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Water for a Healthy Country

Biogeochemistry of the Coorong

Review and identification of future research requirements

Phillip W Ford

CSIRO

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Foreword

The environmental assets of the Coorong, Lower Lakes and Murray Mouth (CLLAMM) region are currently under threat as a result of the ongoing changes in the hydrological regime of the Murray–Darling River. While a number of initiatives are underway to halt or reverse this environmental decline, such as the Murray-Darling Basin Commission’s Living Murray initiative, rehabilitation efforts are hampered by the lack of knowledge about the links between flows and ecological responses in this system.

As a component of the Water for a Healthy Country National Research Flagship, CSIRO has developed a collaborative research program with the aim of producing a decision-support framework for environmental flow management for the CLLAMM region. This involves understanding the links between the key ecosystem drivers for the region (such as water level and salinity) and key ecological processes (generation of bird habitat, fish recruitment, etc.). A second step will involve the development of tools to predict how ecological communities will respond to manipulations of the 'management levers' for environmental flows in the region. These include flow releases from upstream reservoirs, the Lower Lakes barrages, and the Upper South East Drainage scheme, and dredging of the Murray Mouth. The framework will attempt to evaluate the social, economic and environmental trade-offs for different scenarios of manipulation of management levers, as well as different climate scenarios in the Murray–Darling Basin.

The research program brings together several institutions as well as researchers from a range of backgrounds. CSIRO provides a core of expertise in the fields of hydrodynamics, biogeochemistry and socioeconomics. Knowledge about the links between ecological drivers and ecosystem responses will be developed with the CLLAMMecology research cluster, a partnership between the University of Adelaide, Flinders University and SARDI Aquatic Sciences supported by the Flagship Collaboration Fund.

This report is part of a series summarising the output from the Water for a Healthy Country Coorong, Lower Lakes and Murray Mouth program. Previous reports and additional information about the program can be found at www.csiro.au/csiro/channel/ich4.html.

Contents

Abbreviations

anions	Cl^-, HCO_3^-, SO_4^{2-}
Ca^{2+}	calcium ions
cations	Na^+, K^+, Ca^{2+}, Mg^{2+}
CFA	calcium-fluoro-apatites
Chl *a*	chlorophyll *a*
Chl *b*	chlorophyll *b*
Cl^-	chloride ions
CLLAMM	Coorong, Lower Lakes and Murray Mouth
CO_2	carbon dioxide
CO_3^{2-}	carbonate
DEH	Department of Environment and Heritage
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nitrogen
DNRA	dissimilatory reduction of nitrate to ammonia
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
DOP	dissolved organic phosphorus
DSC	dissolved salts calculated
DWLBC	Department of Water, Land and Biodiversity Conservation
FRP	filterable reactive phosphorus
HCO_3^-	bicarbonate
Mg^{2+}	magnesium ions
N	nitrogen
NH_4^+	ammonium

NO_2^-	nitrite
NO_3^-	nitrate
NO_x	oxides of nitrogen (sum of NO_2^- and NO_3^-)
P	phosphorus
PN	particulate nitrogen
POC	particulate organic carbon
SO_4^{2-}	sulfate
TKN	total Kjehldahl nitrogen
TOC	total organic carbon
TP	total phosphorus
USE	Upper South East

Acknowledgements

My colleagues in the Water for a Healthy Country Coorong, Lower Lakes, and Murray Mouth Project – Dr Perran Cook, Dr Evelyn Krull, Dr Sébastien Lamontagne, Dr Barbara Robson and Dr Ian Webster – provided most helpful critical and constructive reviews of an earlier version of this report. The thorough and most helpful review of the penultimate version of this report by Dr Ralf Haese (Geosciences Australia) is gratefully acknowledged.

Dr Michael Geddes (University of Adelaide) kindly collected samples within the Coorong for the total organic carbon (TOC) and dissolved organic carbon (DOC) measurements and provided information on the characteristics of the dominant phytoplankton species.

Summary

The South Australian Departments of Environment and Heritage, and of Water, Land and Biodiversity Conservation have been collecting data on water column chemistry at multiple stations in the Coorong since 1997. Initially the observations occurred every three months, and the frequency subsequently increased to monthly intervals. This report examines the data from 1997 to 2003 from the perspective of developing an understanding of the major biogeochemical processes controlling the availability of nutrients and pelagic primary production. (This approach is motivated by the need to understand how the basic biogeochemical behaviour of the Coorong can be manipulated to achieve the desired ecological outcomes of increased recreational fisheries and greater use by migratory birds).

For most of the study period, there have been strong seasonal gradients of salinity increasing southward along both lagoons of the Coorong. These gradients vary seasonally and arise from the combination of low rainfall and high evaporation together with limited inputs of freshwater from the Lower Lakes. Interpretation of observed temporal changes in nutrient concentration as arising simply from the operation of sources and sinks of dissolved nutrients is precluded by the changes in concentration due solely to evaporation.

Chlorophyll *a* (and the accessory pigment chlorophyll *b*) may be taken as a measure of primary producer biomass in the water column in the Coorong. The concentration of chlorophyll *a* shows a pronounced spatial variation increasing from the northern end to the southern end where concentrations exceed 100 μgL^{-1} for most of the observations. The nature of the principal pelagic primary producer(s) is, as yet, unknown. Most of the water column particulate organic carbon is embodied in the phytoplankton assuming that it is of Redfield ratio composition. There is more particulate nitrogen (N) and phosphorus (P) in the water column than required of Redfield composition material suggesting that there is additional N and P containing detrital material. The concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) all increase southwards along the Coorong faster than the salinity increases indicating that there are sources of these materials in the southern lagoon. There is considerably more DOC than particulate organic carbon in the water column.

In contrast to the relatively high concentrations of nutrients embodied in organic forms, the concentrations of bioavailable species – ammonia, nitrate, and phosphate are low – about half of all observations are below the minimum levels of analytical detection and the longitudinal concentration gradients (after taking account of evaporative concentration changes) are not nearly as pronounced as for the particulate or dissolved organic matter. This leads to the paradoxical situation of having a high phytoplankton biomass but low dissolved nutrient concentrations which appear insufficient to support the biomass production. This can only be resolved by postulating an extensive and tight cycling of nutrients between the organic and inorganic forms, or that the system is either light or nutrient limited and the rate of biomass production is much less than the theoretical maximum.

Many of the biogeochemical processes involved in the cycling of the limiting nutrients N and P are subject to the effects of changing salinity (and the concomitant increases in both sulfate concentration and sediment sulfate reduction to sulfide). Consequently changes in salinity through freshwater/seawater inflows or evaporation will have effects on nutrient availability quite apart from the nutrients introduced in the entering waters. Increasing salinity leads to the abiotic formation of low solubility phosphorus-containing minerals that are an irreversible sink for phosphate. The data suggests that calcite precipitation occurs under hypersaline conditions and additional phosphate is removed through adsorption/inclusion in the calcite crystals. This may be released if the calcite redissolves.

Many of the biogeochemical processes involved in nitrogen cycling occur in the sediments and are affected by the higher sulfide concentrations under elevated salinities. Both nitrification and denitrification are inhibited, while dissimilatory nitrate reduction to ammonia (DNRA) and nitrogen fixation are stimulated by sulfide. Consequently high salinity waters such as occur in

the southern lagoon will favour a high ammonium:nitrate ratio in the water column and an increase in organic nitrogen stored in detrital material, while low salinity waters arising from freshwater inflows are more likely to be dominated by nitrate and have significant losses of bioavailable nitrogen through denitrification. Algal mats have the potential to play an important role in the nitrogen balance of the Coorong but their spatial extent and response to changes in water levels and salinity are unknown.

Six areas where research could strengthen the scientific underpinnings of improved management of the Coorong have been identified. They are:

- quantification of nutrient fluxes and budgets
- extent and functioning of algal mats
- contribution of algal mats to the food web
- nature of the pelagic primary producers, and the scale of and constraints on pelagic primary production
- spatial variation and controls on dissolved phosphate and
- microbial reactivity of dissolved organic carbon, nitrogen and phosphorus.

1. Introduction

The Coorong is a highly diverse and dynamic ecosystem. Its diversity and dynamics are coupled – the changes in salinity and water levels driven by the interaction between changing sea level (Webster 2005), rainfall and evaporation, and the now infrequent major riverine (freshwater) inflows, produce a changing mosaic of permanently inundated areas and intermittently wetted and dried areas subject to varying salinities. The different inflow sources (Murray or Darling rivers, Upper South East [USE] drainage waters, Adelaide Hills flows via Lake Alexandrina and the sea) have their own dissimilar concentrations of particulate and dissolved nutrients, as well as differing salinity. This supply of water of varying nutrient content and salinity creates zones within the Coorong with differing biogeochemical and ecological characteristics. As a consequence, there are spatial and slowly varying temporal, differences in the relative abundance, growth rates and speciation of macroalgae, phytoplankton and zooplankton, as well as differences in the relative importance of microbial processes involved in the transformation of nutrients. While salinity is a major driving factor, there is no simple relationship between nutrient availability and salinity. Hence it is necessary to understand both salinity and biogeochemical impacts if we are to make realistic predictions of ecological outcomes arising from manipulation of inflows into the Coorong.

The biogeochemical functioning of the Coorong has received only limited attention with very little detail in the literature. This review aims to develop a biogeochemical description on how the Coorong functions. We draw inferences about the biogeochemical functioning of the system from the extensive database of observations of water column physical characteristics (summarised in Thomas & Lang 2003). We note that parts of the Coorong are, for at least part of the time, hypersaline and we rely on analogies between the Coorong and more intensively studied hypersaline systems elsewhere. Similarly we draw on analogies with estuarine and marine systems for other parts of the Coorong where this is appropriate as well as descriptions of systems subject to the episodic inputs of freshwater into marine systems in arid environments. Clearly there are limits to the extent we can definitively elucidate the main biogeochemical functions purely by inference from other systems. Within these constraints this report aims to provide an integrated interpretation of how the Coorong functions biogeochemically – describing the spatial patterns of nutrient availability, possible major controls on nutrient transformations, and the response of the pelagic primary producers that fuel the whole process.

The examination of the data against the background of the Coorong's unique characteristics leads to the recognition of specific topics where further research is needed if the evaluation of management options is to be firmly based on an adequate scientific understanding. We make suggestions of critical research areas at the end of this review.

2. Data sources

The water quality data used in this paper have been provided by the South Australian Departments of Environment and Heritage (DEH) and Water, Land, and Biodiversity Conservation (DWLBC). They are the product of a water quality monitoring program that was established by DEH in June 1997 and that has continued to the present. The motivation for the program was to establish baseline conditions in the Coorong before the start of releases of waters from the USE Drainage Scheme via Morella Basin and Salt Creek into the southern lagoon of the Coorong. The initial observations, covering the period June 1997 to December 1998 are summarised in a report from the Australian Water Quality Centre (1999). A subsequent report (Thomas & Lang 2003) extends the data coverage to June 2003, as well as giving guidance on the sample collection and preservation procedures used in the investigations and providing a statistical summary of the results.

Samples were collected at 12 sites along the Coorong (Figure 1) together with additional sites in Salt Creek, Blackford Drain, Fairford Drain and Morella Basin which provide data on the drainage inputs into the Coorong. The initial sampling was at approximately three-month intervals (June 1997 to December 1998). There is a one-year gap from December 1998 to December 1999 when the three-monthly sampling recommenced. Since February 2003, sampling has been at monthly intervals The parameters measured are:

- nutrients (ammonia, total Kjehldahl nitrogen [TKN], oxides of nitrogen [NO_x], total phosphorus [TP], filterable reactive phosphorus [FRP]and dissolved silica [DSi])
- turbidity
- chlorophyll *a* and *b* (Chl *a* and Chl *b*)
- major cations (Na^+, K^+, Ca^{2+} and Mg^{2+})
- anions (Cl^-, HCO_3^- and SO_4^{2-})
- heavy metals and
- electrical conductivity.

The dissolved salts calculated (DSC) was calculated from the complete chemical analysis of all the significant cations and anions. DSC is generally a more accurate measurement of salinity (mass of dissolved salts in unit mass of solution) than total dissolved solids [TDS]) determined by empirical relationships between conductivity and salinity, or by evaporating a known volume of filtered water to dryness. In addition, sediment samples were collected from the 12 sample sites in the Coorong on three dates between April 1998 and March 2002 but analysed for heavy metals only. Water samples were also analysed for pesticides. The heavy metal or pesticide data have not been used in this report.

The DEH data are the most systematic and extended water quality dataset extant for the Coorong. They are a valuable resource for understanding the coupled biological, chemical and hydrodynamic processes and their continuation will be an important element in assessing the effectiveness of management measures introduced in the future. A major gap in the total suite of Coorong data is the absence of water quality measurements of comparable spatial and temporal coverage for the Lower Lakes (Lakes Alexandrina and Albert). Some monitoring occurs along the margins of the Lower Lakes. The adequacy of this data for quantifying nutrient inputs into the Coorong from freshwater flows over the barrage is currently being assessed.

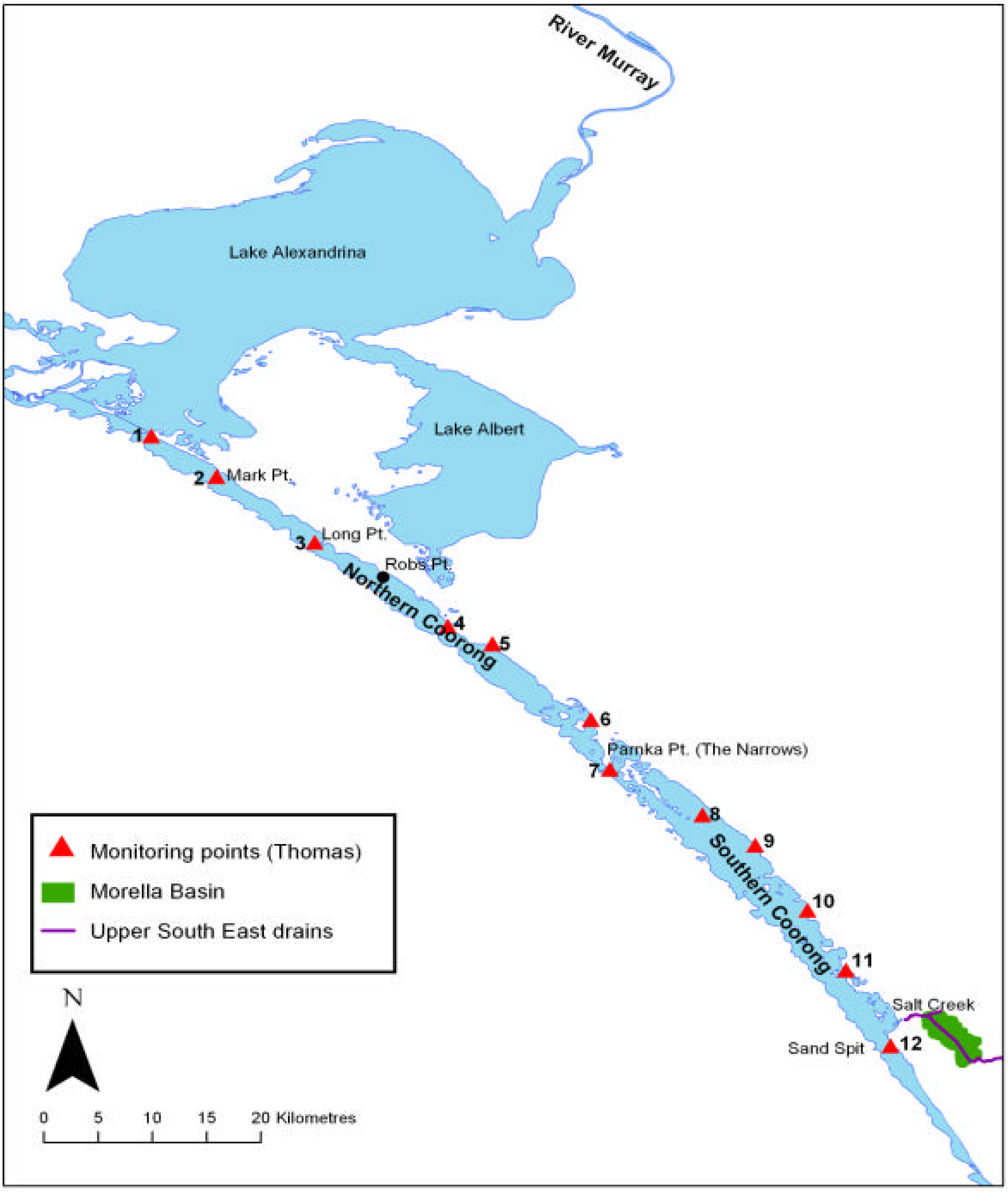

Figure 1. Water quality sampling sites within the Coorong.

3. Method of approach and data overview

The elements carbon, nitrogen, phosphorus, sulfur, silicon, iron and oxygen in a variety of different chemical combinations play a critical and determining role in biogeochemical cycling. We focus on describing the major biogeochemical processes that are involved in the cycling of these elements and the constraints under which they operate. Other trace elements such as manganese, zinc. molybdenum, selenium and the major cations (sodium, potassium, magnesium and calcium) are also critical to biochemical processes but, as the data for the trace elements are limited and some of the major processes involving the cations are covered in the discussion of the macro elements, these will not be dealt with separately in this review.

There are only limited data on primary production in the Coorong: chlorophyll *a* and *b* concentrations in the surface layer – a measure of the biomass of viable phytoplankton. These data are not, however, a measure of the rate of photosynthesis. Thus we only have estimates of the 'stock' of phytoplankton, not rates of their formation or removal.

One of the major characteristics of the Coorong is the wide range of salinities arising from the limited exchanges with either freshwater or marine sources coupled with the high evaporation rate. As a consequence, measured concentrations can change solely due to evaporation removing water from the system. To avoid perceiving these concentration changes as due to the operation of nutrient sources or sinks, in our discussion of dynamics of the concentrations of the main nutrients, we normalise the nutrient concentration by a conservative species such as the chloride ion. Thus when there is no production or consumption of the nutrient, the normalised concentration remains unchanged, but consumption appears as a decrease of the normalised concentration, while production is marked by an increase of the normalised variable.

3.1. Carbon

3.1.1. Organic carbon and primary production

In situ primary production is probably the principal carbon and energy source that supports the food web within the Coorong for most of the time. Inputs from the riverine side are too infrequent and have a too low concentration of readily metabolisable organic carbon to be a long-term (seasonal and longer) major contributor. Inputs from the sea also have a too low organic carbon concentration. The *Ruppia* spp. macrophytes are clearly an important potential contributor to primary production but quantitative data on their productivity and standing biomass are not available so their contribution is not discussed in detail here. There is, however, reliable anecdotal evidence that the relative abundance of the macrophytes in both lagoons has declined markedly over the past decade. Furthermore there has been a reduction in the seagrass coverage (predominantly located in the north lagoon). These changes are likely to have caused a shift in the dominant primary producer groups from macrophytes/seagrasses (plus attached epiphytes) to pelagic phytoplankton, microphytobenthic organisms, and algal mats. These changes are of profound ecological significance for the higher trophic levels such as fish and birds, but they may not be strongly reflected in the available data on the water column chemistry. There is certainly strong evidence of a large pelagic phytoplankton biomass.

The water column contains high concentrations (up to 150 μgL^{-1}) of chlorophyll *a* together with lower concentrations of the accessory pigment chlorophyll *b*. There is a clear spatial gradient of abundance of chlorophyll *a*, with the highest concentrations present in the southern lagoon and much lower concentrations in the northern lagoon. In the southern lagoon, the water column contains floating macroalgae (Phillip Ford pers. obs.) as well as small (~2 µm diameter) pelagic phytoplankton (Mike Geddes pers. comm.) identified as a prochlorophyte (Peter Baker pers. comm.). This identification is consistent with the presence of the chlorophyll *b*. While most of the pelagic chlorophyll *a* is probably embodied in these two groups of organisms, their contributions to net primary production is not defined and we have a poor understanding, at present, of the relative significance of light and nutrient limitation on the overall productivity of the pelagic organisms. These uncertainties about the dominant primary producers (see also later section on algal mats) underlines the need for investigations to define relative contributions of the different producers more thoroughly.

There is some seasonality (Figure 2) in the abundance of the phytoplankton with the highest concentrations occurring in early spring and late summer. In spring of 2000, there was a barrage release and this is associated with a marked decrease in chlorophyll *a* in the southern lagoon and a brief but substantial increase in chlorophyll *a* in the northern lagoon indicating an increase in pelagic phytoplankton. This response was especially marked at the Stations 1 and 2 which would be most affected by the freshwater inputs. This increase may represent the delivery of phytoplankton from the Lower Lakes or enhanced in situ production due to the supply of additional bioavailable nutrients.

The high chlorophyll *a* concentration in the southern lagoon would be expected to lead, in the absence of limitations, to high rates of primary production. Using a chlorophyll *a*-specific photosynthetic rate of 0.75 mg C (mg Chl *a*)$^{-1}$ h^{-1} (Reynolds 1984) and assuming a 10-hour day and no light limitation, the concentration of carbon and chlorophyll *a* embodied in the phytoplankton would double in the lagoon in approximately seven days. This would require the uptake of approximately 120 µgL^{-1} of P. Such standing concentrations of bioavailable P have not been measured in the water column. This discrepancy suggests that the pelagic phytoplankton growth is constrained by nutrient (specifically P) availability. It is possible that P uptake and the production of bioavailable P are tightly coupled and that the inferred high rates of primary production can be sustained while the measured bioavailable P concentrations remain low. However, the chlorophyll *a* concentration changes very slowly over a seasonal time scale, and it is necessary to invoke a mechanism to rapidly remove the phytoplankton and release the P for this process to be feasible.

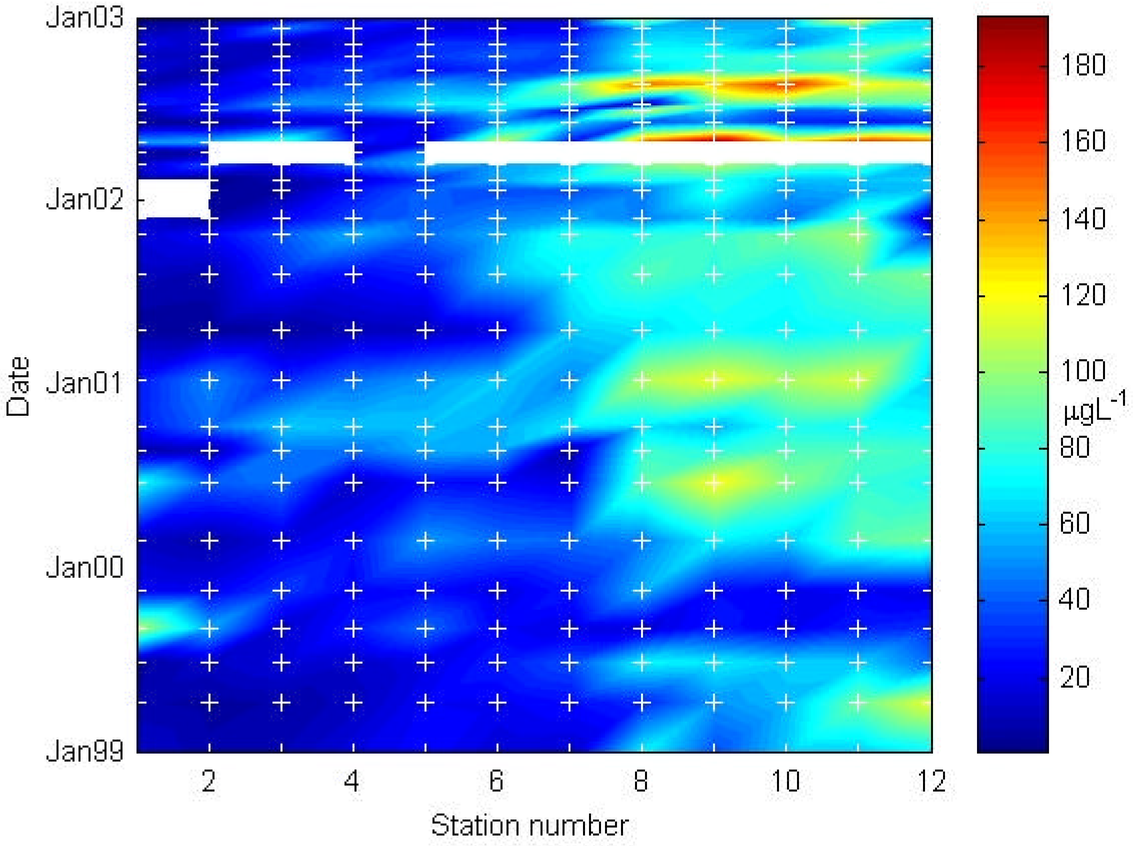

Figure 2. Spatial and temporal variation in pelagic chlorophyll *a* concentrations in the Coorong.

There are limited data (Figure 3) on the overall abundance of particulate and dissolved organic carbon (POC & DOC). Dissolved organic carbon is clearly the dominant organic carbon fraction (DOC:POC ~7:1) in the water column of the Coorong and there is a clear increasing DOC gradient from the north to the south lagoon. Most of the POC can be accounted for by the phytoplankton, based on the measured chlorophyll *a* concentration and using a C:Chl ratio of 50:1 (Reynolds 1997). In this dataset and that for the following two years (sampled in July 2005 and July 2006) (Phillip Ford unpubl. data), the DOC:DIC (dissolved inorganic carbon) ratio increases southwards along the Coorong indicating that DOC is being produced, not merely concentrated by evaporation. Inputs from the USE cannot account for this increase.

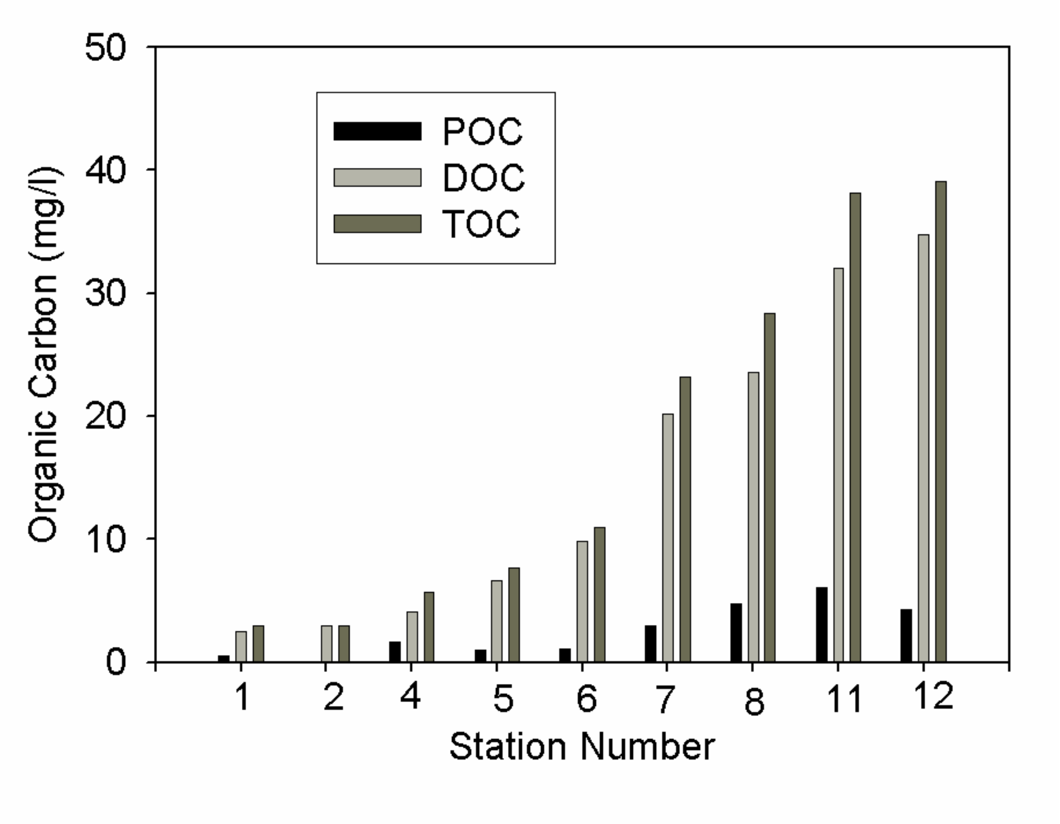

Figure 3. POC, DOC, and TOC concentrations at DEH monitoring stations along the Coorong – July 2004. Station 1 is the northern-most station and station12 is the southern-most at Salt Creek.

The measured concentrations of TKN and TP are considerably higher than would be consistent with all the N and P being incorporated by pelagic phytoplankton of Redfield composition ($C_{106} N_{16}P_1$) suggesting that there are other particulate and dissolved fractions that contain significant amounts of N and P present in the water column. The presence of high concentrations of dissolved organic nitrogen (DON) noted below is consistent with this observation.

Dissolved organic carbon (as opposed to particulate organic carbon) is the dominant form of organic carbon in the water column and increases in concentration from the northern to the southern lagoon. The southern lagoon DOC concentrations (~35 mgL^{-1}) are relatively high compared to most estuarine waters (Cauwet 2002). The probable source of this material (note that it is a complex mixture of individual organic compounds) is organic matter lost from the pelagic phytoplankton and secreted by the algal mats (see Section 3.4). The composition and reactivity of this material is unknown although potentially it could be a major food source for bacteria (Azam et al. 1983). Bacterial breakdown of this organic matter, can occur in either the water column or the sediments, and would release bioavailable forms of N and P as well as refractory dissolved organic matter.

Photochemical processes can play a role in splitting refractory organic materials into more reactive smaller fragments as well as in mineralising nitrogen, phosphorus and sulfur (reviewed in Mopper & Kieber 2002) contained in this material. The inorganic forms of released N, P and sulfur (S) are available for immediate uptake by the phytoplankton. There is thus efficient recycling of these elements. The smaller organic fragments produced can be more readily metabolised by bacteria, while the larger fragments are less biologically reactive than the parent material. The relative importance of this process especially the production of unreactive organic material is unknown in the Coorong. The relative size/rates of the various pathways producing and using the photofragmented DOC have important implications for the overall structure of the food web. Where the photofragmentation products are readily metabolised, they will be rapidly incorporated into bacteria creating an ample food source for protists and small flagellates which consume the bacteria, with the energy available to be passed up the food chain. Where the fragmented material is unreactive, it will just accumulate. DOC concentrations will build up, but little of the photosynthetic energy encapsulated in the initial fragmentation products will be available for transmission up the food chain. The food chain will be then primarily based on grazers of the pelagic phytoplankton. The cycling of DOC in this (hypothetical at present) model of the Coorong is shown diagramatically in Figure 4.

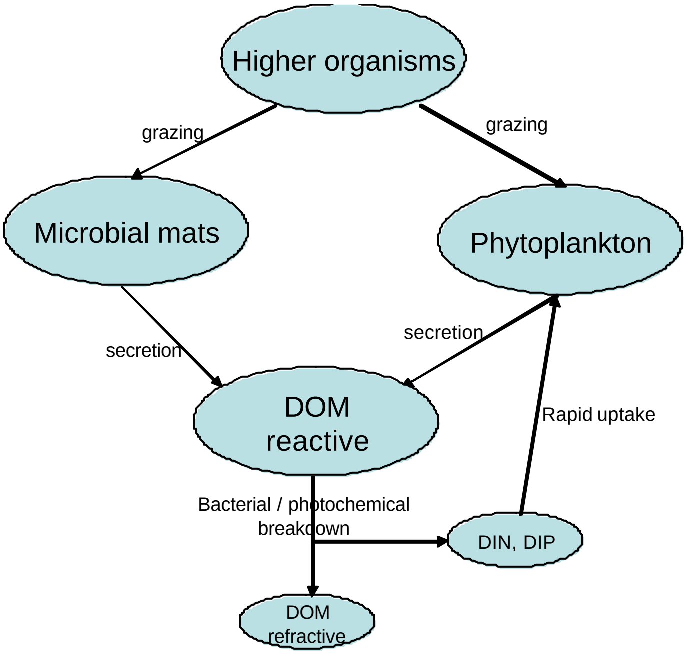

Figure 4. Sources and transformations of DOC proposed to be operating in the Coorong. (Diagram: courtesy Dr Ralf Haese, Geosciences Australia)

3.1.2. Inorganic carbon

We consider here total dissolved carbon dioxide (CO_2), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). These species are in chemical equilibrium and their relative proportions depend on the pH and ionic strength of the water. Bicarbonate is the dominant species at the pHs reported in the Coorong. Carbon dioxide is used by the phytoplankton and the algal mats for photosynthesis while the carbonate is precipitated with calcium as calcite/aragonite when the appropriate solubility product is exceeded. Although sea water is supersaturated with calcite the precipitation is not immediate. The precipitation process is inhibited by magnesium ions (Mg^{2+}) and by the presence of organic matter, and the supersaturated state can persist for extended times.

The formation of carbonate minerals has important implications for the availability of nutrients in the Coorong, in particular P. Interaction between calcite and orthophosphate leads, initially, to the adsorption of phosphate to the calcite and aragonite surfaces, and subsequently, to incorporation into the calcite crystal lattice (Froelich et al. 1980). This material can be subsequently transformed into apatite (summarised in Lopez & Morgui 1992). There is thus a biogeochemical feedback system operating with these components. The CO_2 concentration affects the amount of calcite, and thus the sequestration/availability of inorganic phosphate. Under non-light limiting conditions (and no nitrogen limitation) the phosphate concentration is the principal control on photosynthesis which consumes dissolved CO_2. As the salinity increases the equilibrium concentration of dissolved CO_2 decreases due to salting out (Rumpf et al. 1994).

In the Coorong all these processes come into play and interact with the variations in salinity in time and space. As the salinity increases due to evaporation the ionic product $a_{Ca^{2+}} \cdot a_{CO_3^{2-}}$ (where a_i is the activity of species i) will increase initially (at high salinities the activity may decrease to ion pairing and other effects) due to the increase in concentration. Consequently the ionic product further exceeds the solubility product (which is also changing due to changes in the ionic composition and strength) and ultimately calcite precipitation occurs. The amount of material that precipitates does not however correspond fully to the excess relative to the solubility product.

The available dataset does not allow us to fully explore these issues but we can gain insights into the significance of these processes by examining the variations in the alkalinity data at all stations (Figure 5), and the calcium (Ca^{2+}) ion concentration (Figure 6) as a function of the increase in salinity. The Ca^{2+} concentrations (Figure 6) have been normalised by Mg^{2+} concentration to facilitate direct comparison with earlier published work on the carbonate system in hypersaline systems (Lazar et al. 1983; Lazar & Erez 1992). The general trend of the alkalinity variation is for an initial linear increase in total alkalinity as the degree of evaporation (calculated from the in situ salinity relative to seawater) increases. However, at degree of evaporation ~2, the data 'flattens out' indicating non-conservative behaviour arising from the removal of alkalinity by the precipitation of calcium carbonate ($CaCO_3$). At higher degrees of evaporation ~6 (Lazar & Erez 1992) calcite precipitation ceases and the gradient of the line increases back to the initial slope indicative of conservative behaviour. The high concentrations characteristic of this second phase of conservative alkalinity are not observed in the main body of the Coorong, but are likely to occur in drying pools and the pore water in sandy sediments as the water retreats during an evaporation phase.

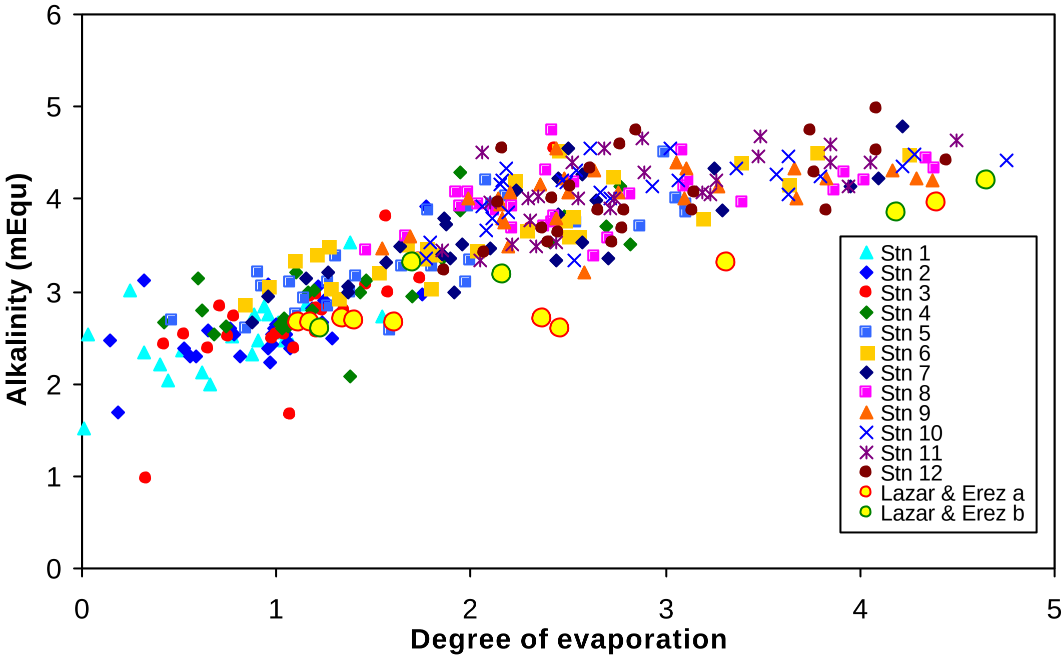

Figure 5. Variation in alkalinity in the Coorong as a function of degree of evaporation. Comparison data for a marine saltern (Lazar & Erez 1992) in winter (yellow circles with black boundaries) and summer (yellow circles with red boundaries) is shown also.

The normalised Ca^{2+} concentration (Figure 6) slowly decreases as the degree of evaporation (here measured as chloride ions [Cl^-] concentration) increases. This is due to the precipitation of calcite and is consistent with the variation in total alkalinity discussed above. At high Cl^- concentrations (>90 000 mgL^{-1} Cl^-~x4 seawater) the removal of Ca^{2+} becomes much more marked due to the precipitation of gypsum ($CaSO_4.2H_2O$) and consuming sulfate from the water column. This is consistent with the data showing that the Ca^{2+} concentration reduction is most pronounced at the southern end (Station 12) of the Coorong.

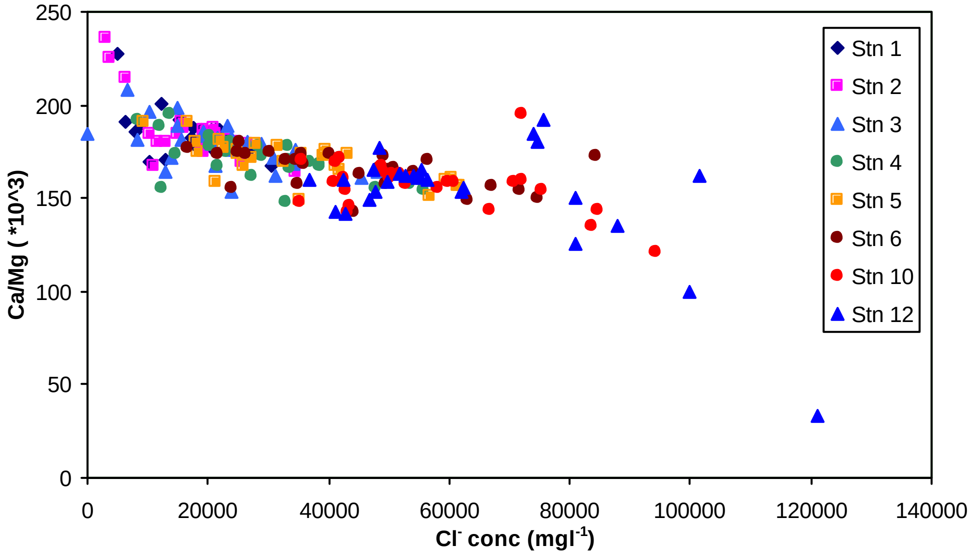

Figure 6. Variation in Ca^{2+}concentration (normalised to Mg^{+2} concentration) as a function of salinity (shown as Cl^- concentration) at different stations along the Coorong.

3.2. Nitrogen

3.2.1. Nitrogen components, cycling, and spatial distribution

Nitrogen occurs in a variety of chemical forms in differing proportions in aquatic systems. The principal components are: ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-). Nitrate and nitrite are often analysed together and reported as oxidised nitrogen (NO_x) – an approach adopted in the DEH dataset. These three species are all soluble in water and are denoted collectively as dissolved inorganic nitrogen (DIN). Nitrogen also exists in chemical combination with carbon and other elements as proteins, amino acids, nucleotides, etc. and cellular detritus and secretions. The soluble nitrogen-containing components are designated as dissolved organic nitrogen (DON) while the solid (insoluble) components are called particulate nitrogen (PN). The available Coorong analytical dataset consists of measurements of NH_4^+, NO_x, and total Kjeldahl nitrogen (TKN). This last parameter encompasses all nitrogen-containing species (both solid and dissolved, inorganic and organic) except NO_x. However, these analytical data are insufficient to infer the magnitude of the PN or DON components. Limited measurements (Phillip Ford unpubl. data) indicate that the DON component is a considerable fraction of the TKN and increases southwards along the Coorong. The DON component appears to be generally larger than the particulate component (PN).

From the biogeochemical perspective, DIN is the key factor in understanding the primary productivity and coupling between the physical processes affecting the Coorong and the ecological response. The DIN is essential for the primary production that drives the whole food chain – its availability determines potential growth and if excessive leads to eutrophication and conditions harmful to many aquatic organisms, and changes in functioning of the system. The relative proportions of $NH_4^+$and NO_x exert a strong influence on the phytoplankton composition in the water column. The sea and the Murray (when it flows) deliver varying amounts of DIN, DON, and PN into the Coorong. Generally, concentrations of NO_x are low throughout the Coorong (more than 50% of the observations < detection limit) and do not increase on moving down the Coorong. In contrast, while ammonia concentrations are also frequently below detection limits at the northern end of the Coorong (changes over time in analytical detection limits in the dataset somewhat obscure this trend), there are intermittent observations of high ammonia concentrations in the southern lagoon that are well above the level that would be produced purely by evaporative processes. This suggests that there is a source of ammonia in the southern lagoon.

The chloride normalised TKN data (Figure 7) indicates that there is considerable temporal variation in TKN and suggests that within this pattern of temporal changes there is a marginal increase of TKN towards the southern end of the Coorong. Isolated inflow events (station 1-left hand side of Figure 7) appear as high normalised concentrations as the chloride content (the denominator in the normalisation) is very small.

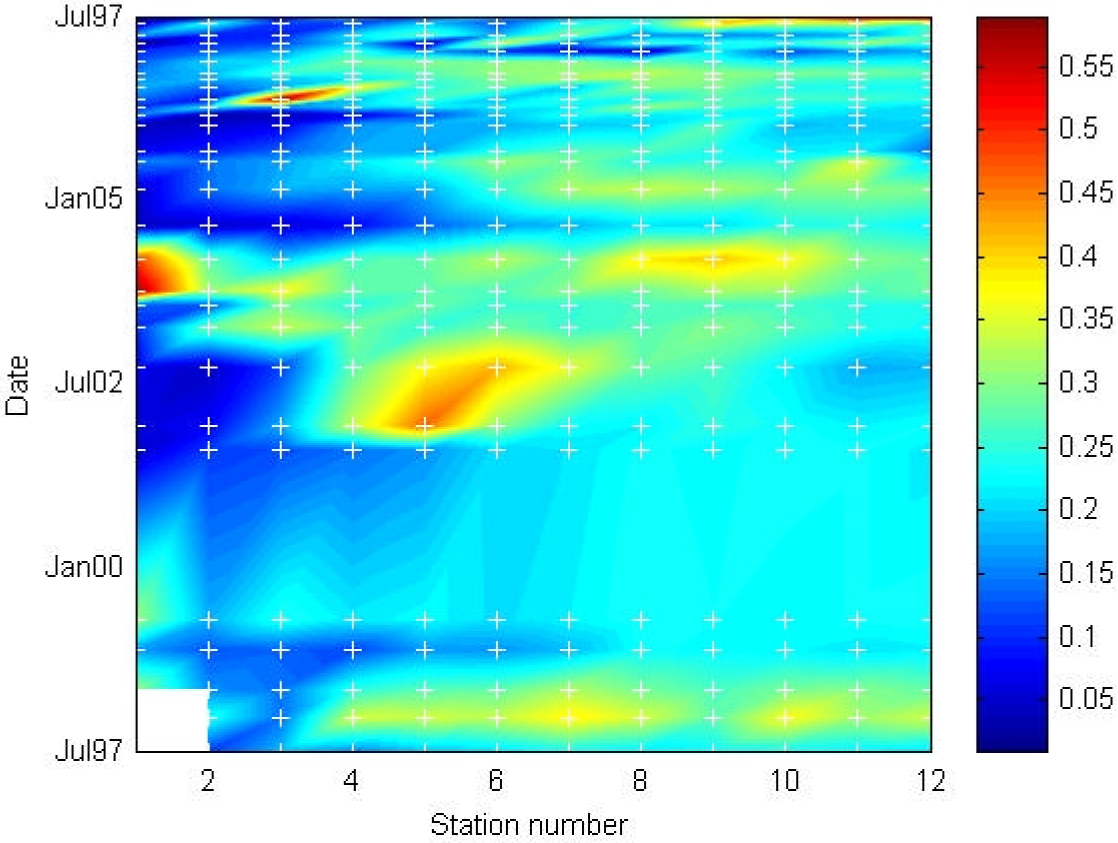

Figure 7. TKN (normalised by Cl^- concentration) at sampling stations (horizontal axis) along the Coorong. The normalised concentration is dimensionless.

3.2.2. Interplay between nitrogen cycling processes and salinity

The breakdown of organic matter to produce DIN occurs mainly through microbial action in the sediments and it is through this step that changes in salinity arising from either evaporation increasing the salinity or freshwater inflows decreasing salinity exercise their initial effects on nitrogen cycling especially the relative amounts of NH_4^+ and NO_x in the water column. The breakdown of organic nitrogen in the sediments first liberates NH_4^+ which can undergo bacterial oxidation to produce NO_x or diffuse out of the sediments as NH_4^+. The DIN can undergo further microbiologically mediated reactions leading to other forms (both organic and inorganic) of nitrogen. In addition nitrogen fixation, both in the water column, and in the algal mats, may introduce additional organic nitrogen into the system. A non-exhaustive (details are given in: Ehrlich 2002; Fenchel, King & Blackburn 1998; Valiela 1995) listing of the processes relevant to the cycling of nitrogen in the Coorong includes:

- organic decomposition: particulate organic matter (PON) → DON → NO_2^-
- nitrification: $NH_4^+ \rightarrow NO_2^-$ and subsequently NO_3^- (NO_x)
- denitrification: $NO_x \rightarrow N_2$
- dissimilatory reduction of nitrate to ammonia (BNRA): $NO_x \rightarrow NH_4^+$
- ANAMMOX: $NO_2^- + NH_4^+ \rightarrow N_2$
- nitrogen fixation: N_2 → particulate organic matter (PON).

The sea waters entering the Coorong contain significant amounts of sulfate (SO_4^{2-}) and the sulfate concentration in the water column rises as the extent of evaporation, and thus the salinity, increases. In the sediments, sulfate is used by the bacteria to breakdown the organic matter and is simultaneously reduced to sulfide ions. Sulfide can have both inhibiting as well as stimulatory effects on the various nitrogen transformation processes (Table 1).

Process	Effect of sulfide	Reference
Nitrification	inhibitory	Hansen et al. 1981; Joye & Hollibaugh 1995; Rysgaard et al. 1999
DNRA	stimulatory	Rysgaard et al. 1996; An & Gardner 2002
Denitrification	inhibitory	Sørensen 1987; Mortimer et al. 2002
ANAMMOX	nil	
Nitrogen fixation	for cyanobacterial mats probably stimulatory	

Table 1. Summary of the effects of sulfide on the nitrogen transformation processes in sediments.

We see that both nitrification and denitrification are inhibited by sulfide. The literature suggests (Jørgensen 1985, Sørensen 1987) that denitrification is more susceptible to sulfide inhibition than nitrification. Thus, under conditions of high salinity and high concentrations of reactive organic matter, the processing of combined nitrogen will be chanelled through the DNRA and ANAMMOX pathways. Direct observation (Gardner et al. 2006) showed that increasing salinity also increases the amount of NO_x being transformed directly to NH_4^+ by DNRA The production of ammonium by this microbial process started at about salinity 10 and continues to increase up to the highest salinity observed. However, net NO_3^- and N_2 fluxes and total denitrification showed no systematic variation with salinity. Overall the release of NH_4^+ from the sediments to the water column increases with salinity. Another aspect of this paper (Gardner et al. 2006) is highly germane to understanding the nitrogen behaviour in the Coorong. Both N fixation and denitrification were quite significant components of the N fluxes across the sediment–water interface and the NET N_2 fluxes into the system were comparable to the NH_4^+ fluxes and greater than the NO_3^- or NO_2^- fluxes. The overall implication for the biogeochemistry of the Coorong is that ammonia will be the dominant DIN species under hypersaline conditions. The available monitoring data suffer from high minimum detection levels but show occasional episodes of higher ammonia in the southern lagoon.

Most of the decrease (~50%) in both nitrification and denitrification occurs as the salinity increases from 0 to 10. These are relatively low salinity values compared to the norm in the Coorong and thus it will be a system where substantial influxes of freshwater will re-establish both nitrification and denitrification, and increase the NO_x:NH_4^+. This contrasts with the effects of inflows of seawater and its subsequent evaporation which will decrease NO_x:NH_4^+ and push the DIN content of the water column towards higher DIN concentrations dominated by ammonia. This additional DIN may be converted into additional biomass if the light climate is suitable and other nutrients are not limiting, and there will be no increase in DIN concentrations.

Nitrogen fixation is unlikely to be negatively affected by increasing salinity or by sulfide inhibition and this process has the potential to deliver additional fixed N, cycling though the biotic N pool. These inputs of fixed nitrogen to the Coorong explains the capability of a system to maintain apparently high levels of N recycling and primary production comparable to highly eutrophic systems despite very low measurable concentrations of DIN, and very infrequent inputs of bioavailable nitrogen from barrage overflows. Generally, algal mats have much higher rates of nitrogen fixation than of denitrification (Stal 2003) and capability underlines the potential importance of these particular ecotypes to the overall biogeochemistry of the Coorong.

The potential complexity of nitrogen cycling in hypersaline mats and the other ecotypes in the Coorong, the sensitivity of the processes to changes in salinity, and the coupling of nutrient availability to biomass production all point to the need for experimental studies that span the range of salinities observed. Quantitative data on these processes will be essential to the parameterisation of predictive models.

Table 2 summarises the consequences for the cycling of the different inorganic nitrogen species of changes in salinity and the associated initiation or cessation of sulfate reduction processes.

Variable	**Value**	**Biogeochemical process change / organism switch**	**Subsidiary requirements/ contingencies / outcomes**
Salinity	Nil	Small green chlorophytes able to assimilate ammonium at low concentrations (a testable hypothesis)	Gradually increases in concentration with increasing salinity but appears ubiquitous. Increasing abundance may reflect reduction in grazing pressure as sulfur rises.
Salinity	~ 10	Inhibition of nitrification and denitrification	Both production and removal rates of NO_3^- decline, NO_3^- gradually disappears from the water column.
Salinity	~ 20	Stimulus of DNRA starts increases with sulfide production	Sediment–water flux of NH_4^+ increases but does not necessarily lead to higher measurable concentrations if taken up by phytoplankton.
Salinity	~ 70 to 80	Inhibition of grazing of algal mats by gastropods. Increased nitrogen fixation but more closely coupled nutrient cycling within the mats leading to paradox of high productivity but very low nutrients in water column. (Farmer 1982; Javour & Castenholz 1981).	Gradual decline in abundance of grazers as salinity increases with some time lag and probably no clear cutoff.
Salinity	Starts at about S = 50 and continues up to S = 200 but mat species changes as S increases (goes through *Lyngbya* to *Phormidium*/ *Beggiatoa*, *Microscscoleus*, *Aphanothece*	Algal mat species that secrete reactive dissolved organic carbon (glycollate or other products of daytime photorespiration or of night-time fermentation) which fuels sulfate reduction (Stal & Caumette1994)	Changing water levels are likely to make the Coorong mats ephemeral as increasing salinity is associated with falling water levels in the southern lagoon. There is a commensurate relationship between the mat-forming cyanobacteria (N fixers) and sulfate-reducing bacteria.
Salinity	~100 to 120	Dissimilatory sulfate reduction optimum (Sorensen et al. 2004)	Frequently achieved in the southern lagoon and persists for months.

Table 2. Biogeochemical processes involving nitrogen species affected by changes in salinity.

3.3. Phosphorus cycling

Figure 8 shows the temporal and spatial variation of normalised TP concentrations at all stations. Normalised concentrations are somewhat higher at the southern end. As more than 50% of the observations of FRP are below detection limits (especially in the southern lagoon), the dissolved component of TP is thus small. The observed spatial distribution of normalised TP thus reflects the particulate P concentrations associated with the higher concentrations of P incorporated into phytoplankton and phytoplankton detritus in the southern lagoon. As the southern lagoon is shallower than the northern lagoon there is likely to be more wind-driven resuspended material. The highest concentrations in the northern lagoon are associated with inflows of freshwater over the barrages. The low concentrations of FRP in the southern lagoon suggest that biogeochemical processes are operating to remove dissolved orthophosphate. Likely candidates are the biological uptake by either the pelagic phytoplankton and algal mats together with abiotic processes removing phosphate through the formation of insoluble P-containing materials. These materials are probably authigenic calcium-fluoro-apatites (CFA) of indeterminate composition. They have been shown to be produced and sequestered in newly forming marine and estuarine sediments (Ruttenberg & Berner 1993). The changing water levels and high evaporation within the Coorong are conducive to the precipitation of these materials in the exposed drying sediments through the evaporative concentration phosphate in the pore waters. In addition, the microbial breakdown of P-containing organic matter will produce higher orthophosphate concentrations in the pore waters. Co-precipitation of phosphate with calcite (Froelich et al. 1980) (see above) will also remove phosphate. The photosynthesis-induced changes in pH within the algal mats can also lead to calcite precipitation (Ludwig et al. 2005). The processes removing phosphate from the water column under increasing salinity conditions are:

- irreversible removal by incorporation into insoluble phosphate-containing minerals (a corollary of this proposition is that sediment P concentrations should increase towards the southern end of the Coorong) and
- adsorption by precipitating calcite. This process should release adsorbed phosphate if the calcite redissolves due to reduction in salinity or decreases in pH.

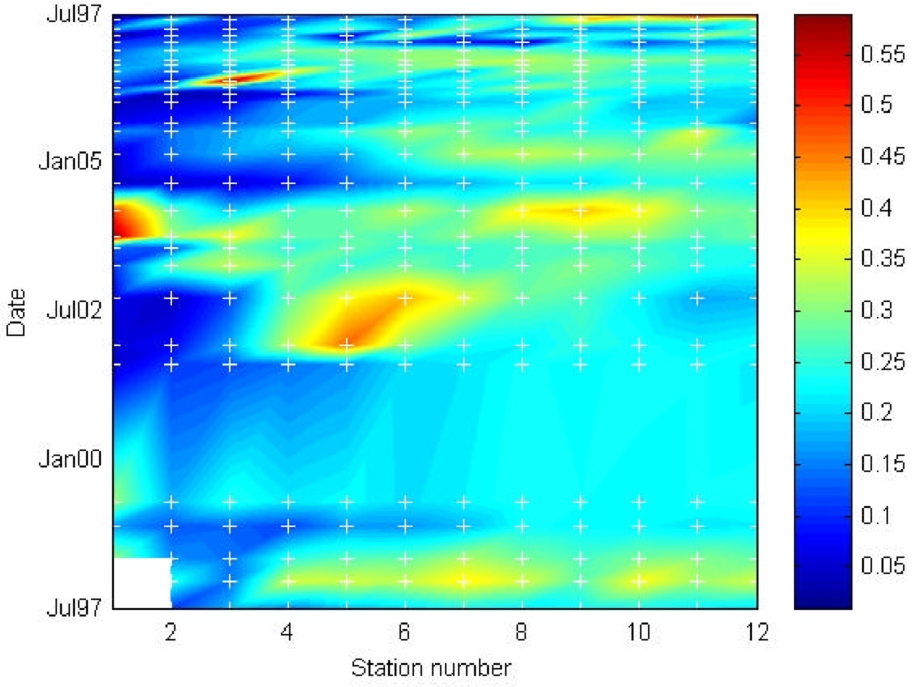

Figure 8. Total phosphorus (TP) concentration normalised by Cl^- at all stations (horizontal axis) along the Coorong.

Exact calculation of the equilibrium orthophosphate concentration in the water column in equilibrium with the sediment CFA is impossible due to uncertainty of the actual composition of the CFA or hydroxy-apatite. It is of heuristic value, however, to assume that the deposited material is calcium hydroxy-apatite (Atlas & Pytkowicz 1977) and use the appropriate solubility product ($Log_{10}K_{sp}$ = -114) (Stumm & Morgan 1995) to calculate the equilibrium phosphate concentration as a function of pH and Ca^{2+}. The results where we have disregarded activity and ion pairing effects (Figure 9) suggest that solubility effects alone can cause significant reductions in the dissolved phosphate concentrations as the salinity increases. These effects consequently will be more pronounced in the southern lagoon. Conversely, freshening of hypersaline waters and sediments may lead to the dissolution of precipitated calcite and release of the sequestered inorganic P. However, the calcium hydroxyl-apatite and insitol hexaphosphate – the end product of microbial transformation of P-containing organic material in hypersaline systems (Degroot & Golterman 1993) – are likely to dissolve much less readily with more of the precipitated P stored in the sediments of the southern lagoon.

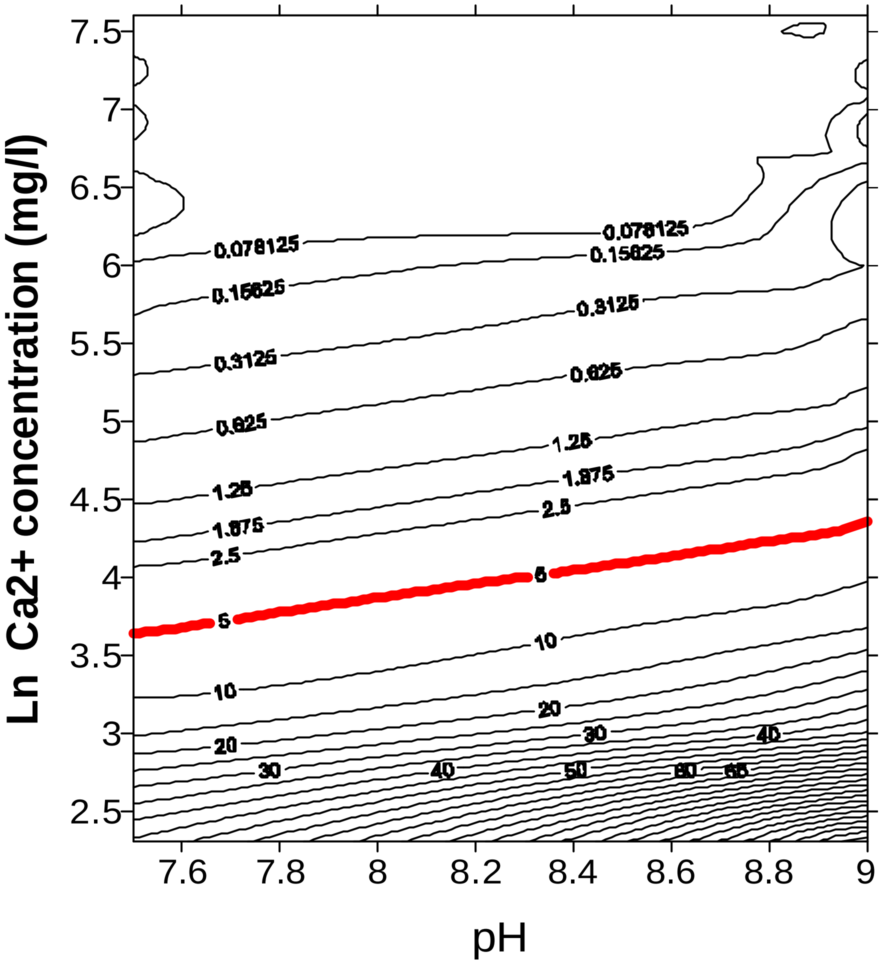

Figure 9. Calculated orthophosphate concentration as a function of Ca^{2+} and pH. The red line indicates the usual analytical detection limit (5 µg P L^{-1}) . In the southern lagoon of the Coorong the pH is usually less than 8.2 while the Ln (Ca^{2+}) is greater than 5. Under these circumstances the equilibrium water column phosphate concentration is seen to be below detection levels.

Further insight into the relative spatial distributions of TKN and TP can be gained by examining the variation in TKN:TP at the various stations along the Coorong (Figure 10). Given the low NO_x concentrations, this ratio is a good approximation for TN:TP. The observed ratio is everywhere above Redfield ratio (N:P; 16:1) characteristic of the composition of pelagic phytoplankton. Going from the northern to the southern lagoon, there is a clear increase in this ratio. The ratio is greatest (~55) in the southern lagoon. As the TKN and TP concentrations include components of detrital solid material, resuspended sediments, and unreactive DON and DOP respectively, no definitive conclusions can be drawn on whether the pelagic phytoplankton growth is actually N or P limited. Considering the abiotic controls on FRP, P limitation seems more likely and this is a hypothesis which can be tested.

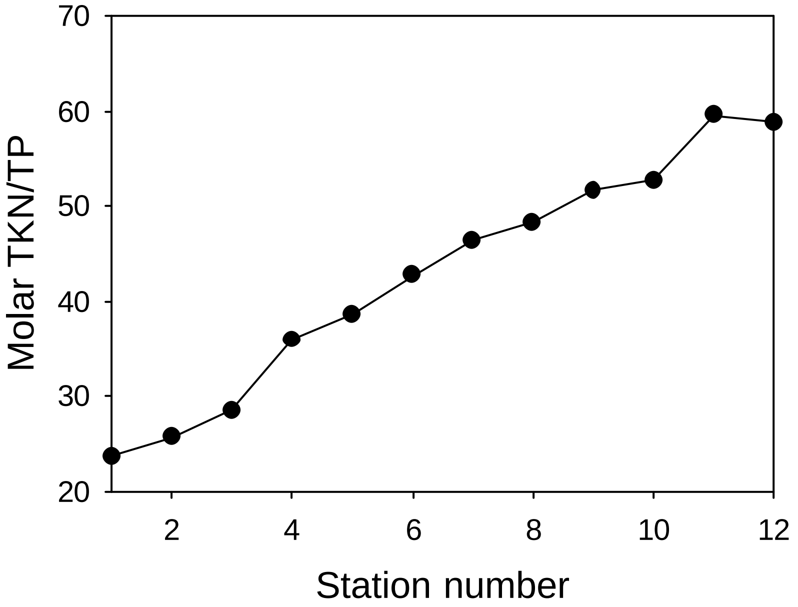

Figure 10. Variation of average TKN:TP (atomic) at stations along the Coorong.

3.4 Role of hypersaline algal mats and potential significance in the Coorong

Algal mats – coherent structured microbial communities whose surface layers are dominated by mixtures of cyanobacteria and diatoms while the underlying layers contain photoautotrophic sulfate-reducing bacteria – are a characteristic of the benthos in shallow hypersaline systems. Their ubiquity arises from specific biochemical mechanisms that allow them to function under high salinity, and the role of the enhanced salinity in suppressing grazing organisms that would limit their abundance. While the Coorong is not hypersaline everywhere all the time, the southern lagoon, especially over the recent past of limited freshwater releases over the barrages, has been hypersaline. Although algal mats are known to be present in the Coorong (J. Mitchell pers. comm.), their extent and variation with season and water level is not documented.

From the work in other hypersaline systems the presence of algal mats has important biogeochemical consequences.

Firstly, the mats, when actively photosynthesising, are characterised by highly efficient capture of dissolved inorganic nutrients generated in the sediments by microbial breakdown of particulate organic matter as well as efficient uptake of the same dissolved inorganic species from the water column. Consequently, under conditions of limited additions of fresh nutrients and active photosynthesis, mats have the capacity to reduce water column dissolved inorganic nutrient concentrations to quite low levels.

Secondly, the presence of the cyanobacteria in the mat may confer the capacity to fix atmospheric nitrogen thus leading to another element (probably either P or Si) becoming the limiting nutrient. As the mats are usually in clear shallow water they can achieve high photosynthetic rates leading to drawdown of bicarbonate and oxygen supersaturation. Under these conditions the cyanobacteria switch to photorespiration excreting glycolic acid thus contributing to the growth of DOC in the water column.

In darkness photosynthesis ceases and the mats rapidly become anoxic and the cyanobacteria turn to fermentation as their energy source using stored glycogen (Stal & Moezelaar 1997). Some of the simple organic compounds produced in the fermentation such as acetate, lactate, and glycollate diffuse into the overlying water column, while the remainder diffuses downward into the sediments. There, these readily metabolisable substances are used by sulfate-reducing bacteria leading to high rates of sulfate reduction within the lower layers of the mat. The sulfide produced reacts with iron oxyhydroxide species (denoted by FeOOH) in the mat, forming iron sulfides that gradually transform to pyrite. The reduced sulfur species are converted to sulfate again when photosynthesis resumes generating high oxygen concentrations in the vicinity of the anoxic zone. Thus algal mats are a mechanism by which interacting carbon, nitrogen, phosphorus, sulfur and iron cycles are interconnected. Changing salinity, which occurs in the Coorong through the annual exchange of seawater, plus the intermittent releases of freshwater from the barrages, impacts on the extent and biogeochemical functioning of the mats in numerous ways:

- changing the species composition of the mat-forming species within the mat – each group has an optimum salinity range and differing capabilities for nitrogen fixation and release of organic carbon
- changing the availability of nutrients – sulfate which is present in high concentrations in seawater, and iron provided in higher concentrations by fine clays delivered by freshwater inflows
- changing the light climate – turbid water will suppress mats, while clear (sea) waters will favour mat photosynthesis and the associated nitrogen fixation and DOC release.

The algal mats may also be a key component of the primary production within the Coorong. They will support populations of grazers such as gastropods and worms. The large amounts of DOC released will support high bacterial populations as much of this material is readily metabolised (DOC from other sources such as messy feeding of flagellates on pelagic phytoplankton), and DOC lost from phytoplankton can undergo photolytic reactions which, while producing more reactive fragments, also produces more recalcitrant organic matter).

As noted earlier the cyanobacteria that form an important element in the microbial mats are capable of fixing nitrogen phototrophically. Given that marine systems are generally nitrogen limited, this input has the potential to change the limiting nutrient from nitrogen to phosphorus as the system becomes increasingly hypersaline. Consequently, changes in physical factors such as salinity or turbidity through changes in the character of the inflows will have the potential to change the mat contribution to the overall nitrogen budget of the Coorong as well as the relative proportions of primary production produced by the benthic and pelagic primary producers.

3.4. Interactions between benthic and pelagic primary production

Inferences from the chemical data indicate that there is a relatively large and persistent biomass of pelagic phytoplankton as well as a potential coverage of much of the permanently wetted surface of the Coorong by algal mats (the extent of the intermittently inundated mats and their contribution to the overall nitrogen budget is an important but unresolved question). These two elements of the primary production in the Coorong have different biogeochemical dependencies and potentially negative interactions. The algal mats, through their tight cycling of dissolved nutrients from the sediments constrain the availability of dissolved nutrients to pelagic phytoplankton. The pelagic phytoplankton reduce the light reaching the benthic mats and thus their overall production. These mutual antagonistic interactions have a spatial character as well. The control of the benthic light intensity by phytoplankton is weakened in the near-shore areas where the optical depth of the water containing the phytoplankton is insufficient to significantly reduce light levels. There will thus be a 'dirty bathwater' effect where the highest benthic primary production occurs in the shallowest water which is most accessible to wading birds. If this analysis is correct, and it is contingent on aerially exposed and dehydrated benthic mats being able to rapidly resume normal biogeochemical function on rewetting, then rapid rises in water level will keep much of the benthic mat beneath the euphotic zone, and limit mat growth to a small rim at the periphery of the lagoon.

Organisms directly or indirectly dependent on the mat as a major food source will be disadvantaged relative to feeders on the pelagic phytoplankton. The phytoplankton will also have an increased source of dissolved nutrients due to the inhibition of mat growth in the deeper parts of the lagoon. These effects will propagate up the food chain. Organisms dependent on pelagic feeders will prosper, while organisms dependent on the benthos will have hard times. Similar arguments apply to changes in the other principal driver – salinity. As the salinity declines the grazing pressure on the mats will increase and pelagic phytoplankton species adapted to lower salinities will be able to grow.

4. Research areas

In the review of the Coorong monitoring data and the associated discussion, we have suggested interpretations of the data that are by no means certain and revealed gaps in our understanding of exactly how the Coorong operates. Rational management to achieve the desired ecological outcomes requires a better understanding of the processes, and especially their response to salinity and water level, the two principal 'levers' that can be manipulated to achieve management goals. These sensitivities cannot be accurately inferred from the reported behaviour of other systems. The differences in climate, bathymetry and inputs make these extrapolations uncertain. Consequently there are areas where research is necessary to elucidate these issues and provide the necessary knowledge underpinning for better management. We set out these areas below.

4.1. Quantification of nutrient fluxes and budgets

It has not been possible using the monitoring dataset to construct accurate nutrient budgets for the northern and southern lagoons, and estimate the fluxes of materials to and from the sediments, as well as quantifying the inputs from the barrages and the sea. Difficulties arise from the dynamic nature of the water levels coupled to the poor temporal resolution of the data. Constructing such budgets through the use of the now operational simple one-dimensional hydrodynamic model coupled with the monthly chemical observations (though see later regarding the need for extended observations) is seen as an important next step. These budgets and fluxes will be an important element in constraining more detailed predictive biogeochemical modelling.

4.2. Extent and functioning of algal mats

While there is indirect and anecdotal evidence for the presence of algal mats in the Coorong and, based on other hypersaline systems, we infer that they can have significant effects on the cycling of organic carbon, the availability of nitrogen through nitrogen fixation and may contribute significantly to the food web, their relative contribution to the overall biogeochemistry of the Coorong is unquantified. As a minimum it is important that we have at least order of magnitude estimates of:

- the contribution to organic carbon production (especially the production of DOC)
- their net contribution to the nitrogen budget of the Coorong on a seasonal scale and
- the susceptibility of these processes to changes in salinity (this includes the persistence of the mats from year to year).

4.3. Algal mats in the food web

Based on the literature and the already assembled data we have suggested that algal mats may be a component of the food chain in the Coorong. It is important to know how the grazing pressure on the mats responds to changes in salinity as this may be a mechanism that limits the transfer of organic carbon from primary production to the higher levels of greatest ecological concern.

4.4. Pelagic primary producers: their identity, productivity and constraints.

The data show large amounts of pelagic phytoplankton biomass especially in the southern lagoon. Identification of the principal pelagic primary producers is a first order requirement. Differentiation between resuspended benthic microalgae, true pelagic phytoplankton, and heterotrophic mixotrophs capable of growing by both photosynthesis and the ingestion of bacteria or dissolved organic nutrients, and estimation of the relative proportions of each component will illuminate the connections between primary production and the higher trophic levels as well as indicating the potential for physical factors to control primary production. Data interpretation implies that this primary production is phosphorus limited, and that the grazing is inhibited by the high salinity. These are important biogeochemical controls and it is important for constructing realistic predictive models that these hypotheses be tested also. The current data on FRP have a too high minimum detection level and DOP is not quantified at all. Sampling and analysis of these analytes will require the adoption of new methods. The intensity of grazing on the pelagic primary production as a function of salinity is a key process in the recycling of nutrients and requires investigation. The diurnal cycle of primary production is not known; the low solubility of oxygen in brines coupled with bubble formation may contribute to overall heterotrophy of the system. The interplay between the algal mats and the pelagic production is unknown.

4.5. Spatial variation in dissolved phosphorus and controls on its availability

Phosphorus appears to play a key role in the growth of pelagic phytoplankton and the stoichiometry of the particulate organic matter. Our analysis (based on the literature) suggests that phosphorus is being removed in the more saline parts of the Coorong as an authigenic mixture of minerals. Given that phosphorus availability is postulated to be a possible limiting factor to pelagic primary production it is important to establish if these processes are operating, and, if phosphorus stored in the sediments can be released once the salinity declines or if it is permanently bound. In addition, growth limitation experiments to establish the limiting nutrient for pelagic phytoplankton production should be undertaken.

4.6. Microbial reactivity of DOC, DON, and DOP

DOC, DON and DOP are merely signifiers for natural mixtures of organic molecules that contain chemically bound carbon, nitrogen and phosphorus. As noted in the review, microbial degradation and photodegradation processes can lead to situations where the organic components are composed predominantly of refractory compounds where the chemically bound nutrients are unavailable and thus represent a sink for bioavailable nutrients. The reactivity of the dissolved organic components should be measured at a range of salinities under both light and dark conditions. In addition, the dissolved organic materials should be fractionated to provide some insights into the identity of the principal individual component molecules and their origin (i.e. algal mat or pelagic phytoplankton).

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