levels less than $600 \ \mu g L^{-1}$ the reproductability decreases as a result of this. The obvious solution is to digest a larger volume of sample, and other steps are being taken to reduce the blank absorbance.

3.2.7 Determination of Chlorophyll a

A known volume of water is filtered through a GFC filter (pore size 1.2μ). The filter is then stored in the dark in a deep freeze until the extraction can be done. The filter plus phytoplankton is then ground and extracted in 90 percent acetone. The optical density of the extract is determined using the spectrophotometer. From this chlorophyll <u>a</u> and phaeophytin are calculated (Strickland and Parson, 1972).

Working Range

This depends on the volume of water filtered.

Precision

at 20 μ gL⁻¹ chlorophyll <u>a</u> (2 σ) 4.2 μ gL⁻¹ at 3 μ gL⁻¹ chlorophyll <u>a</u> 0.6 μ gL⁻¹ 3.2.7 (Cont'd) at $5 \ \mu g L^{-1}$ phaeophytin (2 σ) 2.8 $\mu g L^{-1}$

at $0.5 \mu g L^{-1}$ phaeophytin $0.2 \mu g L^{-1}$

3.3 Interlaboratory Comparison

3.3.1 Orthophosphate

Two sets of samples were collected in Whirl Paks; one set was analysed in the Botany Department, and the other sent to Mr. N. Dyson, CSIRO, Marmion, Western Australia.

Samples size 28. Range of concentration 10 to 300 $\mu g L^{-1}$. The mean difference was 3.2 $\mu g L^{-1}$.

3.3.2 Nitrate

Similarly, two sets of samples (n=26) were collected and one set sent to each laboratory. For the range of concentration 1.4 to $12.0 \ \mu g L^{-1}$ the mean difference was $2.1 \ \mu g L^{-1}$. Although this correlation was not entirely satisfactory, the techniques at the two laboratories differed, and the one at CSIRO was designed with a higher detection limit than that in use here.

3.3.3 Total Phosphorus

Comparison with Government Chemical Laboratories (Plan Street, Perth) gave the same result, $20.0 \ \mu g L^{-1}$, for a single sample.

3.4 General Comments

A more complete programme of inter-laboratory comparison involving more than one other laboratory would be of great benefit to this laboratory and the research projects it supports.

The foregoing data on method performance are somewhat tentative, and more detailed analyses are being made. However, the detection limits and precision should not be compared too closely with those given in the literature. The laboratory is at present processing samples in batches of 50 and 100 and sometimes more, and this results in a reduction of precision. If necessary, detection limits and precision can be improved by handling samples in smaller batches and using longer path length cells. When designing sampling programmes attention must be given to the level of precision required to give validity to the data, with respect to trends and background noise.

4. PHYTOPLANKTON COUNTING AND IDENTIFICATION

The membrane filter method is used for both counts and identification

A cellulose nitrate filter (Gelman, 0.45μ pore size, 13 mm diam.) is placed in a filter holder (Millipore "Swinnex-13") attached to a hand operated vacuum pump. An aliquot of sample is drawn through the system under a pressure not exceeding 150 mm Hg (0.2 ATM), followed by a rinse with distilled water. This serves two purposes: to wash any organisms adhering to the pipette on the filter; and to prevent the formation of salt crystals. The volume of sample used is dependent on cellular density, and ranges from 2 ml at the height of a bloom to 100 ml for some Owen Anchorage samples. The filter is then placed on a clean dry slide on a hotplate for about 15 minutes, and mounted in immersion oil. This technique is a modification of Steel (1969). The slides are examined under a phase contract microscope with the same slides being used for counts and identification.

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APPENDIX I.

TABLE I.1

NUTRIENT ADDITIONS MADE TO SAMPLE WATER FOR EACH ASSAY TREATMENT

Treatment	Nutrient Used	Additional Amount Added
С	-	-
Р	KH ₂ PO ₄	300 µg -P/1
N	NH4NO3	700 µg -N/1
NP	KH2 PO4 NH4 NO3	300 μg -P/1 700 μg -N/1
EM	KH_2PO_4 NH_4NO_3 FeNaEDTA $CuSO_4$ $ZnSO_4$ $CoCI_2$ $MnCI_2$ Na_2MoO_4 $Na_2S_2O_3$ Thiamine HCl Biotin Vitamin B ₁₂	300 μg -P/1 700 μg -N/1 0.050 mg/1 Fe 0.005 mg/1 Cu 0.010 mg/1 Zn 0.005 mg/1 Co 0.100 mg/1 Mn 0.005 mg/1 Mo 225 μg - S/1 0.1 mg/1 0.5 μg/1

TABLE I.2

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DESIGN AND CONCENTRATIONS USED IN MULTIPLE LEVEL N + P ALGAL ASSAYS

	С	Nı	N ₂	N ₃	N4
C	-	+ _ `	+ -	+	+ -
P ₁	-	+	+	+	+
	+	+	+	+	+
P ₂	-	+	+	+	+
	+	+	+	+	+

Pı	Ħ	150 μg/l	KH2PO4
P ₂	æ	300 μg/l	$\rm KH_2PO_4$
Nı	=	175 µg/l	$\rm NH_42NO_3$
N ₂	=	350 μg/l	$\rm NH_42NO_3$
N₃	=	525 µg/l	$NH_4 2NO_3$
N4	=	700 μg/1	$NH_4 2NO_3$



EFFECT OF DCMU ON MEASUREMENT OF CHLOROPHYLL a USING IN-VIVO FLUORESCENCE

Figure I-1

APPENDIX II

Means, Standard deviations, and ranges for the stations in the four geographic areas for each cruise (ref. Figure II.1 over).

CS - Cockburn Sound (22 stations)

OA - Owen Anchorage (5 stations)

WS - Warnbro Sound (1 station x 3 samples)

GI - Coastal station
To west of Garden Island (1 station x 3 samples)

The statistics were derived by using the depth averaged means for each station in the same geographic area.

In the tables the data are shown thus:-

mean (standard deviation) range from — to



CRUISE NO.

PO₄-P (µg/1)

LOC'N	1	2	3	4	5	6	7	8	9
C.S.	19(27)	63(38)	50(11)	50(25)	72(31)	50(37)	53(39)	68(38)	46(11)
	6 - 239	5 - 220	21 - 115	9 - 101	8 - 197	10 - 153	12 - 155	17 - 221	15 - 79
0.A.	4 (2)	35 (6)	39 (7)	57 (6)	35 (3)	14 (6)	11 (4)	28(10)	21 (1)
	1 - 6	30 - 60	20 - 60	49 - 73	30 -39	9 - 29	4 - 18	18 - 46	18 - 28
W.S.	6 (2)	4 (1)	5 (1)	4 (1)	3 (1)	9 (1)	6 (2)	9 (1)	3 (1)
	3 - 10	2 - 6	3 - 7	3 - 5	1 - 5	8 - 11	3 - 10	8 - 12	2 - 6
G.I.	6 (0)	<1 (0)	5 (1)	3 (2)	5 (2)	12 (1)	7 (2)	7 (0)	6 (3)
	5 - 7	1 - 2	3 - 8	3 - 7	1 - 8	8 - 17	5 - 9	7 - 8	3 - 12

CRUISE NO.

TOTAL PHOSPHORUS $(\mu g/1)$

LOC 'N	1	2	3	4	5	6	7	8	9
C.S.	28(27)	85(39)	56(12)	60(34)	110(80)	63(42)	100(57)	76 (40)	60(12)
	8 - 145	30 - 189	33 - 92	15 - 128	11 - 576	15 - 208	10 - 131	16 - 182	28 - 89
0.A.	16 (2)	59 (9)	53(14)	66(11)	90(63)	38 (8)	70(48)	27(11)	36 (6)
	14 - 19	35 - 78	27 - 75	50 - 90	34 - 300	21 - 60	32 - 164	14 - 49	29 - 44
W.S.	21 (5)	18 (<1)	13 (3)	22 (6)	8(10)	25(14)	99(86)	26 (5)	9 (4)
	14 - 30	17 - 19	7 - 10	15 - 33	1 - 35	12 - 50	15 - 241	23 - 29	9 - 13
G,I,	8 (2)	12 (<1)	8 (1)	18 (3)	5 (5)	37(42)	29(21)	16 (4)	5 (1)
	6 - 12	11 - 13	7 - 9	13 - 24	1 - 13	13 - 136	19 - 85	11 - 22	3 - 7

CRUISE NO.

NH₄-N (μg/1)

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LOC'N	1	2	3	4	5	6	7	8	9
C.S.	4 (3)	10 (9)	9 (4)	6 (2)	48(27)	11(10)	57(38)	5 (6)	7 (3)
	1 - 17	3 - 20	3 - 60	2 - 26	2 - 95	1 - 46	10 - 172	1 - 26	3 - 34
0.A.	5 (1)	6 (2)	10 (8)	6 (1)	13 (4)	13 (5)	27 (4)	9 (1)	5 (2)
	4 - 8	4 - 11	5 - 30	5 - 9	7 - 19	6 - 22	13 - 43	2 - 17	3 - 8
W.S.	4 (1)	5 (1)	8 (1)	5 (2)	12 (5)	8 (1)	7 (4)	14 (2)	7 (3)
	2 - 6	3 - 7	6 - 10	3 - 7	8 - 33	6 - 15	3 - 13	10 - 29	5 -14
G.I.	4 (1)	5 (2)	8 (1)	7 (3)	7 (2)	7 (1)	14 (4)	2 (1)	1 (0)
	3 - 6	3 - 12	6 - 9	3 - 20	2 - 13	6 - 8	8 - 19	2 - 9	3 - 6

CRUISE NO.

NO₃-N (μg/1)

LOC'N	1	2	3	4	5	6	7	8	9
C.S.	3 (2)	3 (2)	3 (1)	4 (2)	11 (5)	8 (6)	65(20)	6(10)	2 (1)
	2 - 4	2 - 15	2 - 7	1 - 16	3 - 26	1 - 42	35 - 230	2 - 17	1 - 5
0.A.	5 (2)	2 (0)	3 (1)	2 (1)	9 (2)	5 (2)	159(66)	4 (1)	2 (1)
	3 - 7	2 - 3	2 - 5	2 - 3	6 - 15	3 - 11	67 - 360	2 - 9	1 - 4
W.S.	2 (0)	2 (0)	3 (0)	2 (1)	5 (0)	4 (0)	19(12)	2 (0)	2 (1)
	2 - 3	2	2 - 3	2 - 4	2 - 10	3 - 6	5 - 37	1 - 3	2 - 4
G.I.	10 (2)	2 (0)	2 (1)	2 (1)	3 (1)	10 (1)	31 (3)	2 (1)	2 (0)
	.7 - 11	2	2 - 3	2 - 4	3 - 4	7 - 15	24 - 34	2 - 8	2

CRUISE NO.

CHLOROPHYLL <u>a</u> (mg/m^3)

LOC'N	1	2	3	4	5	6	7	8	9
C.S.	2.9(1.0) .9 - 5.5	4.8 (3.1) 0.4 - 10.2	1.8 (0.9) .5 - 4.0	3.1 (2.3) .1 - 9.4	1.8 (1.0) .3 - 6.6	2.7 (2.0) .1 - 7.5	3.8 (0.2) .8 - 13.8	4.2(2.4) .3 - 12.5	2.4(1.3) .3 - 9.3
0.A.	3.7(1.5) 1.6 - 5.4	4.2 (.9) 2.9 - 6.0	$ \begin{array}{r} 1.2 \\ (0.3) \\ .3 - 3.2 \end{array} $	3.0 (0.6) 2.2 - 4.0	$2.4 \\ (1.2) \\ 1 - 4.8$	1.0 (0.3) .6 - 1.6	3.4(2.5) 2.0 - 5.2	3.8(0.6) 2.9 - 5.9	1.2 (0.5) .3 - 2.5
W.S.	1.2 (0.2) .9 - 2.4	.3(.1) .2 - 1.0	0.3 (0.1) .16	1.2(0.9) .6 - 3.5	0.7 (0.2) .2 - 1.0	0.9 (0.2) .7 - 1.1	2.6 (.3) 2.2 - 3.0	.2(.6) <.13	.3(.1)
G.I.	0.4 (0.1) .17	0.2 (0.0) 0.1 - 1.0	0.1 (0.0) .12	0.3(0)	0.5 (0.3) .2 - 1.3	0.5 (0.1) .1 - 1.2	0.6 (0.2) .29	0.3 (0.2) .27	0.4 (0.5) <.1 - 1.0

CRUISE NO.

N:P RATIO

LOC'N	1	2	3	4	5	6	7	8	9
C.S.	.64 (.45)	.48 (.20)	.51 (.18)	.53 (.27)	1.81 (0.70)	1.06 (.97)	6.54 (3.17)	.29 (.22)	.43 (.15)
0.A.	2.17 (.36)	.57 (.19)	.75 (.55)	.33 (.06)	1.37 (.34)	3.98 (2.84)	45.66 (37.13)	1.5 (.8)	.88 (.21)
W.S.	3.13	3.62	4.47	4.92	12.00	3.14	10.76	3.4(.7)	8.24 (3.4)
G.I.	1.29	44.6(26)	4.33	7.89	5.00	28.5	17.37	2.6(.7)	3.02 (1.62)

ATTENUATION CO-EFFICIENTS (E (m^{-1}))

LOC'N	1	2	3	4	5	6	7	8	9
C.S.	.10 (.04)	.10 (0.03)	.13 (.06)	.12 (.03)	.15 (.05)	.15 (.03)	.16 (.03)	.16 (.02)	.13 (.03)
0.A.	.15 (0.02)	.14 (0.03)	.11 (.02)	.20 (.08)	.14 (0.2)	.15 (.01)	.31 (.15)	.20 (.01)	.11 (.03)
W.S.	.11	-	.06	-	.08	.12 (.02)	.15(0)	.10 (0)	.06 (0)
G.I.	0.7	-	.06	.06	.08	.07	.08 (0)	.05 (0)	.06 (0)

CRUISE NO.

TEMPERATURE ^OC

LOC 'N	1	2	3	4	5	6	7	8	9
c.s.	15.5 (0.4)	19.0 (0.7)	23	22.5	20.5	18.5	14.0	16.0	20.0
0.A.	16 (0.0)	19 (0.5)	22	22.5	-	19.0	14.0	16.0	21.0
W.S.	17	18.5	-	23	22	18	N.D.		20.0
G.I.	17	19.0	-	22	20	20	15	18.5	19.0